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REGULAR ARTICLE

A potential energy surface survey of OB_6: global minima and isomerization stability

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Abstract In light of the very recent significant discrepancies on the global isomer of the sept-atomic molecule OB_6, we performed a detailed potential energy surface survey of OB_6 covering various isomeric forms. We showed that at the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d) level, the planar knife-like isomer **01** with a –BO moiety has the lowest energy, followed by the planar belt-like isomer **02** at 22.6 kcal/mol. Another isomer **05** at 33.1 kcal/mol can be viewed as the direct O-adduct of the pentagonal pyramid B_6. Kinetically, the three isomers **01**, **02** and **05** all have considerable barriers (19–29 kcal/mol) (obtained at B3LYP/6-311+G(d) level) against isomerization. However, other isomers either have much higher energy or possess much smaller conversion barriers and are thus of little likeliness for isolation. Moreover, though being isoelectronic to the well-known CB_6^{2-} molecule, OB_6 does not have any kinetically stabilized wheel-like isomers with O or B centers. The three OB_6 isomers **01**, **02** and **05** await future laboratory studies. The detailed results reported in this paper are expected to provide useful information for understanding the growing process of boron oxides, O-doping and oxidation mechanism of boron clusters.

Keywords OB_6 · Molecular wheel · Isomerization · Potential energy surface

1 Introduction

Small clusters form a bridge between atoms and larger clusters (even bulk materials). Boron-related clusters have been the focus of both theoretical and experimental studies [1–6]. Being electron deficient and able to form strong covalent bonding, boron is well known to be associated with a rich structural diversity in its compounds [6, 7]. For small boron or binary boron-rich clusters, some interesting phenomena have been revealed, among which is the postulation of planar/quasi-planar hyper-coordinated atomic-centered molecules [8–10]. CB_6^{2-}, a 6π-electron system with a planar hexa-coordinated carbon center, was first theoretically designed in 2000 [8]. Since then, a large number of publications have focused on CB_6^{2-} and related molecular species with hyper-coordinated centers [11–16]. These species have been given a vivid name “molecular wheel” [1], of which, B_9^- and CB_7^- were first theoretically suggested [9] and later the existence of the sept-membered (B_8^{2-} and CB_7^-) [1, 10] and octa-membered (B_9^-) [1, 17] B-centered wheels has been successfully verified in laboratory. The calculated high aromaticity of these boron-rich species has led chemists to predict that they might resemble the well-known organic aromatic cyclopentadienyl unit (i.e., $C_5H_5^-$ or Cp^-) to act as potential building blocks for more complex materials [18]. The sandwich-like compounds based on the C and N-centered molecular wheels (i.e., CB_6^{2-} and NB_6^-, respectively) have been theoretically devised [19–24]. We should note that due to the existence of other lower-lying isomers [8, 25, 26], the kinetically stabilized C-centered hyper-coordinated molecular wheels still await experimental verification [26]. Due to the fundamental interest and potential in materials, any new finding of such species should continue to be attractive and would enrich the “flat chemistry”.

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In the present work, we choose to study a sept-atomic boron-rich binary cluster OB_6, which is isoelectronic to the milestone molecule CB_6^{2-} [8]. Very recently, two groups have investigated its structures and energetics. At the GGA-PW91/6-311G(d) level, Drummond et al. [27] found that the lowest energy isomer of OB_6 is a planar knife-like isomer with a boronyl handle (see structure **a** in Fig. 1). However, at the B3LYP/6-311+G(d) level, Feng et al. [28] predicted a belt-like isomer as the lowest-energy OB_6 form followed by an O-adducted pentagonal pyramid B_6 at 0.45 eV (see structures **b** and **c**, respectively, in Fig. 1). Clearly, there exists a sharp discrepancy between the studies of the two groups. Drummond et al.'s work seems to support recent studies that –BO can be viewed as a rigid structural unit [29–32], whereas Feng et al.'s work appears to be consistent with the very recent results of the isoelectronic CB_6^{2-} [25, 26]. In this paper, we will report the first detailed isomerism potential energy survey of OB_6 by considering various isomeric forms. It is clear that during the formation process of any cluster **A** (e.g., chemical vaporization deposition, or elimination reactions like $\mathbf{B} + \mathbf{C} \rightarrow \mathbf{A} + \mathbf{D}$), various isomeric forms would be experienced. If one isomer ($\mathbf{A_i}$) of the cluster **A** possesses high barriers against isomerization and fragmentation (we call "kinetic stability"), $\mathbf{A_i}$ could have sufficient lifetime of existence, which might influence the nucleation of clusters. Isomers with good kinetic stability should be isolated under appropriate circumstances. Through the potential energy surface study of OB_6, we want to address the following issues. (1) Among the isomers **a**, **b**, **c** in Fig. 1 or other forms, which is the lowest energy isomer of OB_6? (2) In addition, are there any isomers that have good kinetic stability? (3) Finally, is there any local minimum structure that features the B or O-centered hexa-coordinated molecular wheel? And if there is, does it possess reasonable kinetic stability to allow laboratory study?

2 Computational methods

For geometrical and frequency calculations of OB_6, the B3LYP method [33, 34] was applied in conjunction with the 6-311+G(d) basis set. The local minimum points have no imaginary frequency, whereas the transition states (TSs) each have only one imaginary frequency. For each transition state, the intrinsic reaction coordinate (IRC) calculations were performed at the same level to check the right correction between designated isomers. Since OB_6 might be associated with electron lone pairs, multi-centered bonding and π bonding, we carried out the more costly CCSD(T) [35] calculations with 6-311+G(2df) basis set on isomers for better energy evaluation. All computational work was done in Gaussian 03 program package [36].

3 Results and discussions

Our initial structural search of OB_6 (with no symmetry constraints) adopts the following strategy. First, we considered seven kinds of basic structural units, i.e., chainlike, branched chainlike, three, four, five, six, and seven-membered rings. Then, based on these structural units, we constructed various pure "B_7" isomers covering 1D, 2D and 3D forms. Finally, through the simple and successive replacement of one B-atom in B_7 by O-atom, we obtained various OB_6 isomers. Via this exhaustive structural search, we could locate many OB_6 isomers at the B3LYP/6-311+G(d) level, of which the former 22 ones are depicted in Fig. 2. To inspect the interrelation between various OB_6 isomers, we located 34 interconversion TSs at the B3LYP/6-311+G(d) level. By means of the isomers and the connected TSs, we drew the schematic potential energy surfaces (PES) of OB_6 calculated at the B3LYP/6-311+G(d) level. Due to the high complexity and for ease of discussion, the PES of OB_6 was divided into two parts, i.e., Figs. 3 and 4. In addition, Since the B3LYP/6-311+G(d) calculations showed that the triplet structures are all higher in energy than the corresponding singlet ones, the details would not be discussed here for simplicity.

3.1 Low-lying OB_6 isomers

The former five low-lying singlet isomers are the planar knife-like **01** (*0.0* kcal/mol) with a –BO handle, planar

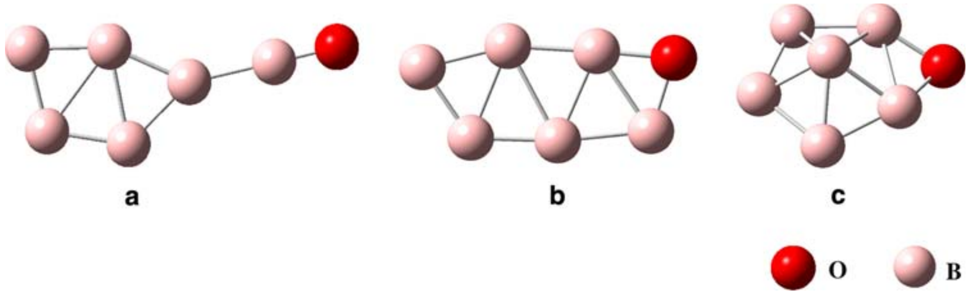


Fig. 1 Lowest-energy and low-lying structures of B_6O, **a** from [27], **b** and **c** from [28]

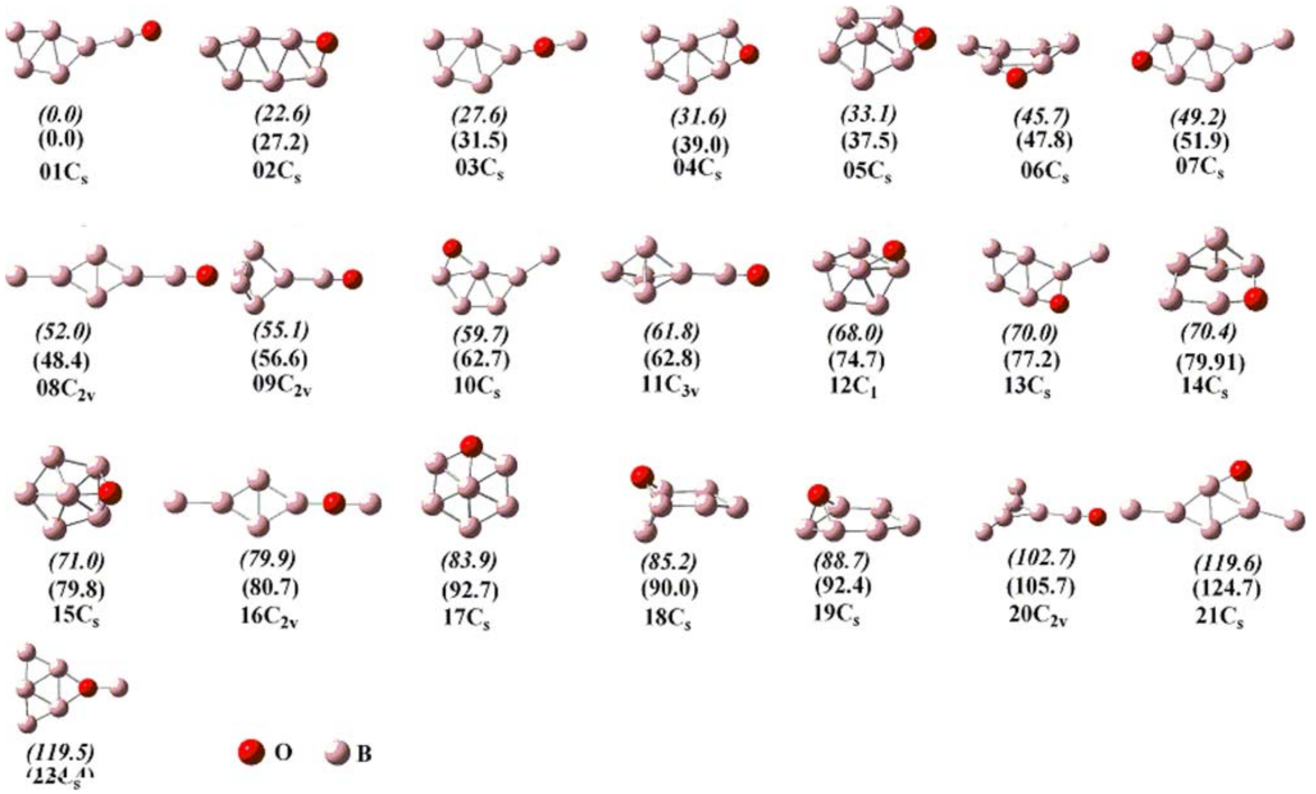


Fig. 2 Calculated structures and relative energies for OB_6 isomers. The upper and lower values obtained at the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d) and B3LYP/6-311+G(d) levels, respectively. The energy values are in kcal/mol

belt-like **02** (*22.6*), planar knife-like **03** (*27.6*) with a –OB handle, planar belt-like **04** (*31.6*), and O-adducted B_6 pentagonal pyramid **05** (*33.1*). The italic values in parentheses are relative energies obtained at the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d) level. Clearly, our calculations well support Drummond et al.'s [27] GGA-PW91/6-311G(d) conclusion, while contrast Feng et al.'s [28] B3LYP/6-311+G(d) results (they predicted **02** and **05** as the respective ground and second-lowing isomers). The neglect of the low-lying isomers **01** and **03** (both with a terminal BO moiety) in Feng et al.'s study might result from the chosen B_6 cluster as a guide for their initial structural search.

Among the five low-lying isomers, the lowest-energy one **01** has the highest kinetic stability with the least conversion barrier being 45.9 kcal/mol (for the **01** → **02** process) (see Fig. 4). The direct conversion of **01** to **03** and to **05** is even more difficult with the barriers of 52.6 and 66.9 kcal/mol, respectively. The second low-lying isomer **02** has the barrier of 18.7 kcal/mol for its rearrangement into the lowest isomer **01.** Considering the conversion to **04** and **03**, isomer **02** has the respective lower barriers of 13.6 and 13.9 kcal/mol. Yet, the reverse conversion is much easier, i.e., 1.8 and 9.6 kcal/mol for **04** → **02** and **03** → **02** conversions, respectively. So, the **02** → **01** conversion should govern the kinetic stability of **02**. For the 3D isomer **05**, the most possible conversion is its transformation into the belt-like isomer **02** with the overall barrier 28.8 kcal/mol (**05** → **04**). The isomers **03** and **04** are considered as unstable in kinetics due to their lower barriers toward conversion into the more stable form **02**, i.e., 9.6 kcal/mol (**03** → **02**) and 1.8 kcal/mol (**04** → **02**), respectively.

3.2 High-lying OB_6 isomers

Figure 3 appears to be very complicated, which covers the diverse isomerization pathways of the remaining nineteen isomers, with the relative energies ranging from 45 to 120 kcal/mol. Seven of them, i.e., **07**, **08**, **10**, **13**, **16**, **20**, and **21**, have the perfect planar structures. From Fig. 3, we can find that each high-energy isomer has the barrier of being lower than 12 kcal/mol toward conversion to lower-lying isomers. Thus, these high-energy isomers can be described as kinetically unstable, and might have little possibility of being isolated under normal nucleation processes.

3.3 OB_6 molecular wheel

The OB_6 cluster is isoelectronic to CB_6^{2-}, which has been famous for its interesting carbon-centered hexa-coordinated planar structure (D_{6h}) [8, 9, 11–16, 26]. Recent

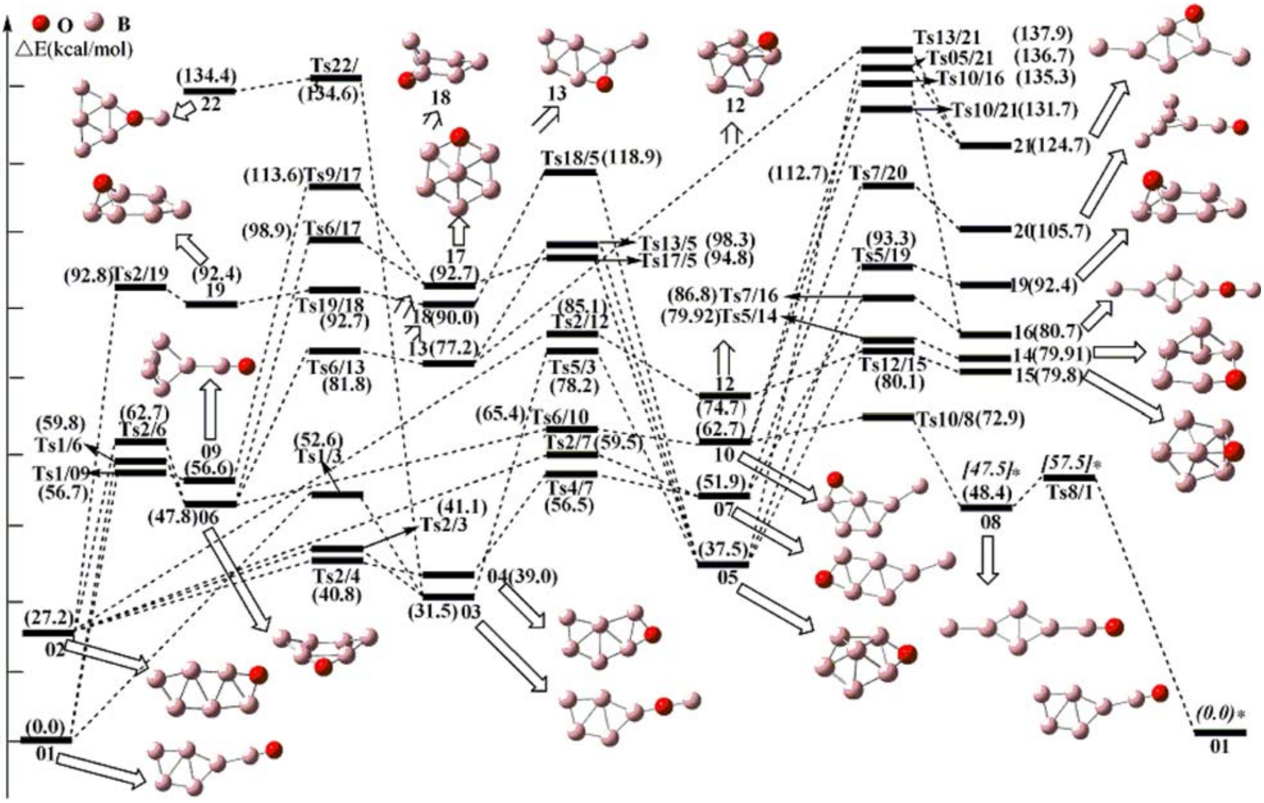
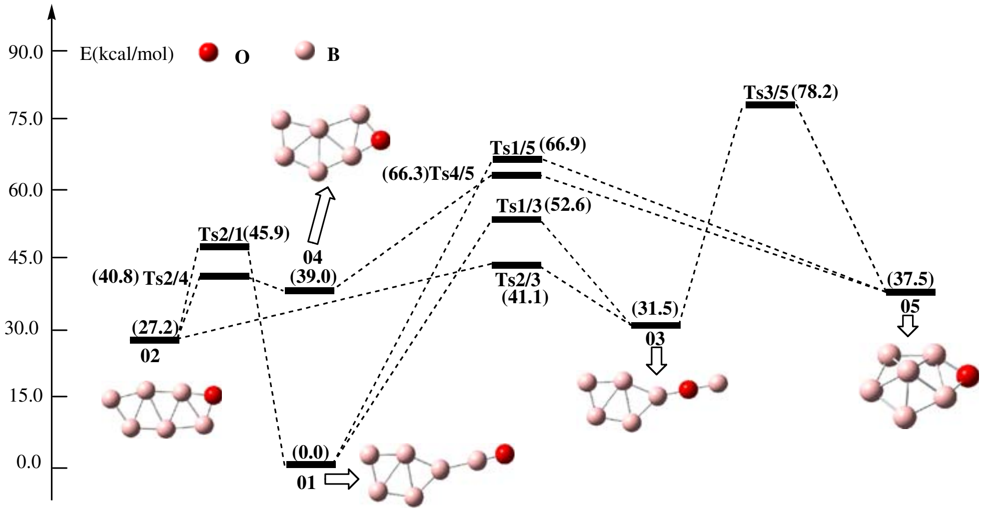


Fig. 3 Schematic potential energy surface of OB_6 at the B3LYP/6-311+G(d) level. *Asterisk* means the structures obtained at the BH&HLYP/6-311+G(d) level

Fig. 4 Schematic potential energy surface of OB_6 at the B3LYP/6-311+G(d) level. The energy values are in kcal/mol



calculations also revealed that the B-centered hexa-coordinated planar structure and two kinds of belt-like isomers are much lower in energy, and the belt-like one is the ground isomer [25, 26]. Up to now, experimental endeavors for carbon–boron binary clusters have characterized the belt-like isomer for CB_6^{2-} [25], and the B-centered sept-coordinated planar wheel-like isomer for CB_7^- [9, 10]. Laboratory confirmation of the C-centered hyper-coordinated planar wheel still remains a great challenge in planar chemistry!

At the B3LYP/6-311+(d) level, the D_{6h}-symmetrized O-centered hexa-coordinated planar wheel structure **24** (see Fig. 5) has two large imaginary frequencies as 757.6 and 757.5 icm^{-1}, which are associated with the sticking-out mode of the planar and the departure from the D_{6h}-center. It is energetically very high-lying at 222.2 kcal/mol

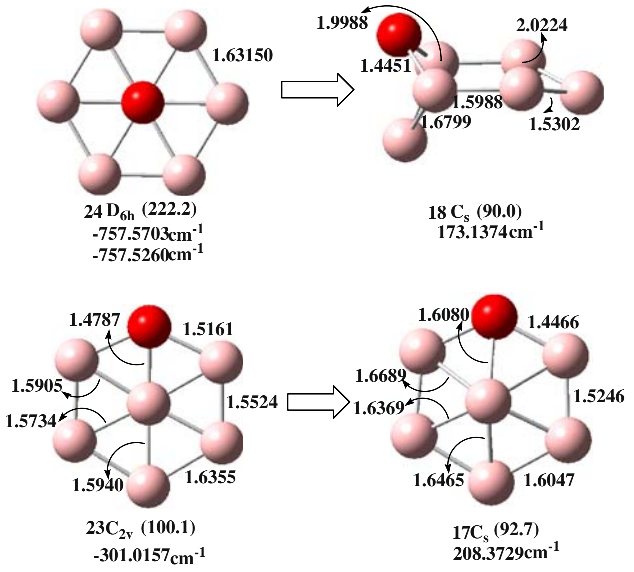


Fig. 5 Structures and relative energies for OB_6 molecular wheel at the B3LYP/6-311+G(d) level. The energy values are in kcal/mol and bond lengths are in angstroms. The values in *parentheses* obtained at B3LYP/6-311+G(d) level

above **01**. Further symmetric relaxation of **24** results in a C_s-structure **18** (at 90.0 kcal/mol) with no imaginary frequencies. As shown in Fig. 3, isomer **18** would easily isomerize to **19** and then to the low-lying belt-like isomer **02** with the overall barrier of only 2.8 kcal/mol (via **TS02/19**). On the other hand, the B-centered hexa-coordinated planar wheel **23** at 100.1 kcal/mol (in C_{2v} symmetry) is not a minimum point, either, with the imaginary frequency 301.0 icm^{-1}, elimination of which leads to a quasi-planar wheel-like isomer **17** at 92.7 kcal/mol. Unfortunately, isomer **17** can be converted very easily to the low-lying isomer **05** via a ring-contraction transition state **TS17/5** (see Fig. 3). The barrier is only 2.1 kcal/mol, indicative of its high kinetic instability. Thus, the present study of OB_6 clearly shows that neither the O-centered nor the B-centered molecular wheels have the fate of being observed. This sharply contrasts the situation of the carbon–boron systems [10] and pure boron clusters [1, 6]. This again demonstrates the importance of the hetero-doping effect in cluster science.

3.4 Bonding properties of 01, 02 and 05

The characteristic orbitals of the three kinetically stabilized isomers **01**, **02** and **05** are depicted in Fig. 6. For isomer **01**, HOMO is mainly a delocalized σ-orbital of the B_5-ring. HOMO-2 is mainly of the delocalized π-bonding over the B_5-ring. Thus, the isomer **01** can be viewed as doubly aromatic (σ and π) within the B_5-ring. We note that isomer **01** also has two π bonding orbitals (HOMO-4 and HOMO-5) that are mainly localized between B and O, which contributes to the unique rigidity of the –BO moiety. Since the ground isomer of neutral B_5 radical also has very similar characteristic orbitals, i.e., delocalized σ in HOMO-1 and delocalized π in HOMO-3 for B_5 (see Fig. 6), we can take OB_6-**01** as the direct addition between B_5 radical and BO radical.

Formally, in view of the structural and bonding resemblance to the bare B_6 isomers, the two OB_6 isomers **02** and **05** can be taken as the direct O-adduct of the two respective low-lying B_6 isomers. For isomer **02**, as shown in Fig. 6, HOMO-1 and HOMO-4 are the delocalized σ orbitals, and they are analogous to the HOMO-1 and HOMO-2 of pure planar belt-like B_6 isomer. HOMO-2 of **02** is the delocalized π orbital of –B_6 moiety, and it resembles HOMO-3 of pure planar belt-like B_6. HOMO-6 is the π-bonding between O atom and adjacent two B atoms, and describes the bonding of O atom with B_6 isomer. For isomer **05**, the HOMO, HOMO-2, HOMO-3 and HOMO-4 orbitals are similar to the HOMO, HOMO-2, HOMO-3 (degenerate with HOMO-4) and HOMO-5 of pentagonal pyramid B_6 isomer, respectively. Clearly, both the σ and π characteristic orbitals of bare B_6 are well inherited to the respective O-adducted structures OB_6-**02** and OB_6-**05**.

3.5 Implications

Now, Via our thorough potential energy surface study, the three questions raised in Sect. 1 can be answered. First, the knife-like isomer **01** is the global structure followed by the belt-like form **02**. Second, three isomers (**01**, **02** and **05**) have good kinetic stability, suggesting their possible isolation. The remaining isomers have much lower conversion barriers toward isomerization to lower-lying forms. Finally, it is hopeless to detect any B or O-centered hexa-coordinated molecular wheel OB_6. Our work confirms the importance of performing the isomerism study for clusters with exotic structures. Moreover, since the three isomers **01, 02 and 05** are separated by high barriers, they should play important roles in the nucleation processes of B-rich boron-oxygen clusters.

4 Conclusions

At the B3LYP/6-311+G(d) and CCSD(T)/6-311+G(2df) calculations, we constructed the first detailed isomerism potential energy surface of OB_6. The lowest-energy isomer was found to be a knife-like form **01** with exocyclic BO moiety, followed by a belt-like isomer **02**. Our results definitively clarified the recent theoretical discrepancy on the OB_6 global minimum structural type. Kinetically, the isomers **01** and **02** as well as the O-adducted pentagonal pyramid B_6 isomer **05** each possess considerable

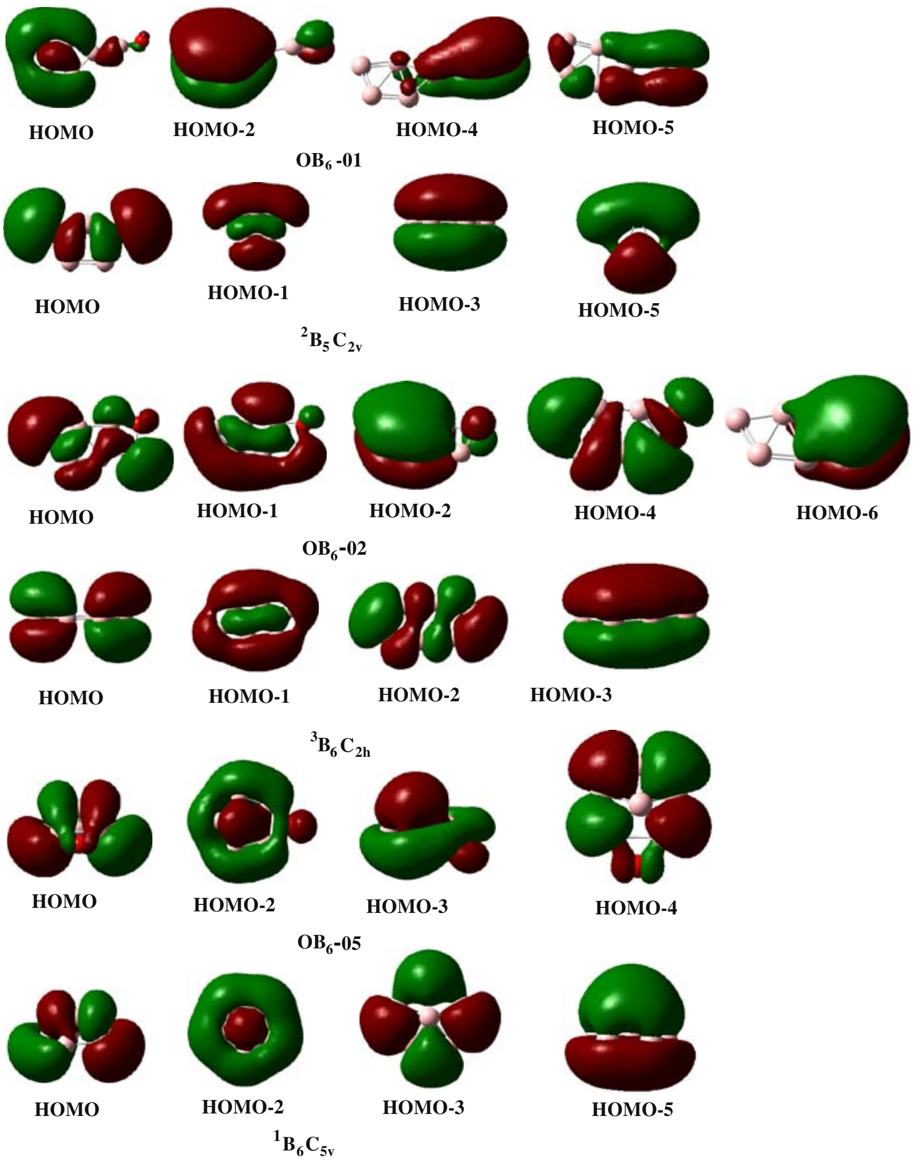


Fig. 6 Characteristic orbitals of OB_6-**01** OB_6-**02** OB_6-**05** and $^2B_5(C_{2v})$, $^3B_6(C_{2h})$, $^1B_6(C_{5v})$ at the B3LYP/6-311+G(d) level

conversion barriers. The remaining isomers are associated with much lower barriers and are thus of little interest for isolation. Amongst, the B- or O-centered molecular wheel could not exist due to the rather low conversion barriers. The results reported in this work might provide useful information for deeply understanding the growth of OB_6 cluster as well as the O-doping and oxidation mechanism of B_6 cluster.

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