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Low-energy boron fullerenes: Role of disorder and potential synthesis pathways

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We show by means of first-principles calculations that in boron nanostructures a large variety of two-dimensional structures can be obtained, all with similar energetic properties. Some of these new structures are more stable than both the B_{80} fullerenes initially proposed by Szwacki *et al.* [Phys. Rev. Lett. **98**, 166804 (2007)] and boron nanotubes. At variance from other systems like carbon, disordered configurations are energetically comparable with ordered ones. Cage-like structures that are not ordered are thus comparable in energy to the more ordered original B_{80} fullerene. A comparison with other more disordered structures like bulk-like boron clusters is also presented. We found that in the presence of other seed structures (like Sc_3 or Sc_3N), some endohedral cage-like structures are energetically preferred over bulk-like clusters. This result opens a new pathway for the synthesis of the B_{80} fullerene as an endohedral fullerene as was done in the case of the C_{80} fullerene.

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Since the pioneering prediction of the existence of quasi-planar boron nanostructures,[1] a lot of work has been done to analyze the properties of these objects both from the theoretical and experimental points of view. In the past decade, both nanosheets,[2,3] and nanotubes[4] have been experimentaly observed, whereas boron fullerene cages have not yet been observed. In the case of the latter nanostructures, the "magic" stability of the B_{80} fullerene was recently assessed by means of density-functional theory (DFT) calculations.[5] This fullerene is of an icosahedral-type symmetry. However, its symmetry (Ih or Th) is still controversial and the object of debate.[6,7] The stability of this B_{80} fullerene was explained[8,9] by its similarity to the stable α boron sheet proposed by Tang and Ismail-Beigi.[10] The same α boron sheet,[11,12] or alternative sheets,[13,14] was used as a pattern for the theoretical design of other cage structures.

It is worth noting that while both B6 and B7 units (filled boron pentagons and hexagons, respectively) were predicted[1] to be building blocks of boron nanostructures, B7-based nanostructures were first found[2] while B6-based nanostructures were unknown until the recent work of Huang *et al.*[3] As a consequence, B6-based fullerenes (that is, with filled pentagons) have never been seen in relation to the proposed pure B7-based (that is, with only filled hexagons) B_{80} fullerene of Szwacki *et al.*[5] Filled pentagons have only been considered in bulk-like clusters called stuffed fullerenes.[15] However, the stuffing leads to a bulky pentagonal-based seven-atom unit (constitutive of the B_{84} building block of bulk boron[15]) rather than to a real pentagonal-B6 unit. The corresponding B_{101} cluster[15] was found to have a lower cohesive energy than the B_{80} fullerene of Szwacki *et al.*[5] The higher stability of such bulk-like boron clusters with respect to boron fullerenes has recently been confirmed for a B_{80} cluster.[16,17] However, the experimental evidence for the existence of both nanosheets[2,3] and nanotubes[4] implies the possiblity of growing some fullerene-like cages. For example, such structures might be stabilized by cutting single-wall nanotube slices as recently proposed for the SiC system.[18] Another possibily lies in the use of standard vaporization techniques,[2,3] which are already used to grow nanosheets, together with the addition of some seed that would favor the fullerene growth around it, leading an endohedral fullerene seed@B_{80}.

In this Rapid Communication we evaluate, by means of DFT calculations, the relative stability of B_{80} fullerenes that contain B6 units. Such isomers can be constructed (theoretically) from concerted boron diffusion at the surface of the original B_{80} structure. These "disordered" structures are then classified in terms of the nature of the elements by which they are constituted. Cage-like structures that are not ordered are comparable in energy to the more-ordered original B_{80} fullerene. A comparison with other more-disordered bulk-like boron clusters is also presented. We therefore have considered how the presence of other objects (like Sc_3 or Sc_3N) alters the configuration space of B_{80} cages in the spirit of the previously mentioned seed@B_{80} strategy. We have found that in the presence of such seed structures, some endohedral cage-like structures are energetically preferred over bulk-like clusters. This result opens a new pathway for the synthesis of the B_{80} fullerene as an endohedral fullerene as was done in the case of the C_{80} fullerene.[19] A discussion about the role of the disorder in other single-layered boron structures of lower dimensionality is then presented.

The DFT calculations are performed with the BigDFT code,[20] which uses a systematic wavelet basis set. The number of basis functions is chosen in such a way that our energy results per boron atom are accurate within 0.5 meV. Geometries are considered optimized when the forces on atoms are less than 2 meV/Å. Our calculations used the PBE exchange-correlation functional[21] and the Hartwigsen-Goedecker-Hutter pseudopotentials[22] in the Krack variant.[23] We have excluded the local density approximation functional due to its apparently less accurate description of nonplanar B_{18} and B_{20} boron clusters.[24]

Isolated boundary conditions are used both for the Kohn-Sham electronic orbitals and the calculation of the electrostatic Hartree potential.[25] Hence no supercell approximation is

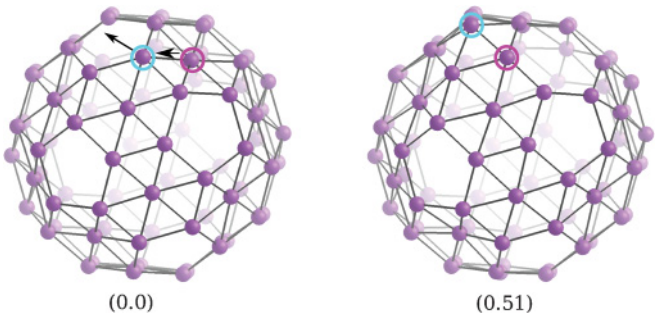

FIG. 1. (Color online) Transformation of $B_{80}^{20:0}$ into $B_{80}^{19:1}$. The numbers below the structures are the total energies (in eV) with respect to $B_{80}^{20:0}$. The two atoms involved in the transformation are highlighted.

needed. Unless otherwise stated, the energies of a given boron fullerene are given relative to the total energy of the B_{80} fullerene of Szwacki.[5] Barrier calculations have been performed using the "nudged elastic band" method as implemented in the BigDFT code.[20]

In the first publication on the B_{80} fullerene, a perfect icosahedral structure was proposed by Szwacki *et al.*[5] as the most stable cage structure based on boron. It consists of a B_{60} fullerene skeleton where all 20 hexagons have been filled by 20 additional boron atoms. This structure can be viewed as a spheroidal network of B7 units. In the same paper, the B_{72} fullerene corresponding to a network of B6 units was also considered. It consists of a B_{60} fullerene skeleton where all 12 pentagons have been filled by 12 additional boron atoms. In addition, the B_{92} fullerene where all pentagons and hexagons are filled was also considered. Both B_{72} and B_{92} were found to be less stable than the B_{80} fullerene. We can name these boron cages in terms of the number of filled hexagons and pentagons of the cage. Both B_{60} and B_{92} are extrema of the set of families that comes from this classification. Indeed, with this classification system, the B_{60} fullerene is made of 20 unfilled hexagons (UH) and 12 unfilled pentagons (UP) while the B_{92} fullerene is made of 20 filled hexagons (FH or B7) and 12 filled pentagons (FP or B6). The original B_{80} is composed of 20 FH and 12 UP. For B_{60+X} fullerenes $N_{\mathrm{FH}} + N_{\mathrm{FP}} = X$ and $N_{\mathrm{UH}} + N_{\mathrm{UP}} = 32 - X$, thus we will just label these cages by their numbers of FH and FP, that is, $B_{80}^{N_{\mathrm{FH}}:N_{\mathrm{FP}}}$, the fullerene of Szwacki *et al.*[5] being $B_{80}^{20:0}$. Of course, this classification can be used for other single-layered structures, for example, the α boron sheet studied in Ref. 10. In this study it has been discussed that the optimal FH to UH ratio $\zeta = 1/3$, which corresponds to the $\eta = 1/9$ value of the α boron sheet.[10] Clearly, for a given value of ζ, plenty of configurations are possible even on a small surface like that of B_{80}.

Interestingly, the presence of the disorder does not affect the energy of the structure in a systematic way. Indeed, if we start from the original $B_{80}^{20:0}$ structure we can introduce a FP defect through the reaction FH + UP → UH + FP. It corresponds to a $B_{80}^{19:1}$ fullerene depicted on the right-hand side of Fig. 1. Its total energy per atom is 6.3 meV higher than the initial $B_{80}^{20:0}$. A two-step process can be found to transform the original $B_{80}^{20:0}$ into this $B_{80}^{19:1}$ by only shifting atoms on the surface of the cage. The migration energy of such a process is found to be ∼1.75 eV. Both the total energy and the barrier to create

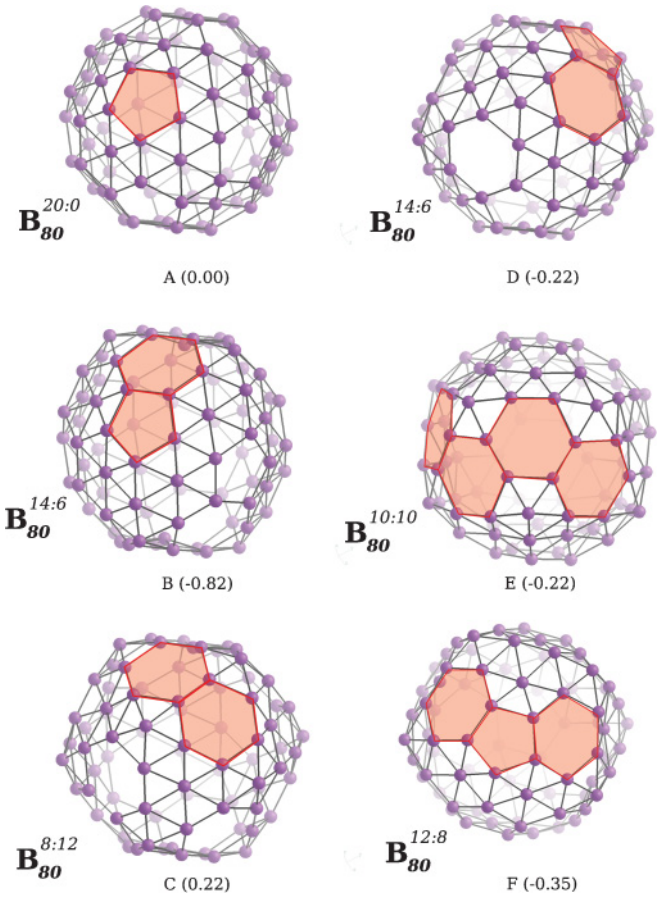

FIG. 2. (Color online) The original B_{80} fullerene proposed by Szwacki[5] labeled $B_{80}^{20:0}$ and five proposed B_{80} isomers: (i) two possible $B_{80}^{14:6}$ isomers (panels B and D) and a $B_{80}^{8:12}$ isomer (panel C) with unfilled pairs of rings (UP-UH or UH-UH), (ii) a $B_{80}^{12:8}$ isomer (panel E) and a $B_{80}^{10:10}$ isomer (panel E) with respect to quadruple and triple unfilled rings (UH-UH-UH-UH and UH-UP-UH) The total energies with respect to $B_{80}^{20:0}$ are reported in electron volts. The pattern of unfilled polygons is highlighted in red.

this FP-UH defect seem to be unfavorable to form such defects under ambient conditions starting from a $B_{80}^{20:0}$. However, if one repeats this transformation three times, the corresponding $B_{80}^{17:3}$ has a total energy per atom that is 0.7 meV *lower* than the initial $B_{80}^{20:0}$. Moreover, introducing three additional FP-UH defects in the $B_{80}^{17:3}$ leads to the stable $B_{80}^{14:6}$ (Fig. 2), which has a total energy per atom 10.2 meV *lower* than the initial $B_{80}^{20:0}$. Finally, by combining 12 times the UP → FP transformation, we end up with $B_{80}^{8:12}$ (Fig. 2) that exhibits the maximum number of possible FP-UH defects. Its total energy per atom is 2.7 meV *higher* than the initial $B_{80}^{20:0}$.

Thus, even if the isolated FP-UH defect is not thermodynamically favorable, some of their combinations lead to a negative binding energy. To show further evidence of this consideration, we have considered six different cage-like structures of B_{80}. In Fig. 2, we have considered $B_{80}^{20:0}$, $B_{80}^{14:6}$, and $B_{80}^{8:12}$ (panels A, B, and C) with also other less symmetric cages of types $B_{80}^{14:6}$, $B_{80}^{10:10}$, and $B_{80}^{12:8}$, respectively (panels D, E, and F). These cages are represented on the left-hand side of Fig. 2 together with their corresponding total energies. Most

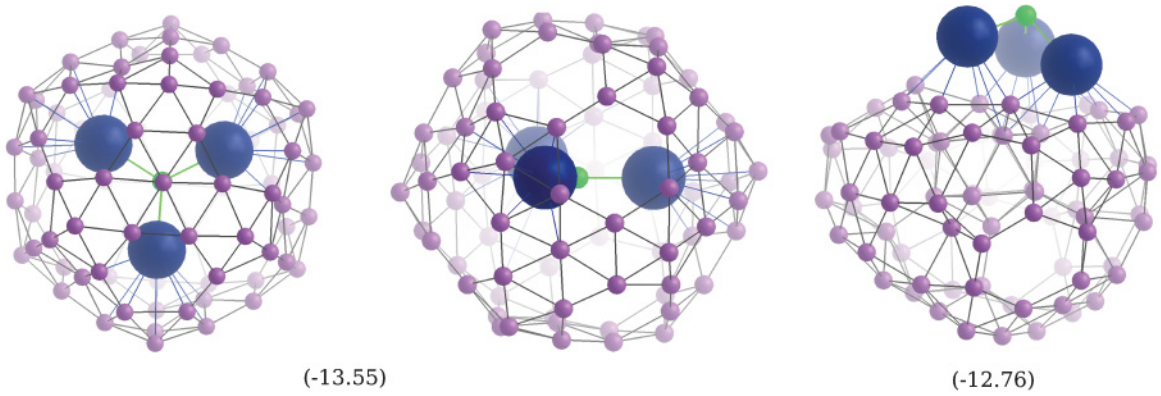

FIG. 3. (Color online) The stable $Sc_3N@B_{80}^{8:12}$ endohedral fullerene (from the top view in the left panel and the side view in the middle panel) and the $Sc_3N@/B_{80}^{Zhao}$ cluster (right panel). The Sc_3N is flat and well centered at the middle of the $B_{80}^{8:12}$ fullerene cage, while it adopts an umbrella form when adsorbed on top of the B_{80}^{Zhao} cluster. The latter form is observed (not shown) for all systems with total energies higher than −13 eV (see Table I). The total energies with respect to $B_{80}^{20:0}$ and isolated Sc_3N are reported in electron volts.

of these cages are found to be more stable than the highly symmetric, "ordered," $B_{80}^{20:0}$.

Since disordered structures may be energetically favored over ordered ones, it is also important to compare the energy with a more disordered sector of the configuration space, that is, bulky clusters of no particular symmetry. As an example, we consider the cluster recently presented by Zhao *et al.*,[16] which will be denoted by B_{80}^{Zhao} in the following. It is found to have a total energy of −1.56 eV, considerably more stable than the previously considered cage-like structures. The situation appears thus to be drastically different from more common cases, for example, the isoelectronic C_{60} system. In this case the most symmetric configuration (C_{60} fullerene) is at the same time a cage and by far the lowest in energy. Less symmetric structures are always less favorable since the fullerene structure is the only one in which all C atoms have pure $sp2$ bonds and all the carbon UP isolated from each other. This situation cannot be verified in boron structures: first of all, at variance from carbon, FP and FH also exist with UP and UH. This fact multiplies the number of possible defects that a cage (more generally, a single-layered structure) may have, without simplifying energetic considerations. Moreover, there is no preferred bonding structure. For example, the competition between two-center and three-center bonds of boron has been already pointed out in Ref. 10. As a matter of fact, bulky structures may have the same energy as cages. This means that the "amorphous" sector of the configuration space of boron should also be considered while thinking of synthesis processes of cages, and it cannot be excluded by simple energetic considerations. Nonetheless, a cage is topologically different from a cluster, and we may wonder whether the possibility of somehow "protecting" the cage-like sector of the B_{80} configuration space exists.

Such a mechanism might be obtained using standard techniques such as those used to grow endohedral carbon fullerenes.[19,26,27] From these papers one can learn that the size of the bare fullerene is a key parameter in determining which possible clusters can be encapsulated inside. The measured diameter of all B_{80} isomers (8.30, 8.36, and 8.43 Å) allows one to stuff them with the same clusters used in the case of the C_{80} or C_{82} fullerenes (≃8.2 Å), for example, with several Sc atoms[26,27] or with trimetallic nitride cluster.[19] To evaluate this hypothesis we have calculated the formation energy of the B_{80} fullerene with three additional Sc atoms inside or with an Sc_3N cluster inside (Table I). We have also considered the absorption of such a cluster on the surface of the stable B_{80}^{Zhao} cluster. As an example, we consider the cages that have up to two unfilled elements close to each other (UP-UH or UH-UH pairs), that is, panels A through D of Fig. 2. The endohedral fullerenes $3Sc@B_{80}^{8:12}$ and $Sc_3N@B_{80}^{8:12}$ (see Fig. 3) are found to be the minimum of each series (Table I). The stability of the bare bulky-like B_{80}^{Zhao} is thus reverted in the presence of Sc clusters. The stabilization upon electron doping of these icosahedral B_{80} fullerenes is similar in several aspects to the C_{80} fullerene situation. For this C_{80} fullerene, the isomer with an icosahedral symmetry Ih is not synthetizible as a bare fullerene. Instead other isomers with lower symmetries are produced. However the introduction of different electron donors during the synthesis process allow its stabilization into this Ih symmetry.[19] This comparison strongly supports the proposed synthetisation pathway for the B_{80} fullerene as an endohedral fullerene, for example, with trimers of Sc atoms or Sc_3N clusters. In this way, the topological "protection" of the cage-like section, related to the fact that the seed is *inside* the cage, is also strengthened by the energetic convenience of an endohedral cage with respect to a bulk-like cluster with the seed in its surroundings.

From the previously mentioned results concerning the effect of disordered patterns in B_{80} fullerenes, we can speculate that "disordered" boron nanotubes might be more stable than

TABLE I. Total energies for different locations of Sc-based clusters inside (@) the three considered B_{80} fullerenes or on (/) the bulky-like B_{80}^{Zhao} cluster. Energies (in electron volts) are measured with respect to the energy of the $B_{80}^{20:0}$ cage plus the energy of the added elements (Sc_3N or Sc_3 clusters, respectively). The lowest energy configuration for each type of cluster is highlighted in bold.

	$B_{80}^{20:0}$ (A)	$B_{80}^{14:6}$ (B)	$B_{80}^{8:12}$ (C)	$B_{80}^{14:6}$ (D)	B_{80}^{Zhao}
$3Sc + B_{80}$	−14.67	−17.05	**−18.86**	−17.62	−17.55
$3ScN + B_{80}$	−9.89	−11.81	**−13.55**	−13.10	−12.76

the ordered boron nanotubes derived from the α boron sheet proposed by Tang and Ismail-Beigi.[10] This might explain the discrepancy[8] between the predicted breathing mode frequency of such ordered nanotubes and the one detected in the Raman spectra of the 3-nm grown nanotube.[4] This breathing mode frequency has been predicted[8] using an extrapolation of the elastic behavior (stiffness and Poisson's ratio) of small ordered nanotubes ($d \leqslant 1.65$ nm). Even at fixed ζ, the number of possible configurations will increase with the radius of the nanotube whereas there is only one possible structure in the case of maximally ordered nanotubes. Thus one would have to directly consider the 3-nm nanotube and find the global minima in the configuration space of $\zeta = 1/3$. Still, the configurational disorder introduced by the presence of FP, FH, UP, and UH at the same time will clearly result in a broadening of the breathing mode frequency of such nanotubes. The study of such large nanotubes via DFT approach is beyond the scope of the present paper.

To summarize, we have shown in this Rapid Communication that in boron nanostructures, energetically preferred configurations are not necessarily ordered. Rather, the electronic properties of boron are so flexible that it is almost impossible to find patterns in the configuration space that can be considered protected by energetic considerations alone. This is much more important if one takes into account entropic effects on these structures.[17] This suggests that the configuration space of boron nanostructures has some features that are rather different from other systems like carbon. A more detailed study of these differences can be found in Ref. 28. For the B_{80} fullerene, we found some ways to protect the cage-like sector of the configuration space against the formation of bulky structures. This fact opens new possible pathways for the synthesis of the B_{80} fullerene as an endoheral fullerene in a way similar to the case of the C_{80} fullerene.[19]

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