

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

- Dedicated to Douglas J. Klein -

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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. Borane polyhedral concatenation of molecules is also considered from a mathematical point of view.

1. Introduction

With one electron fewer than carbon, boron engenders a very rich chemistry which ranges from the solid state – in combination with metals and non-metals – to molecular organic and inorganic chemistry.¹ The transition from two-dimensional to three-dimensional structures in boron is a notable feature of boron chemistry: for instance, solid MgB_2 is a superconductor² 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 pyramids³ and MgB_6 is based on octahedral $\{\text{B}_6\}$ moieties.⁴ Here it is noted that the similarity of pentagonal pyramidal $\text{C}_6\text{H}_6^{2+}$ and the pentagonal pyramids in solid MgB_4 have been rationalised⁵ by means of structural correlations between boron and carbon compounds.⁶

Several allotropes of elemental boron exist, where $\{\text{B}_{12}\}$ icosahedra are connected in different ways.⁷ When combined with other elements from the Periodic Table, the chemistry of boron is expanded to yield a very rich library of architectural constructs in any dimension.⁸

The combination of boron with hydrogen leads to the well-known B_xH_y deltahedral structures⁹ – the boranes. In 1980, William Lipscomb described examples of possible polymeric borane structures;¹⁰ at least ten different bonding schemes between polyhedral species can now be categorised, for example: (1) a single $\text{B}\cdots\text{B}$ bond in¹¹ $\text{B}_{10}\text{H}_{16}$, which is a dimer of B_5H_8 (Figure 1a), (2) a single three-center BHB bond in¹² $\text{B}_{20}\text{H}_{19}^{3-}$, (3) two BHB bridges as in^{!Error! Marcador no definido.}¹³ photo- $\text{B}_{20}\text{H}_{18}^{2-}$, (4) one three-center BBB bond, as in¹⁴ $\text{B}_{15}\text{H}_{23}$ and in $\mu\text{-Fe}(\text{CO})_4\text{B}_7\text{H}_{12}^-$, (5) two three-center BBB bonds, as in^{15,16,17} $\text{B}_{20}\text{H}_{18}^{2-}$, (6) one shared atom, as in¹⁸ $(\eta^5\text{-C}_5\text{H}_5)\text{CoC}_2\text{B}_{10}\text{H}_{10}\text{CoC}_2\text{B}_{10}\text{H}_{10}^-$, (7) two shared boron atoms, which can result in different configurations, *e.g.* *cis* as in^{19,20} $\text{B}_{14}\text{H}_{20}$ (Figure 1b) and *trans* as in²¹ *anti*- $\text{B}_{18}\text{H}_{22}$ (see section 2 below), (8) three shared boron atoms, as in²² $\text{B}_{20}\text{H}_{16}(\text{NCCCH}_3)_2$, in²³ $\text{B}_{21}\text{H}_{18}^-$, and as in²⁴ solid-state $\alpha\text{-AlB}_{12}$ and a related structure²⁵ for boron, (9) four shared boron atoms, as in²⁶ $\text{B}_{20}\text{H}_{16}$, and (10) a “double cap” join, as in²⁷ $(\text{CH}_3)_4\text{C}_4\text{H}_8\text{FeCo}(\eta^5\text{-C}_5\text{H}_5)$.

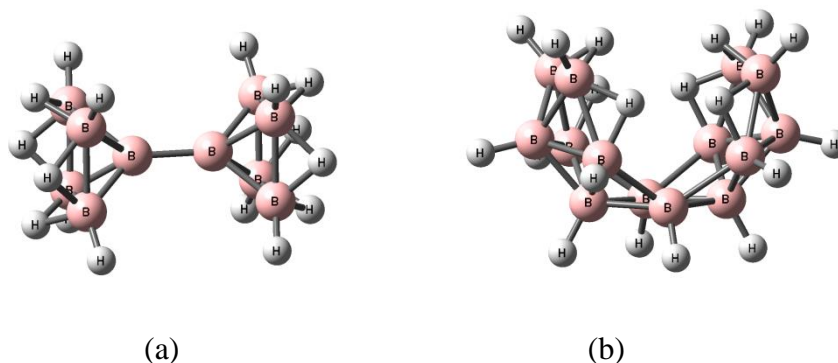


Figure 1. Example of (a) single B-B bond in $B_{10}H_{16}$, and (b) two shared boron atoms in *cis* $B_{14}H_{20}$. B3LYP/6-31G* optimized geometries (energy minima).

When considering the extension of known borane structures²⁸ in the search for potential novel cluster macromolecules²⁹ one can proceed as follows:

- (a) Reasonable extrapolation of known bonding e.g. ethane to polyethylene.
- (b) By 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 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 use of procedure (a) above in order to introduce new *open* and *cyclic* molecular constructs with Lipscomb's bonding mode (7) as also delineated above, namely, building-up extended polyhedral structures based on two shared boron atoms³¹ in the particular case of fused pentagonal pyramids, following extensions of the known isomers of $B_{18}H_{22}$, namely *anti*- $B_{18}H_{22}$ and *syn*- $B_{18}H_{22}$.

2. New isomers derived from $B_{18}H_{22}$

To date, two isomers of the $B_{18}H_{22}$ borane are known:³² the *anti*- $B_{18}H_{22}$ isomer (**1**), *anti-transoid*, with C_i symmetry, and the *syn*- $B_{18}H_{22}$ isomer (**2**), *syn-transoid*, with C_2 symmetry. Figure 2 depicts the geometries of the two isomers.

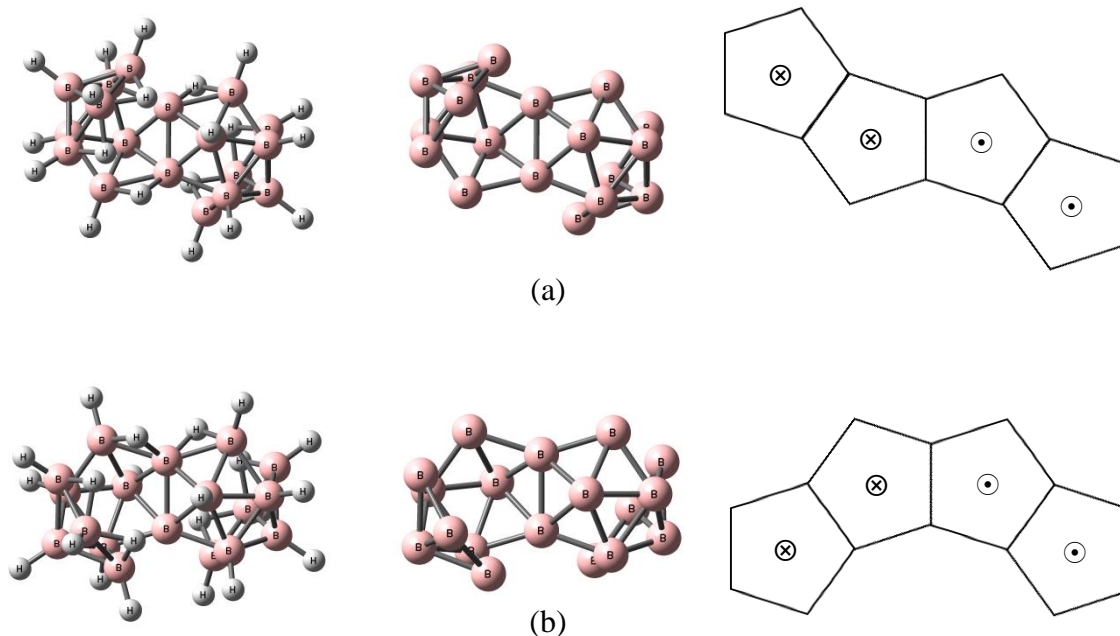


Figure 2. Optimized structures of (a) *anti-transoid* or simply *anti*- $B_{18}H_{22}$ (**1**), C_i symmetry, and (b) *syn-transoid* or simply *syn*- $B_{18}H_{22}$ (**2**), C_2 symmetry. *Transoid* refers to the connecting mode between the two central pentagons. We show from left to right: the whole structure, the molecule with hydrogens removed for clarity and a simplified 2D unfolded representation of the $\{B_{18}\}$ units. The symbols \odot and \otimes mean respectively a boron atom above and below the projection plane in a 2D projection. B3LYP/6-31G* computations.

At this point it is noted that, since the synthesis and the description of absorption bands of both isomers,³³ it has been known that *anti*- $B_{18}H_{22}$ (**1**) fluoresces but *syn*- $B_{18}H_{22}$ (**2**) does not, thus the two isomers have distinct photophysics. Recently, we explained this natural phenomenon by means of high-level quantum-chemical computations.³²

Taking into account the 2D unfolded projections from Figure 2, it is reasonable to speculate an extension of the $B_{18}H_{22}$ structures by the addition of further pentagons, starting off from the two central fused pentagonal pyramids, as shown in Figure 3.

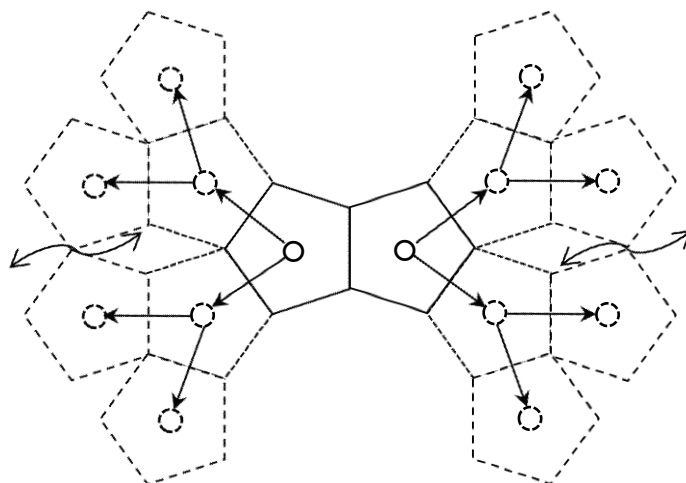


Figure 3. Proposed extension patterns starting off from two fused pentagonal pyramids – solid lines. The curved double arrows indicate that structures with steric clashes should be avoided. The empty circles in the center of each pentagon indicate that in the 2D projection the boron atom can be above (\odot) or below (\otimes) the 2D projection plane.

The extended structures follow the arrows on each direction in such a way that no two pentagons' vertices 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.* two fused pentagonal pyramids – original unit – it is also necessary to consider the positioning of the top (apical, axial) vertices of the pentagonal pyramids, e.g. as in Figure 2, where the symbols \odot or \otimes mean respectively that, in the 2D projection of the structure, the apical vertex is above or below the projection plane. Thence, the consideration of different positions of the central axial atoms in the pentagonal pyramids, and the projections of these vertices unto the projection plane, other than those found in the known *anti*- $B_{18}H_{22}$ and *syn*- $B_{18}H_{22}$ isomers, leads to two so far experimentally unknown isomers with the $B_{18}H_{22}$ formulation. Specifically, starting from 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 screen plane (\otimes) are changed to positions *above* the plane

(\odot), then two new isomers (**3**) and (**4**) result, the *anti-cisoid* and the *syn-cisoid* $B_{18}H_{22}$ structures respectively, as depicted in Figure 4.

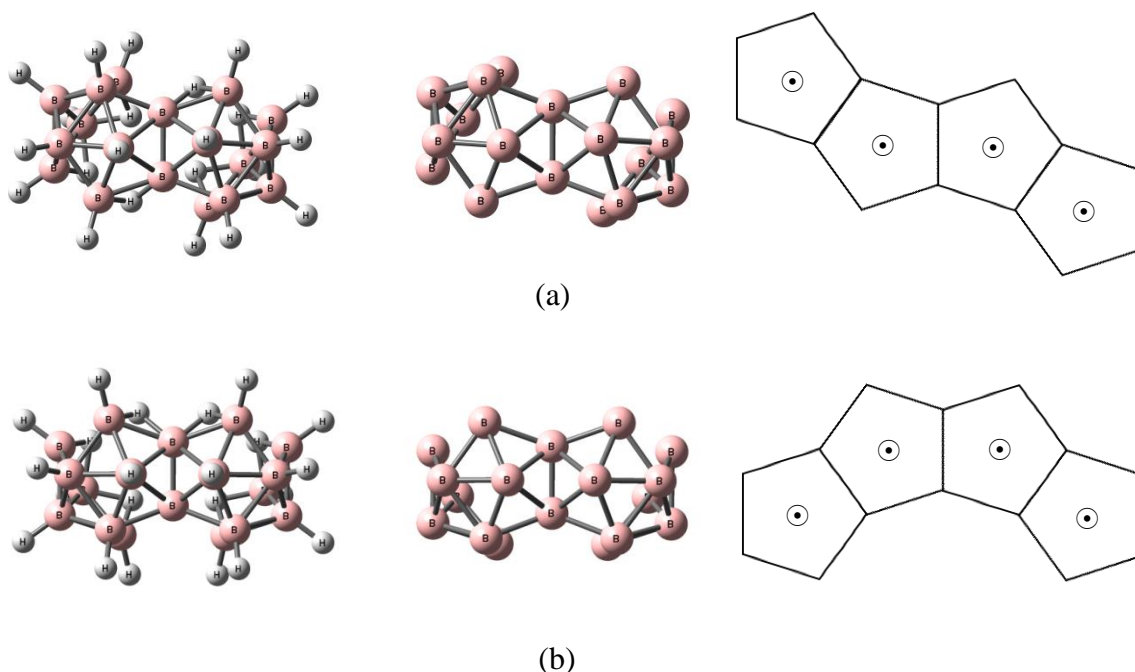


Figure 4. Optimized geometry of the (a) *anti-cisoid* $B_{18}H_{22}$ (**3**) with C_2 symmetry, and (b) *syn-cisoid* $B_{18}H_{22}$ (**4**) with C_s symmetry. In (**3**) and (**4**) the mutual orientation of boat-like hexagonal belts of the respective decaborane units are *cisoid*, whereas in (**1**) and (**2**) such an orientation is *transoid*. We show from left to right: the whole structure, the molecule with hydrogens removed for clarity, and a simplified 2D unfolded projection. The symbol \odot means that the boron atom is above the screen plane in the 2D unfolded projection. B3LYP/6-31G* computations.

Quantum-chemical computations show that isomers (**3**) and (**4**) are energy minima, but quite 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.

Table 1. Energies and energy differences for the different isomers of $B_{18}H_{22}$. We also gather energies for cyclic structures (**6**) and (**7**) – see Section 4 below. B3LYP/6-31G* computations. The geometries of all molecules correspond to energy minima at this level of theory.

$B_{18}H_{22}$	Symmetry	Energy (au)	ΔE (kJ·mol ⁻¹)
<i>anti-transoid</i> (1)	C_i	-460.703685	0.0
<i>syn-transoid</i> (2)	C_2	-460.701612	5.4
<i>anti-cisoid</i> (3)	C_2	-460.620937	217.3
<i>syn-cisoid</i> (4)	C_s	-460.612636	239.0
<i>isomer</i> (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	---

An alternative factorization of the structures of the $B_{18}H_{22}$ isomers is that they result from the formal fusions of *nido*- $B_{10}H_{14}$ units with two atoms held in common – this in fact best represents the chemistry itself, as each $B_{18}H_{22}$ subcluster 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), $B_{26}H_{30}$, $B_{34}H_{38}$...namely the $B_{8n+2}H_{8n+6}$ series ($n = 1, 2, 3, \dots, \infty$).

We also considered a further isomer derived from $B_{18}H_{22}$ (5), following a different ‘fusion’ scheme, as depicted in Figure 5, which also results an energy minimum.

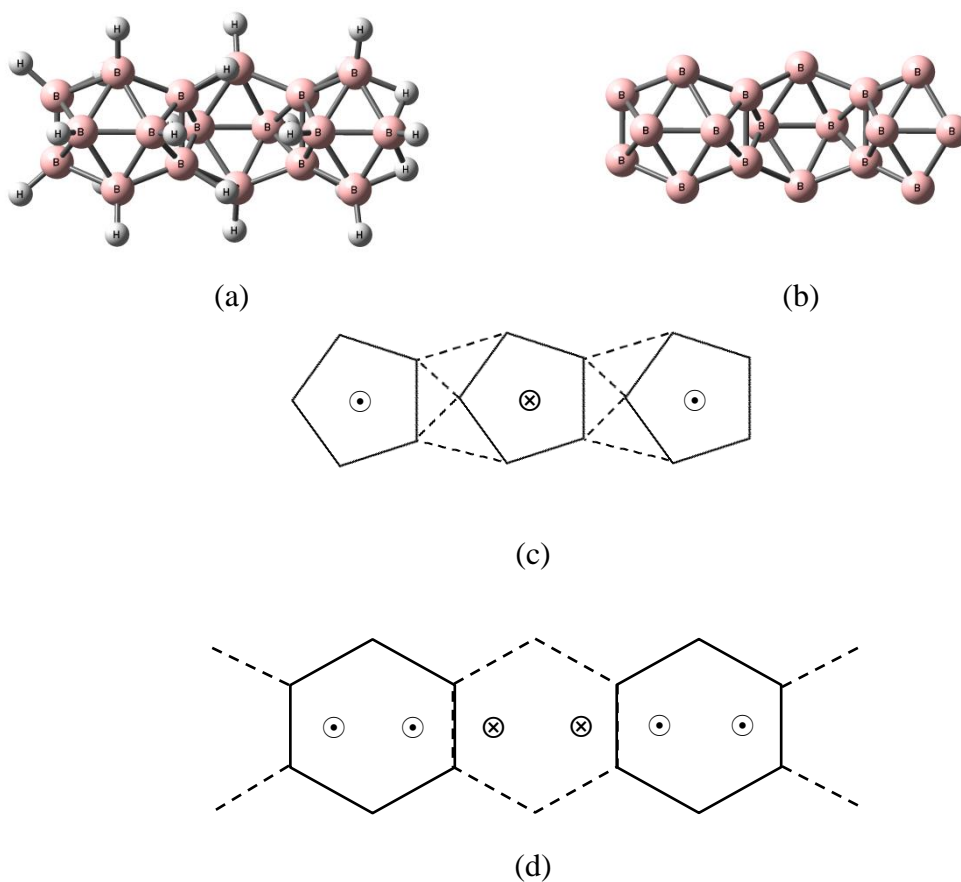


Figure 5. Optimized geometry of an additional isomer of $B_{18}H_{22}$ (5), C_s symmetry, following a different extension pattern. We show (a) the whole structure (B3LYP/6-31G* computations), (b) the molecule without hydrogens for clarity, and (c) a 2D unfolded projection of the isomer using pentagons. 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 \odot and \otimes indicate respectively that the central boron atom in the pentagon is located above and below the 2D projection plane.

In this latter case we observe a natural way of extending in 1D the isomer from Figure 5c(d) to an infinite structure, provided that the atoms at the center of the pentagon(hexagon) follow the pattern $\{...\odot(\odot)\otimes(\otimes)\odot(\odot)\otimes(\otimes)...\}$.

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 – can lead to novel cluster macromolecules with different properties. It is reasonable to predict the future isolation of such species, but at present with no transferable generic routes for borane cluster fusion chemistry, it is not clear how this may be effected.

The question we now put forward is ‘how many isomers/conformers can we enumerate given a number of pentagons, and following a given extension pattern?’.

3. Mathematical considerations for extension of borane molecules. Cyclic constructions

As we have seen from the above results, borane chemistry can lead to interesting patterns derived from original units, corresponding to existing boranes. Thus, two extension patterns – Figure 3 and Figure 5 – can lead to novel cluster macromolecules with different properties.

A more general question is ‘how many isomers/conformers can we sample 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 involved³⁴. In this section we motivate this fact rephrasing the problem into the context of self-avoiding walks, and we make explicit constructions when dealing with cyclic configurations.

As pointed out by the chemist P. Flory,³⁵ there exists a deep connection between combinatorial models and chemical configurations. Flory proposed³⁵ considering self-avoiding walks (i.e., walks visiting every vertex at most once) on a lattice as a model for spatial position of polymer chains. Self-avoiding walks turned out to be very interesting mathematical objects, leading to challenging questions in such research fields as probability, statistical mechanics and combinatorics.³⁶ In fact, the topology of the lattice base configurations – triangular, square and hexagonal³⁷ (honeycomb) – has played a central role in this area. Using the lace expansion technique, the model has been studied

in dimensions greater than four: in this case, it behaves like simple random walks. In two and three dimensions, the model remains mysterious. The difficulty to study self-avoiding walks comes from the fact that the process is not markovian, and consequently standard probability techniques are unefficient.

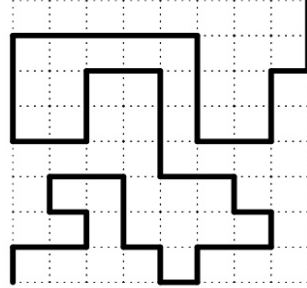


Figure 6. A self-avoiding walk on the square lattice with 48 steps.

When considering cyclic structures, one can relate the study with the enumeration of the so called *polyominos*. Similarly, enumerative formulas for general families are not known³⁸. However, we can obtain partial results in our context which are discussed in the following lines.

Given an infinite number of regular polygons, the 2D space can be ‘filled in a regular mesh’ with triangles, squares and hexagons. If we use octagons or dodecagons, one can also fill a 2D mesh but with interstitial squares and equilateral triangles – see Figure 7. Pentagons are quite an interesting exception to this rule.

Although objects themselves may appear to have 5-fold, 7-fold, 8-fold, or higher-fold rotation axes, these are not possible in 2D and 3D periodic systems, i.e. in crystals. The reason is that the external shape of a crystal is based on a geometric arrangement of atoms, and that periodic lattices must be space filling. There are only 32 symmetry classes (point groups) in crystals. These 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 number, and φ is 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 summary, only -1 , $-1/2$, 0 , $+1/2$, $+1$ are possible values for $\cos(\varphi)$, corresponding to 2-, 3-, 4-, 6- and 0-fold rotation axes, respectively.

Given a regular 2D polygon with number of edges $n = (5, 6, 8, 12)$, then if one joins the same polygon by an edge to form a regular cyclic structure, then the external (α) and internal (β) angles, and number of inner edges (χ) 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 $n = (5, 6, 8, 12)$. If we take a close look to the extension pattern from Figure 3, one can readily see that cyclic or ‘closed’ structures – ‘animals’ as described by mathematicians – are also possible. A very simple case is the smallest cyclic regular structure that can be made up using fused/connected pentagons, as displayed in Figure 7a.

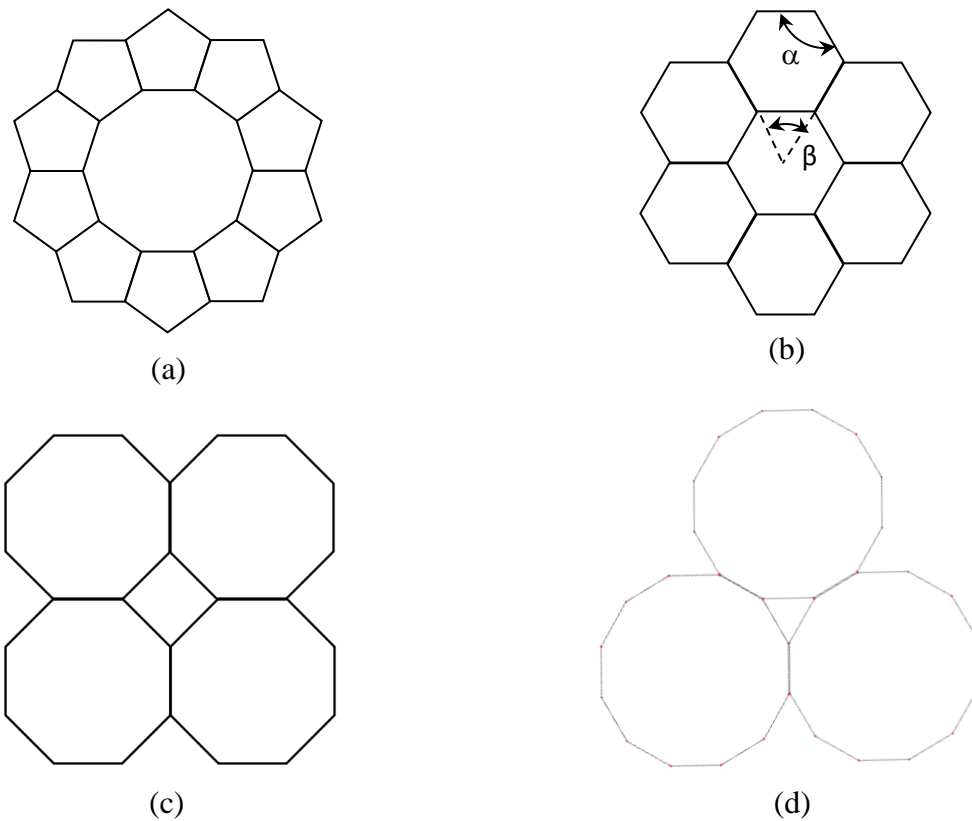


Figure 7. Examples of cyclic ‘fused’ regular polygons. (a) $n = 5$, ten pentagons, (b) $n = 6$, six hexagons, (c) $n = 8$, four octagons, (d) $n = 12$, three dodecagons.

In the search for a potential realizable ‘cyclic’ boranes derived from fused pentagons, we proceeded as follows. First, taking into account that neutral B_6H_{10} exists – Figure 8a – one could think of fusing ten such pentagonal pyramids with an \cdots up-down-up-down \cdots sequence for the axial ‘top-vertex’ vertices – Figure 8b. Then, maintaining the encircled hydrogen atoms from Figure 8a, one could add additional hydrogen atoms, reasonably placing them in bridging positions akin to those in the known $B_{18}H_{22}$ isomers. Note, however, that given the structure from Figure 8b, certain bridging (three-center) hydrogen atoms cannot longer be located in the same position given the symmetry of the cycle. Thus bridging hydrogen atoms also follow alternately down and up sequence (Figure 8c). We tried different positionings for the remaining hydrogen atoms and finally found an energy minimum with D_{5d} symmetry for the cyclic structure $B_{40}H_{40}$ (**6**), as displayed in Figure 8c. No energy minima could be found by adding bridging or bound-to-boron hydrogen atoms to the inner $\{B_{10}\}$ decagon from the cyclic system of Figure 8c.

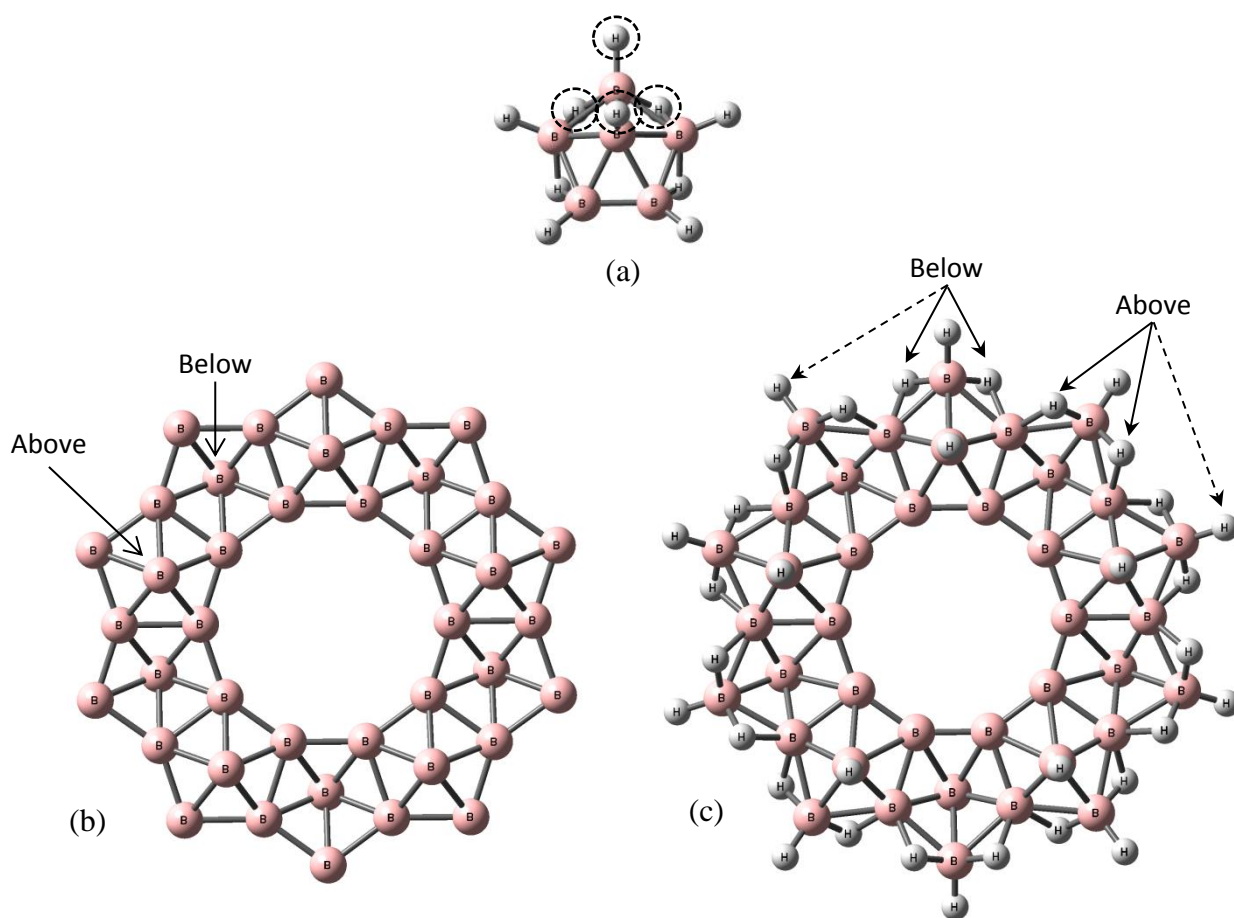


Figure 8. (a) Structure of B_6H_{10} , with a pentagonal pyramidal structure; (b) cyclic $\{B_{40}\}$ structure with ten fused pentagonal pyramids following an alternating “...up·down·up·down...” series for the top/bottom-vertex boron atom at the center of each pentagon in the projection, as shown by arrows, and (c) addition of hydrogen atoms to the former structure leading to the $B_{40}H_{40}$ formulation - cyclic structure (6) - with D_{5d} symmetry and corresponding to an energy minimum. B3LYP/6-31G* computations.

We tried using another borane in order to produce a cyclic structure with ten pentagons: specifically we started from the known *closo* (closed polyhedral) structure of the $[B_7H_7]^{2-}$ dianion, depicted in Figure 9a. Fusing ten such structures with the two-boron-atoms-in-common conjunction, and maintaining the encircled hydrogen atoms from Figure 9a, leads to a structure of D_{10h} symmetry, which is depicted in Figure 9b. A geometry optimization of this structure, with total charge zero, *i.e.* neutral $[B_{50}H_{30}]$, leads to an energy minimum, independently from the method or basis-set used.³⁹ The structure from Figure 9b corresponds to the energy minimum obtained with the B3LYP/6-31G* quantum chemical method. The energies of cyclic structures (6) and (7) are gathered in Table 1 above.

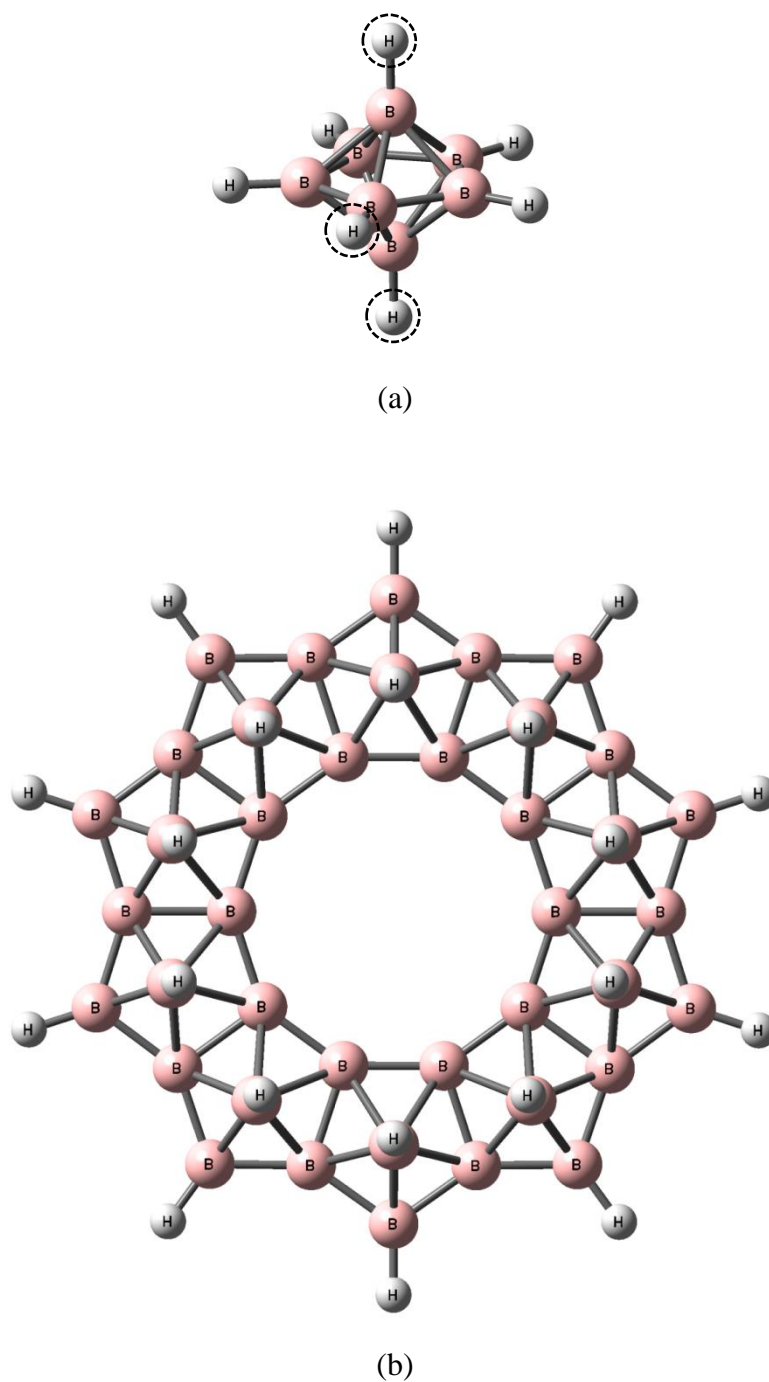


Figure 9. (a) Structure of $B_7H_7^{2-}$, with a pentagonal bipyramidal structure; (b) 2D projection, perpendicular to the C_{10} axis of rotation, of the cyclic structure $B_{50}H_{30}$ of D_{10h} symmetry, derived by the two-borons-in-common fusing of ten pentagonal bipyramidal $\{B_7H_7\}$ units by the edges of the boron atoms bound to the non-encircled hydrogen atoms from (a); B3LYP/6-31G* computations. Not shown are the hydrogen atoms below each pentagonal bipyramid. Both structures correspond to energy minima. Only structure (a) is known.

Electronic structure computations on the above two cyclic structures $B_{40}H_{40}$ (D_{5d}) and $B_{50}H_{30}$ (D_{10h}) by means of Natural Population Analysis (NPA)^{40,41} revealed interesting features. Whereas that based on ten *nido*- $B_6H_6^{(4-)}$'s shows mainly three-center bonding with an exception of B-B nearest-neighbour separations that forms 10-membered inner ring (B atoms are approximately sp^2 -hybridized), the second structure formed by edge-shared *closo*- $B_7H_7^{(2-)}$'s provides a different picture. Apart from B-B bonds being parts of the above 10-membered inner ring, the joint edges are also based on 2c-2e bonds with approximate sp^3 -hybridized B atoms. Boron triangles in which one side coincides with a body-diagonal of the bipyramid are based on 3c-2e bonds.

*The mno rule*⁴² applied to new cyclic structures $B_{40}H_{40}$ and $B_{50}H_{30}$

A more generally applicable electron-counting rule, the *mno* rule that reveals also the ground for the existence of the so-called macropolyhedral boranes, is used in the following to verify the correctness of neutral charge for these two predicted macropolyhedral boron clusters. In this concept *m* represents the number of polyhedra, *n* is related to the number of vertices, and *o* is the number of single-vertex-sharing condensation. Note that Wade's *n* + 1 rule stems from the *mno* rule for *m* = 1 and *o* = 0.

According to this *mno* rule $B_{40}H_{40}$ (**6**) is neutral since 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 building the macropolyhedra) are needed to compensate 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 groups give 20 electron pairs, and twenty bridging hydrogens give 10 electron pairs to the skeletal bonding. Of 10 joint edges each give three electrons (all its valence electrons because there is no *exo*-2c-2e bond) to make the total electron pairs 60. $B_{50}H_{30}$ (**7**) and the fifth isomer $B_{18}H_{22}$ (**5**) are worked out in a similar manner. For $B_{50}H_{30}$ we have *m* = 10, *n* = 50 and *o* and *p* = 0 for *closo* (closed cages) systems, namely, corresponding to 60 electron pairs: 30 BH terminal bonds provide 30 electron pairs, and 10 edges (20 atoms) also provide 30 electron pairs (in analogy with polynido). Therefore, the total number of electron pairs is 60.

As for the five $B_{18}H_{22}$ isomers, the *mno* rule was applied to known *syn*- $B_{18}H_{22}$ and *anti*- $B_{18}H_{22}$ isomers.⁴³ The two additional isomers (**3**) and (**4**) follow entirely the same

reasoning. For the fifth isomer, **5**, we have $m = 3$, $n = 18$, $o = 0$, $p = 3$ (*nido*) = 24 electron pairs, with 14 B-H bonds = 14 electron pairs, two edges $(4 \times 3)/2 = 6$ electron pairs, and 8 bridges = 4 pairs, i.e. $14 + 6 + 4 = \underline{24}$.

5. Conclusions

Borane molecules B_xH_y are well known and varied. These molecules form a rich variety of architectures with open and closed polyhedral structures. In this work we present computational work suggesting three new additional isomers of $B_{18}H_{22}$. These new structures are higher in energy than the well known *anti*- and *syn*- isomers of $B_{18}H_{22}$, but, in view of the stability of the known isomers, it is reasonable to predict that these new isomers will be isolatable when appropriate synthetic chemistry is developed. In the search for a stable cyclic structure built up by edge-fusing “up-down-up-down...” ten B_6H_{10} pentagonal pyramids we found an energy minimum structure with the corresponding D_{5d} symmetry for the resulting ‘*polynido*’ neutral species $B_{40}H_{40}$. Similarly, when fusing ten B_7H_7 pentagonal bipyramids to give *cyclo*- $B_{50}H_{70}$ we were able to find an energy-minimum cyclic structure with D_{10h} symmetry and total charge zero (and spin zero). This finding opens up different ways of extending “cyclic” structures, as depicted in Figure 10, where different modes of building up cyclic structures are proposed.

We also considered from a mathematical point of view the challenges involved in the extension of borane molecules when considering different extension units and ways of counting the extended molecules. For instance, Figure 3 displays extension patterns starting from two edge-fused pentagons.

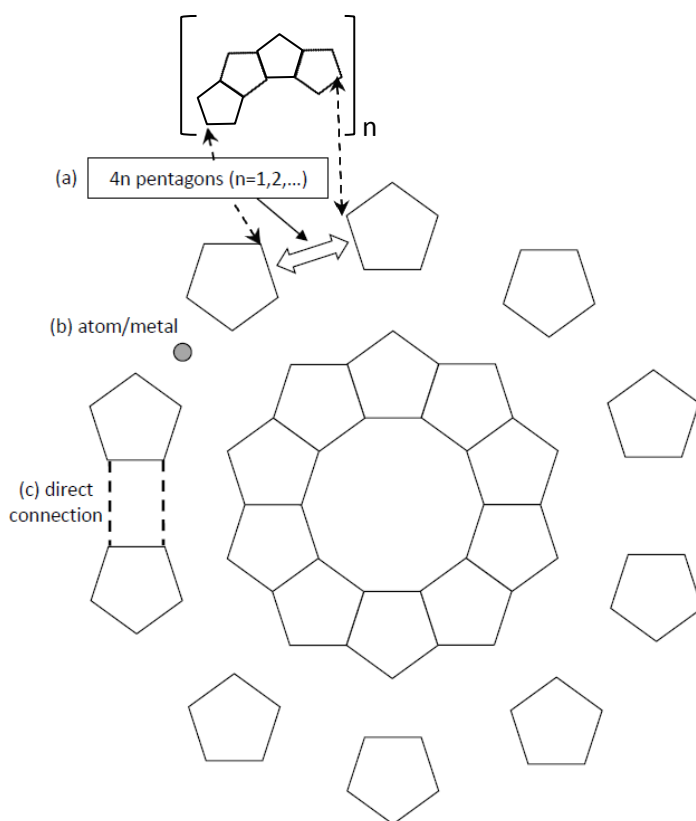


Figure 10. Extension of cyclic structures based on pentagons and using different connecting patterns with a C_{10} rotation axis. Mode (a) of connection corresponds to addition of $4n$ pentagons fused as described in the square brackets. Mode (b) corresponds to an addition of a single atom/metal between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

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References

- ¹ Contemporary Boron Chemistry, (eds) M. G. Davidson, K. Wade, T. B. Marder, A. K. Hughes, 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) 1521-1523.
- ³ R. Naslain, R. Guette, and M. J. Barret, *J. Solid State Chem.* **8** (1973) 68 – 85.
- ⁴ P. Blum and F. Bertaut, *Acta Crystallogr.* **7** (1954) 81-86.
- ⁵ E. D. Jemmis and E. G. Jayasree, *Acc. Chem. Res.* **36** (2003) 816-824.
- ⁶ The Borane Carborane Carbocation Continuum, Ed. J. Casanova, Wiley, New York, 1998.
- ⁷ E. Amberger (1981). "Elemental boron". In Buschbeck, K. C. 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) 1239-1248.
- ⁹ W. N. Lipscomb, in *Boron Hydrides*, Benjamin, New York, 1963.
- ¹⁰ W. N. Lipscomb, *Inorg. Chem.* (1980) 1415-1416.
- ¹¹ R. N. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. USA* **47** (1961) 996-999.
- ¹² M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.* **88** (1966) 3873-3874.
- ¹³ B. G. DeBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.* **7** (1968) 1085-1090.
- ¹⁴ J. Rathke and R. Schaeffer, *Inorg. Chem.* **13** (1974) 3008-3011.
- 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) 194-196.
- 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) 234-245.
- ¹⁹ J. C. Huffman, D. C. Moody, and R. Schaeffer, *J. Am. Chem. Soc.* **97** (1975) 1621-1622.
- ²⁰ J. C. Huffman, D. C. Moody, and R. Schaeffer, *Inorg. Chem.* **20** (1981) 741-745.
- ²¹ P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.* **39** (1963) 26-34.
- ²² J. H. Enemark, L. B. Friedman, and W. N. Lipscomb, *Inorg. Chem.* **5** (1966) 2165-2172.
- ²³ E. Bernhardt, D. J. Brauer, M. Finze, H. Willner, *Angew. Chem. Int. Ed.* **46** (2007) 2927-2930.
- ²⁴ I. Higashi, T. Sakurai, and T. Atoda, *J. Solid State Chem.* **20** (1977) 67-77.
- ²⁵ M. Vlasse, R. Naslain, J. S. Kasper, and K. Ploog, *J. Solid State Chem.* **28** (1979) 289-301.
- ²⁶ R. D. Dobrott, L. B. Friedman, and W. N. Lipscomb, *J. Chem. Phys.* **40** (1964) 866-872.
- ²⁷ W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.* **98** (1976) 3490-3495.
- 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) 93-144.
- ³⁰ J. M. Oliva and A. Vegas, *Chem. Phys. Lett.* **533** (2012) 50-55.
- ³¹ F. A. Kiani and M. Hofmann, *Dalton Trans.* (2007) 1207–1213
- ³² M. G. S. Londesborough, D. Hnyk, J. Bould, L. Serrano-Andrés, V. Saurí, J. M. Oliva, P. Kubat, T. Polívka, K. Lang, *Inorg. Chem.* **51** (2012) 1471-1479.
- ³³ A. R. Pitochelli, M. F. Hawthorne, *J. Am. Chem. Soc.* **84** (1962) 3218-3218.
- 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. Geim, A. K. and Novoselov, K. S. (2007). *Nature Materials* **6** (3): 183–191. Graphene may exhibit ‘exotic superconductivity’.
- ³⁸ M. Bousquet-Mélou, *Disc. Math.* **180** (1996) 73-106.
- ³⁹ We used Hartree-Fock and B3LYP methodologies combined with basis sets STO-3G, STO-3G*, 6-31G* and 6-31G**.
- ⁴⁰ E. D. Glendening, C. R. Landis, and F. Weinhold, in *Natural Bond Orbital Methods*, Wiley Interdisciplinary Reviews **2** (2102) 1-42.
- ⁴¹ J. Z. Dávalos, J. González, A. Guerrero, D. Hnyk, J. Holub, and J. M. Oliva, *J. Phys. Chem. C* **117** (2013) 1495-1501.
- ⁴² E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *J. Am. Chem. Soc.* **123** (2001), 4313-4323.

⁴³ E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *Inorg. Chem.* **40** (2001) 1730-1731.