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A systematic examination of classical and multi-center bonding in heteroborane clusters

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A systematic examination of classical and multi-center bonding in heteroborane clusters†

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This paper presents a systematic study of multicenter and classical bonding on a broad series of experimentally known heteroboranes covering closo, nido, arachno and hypno types of cages with incorporated tetræ, prætægan or chalcogen heterovertices up to the third-row elements. The nature of bonding is studied using a novel quantum-chemical tool, the intrinsic atomic/bond orbital (IAO/IBO) approach, which provides a direct connection between quantum chemistry and chemical concepts. We also discuss how the computed IBO properties are related to molecular observables such as interatomic distances, molecular electrostatic potential surfaces and dipole moments.

Introduction

Bonding in boron clusters (boron hydrides, boranes) is predominantly of multicenter nature, and usually referred to as 3-center-2-electron (3c2e) bonding.1–4 Two types of 3c2e bonds, B–B–B and B–H–B triangles, occur in boranes. The bridging B–H–B triangles of B2H6 led W. N. Lipscomb to formulate the concept of multicenter bonding. The Nobel Prize was awarded to him for the explanation of the differences between boranes and analogous organic compounds. The geometries of boranes and hydrocarbons are not compatible even in the case of simple B2H6 and C2H6 molecules. B2H6 with D3d symmetry differs from the ethane structure with D2h symmetry. Conceivably, B2H6 could be fitted to the electron diffraction data only when a hydrogen-bridge-based model of D2h symmetry is considered.5

Multicenter bonding is not limited to boranes. It has been shown by using high-angle X-ray diffraction that the bonding in the trimethylaluminium dimer (Al2Me6) has multicenter character.6 Multicenter bonding was also proposed for heteroborane clusters. W. N. Lipscomb et al. studied the nature of bonding in closo-carboranes at the semiempirical quantum chemical level (the partial retention of diatomic differential overlap/PRDDO/method).7 In Lipscomb’s classical view of 3c2e bonding, n atomic orbitals are combined into 3c2e bonds by forming only n/3 bonding orbitals. Extra electrons would have to occupy antibonding orbitals. A valence pattern for a given number of atoms is thus restricted to a few well-defined possibilities. Further attention has been paid to smaller cages such as closo-1,2-Y2B3H5 (Y = CH, N, P), where it has been known that both 3c2e and 2c2e alternatives are possible.9 Since the effort to study the bonding of heteroboranes has focused mainly on smaller closo-carboranes, the knowledge of bonding in other heteroborane architectures is very limited. Recently, it has also been possible to analyze bonding patterns using a novel quantum-chemical tool, the intrinsic atomic/bond orbital (IAO/IBO) method.10 This method provides a direct connection between quantum chemistry and intuitive chemical concepts. It helps in determining the nature of chemical bonding from first principles calculations and computes the nature and shape of chemical bonds in terms of connecting quantitative SCF wave functions to a qualitative chemical picture (see Scheme 1).

Generally speaking, the bonding character illustrated (e.g. in the form of not assumed Lewis structures) thus naturally emerges. This procedure thus goes beyond the standard natural bond orbital (NBO) approach,11 which assumes a spherical symmetry of AOs and Lewis bonding patterns. Boldyrev has also

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† Electronic supplementary information (ESI) available: The summarized IBO data for 7-, 9- and 11-vertex closo-heteroboranes and the NBO results for selected representative boranes. See DOI: 10.1039/c7cp07422k

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**Scheme 1**  Simplification of the intrinsic bond orbital (IBO) methodology.
introduced a tool known as adaptive natural density partitioning (AdNP), a method that analyzes the first-order reduced density matrix, which inherently contains some assumptions. However, this approach works well for various boron rings such as boron molecular Wankel motors, boron fullerenes and 2D boron sheets. The wave function used for IBOs is initially calculated using canonical molecular orbitals (MOs) from the SCF procedure, and their subsequent unitary transformation yields the desired IBOs, which clarifies the nature of the corresponding bonding pattern. The point is that basis set functions are not associated with any atom. In the case of expanding MOs over a minimal basis set of free-atom AOs (known from any textbook of general chemistry), the resulting wave function can easily be interpreted. However, such a wave-function would be imprecise because the free-atom AOs do not undergo any polarization from the corresponding surroundings. On that basis, an accurate wave function is calculated and a set of polarized AOs is formed in terms of splitting free-atom AOs (known from any textbook of general chemistry), the resulting wave function can easily be interpreted. The outputs were examined using the IBOview program packages. The numbers of both atoms can thus be considered as an indication of classical bonding. However, it might be questionable whether a larger interatomic distance necessarily indicates multicenter bonding. It might also be a consequence of electron deficiency in the case of electron unsaturated boranes. In this study, the obtained IBO results are compared with the interatomic distances refined either from the experimental electron diffraction or from the combined ab initio/GIAO/NMR approach. Secondly, classical bonding follows the established electronegativity concept, which is not true for multicenter bonding. We have thus computed and analyzed the molecular electrostatic potential (ESP) surfaces and the dipole moments of selected representative molecules.

Methods

In the first step, the IBO method was validated on a series of organic and inorganic compounds with well described either covalent or multicenter bonding: ethane, elemental white phosphorus P₄ and hydrogen disulfide (containing classical, 2c2e bonding), trimethylaluminium dimer, diboran, closo-B₁₂H₁₄, nido-B₉H₁₄, arachno-B₁₄H₂₄, closo-B₁₀H₁₀, closo-B₁₀H₈, closo-B₉H₇, closo-B₉H₈, closo-B₈H₇, closo-B₈H₈, and tetra-tert-butylditetrabora-tetrahedrane. In the second step, we used the IBO method to investigate the nature of bonding in a series of experimentally known heteroboranes containing only up to third-row elements, specifically: closo-I-B₁₂H₁₂, closo-I-B₁₁H₁₁, closo-I-B₁₀H₁₀, closo-I-B₈H₈, closo-II-B₁₁H₁₁, closo-II-B₁₀H₁₀, closo-II-B₈H₈, closo-III-B₁₁H₁₁, closo-III-B₁₀H₁₀, closo-III-B₈H₈, closo-IV-B₁₁H₁₁, closo-IV-B₁₀H₁₀, and closo-IV-B₈H₈. Sheets

Fig. 1 The numbering scheme for the following studied cages: closo-B₁₂H₁₂ (A), closo-I-B₁₂H₁₂ (B), closo-I-B₁₁H₁₁ (C), closo-I-B₁₀H₁₀ (D), closo-III-B₁₁H₁₁ (E), closo-II-B₁₁H₁₁ (F), closo-III-B₁₀H₁₀ (G), closo-IV-B₁₁H₁₁ (H) and nido-B₁₂H₁₂ (I).
Results and discussion

Benchmarks

To validate the IBOs and illustrate the difference between the 2c2e and 3c2e types of bonding, we first applied the IBO approach to a series of organic/inorganic compounds with 2c2e bonding and closo-borane clusters with 3c2e bonding. In addition, we considered the bridging Al–C bonds in Al2(CH3)6, because the multicenter bonding of this molecule had been confirmed experimentally.6

The IBOs for the benchmark organic/inorganic compounds and the selected boron clusters are summarized in Fig. 2. The IBOs clearly demonstrated classical bonding in ethane, elemental white tetraphosphorus P4, and disulfide hydrogen (Fig. 2A–C). The IBOs also confirmed multicenter bonding in Al2(CH3)6 (Fig. 2D) in accordance with the experimental data. In addition, the hydrogen bridging in diborane was also shown to be of multicenter nature (Fig. 2E). The interatomic distances are slightly elongated in the shown multicenter bonds. The B–H, B–B and C–Al separations are 4–14% longer than the sum of the covalent radii (\(\Sigma_{\text{cov}}\)) of both atoms, i.e. distances of 1.334, 1.770 and 2.125 Å, respectively. For comparison, the classical 2c2e B–H and C–Al bonds of the same molecules are closer to \(\Sigma_{\text{cov}}\), i.e. 1.187 and 1.953 Å, which correspond to 101.5 and 97.2% of \(\Sigma_{\text{cov}}\), respectively.

In the series of various borane clusters, the presence of multicenter bonding was confirmed (Fig. 2F and G). Besides the 3c2e bonds, this approach also revealed 4-center-2-electron (4c2e) bonds of the B–B–B type in closo-B6H12 \(n\) \(=\) 12, 10 and 8, nido-B14H11 \(4^{+}\) and arachno-B16H14 \(2^{–}\). This unique 4c2e bonding has already been known for some borane compounds.60,61 However, this bonding has only been reported as 4c2e B–B–B–H with no evidence for 4c2e B–B–B–B bonding. The presence of the 4c2e bond in closo-B12H12 \(2^{–}\) is shown in Fig. 2F. The number of 4c2e bonds increased with the size of the cluster (e.g. closo-B10H10 \(2^{–}\) and closo-B12H12 \(2^{–}\) had one and three 4c2e bonds, respectively).

In the case of tetra-tert-butyl-tetrabora-tetrahedrane, B4(\(t\)-Bu)4 (see Fig. 2H), the IBO approach clearly indicated the presence of four multicenter 3c2e bonds (B–B–B triangles). The other bonds, including the B–C, C–C and C–H bonds, were confirmed by the IBOs to be of classical 2c2e nature. The observed presence of 3c2e bonding corresponded well with the published study on B4H4 and B4(\(t\)-Bu)4.62

Bonding in heteroboranes

It is important to consider the differences between various boron architectures when analyzing the results for multidimensional boron compounds – e.g. closo-1-SB11H11 differs in many respects from closo-1-SB12H12.63 The IBO results of icosahedral heteroboranes are summarized in Table 1. Furthermore, the IBOs of selected closo-heteroborane clusters are shown in Fig. 3. When the icosahedral cluster only contained a single heteroatom, the heteroatom was mostly part of multicenter bonding. For instance, the C atom of closo-1-CB11H12 participated in three bonds, one of 4c2e nature (B–B–C) and two of 3c2e nature (B–B–C, see Fig. 3A). This bonding was thus analogous to the parent closo-B11H12, which also contained one 4c2e and two 3c2e bonds in the same location. Similarly, the S atom of closo-1-SB11H11 (see Fig. 3B) took part in two multicenter (3c2e) bonds of B–S–B type and one bond of B–B–S–B type of 4c2e nature. Such a bonding pattern corresponded to a B–S distance of 2.010 Å (106.9% of \(\Sigma_{\text{cov}}\)).26

More interestingly, it could also help in explaining the highly...
positive σ-holes ($V_{S,\text{max}}$ of 28.2 kcal mol$^{-1}$) on the S atom, which are known to be important for its crystal packing.$^{64}$ This $V_{S,\text{max}}$ value is unusually high considering the low electronegativity of boron atoms. $\text{closo-1-NB}_{11}\text{H}_{12}$ contained two 3c2e B–N bonds and one 2c2e B–N bond. However, it should be mentioned that the 2c2e bonding was debatable in the case of $\text{closo-1-NB}_{11}\text{H}_{12}$ (see Fig. 3C). The bond evaluated as a classical covalent bond was less localized than a typical 2c2e bond (Fig. 2) and could also be seen as a crossing between the 2c2e and 4c2e bonds. Such a bonding pattern would also better correspond to a B–N distance of 1.716 Å (110.0% of $\Sigma_{c,\text{cov}}$).$^{23}$

$\text{closo-1,7-C}_{2}\text{B}_{10}\text{H}_{12}$ and $\text{closo-1,7-P}_{2}\text{B}_{10}\text{H}_{10}$ have two heteroatoms that are not adjacent. They can thus be considered as a crossing between heteroboranes with one and more heterovertices. In contrast to $\text{closo-1-CB}_{11}\text{H}_{12}$, the C atoms of $\text{closo-1,7-C}_{2}\text{B}_{10}\text{H}_{12}$ did not form 4c2e B–C–B–B bonds. Instead, they only formed B–C–B 3c2e multicenter bonds. $\text{closo-1,2-C}_{2}\text{B}_{10}\text{H}_{12}$ has two adjacent C atoms, which form 3c2e B–C–B bonds and a classical C–C bond (see Fig. 3D). This pair of adjacent C–C atoms is known to act as an electron donor and becomes the center of the partial positive charge in the molecule. This has

| Compound          | Bonding       | Multicenter    | Classical      |
|-------------------|---------------|----------------|----------------|
| $\text{closo-1-CB}_{11}\text{H}_{12}$ | 2 × B–C–B; 1 × B–C–B–B | —               | —              |
| $\text{closo-1-SB}_{11}\text{H}_{11}$ | 1 × B–C–B; 1 × B–C–B–B | —               | —              |
| $\text{closo-1-NB}_{11}\text{H}_{12}$ | 2 × B–N–B; 1 × B–N–B | —               | —              |
| $\text{closo-1,7-C}_{2}\text{B}_{10}\text{H}_{12}$ | 6 × B–C–B | —               | —              |
| $\text{closo-1,7-P}_{2}\text{B}_{10}\text{H}_{10}$ | 3 × B–P–B; 3 × B–P–B | —               | —              |
| $\text{closo-1,2-C}_{2}\text{B}_{10}\text{H}_{12}$ | 4 × B–C–B; 1 × C–C | —               | —              |
| $\text{closo-1,2-P}_{2}\text{B}_{10}\text{H}_{10}$ | 4 × B–P–B; 1 × P–P–B | —               | —              |

**Table 1** The summarized IBO data for the icosahedral heteroboranes. For the sake of clarity, the B–B–H and B–B–B multicenter bonds are not included.

**Fig. 3** Calculated IBOs for the following heteroboranes: $\text{closo-1-CB}_{11}\text{H}_{12}$ (A), $\text{closo-1-SB}_{11}\text{H}_{11}$ (B), $\text{closo-1-NB}_{11}\text{H}_{12}$ (C), $\text{closo-1,2-C}_{2}\text{B}_{10}\text{H}_{12}$ (D), $\text{closo-1,2-P}_{2}\text{B}_{10}\text{H}_{10}$ (E), $\text{closo-2,3-C}_{2}\text{B}_{9}\text{H}_{11}$ (F), $\text{closo-2,1-PCB}_{8}\text{H}_{9}$ (G), $\text{closo-1-SB}_{9}\text{H}_{9}$ (H), $\text{closo-1-CB}_{7}\text{H}_{8}$ (I), $\text{closo-1-CB}_{7}\text{H}_{8}$ (J), $\text{closo-1-2-P}_{2}\text{B}_{8}\text{H}_{8}$ (K), $\text{closo-1,5-C}_{2}\text{B}_{5}\text{H}_{5}$ (L) and $\text{closo-1,2-C}_{2}\text{B}_{5}\text{H}_{5}$ (M). The orbitals that are not shown in this figure are analogous to those rendered. The orbital color coding is as follows: dark blue/purple – classical 2c2e bonding; red/pink – multicenter 3c2e bonding; yellow – multicenter 4c2e bonding.
already been determined experimentally. It might thus be considered important experimental evidence supporting the 3c2e B–C–B bonding. The C–C bond of closo-1,2-C$_2$B$_6$H$_{12}$ was the only classical bond found by the IBO approach among theicosahedral heteroboranes besides the debatable case of closo-1-1NB$_{11}$H$_{12}$ described above. Similar to the B–N bond of closo-1-NB$_{11}$H$_{12}$, the C–C bond of closo-1,2-C$_2$B$_6$H$_{12}$ was less localized and longer (1.624 Å) than the C–C classical bonds in the validation data set, e.g. in ethanol (1.540 Å). It also corresponds to LMO results obtained by Lipscomb et al. The studiedicosahedral cluster with adjacent P atoms, closo-1,2-P$_2$B$_{10}$H$_{10}$ (see Fig. 3E), did not form a classical bond between the P atoms; instead, it formed a multicenter B–P–P–B 4c2e bond. This bonding could be compared to B–B–B–B obtained in theparent closo-B$_{12}$H$_{12}$. The P–P distance in closo-1,2-P$_2$B$_{10}$H$_{10}$ is 2.310 Å (104.1% of $\Sigma_{\text{con}}$). The most positive molecular ESP surface is located between the two P atoms ($V_{S_{\text{max}}}$ = 28.2 kcal mol$^{-1}$) which is analogous to closo-1,2-C$_2$B$_{12}$H$_{12}$.

The bonding patterns of the 11-vertex closo-carboranes were similar to those of the 12-vertex cages (compare Table 1 and Table S1, ESII†). The IBO results did not reveal any difference in bonding between closo-2-C$_{10}$H$_{11}$ and the above-discussed closo-1-C$_{10}$H$_{11}$. However, some difference was found between closo-2,3-C$_2$B$_7$H$_{11}$ and closo-1,7-C$_2$B$_{10}$H$_{10}$ (separated C atoms in both clusters) as seen in Fig. 1. The C atoms of closo-2,3-C$_2$B$_7$H$_{11}$ (see Fig. 3F) participated in a classical B–C bond besides the two B–C–B 3c2e bonds. On the other hand, closo-1,7-C$_2$B$_{12}$H$_{12}$ only had 3c2e B–C–B bonds.

The bonding patterns obtained in the 10-vertex closoheteroboranes (see Table 2) were also overall similar to those in theicosahedral cages. closo-1-C$_{10}$B$_{10}H_{10}$ and closo-1,2-C$_2$B$_7$H$_{10}$ had analogous bonding patterns to closo-1-C$_{10}$B$_{10}H_{10}$ and closo-1,2-C$_2$B$_{12}$H$_{12}$, respectively. It should be mentioned, however, that the C–C bond of closo-1,2-C$_2$B$_{10}$H$_{10}$ is shorter than that bond in closo-1,2-C$_2$B$_{10}$H$_{12}$ (1.538 Å vs. 1.624 Å). In addition, the bonding in closo-2,1-P$_2$B$_{10}$H$_{10}$ (see Fig. 3G) was similar to closo-1,2-C$_2$B$_{12}$H$_{12}$. Besides closo-1,2-C$_2$B$_{12}$H$_{12}$, two other isomers of closo-1,2-C$_2$B$_{12}$H$_{12}$ were studied, both with non-adjacent C atoms.

### Table 2

The summarized IBO data for various closo-heteroboranes. For the sake of clarity, B–B–H and B–B–B multicenter bonds are not included.

| Compound                  | Multicenter | Classical |
|---------------------------|-------------|-----------|
| 10-vertex                 |             |           |
| closo-1-C$_{10}$B$_{10}$H$_{10}$ | 2 × B–C–B; 1 × B–C–B | —         |
| closo-1,2-C$_2$B$_7$H$_{10}$ | 4 × B–C–B | 1 × C–C |
| closo-1,6-C$_2$B$_7$H$_{10}$ | 5 × B–C–B | 1 × B–C–B |
| closo-1,10-C$_2$B$_{10}$H$_{10}$ | 5 × B–C–B | 1 × B–C–B |
| closo-1-NB$_{11}$H$_{12}$ | 2 × B–N–B | 1 × B–N |
| closo-2,1-P$_2$B$_{10}$H$_{10}$ | 2 × B–P–B; 2 × B–C–B | 1 × C–P |
| closo-6,1-P$_2$B$_{10}$H$_{10}$ | 3 × B–C–B; 2 × B–P–B; 1 × B–P–B–B | — |
| closo-1-SB$_9$H$_9$ | 2 × B–S–B | 1 × B–S |
| 8-vertex                  |             |           |
| closo-1-B$_{11}$H$_{12}$ | 2 × B–C–B | 1 × B–C |
| closo-1,2-C$_2$B$_8$H$_{8}$ | 4 × B–C–B | 1 × C–C |
| closo-1,7-C$_2$B$_8$H$_{8}$ | 4 × B–C–B | 1 × B–C–B–B |
| closo-1,6-C$_2$B$_8$H$_{8}$ | 4 × B–C–B | 1 × B–C–B–B |

Both clusters only formed multicenter bonds of either 3c2e or 4c2e nature. The fact that these molecules formed a 4c2e bond corresponded to the parent closo-B$_{10}$H$_{12}$, in which a 4c2e bond occurred as well. The analysis of closo-1-NB$_{11}$H$_{12}$ revealed very similar results to the above-discussed closo-1-NB$_{11}$H$_{12}$. Both of these molecules had a single 2c2e B–N bond. This might be in accordance with closo-1-SB$_9$H$_9$, where two multicenter B–S–B bonds and one classical B–S bond were found. When closo-1-SB$_{11}$H$_{11}$ (see Fig. 3H) was compared to closo-1-SB$_{11}$H$_{11}$, one classical B–S bond was formed instead of a B–S–B 4c2e bond. This finding might help to rationalize the less positive $\Sigma_{\text{con}}$ of 4c2e bonding in closo-1-SB$_{11}$H$_{11}$ could be caused by differences in the architecture of the cage. Otherwise, the data were in agreement with the results obtained for the larger closo-cages, discussed above.

The bonding patterns observed across the 8- and 7-vertex closo-carboranes were overall similar to the bigger ones (see Tables 1 and 2). However, one significant difference was found. While the IBOs did not show any C–B classical bonding in the bigger closo-C$_{10}$H$_{11}$H$_{11}$ (n = 9–12) cages, the C atom of closo-C$_{10}$H$_{11}$H$_{11}$ (n = 7–8) formed a classical 2c2e B–C bond as well as multicenter bonds.

The 6- and 5-vertex closo-dicarbaboranes showed different trends from the bigger ones. Classical bonding was still more frequent in the smaller cages. In addition to the C–C and B–C bonds, the classical B–B bond was also found in closo-1,6-C$_2$B$_8$H$_{8}$ and closo-2,3-C$_2$B$_7$H$_{8}$ (see Table 3 and Fig. 3). Furthermore, the IBOs even disproved the presence of any multicenter bonding in closo-1,5-C$_2$B$_9$H$_9$. All bonds appeared to be B–C classical bonds. Such a bonding pattern would correspond to the localized molecular orbital (LMO) structures, which were already used to question the presence of the multicenter nature of the C–B–C bonding in closo-1,5-C$_2$B$_9$H$_9$. Note that the small cluster dimensions are problematic cases in terms of $^{11}$B NMR computations. In addition, the interatomic distances and charge distribution should reflect the classical bonding pattern. The short C–B separation (1.553 Å) supports the classical bonding pattern. It should also be mentioned that...
The IBO results of closo-1,2-C₂B₉H₆ did not differ from the IBO results of the bigger closo-1,2-C₆B₉n=2H₆ (n = 12, 10, 8), in contrast to the other smaller compounds. The C atom participated in four B–C–B bonds and one C–C bond in all of these closo-1,2-C₂B₉n=2H₆ (n = 12, 10, 8, 6) molecules. The IBO results of closo-1,2-C₂B₉H₆ nicely resembled the LMO structures on the PRDDO level obtained using the Boys criteria.

The bonding results for nido- are summarized in Table 4. The calculated IBOs for the selected heteroborane clusters are included in Fig. 5 to illustrate their bonding. The results show that the nature of bonding is heavily dependent on the position of the heteroatom in the nido-cages. Covalent bonds were found exclusively in the open face. For example, nido-2,9-C₂B₉H₁₂ and nido-2,7-C₂B₇H₁₂, which had one C atom located in the open face and one in the closed face, only formed the classical B–C bonds on the open belt, whereas the carbon in the closed face only participated in bonding of 3c2e nature. Moreover, although nido-2,7-C₂B₇H₁₂ had adjacent carbon atoms, the classical C–C bonding did not occur. Instead, C–C–B bonding of 3c2e nature was formed. On the other hand, when a nido-cage contained at least one heteroatom in the open pentagonal belt, evidence for classical covalent bonding was found. nido-Carboranes with two C atoms in the face formed B–C–B, B–C and C–C bonds. nido-7,9-C₂B₉H₁₂ contained adjacent C atoms and thus formed one C–C and two B–C bonds of classical 2c2e nature. nido-2,7-C₂B₇H₁₂ with separated C atoms formed four B–C bonds of 2c2e nature, all in the open face. The 3c2e bonds were formed in B–C–B triangles, when both B atoms were located under the C atom.

The bonding patterns of the nido-cages with other incorporated heteroatoms were very similar to the already-described nido-carboranes. Any heteroatom incorporated into the open face...
was a source of classical bonding. This resulted in a variety of bonding. For example, the open belts of nido-7,8,10-C2SB8H10, nido-7,8,9,10-P3CB7H8, nido-7,8,9,10-P3CB7H8 and nido-9,11,7,8-P2C2B7H9 were formed exclusively via the classical covalent bonds. There was evidence for S–B, P–P, C–C, C–P, B–C and P–B classical bonds. The length of these bonds ranged from 98.3 to 102.0% of $S_{cov}$, thus supporting the classical bonding pattern.47–49 Besides the classical bonds in the open face, the nido-heteroboranes also contained multicenter bonds of 3c2e nature with the participating heteroatom in agreement with the above-described nido-carboranes. In nido-8,9,7,11-P3CB7H9, the 3c2e B–P–B bonds were formed in the triangles 3–4–8 and 4–5–9 (the numbering of this cage is shown in Fig. 1). Similarly, B–C–B 3c2e bonds were formed in the 2–6–11 and 2–3–7 triangles. The interatomic distances ranged from 103.9 to 108.7% of $\Sigma_{cov}$ in these triangles.48 nido-9,11,7,8-P2C2B7H9 had an analogous bonding pattern even though the P atoms were not adjacent.

When the two heteroatoms were adjacent to each other, two 3c2e bonds of B–Z–B (Z = various heteroatoms) were formed. Here, one boron atom was shared by both of the triangles. This one lay on the under-belt under the middle of the Z–Z covalent bonding. When the heteroatoms were not located adjacent to each other, the 3c2e triangles were still formed. The heteroatoms and boron atoms lying under them are involved in this kind of bonding. The computed dipole moments and molecular ESP surfaces of the representative nido clusters show that the heterovertices located in the open pentagonal face act as an electron donor and become the center of a partial positive charge of the molecule (Fig. 6), which supports the existence of the B–Z–B 3c2e bonds. Moreover, the crystal packing of nido-7,8,9,11-Sb2C2B7H9 is predominantly dictated by the very strong Sb2····H–B σ-hole interaction.48b

We also applied the IAO method to nido-6,7-C2B7H9 as a representative of the 9-vertex nido-heteroboranes. Two B–C–B bonds of 3c2e nature and B–C and C–C 2c2e bonds suggested that bonding in the 9-vertex is not different from the 11-vertex nido-clusters.

The IBO results of the arachno-clusters are summarized in Table 4 and some of them have also been selected for Fig. 5, where the IBO results are illustrated. The results were similar to

Fig. 5 Calculated IBOs for the following heteroboranes: nido-2,9-C2B9H12^- (A), nido-2,7-C2B9H12^- (B), nido-7,8-C2B9H12^- (C), nido-7,9-C2B9H12^- (D), nido-7,8,9,10-P2C2B7H9 (E), nido-7,9,8,10-P2C2B7H9 (F), arachno-1,8,11-NC2B9H13 (G), arachno-6,9-CSB8H12 (H), hypho-7,8-NSB8H12 (I) and hypho-7,8-S2B4H4 (J). The orbitals that are not shown in this figure are analogous to those rendered. The orbital color coding is as follows: dark blue/purple – classical 2c2e bonding; red/pink – multicenter 3c2e bonding; yellow – multicenter 4c2e bonding.
those of the nido-clusters. The C atoms were bonded via 3c2e B–C–B bonds in the arachno-clusters. In the case of arachno-
1,8,11-NC2B8H13 with adjacent carbon atoms, the classical C–C
bond was formed. At the same time, two B–C–B multicenter
bonds were formed as well (see Fig. 5G). The other heteroatoms
only formed classical bonds, e.g. the S atom of arachno-4,6,5-
C2SB6H10 or the N atom of arachno-1,8,11-NC2B8H13.

The calculated IBOs for hypho-clusters are summarized in
Table 4. Their IBOs are shown in Fig. 5. Bonding of the
heteroatoms was dominated by classical bonding in the studied
hypho-clusters. With the exception of hypho-C2B8H13, the IBOs
did not reveal any bonds of multicenter nature with the exception
of the B–B–B and B–B–H bonds. Each of the heteroatoms formed
two covalent bonds with a boron atom of 2c2e nature.

In contrast to closo-1-SB11H11, the S atom of hypho-7,8-
NSB6H11 is incorporated into the hypho-cluster network exclusively
via classical B–S bonds and consequently acts as an electron
acceptor. This S atom thus has a negative electrostatic potential
(ESP) surface without areas of positive ESP (see Fig. 7).

Table S2 (ESI†) shows the results for a selected series of
representative compounds obtained by the most widely used
orbital localization scheme, the NBO methodology. The NBO
and IBO results are overall similar with many small differences.
The majority of the differences are due to the different localization
techniques used. While IBO only minimizes the spread of bond
orbitals over the atoms (i.e. maximizes their localization), the
NBOs explicitly search for the predefined Lewis structures most
closely matching the given wave function. Consequently, 4c2e
bonds naturally emerged in the IBO analysis of many heteroborane
clusters. On the other hand, the NBO analysis was limited to 2c2e
and 3c2e bonds. Other nonsystematic differences could be found
between the IBO and NBO methods. However, an exhaustive
comparison of the IBO with other methods is beyond the scope
of this study.

Conclusions

The nature of bonding has been systematically studied on a
broad series of heteroboranes using a novel quantum chemical
tool, the intrinsic bond orbital (IBO) approach. The results have
shown that the bonding of heteroatoms in icosahedral clusters
is mainly of multicenter nature. The role of classical bonding
increases with the decreasing size of the closo-heteroborane
cages. An extreme case is closo-1,5-C2B3H5, where the IBOs
have disproved the presence of any multicenter bonding. The nature
of bonding in the nido- and arachno-cages heavily depends on
the position of the heteroatom, and covalent bonds have been
found exclusively in the open face in nido- and arachno-cages.
However, classical bonds are more common in clusters with
open faces than in closo-heteroboranes.

It has also been shown in the studied architectures that the
nature of bonding is reflected in the molecular observables
such as the molecular electrostatic potential surface. Roughly
speaking, where electron distribution is opposed to the classical
electronegativity complex, such an electron distribution might
be attributed to multicenter bonding. On the other hand, the classical bonding indicates the classical electronegativity concept. Vector analyses of the experimental and computed dipole moments support such an observation.

Conflicts of interest

There are no conflicts to declare.

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