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*Original Scientific Article*

# Borane Polyhedra as Building Blocks for Unknown but Potentially Isolatable New Molecules – Extensions based on Computations of the Known $B_{18}H_{22}$ Isomers[†]

**Josep M. Oliva,[a,*] Juanjo Rué,[b] Drahomír Hnyk,[c]**
**John D. Kennedy,[c,d] and Vladimir R. Rosenfeld[e]**

[a]*Instituto de Química-Física "Rocasolano", CSIC, 28006 Madrid, Spain*
[b]*Instituto de Ciencias Matemáticas (CSIC – UAM – UC3M – UCM),*
*Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[c]*Institute of Inorganic Chemistry of the AS CR, v.v.i., 250 68 Husinec-Řež, Czech Republic*
[d]*The School of Chemistry of the University of Leeds, Leeds LS2 9JT, UK*
[e]*Texas A&M University, Galveston, TX 77553, USA*

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*Abstract.* Known borane polyhedral cluster characteristics can be used for predicting new architectural constructs. We propose additional structures derived from $B_{18}H_{22}$ : three positional isomers different from the well-known *anti*-$B_{18}H_{22}$ and *syn*-$B_{18}H_{22}$ boranes. We have also derived two new cyclic structures based on the condensation of borane pentagonal pyramids and bipyramids. The concatenation of polyhedral borane molecules is also considered from a mathematical point of view. (doi: 10.5562/cca2304)

*Keywords:* boranes, bond, $B_{18}H_{22}$, quantum chemistry, mathematical chemistry

## INTRODUCTION

With one electron fewer than carbon, boron engenders a very rich chemistry which, in combination with metals and non-metals, ranges from the solid state to molecular organic and inorganic chemistry.[1] The transition from two-dimensional to three-dimensional structures is a notable feature of boron chemistry: in the solid state, for instance, $MgB_2$ is a superconductor[2] with a two-dimensional graphite-like (honeycomb) boron layer separated by Mg atoms, $MgB_4$ is a three-dimensional system based on edge-shared pentagonal pyramides,[3] and $MgB_6$ is based on octahedral $\{B_6\}$ moieties.[4] Here it is noted that the similarity of pentagonal pyramidal $[C_6H_6]^{2+}$ and the pentagonal pyramids in solid $MgB_4$ has been rationalised[5] by means of structural correlations between boron and carbon compounds.[6] Further, the pentagonal pyramidal motif is also that of the binary borane *nido*-$B_6H_{10}$, isoelectronic with the $[C_6H_6]^{2+}$ dication.

Several allotropes of elemental boron exist, in which $\{B_{12}\}$ icosahedra are connected in different ways.[7] When combined with other elements from the Periodic Table, the chemistry of boron expands to yield a very rich library of architectural constructs in any dimension.[8]

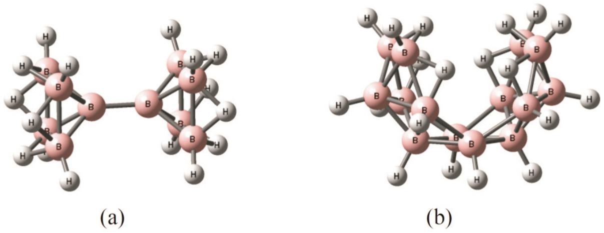

**Figure 1.** Examples of intercluster linkages: (a) single B−B bond in $B_{10}H_{16}$, and (b) two shared boron atoms in *cis*-$B_{14}H_{20}$. These representations are from B3LYP/6-31G* optimized geometries (energy minima).

The combination of boron with hydrogen leads to the well-known $B_xH_y$ deltahedral structures[9] – the boranes. In 1980, William Lipscomb described examples of possible polymeric borane structures.[10] In such polymeric and oligomeric species, at least ten different bonding schemes between polyhedral species can now be categorised, for example: (1) a single B−B bond as in $B_{10}H_{16}$,[11] which is a dimer of $B_5H_8$ (Figure 1a), (2) a single three-center BHB bond as in the $[B_{20}H_{19}]^{3-}$ trianion,[12] (3) two BHB bridges as in the [photo-

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[†] Dedicated to Professor Douglas Jay Klein on the occasion of his 70th birthday.
[*] Author to whom correspondence should be addressed. (E-mail: j.m.oliva@iqfr.csic.es)

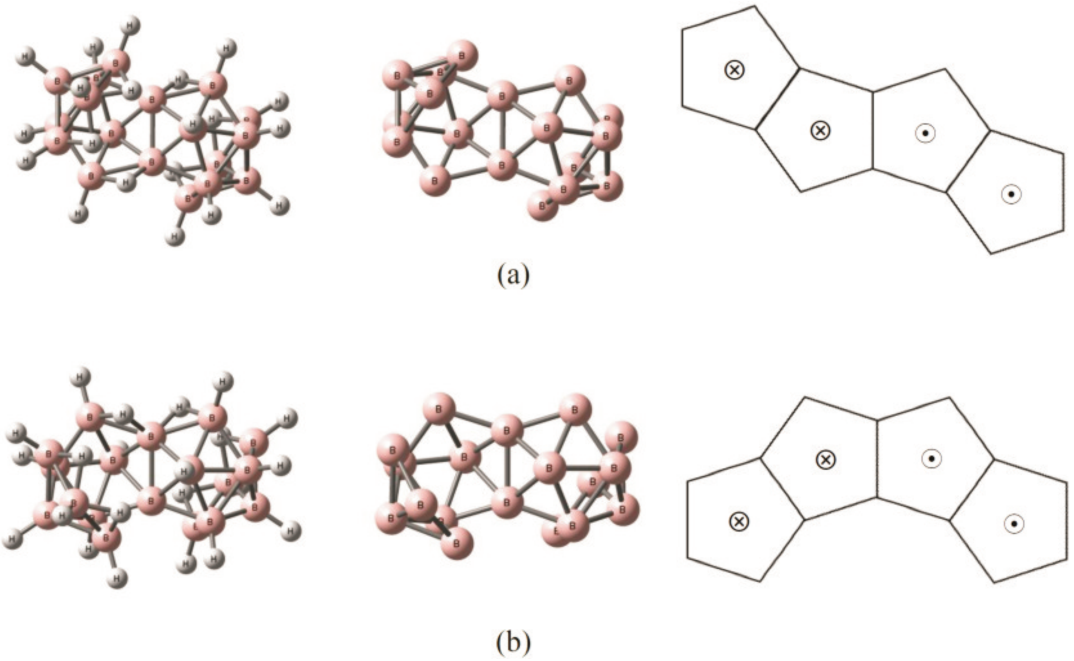

**Figure 2.** Optimized structures of the known isomers of $B_{18}H_{22}$ from B3LYP/6-31G* computations: (a) the *anti-transoid* isomer *anti*-$B_{18}H_{22}$ **1** of $C_i$ symmetry, and (b) the *syn-transoid* isomer *syn*-$B_{18}H_{22}$ **2** of $C_2$ symmetry. *Transoid* refers to the connecting mode between the two central pentagonal pyrammids. Shown from left to right: the whole molecular structure, the molecule with hydrogen atoms removed for clarity, and a simplified two-dimensional (2D) 'unfolded' representation of the pentagonal pyramidal sub-units of the $\{B_{18}\}$ frameworks. The symbols ⊙ and ⊗ signify respectively boron atoms above and below the projection plane in the 2D projection, and implies that the two open faces of the two pairs of pentagonal pyramids are on opposite sides of the molecule, *i.e. transoid*.

$B_{20}H_{18}]^{2-}$ dianion,[13] (4) one three-center BBB bond, as in $B_{15}H_{23}$,[14] and in the $[\mu\text{-Fe(CO)}_4B_7H_{12}]^-$ anion, (5) two three-center BBB bonds, as in the non-photo $[B_{20}H_{18}]^{2-}$ dianion,[15–17] (6) one shared atom, as in the $[(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{10}CoC_2B_{10}H_{10}]^-$ anion,[18] (7) two shared boron atoms, which can result in different configuratons, *e.g. cis* as in $B_{14}H_{20}$ (Figure 1b)[19,20] and *trans* as in *anti*–$B_{18}H_{22}$,[21] (see section 2 below), (8) three shared boron atoms, as in $[B_{20}H_{16}(NCCH_3)_2]$,[22] in the $[B_{21}H_{18}]^-$ anion,[23] and as in solid-state α-$AlB_{12}$,[24] and a related structure for elemental boron,[25] (9) four shared boron atoms, as in $B_{20}H_{16}$,[26] and (10) a "double cap" join, as in $[(CH_3)_4C_4H_8FeCo(\eta^5\text{-}C_5H_5)]$.[27]

In the consideration of the extension of known borane structures[28] in the search for potential novel cluster macromolecules,[29] one can proceed as follows:

(*a*) Reasonable extrapolation of known bonding modes, as exemplified by ethane to polyethylene in carbon hydride chemistry.
(*b*) By the recognition that many macromolecules can be regarded as fragments of solid-state matrices,[30] but with peripheral valencies tied up by ligands (ligands in the general sense) rather than being surrounded by more matrix, *e.g*. benzene, naphthalene, anthracene etc from graphite, adamantane from diamond, polyoxometallate species from metal oxide ceramics, carbonyl metal cluster compounds from metal matrices, boranes from crystalline elemental boron, etc.
(*c*) Speculation based on the principle that novel macromolecular architectures may not have structural parallels in known molecular species or solid-state matrices (see section 3 below).

The goal of this work is the of use of procedure (*a*) above in order to introduce new *open* and *cyclic* molecular constructs that make use of Lipscomb's bonding mode (7) as delineated above, namely, the building-up or *Aufbau* of extended polyhedral structures based on two shared boron atoms.[31] We apply the principle to the particular case of fused pentagonal pyramids, to generate extensions of the two known *anti* and *syn* isomers of $B_{18}H_{22}$.

## NEW ISOMERS DERIVED FROM $B_{18}H_{22}$

To date, two isomers of the binary borane $B_{18}H_{22}$ are known:[32] the *anti*-$B_{18}H_{22}$ isomer **1** of $C_i$ symmetry, which we can describe as *anti-transoid*, and the *syn-transoid* isomer *syn*-$B_{18}H_{22}$ **2** of $C_2$ symmetry. Figure 2 depicts the geometries of the two isomers.

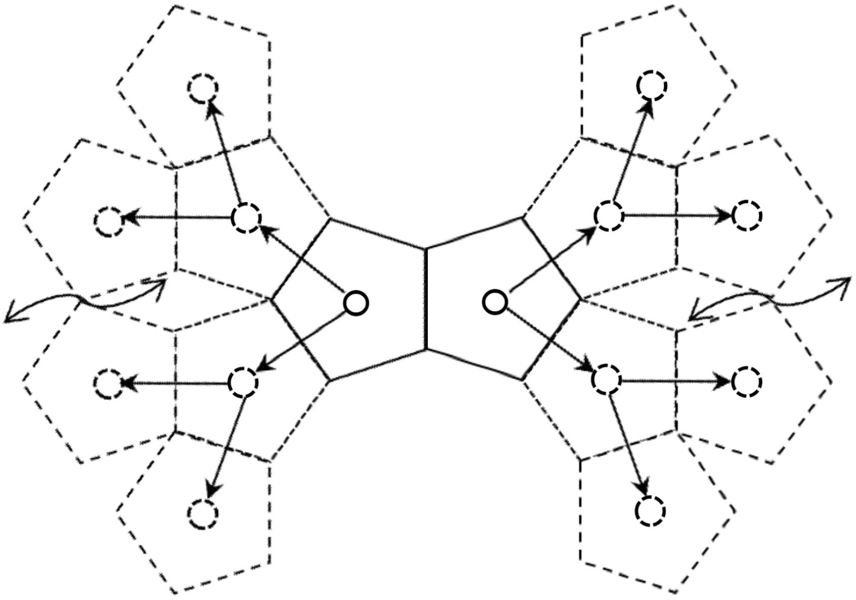

**Figure 3.** 2D representations of proposed extended structural patterns (hatched lines) based on two fused pentagonal pyramids (solid lines). The curved double arrows indicate that structures with steric clashes should be avoided. The empty circles in the center of each pentagon indicate that in this 2D projection the apical boron atoms can be above (⊙) or below (⊗) the formal 2D projection plane.

At this point it is noted that, since the initial report of the synthesis and the description of absorption bands of both of these isomers,[33] it has been known that *anti*-$B_{18}H_{22}$ **1** fluoresces but *syn*-$B_{18}H_{22}$ **2** does not; the two isomers therefore have distinctly different photophysical properties, and we have recently elucidated the origins of this interesting natural phenomenon by means of high-level quantum-chemical computations.[32]

From a consideration of the two-dimensional (2D) ‘unfolded’ projections from Figure 2, it is reasonable to speculate an extension of the $B_{18}H_{22}$ structural principle by the addition of further pentagonal pyramids, using the two central fused pentagonal pyramids as a starting structure, as represented schematically in Figure 3.

The extended structures follow the arrows on each direction in such a way that no vertices of any two pentagons can touch each other, as shown by the double curved arrow in Figure 3. The central (top/bottom vertex) boron atom from each pentagon can be above or below the screen plane. Thus the *anti*-$B_{18}H_{22}$ **1** and *syn*-$B_{18}H_{22}$ **2** isomers can be described as a simple extension of the original unit (two fused pentagonal pyramids) by adding a further pentagon down or up, provided that the two central boron atoms on each side are above and below the screen plane respectively in the 2D projection.

In the consideration of extensions of the original units, *i.e.* the starting unit of two fused pentagonal pyramids, it is also apposite to explore the positionings of the top (apical, axial) vertices of the pentagonal pyramids, other than those that lead to the known *syn* and *anti* $B_{18}H_{22}$ isomers. Thus, from Figure 2, where the symbols ⊙ or ⊗ mean respectively that, in the 2D projection of the structure, the apical vertex is above or below the projection plane, it can be seen that alterative positions of the central axial atoms in the pentagonal pyramids above and below the 2D plane lead to two so far experimentally unknown isomers with the $B_{18}H_{22}$ formulation. Specifically, compared with the *anti* and *syn* isomers shown in Figure 2a and Figure 2b (see the 2D projections), if the positions of the central boron atoms which are ***below*** the nominal 2D plane (⊗) are changed to positions ***above*** the plane (⊙), then two new isomers **3** and **4** result. These can be described as *anti-cisoid* $B_{18}H_{22}$ **3** with $C_2$ symmetry and *syn-cisoid* $B_{18}H_{22}$ **4** with $C_s$ symmetry, as depicted in Figure 4.

Quantum-chemical computations show that isomers **3** and **4** are energy minima, but significantly higher in energy than the known isomers *anti*-$B_{18}H_{22}$ **1** and *syn*-$B_{18}H_{22}$ **2**, as shown in Table 1.

An alternative factorization of the structures of the $B_{18}H_{22}$ isomers is that they result from the formal fusions of *nido* $B_{10}H_{14}$-type units with two atoms held in common. This factorization in fact better represents the chemistry itself, as each $\{B_{10}H_{11}\}$ subcluster of the $B_{18}H_{22}$ isomers has properties closely related to those of $B_{10}H_{14}$. Extension of this concept engenders the sequence $B_{10}H_{14}$, $B_{18}H_{22}$ (Figure 5), $B_{26}H_{30}$, $B_{34}H_{38}$, and so on, *i.e.* the series $B_{8n+2}H_{8n+6}$, where $n = 1, 2, 3, \ldots, \infty$.

Following a different intercluster fusion scheme, as depicted in Figure 5, we also considered a further isomer

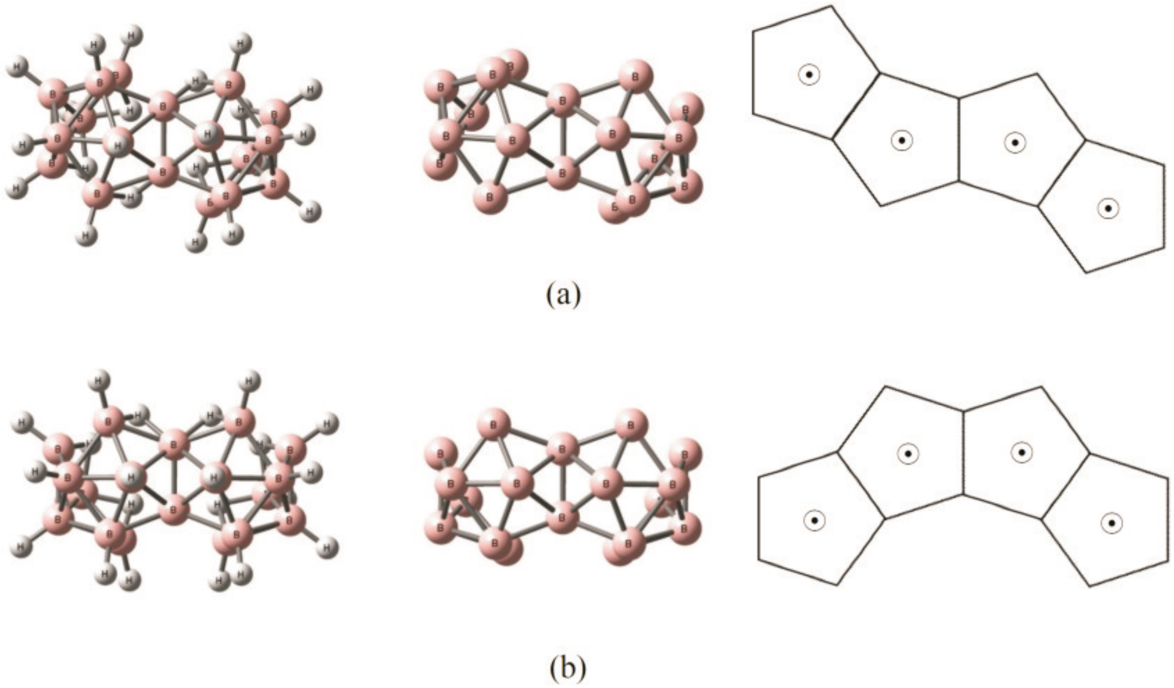

**Figure 4.** Optimized B3LYP/6-31G* geometries of (a) *anti-cisoid* $B_{18}H_{22}$ **3** of $C_2$ symmetry, and (b) *syn-cisoid* $B_{18}H_{22}$ **4** of $C_s$ symmetry. In **3** and **4** the mutual orientation of boat-like hexagonal belts of the respective decaborane sub-units are *cisoid*, *i.e.* the open faces of the pentagonal pyramids are all on the same side of the molecule, whereas in known *anti-transoid* **1** and *syn-transoid* **2** the relative orientation is *transoid*. Shown from left to right: the whole structures, the molecule with hydrogen atoms removed for clarity, and simplified 2D 'unfolded' projections. The symbol ⊙ means that the apical boron atom is above the projection plane in the 2D unfolded projections.

**5** derived from $B_{18}H_{22}$, which also results an energy minimum, abeit some 360 kJ·mol$^{-1}$ higher than the thermodynamically most stable isomer, *anti*-$B_{18}H_{22}$ **1**.

In this derivation of **5** we observe a natural way of extending in one dimension the isomer from Figures 5c and 5d to an infinite structure, provided that the apical atoms follow the pattern {...⊙⊗⊙⊗...} (using the pentagonal motif) or {...(⊙⊙)(⊗⊗)(⊙⊙)(⊗⊗)...} (using the hexagonal motif).

These results clearly show that extensions from known borane architectures can lead to interesting patterns for possible new species that derive from original units that correspond to existing boranes. Thus, two extension patterns (Figure 3 and Figure 5) readily lead to predictions of novel cluster macromolecules that will have new, different properties. It is reasonable to predict the future isolation of such species, but at present with no transferable generic routes for borane

**Table 1.** Energies and energy differences from B3LYP/6-31G* computations for the different isomers of $B_{18}H_{22}$. Also given are energies for cyclic structures **6** and **7** (see Section 4 below). The computed geometries of all molecules, as illustrated in Figures 2, 4, 5, 8 and 9, correspond to energy minima at this level of theory

| $B_{18}H_{22}$ | | Symmetry | Energy / a.u. | $\Delta E$ / kJ·mol$^{-1}$ |
|---|---|---|---|---|
| *anti-transoid* | **1** | $C_i$ | −460.703685 | 0.0 |
| *syn- transoid* | **2** | $C_2$ | −460.701612 | 5.4 |
| *anti-cisoid* | **3** | $C_2$ | −460.620937 | 217.3 |
| *syn-cisoid* | **4** | $C_s$ | −460.612636 | 239.0 |
| *isomer* | **5** | $C_s$ | −460.565627 | 362.5 |
| Cyclic Structures | | | | |
| $B_{40}H_{40}$ | **6** | $D_{5d}$ | −1018.141787 | --- |
| $B_{50}H_{30}$ | **7** | $D_{10h}$ | −1260.624475 | --- |

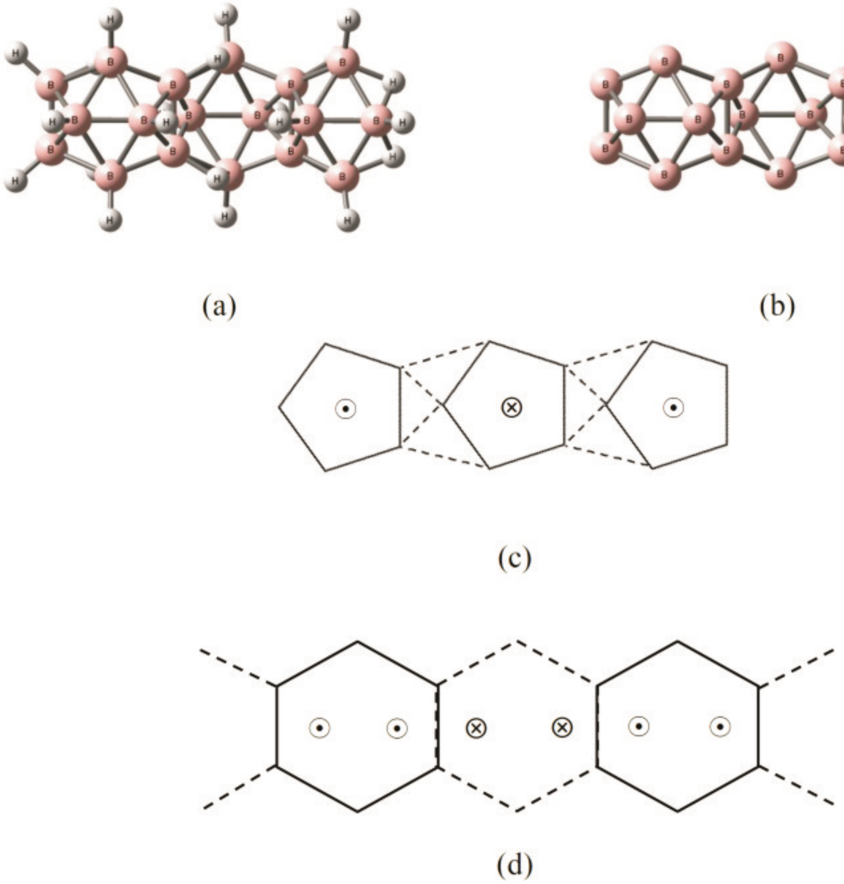

**Figure 5.** Optimized geometry of an additional isomer of $B_{18}H_{22}$ (**5**), $C_s$ symmetry, following a different extension pattern. We show (a) the whole structure (B3LYP/6-31G* computations), (b) the molecule without hydrogen atoms for clarity, and (c) a 2D unfolded projection of the isomer using pentagons. The hatched lines connect the pentagons from structure in (b). Diagram (d) shows another 2D projection using hexagons to illustrate an infinite 1D extension of isomer (**5**). The symbols ⊙ and ⊗ indicate respectively that the central boron atoms associated with the pentagons or hexagons are located above and below the 2D projection plane.

cluster fusion chemistry, it is not clear how this may be effected. Although the three new $B_{18}H_{22}$ isomers **3**, **4** and **5** are higher in energy than the two known isomers **1** and **2** (Table 1), it is likely that they will be kinetically stable and thence ultimately synthesisable by directed chemistry.

## Mathematical Considerations for Extension of Borane Molecules. Cyclic Constructions

As can be seen from the above results, extension of just two known structural patterns in borane chemistry can lead to interesting new patterns based on the original units that correspond to existing boranes. It has been shown that the two extension patterns (Figure 3 and Figure 5) readily lead to the prediction of novel cluster macromolecules which will have new properties.

More generally, it is thence reasonable to speculate, based on these two extension patterns, about how many isomers or conformers can be enumerated, given a number of pentagons, and following a given extension pattern. The problem of sampling all possible configurations that can be defined by means of concatenated molecules is very involved.[34] In this section we address this factor by phrasing the problem into the context of self-avoiding walks (*i.e.* Figure 6), and by making explicit constructions when dealing with cyclic configurations.

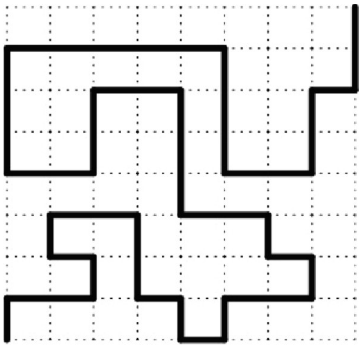

**Figure 6.** A self-avoiding walk on the square lattice with 48 steps.

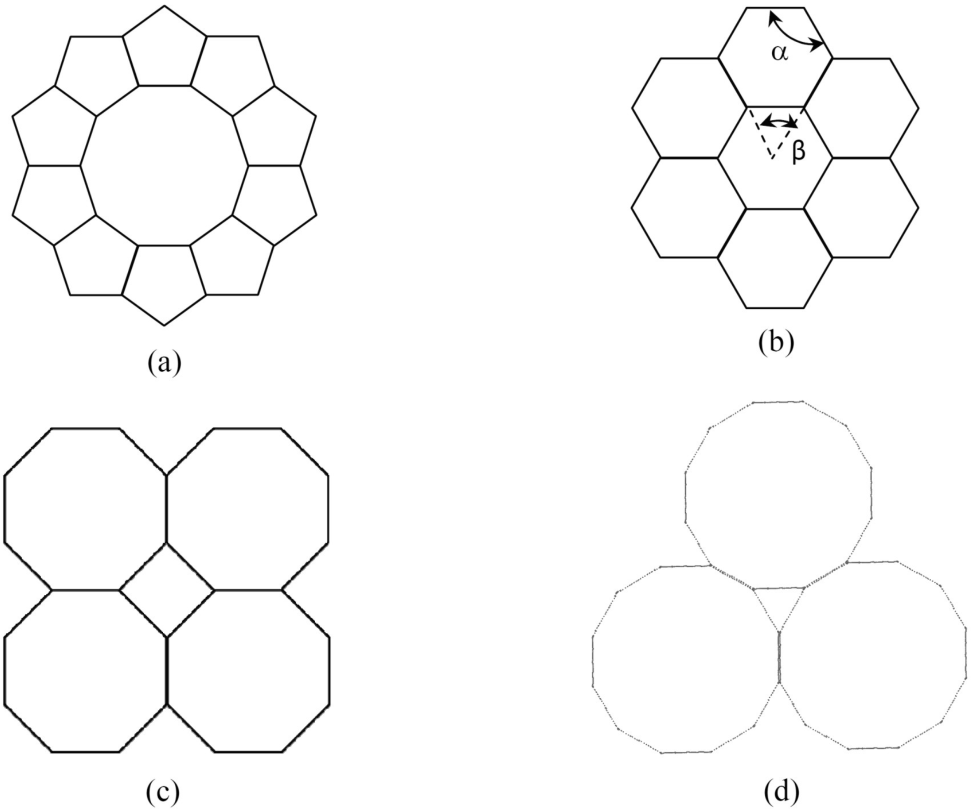

**Figure 7.** Examples of cyclic ‘fused’ regular polygons. (a) $n = 5$, ten pentagons, (b) $n = 6$, six hexagons, (c) $n = 8$, four octagons, (d) $n = 12$, three dodecagons.

As pointed out by Flory some 60 years ago,[35] there is a deep connection between combinatorial models and chemical configurations. Flory proposed[35] the consideration of ‘self-avoiding walks’ on a lattice (*i.e.* walks that visit each vertex only once) as a model for the spatial positioning of polymer chains. The approach of using self-avoiding walks turns out to be a very interesting mathematical object, leading to challenging questions in research fields such as probability, statistical mechanics and combinatorics.[36] Here the topologies of the fundamental lattice base configurations, *viz.* triangular, square and hexagonal[37] (honeycomb), play a central role. Using the technique of lace expansion,[38] the model has been studied in dimensions greater than four: in these settings, the model behaves essentially like simple random walks. In two and three dimensions, the model still remains mysterious. The difficulty to study self-avoiding walks derives from that the process is not Markovian, and consequently standard probability techniques are inefficient.

In the consideration of cyclic structures, one can initiate a study with the enumeration of the so called *polyominos*. However, although enumerative formulae for general families are not known,[39] we can nevertheless obtain partial results in our context, as discussed in the following paragraphs.

Given an infinite number of regular polygons, the two-dimensional (2D) space can be completely filled in a regular mesh with triangles, squares and hexagons. If we use octogons or dodecagons, one can also generate a 2D regular mesh, but now with interstitial squares and equilateral triangles (Figure 7). Pentagons are quite an interesting exception to this rule.

Although objects themselves may appear to have five-fold, seven-fold, eight-fold, or higher-order rotation axes, these are not possible in 2D and 3D periodic systems, *e.g.* in crystals. This is because the external shape of a crystal is based on a geometric arrangement of its constituents (atoms), and because periodic lattices must be space filling. There are only 32 symmetry classes (point groups) in crystals. That there are only 32 symmetry classes for the external forms of crystals is a definite restriction, and the translation periodicity limits the symmetry elements that may be present in a crystal. There is a goniometric equation $m\cdot t = t + 2\cdot t\cdot\cos(\varphi)$, where $t$ is a period, $m$ an integer, and φ the rotation angle in the lattice, $\cos(\varphi) = (m - 1)/2$. As the cosine function is only allowed in the range $-1 \leq \cos(\varphi) \leq +1$, only five kinds of rotation axes are compatible with a lattice. Thus, not only is five-fold symmetry not allowed in crystal structures, but all periods larger than six are impossible. In sum, only −1, −1/2, 0, +1/2, +1 are pos-

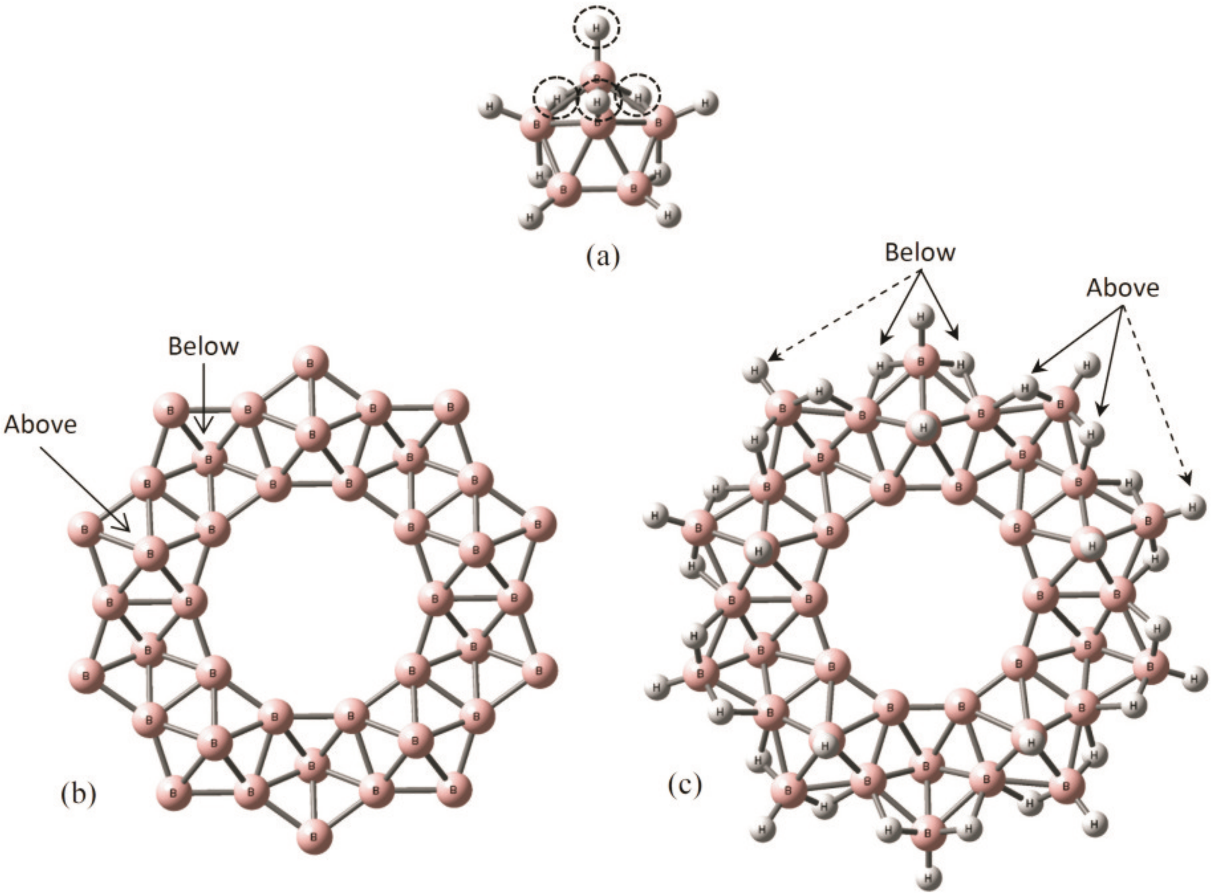

**Figure 8.** (a) Structure of *nido*-$B_6H_{10}$, which has the basic pentagonal pyramidal structure; the encircled hydrogen atom positions are carried forward to generate the structure shown in 8c; (b) the cyclic $\{B_{40}\}$ structure that has ten fused pentagonal pyramids following an alternating "···up·down·up·down···" sequence (as shown by arrows) for the apical-vertex boron atoms at the centers of the pentagons in this projection, and (c) addition of hydrogen atoms to the last structure leading to the overall cyclic $B_{40}H_{40}$ formulation **6** that has $D_{5d}$ symmetry and that corresponds to an energy minimum in B3LYP/6-31G* computations.

sible values for $cos(\varphi)$, corresponding to two-, three-, four-, six- and zero-fold rotation axes, respectively.

Given a regular 2D polygon with number of edges $n$ (where $n$ is 5, 6, 8, or 12), then if one joins it to an identical polygon by an edge to form a regular cyclic structure, then the external ($\alpha$) and internal ($\beta$) angles, and number of inner edges ($\chi$) are defined as:

$$\alpha = \frac{\pi(n-2)}{n}$$

$$\beta = \frac{\pi(n-4)}{n}$$

$$\chi = \frac{2n}{n-4}$$

Figure 7 depicts the cases for regular polygons where $n$ is 5, 6, 8 and 12. In this context, consideration of the extension pattern from Figure 3 thence readily shows that cyclic or 'closed' structures ('animals' as described by some mathematicians) are also possible. Here a very simple case is the smallest cyclic regular structure that can be made up using fused/connected pentagons, ten in number, as displayed in Figure 7a.

Thence, in the search for potentially realizable macrocyclic boranes based on the fused pentagonal motif, we proceeded as follows. First, taking into account that the neutral compound *nido*-$B_6H_{10}$ exists (Figure 8a) the fusion of ten such *nido*-shaped $\{B_6\}$ pentagonal pyramids with an ···up-down-up-down··· sequence for the axial vertices can be visualized, as in Figure 8b. Then, including for each unit the two unique encircled BH(*exo*) hydrogen atoms from Figure 8a, one can also include two bridging hydrogen atoms per unit, also encircled in 8a, reasonably placing them in bridging positions akin to those seen in the known $B_{18}H_{22}$ isomers, to generate a $B_{40}H_{40}$ cyclic entity **6**. Note, that the bridging hydrogen atoms must occupy *endo* positions on the open faces of the pentagonal pyramids, so the pairs of bridging hydrogen atoms also follow an alternately down and up sequence (Figure 8c). Different positionings for these remaining hydrogen atoms were tried, but the energy minimum was in fact found for the cyclic structure of $D_{5d}$ symmetry shown in Figure 8c. No energy minima could be found by adding B−H−B bridging or B−H(*exo*) hydrogen atoms to the inner $\{B_{10}\}$ decagon from the cyclic system of Figure 8c.

We thence examined another borane in order to produce a cyclic structure based on the cyclic ten-pentagon motif of Figure 7a, now starting from the known *closo* (*i.e.* closed deltahedral) structure of the $[B_7H_7]^{2-}$ dianion, as depicted in Figure 9a. The fusion of ten such structures with the two-boron-atoms-in-common mode of conjunction, and with the retention of the encircled hydrogen atoms from Figure 9a, thence leads to a structure **7** of $D_{10h}$ symmetry (Figure 9b). Geometry-energy optimizations of this structure, with total charge zero, *i.e.* neutral $[B_{50}H_{30}]$, lead to similar energy minima independently of the method or basis-set used.[40] The structure shown in Figure 9b corresponds to the energy minimum obtained using the B3LYP/6-31G* quantum chemical method. The energies of minimised cyclic structures for **6** and **7** are in Table 1 above.

Computations by means of Natural Population Analysis (NPA) of the electronic structures of the above two cyclic structures $B_{40}H_{40}$ **6** ($D_{5d}$) and $B_{50}H_{30}$ **7** ($D_{10h}$)[41,42] revealed interesting features. That of **6**, based based on ten fused $\{B_6\}$ *nido* shapes, shows mainly three-center bonding, with the exception of the ten B−B nearest-neighbour separations that form the ten-membered inner ring; these ten boron atoms are approximately $sp^2$-hybridized, and show strong direct two-center B−B bonding. Here it is noted that the corresponding unbridged position in *nido*-$B_6H_{10}$ itself is well known to be also essentially of two-electron two-centre character. By contrast, the second structure **7**, based on the fusion of $\{B_7\}$ *closo* shapes provides a different picture. Apart from strong two-center B−B bonds characterising the ten-membered inner ring, the joint edges are also based on two-centre two-electron bonds, now with approximately $sp^3$-hybridized B atoms. The $\{B_3\}$ triangles in which one side coincides with a body-diagonal of the bipyramid are based on three-centre two-electron bonds.

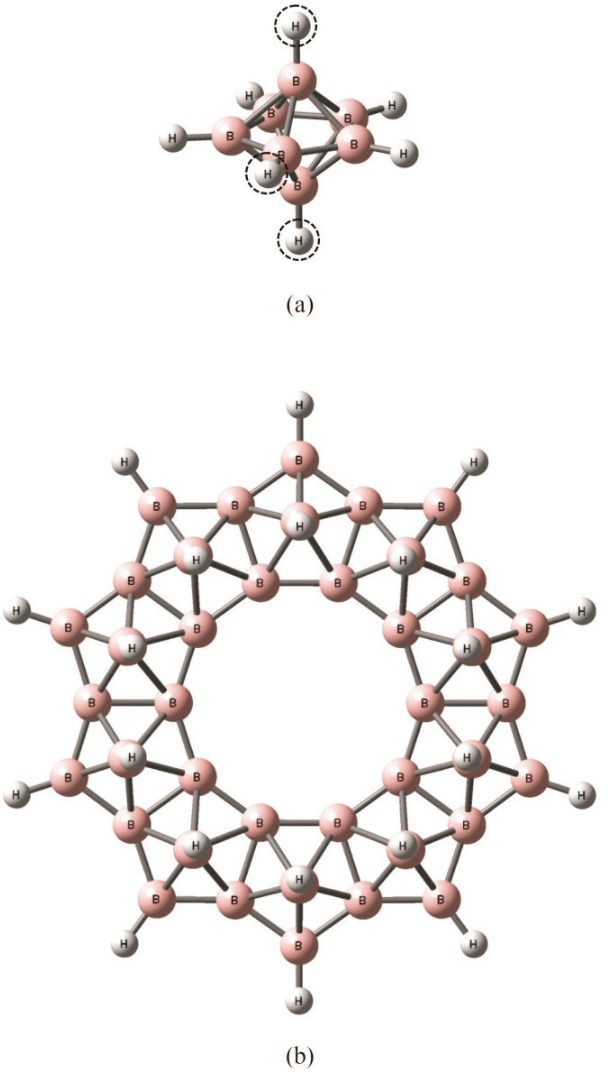

**Figure 9.** (a) Structure of the known dianionic species $[B_7H_7]^{2-}$, which has a pentagonal bipyramidal structure; (b) 2D projection, perpendicular to the $C_{10}$ axis of rotation, of the at present hypothetical cyclic structure $B_{50}H_{30}$ **7** of $D_{10h}$ symmetry, derived by the two-borons-in-common fusion of ten pentagonal bipyramidal $\{B_7H_7\}$ units by the edges of the boron atoms bound to the non-encircled hydrogen atoms from (a); the bottom BH units in each pentagonal bipyramid are eclipsed in this projection, and not visible. Both structures correspond to B3LYP/6-31G* computational energy minima.

## The *mno* rule[43] Applied to New Cyclic Structures $B_{40}H_{40}$ 6 and $B_{50}H_{30}$ 7

A structure-electron-counting correlation, the so-called *mno* 'rule', can be used in macropolyhedral boron-containing molecules to correlate the cluster structures with the formal cluster electron-counts, and it is of interest to consider this approach in relation to the neutral charges of the computed macrocyclic macropolyhedral species $B_{40}H_{40}$ **6** and $B_{50}H_{30}$ **7**. In the *mno* concept, *m* represents the number of polyhedra, *n* is related to the number of vertices, and *o* is the number of single-vertex-sharing condensations. Here it may be noted that the *mno* rule for $m = 1$ and $o = 0$ corresponds to the $n + 1$ electron-pair category in the more familiar Wade's rules.

Thus, in terms of the *mno* concept, for neutral $B_{40}H_{40}$ **6** the number of shared units (*m*) is 10, the number of atoms ($n$) is 40, the number of single-vertex-sharing condensations ($o$) is 0 and, finally, 10 electron pairs (often designated as $p$ in *nido* and *arachno* clusters that build the macropolyhedra) are needed to compensate for the absent ten vertices (in terms of a *nido* building block), *i.e.* the polyhedral *polynido* skeleton requires $m + n + o + p =$ **60** electron pairs. The 20 B−H units give 20 cluster electron pairs, and twenty bridging hydrogen atoms give 10 electron pairs to the skeletal bonding. Of 10 joint edges, each edge gives three electrons (*i.e.* all of its valence electrons because there is no *exo*-2c-2e bond) to make the total electron pairs also **60**, in accord with the *mno* sum. Neutral $B_{50}H_{30}$ (**7**) and the fifth $B_{18}H_{22}$ isomer **5** can be treated in a similar manner. For $B_{50}H_{30}$ we have $m = 10$, $n = 50$ and $o$ and $p = 0$ for *closo* (closed-cage) systems, again corresponding to **60** electron pairs: 30 B−H terminal groups provide 30 cluster electron pairs, and 10 edges (20 atoms) also provide 30 electron pairs, as with the *polynido* structure of **6**. Therefore, the total number of electron pairs is **60**, again in accord with the *mno* sum.

As for the five $B_{18}H_{22}$ isomers, the known *syn*-$B_{18}H_{22}$ and *anti*-$B_{18}H_{22}$ isomers were dealt with in one of the original papers on the *mno* concept,[44] and the two additional isomers **3** and **4** follow entirely the same reasoning. For the fifth isomer, **5**, $m = 3$, $n = 18$, $o = 0$, and $p = 3$ (*nido*), giving **24** electron pairs as the *mno* sum. Fourteen B−H(*exo*) units provide 14 cluster electron pairs, two edges (4 x 3)/2 provide 6 electron pairs, and 8 bridges provide 4 pairs, *i.e.* 14 + 6 + 4 = **24**, consistent with the *mno* sum.

## CONCLUSION

Borane molecules $B_xH_y$ are well known and varied, both as neutral and ionic species. The boranes, together with their metallaborane, main-group-heteroborane, and metallaheteroborane congeners, engender a rich variety of architectures with open and closed polyhedral structures. In this work, via the extension of known borane structural principles, we have presented computational work that suggests that three new additional isomers of $B_{18}H_{22}$ may be feasible. The new structures of these new species are higher in energy than their well known *anti*- and *syn*- isomers, but, in view of the kinetic stability of the known isomers, it is reasonable to predict that these new isomers will also be kinetically stable, and thence ultimately isolatable when appropriate synthetic chemistry is developed. In a further extension of the same structural priciples, in a search for a stable cyclic structure built up by the "…up-down-up-down…" edge-fusing of ten *nido*-$B_6H_{10}$-based pentagonal pyramidal units we found an energy-minimum structure with $D_{5d}$ symmetry for the resulting '*polynido*' neutral species *cyclo*-$B_{40}H_{40}$. Similarly, the fusion of ten $\{B_7H_7\}$-based *closo* pentagonal bipyramids gave *cyclo*-$B_{50}H_{70}$ with an energy-minimum cyclic structure with $D_{10h}$ symmetry and total charge zero (and spin zero). We have also considered from a mathematical point of view the challenges involved in the extension of the structural principles of borane molecules by the consideration of different extension units and ways of counting the extended molecules. For instance, Figure 3 displays extension patterns starting from two edge-fused pentagonal pyramids, the pentagonal pyramid being an ubiquitous structural feature of most single-cluster boron-containing cluster species. Overall, the findings point the way to further applications of different ways of extending known structures to predict new linear and cyclic species. Possibilities in the area of cyclic structures based on a pentagonal motif are depicted in Figure 10, in which different modes of building up cyclic structures are proposed.

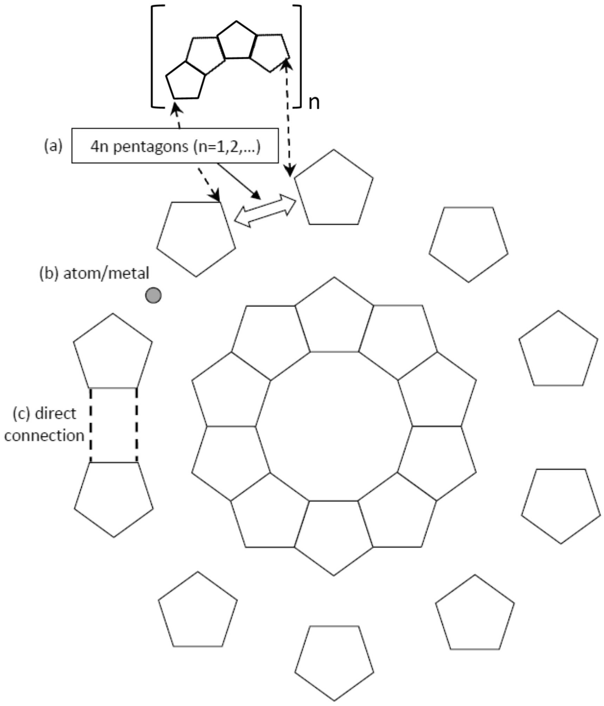

**Figure 10.** Extension of cyclic structures based on pentagons and using different connecting patterns with a $C_{10}$ rotation axis. Mode (a) of connection corresponds to addition of 4n pentagons fused as described in the square brackets. Mode (b) corresponds to an addition of a single atom/metal between pentagons, and mode (c) to a direct connection using one or more atoms in a parallel fashion, e.g., with two –CH=CH– moieties.

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## REFERENCES

1. M. G. Davidson, K. Wade, T. B. Marder, and A. K. Hughes, *Contemporary Boron Chemistry*, The Royal Society of Chemistry, Cambridge, 2000.
2. W. N. Kang, H.-J. Kim, E.-M. Choi, C. U. Jung, and S.-I. Lee, *Science* **292** (2001) 1521.
3. R. Naslain, R. Guette, and M. J. Barret, *J. Solid State Chem.* **8** (1973) 68.
4. P. Blum and F. Bertaut, *Acta Crystallogr.* **7** (1954) 81.
5. E. D. Jemmis and E. G. Jayasree, *Acc. Chem. Res.* **36** (2003) 816.
6. J. Casanova, *The Borane Carborane Carbocation Continuum,* Wiley, New York, 1998.
7. E. Amberger, *Elemental boron*, in K. C. Buschbeck (Ed.), *Gmelin Handbook of Inorganic and Organometallic Chemistry*: B Boron, Supplement 2 (8th ed.), Berlin: Springer-Verlag. pp. 1–112.
8. S. L. Shea, J. Bould, M. G. S. Londesborough, S. D. Perera, A. Franken, D. L. Ormsby, T. Jelínek, B. Stíbr, J. Holub, C. A. Kilner, M. Thornton-Pett, and J. D. Kennedy, *Pure Appl. Chem.* **75** (2003) 1239.
9. W. N. Lipscomb, in *Boron Hydrides*, Benjamin, New York, 1963.
10. W. N. Lipscomb, *Inorg. Chem.* (1980) 1415.
11. R. N. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. USA* **47** (1961) 996.
12. M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.* **88** (1966) 3873.
13. B. G. DeBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.* **7** (1968) 1085.
14. J. Rathke and R. Schaeffer, *Inorg. Chem.* **13** (1974) 3008.
15. R. L. Pilling, M. F. Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.* **86** (1968) 3568.
16. C. H. Schwalbe and W. N. Lipscomb, *J. Am. Chem. Soc.* **91** (1969) 194.
17. There are four isomers, according to type of contacts of two $B_{10}H_{10}{}^{(2-)}$ units + so-called *fac*-$B_{20}H_{18}{}^{(2-)}$ with three shared B-vertices.
18. G. Evrard, V. A. Ricci, Jr., I. Bernal, W. J. Evans, D. F. Dustin, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.* (1974) 234.
19. J. C. Huffman, D. C. Moody, and R. Schaeffer, *J. Am. Chem. Soc.* **97** (1975) 1621.
20. J. C. Huffman, D. C. Moody, and R. Schaeffer, *Inorg. Chem.* **20** (1981) 741.
21. P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.* **39** (1963) 26.
22. J. H. Enemark, L. B. Friedman, and W. N. Lipscomb, *Inorg. Chem.* **5** (1966) 2165.
23. E. Bernhardt, D. J. Brauer, M. Finze, and H. Willner, *Angew. Chem. Int. Ed.* **46** (2007) 2927.
24. I. Higashi, T. Sakurai, and T. Atoda, *J. Solid State Chem.* **20** (1977) 67.
25. M. Vlasse, R. Naslain, J. S. Kasper, and K. Ploog, *J. Solid State Chem.* **28** (1979) 289.
26. R. D. Dobrott, L. B. Friedman, and W. N. Lipscomb, *J. Chem. Phys.* **40** (1964) 866.
27. W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.* **98** (1976) 3490.
28. Systematization and structures of the boron hydrides, L. Barton, New Trends in Chemistry, Topics in Current Chemistry Volume 100 (1982) pp 169-206: from $BH_3$ to icosaborane(16), $B_{20}H_{16}$ and oligomeric *closo*-Borane anions.
29. E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *Chem. Rev.* **102** (2002) 93.
30. J. M . Oliva and A. Vegas, *Chem. Phys. Lett.* **533** (2012) 50.
31. F. A. Kiani and M. Hofmann, *Dalton Trans.* (2007) 1207.
32. M. G. S. Londesborough, D. Hnyk, J. Bould, L. Serrano-Andrés, V. Saurí, J. M. Oliva, P. Kubat, T. Polívka, and K. Lang, *Inorg. Chem.* **51** (2012) 1471.
33. A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.* **84** (1962) 3218.
34. M. Bousquet-Mélou, On the importance sampling of self-avoiding walks, ArXiv 1106.1876.
35. P. A. Flory, in *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953.
36. N. Madras and G. Slade, *The Self-Avoiding Walk, Probab. Appl.*, Birkhauser, Boston, MA, 1993.
37. See for instance, the exotic properties of graphene. A. K. Geim and K. S. Novoselov *Nature Materials* **6** (3) (2007) 183. Graphene may exhibit 'exotic superconductivity'.
38. G. Slade, in *The Lace Expansion and its Applications*, Lecture Notes in Mathematics 1879, Springer, Berlin (2006).
39. M. Bousquet-Mélou, *Disc. Math.* **180** (1996) 73.
40. We used Hartree-Fock and B3LYP methodologies combined with basis sets STO-3G, STO-3G*, 6-31G* and 6-31G**.
41. E. D. Glendening, C. R. Landis, and F. Weinhold, in *Natural Bond Orbital Methods*, Wiley Interdisciplinary Reviews **2** (2012) 1.
42. J. Z. Dávalos, J .González, A. Guerrero, D. Hnyk, J. Holub, and J. M. Oliva, *J. Phys. Chem. C* **117** (2013) 1495.
43. E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *J. Am. Chem. Soc.* **123** (2001) 4313.
44. E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *Inorg. Chem.* **40** (2001) 1730.