Boron aggregation in the ground states of boron-carbon fullerenes

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We present unexpected structural motifs for boron-carbon nanocages of the stoichiometries $B_{12}C_{48}$ and $B_{12}C_{50}$, based on first-principles calculations. These configurations are distinct from those proposed so far because the boron atoms are not isolated and distributed over the entire surface of the cages, but rather aggregate at one location to form a patch. Our putative ground state of $B_{12}C_{48}$ is 1.8 eV lower in energy than the previously proposed ground state and violates all the suggested empirical rules for constructing low-energy fullerenes. The $B_{12}C_{50}$ configuration is energetically even more favorable than $B_{12}C_{48}$, showing that structures derived from the C_{60} buckminsterfullerene are not necessarily magic sizes for heterofullerenes.

Since its discovery by Kroto *et al.* in 1985 [1], the C_{60} fullerene has found a wide range of applications as a building block in the field of nanoscience. For instance, it is possible to directly form solids out of it [2] or to dope it by adding substitutional or endohedral atoms, e.g., in the context of hydrogen storage [3].

For future applications, it would be advantageous to have more such basic building blocks. One possibility is to modify the original carbon fullerene by substitutional doping. Boron and nitrogen are very popular choices for the dopant atoms since they are neighbors to carbon in the Periodic Table. Various boron-carbon heterofullerenes have been observed experimentally [4,5]. The existence of cross-linked $N_{12}C_{48}$ fullerenes could explain experimental measurements of thin solid films [6]. The case of boron is of particular importance as it is the *p*-type counterpart of the *n*-type nitrogen doping in fullerene and graphene used to tune their electronic or catalytic properties [7,8].

To determine the energetically most favorable structure, it is in principle necessary to perform a numerically costly unbiased global structure search, which became possible only very recently [9–12]. Previous work on heterofullerene cages was therefore based on biased searches that constrained the exploration of the energy landscape to certain structural motifs. For the stoichiometries B_nC_{60-n} this constraint typically consisted in starting the search from the perfect C_{60} fullerene and substituting *n* carbon atoms by boron. Garg *et al.* [13] extensively investigated the geometries B_nC_{60-n} for *n* = 1–12. They concluded that the boron is arranged such that a pentagon ring does not contain more than one and a hexagon not more than two boron atoms (at nonadjacent sites). Putting more boron atoms in a ring increases the bond lengths and decreases the stability. A study by Viani and Santos [14] on various smaller fullerenes again confirmed that boron atoms are most preferably situated at opposite sites in a hexagon, thereby increasing the bond lengths in their neighborhood. For the heterofullerene $B_{12}C_{48}$, which will be one of the two stoichiometries investigated in this paper, Manaa *et al.*

[15] performed a detailed study; they claimed that the best structure was the same as the one previously found for $N_{12}C_{48}$ [16], thereby again confirming the previous results stating that the boron atoms should be spread over the entire carbon cage and isolated. We will refer to this class of structures as "diluted."

We reinvestigated the boron-carbon heterofullerenes by performing a systematic and unbiased search for low-energy minima for the stoichiometries $B_{12}C_{48}$ and $B_{12}C_{50}$.

The minima hopping method [12] (MHM) was used for our unbiased search of new configurations. It can efficiently find low-energy structures by exploiting the Bell-Evans-Polanyi principle for molecular dynamics [17]. All calculations were done at the level of density functional theory using the BIGDFT package [18]. This code uses Daubechies wavelets [19] as a basis set and Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials [20,21] to simulate the core electrons. The exchange correlation part was described by the Perdew-Burke-Ernzerhof (PBE) functional [22], which has been shown to give highly reliable energy differences between different structural motifs in boron [23] and is therefore used [24] in this work. Convergence parameters in BIGDFT were set such that total energy differences were converged up to 10^{-4} eV and all configurations were relaxed until the maximal force component on any atom reached the noise level of the calculation, which was of the order of 1 meV/Å.

To speed up our exhaustive configurational search, we started both from diluted and aggregated configurations with a wide structural diversity, based on various C_n backbones (with *n* = 60, 58, or 48). For aggregated configurations, we considered both filled hexagons and filled pentagons as they were demonstrated to be the building blocks [25,26] in the B_{80} boron fullerene [27]; furthermore, we have inserted compact boron icosahedrons in opened C_{60} fullerenes. In addition, we generated structures of high symmetry for the stoichiometry C_{48} and added 12 boron atoms at locations where it seemed appropriate by intuition. Some short MHM runs starting from the energetically most promising configurations allowed us to see trends leading to an energy lowering. From these, a second set was derived by applying additional modifications (e.g., exchanging boron and carbon atoms) in order to speed

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up the exploration in a second step of MHM. Finally, we systematically exchanged boron and carbon atoms up to second-nearest neighbors for the most favorable structures emerging from this process. In this way, we could generate more than 1000 configurations containing a large variety of structural motifs.

Among our $B_{12}C_{48}$ structures obtained in this way, we found several being considerably lower in energy than the three most favorable ones identified by Manaa *et al.* [15] Whereas our configurations agree with theirs in the overall shape exhibiting a cagelike structure, they differ substantially by the fact that the boron is not distributed over the entire cluster, but aggregated in a patch, thereby separating the surface of the compound in a boron-rich and a boron-poor part. This is in strong contrast to the widely accepted belief that the boron atoms should be isolated [8,13–15,28–33], i.e., be always separated by one or several carbon atoms. We will refer to our structural motif as "patched."

The low-energy part of the spectrum that we have explored is shown in Fig. 1, together with the structures of the 12 lowest isomers that we have found, the lowest structure exhibiting a filled pentagon (no. 27) and the three most favorable diluted structures (nos. 144, 295, and 453). The latter turned out to be identical to the three lowest structures identified by Manaa *et al.* In total, we found 143 structures that are lower in energy than the putative ground state proposed so far. We made, however, no effort to find all the structures in this energy interval, and so more than 143 structures are expected to exist. The energy levels are colored on a scale from 0 to 1 which describes the relative amount of carbon atoms being first neighbors to boron. Thus a value of 0 (red) means that the boron atoms are only surrounded by boron—which can obviously not happen—whereas a value of 1 (blue) means that the boron atoms are only surrounded by carbon. Consequently, the coloring of the patched structures tends toward red values, while the coloring of the diluted ones tends toward blue values. In the lowest structures, the boron atoms form a patch with frayed boundaries, which results in astonishing configurations where carbon atoms have four boron atoms as first neighbors. Furthermore, it is surprising that the lowest structure exhibits a heptagon, which is usually less favorable than the pentagons and hexagons, and twice two adjacent pentagons, which is in general very disadvantageous [34]. However, these pentagons not only consist of carbon, but there are some substitutional boron atoms contained within them as well. A detailed analysis shows that there is a fair delocalization of the charge within the boron patches; this is also characteristic of aromatic systems which are known to exhibit a particularly high stability. (See the Supplemental Material in Ref. [42].) Furthermore, for the putative ground state, we can observe the same delocalization, but there is in addition a strong concentration of the charge on those carbon atoms that are surrounded by four boron atoms. Since this pattern is present in all low-energy structures, it is expected to contribute considerably to the stability of these configurations.

Table I gives some more information about the structures shown in Fig. 1. The first column shows the energy separation ΔE of the configurations with respect to the lowest structure. One can see that our ground state is 1.8 eV lower in energy than the putative ground state proposed so far. In the second
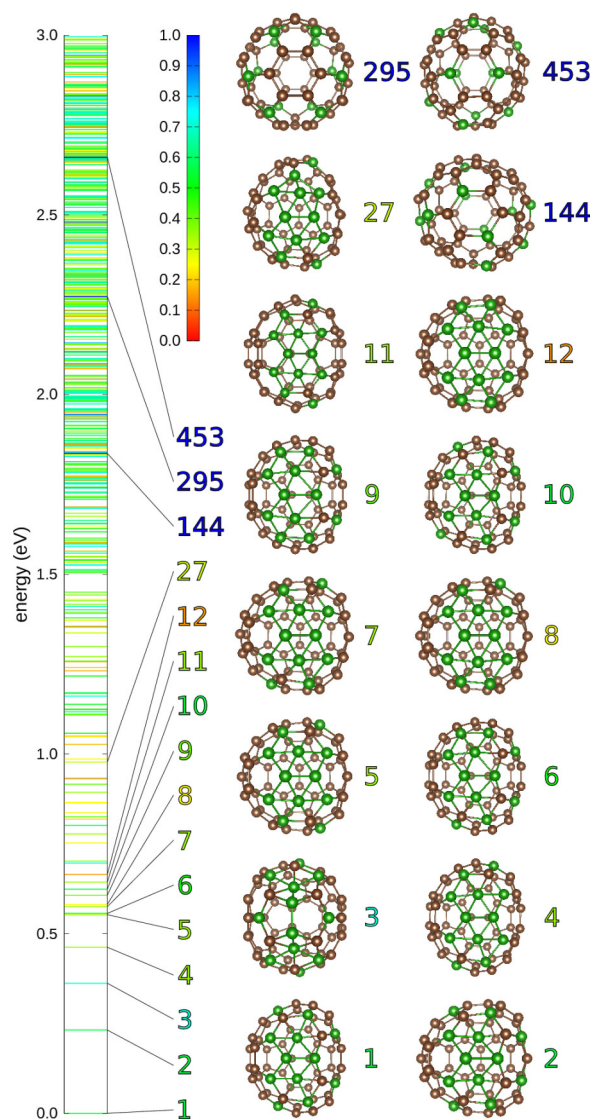

FIG. 1. (Color online) Plot of the 12 energetically most favorable structures, the most favorable one containing a filled heptagon and the three lowest diluted configurations for $B_{12}C_{48}$, together with the low-energy part of the spectrum. The coloring scheme is explained in the text.

column, we present the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gaps of the structures. The values range from 0.2 to 0.7 eV, thus being rather small, and they do not exhibit any special pattern. In particular, there is no notable difference between the class of the patched and the diluted structures. The fact that the lowest structure does not exhibit the largest gap might be unexpected, but is also found in numerous other systems such as in Ref. [35].

The next column shows the formation energies per atom ΔH with respect to the bulk conformations of boron and carbon (α-boron and cubic diamond, respectively), which are defined by $\Delta H = (E - n_B E_B^0 - n_C E_C^0)/(n_B + n_C)$, with E being the energy of the compound and E_X^0 and n_X being the energy per atom of the reference configurations and the number of atoms, respectively. In the next column, we give

TABLE I. Properties of the structures shown in Fig. 1.

	ΔE (eV)	Gap (eV)	ΔH (eV)	PG	RMSD (bohr)
1st	0.000	0.457	0.340	C_s	0.000
2nd	0.232	0.477	0.344	C_s	1.003
3rd	0.362	0.646	0.346	C_s	1.717
4th	0.462	0.645	0.348	C_1	1.092
5th	0.553	0.295	0.350	C_s	1.589
6th	0.557	0.236	0.350	C_1	0.558
7th	0.575	0.247	0.350	C_1	1.486
8th	0.582	0.452	0.350	C_1	1.579
9th	0.607	0.604	0.350	C_s	0.783
10th	0.624	0.378	0.351	C_1	0.533
11th	0.644	0.616	0.351	C_s	1.344
12th	0.665	0.644	0.351	C_s	1.490
27th	0.978	0.695	0.357	C_1	1.678
144th	1.836	0.494	0.371	S_6	3.465
295th	2.273	0.316	0.378	D_{3d}	3.501
453th	2.661	0.302	0.385	S_6	3.442

the point groups (PG) of the structures. Whereas the diluted structures are rather symmetric (point groups S_6 and D_{3d}), the new structures are of much lower symmetry (C_s and C_1). Finally, we present the root mean square distance (RMSD) [36] of the structures with respect to the new putative ground state, which is defined as the global minimum over all translations, rotations, and permutations of all the identical species among the N atoms of structure $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ with respect to the ground state $\{\mathbf{r}_1^0, \dots, \mathbf{r}_N^0\}$: $\text{RMSD} = \frac{1}{\sqrt{N}}\sqrt{\sum_{j=1}^{N}(\mathbf{r}_j - \mathbf{r}_j^0)^2}$. It is obvious that there is a clear separation between the patched structures and the diluted ones. Within the patched ones, however, there is no relation between the energy and the RMSD.

A more complete overview of the energies and the corresponding RMSD values is shown in Fig. 2. Here we plot for all structures up to 8 eV the energy difference and the RMSD with respect to the putative ground state. As can be seen, there is a broad range with favorable structures whose energies are completely uncorrelated to the value of the RMSD. However,
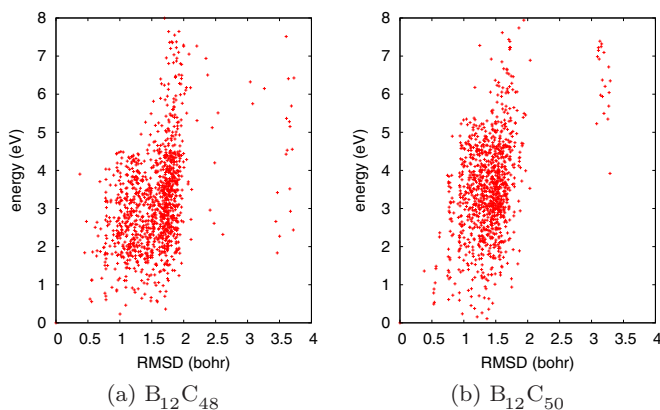
this range is sharply bounded at a value of about 2 bohr, separating it from energetically higher configurations.

By filling the heptagon in the putative ground state of $B_{12}C_{48}$ by two carbon atoms—thus modifying it into a pentagon and a hexagon—the two adjacent pentagons which are present twice on both sides of the heptagon are turned into a pentagon and a hexagon each. Since this structure consists only of pentagons and hexagons and furthermore respects the isolated pentagon rule, it is a promising candidate for the global minimum of the stoichiometry $B_{12}C_{50}$.

To confirm this assumption, we again performed an extended and unbiased search for the ground state. Once more we used several approaches to generate many different input structures: We added two atoms to the lowest isomers of $B_{12}C_{48}$ as described; we replaced ten carbon atoms by boron in a C_{60} and added two additional interstitial boron atoms at appropriate positions; and we replaced 12 carbon atoms with
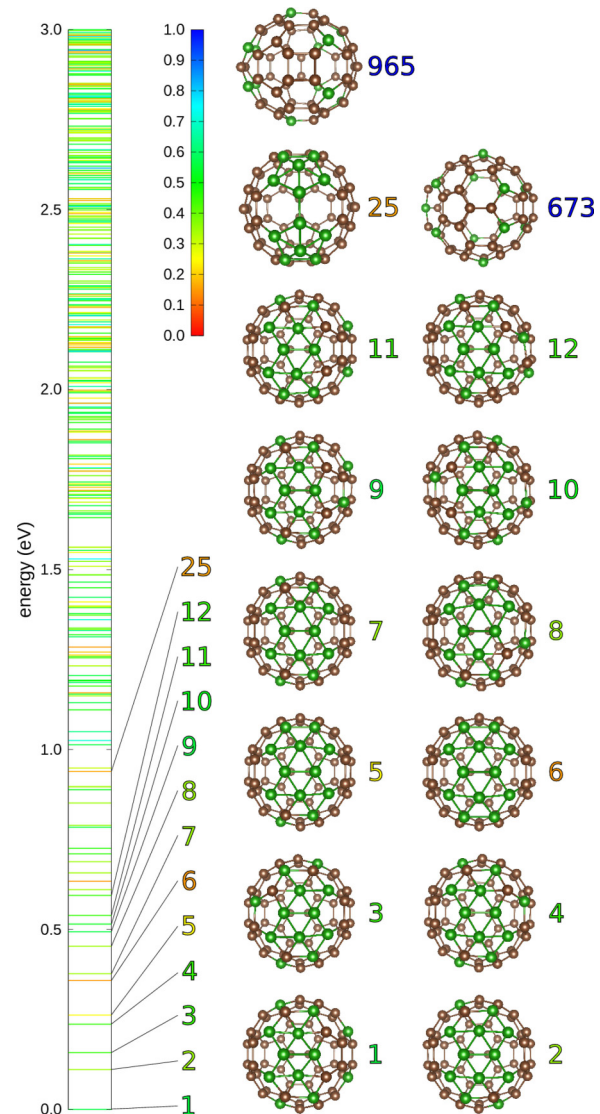

FIG. 2. (Color online) The energy difference vs the RMSD, both with respect to the putative ground states.

(a) $B_{12}C_{48}$

(b) $B_{12}C_{50}$

FIG. 3. (Color online) The low-energy part of the spectrum for $B_{12}C_{50}$, together with figures of the 12 energetically lowest structures, the most favorable one containing a filled pentagon and the two most favorable diluted configurations.

TABLE II. The same data as in Table I, this time for the structures shown in Fig. 3.

	ΔE (eV)	Gap (eV)	ΔH (eV)	PG	RMSD (bohr)
1st	0.000	0.534	0.322	C_s	0.000
2nd	0.110	0.416	0.324	C_2	1.363
3rd	0.158	0.434	0.325	C_1	1.209
4th	0.237	0.283	0.326	C_1	0.976
5th	0.262	0.338	0.327	C_1	1.285
6th	0.358	0.308	0.328	C_{2v}	1.390
7th	0.377	0.154	0.328	C_s	1.168
8th	0.453	0.215	0.330	C_1	1.113
9th	0.494	0.249	0.330	C_1	0.530
10th	0.515	0.380	0.331	C_1	1.451
11th	0.539	0.227	0.331	C_1	0.539
12th	0.595	0.363	0.332	C_1	0.931
25th	0.939	0.296	0.337	C_{2v}	1.750
673th	3.921	0.204	0.386	C_s	3.289
965th	5.227	0.458	0.407	C_s	3.080

boron starting from a C_{62} fullerene. For this last approach, we took two examples that were first described by Ayuela *et al.* [37] and Qian *et al.* [38] and turned out to be the most stable C_{62} isomers in a study by Cui *et al.* [39] As for the case of $B_{12}C_{48}$, we again continued by either manually rearranging the atoms or by using the configurations as input for subsequent MHM runs.

It turned out that the structure that we constructed by hand from the ground state of $B_{12}C_{48}$ is energetically the most favorable one. In addition, at least 673 patched structures are lower in energy than the most favorable diluted configuration, which is 3.9 eV higher in energy than our ground state. The low-energy part of the spectrum is shown in Fig. 3, together with figures of the 12 structures being lowest in energy, the most favorable one containing a filled pentagon and the two most favorable diluted configurations. The energy levels are coded in colors analogous to Fig. 1. As for the case of $B_{12}C_{48}$, it is clear that all low-lying minima correspond to the same structural motif where the boron is aggregated in a patch.

In Table II we present some more information about the structures shown in Fig. 3. The HOMO-LUMO gaps are—except for the few lowest structures—in general smaller

than the ones for $B_{12}C_{48}$; again there is no notable difference between the patched and the diluted structures. The values for the formation energy ΔH are slightly lower than their counterparts for $B_{12}C_{48}$ in Table I, indicating that it is more likely to encounter experimentally the stoichiometry $B_{12}C_{50}$ than $B_{12}C_{48}$. The point groups exhibit a wider variation compared to the case of $B_{12}C_{48}$; the energetically most favorable structures have the point groups C_1, C_2, C_s, and C_{2v}. On the other hand, the diluted structures are of lower symmetry than their counterparts for $B_{12}C_{48}$ and exhibit only the point group C_s. The RMSD behaves similar for $B_{12}C_{48}$. A more complete overview of the energy versus the RMSD—analogous to the one shown in Fig. 2—is given in Fig. 3. Both the last column of Table II and Fig. 3 show again a clear separation between the patched and the diluted configurations.

In conclusion, we have shown that the ground state of boron-carbon heterofullerenes is fundamentally different from what was thought previously. It consists of incomplete carbon cages whose openings are filled with boron patches. In a broader context, our results show that doping in sp^2 materials is not yet well understood and that no universally valid rules are available to predict which structural motifs are the most stable ones in such doped structures. Our results could also give guidance to synthesis efforts [40] for such heterofullerenes. The steep rise of the energy of metastable configurations as a function of the distance from the ground state shown in Fig. 2 indicates that there is a substantial driving force toward low-energy motifs with patches and suggests that a synthesis of patched structures should be possible. The energy gap between the ground state and the lowest metastable state (0.2 eV for $B_{12}C_{48}$ and 0.1 eV for $B_{12}C_{50}$) is, however, much smaller than in C_{60} (1.6 eV), and reaching the ground state might therefore be difficult. A synthesis procedure based on the substituting [5] of carbon atoms by boron atoms is unlikely to succeed for heterofullerenes containing a larger number of boron atoms which then form patches. Planar boron clusters that are structurally similar to the boron patches found in our ground state can, however, be synthesized experimentally [41] and might form growth nuclei for such heterofullerenes in a carbon-rich spark or vapor chamber.

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