Selecting Boron Fullerenes by Cage-Doping Mechanisms

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(Dated: 19 February 2013)

So far, no boron fullerenes were synthesized: more compact \( sp^3 \)-bonded clusters are energetically preferred. To circumvent this, metallic clusters have been suggested by Pochet et al. [Phys. Rev. B 83, 081403(R) (2011)] as “seeds” for a possible synthesis which would topologically protect the \( sp^2 \) sector of the configuration space. In this paper, we identify a basic pentagonal unit which allows a balance between the release of strain and the self-doping rule. We formulate a guiding principle for the stability of boron fullerenes, which takes the form of an isolated filled pentagon rule (IFPR). The role of metallic clusters is then reexamined. It is shown that the interplay of the IFPR and the seed-induced doping breaks polymorphism and its related problems: it can effectively select between different isomers and reduce the reactivity of the boron shells. The balance between self and exterior doping represents the best strategy for boron buckyball synthesis.

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I. INTRODUCTION

Boron analogues to carbon $sp^2$ structures usually take the form of compounds where an other element acts as an electron donor. In these structures, the B$^-$ anions behave like carbon atoms. This is the case of MgB$_2$, the boron analogue of graphite. For less extended structures this purely exterior doping can be unfeasible and impractical, e.g. giving 60 electrons to a boron buckyball is no simple task. Fortunately, simulations have shown that pure boron systems can partially overcome the low electron count on their own through self-doping. This mechanism explains the stability of small planar $sp^2$ clusters, the relative stability of the all boron $\alpha$-sheet and other structures. In contrast with carbon, these all-boron structures were also expected to display polymorphism and multi-center bonding thus allowing new behaviors for well-known structures. On this basis, the B$_{80}$ fullerene has attracted a lot of attention.

However, no boron fullerene were observed experimentally. Consequently, it was shown that other less symmetric bulk-like precursors, dubbed core-shell structures, are energetically preferred. Self-doping is thus insufficient to guarantee $sp^2$ bonding in extended boron. Nevertheless, it can be argued that synthesis of these systems remains possible if both self and exterior doping are present. Endohedral metallaborofullerenes were found to be energetically more stable than the corresponding core-shell clusters, suggesting a possible synthesis pathway which is very similar to the one used in the synthesis of endohedral carbon fullerenes. The recent observation of boron nanotubes inside Mg rich catalytic pores or on catalytic surfaces give even more weight to this scenario.

Yet, some problems would remain. The polymorphism of boron can also prove to be a problem since there would be no energetically motivated driving force towards some well-defined structure. A successful synthesis would lead to disordered structures which could negatively impact their characterization and properties. Furthermore, polymorphism is also related to high reactivity: endohedral boron fullerenes could still have the possibility of forming outward $sp^3$ boron structures by merging with other boron clusters during synthesis.

In our paper, we offer a critical reassessment of the role of doping in the boron fullerenes and show how it can overcome the above mentioned problems. We first rationalize the role of self-doping in the pure B$_{80}$ borofullerene. The different B$_{80}$ fullerene isomers are formed of a B$_{60}$ backbone with an additional 20 filling boron atoms, which can be placed in the
FIG. 1. Wannier functions representing the bonding pattern of a filled pentagon for the C$_3$ 17-3 isomer. The 3c-2e Wannier functions are represented in red and the 4c-2e Wannier functions are in blue. The neighboring filled hexagons are shaded to clarify the local environment. A schematic representation of this pentagonal environment is shown at the bottom right. This coloring scheme is reused in Figure 2.

center of hexagons or pentagons. These boron atoms act as dopants. We show that filled pentagons contribute to lower the global strain of the fullerene, but a specific type of local environment is necessary to satisfy the electron-counting issues arising from the self-doping rule for filled pentagons. Additionally, it will be shown that delocalized $\pi$ bond percolation (partial aromaticity) plays a stabilizing role in these isomers. All of these findings support the fact that, for these open-shell clusters, the pentagonal pyramids represent the crucial building block for the stability of the B$_{80}$ fullerenes. This leads us to formulate a generalized isolated filled pentagon rule (IPFR). Having understood the consequences of the strain and of self-doping in pure borofullerenes, we then focus on the role of exterior doping, i.e. charge transfer via endohedral centers (seeds) or anions. We show that exterior doping not only further stabilizes these clusters but also diminishes their reactivities. Furthermore, the overall polymorphism can be broken by the interaction with a seed. Hence, endohedral metalloborofullerenes possess all the required properties to overcome the known hurdles inhibiting borofullerene synthesis.
FIG. 2. The different $B_{80}$ isomers with increasing number of filled pentagons. They were chosen to exemplify the role of the filled pentagonal unit inside these structures. The different local environments of the filled pentagons which are present in each isomer are sketched below them along with their frequency. The colored sections of these sketches represent a neighboring filled hexagon. Also displayed is the energy difference ($\Delta E$ in meV) between the isomer and the $I_h$ 20-0, its HOMO-LUMO gap ($E_G$ in eV) and its average pyramidalization angle ($\Theta$).

II. METHODS

We use the Kohn-Sham approach to density-functional theory (DFT) as implemented in the BigDFT code\textsuperscript{36}, which uses a systematic real-space wavelet basis. We considered the basis converged when an accuracy of 0.5 meV/atom was reached for the total energy and 1 meV/Å for the forces. This corresponds to a uniform wavelet grid with a spacing of 0.4 bohrs with an extent of 11.5 bohrs for the coarse grid and 2.9 bohrs for the fine grid. The structural relaxations used the FIRE algorithm\textsuperscript{37} and were stopped when the forces were below 5 meV/Å. In addition HGH pseudopotentials\textsuperscript{38} in the Krack variant\textsuperscript{39} were used with isolated boundary conditions. Hence, no supercell approximation was needed.

Our calculations used the GGA-PBE\textsuperscript{40} exchange-correlation functional, which was shown to give the same energy organization as coupled cluster methods for small boron clusters.
(in contrast to other hybrid functionals\textsuperscript{21}. The GGA-PBE was also shown to yield more accurate results than LDA in these systems, even if some deviation from diffusion quantum Monte Carlo was seen\textsuperscript{21}.

The Wannier functions were extracted from the Kohn-Sham wavefunctions using the Wannier90 code\textsuperscript{32}. They were considered converged when the total spread varied by less than $10^{-12}$ Å$^2$. An initial projection on $sp^2$ functions located on the atoms and with the $z$ axis pointing along the radial direction was needed. In order to quantify the degree of strain inherent to each isomer, we have used the Pi Orbital Axis Vector (POAV2) method\textsuperscript{42} developed for carbon fullerenes. The POAV2 analysis of the structure was also done with a code developed for this purpose. The pyramidalization angle is defined as the mean deviation from perfect orthogonality between the $\sigma$ and $\pi$ orbitals. The multi-center bonding revealed by the Wannier analysis (or other local orbitals analysis\textsuperscript{15}) coupled to the high coordination number of boron atoms (5 or 6) adds some difficulties in the POAV analysis of these systems. Luckily, a study of the Wannier functions revealed that the filling atoms do not possess local orbitals with $\pi_z$ character. They thus literally behave as doping atoms which contributes $\sigma$ electrons in three 3c-2c bonds. Hence, there is no point in evaluating there $\pi$ misalignment. On the other hand, the backbone atoms do possess $\pi_z$ character and the POAV2 analysis was done only for these atoms. The still relatively high coordination of these atoms (5) did not pose a problem because the 3c-2e Wannier centers were located on the plane defined by the corresponding three atoms and thus using any of these atoms yields the same pyramidalization angle. Thus, for simplicity, only the backbone atoms were used for this analysis which reduced the effective coordination to three.

In order to be concise, we do not discuss the pseudo-Jahn-Teller distortion\textsuperscript{43} which was found to yield a slightly more stable $T_h$ 20-0 fullerene. This distortion has no impact on the conclusion of this work. The associated puckering of the filling atoms does not impact the global pyramidalization angle because they are alternatively moved inside and outside the structure. Alternatively, this distortion can be understood in the IFPR since for the 20-0 structure the filling atoms are the most reactive sites. In the rest of the text, the fullerenes are referenced according to their symmetry and their number of filled hexagons and pentagons\textsuperscript{19}. For example, the first proposed fullerene\textsuperscript{19} becomes the $I_h$ 20-0 and the volleyball structure\textsuperscript{19} becomes the $T_h$ 8-12.
III. RESULTS AND DISCUSSION

A. Effect of filled pentagons on pure borofullerenes

In the fullerene structure, the role of the pentagons is to allow for curvature by increasing the pyramidalization of its corners. Hence, most of the strain is stored in the pentagons. In carbon, this leads to the isolated pentagon rule (IPR) which is a rather strong requirement on the stability of pure neutral carbon fullerenes. In the boron fullerenes, the pentagons essentially play the same role. The only caveat is that the filling boron atoms can be placed to lower the global strain of the fullerene by increasing their pyramidalization angle. Since these atoms serve mostly as dopants they are not constrained to a $sp^2$ bonding pattern, in a way reminiscent of the carbon atoms in $\eta^2$-complexes of carbon fullerenes, and they do not contribute to the strain. The strain is characterized by the average pyramidalization angle (see Methods) and is presented in Figure 2. As can be seen, the inclusion of filled pentagons always releases strain and the energetically preferred structure ($D_{3d}$ 14-6) sports the smallest angle of all the isomers.

Nevertheless, not all the isomers are stabilized when compared to the $I_h$ 20-0. Indeed, the position of the 20 filling atoms with respect to the 60 atoms backbone cage appears to be crucial. They should be distributed such that the self-doping rule for boron $sp^2$ systems is satisfied: filled rings should be bordered by alternating filled and empty neighbor rings. Of course, this cannot be realized for the filled pentagons and they will thus inevitably be frustrated. The most stable local environment for filled pentagons, presented in Figure 1, is the closest one can find to the self-doping requirement: almost all backbone atoms contribute half their electrons to the pentagon, except the atom located at the junction of the two filled neighbors which contributes only one. This atom has a coordination number of six, instead of a coordination of five which is normally found in the backbone. It thus behaves more like a dopant atom than like a backbone atom and we can see this side of the pentagon has three inter-penetrating filled-hexagons (see supplementary information). It is this boron atom which sports the largest pyramidalization angle but because of its almost dopant nature, it does not contribute to the strain.

These two considerations (strain and self-doping) explain the total energy differences observed in Figure 2. The inclusion of only one or two filled pentagons always results in a
FIG. 3. Schlegel diagrams with superposed Wannier states for the $Ih$ 20-0 and both $C_{3v}$ 14-6 structures. The 3c-2e bonds are in red and the 4c-2e bonds are in blue. The delocalized $\pi_z$ bonds are displayed in green on the right panels. For clarity, the filling atoms are shown as big purple circles. The $Ih$ 20-0 is formed of alternating 3c-2e bonds and 4c-2e bonds in the same Kékulé structure then the one observed in $C_{60}$. In the case of the $D_{3d}$ 14-6, we can see a complete percolation of the $\pi_z$ states on the equator. For the $D_{3d}$ 14-6(B), the $\pi_z$ states span out of the poles in three lightning shaped arms that do not meet.

destabilized fullerene because the self-doping rule cannot be achieved. The first stabilized fullerene is the $C_3$ 17-3, where the three-filled pentagons are clustered around one hexagon which becomes the pole of symmetry. All other stabilized structures, are completely formed of pentagons with the same local environment, except the $D_{3d}$ 10-10 which also possess other types of pentagons but which are placed to complement each other. This demonstrates that such an environment is the most stable for the $B_{80}$ and that the increased stability in these isomers stems mostly by global release of strain as denoted by their decreased average pyramidalization angles. This balance between strain and electronic issues form a generalization of the IPR, which we call the isolated filled pentagons (IFPR) rule, in the borofullerenes.
B. Partial aromaticity and reactivity

To quantify the \(sp^2\) character of the cages, we perform a decomposition of its orbitals in terms of localized bonds via the Wannier transformation\(^{32}\) (see Methods section). The Kékulé bonding pattern found in the original \(Ih\) 20-0 is similar to the one found in \(C_{60}\) except for the multi-center character of the bonds: there is a double four-center-two-electron (4c-2e) \(\sigma\)-bond located between two adjacent filled-hexagons and a three-center-two-electron (3c-2e) \(\sigma\)-bond located on the edge of the empty pentagons, as seen on the Schlegel diagrams of Figure 3. This is also similar to the bonding pattern found in the boron \(\alpha\)-sheet\(^{15}\), with one notable exception: the \(\pi_z\) states are now partly localized inside the double 4c-2e bonds. This lowering of the aromaticity\(^{33}\) further destabilizes fullerene structures with respect to their planar counterparts.

For the other isomers, the bonding pattern of the filled pentagons slightly changes because of the differing symmetry, i.e. not all surrounding hexagons are necessarily equivalent. Nevertheless, a Wannier analysis shows that most states remain the same. Notable changes stems from local release of strain which are associated to the presence of strongly delocalized \(\pi_z\) 7c-2e states. As can be seen in Figure 3 in the \(D_{3d}\) 14-6 these delocalized \(\pi_z\) electrons percolate around the equator of the isomer. This equatorial aromaticity is analogous to the one observed in \(C_{70}\), albeit weaker: the equatorial angles are of 10.5\(^\circ\) for this isomer while they are of 8.75\(^\circ\) for \(C_{70}\). Consequently, the atoms of the equator are thus expected to be less reactive than their \(Ih\) 20-0 counterparts. At the same time, other sections of this isomer seem far more prone to reactions. The chemical hardness, determined by the HOMO-LUMO gap, can be used on the DFT level as a good representation of the reactivity trends in these isomers. Furthermore, the local strain coupled with the atomic contributions to frontier orbitals was shown to yield accurate reactivity maps for convex clusters\(^{34}\). The local strain on the backbone atoms of the poles (11.92\(^\circ\)) is larger than for the \(Ih\) 20-0 (11.46\(^\circ\)) which leads to a higher strain activated reactivity. The non-degenerate LUMO level of this isomer is also located near these atoms suggesting that they indeed represents the preferred sites for reduction reactions.

One can thus wonder if a different distribution of the same number of filled pentagons can lead to a decreased reactivity while maintaining the global release of strain. The IFPR suggests that this is not possible because release of global strain is associated with its
local increase in some zone of the structure. Thus increased stability comes at the price of increased reactivity. This is demonstrated within a second D$_{3d}$ 14-6(B) isomer. This structure is formed with exactly the same pentagonal environment but the filled pentagons now lie on the equator. This corresponds to the maximally separated uniform distribution of filled pentagons. In this case, both the global pyramidalization angle (11.35°) and the minimal angle (10.60°) are higher than the ones of the D$_{3d}$ 14-6. Now, its HOMO-LUMO gap is almost five times higher suggesting a much lower reactivity. An inspection of its doubly degenerated LUMO reveals that it is now delocalized on the equator, suggesting that it possesses less specific reactive sites. The same kind of delocalized π$_z$ electrons is seen in this isomer, but because of the new pentagonal arrangement, they are this time arching from the poles in three lightning shaped arms that terminate on the filled pentagons (represented in the lower right section of Figure 3). This points to a lower reactivity of the poles. These π$_z$ states do not percolate leading to a lower resonance energy then the D$_{3d}$ 14-6. The increased strain and reduced resonance energy explain the energy difference between the two 14-6 isomers.

C. Exterior v.s. self-doping

Having identified the consequences of strain and self-doping, we can now address the influence of exterior doping, i.e. the interaction with non boron atoms. As mentioned earlier, metallic clusters are envisioned to act as growth centers for endohedral metalloborofullerenes. The induced stabilization of each endohedral isomer will depend greatly on the nature, symmetry and orientation of the seed. Thus, the identification of a good candidate for

|                       | Sc$_3$N@B$_{80}$ | B$_{80}^{-2}$ |
|-----------------------|------------------|--------------|
|                       | ΔE [eV] | $E_G$ [eV] | ΔE [eV] | $E_G$ [eV] |
| Ih 20-0               | -10.859 | 0.592      | -3.563 | 0.132      |
| D$_{3d}$ 14-6         | -10.973 | 0.229      | -4.591 | 0.550      |
| D$_{3d}$ 14-6(B)      | -12.976 | 0.385      | -4.286 | 0.175      |

TABLE I. Binding energies and HOMO-LUMO separation for the endohedral Sc$_3$N@B$_{80}$ fullerene and the B$_{80}^{-2}$ ion. Binding energies are measured with respect to the energy of the pristine cage (plus the energy of the added cluster).
synthesis would necessitate a complete zoology of metallic clusters coupled with their effect on different isomers. This is beyond the scope of this paper. We will rather focus on the general effects of the inclusion of the metallic clusters on the pentagonal unit, by considering two basic examples: the Sc$_3$N cluster and the B$_{80}^{-2}$ anions.

As can be seen in Table I, all isomers are stabilized by the inclusion of the Sc$_3$N “seed”.

For the I$_h$ 20-0, we find that the nitrogen atom departs from the plane formed by the Sc to form a covalent bond with a filling boron atom, thus reproducing the results of Peng et al.\textsuperscript{26} This is consistent with the reactivity picture described by the LUMO and the strain. A Bader analysis of the electron density reveals that the Sc atoms have lost 1.5 electrons while the N atom gained 2.5 electrons. This corresponds to a net transfer of 2 electrons to the boron system. A Jahn-Teller deformation is observed at this filling since the LUMO of the I$_h$ 20-0 is threefold degenerate. This reduces the symmetry of the system to $C_1$ leading to a decrease of the HOMO-LUMO gap of the system to 0.592 eV. The global pyramidalization angle remained the same (11.46°) showing that the endohedral cluster in the I$_h$ 20-0 do not impact the global strain. Since the symmetry is decreased, there is now a greater scatter in the local strain leading to some preferred reactive sites which are located close to the N-B bond.

In the D$_{3d}$ 14-6 isomers, things are quite different. The metallic cluster adopts a quasi-planar structure which places itself on the plane containing the equator. This shows that no covalent bonds between the cluster and the fullerenes are formed, which is confirmed by the electronic density. This also agrees with the previous reactivity picture: the LUMO of these systems is formed of backbone $\pi_z$ states. Interior covalent bonding with these atoms is therefore unlikely: it inevitably leads to an increase of the global strain which greatly destabilizes these states. This is the origin of the “topological” protection invoked in the literature\textsuperscript{20}. Nevertheless, the global pyramidalization angle of the D$_{3d}$ 14-6(B) was greatly reduced (11.09°) and is now similar with the D$_{3d}$ 14-6. Consequently, as we can see in Table I, the stability of the D$_{3d}$ 14-6(B) is greatly increased. It becomes the most energetically stable isomer. This can be traced to electrostatic effects. A Bader analysis of the charge density displays a 3.2 electron transfer from the cluster to the cages (with +1.6e Sc atoms and -1.6e N atom). These extra electrons are mostly clustered around the equator which maximizes the electrostatic interaction with the positively charged Sc atoms. Its increased stability is thus a consequence of the planar geometry of the seed. By maximizing the
electrostatic interactions, by varying the shape and the symmetry of the metallic clusters, it is thus possible to maximize the driving force which will select a given fullerene structure during growth.

Interestingly, the seed increases the HOMO-LUMO gap of the D_{3d} 14-6 suggesting a decrease in reactivity. This can be maximized if the metallic cluster is chosen to yield an electron count that matches the distribution of the electronic levels of the neutral fullerene. To this end, we have studied the corresponding B_{80}^2 ions. Here, we see that the stabilization caused by the population of the π_{z} electrons is maximal for the D_{3d} 14-6 which stays the most energetically favored isomer. Since the LUMO of this isomer is not degenerate, there is no Jahn-Teller deformation in this system and the pyramidalization angles stays the same. The rigid band approximation works well in these systems, since a difference of the anion and neutral densities show that the extra charge is located on the LUMOs and the energy levels are basically unperturbed. The extra electrons are thus distributed in the π states of the backbone atoms of the poles of the D_{3d} 14-6 and it is the increased resonance energy which is responsible for the stabilization and decreased reactivity of the structure. Unsurprisingly, in the case of the D_{3d} 14-6(B), there is a Jahn-Teller deformation since in its neutral state the LUMO is twice degenerated. This deformation allows it to decrease its global pyramidalization angle (11.27°) which is responsible for its further stabilization.

IV. SUMMARY AND CONCLUSIONS

To rationalize the effect of exterior and self-doping, we carried out simulations on the B_{80} isomers. This has lead us to formulate the generalized isolated filled pentagon rule (IFPR) which states that a peculiar environment is necessary for the stability of the filled pentagons. Because of polymorphism, the IFPR is not a strong constraint on stability, as the IPR, but rather a guideline for constructing the most stable known structures. It is also shown that increased π conjugation enabled by local decrease of strain plays a large role in the stabilization of certain isomers. The IFPR isomers are thus reminiscent of C_{70} where equatorial aromaticity plays a stronger role. This is in good agreement with the simulated ring currents for the I_{h} 20-0 \textsuperscript{[23]} Further study of the effect of filled pentagons on the ring currents of B_{80} would be needed. Furthermore, the IFPR clearly indicates that the synthesis of pure borofullerenes faces difficult challenges because increased stability comes at the price
of increased strain induced reactivity.

The IFPR should be valid for larger boron fullerenes. In this case, the increase of the hexagon to pentagon ratio enables greater freedom to determine the local environment of the filled pentagons. It then becomes possible to maintain a same filling pattern than the α-sheet, or other stable sheets, for the hexagons located far from the pentagons all the while modifying the ones close to the pentagons to maximize stability. However, the relative energy differences should drop as the size of the fullerene increases since the effect of the curvature diminishes. Larger fullerenes are thus expected to have a denser energy spectrum recovering the stronger polymorphism of the boron sheets.

Self-doping alone is not enough to guarantee the existence of the fullerene structures. It is thus necessary to explore other means of stabilizing these structures. The use of endohedral “seeds” for cluster growth could provide further doping leading to greater stabilization. In an effort to understand if a future synthesis of endohedral borofullerenes is feasible, we have studied the effect of this exterior doping on the IFPR. Of course, we have restricted ourself to IPR fullerenes and one must keep in mind that in endohedral carbon fullerenes departure from the IPR is well-known and that this can also be the case in endohedral borofullerenes. In the two cases considered, namely the Sc$_3$N cluster and the $B_{80}^2$ anions, the stability of the isomers were systematically increased. The effect of the IFPR was found to inhibit direct reaction with the endohedral cluster since they would inevitably increase the strain of the fullerene shell. Furthermore, it is shown, that during growth, the symmetry of the metallic cluster will select a given isomer which will minimize the electrostatic effects. In other words, the “seed” can restore a greater energetically motivated (2 eV) driving force. We have also demonstrated that electron addition can decrease the reactivity of the borofullerenes thus reducing the probability of forming outwards $sp^3$ structures during synthesis. We thus show that a metallic seed has all the requirements needed to solve the difficulties restricting the synthesis of boron fullerenes.

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V. ACKNOWLEDGEMENTS

We acknowledge support by the ANR through the NANOSIM-GRAPHENE project and NEWCASTLE. This work was performed using HPC resources from the GENCI-CINES (Grant 6194).