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Structure and Energetics of Fragments of the Planar α and β Boron Sheets

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Large scale first principles calculations based on density functional theory and using hybrid exchange-correlation functionals have been performed in order to study the structural properties and the relative stability of fragments of the planar α and β boron sheets. Based on the considered structures, we show that, in contrast to the fragments of the α-sheet, all the fragments of the β-sheet, having more than ≈30 atoms, are fully planar regardless of their shape. We conclude that the β-sheet is the only planar boron sheet reported so far that retains planarity even if it is reduced to relatively small fragments.

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1. Introduction

Experimental and theoretical studies indicate that small boron clusters B_n, $n < 20$, assume planar or quasi-planar structures [1]. The structural transition from 2D quasi-planar clusters to 3D was established to happen for neutral structures at $n = 20$ [2]. More recently, however, a quasi-planar cluster containing 36 boron atoms has been reported experimentally [3]. It is also reported in a theoretical study that a much larger B_{84} cluster adopts a quasi-planar shape [4]. On the other hand, a planar monolayer of boron comprised of B_7 motifs, the so-called α-sheet, have been investigated and found to be more stable than the buckled triangular sheet that was thought to be, for a long time, the most stable 2D arrangement of boron atoms [5]. The α-sheet is, however, less stable than the recently reported 2D crystal with a nonzero thickness [6]. In a context of a different study, it has been introduced a novel sheet [7], labeled as the β-sheet, that is made up of B_{12} planar motifs that, if isolated, are known to be a very stable quasi-planar structures [1]. This planar β-sheet will be a topic of the present study. Both sheets, α and β, have the same as graphene plane group symmetry $p6mm$, although are constructed from planar motifs, B_7 and B_{12}, that have different point group symmetries (D_{6h} and D_{3h}, respectively). The isolated and structurally optimized B_7 and B_{12} clusters are shown in the top-left and top-right part of Fig. 1, respectively. We investigate the structure and relative stability of fragments of the α and β boron sheets. It is shown that small α-fragments, with less than ≈30 atoms, are quasi-planar and less stable than the β-fragments. Furthermore, relatively large α-fragments do not keep planarity and undergo structural distortions contrary to the β-fragments that are perfectly planar.

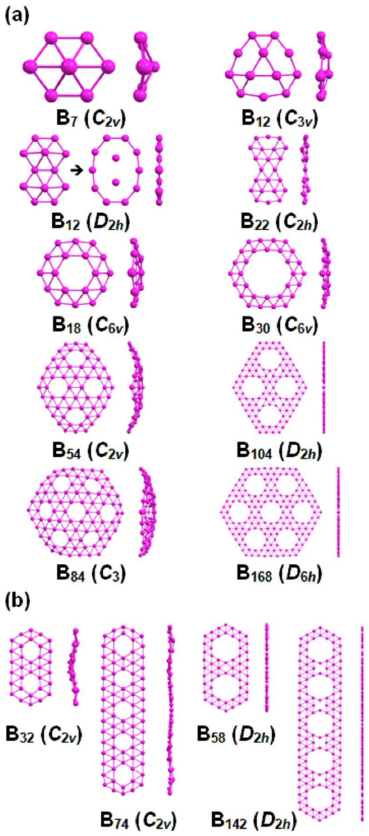

Fig. 1. Compact (a) and elongated (b) boron structures. In each case front and side views of the optimized fragments of boron sheets are shown. α-fragments (β-fragments) are at the left (right) column. The B_{12} cluster on the left is shown before and after structural relaxation. The symmetry of each depicted cluster is indicated in parenthesis.

2. Theoretical approach

The calculations are carried out using the NWChem code suite [8]. All the studied structures are initially optimized at the B3LYP/4-31G level of theory with no symmetry constraints. To check that each structure is in its true local minimum, we expose the clusters to small atomic displacements in the direction perpendicular to the plane of the cluster and optimize the resulting structures. Some of the studied fragments of the boron sheets restore the planarity after structural optimization and some of them undergo structural distortions.

The structures obtained in such a way are further optimized using the 6-31G basis set and the PBE0 hybrid functional. The last calculations are done with some symmetry constraints imposed for larger clusters to reduce computational time. To minimize the effects of the edges on the calculations, all the clusters have boron double-chain stripes at the edges. The output files are analyzed and visualized using the ChemCraft program [9].

3. Results and discussion

We have optimized fragments of boron α-sheets of compact shapes with D_{2h} or D_{6h} symmetries as well as elongated structures that can be considered fragments of boron nanoribbons [10]. The compact and elongated structures are shown in the left column of Fig. 1a and b, respectively. In an attempt to compare the structural stability of fragments of two different sheets, we have optimized fragments of the boron β-sheet that have similar structural characteristics as the α-fragments. The considered β-fragments are shown in the right column of Fig. 1. The structural characteristics that have been taken into account are: symmetry, number of "holes", and shape, and these common features have the initial clusters that after structural optimization are shown in Fig. 1, except for the B_7 (C_{2v}) and B_{12} (C_{3v}) clusters (building motifs). From this figure, we can see that the α-fragments [with the exception of B_{12} (D_{2h})] are not longer planar when isolated from the α-sheet and can be categorized as quasi-planar instead. This result is in accord with a recent study in which it was demonstrated that fragments of the α-sheet that have boron triple-chain stripes at the edges are bowl-shaped quasi-planar clusters [4]. This is, however, not the case of the β-fragments (larger than B_{30}) that preserve their planarity, even if isolated from the infinite matrix. The next step in our analysis was to compare the total energies of the clusters shown in Fig. 1.

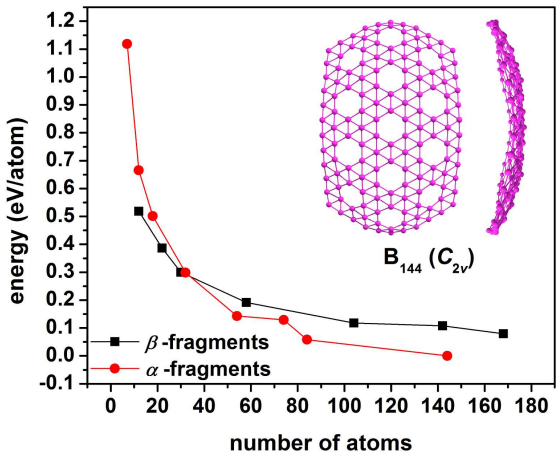

Fig. 2. Total energies (per atom) of the clusters depicted in Fig. 1 versus the number of boron atoms. The energies are given relative to the energy of B_{144} (C_{2v}) shown in the inset, which is the largest α-fragment considered in this work.

The results are presented in Fig. 2, where we plotted the total energies (per atom) versus the number of atoms in the clusters. From this figure, we can see that the α-fragments are less stable than the β-fragments for clusters having less than ≈30 atoms. For larger clusters, the α-fragments are lower in energy and this is consistent with previous results, since the β-sheet has a smaller cohesive energy than the α-sheet by 140 meV/atom [7]. Finally, it should be mentioned that small fragments of the β-sheet sheet can become planar by addition of hydrogen atoms. This was done successfully for the quasi-planar clusters B_{12} (C_{3v}) and B_{22} (C_{2h}) shown in Fig. 1a (right column), which become completely planar with the hydrogen atoms attached [11].

4. Summary

We have investigated the structure and relative stability of fragments of α and β sheets. We have found that small β-fragments are more stable than the α-fragments. Moreover, the β-fragments larger than B_{30} are fully planar in contrast to the α-fragments that are quasi-planar. Finally, to our knowledge, the β-sheet is the only planar boron sheet reported so far, whose fragments are also planar.

Acknowledgments

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