



Structural Motifs and Evolution of Boron Nanoclusters

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Abstract

Boron is a chemically versatile element, capable of forming diverse chemical bonds (e.g., single, double, triple, 3-center 2-electron bonds, and more), which determines its chemical behavior as a pure substance and in compounds with other elements. Electron deficiency and tendency to form multicenter bonds give rise to the ubiquitous presence of clusters in structures of boron allotropes and of many boron compounds in bulk and molecular forms. Here we investigate a wide range of neutral boron clusters B_n ($n = 2\text{--}60$) using the first-principles evolutionary algorithm USPEX. We find clear preference for planar structures for $n < 10$, while there is a competition between planar, cage, bilayer, and tubular structures for $n > 10$. We identify magic clusters as those having positive second-order differences of the total energy (and additionally analyze their fragmentation energy and HOMO–LUMO gap). Most of the magic clusters have even n , the most notable exception being magnetic cluster B_{39} with cuboctahedral shape. Investigating the concept of aromaticity of inorganic compounds, we applied such approaches as nuclear independent chemical shift (NICS) and adaptive natural density partitioning (AdNDP) to a number of boron clusters and found that two clusters, B_{10} and B_{13} , are aromatic (the former being magic).

Keywords Boron clusters · USPEX · Aromaticity · Antiaromaticity · Multicenter indexes · Adaptive natural density partitioning

Introduction

For many decades chemists, physicists and materials scientists have been attracted and fascinated by unusual bonding, unique structures and interesting properties of boron and its compounds. Boron's chemical complexity is caused by its chemical frustration, as we explained in work by Oganov and Chen et al. [1]: located between metals and nonmetals in the Periodic Table, it has only three valence electrons and therefore could be a metal, if its valence electrons were not localized so close and attracted so strongly to the nucleus. As a result of this frustration, all five established crystal structures of boron allotropes are complex [1–3]. Rhombohedral β - B_{106} , which is the most common crystalline phase,

is a superhard material with a high melting point (2453 K) [4].

In the recently discovered¹ structure of γ - B_{28} (and likely also in β - B_{106}) some boron atoms have significant fractional positive and negative charges. Due to electron deficiency of boron, multicenter covalent bonding is widespread: 3c–2e [5, 6] bonds are present within boron icosahedra in boranes and bulk boron; a 12c–2e bond has been found in the $[B_{12}H_{12}]^{2-}$ cluster [7]. To get better understanding of such compounds, one can use the electron counting rules proposed by Wade and extended by Jemmis [8, 9]. Electron deficiency can be removed when a boron atom accepts a whole electron. According to the Zintl-Klemm [10] rule, the structural behavior of a negatively charged boron atom is similar to that of a carbon atom, which is illustrated by the structure of graphene-like boron layers observed in MgB_2 [11] and in lonsdaleite-like boron framework in its predicted high-pressure phase [12].

While solid boron is non-magnetic, magnetism can appear in low-dimensional forms of this element: e.g., isolated boron atom is magnetic, and magnetic moments have

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been predicted in some low-energy forms of borophene [13]. Some boron clusters can be magnetic as well.

Boron nanoclusters get increasing attention due to their potentially interesting electronic and chemical (e.g., catalytic) properties. Boron-containing compounds are widely utilized in luminescent materials, liquid crystals, polymers, sensors, nonlinear optics, and coordination polymers. In addition to these applications, boron is notable for its exceptionally high gravimetric and volumetric energy densities (for example, in combustion processes) among elements. This makes it a valuable additive to traditional hydrocarbon fuels, such as n-decane and kerosene, to enhance their energy density and improve combustion efficiency. Boron can significantly increase the combustion temperature due to its high heat of combustion, resulting in improved thermal efficiency and greater thrust or energy output of the fuel. While crystalline boron allotropes contain icosahedral B_{12} groups, structures of small boron nanoclusters are quite different [14]. So, it is interesting to find at which size boron clusters become similar to the structures of bulk boron allotropes. Pure boron nanoparticles are expected to form single-atom planar sheets, cages, or nanotubes, which has been confirmed by many theoretical and experimental studies. The preferred geometry (planar [14], tubular [14–16], bilayer [17], cage [17], and core–shell [18]) depends on the cluster size. Small clusters (with up to 20 atoms) have been mostly found to exist in planar configurations [19, 20]. In medium-sized clusters, there is a competition between two structural motifs [17, 21]. For example, the well-known quasi-planar structure B_{36} is known from experiment and is thought as a building block for producing a single-atom borophene sheet [22]. The smallest tubular boron structure seen in the experiment consists of 20 atoms and is a potential precursor for single-walled boron nanotubes [22]. Boron cages have also been subject of great interest, with B_{40} being the first synthesized. Accurate calculations have confirmed that clusters containing 46, 48, and 50 atoms exist in three competitive structures: core–shell, bilayer, and quasi-planar [17]. Larger clusters have been demonstrated to form core–shell, rather than hollow-cage structures [18]. First-principles studies of B_{80} , B_{68} , and B_{74} have established the existence of a B_{12} icosahedral core which makes the core–shell geometry more stable than cage [18]. These large clusters can be viewed as already reminiscent of the structures of bulk boron allotropes.

An interesting and for now elusive aspect of inorganic molecules and nanoclusters is aromaticity. The very concept of aromaticity is rather ambiguous, and has led to six criteria [23] to determine if a compound is aromatic, non-aromatic, or antiaromatic (i.e., having $4n$ π -electrons that destabilize cyclic systems and make them more reactive [24]): electronic, energetic, geometric, magnetic, and the ones based on reactivity and spectroscopy. In the case of

inorganic compounds, the final conclusion about aromaticity is considered reliable only after careful consideration when multiple criteria are met. For some compounds, aromaticity, antiaromaticity, and non-aromaticity can be evaluated directly from the calculated current density maps. According to this criterion, strongly diatropic rings mean that the molecule is aromatic, strongly paratropic—antiaromatic; if there is no ring, the conclusion about non-aromaticity can be made [25]. Here it is important to remember that the ground state of the nanocluster could be in the triplet state and Baird's rule is applied. According to this rule, planar cyclic structures are aromatic in their lowest triplet state if they have $4n$ π -electrons, and antiaromatic if they have $4n+2$ π -electrons. This is the photochemical counterpart to Hückel's rule, which applies to the singlet ground state.

For boron clusters, in the absence of relevant experimental data, only four criteria can be evaluated—magnetic, spectroscopic, bonding analysis, and resonance energy. Similar approach to assess structural evolution and stability was used in a number of previous works [26–30]. In this work, we want to get a full understanding of the B_n clusters' behavior through an investigation of their optimal and low-energy metastable structures in a wide range of compositions ($n = 2$ –60). Structural competition and evolution as a function of the number of atoms were investigated and compared with the previously reported results. Another goal of our study is to determine magic clusters (and factors stabilizing them), explore the evolution of the type of structure with increasing number of atoms, and check the possible effect of aromaticity on stabilization of clusters.

Computational Details

The initial search for lowest-energy boron clusters was performed using the first-principles evolutionary algorithm USPEX [21, 31, 32]. This method offers an important advantage of enabling simultaneous prediction of structures of different composition, taking advantage of their evolutionary competition and exchange of structural information. This leads to a significant speedup of the calculations, relative to traditional approach of predicting structures for each composition separately [33]. Our approach allows one to efficiently determine not only the ground-state structures for each composition, but also many low-energy isomers, which allows one to study competition between different structure types.

The local geometry relaxations during global optimization search were performed within density functional theory (DFT) using PAW method [34] and Perdew–Burke–Ernzerhof (PBE) functional [35], as implemented in the VASP code [36, 37]. Subsequently, the 10 lowest-energy isomers from each composition were selected for further refinement using the GAUSSIAN software [38], applying the

PBE0 hybrid functional [39] and the Def2-TZVPP basis set [40], finding spin multiplicity corresponding to lower electronic state ($M=1$, $M=2$ or $M=3$). All energetic characteristics and HOMO-LUMO gaps were calculated using the same level of theory.

To identify particularly stable clusters, expected to have particularly high abundances, we computed the second-order differences in the total energies $\Delta^2 E$. As additional criteria, we used the fragmentation energies and HOMO-LUMO gaps. We also investigated the aromaticity in boron clusters following different criteria that can be evaluated for inorganic compounds: adaptive natural density partitioning method (AdNDP) [41–45], and nuclear independent chemical shift (NICS) [46].

Results and Discussion

Structure

All predicted clusters were divided into the planar, cage, tubular, core-shell, and bilayer groups. A cluster is considered planar when all its atoms lie approximately in the same plane. Another type is tubular clusters, including clusters with one or two atoms sticking out of the tube. Three-dimensional structures consisting of a shell and core containing fewer than five atoms were classified as cage structures. Structures consisting of two connected planes were classified as bilayer ones. Finally, boron shells encapsulating an icosahedral B_{12} core were classified as core-shell structures. These five types were discerned among 5100 structures of boron clusters containing from 10 to 60 atoms (50 different

compositions with 100 isomers for each) that were found through evolutionary search.

All obtained ground-state structures of B_n clusters ($n = 2–60$) are shown in Fig. 1. The xyz coordinates of all calculated ground-state structures are provided in ESI Section S2. The clusters, containing 3–5, 8, 10, 11, 13, 15–18 atoms are planar, clusters with 6, 7, 9, 12, 23 and 36 atoms are quasi-planar (exhibit a nearly planar geometry with slight deviations), all the rest are attributed to non-planar clusters. For further study, we have selected clusters containing 10–60 atoms, where the structure competition occurs. For these structures, we looked at the structural tendencies of boron cluster isomers (Fig. 2) as a function of structural patterns from the number of atoms in each cluster plotted as energy difference between structures and their ground states. Boron clusters with 10–20 atoms adapt mostly planar structure with exceptions of B_{14} , B_{19} , which are cage, and tubular B_{20} . B_n clusters with $n = 21–40$ showed the tendency to be cage with the exception of tubular B_{21} , quasi-planar B_{23} and B_{36} , the latter being highly symmetric. Clusters with 41–60 atoms usually are bilayer, except B_{41} in cage form and B_{59} with core-shell structure.

Our results on the structural competition agree with those previously reported.[19–21, 47, 48] The remarkable magnetic cluster B_{39} , first found by Wu and colleagues [21] and characterized by a highly symmetric cage (O_h) of 38 atoms around the central boron atom, was also predicted in our calculations.

For compositions B_{31} , B_{32} , B_{33} , B_{35} , B_{37} , B_{38} , B_{41} , B_{43} , B_{44} , B_{45} , B_{49} and B_{50} we identified ground-state structures not previously described in the literature.[21] These clusters exhibit lower energy by $\sim 0.3–1.2$ eV and mostly have low-symmetry structures, except B_{50} with D_{2d} symmetry.

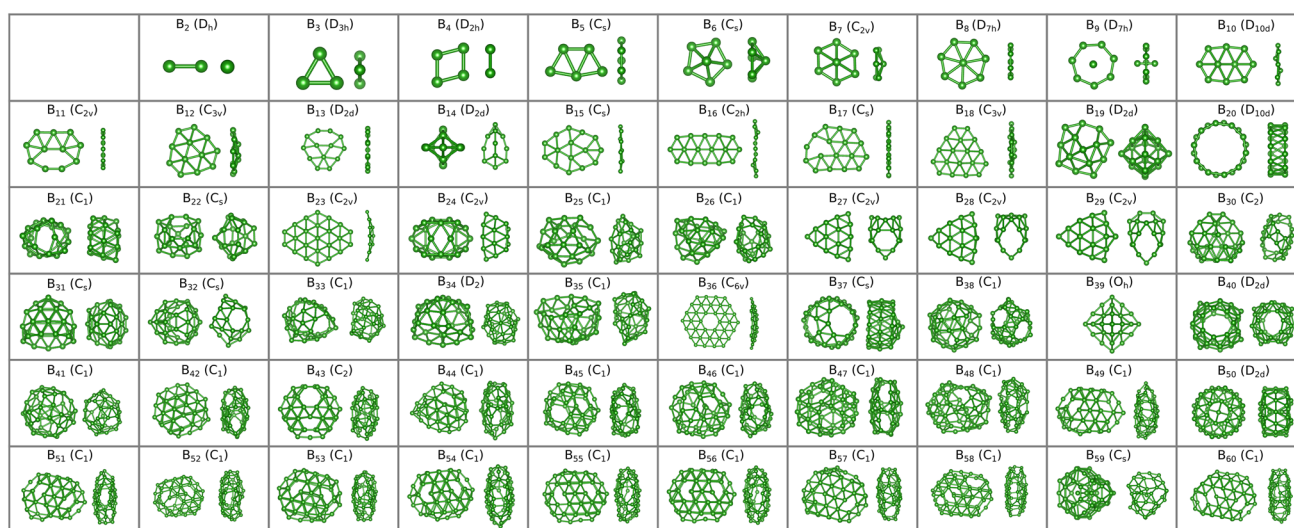


Fig. 1 Ground-state structures of B_n clusters ($n = 2–60$) in two projections with their point groups

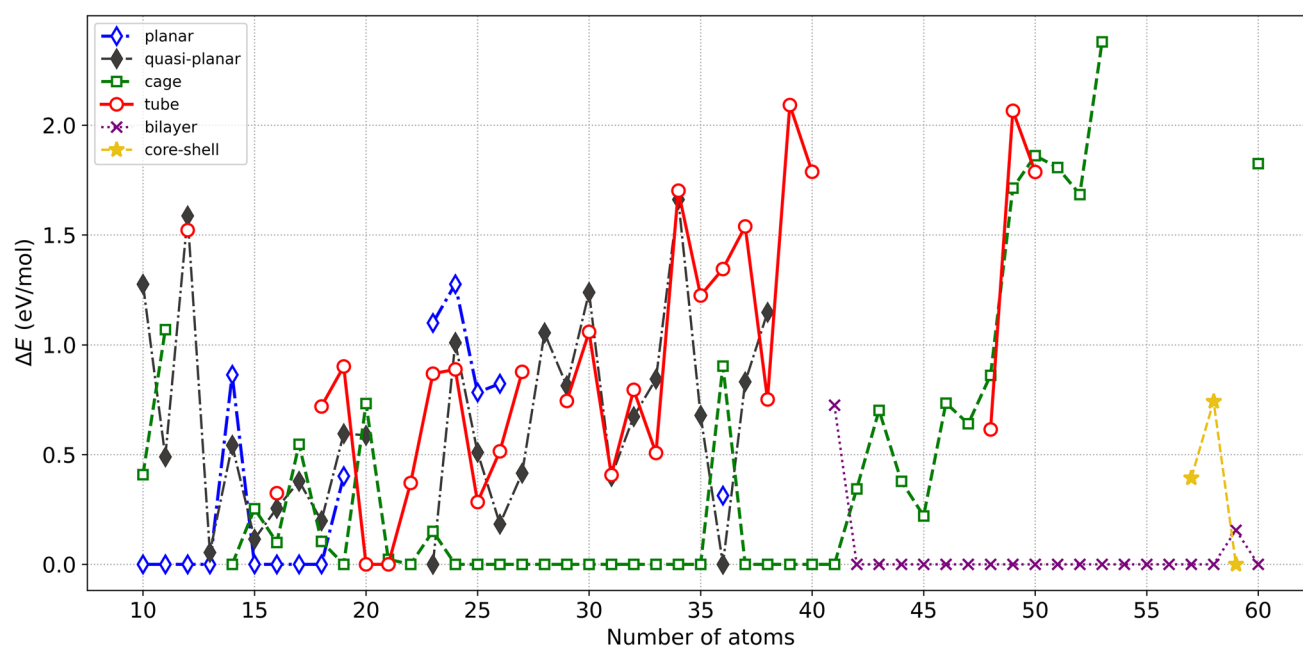


Fig. 2 Structural competition in the B_n clusters ($n = 10$ – 60). Vertical axis represents ΔE between different structures and the most stable structure at each atomic composition n .

Indeed, lowest-energy structures are not always bound to demonstrate high symmetry, and USPEX algorithm is capable of discovering such clusters.

Energetics

One should remember that any cluster is higher in energy than its infinite periodic counterpart—the bulk crystal, and therefore stability of clusters should be discussed not in terms of the lowest possible energy, but using local criteria (comparing a given cluster with clusters of similar size). Second-order differences in the total energy $\Delta^2 E$ have been shown to work well for this purpose [49, 50], while additional insight is also provided by the fragmentation energy (the minimum energy required to split a given cluster into two smaller clusters) and the HOMO–LUMO gap. In addition to evaluating stability of our clusters, we were interested in the trends—spin states (singlet, doublet or triplet), point group symmetries, and wanted to know how our results agree with previous studies [19–21, 47, 48, 51].

These criteria of stability have been successfully used in our previous studies [33, 52–59]. In the first criterion, we consider the stability with respect to the exchange of one boron between two identical nanoclusters B_n . This corresponds to the so-called second energy difference (discrete analog of the second derivative of the energy) and can be written as:

$$\Delta^2 E = E[B_{n+1}] + E[B_{n-1}] - 2E[B_n] \quad (1)$$

A cluster with n atoms is considered stable (“magic”) when two clusters B_n have lower energy than two clusters of neighboring compositions— B_{n+1} and B_{n-1} . Physically, this means that a collision of two such clusters will not lead to transfer of an atom from one cluster to the other, and such clusters can accumulate in significant concentrations. Mathematically, such stability is expressed by positive second-order energy difference $\Delta^2 E$, which reveals 30 “magic” boron clusters (Fig. 3a), most of which have even numbers of boron atoms (and, consequently, even numbers of electrons). The magic clusters B_n with $n = 4, 10, 12, 14, 16, 18, 20, 22, 24, 28, 30, 32, 34, 36, 40, 46, 52, 54, 56, 58$ are in the singlet state, those with $n = 3, 5, 7, 27, 39, 43, 49, 51, 59$ have an odd number of electrons (i.e., are open-shell and magnetic), and are in the doublet state, and the unique case $n = 8$ corresponds to a cluster with an even number of electrons in the triplet state. Total energies and magnetic moments are given in Section1, Table S2, Supplementary Information.

Additionally, we have used the second criterion—the HOMO–LUMO gap. A wide HOMO–LUMO gap is usually associated with increased stability, but it is not expected to be completely correlated with $\Delta^2 E$. The HOMO–LUMO gaps (Fig. 3b) have particularly high values for the following eleven magic clusters: $B_3, B_4, B_6, B_8, B_9, B_{12}, B_{14}, B_{24}, B_{30}$ and B_{40} . Wide HOMO–LUMO gaps are related to low electronic polarizability, which implies relatively low reactivity and high kinetic stability.

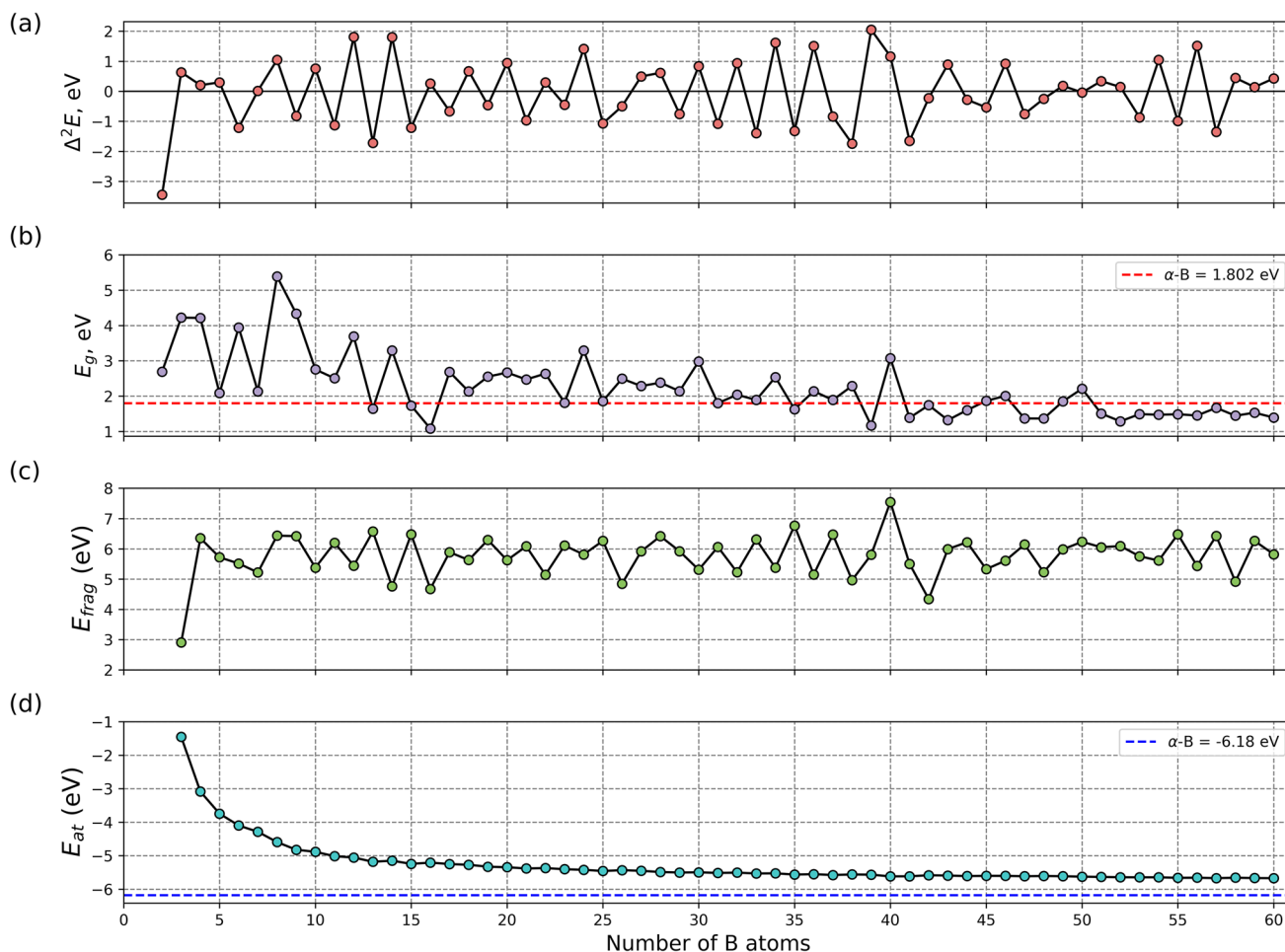


Fig. 3 **a** Second-order differences of energy $\Delta^2 E$, **b** HOMO–LUMO gaps, **c** fragmentation energies ΔE_{frag} and **d** atomization energies E_{at} of the ground-state structures of the B_n clusters ($n = 2\text{--}60$). The theoretical band gap of α -boron is equal to 1.802 eV, and the calcu-

lated atomization energy of crystalline α -B is -6.18 eV; one can see how the band gaps and atomization energies of large boron clusters asymptotically approach bulk values.

Another stability criterion characterizes resistance to fragmentation. Here we identify molecules that could spontaneously decompose. To this end, we consider all possible channels of fragmentation of a given molecule for the decomposition into two fragments:

$$B_n = B_{n-a} + B_a, \text{ where } 0 \leq a \leq n \quad (2)$$

The energy of each fragmentation reaction $n \rightarrow a + (n-a)$ is found as:

$$E_{\text{frag}}(n, a) = E(a) + E(n-a) - E(n) \quad (3)$$

We are looking for the decomposition into the most stable fragments, hence, we calculated the minimal value of all fragmentation energies:

$$E_{\text{frag}}(n) = \min_a E_{\text{frag}}(n, a) \quad (4)$$

Interestingly, the lowest-energy fragmentation path for all boron clusters is the removal of one boron atom. The dependence of the fragmentation energy on the number of atoms is shown in Fig. 3c. Again, we see that clusters with even numbers of boron atoms tend to have particularly high fragmentation energies. Interestingly, clusters with high energy of removal of one boron atom also have high values of $\Delta^2 E$ (the exception is B_{23} with high E_{frag} and nearly zero $\Delta^2 E$). The energy of removal of one B atom is the structural analog of the ionization potential (energy of removal of one electron). Its high values are indicative of a closed structural shell.

To obtain a full picture, the atomization energy (Fig. 4d) was calculated using the formula:

$$E_{\text{at}}(n) = (E[B_n] - nE[B_1])/n, \quad (5)$$

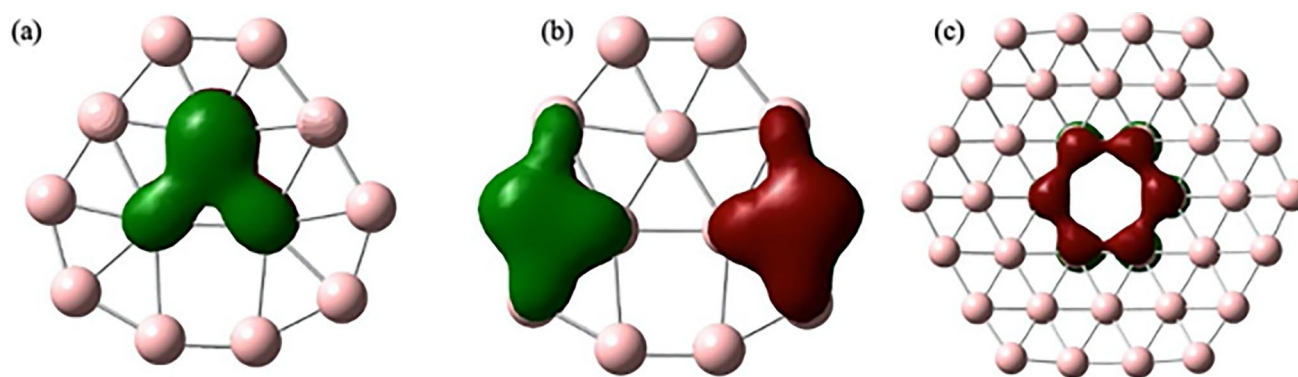


Fig. 4 AdNDP analysis of **a** 3c–2e and **b** 4c–2e bonds of B_{13} , and **c** 6c–2e bond of B_{36}

where $E[B_1]$ is the energy of an isolated boron atom, $E[B_n]$ is the total energy of the cluster, and n is the number of atoms. As expected, E_{at} decreases with the number of atoms, approaching the bulk value, and bulk crystal has lower energy than any cluster.

Summarizing the results analyzed above, energetic criteria show that mostly even-numbered clusters are showing special stability. These are B_8 , B_{10} , B_{12} , B_{14} , B_{20} , B_{24} , B_{30} , B_{32} , B_{34} , B_{36} , B_{40} . It is worth mentioning that B_8 has a triplet ground state, and hence, due to Baird's rule, is aromatic (has $4n$ π -electrons). The symmetry of magic clusters is higher than that of the neighboring non-magic ones. Magicity stems from closed electronic and/or structural shell—the former implies singlet state, whereas the latter implies high symmetry.

Aromaticity

Aromaticity is an important property of a molecular cluster that can often be understood by analyzing the characteristic features of its individual fragments [60]. In some cases, the overall aromaticity of a system can be approximated as the sum of the aromaticities of its constituent parts. In this study, we aim to explore the relationship between aromaticity and magicity in boron clusters by analyzing both magic and non-magic species. Specifically, we selected several representative clusters (B_{10} , B_{11} , B_{12} , B_{13} , B_{15} , B_{16} , B_{18} and B_{36}) to determine whether their stability (magicity) correlates with their possibly aromatic character.

To assess aromaticity, we employed the Nuclear Independent Chemical Shift (NICS) method [46], which falls under the magnetic criteria of aromaticity introduced by Paul v. R. Schleyer in 1996. The NICS approach is based on the response of an aromatic system to an external magnetic field, allowing for the quantification of aromatic character. For the selected boron clusters, we computed NICS values at their geometric centers to determine the extent of electron delocalization, which is often associated with enhanced

stability. If a cluster exhibits a significant negative NICS value, it suggests a strong aromatic character due to electron delocalization in closed circuits.

Our results presented in Table 1 reveal that, among the studied clusters, only B_{10} and B_{13} exhibit negative NICS values, indicating their aromatic nature. Interestingly, despite its pronounced aromaticity, B_{13} is classified as a non-magic cluster, suggesting that aromaticity has very limited effect here and alone does not necessarily dictate the overall stability of boron clusters. B_{10} is both aromatic and magic.

In addition to NICS analysis, we applied the Adaptive Natural Density Partitioning (AdNDP) method to further investigate the electronic structure and bonding patterns within these clusters. AdNDP provides an insightful representation of molecular bonding by identifying localized and delocalized electron pairs. The method systematically recovers traditional Lewis bonding elements (such as 1c–2e and 2c–2e bonds) while also revealing multicenter delocalized bonding patterns (for $n > 2$), which are strongly linked to aromaticity.

As shown in Fig. 4, our AdNDP analysis of B_{13} highlights the presence of multicenter 3c–2e and 4c–2e bonds, reinforcing its aromatic character. Meanwhile, B_{36} features a prominent 6c–2e bond, suggesting delocalization effects that may contribute to its stability.

Table 1 Calculated NICS values of corresponding clusters at the geometry center, 1 Å and 2 Å above were computed, given in ppm.

Cluster	NICS(0)	NICS(1)	NICS(2)
B_{10}	– 52.836	– 21.097	– 4.168
B_{11}	25.995	19.158	7.912
B_{12}	27.743	14.385	8.541
B_{13}	– 12.363	– 8.439	– 7.695
B_{15}	15.660	11.592	2.944
B_{16}	24.012	15.898	5.827
B_{18}	25.683	21.897	6.731

Overall, our findings suggest that while aromaticity plays a role in the electronic structure and bonding of boron clusters, it does not always correlate directly with their magicity.

Conclusions

In this study, we investigated a wide range of boron clusters and identified clear trends in their structural motifs. As the number of atoms increases from 10 to 60, boron clusters predominantly adopt planar, cage, or bilayer structures, with only a few tubular structures observed. For clusters containing more than 60 atoms, structural diversity diminishes, and core-shell structures become the only motif present, resembling bulk boron structures. We identified previously undescribed ground-state structures for the compositions B_{31} , B_{32} , B_{33} , B_{35} , B_{37} , B_{38} , B_{41} , B_{43} , B_{44} , B_{45} , B_{49} , and B_{50} . These newly identified structures are ~ 0.3 – 1.2 eV lower in energy compared to alternatives reported in the literature, and most exhibit low symmetry, with the exception of B_{50} , which exhibits D_{2d} symmetry. To evaluate stability of the clusters, we employed a simple approach by calculating the second derivative of the cluster energy with respect to composition. This analysis revealed magic clusters, including B_8 , B_{10} , B_{12} , B_{14} , B_{20} , B_{24} , B_{30} , B_{32} , B_{34} , B_{36} , and B_{40} and some others. The symmetry of these magic clusters is generally higher than that of their non-magic neighbors. Notably, B_8 has a triplet ground state and is aromatic due to Baird's rule, possessing $4n$ π -electrons. To further investigate, we tested the concept of aromaticity on several magic B_n clusters ($n = 10$ – 60) using a nuclear independent shift approach. Our findings indicate that only two clusters, B_{10} and B_{13} , are aromatic, with B_{10} being the only one classified as magic. Thus, aromaticity plays a minor role in the stabilization of boron clusters (magicity). Instead, the dominant factors are a closed-shell electronic structure, characterized by large HOMO-LUMO gaps and an even number of electrons, and a closed-shell atomic structure.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10876-025-02815-0>.

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Author contributions Ekaterina D. Anisimova—conceptualization, data curation, validation, visualization, writing—the original draft, and writing—review and editing. Elizaveta E. Vaneeva—global optimization, data curation, validation, methodology and writing—review and editing. Vladimir S. Baturin—formal analysis, investigation, and writing—review and editing. Sergey V. Lepeshkin—investigation, validation, methodology and writing—review and editing. A. R.

Oganov—conceptualization, writing—review and editing, and supervision. All co-authors contributed to the discussion of the data. All authors have given approval to the final version of the manuscript.

Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

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