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Nunes, João Pedro F, Holub, Josef, Rankin, David W H et al. (2 more authors) (2015) A computational analysis of the apparent nido vs. hypho conflict:are we dealing with six- or eight-vertex open-face diheteroboranes? Dalton Transactions. pp. 11819-11826. ISSN 1477-9234

https://doi.org/10.1039/c5dt01460c

A computational analysis of the apparent *nido* vs. *hypho* conflict: are we dealing with six- or eight-vertex open-face diheteroboranes? †‡

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Abstract

A series of computational studies have been undertaken to investigate the electronic structures and bonding schemes for six hetero-substituted borane cages, all of which have been presented in the literature as potential *hypho* structures. The six species are *hypho*-7,8-$[C_2B_6H_{13}]^-$ (**1a**), *hypho*-7,8-$[CSB_6H_{11}]^-$ (**1b**), *hypho*-7,8-$[S_2B_6H_9]^-$ (**1c**), *hypho*-7,8-$[NSB_6H_{11}]$ (**1d**), *exo*-7-Me-*hypho*-7,8-$[NCB_6H_{12}]$ (**1e**), and *endo*-7-Me-*hypho*-7,8-$[NCB_6H_{12}]$ (**1f**) and the so-called *mno* rule has been applied to each of them. As no structural data are known for the carbathia-, azathia-, and dithiahexaboranes, we have also applied the *ab initio*/GIAO/NMR structural tool for **1b**-**1d**, with **1c** having been prepared for this purpose. We conclude that an *mno* count of 10 means that **1a**, **1b**, **1d**, **1e**, and **1f** should be termed *pseudo-nido* or *pseudo-hypho*. Only **1c** can be considered to be correctly termed *hypho*-7,8-$[S_2B_6H_9]^-$.

† Electronic supplementary information (ESI) available: Cartesian coordinates for the structures of **cB11**, **nB10**, and **aB9** (Tables S1-S3), **1a**-**1f** (Tables S4-S9), and *nido*-$[B_6H_{11}]^+$ (Table S10), the s character, p character, and resultant hybridisation of **1a**-**1f** for all levels of theory (Tables S11-S13), and charges on the heteroatoms of **1a**-**1f** (Table S14). The molecular structures of **1a**-**1f** with full atom numbering (Figure S1), the equivalent for the *closo-nido-arachno-hypho* relationship for $n = 11$ with full atom numbering (Figure S2), and the molecular structure of *nido*-$[B_6H_{11}]^+$ with full atom numbering (Figure S3).

‡ Dedicated to the memory of Professor Ken Wade.

Introduction

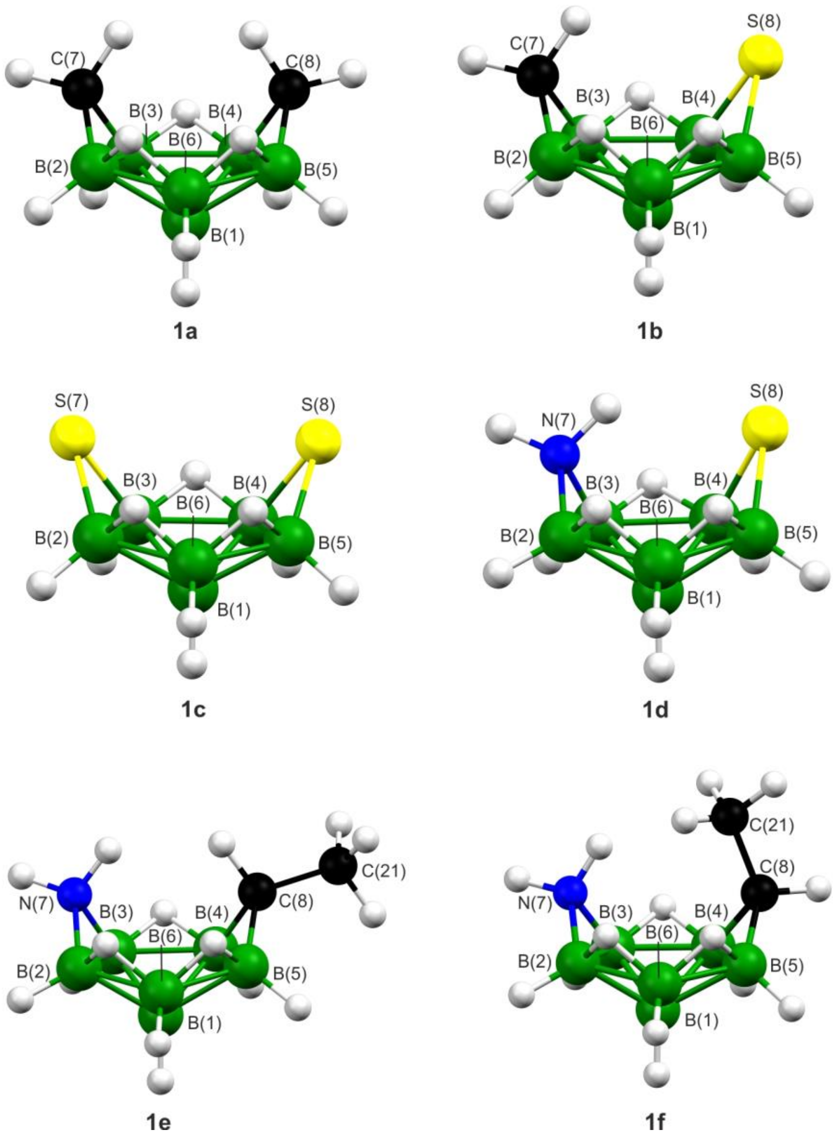
Polyhedral boranes and heteroboranes have long provided interest covering a range of chemical research,[1] where their unexpected structures, innovative bonding schemes, and unusual chemical properties have resulted in them being considered promising candidates for use in medicinal and materials applications. For decades now an understanding of the molecular architectures of these species has led directly and indirectly to practical uses for boranes and future structural studies will undoubtedly lead to potential further uses being identified.

The variety of bonding schemes exhibited by polyhedral boranes and heteroboranes was initially noted by Lipscomb,[2] with Williams[3] and Wade[4] also making significant contributions. Williams reported a major breakthrough by recognising that the experimentally isolated *nido*, *arachno*, and *hypho* boranes could be derived from the nearest *closo* structures by the removal of one, two, and three $\{BH\}^{2-}$ vertices, respectively. This led to the derivation of Wade's $n + 1$ electron-pair rule for a *closo*-type cluster, where n is the number of vertices.[4,5] Subsequently, the number of skeletal electron pairs required for stable *nido*, *arachno*, and *hypho* skeletons was determined to be $n + 1 + p$, where p is the number of missing vertices; it follows that *closo*-$[B_nH_n]^{2-}$ requires such a formal charge to comply with Wade's rule. It should be noted that *closo* systems are known experimentally for n = 5-12, where the icosahedral cluster with I_h point-group symmetry (n = 12) is the most stable of the *closo* series.

The unusually high stability of *closo*-$[B_{12}H_{12}]^{2-}$, as well as the existence of condensed B_{12} units (for example, in the so-called macropolyhedral boron clusters $B_{20}H_{16}$ [6] and $B_{21}H_{18}^{-}$ [7]), meant that a generalisation of the electron-counting rules was required since such structures are beyond the scope of the Williams-Wade formalism. A generally applicable electron-counting rule – the so-called *mno* rule – was derived by Jemmis;[8] based on Hückel's rule it allows the structures of macropolyhedral boranes and metallaboranes to be characterised alongside simple boranes. According to the *mno* rule, $m + n + o$ electron pairs are necessary for a macropolyhedral system to be stable, where m is the number of individual polyhedral subclusters from which a macropolyhedral cluster is composed, n is the number of vertices, and o is the number of single-vertex-sharing condensations. For *nido*, *arachno*, and *hypho* arrangements, one, two, and three additional pairs of electrons are required. Wade's $n + 1$ rule can be considered as a special case of the *mno* rule, where $m = 1$ and $o = 0$.

Some *hypho* and *nido* complexes have very similar structures and electronic structure investigation would seem sensible to ensure clusters are not wrongly classified. In this work we have performed *ab initio* and DFT analyses of the bonding schemes for six potential *hypho* structures {*hypho*-7,8-$[C_2B_6H_{13}]^-$ (**1a**), *hypho*-7,8-$[CSB_6H_{11}]^-$ (**1b**), *hypho*-7,8-$[S_2B_6H_9]^-$ (**1c**), *hypho*-7,8-$[NSB_6H_{11}]$ (**1d**), *exo*-7-Me-*hypho*-7,8-$[NCB_6H_{12}]$ (**1e**), and *endo*-7-Me-*hypho*-7,8-$[NCB_6H_{12}]$ (**1f**)}, also employing the *mno* rule to see what results it yields. All six structures are shown in Figure 1, while Figure S1 also gives the hydrogen atom numbering. As no structural data are currently available for the carbathia-, azathia-, and dithiahexaboranes, we have also applied the *ab initio/*GIAO/NMR structural method for **1b**-**1d**.

Figure 1 The molecular structures of eight-vertex diheteroboranes that have been proposed as *hypho*-type clusters. For clarity hydrogen-atom numbering has been omitted. The molecules are *hypho*-7,8-$[C_2B_6H_{13}]^-$ (**1a**), *hypho*-7,8-$[CSB_6H_{11}]^-$ (**1b**), *hypho*-7,8-$[S_2B_6H_9]^-$ (**1c**), *hypho*-7,8-$[NSB_6H_{11}]$ (**1d**), *exo*-7-Me-*hypho*-7,8-$[NCB_6H_{12}]$ (**1e**), and *endo*-7-Me-*hypho*-7,8-$[NCB_6H_{12}]$ (**1f**).



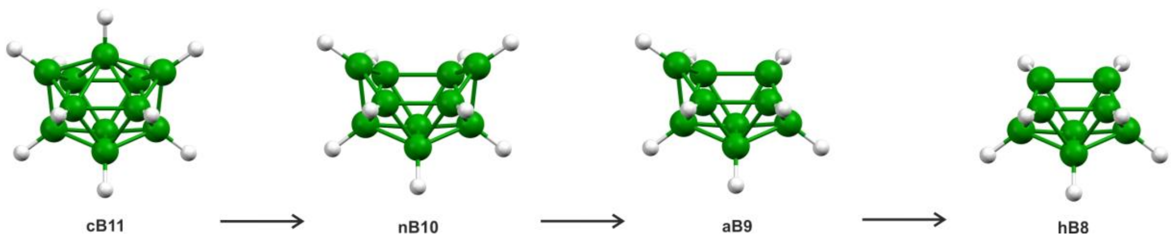
Experimental section

NMR

Experimental ^{11}B NMR chemical shifts for **1b** and **1d** were taken from references 9 and 10, respectively; **1c** was prepared according to reference 11.

Quantum chemical calculations

The geometries of *closo*-$[B_{11}H_{11}]^{2-}$ (**cB11**), *nido*-$[B_{10}H_{10}]^{4-}$ (**nB10**) and *arachno*-$[B_9H_9]^{6-}$ (**aB9**) were fully optimised using Gaussian09.[12] Each of these structures, as well as that of the related hypho species (**hB8**) are depicted in Scheme 1. (The scheme is reproduced in Figure S2, where the atom numbering is given.) The geometry optimisations for each of **cB11**, **nB10**, and **aB9** were performed at the B2PLYP,[13] MP2,[14-18] B98,[19] B97d,[20] PBE,[21,22] PW91,[23-27] and HFS[28-30] levels of theory using the 6-311+G(d,p)[31,32] basis set on all atoms; the nature of any stationary points on the potential-energy surfaces were investigated using frequency calculation. The initial geometries for **nB10** and **aB9** were optimised from geometries obtained by removing one and two vertices from **cB11**, respectively, using GaussView 5.0.[33] The bonding orbitals for **cB11**, **nB10**, and **aB9** were investigated using natural bond orbital (NBO) analyses to look for three-centre bonds and resonance structures.



Scheme 1 Schematic representation of the *closo-nido-arachno-hypho* relationship for $n = 11$.

The geometries of the heteroboranes **1a**-**1f** were also fully optimised using Gaussian09 and the method and basis set combinations described above, with the character of each stationary point verified by frequency calculations. Magnetic shieldings were calculated for **1b-1d** by running GIAO[34] jobs with TZP basis set II by Huzinaga,[35] which is well suited for this purpose. In order to investigate the relationships between **1a**-**1f** and their true borane analogues, the heteroatoms for each borane cage were replaced by hydrogen atoms using GaussView 5.0. The geometries of the species formed by the inclusion of hydrogen atoms in place of heteroatoms were optimised using the same levels of theory and basis sets previously employed, and frequency calculations were performed to verify the nature of any stationary points; the distances between the substituted hydrogen atoms and the boron-cage atoms were fixed at values optimised for the B–C/N/S distances. NBO analyses were also performed for all of the H-substituted structures.

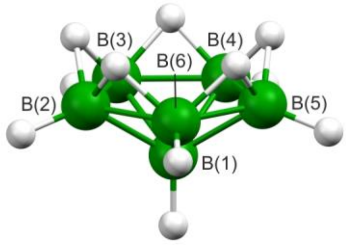
Calculating mno values

The *mno* rule is used to determine the number of pairs of electrons required for a species to be considered stable by calculating $m + n + o$ (for the meanings of m, n, and o, see above). As an illustration the *mno* rule is applied to an icosahedral borane by taking the values $m = 1$, $n = 12$, and $o = 0$, yielding $m + n + o = 13$ electron pairs, the same result as the $n + 1$ electron-pair rule. Each vertex with one terminal atom contributes all-but-one of its electrons to cluster bonding, with the remaining electron involved in the *exo* covalent bond. However, in the three isomeric icosahedral carbaboranes *closo*-$C_2B_{10}H_{12}$, the BH groups each donate one pair of electrons and each CH moiety contributes three electrons (1.5 electron pairs) to the polyhedral bonding, thus satisfying the *mno* rule [*i.e.* $10 + (2 \times 1.5) = 13$ for this neutral carbaborane].[36] Similarly, in the icosahedral azaborane *closo*-$NB_{11}H_{12}$ [37] there are eleven BH groups that contribute eleven electron pairs as well as an NH group that donates two electron pairs to the skeletal bonding. Considering molecules containing third-row elements, the neutral icosahedral *closo*-$SB_{11}H_{11}$ thiaborane is known,[38] in which BH groups provide eleven electron pairs; sulfur has tendency to retain one of its lone pairs, contributing four electrons (two electron pairs) to the cluster.

The following *closo* dianions, presented in order of stability, $B_{12}H_{12}^{2-}$, $B_{11}H_{11}^{2-}$, and $B_5H_5^{2-}$, can be used to derive *nido*, *arachno*, and *hypho* heteroboranes *via* the removal and substitution of vertices.[39] However, according to the Williams-Wade concept, heteroboranes cannot exist with two, three, or four BH moieties. *Closo*-$[B_5H_5]^{2-}$ is, therefore, not a suitable "parent" species for any of the *nido*, *arachno*, or *hypho* heteroborane structures.

There are heteroboranes with molecular shapes based on *nido*-$[B_{10}H_{10}]^{4-}$ (**nB10**)[40] and *arachno*-$[B_9H_9]^{6-}$ (**aB9**),[41] which are derived from the C_{2v}-symmetric *closo*-$[B_{11}H_{11}]^{2-}$ (**cB11**), as shown in Scheme 1. As well as *closo*, *nido*, and *arachno* clusters, Scheme 1 depicts the hypothetical *hypho*-$[B_8H_8]^{8-}$ (**hB8**). In contrast, our so-called *hypho* eight-vertex-type heteroboranes resemble the six-vertex arrangement adopted by *nido*-$[B_6H_{11}]^{+}$ (**nB6**),[42] shown in Figure 2. (Figure S3 depicts the same structure but also includes hydrogen atom numbering.)

Figure 2 The molecular structure of *nido*-$[B_6H_{11}]^+$, whose structure resembles a *hypho* eight-vertex heteroborane. For clarity hydrogen-atom numbering has been omitted.



nB6

The molecule *hypho*-7,8-$[C_2B_6H_{13}]^-$ (**1a**) has previously been structurally characterised by applying the *ab initio/*GIAO/NMR structural tool,[43] which confirmed its C_s-symmetric "helmet-like" structure (Figure 1). Three other proposed *hypho* species (also shown in Figure 1) have been calculated to have the same structural motif as **1a**; these are *hypho*-7,8-$[CSB_6H_{11}]^-$ (**1b**),[9] *hypho*-7,8-$[S_2B_6H_9]^-$ (**1c**),[11] and *hypho*-7,8-$[NSB_6H_{11}]$ (**1d**).[10] The last of these examples (**1d**) illustrates how nitrogen can be accommodated in an eight-vertex *hypho* arrangement, with the same arrangement found in *exo-* and *endo*-7-Me-*hypho*-7,8-$[NCB_6H_{12}]$ (**1e** and **1f**, respectively). Again, GIAO calculations of the shielding tensors have been used for structural characterisation.[44]

Results and discussion

Calculations were initially performed to investigate the bonding patterns of the parent **cB11**, **nB10**, **aB9**, and **hB8** systems, as shown in Scheme 1. Apart from the standard HF calculations perturbed with the MP2 model chemistry, we employed six density functional theory (DFT) approaches to span all the possibilities afforded by DFT, *i.e.* B98 (stand-alone hybrid functional), B97D (stand-alone pure functional), HFS (exchange-only functional), PW91 (correlation functional), PBE (exchange-combined functional), and B2PLYP (double-hybrid functional), the latter utilising HF exchange and an MP2-like correlation. All seven model chemistries used the 6-31G(d) basis set for the initial geometry optimisations. However, all attempts to identify a minimum on the potential-energy hypersurface of **hB8** failed because of the formation of either a series of flattened triangular borane architectures or a random assembly of eight boron atoms. The final basis set used for optimising **cB11**, **nB10**, and **aB9** was 6-311G(d,p). Cartesian coordinates for these structures are given in Tables S1-S3. Attempts to use extra diffuse functions on these basis sets caused the optimisations to diverge. Second-derivative analyses of these systems showed that they represented minima on the respective potential-energy hypersurfaces. The seven model chemistries were also used to calculate Hartree-Fock and Kohn-Sham natural orbitals and no two-centre two-electron (2c-2e) bonds were predicted for the cage motifs, only for the terminal B–H bonds.

In order to get a deeper insight into the bonding patterns of **1a**-**1f**, we performed entirely the same computational procedures as for **cB11**, **nB10**, **aB9**, and **hB8**. All of these diheterohexaboranes structures were identified as potential minima at *ab initio* and all DFT levels. Cartesian coordinates relating to the MP2/6-311+G(d,p) calculations are given in Tables S4-S9. The strong resemblance of each of the **1a**-**1f** molecular geometries to that of *nido*-$[B_6H_{11}]^+$ prompted us to replace each heteroatom with a hydrogen atom (H_r), with the B–H_r distances fixed at the values optimised for the B–C/N/S bond lengths. Any substituents originally bonded to C or N were omitted. The new structures generated were termed **1a/H**-**1e/H** (no calculations were required for **1f/H** which is identical to **1e/H**). The structure of *nido*-$[B_6H_{11}]^+$ (Figure 2) was calculated as a comparison as it has the same arrangement of H-bridges; Cartesian coordinates relating to its geometry at the MP2/6-311+G(d,p) level are given in Table S10. As might be expected, frequency calculations performed for each of **1a/H**-**1e/H** showed imaginary frequencies relating to the H_r atoms.

Performing NBO analyses for each of **1a/H**-**1e/H** revealed that three-centre two-electron (3c-2e) bonding is present throughout each of the clusters, *i.e.* also in B–H_r–B bridges. When these structures were allowed to relax further by optimising the B–H_r distances, 3c-2e bonding persisted for all five species **1a/H**-**1e/H**. The geometry optimisations performed using the 6-311+G** basis sets demonstrate that 3c-2e bonding exists regardless of the lengths of the B–H bridging distances; this was true for all seven methods employed. Similar analyses for **1a**-**1f** (where the heteroatoms are present) showed a different picture, where all B–C/N/S distances were classified as 2c-2e bonds. If the NBO analyses had revealed 2c-2e bonds for B–H_r–B bridges in **1a/H**-**1e/H**, we could have stated that the heteroatoms present in **1a**-**1f** were *not* part of multicentre bonding. However, this was not the case we therefore had to follow another way of finding the nature of bonding in **1a**-**1f**.

Table 1 shows the hybridisation of the heteroatoms in **1a**-**1f** when transforming canonical orbitals to natural ones using NBO analysis. (Such calculations were performed for all levels of theory specified in the experimental section and then averaged. The range of values is also shown. The characters and hybridisations of the B–C/N/S bonds for each of **1a**-**1f** at all levels of theory are given in Tables S11-S13.) Table 1 shows that the heteroatoms in each species are more or less sp^3-hybridised, as is the case for textbook examples such as CH_4, NH_3, and H_2S. This means that, as well as 2c-2e bonds to boron atoms, all of the heteroatoms are covalently bonded to hydrogen atoms and any carbon atoms that are external to the cage motif. In addition, NBO analyses showed that heteroatoms in **1a**-**1f** are negatively charged. The average calculated charges are presented in Table 2 (with the corresponding values for each level of theory in Table S14) and are in line with those values for classical covalent species such as CH_4, NH_3, and H_2S. However, such an observation is in contrast to the electron distribution experimentally determined for the icosahedral species, in which the midpoint of CC vector and sulfur atom were found to be positively charged as revealed by vector algebra of experimental dipole moments measured for the *exo*-substituted icosahedra.[36d,38b]

Table 1 Table showing the hybridisation of the heteroatoms (C/N/S) bonded to the boron atoms. The bond characters were calculated using NBO analyses and are averaged across all levels of theory specified in the experimental section.[a]

	Bond	s character / %	p character / %	Hybridisation[b]
1a	B(2)–C(7)	28.45	71.53	2.51 ± 0.01
	B(3)–C(7)	26.84	73.14	2.73 ± 0.06
	B(4)–C(8)	26.84	73.14	2.73 ± 0.06
	B(5)–C(8)	28.45	71.53	2.51 ± 0.01
1b	B(2)–C(7)	28.62	71.34	2.49 ± 0.01
	B(3)–C(7)	26.08	73.89	2.83 ± 0.07
	B(4)–S(8)	16.96	82.87	4.91 ± 0.37
	B(5)–S(8)	18.49	81.22	4.40 ± 0.24
1c	B(2)–S(7)	18.50	81.31	4.40 ± 0.23
	B(3)–S(7)	16.72	83.10	4.99 ± 0.36
	B(4)–S(8)	16.72	83.10	4.99 ± 0.36
	B(5)–S(8)	18.50	81.31	4.40 ± 0.23
1d	B(2)–N(7)	29.38	70.61	2.40 ± 0.02
	B(3)–N(7)	27.46	72.53	2.64 ± 0.06
	B(4)–S(8)	16.61	83.20	5.02 ± 0.32
	B(5)–S(8)	17.08	82.71	4.86 ± 0.32
1e	B(2)–C(8)	26.28	73.70	2.80 ± 0.03
	B(3)–C(8)	25.80	74.19	2.88 ± 0.05
	B(4)–N(7)	28.69	71.31	2.49 ± 0.05
	B(5)–N(7)	29.48	70.52	2.39 ± 0.02
1f	B(2)–C(8)	26.12	73.85	2.83 ± 0.03
	B(3)–C(8)	26.00	73.98	2.85 ± 0.05
	B(4)–N(7)	28.49	71.50	2.51 ± 0.05
	B(5)–N(7)	29.41	70.59	2.40 ± 0.02

[a] The characters and hybridisations from each of the individual calculations are given in Tables S11-S13. [b] The errors quoted are the standard deviation of the values calculated for the different model chemistries.

Table 2 Table showing the atomic charges of the heteroatoms (C/N/S) within the borane cage motif. The charges are averaged across all levels of theory specified in the experimental section.[a]

	Atom	Charge[b]		
1a	C(7)	–0.92	±	0.02
	C(8)	–0.92	±	0.02
1b	C(7)	–0.91	±	0.02
	S(8)	–0.27	±	0.03
1c	S(7)	–0.22	±	0.03
	S(9)	–0.22	±	0.03
1d	N(7)	–0.95	±	0.02
	S(8)	–0.18	±	0.04
1e	N(7)	–0.93	±	0.02
	C(8)	–0.73	±	0.02
1f	N(7)	–0.94	±	0.02
	C(8)	–0.74	±	0.02

[a] The charges from each of the individual calculations are given in Table S14. [b] The errors quoted are the standard deviation of the values calculated for the different model chemistries.

Armed with these results, we applied the *mno* rule to *nido*-$[B_6H_{11}]^+$ as well as to **1a**-**1f**. For *nido*-$[B_6H_{11}]^+$ $m = 1$, $n = 6$, $o = 0$, and $p = 1$, meaning that eight electron pairs are required to stabilise this system. There are six B–H fragments, each of which contributes one electron pair. The remaining two electron pairs are available from the five bridging hydrogen atoms with one spare electron present; the total number of electron pairs is 6 + 2.5 = 8.5. As there is one excess electron the hypothetical *nido*-$[B_6H_{11}]^+$ is obviously a cation. (For *nido*-B_6H_{10} we have eight electron pairs and, consequently, the molecule is neutral.)

To apply the *mno* rule to **1a**-**1f** we need to distinguish whether they adopt a *hypho* or a *nido* electron count.

Let's start by supposing that they are considered to be *hypho*, giving $m = 1$, $n = 8$, $o = 0$, $p = 3$, meaning that 12 electron pairs are required. In order to comply with a *hypho* electron count the heteroatoms must contribute the following number of electron pairs: sulfur 2, carbon 2, and nitrogen 2.5 for the charges to be "*hypho*" correct.

Therefore, for **1a** we have 7.5 + 4 = 11.5 electron pairs, thus requiring one extra electron to stabilise the system. This C_s skeleton is therefore characterised with a single negative charge. The same applies to the other non-nitrogen-containing compounds (**1b** and **1c**), where sulfur and/or carbon contributes 4 electron pairs, resulting in an overall single negative charge for these species. However, such electron pair contributions from the heteroatoms are in conflict with the NBO results shown in Table 1, where C, N, and S are more or less sp^3-hybridised and are connected to the boron atoms by conventional 2c-2e bonds. Moreover, the carbon and nitrogen atoms are not naked, but rather are bonded also to two *exo* atoms or groups, *i.e.* the corresponding one electron pair from each of these heteroatoms cannot contribute to the skeletal moieties.

Secondly, we may formally consider **1a-1f** to be *nido* clusters, where values of n = 6, m = 1, o = 0, and p = 1 yields an *mno* value of eight and, consequently, eight electron pairs are required to stabilise these molecules, as was the case for *nido*-$[B_6H_{11}]^+$. In the latter, six B–H bonds contribute six electron pairs, and five hydrogen bridges contribute 2.5 electron pairs, *i.e.* this system must have a single positive charge (6 + 2.5 =8.5 and so one electron must be removed to get 8). There is also another hypothetical system, *nido*-$[B_6H_9]^-$, which has *three* H-bridges and complies with the *mno* rule (*mno* = 8; 6 + 1.5 = 7.5, so the formal charge is –1). On that basis, there is no scope for the two additional bridging bonds that would be required for this to be a *nido* system with a single negative charge. Such a charge is, however, unambiguously observed for **1a**, **1b**, and **1c**, in which there are *five* bridges (three B–H–B bridges and two B–C/S–B bridges. The same argument can be applied to relate the neutral molecules **1d**, **1e**, **and 1f** to *nido*-B_6H_{10} (6 + 4/2 = 8; there is no scope for further bridge-type bonding to comply simultaneously with the *nido* electron count requirement and to keep the system neutral).

Only **1c** can truly be considered to be correctly classified as *hypho*-7,8-$[S_2B_6H_9]^-$, since **1c** can afford to accept four electron pairs from the sulfur atoms into cluster bonding leaving one lone pair of electrons on each sulfur atom.

We must therefore conclude that **1a**, **1b**, **1d**, **1e**, and **1f** are, in reality, neither formally *hypho* skeletons nor *nido* structures. To be formally *hypho*, an *mno* value of 12 should be satisfied for **1a**, **1b**, **1d**, **1e**, and **1f**. Moreover, we would actually need to have *mno* = 10 to "accommodate" two extra B–C/N/S–B bridges and to comply with *nido* requirement. Since each of **1a**, **1b**, **1d**, **1e** and **1f** is analysed in terms of having a *mno* value of 12 or 8 (and not 10), we might call these systems *pseudo-nido* or *pseudo-hypho*. As stated above, **1c** can be correctly classified as *hypho*-7,8-$[S_2B_6H_9]^-$.

Small clusters are known to be very sensitive to the inclusion of electron dynamic correlation when shielding tensors are being calculated.[45] The GIAO-MP2 calculations predict ^{11}B chemical shifts that compare well with experimental values. Table 3 compares computed and experimental ^{11}B chemical shifts for **1b-1d**.

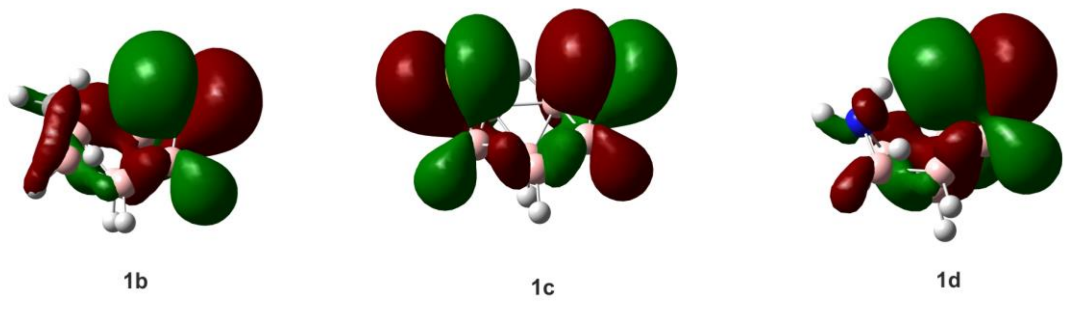
Table 3 Computed (GIAO) and experimental NMR chemical shifts for **1b**-**1d**.

	Vertex					
	B(1)	B(3)	B(6)	B(4)	B(2)	B(5)
1b GIAO[a]	–56.5	–36.3	–33.5	–25.1	–4.6	3.1
Exp.[b,c]	–54.8	–33.2	–29.4	–23.9	–3.1	2.0
1c GIAO[a]	–55.8	5.3	–26.1	–31.4	–26.1	5.3
Exp.[b,d]	–52.2	6.8	–22.4	–25.0	–22.4	6.8
1d GIAO[a]	–56.3	–26.4	–24.9	–21.7	–2.0	2.2
Exp.[b,e]	–55.1	–25.6	–22.4	–20.8	–1.6	1.8

[a] GIAO-MP2/II//6-311+G**. [b] Measured in $CDCl_3$. [c] Ref. 9. [d] This work. [e] Ref. 10.

While the computed and experimental ^{11}B NMR chemical shifts generally compare well, the presence of sulfur in **1b**-**1d** makes these fits for some atoms slightly worse than for clusters reported in the literature that do not contain a third-row element. Such discrepancies can be attributed to the inadequacy of using a triple-zeta Huzinaga type-II basis set on sulfur.[46] The most striking features of the individual spectra are shifts to low frequencies for the "bottom" boron atom, B(1). When comparing these values we clearly see the difference between the nature of the ^{11}B chemical shifts for B(2) and B(3) in **1b** and **1d** and those of **1c**. Inspecting the highest occupied molecular orbitals (HOMOs; see Figure 3) for **1b**-**1d** offers an explanation in terms of the entirely different shieldings of B(2) and B(3) when comparing **1b** and **1d** with C_s-symmetric **1c**.

Figure 3 HOMO for **1b**-**1d** at HF/6-311+G(d,p).



The decent agreement between theory and experiment suggests that MP2/6-311+G(d,p) geometries serve as valid representations of the molecular geometries in solution, which are characterised by very long B–B distances (values are between 1.94 and 1.98 Å) bridged by heteroatoms.

Conclusions

According to these computational efforts, we have concluded that *hypho*-7,8-$[S_2B_6H_9]^-$ (**1c**) is correctly classified as a formal *hypho* structure. However, the other compounds studied here should be considered as *pseudo-hypho* or *pseudo-nido*, *i.e.* there is a *nido* vs. *hypho* conflict, and also a disagreement with the literature. Conceivably, according to the *mno* rule *all* valence electrons of carbon and nitrogen are accounted for in skeletal bonding when assuming *hypho* electron count. On the contrary, we would need to have 10 electron pairs instead of eight to comply with the formal *nido* electron count while also having sufficient electrons to allow for the bonding of carbon and nitrogen cage atoms to *exo* carbon and hydrogens atoms. The fact that *hypho*-$[B_8H_8]^{8-}$ has been shown not to exist complements such a conclusion.

Acknowledgements

D.A.W. thanks the EPSRC for funding a Career Acceleration Fellowship (EP/I004122), and for partially funding, along with the Department of Chemistry, University of York, a studentship for J.P.F.N. We acknowledge the use of the EPSRC National Service for Computational Chemistry Software hosted at Imperial College in carrying out this work, which also made use of the York Advanced Research Computing Cluster (YARCC) provided by the University of York. We acknowledge the Czech Science Foundation (project number P207/11/07505) for financial support. All data supporting this study are provided either in the results section of this paper or as supplementary information accompanying this paper.

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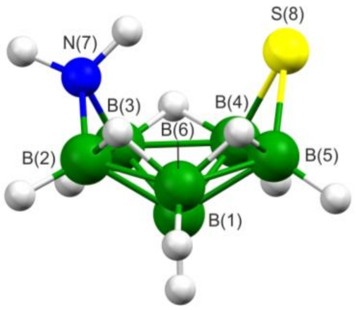
Graphical Abstract



Computational studies have been undertaken to investigate the electronic structures of six hetero-substituted borane cages, concluding that *hypho*-7,8-$[S_2B_6H_9]^-$ is the only true *hypho* species in this series.