Boron aggregation in the ground states of boron-carbon fullerenes

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We present novel structural motifs for boron-carbon nano-cages of the stochiometries $\mathrm{B}_{12}\mathrm{C}_{48}$ and $\mathrm{B}_{12}\mathrm{C}_{50}$, based on first principle calculations. These configurations are distinct from those proposed so far by the fact that 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 $\rm B_{12}C_{48}$ 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 $\rm B_{12}C_{50}$ 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.

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13 it by adding substitutional or endohedral atoms, e.g. in 14 the context of hydrogen storage [3].

For future applications it would be advantageous to 16 have more such basic building blocks. One possibility is 17 to modify the original carbon fullerene by substitutional 18 doping. A very popular choice for the dopant atoms are 19 boron and nitrogen since they are neighbors to carbon in 20 the periodic table. Various boron-carbon heterofullerenes 21 have been observed experimentally [4, 5]. The existence $_{22}$ of cross-linked $N_{12}C_{48}$ fullerenes could explain experi-23 mental measurements of thin solid films [6]. The case 24 of boron is of particular importance as it is the p-type 25 counterpart of the n-type nitrogen doping in fullerene 26 and graphene used to tune their electronic or catalytic properties [7, 8].

In order to determine the energetically most favorable structure, it is in principle necessary to perform a nu-30 merically 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 34 of the energy landscape to certain structural motifs. For 35 the stochiometries $B_n C_{60-n}$ this constraint typically con- $_{36}$ sisted in starting the search from the perfect C_{60} fullerene $_{37}$ and substituting n carbon atoms by boron. Garg et $_{38}$ al. [13] extensively investigated the geometries $\mathrm{B_{n}C_{60\text{-}n}}$ ₃₉ for n=1-12. They concluded that the boron is ar-40 ranged such that a pentagon ring does not contain more 77 figurations with a wide structural diversity, based on var-41 than one and a hexagon not more than two boron atoms 78 ious C_n backbones (with n=60, 58 or 48). For aggre-42 (at non-adjacent sites). Putting more boron atoms in a 79 gated configurations we considered both filled hexagons 43 ring increases the bond lengths and decreases the sta- 80 and filled pentagons as they were demonstrated to be the ⁴⁴ bility. A study by Viani and Santos [14] on various ⁸¹ building blocks [23, 24] in the B₈₀ boron fullerene [25];

Since its discovery by Kroto et al. in 1985 [1], the 46 most preferably situated at opposite sites in a hexagon, 10 C $_{60}$ fullerene has found a wide range of applications as a 47 thereby increasing the bond lengths in their neighbor-¹¹ building block in the field of nano-science. For instance ⁴⁸ hood. For the heterofullerene B₁₂C₄₈, which will be 12 it is possible to directly form solids out of it [2] or to dope 49 one of the two stochiometries investigated in this pa-50 per, Manaa et al. [15] performed a detailed study; they 51 claimed that the best structure was the same that was ₅₂ previously found for N₁₂C₄₈ [16], thereby again confirm- $_{53}$ ing the previous results stating that the boron atoms 54 should be spread over the entire carbon cage and isolated. 55 We will refer to this class of structures as "diluted".

> We reinvestigated the boron-carbon heterofullerenes 57 by performing for the first time a systematic and unbi- $_{58}$ ased search for low energy minima for the stochiometries 59 B₁₂C₄₈ and B₁₂C₅₀.

> The Minima Hopping Method (MHM) [12] was used 61 for our unbiased search of new configurations. All cal-62 culations were done at the level of Density Functional 63 Theory, using the BigDFT package [17]. This code uses 64 Daubechies wavelets [18] as basis set and HGH pseudopo-65 tentials [19] to simulate the core electrons. The exchange 66 correlation part was described by the PBE functional ₆₇ [20], which has shown to give highly reliable energy dif-68 ferences between different structural motifs in boron [21] 69 and is therefore used [22] in this work. Convergence pa-70 rameters in BigDFT were set such that total energy dif- $_{71}$ ferences were converged up to $10^{-5}\,\mathrm{Ha}$ and all configu-72 rations were relaxed until the maximal force component 73 on any atom reached the noise level of the calculation, 74 which was of the order of 1 meV/Å.

In order to speed up our exhaustive configurational 76 search we started both from diluted and aggregated con-45 smaller fullerenes again confirmed that boron atoms are 82 furthermore we have inserted compact boron icosahe $_{\rm 83}$ drons in opened $\rm C_{60}$ fullerenes. In addition we generated structures of high symmetry for the stoichiometry C_{48} $_{85}$ and added 12 boron atoms at locations where it seemed 86 appropriate by intuition. Some short MHM runs start-87 ing from the energetically most promising configurations 88 allowed us to see trends leading to an energy lowering. From these ones a second set was derived by applying additional modifications (e.g. exchanging boron and carbon 91 atoms) in order to speed up the exploration in a second 92 step of MHM. Finally we systematically exchanged boron and carbon atoms up to second-nearest neighbors for the 94 most favorable structures emerging from this process. In 95 this way we could generate more than thousand configurations containing a large variety of structural motifs.

Among our B₁₂C₄₈ 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 the new configurations agree with them in the overall shape exhibiting a cage-like structure, they differ 102 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 [26], i.e. be always separated by one or several carbon atoms. We will refer to our novel structural motif 109 as "patched".

The low energy part of the spectrum that we have explored is shown in Fig. 1, together with the structures 112 of the 12 lowest isomers that we have found, the lowest structure exhibiting a filled pentagon and the three most favorable diluted structures. The latter ones turned out to be identical to the three lowest structures identified by Manaa et al. In total we found 143 new structures 117 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 121 are colored on a scale from 0 to 1 which describes the 122 relative amount of carbon atoms being first neighbors to 123 boron. Thus a value of 0 (red) means that the boron 124 atoms are only surrounded by boron – which can obvi-125 ously 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 towards red values, while the coloring of the diluted ones tends towards blue values. In the lowest structures the boron atoms form a patch with frayed boundaries, which 131 results in astonishing configurations where carbon atoms have four boron atoms as first neighbors. Furthermore 139 135 hexagons, and twice two adjacent pentagons, which is in 142 the lowest structure. We can see that our new ground 136 general very disadvantageous [27]. However these pen- 143 state is 1.8 eV lower in energy than the putative ground 137 tagons do not only consist of carbon, but there are some 148 state proposed so far. In the second column we present 138 substitutional boron atoms contained within them.

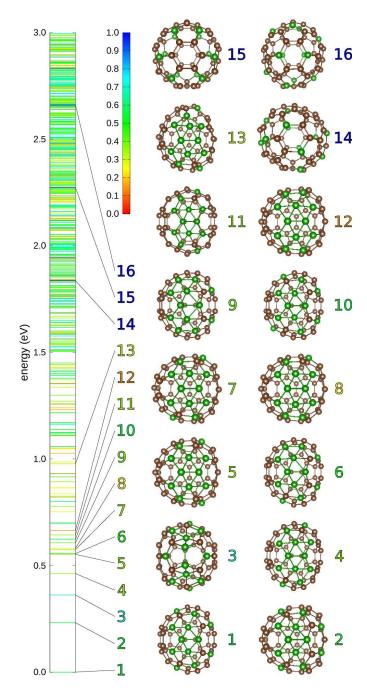


FIG. 1. Plot of the 12 energetically most favorable structures, the most favorable one containing a filled heptagon and the three lowest diluted configurations for $\mathrm{B}_{12}\mathrm{C}_{48},$ together with the low energy part of the spectrum. The coloring scheme is explained in the text.

Tab. I gives some more information about the strucit is surprising that the lowest structure exhibits a hep- 140 tures shown in Fig. 1. The first column shows the entagon, which is usually less favorable than the penta- and $_{141}$ ergy separation ΔE of the configurations with respect to 146 the HOMO-LUMO gaps of the structures. The values

	ΔE	gap	ΔH	PG	RMSD
	(eV)	(eV)	(eV)		(bohr)
1st	0.000	0.457	0.340	$C_{\rm s}$	0.000
2nd	0.232	0.477	0.344	$C_{\rm s}$	1.003
3rd	0.362	0.646	0.346	$C_{\rm s}$	1.717
4th	0.462	0.645	0.348	C_1	1.092
5th	0.553	0.295	0.350	$C_{\rm s}$	1.589
6th	0.557	0.236	0.350	C_1	0.558
$7 \mathrm{th}$	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	$C_{\rm s}$	0.783
10 th	0.624	0.378	0.351	C_1	0.533
11th	0.644	0.616	0.351	$C_{\rm s}$	1.344
12th	0.665	0.644	0.351	$C_{\rm s}$	1.490
$27 \mathrm{th}$	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

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

147 range from 0.2 eV to 0.7 eV, thus being rather small, 185 148 and do not exhibit any special pattern. In particular 186 formed an extended and unbiased search for the ground 149 there is no notable difference between the class of the 187 state. We again used several approaches to generate 150 patched and the diluted structures. The next column 188 many different input structures: We added two atoms to shows the formation energies per atom ΔH with respect 189 the lowest isomers of $B_{12}C_{48}$ as described; we replaced 153 and cubic diamond, respectively), which is defined by 191 tional interstitial boron atoms at appropriate positions; $_{154}$ $\Delta H = (E - n_B E_B^0 - n_C E_C^0)/(n_B + n_C)$ with E being $_{192}$ and we replaced 12 carbon atoms by boron starting from 155 the energy of the compound and E_X^0 and n_X being the 193 a C_{62} fullerene. For this last approach we took two ex-156 energy per atom of the reference configurations and the 194 amples that were first described by Ayuela et al. [29] and 157 number of atoms, respectively. In the next column we 195 Qian et al. [30] and turned out to be the most stable C₆₂ 158 give the point groups of the structures. Whereas the di- 196 isomers in a study by Cui et al. [31]. As for the case of $_{159}$ luted structures are rather symmetric (point groups S_{6} $_{197}$ $B_{12}C_{48}$ we again continued by either manually rearrang-160 and D_{3d}), the new structures are of much lower symme- 198 ing the atoms or by using the configurations as input for 161 try (C_s and C₁). Finally we present the RMSD [28] of the 199 subsequent MHM runs. $_{162}$ structures with respect to the new putative ground state. $_{200}$ It turned out that the structure that we constructed $_{163}$ It is obvious that there is a clear separation between $_{201}$ by hand from the ground state of $\mathrm{B}_{12}\mathrm{C}_{48}$ is energetically 164 the patched structures and the diluted ones. Within the 202 the most favorable one. In addition, at least 673 patched energy and the RMSD.

169 plot for all structures up to 8 eV the energy difference and 207 being lowest in energy, the most favorable one contain-170 the RMSD with respect to the putative ground state. As 208 ing a filled pentagon and the two most favorable diluted $_{172}$ energies are completely uncorrelated to the value of the $_{210}$ analogy to Fig. 1. As for the case of $\mathrm{B}_{12}\mathrm{C}_{48}$ it is clear that of about 2 bohr, separating it from energetically higher 212 motif where the boron is aggregated in a patch. configurations.

 $_{177}$ $\mathrm{B}_{12}\mathrm{C}_{48}$ by two carbon atoms – thus modifying it into a $_{216}$ – except for the few lowest structures – in general smaller 178 pentagon and a hexagon – the two adjacent pentagons 217 than the ones for $B_{12}C_{48}$; again there is no notable dif-179 which are present twice on both sides of the heptagon 218 ference between the patched and the diluted structures. ₁₈₀ are turned into a pentagon and a hexagon each. Since ₂₁₉ The values for the formation energy ΔH are slightly ₁₈₁ this structure consists only of pentagons and hexagons ₂₂₀ lower than their counterparts for $B_{12}C_{48}$ in Tab. I, in-182 and furthermore respects the isolated pentagon rule, it 221 dicating that it is more likely to encounter experimen-

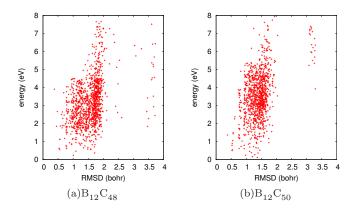


FIG. 2. The energy difference versus the RMSD, both with respect to the putative ground states.

183 is a promising candidate for the global minimum of the 184 stoichiometry $B_{12}C_{50}$.

In order to confirm this assumption we again perto the bulk conformations of boron and carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional conformations of boron and carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional conformations of boron and carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon atoms by boron in a C_{60} and added two additional carbon (lpha-boron $_{190}$ ten carbon (lpha-boron

patched ones, however, there is no relation between the $_{203}$ structures are lower in energy than the most favorable di-204 luted configuration which is 3.9 eV higher in energy than A more complete overview of the energies and the cor- 205 our ground state. The low energy part of the spectrum is responding RMSD values is shown in Fig. 2(a). Here we 206 shown in Fig. 3, together with figures of the 12 structures can be seen there is a broad range with structures whose 209 configurations. The energy levels are coded in colors in RMSD. However this range is sharply bounded at a value 211 all low lying minima correspond to the same structural

In Tab. II we present some more information about the By filling the heptagon in the putative ground state of 216 structures shown in Fig. 3. The HOMO-LUMO gaps are

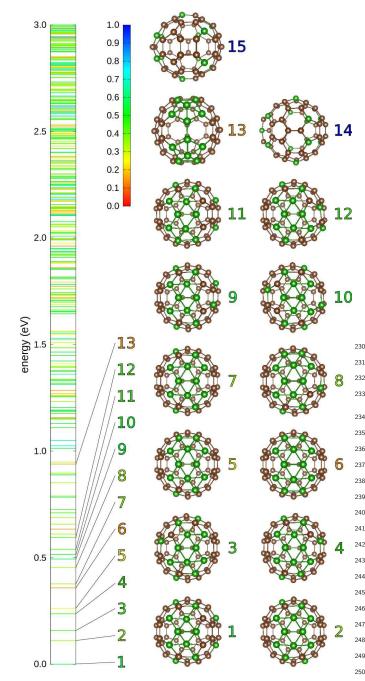


FIG. 3. The low energy part of the spectrum for $B_{12}C_{50}$, together with figures of the 12 energetically lowest structures, the most favorable one containing a filled pentagon and the 253 be difficult. The standard synthesis procedure of substitwo most favorable diluted configurations.

 $_{222}$ tally the stoichiometry $\mathrm{B}_{12}\mathrm{C}_{50}$ than $\mathrm{B}_{12}\mathrm{C}_{48}$. The point 223 groups exhibit a wider variation compared to the case of 224 B₁₂C₄₈; the energetically most favorable structures have $_{225}$ the point groups $\mathrm{C}_{1},\,\mathrm{C}_{2},\,\mathrm{C}_{s}$ and $\mathrm{C}_{2v}.$ On the other hand 226 the diluted structures are of lower symmetry than their $_{\rm 227}$ counterparts for $\rm B_{12}C_{48}$ and exhibit only the point group $_{\rm 262}$ ²²⁸ Cs. The RMSD behaves similar as for B₁₂C₄₈. A more ²⁶³ Computing time was provided by the CSCS and GENCI 229 complete overview of the energy versus the RMSD – anal- 264 (grant 6194).

	ΔE	gap	ΔH	PG	RMSD
	(eV)	(eV)	(eV)		(bohr)
1st	0.000	0.534	0.322	$C_{\rm s}$	0.000
2nd	0.110	0.416	0.324	C_2	1.363
3rd	0.158	0.434	0.325	C_1	1.209
$4 \mathrm{th}$	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
$7 \mathrm{th}$	0.377	0.154	0.328	$C_{\rm s}$	1.168
8th	0.453	0.215	0.330	C_1	1.113
9th	0.494	0.249	0.330	C_1	0.530
$10 \mathrm{th}$	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	$C_{\rm s}$	3.289
965th	5.227	0.458	0.407	$C_{\rm s}$	3.080

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

230 ogous to the one shown in Fig. 2(a) – is given in Fig. 2(b). 231 Both the last column of Tab. II and Fig. 2(a) show again 232 a clear separation between the patched and the diluted configurations.

In conclusion, we have shown that the ground state of 235 boron-carbon heterofullerenes is fundamentally different from what was thought previously. It consists of incomplete carbon cages whose openings are filled with boron 238 patches. In a broader context our results show that 239 doping in sp²-materials is not vet 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 [32] for such heterofullerenes. The steep rise of the energy of metastable configurations $_{245}$ as a function of the distance from the ground state 246 shown in Fig. 2 indicates that there is a substantial ²⁴⁷ driving force towards low energy motifs with patches and suggests that a synthesis of patched structures should 249 be possible. The energy gap between the ground state $_{\mbox{\tiny 250}}$ and the lowest metastable state $(0.2\,\mbox{eV}$ for $\rm B_{12}C_{48}$ and $_{251}$ 0.1 eV for $\mathrm{B_{12}C_{50}}$) is however much smaller than in $\mathrm{C_{60}}$ $(1.6\,\mathrm{eV})$ and reaching the ground state might therefore 254 tuting [5] carbon atoms by boron atoms is unlikely to 255 succeed for heterofullerenes containing a larger number 256 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 [33] and might form growth nuclei for such heterofullerenes in a carbon rich spark or vapor chamber.

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