Energy Landscape of Fullerene Materials: A Comparison of Boron to Boron Nitride and Carbon

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Using the minima hopping global geometry optimization method on the density functional potential energy surface we show that the energy landscape of boron clusters is glasslike. Larger boron clusters have many structures which are lower in energy than the cages. This is in contrast to carbon and boron nitride systems which can be clearly identified as structure seekers. The differences in the potential energy landscape explain why carbon and boron nitride systems are found in nature whereas pure boron fullerenes have not been found. We thus present a methodology which can make predictions on the feasibility of the synthesis of new nanostructures.

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The experimental synthesis of fullerenes is a very difficult task. Carbon fullerene structures were therefore theoretically predicted [1] long before they could be produced in the lab [2]. Many more hollow and endohedrally doped fullerene structures made out of elements different from carbon have also been proposed since then theoretically [3] in searches of other possible building blocks for nanosciences. It is, however, surprising that since the experimental discovery of carbon fullerenes some 25 years ago no other fullerenes have been synthesized. So the question is whether experimentalists have just not yet found a way to synthesize these theoretically predicted fullerenes, or whether they do not exist at all in nature. We have recently shown [4] that all the theoretically proposed endohedral Si_{20} fullerenes are metastable and can thus most likely not be found in nature. In this Letter we investigate in detail boron clusters.

Following the B_{80} fullerene structure proposed by Szwacki *et al.* [5] various other fullerene [6] and stuffed fullerene structures [7] were proposed. Subsequently it was however shown for B_{80} that there exist nonfullerene structures [8] which are lower in energy. We will contrast the characteristics of the potential energy landscape of these boron clusters with those of systems found in nature, namely, carbon and boron nitride fullerenes and find that there are important differences.

To explore the energy landscape of the boron, carbon, and boron nitride clusters we do global geometry optimizations on the density functional potential energy surface with the minima hopping algorithm [9]. This algorithm can render the global minimum configuration as well as many other low energy metastable structures. All the density functional calculations are done with the BIGDFT electronic structure code [10] which uses a systematic wavelet basis together with pseudopotentials [11] and the standard local-density approximation (LDA) [11] and Perdew-Burke-Ernzerhof (PBE) [12] exchange correlation functionals.

We start out by analyzing the $B_{16}N_{16}$ cluster which was found to be short lived in experiments [13]. In this system structural rigidity is imposed by a strong preference for sp_2 hybridization [14] as well as by the requirement that bonds are only formed between atoms of different type. This leads to a small configurational density of states. As shown in Fig. 1 there exists a fairly large energy interval in which only cagelike structures exist. Hence there is a strong driving force towards the ground state cage structure and minima hopping can find it rapidly. This driving force also allows the formation of $B_{16}N_{16}$ in nature.

Using the same methods, we went on to study medium size boron clusters with 32–36 atoms. In this size range the clusters show a strong tendency to form cages and all the numerous low energy structures we found are cagelike. This is in agreement with a recent study [15] where the ground state was found to be cagelike. Three representative ground state structures are shown in Fig. 2. These medium size clusters contain well-known structural motifs, [16] namely, empty and filled hexagons as well as empty and filled pentagons. But, in addition, they contain numerous other structural motifs such as single atoms connecting filled hexagons or rings containing more than 6 atoms. The inclusion of these other structural motifs does not increase the energy significantly and the first metastable structure is typically only 0.1 eV higher in energy than the global minimum. For B_{32} we found for instance some 100 cagelike isomers in an energy interval of only 1 eV above the global minimum and even more isomers presumably exist in this interval. The number of nearest neighbors in these structures varies from 4 to 6 and the bond angles vary from 90° for some fourfold coordinated corner atoms to 60° for sixfold coordinated atoms in the center of a planar hexagon. This is in contrast to the structural rigidity imposed by the sp_2 hybridization on all the carbon fullerene structures we have generated. Even though one can find in our 60 atom carbon structures rectangles and heptagons in addition to hexagons and pentagons, all the atoms have, without any

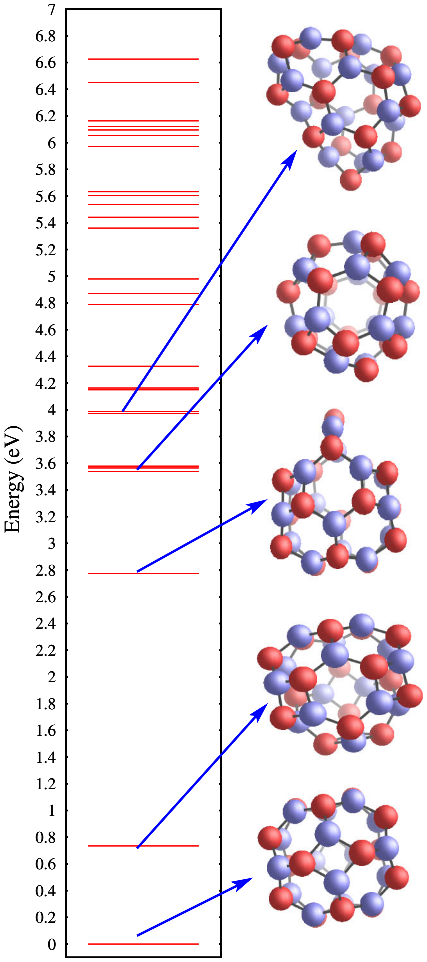

FIG. 1 (color online). The configurational energy spectrum of $B_{16}N_{16}$. Boron atoms are shown in blue (dark gray) and nitrogen atoms in red (medium gray). The higher energy cage structures can be described as a "basket" with a "handle" made out of a chain of 4 atoms (two of each type).

exception, 3 nearest neighbors in structures that are less than 20 eV above the ground state. As a consequence we expect the configurational density of states to be much smaller for carbon cages than for boron clusters. This is indeed the case as will be shown in more detail later.

Next we did global geometry optimization runs for the B_{80} cluster. A first run started from the Szwacki fullerene, which consists of the C_{60} fullerene with 20 additional atoms filled into the hexagons. It thus consists of 20 filled hexagons and 12 empty pentagons. The insertion of the 20 atoms can be viewed as some kind of doping which stabilizes the two-dimensional boron network [17]. During a long period the cage structure was not destroyed in the minima hopping run. Instead minima hopping explored the defect structures that we have described previously [18] as well as other cage structures which are slightly lower in energy than the Szwacki fullerene. Since there is a very large number of possible defect structures this cage funnel contains a very large number of local minima and it takes longer for minima hopping to escape from it.

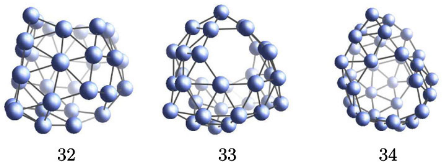

FIG. 2 (color online). Global minima of B_{32}, B_{33}, and B_{34}.

Once one escapes from the fullerene funnel one finds significantly lower energy structures. These structures contain the icosahedral B_{12} motif which is the basic building block of elemental boron. This icosahedron is in most cases at the base of a domelike structure or otherwise at the center of a spherical cage. Both the domes and the cages consist mainly but not exclusively of filled and empty hexagons and pentagons. Figure 3 shows the configurational density of states for the B_{80} cluster. The majority of

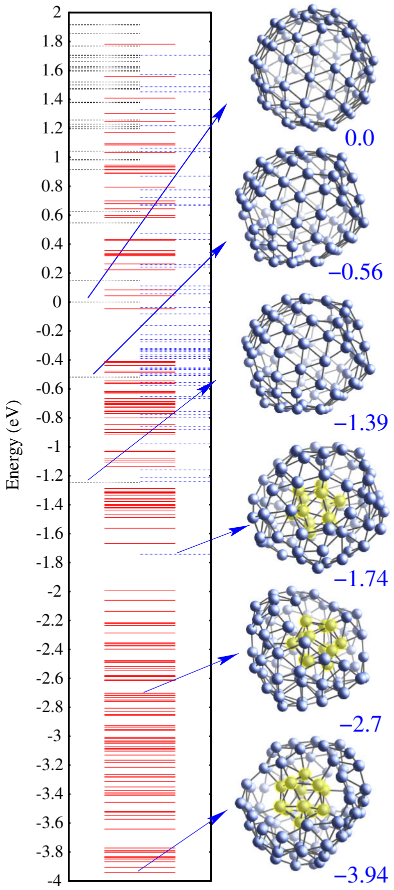

FIG. 3 (color online). The configurational energy spectrum of B_{80}. The energy of the Szwacki fullerene is taken to be zero. The energy levels of the icosahedron-dome structures are centered whereas the levels shifted to the left are fullerenelike structures. The levels on the right correspond to centered icosahedron structures. The atoms of the icosahedra are shown in yellow (light gray). The structure at an energy of -2.7 eV is the putative global minimum from Ref [8]. The energy per atom of our lowest energy B_{80} structure is about 0.13 eV per atom higher in energy than the sheet structure of Tang and Ismail-Beigi [17].

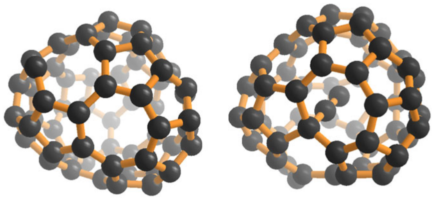

FIG. 4 (color online). Two high energy C_{60} cage structures. The structure on the left has only threefold coordinated atoms even though it contains two seven-member rings. It is 20.5 eV above the ground state. Structures that are even higher in energy can possess some chains with twofold coordination and anchor atoms for these chains with fourfold coordination. The structure on the right is an example of such a cage and is 25 eV higher than the ground state.

the structures are of the dome type and the energies of dome-type and fullerene-type structures overlap. Like for the medium size boron clusters, many structural building blocks can be combined to form clusters of very similar energy. Hence the energy difference between the low energy isomers is again very small. The lowest energy structure we found is considerably lower in energy than the recently proposed compact B_{80} structure [8], both within the LDA and PBE functionals.

Let us contrast the configurational energy spectrum of B_{80} clusters with the one of C_{60} clusters. For C_{60} the first metastable structure is a Stone-Wales [19] point defect which is 1.6 eV higher in energy than the fullerene ground state. Various defects can be combined to form cages of higher and higher energy. Two high energy structures are shown in Fig. 4. The lowest non-cage-like structures are however some 25 eV higher in energy than the ground state. This shows that in contrast to B_{80} the cagelike and non-cage-like structures are widely separated in energy. There is consequently a strong driving force towards cagelike structures and finding the ground state for C_{60} is much easier than for B_{80}.

The differences in the potential energy landscape between B_{80} and C_{60} are also well illustrated by the following computer experiment. If one does a local geometry optimization for 80 boron atoms starting from random positions one obtains disordered structures which are already fairly low in energy, namely, about 10 eV higher than the ground state. This is in contrast to the case of 60 carbon atoms where a local geometry optimization starting from random positions gives structures which are about 50 eV above the ground state unless they happen to be cagelike. This shows again that the boron potential energy landscape has a glassy character with a lot of disordered low energy structures. The energy landscape of C_{60} on the other hand has a broad and deep funnel which leads to the ground state fullerene.

The glassy energy landscape of bulk boron has been explained by the frustrated bonding features of boron where 2-center bonds have to coexist with 3-center bonds [20]. The glassy energy landscape of the medium size boron clusters can also be explained in this way. Figure 5 shows the coexistence of these two types of bonds in our lowest energy B_{80}.

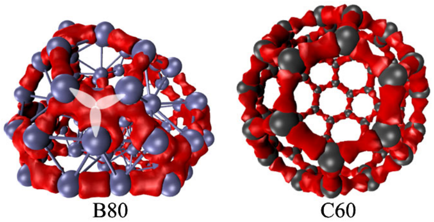

FIG. 5 (color online). The isosurfaces of the valence charge density in our lowest B_{80} cluster and the C_{60} fullerene. They are evaluated at 70% of the maximum value (0.12 a.u. respectively 0.24 a.u.). Whereas in C_{60} we see only two center bonds, both 2 and 3 center bonds are visible in B_{80}.

In addition to the B_{80} cluster we also examined the B_{92} and B_{100} cluster. A structure with a icosahedron in the center of a 80 atom Szwacki fullerene is 7.7 eV lower than the fullerene which was obtained by filling the 12 pentagons [5]. The lowest energy structure, however, does not have high symmetry anymore. A stuffed fullerene structure was proposed for B_{100} [21]. Doing minima hopping runs starting from this configuration some structures with lower energy and lower symmetry were found as well. These structures were also about 10 eV lower in energy than the recently proposed B_{100} fullerene [22]. This shows that disordered cages with an icosahedron inside are the basic structural motif for boron clusters in this size range.

Among all the ground state structures of boron clusters of any size, we could not find any high symmetries. Hence the vibrational modes have no or only low degeneracy. Employing some mode following method will therefore in general lead to different transition states with different barrier heights. Since the height of the barrier correlates with curvature along the starting mode [23], one can expect for a cluster of low symmetry a broader distribution of barrier heights and therefore a larger probability of finding low energy barriers [24]. If low barriers exist a small modification of the external environment such as the presence of another cluster can make these barriers disappear. Hence it is not surprising that all boron structures that we examined, independently of whether they are medium size, large, cagelike or not, turned out to be chemically reactive with other boron clusters when they are brought into contact. During such a chemical reaction with another cluster several chemical bonds are formed which leads to a considerable lowering of the energy and to a large distortion or even destruction of the original structures. This means that even though medium size clusters have a strong tendency for cage formation in isolation, it is unlikely that such boron cages exist in nature. This behavior is also in contrast to the behavior of the C_{60} and $B_{16}N_{16}$ fullerenes. They are only weakly interacting and do not form chemical bonds when they are brought into contact. The chemical reactivity of the boron clusters can also be rationalized in a local picture. If many different structural motifs can be used as a building block of a low symmetry cluster, it is very likely that some atoms have some dangling bonds which are chemically reactive.

Our results explain why boron fullerenes have not been found experimentally. Boron clusters are frustrated systems which do not have enough electrons to fill all electronic orbitals in a chemical bonding based on pure sp_2 hybridization and they consequently do not exhibit some clear preference for a simple structural motif. Hence, from an energetical perspective, there is no driving force towards some well-defined structure. Instead one finds a glassy energy landscape with a large number of different low energy structures whose energies are very similar. These structures are chemically reactive and will therefore not be found under experimental conditions.

The fact that no elemental boron but only compounds containing boron can be found on earth however indicates the possibility of synthesizing more complicated boron cages such as metal doped boron fullerenes.

Such a doping can energetically pull down the cagelike part of the configurational space of boron clusters [18].

Our simulations demonstrate that one can make theoretical predictions about the feasibility of an experimental synthesis. In order to judge whether a system can be formed in nature, it is not necessary to simulate its synthesis process explicitly by molecular dynamics or similar methods.

A global geometry optimization with the minima hopping algorithm indicates whether the system being simulated is a structure seeker or a system with a glasslike potential energy surface. For a glassy system finding the global minimum is slow because one has to explore energetic regions with a large density of minima whose energies are very similar. For a structure seeker, on the other hand, the energy goes down rapidly and by significant amounts as one approaches the ground state. Only for these latter systems, it is to be expected that synthesis pathways can be found.

Our work thus clearly shows that theoretical cluster structure prediction has to be based on global geometry optimization because only this approach gives the necessary information on the potential energy landscape. The standard approach based on structures, obtained from educated guesses, that were subsequently locally relaxed, gives only a very incomplete characterization of a system. A ground state structure predicted by global geometry optimization has a reasonable chance of being found in nature in significant quantities only if it is (a) at the bottom of a broad and deep funnel, (b) is significantly lower in energy than the other low energy metastable structures and (c) has high symmetry.

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