

Cite this: *Dalton Trans.*, 2025, **54**,
239

Heats of formation on the way from B₂H₆ to B₂₀H₁₆: thermochemical consequences of multicenter bonding in *ab initio* and DFT methods†

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The objective of this study is to evaluate the effectiveness of various computational methods in reproducing the experimental heats of formation of boron hydrides using the atomization energy approach. The results have demonstrated that the empirical dispersion combined with the BJ damping function provided too large intramolecular dispersion energies, thereby compromising the accuracy of the outcomes produced by the DFT-D3 methods. Additionally, the CCSD(T) method has reproduced the experimental values only when combined with a basis set optimized for an accurate description of the core-valence correlation effect. Furthermore, the number of multicenter bonds present in the molecules under examination has also reflected their stability, as indicated by the heats of formation. Finally, a five-center two-electron (5c–2e) bond has emerged in B₅H₉, by applying the intrinsic bond orbital (IBO) method.

Received 10th September 2024,

Accepted 4th November 2024

DOI: 10.1039/d4dt02589j

rsc.li/dalton

1 Introduction

Boron hydrides represent a vast chemical space and an astonishing variety of stable structures of various shapes. The shapes are dictated by the formation of three-center two-electron (3c–2e) bonds,¹ leading to 3D aromaticity.^{2,3} Therefore, they differ dramatically from aliphatic hydrocarbons, which only exhibit two-center two-electron (2c–2e) bonds. In aromatic hydrocarbons, the 2c–2e bonds are complemented by π electron clouds, which form the background of 2D aromaticity.

The gas-phase enthalpy of formation ($\Delta_f H^\circ$) of a chemical substance is a fundamental observable in chemical sciences. In addition to its use in thermochemistry, $\Delta_f H^\circ$ has been actively employed in the development, parameterization and evaluation of the methods of electronic structure theory, in particular density functional theory (DFT) and semiempirical quantum mechanical (SQM) methods. For instance, the most prevalent SQM techniques, including the PM6 and PM7 methods, have been parameterized against $\Delta_f H^\circ$. Such calibrations are typically,

although not exclusively, based on experimental $\Delta_f H^\circ$ data.^{4,5} It is noteworthy that even high-level computational methods exhibit greater discrepancies in the reproduction of the $\Delta_f H^\circ$ of boron hydrides than that of hydrocarbons.^{6,7} For instance, the mean absolute errors (MAEs) of the B3LYP-D3, ω B97X-D3 and DLPNO-CCSD(T) methods for a comprehensive set of 113 organic molecules have been documented to be 6.0, 3.2 and 1.6 kcal mol⁻¹, respectively.⁸ For boron hydrides, the reported MAEs for B3LYP-D2, G3, CCSD(T) and G4 were 13.3, 10.0, 6.6 and 3.6 kcal mol⁻¹, respectively.⁶ This limitation of higher-level computational methods represents a significant obstacle to the advancement of approximate techniques for the accurate representation of boron hydrides. It is thus evident that the benchmark computational methods capable of reproducing the experimental $\Delta_f H^\circ$ of boron hydrides are a prerequisite for the further development of more reliable approximate methods. The lack of computational methods applicable to molecular systems containing boron atoms poses a significant challenge when dealing with extended molecular systems. This limitation is frequently addressed through the implementation of simplistic solutions, such as the substitution of boron atoms with carbon atoms in protein–ligand docking of boron-containing compounds.^{9,10}

In this study, we have evaluated the efficacy of computational methods in reproducing the experimental $\Delta_f H^\circ$ of boron hydrides using the atomization energy approach and proposed a novel benchmark methodology for these calculations, which can be employed for generating reference data for the development of more approximate methods. Furthermore, we sought to gain deeper insights into the bonding of boron hydrides by applying

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† Electronic supplementary information (ESI) available: A comparison of experimental and computed bond lengths in B₂H₆, B₄H₁₀, B₅H₁₁ and B₆H₁₂, a summary of computed $\Delta_f H^\circ$ values and the coordinates for the optimized structures of the studied molecules are provided. See DOI: <https://doi.org/10.1039/d4dt02589j>



the intrinsic bond orbitals (IBOs) bonding analysis to a series of binary boron hydrides and also to electron-precise (with a sufficient number of electrons to form conventional electron-pair bonds between the linked atoms) boron compounds.

It is noteworthy that boron hydrides have garnered significant interest in thermochemistry as a potential rocket fuel.¹¹ There are experimental $\Delta_f H^\circ$ for eight boron-hydride compounds documented in the literature, as presented in Table 1. For the archetypal boron hydride, diborane B_2H_6 , the JANAF tables provide a $\Delta_f H^\circ$ value of 9.8 kcal mol⁻¹.¹² This value is in close agreement with those determined by Gunn (8.6 kcal mol⁻¹)¹³ and by Prosen *et al.*¹⁴ (7.5 kcal mol⁻¹, derived from 6.7 kcal mol⁻¹ for conversion to amorphous B and applying the 0.4 kcal mol⁻¹ estimate for amorphous B¹⁵). Gunn and Green have reported a lower value of 5.8 kcal mol⁻¹, determined by explosive decomposition.¹⁶ We use the average value of 7.9 kcal mol⁻¹ for B_2H_6 in this study (see Table 1). Gunn and Green have determined the $\Delta_f H^\circ$ of B_4H_{10} , B_5H_9 , B_5H_{11} and B_6H_{10} by explosion of mixtures with SbH_3 (the $\Delta_f H^\circ$ of 13.8, 15.4, 22.2 and 19.6 kcal mol⁻¹, respectively).¹⁷ Prosen *et al.* have determined a $\Delta_f H^\circ$ value of 15.0 kcal mol⁻¹ for B_5H_9 ,^{14,15} and the JANAF tables give the $\Delta_f H^\circ$ value of 17.5 kcal mol⁻¹ for B_5H_9 .¹² We utilize the average value of 16.0 kcal mol⁻¹ for B_5H_9 (Table 1). Gunn and Kindsvater have measured the $\Delta_f H^\circ$ of B_6H_{12} , $B_{10}H_{14}$ and $B_{10}H_{16}$ calorimetrically by explosion and obtained the $\Delta_f H^\circ$ of 26.5, 4.4 and 34.8 kcal mol⁻¹, respectively.¹⁸ Johnson *et al.*¹⁹ and Galchenko *et al.*²⁰ have studied $B_{10}H_{14}$ by pyrolysis methods, and when combined with the heat of sublimation by Miller,²¹ similar $\Delta_f H^\circ$ values of 2.5 and 4.3 kcal mol⁻¹ were obtained. However, the JANAF tables give a higher value of 11.3 kcal mol⁻¹.¹² Because of this discrepancy, we did not include $B_{10}H_{14}$ in the evaluation of calculation methods. In order to assess the impact of multicenter bonding on computational estimation more accurately, we also utilized eight electron-precise boron compounds (B_2Cl_4 , B_2F_4 , B_2O_3 ,

$B_3N_3H_6$, BCl_3 , BF_3 , HO-BO and BO_3H_3), for which experimental $\Delta_f H^\circ$ data are available (see Table 1).

2 Methods

All the compounds were optimized using the B3LYP/DZVP-DFT (the DZVP-DFT basis set²⁴ is available through the basis set exchange repository, <https://www.basissetexchange.org>, as dgauss-DZVP) and MP2/cc-pVDZ levels and the LBFSGS algorithm with strict optimization criteria, namely the energy change below 0.0006 kcal mol⁻¹, the largest gradient component below 0.12 kcal mol⁻¹ Å⁻¹ and the root-mean-square gradient below 0.06 kcal mol⁻¹ Å⁻¹. Cuby4^{25,26} was utilized for gradient optimizations. The Cuby4 program used Turbomole 7.3²⁷ for the MP2 and B3LYP calculations.

The $\Delta_f H^\circ$ values were computed using the atomization energy approach as described in ref. 28. We utilized the Cuby4 framework.^{25,26} The Cuby4 program used Turbomole 7.3²⁷ for the CCSD(T), MP2, B3LYP and BLYP calculations. For the ω B97X calculations, Cuby4 utilized ORCA 5.0.3.²⁹ Harmonic vibrational calculations providing the ZPVE and other thermodynamic contributions necessary for the evaluation of $\Delta_f H^\circ$ were performed at the same level as gradient optimizations, namely at the B3LYP/DZVP-DFT and MP2/cc-pVDZ levels. The energy calculations of the studied molecules and their constituent atoms were performed at the all-electron CCSD(T) and various DFT levels. The DFT calculations were carried out in combination with the def2-QZVP basis set. The impact of empirical dispersion (D3)^{30,31} with Becke–Johnson (BJ) and zero (0) damping functions on DFT was tested. Unless otherwise stated, the BJ damping function was used as the default option. In the case of CCSD(T), we utilized the cc-pVQZ basis set. In the method abbreviated as CCSD(T)', we used cc-pwCVQZ³² for boron atoms and cc-pVQZ for all the other elements (H, F, Cl, N, and O) and abbreviated it as CCSD(T)'. In the case of larger molecules, namely B_8H_{12} , B_9H_{15} , $B_{10}H_{14}$, $B_{10}H_{16}$ and $B_{20}H_{16}$, a composite approach was employed to compute CCSD(T). The CCSD was evaluated with cc-pwCVQZ and cc-pVQZ basis sets, while the perturbative triples (T) were evaluated using the smaller cc-pwCVTZ and cc-pVTZ basis sets.

The intrinsic bond orbitals (IBOs) method was used to link the quantitative SCF wave functions to a qualitative chemical picture.³³ In other words, a projection operator projected IBO orbitals from the canonical ones. The IBOview program³⁴ was utilized for this purpose. The corresponding input files for the latter were generated at the B3LYP/def2-TZVP level using the Turbomole 7.3²⁷ program package.

3 Results and discussion

3.1 Bonding properties

As far as the electronic structure is concerned, the compounds listed in Table 1 have been investigated in terms of the IBOs.³³ The bonding in the electron-precise boron compounds is strictly

Table 1 The experimental gas-phase enthalpy of formation ($\Delta_f H^\circ$) of boron compounds in kcal mol⁻¹. The molecular structures of boron hydrides are shown in Fig. 1

Molecule	Exp. $\Delta_f H^\circ$	Avg. exp. $\Delta_f H^\circ$
Boron hydrides		
B_2H_6	9.8, ¹² 8.6, ¹³ 7.5, ^{14,15} 5.8 ¹⁶	7.9 ± 1.7
B_4H_{10}	13.8 ¹⁷	13.8
B_5H_9	15.4, ¹⁷ 15.0, ¹⁴ 17.5 ¹²	16.0 ± 1.3
B_5H_{11}	22.2 ¹⁷	22.2
B_6H_{10}	19.6 ¹⁷	19.6
B_6H_{12}	26.5 ¹⁸	26.5
$B_{10}H_{14}$	11.3, ¹² 4.4, ¹⁸ 2.5, ^{19,21} 4.3 ^{20,21}	5.6 ± 3.9
$B_{10}H_{16}$	34.8 ¹⁸	34.8
Other boron compounds		
B_2Cl_4	-116.9 ¹²	-116.9
B_2F_4	-342.2 ¹²	-342.2
B_2O_3	-199.8 ¹²	-199.8
$B_3N_3H_6$	-121.9, ¹² -124.1 ²²	-123.0 ± 1.6
BCl_3	-96.3, ¹² -97.5 ²³	-96.9 ± 0.9
BF_3	-269.7, ¹³ -271.6 ¹²	-270.7 ± 1.3
HO-BO	-134.0 ¹²	-134.0
BO_3H_3	-237.2 ¹²	-237.2



dominated by 2c–2e bonds only. In the case of cyclic borazine, the 2c–2e bonds are complemented by pseudo 3c–2e bonds, which form the classical π electron clouds (the corresponding expansion coefficients, ECs: N 1.51, B 0.23 and B 0.23). Bonding properties in borazine are of 3c–2e-like in terms of the multicenter bonding approach. As a consequence, these two 3c–2e-like bonds form “ π -bonds” (see Fig. 2, the violet vs. pink regions visu-

alize the different phases). However, the wave function of this kind changes its sign in contrast to genuine 3c–2e bond appeared in the polyhedral boron clusters in which these orbitals have exclusively one sign.

In the case of boron hydrides, there used to be a concept of two kinds of 3c–2e bonds, namely central and open. The structures of B_2H_6 , B_4H_{10} , B_5H_{11} and B_6H_{10} were well described using open three-center bonds.³⁵ However, the bonding schemes in B_5H_9 and $B_{10}H_{14}$ required a resonance hybrid of four valence structures and 24 valence structures, respectively, when open 3c–2e bonds were omitted. We have made efforts to unify these concepts by analyzing the bonding properties using the above approach, which has given rise to not only three- but also four- and even five-center bonding. The four-center bonding concept was found during the bonding analysis of a series of heteroboranes with the EB_{11} (E = S, Se, Te) *closo*-icosahedral core.^{36–38} The results have demonstrated that all the boron hydrides with bridging and terminal hydrogens have 3c–2e BHB and 2c–2e BH bonds, respectively. They are exemplified for the case of B_2H_6 . The rest of the bonds in the remaining seven cases consist of a mixture of 3c–2e and 4c–2e bonds. In addition, the bond description of B_5H_9 even appears to have a 5c–2e bond (see Fig. 3), a motif that has been earlier observed by Lipscomb by Extended Huckel Theory (EHT).³⁹ The corresponding ECs in this IBO have been computed as B 0.79, B 0.74, B 0.16, B 0.16 and B 0.11. B_4H_{10} serves as an example of the 4c–2e bonding scheme (EC: B 0.80, B 0.80, B 0.18 and B 0.18). The most commonly

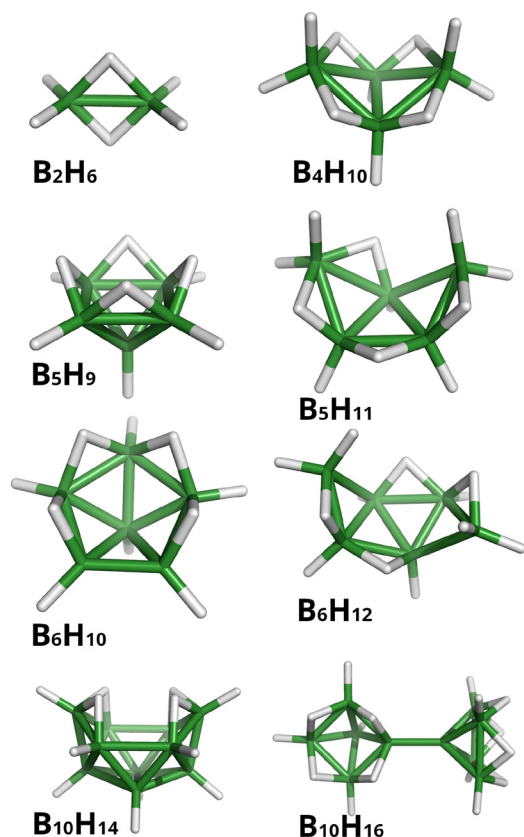


Fig. 1 Molecular structures of boron hydrides with experimentally determined $\Delta_f H^\circ$.

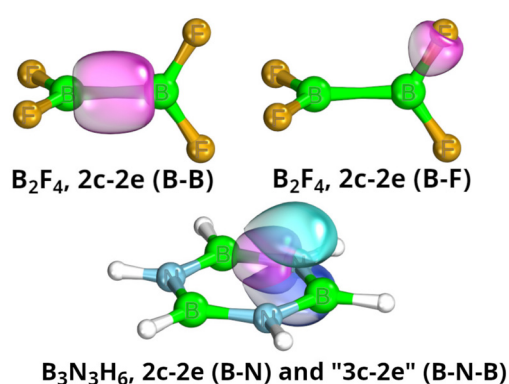


Fig. 2 Examples of bonding as revealed in electron-precise boron compounds by the application of the IBO computational approach. Color coding: pink – 2c–2e, violet – 3c–2e.

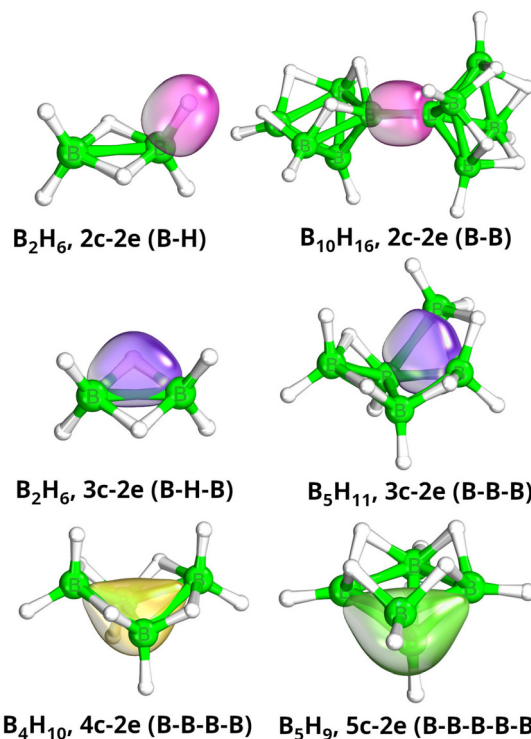


Fig. 3 Examples of bonding as revealed in boron hydrides by the application of the IBO computational approach. Color coding: pink – 2c–2e, violet – 3c–2e, yellow – 4c–2e, green – 5c–2e.



Table 2 The mean absolute error (MAE) and Pearson correlation coefficient (R) of the computed gas-phase enthalpy of formation ($\Delta_f H^\circ$) for boron hydrides (B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , B_6H_{12} and $B_{10}H_{16}$) and other boron compounds (B_2Cl_4 , B_2F_4 , B_2O_3 , $B_3N_3H_6$, BCl_3 , BF_3 , HO-BO and BO_3H_3) in kcal mol $^{-1}$. The CCSD(T)//MP2 approach entails the utilization of CCSD(T) for the evaluation of energy, whereas MP2 is employed for the determination of gradients and the calculation of other thermodynamic contributions, which are essential for the evaluation of $\Delta_f H^\circ$

Method	MAE	R	MAE	R
	Boron hydrides		Other boron compounds	
CCSD(T)//MP2	12.1	0.71	2.2	0.999
CCSD(T)'/MP2	1.4	0.99	1.9	0.999
B3LYP	3.2	0.98	4.6	0.998
B3LYP-D3//B3LYP	23.0	-0.12	3.4	0.997
B3LYP-D3-0//B3LYP	11.9	0.91	4.2	0.998
BLYP//B3LYP	14.8	0.98	7.2	0.996
BLYP-D3//B3LYP	9.8	0.58	8.3	0.996
BLYP-D3-0//B3LYP	4.0	0.98	7.7	0.997
ω B97X-D3BJ//B3LYP	23.5	-0.58	5.1	0.998
ω B97X-D3-0//B3LYP	17.1	-0.06	2.9	0.999
ω B97X-V//B3LYP	19.7	-0.26	4.9	0.999

used $B_{10}H_{14}$ has such bonding schemes with the ECs of B 0.74, B 0.71, B 0.22 and B 0.22. Interestingly, a classical 2c-2e B-B bond has been identified in the *conjuncto* $B_{10}H_{16}$ system (Fig. 3).

Furthermore, the number of multicenter bonds present in the molecules under study also reflects their stability, as indicated by the $\Delta_f H^\circ$. It is evident that an increase in the number of multicenter bonds results in enhanced system stability with respect to this thermochemical parameter. Decaborane(10), $B_{10}H_{14}$, a fundamental component of boron chemistry, is distinguished by its exceptional stability among binary boron hydrides, which is attributable to its nine multicenter bonds (six 3c-2e BBB and three 4c-2e BBBB). In contrast, B_5H_{11} and B_6H_{12} have only two multicenter bonds (one 3c-2e BBB and one 4c-2e BBBB) and three multicenter bonds (two 3c-2e BBB and one 4c-2e BBBB), respectively, which is indicative of a lack of stability, consistent with the observed heats of formation.

3.2 Thermochemical properties

Whereas in the previous section, we evaluated the studied molecules in terms of the nature of the bonds, in this section, we are going to focus on the energetic contributions of these motifs when reproducing experimental $\Delta_f H^\circ$ as precisely as possible. First, we evaluated the correctness of the optimized geometries employed for the $\Delta_f H^\circ$ calculations. Both methods utilized for the optimizations, namely MP2/cc-pVDZ and B3LYP/DZVP-DFT, were in good agreement with the experi-

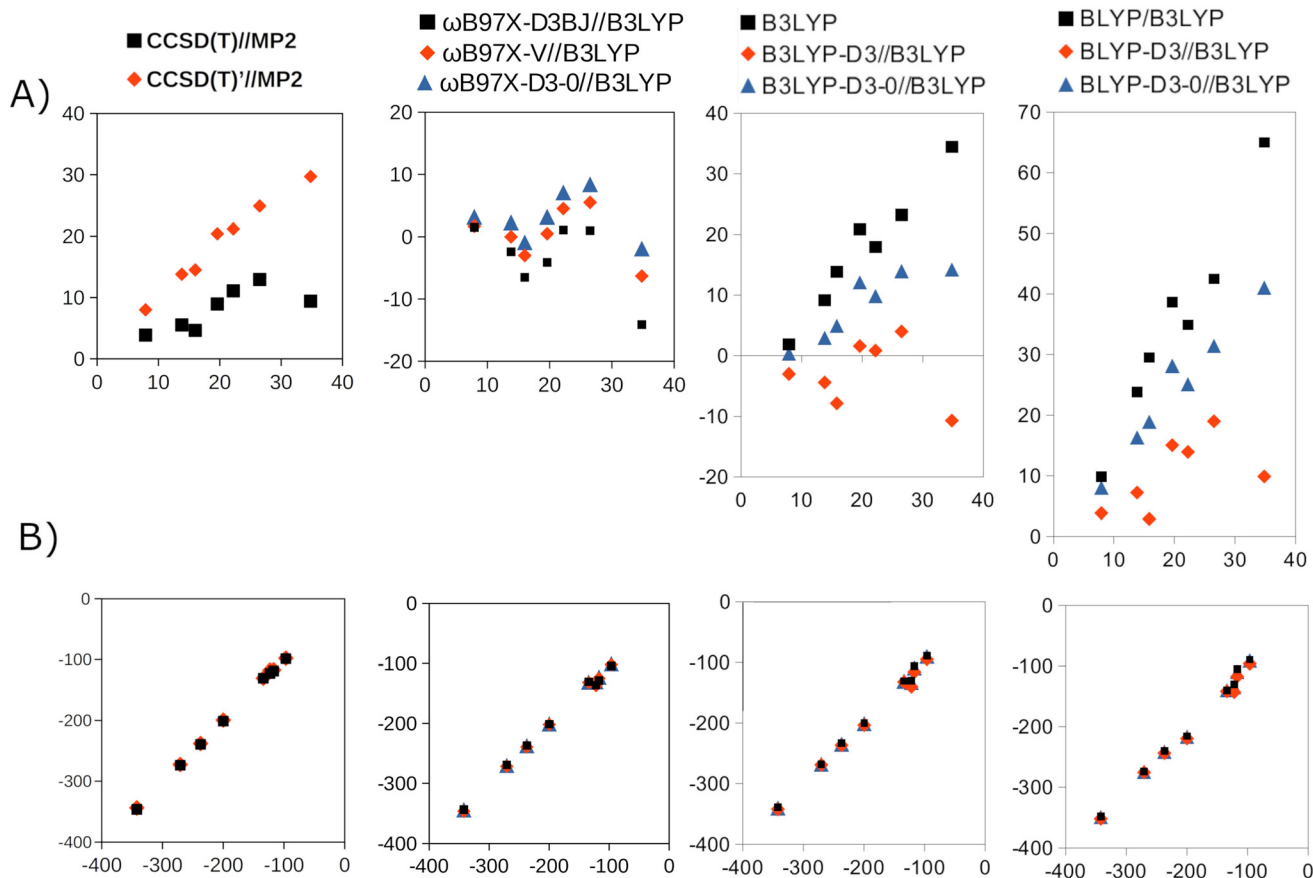


Fig. 4 The computed gas-phase enthalpy of formation ($\Delta_f H^\circ$) for (A) boron hydrides (B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , B_6H_{12} and $B_{10}H_{16}$) and (B) other boron compounds (B_2Cl_4 , B_2F_4 , B_2O_3 , $B_3N_3H_6$, BCl_3 , BF_3 , HO-BO and BO_3H_3) plotted against the experimental $\Delta_f H^\circ$. All in kcal mol $^{-1}$.



mental structures of B_2H_6 , B_4H_{10} , B_5H_{11} and B_6H_{12} determined by electron diffraction,^{40–42} with the MAEs in the bond lengths being 0.015 and 0.020 Å, respectively (see Table S1†). We have also tried a larger basis set for MP2 calculations, specifically cc-pVTZ, but the obtained geometries had a larger MAE of 0.023 Å.

In the case of electron-precise boron compounds, the $\Delta_f H^\circ$ computed by all the tested methods was in good agreement with the experimental values, with the Pearson coefficient R being higher than 0.995 (see Table 2 and Fig. 4). The MAEs of the $\Delta_f H^\circ$ of the DFT-based methods were between 2.9 and 8.3 kcal mol⁻¹, with the best performance among the DFT methods achieved by ω B97X-D3-0//B3LYP. The empirical dispersion D3 did not dramatically change the MAE in any case. CCSD(T)//MP2 and CCSD(T)//MP2, with the MAE for the $\Delta_f H^\circ$ being 2.2 and 1.9 kcal mol⁻¹, respectively, approached the experimental accuracy. A comparison of the MAE obtained for the individual molecules across all the evaluated computational methods, as presented in Table 3, revealed that $B_3N_3H_6$ was the most challenging electron-precise boron compound for the computational reproduction of $\Delta_f H^\circ$. This is consistent with the established difficulty of $B_3N_3H_6$ in this context.⁴³ Surprisingly, another molecule that is known to be challenging, B_2F_4 ,^{44,45} had the MAE comparable to other electron-precise compounds.

In the case of boron hydrides, all compounds were computed with a similar average error (Table 3), but the performance of the tested methods exhibited notable discrepancies. DFT-D3 methods combined with the BJ damping function had a large MAE in the range of 9.8 to 23.5 kcal mol⁻¹ and Pearson correlation in the range of -0.58 to 0.58. The D3 dispersion was excessively attractive, resulting in too low $\Delta_f H^\circ$, Table 2 and Fig. 4. Using the zero-damping function instead of BJ improved the results, with MAE in the range of 4.0 to 17.1 kcal mol⁻¹ and Pearson correlation in the range of -0.06 to 0.98. In agreement with our results, Becke has recently found that BJ damping may give too large (in absolute value) intramolecular dispersion energies in some alkaline clusters, in particular in Li_8 and Na_8 clusters. It has been shown that it is due to the too-small effective van der Waals interatomic separation ($R_{vdw,ij}$) that is linearly related to a critical interatomic separations ($R_{c,ij}$).⁴⁶

Table 3 The mean absolute error (MAE) of the computed gas-phase enthalpy of formation ($\Delta_f H^\circ$) divided by molecular weight (M). $\Delta_f H^\circ M^{-1}$ in kcal g⁻¹

Molecule	MAE	Molecule	MAE
Boron hydrides		Other boron compounds	
B_2H_6	0.17	B_2Cl_4	0.04
B_4H_{10}	0.18	B_2F_4	0.05
B_5H_9	0.20	B_2O_3	0.07
B_5H_{11}	0.18	$B_3N_3H_6$	0.15
B_6H_{10}	0.16	BCl_3	0.04
B_6H_{12}	0.17	BF_3	0.03
$B_{10}H_{16}$	0.21	HO-BO	0.09
		BO_3H_3	0.04

CCSD(T)//MP2 had surprisingly large MAE for boron hydrides of 12.1 kcal mol⁻¹. In contrast, CCSD(T)//MP2 had a small MAE of 1.4 kcal mol⁻¹, being thus close to the experimental accuracy also for this class of compounds. In analogy with our observations, the incorporation of core-correlation functions, as exemplified by the cc-pwCVnZ basis sets, also led to an improvement in the computational description of $\Delta_f H^\circ$ in complexes comprising alkali and alkaline earth metals.⁴⁷ We propose CCSD(T)//MP2 as the benchmark method for the computational evaluation of $\Delta_f H^\circ$ data for the boron compounds for which no experimental determinations are available or in cases where there are discrepancies between several experimental measurements. Consequently, we have applied this method to B_8H_{12} , B_9H_{15} , $B_{10}H_{14}$ and $B_{20}H_{16}$ (see Table 4 and Fig. 1, 5). The computed $\Delta_f H^\circ$ of -2.5 kcal mol⁻¹ for $B_{10}H_{14}$ thus preferred, among several experimental values, the smallest one of 2.5 kcal mol⁻¹, reported by Prosen *et al.*¹⁹ Although the X-ray crystal structures of B_8H_{12} and B_9H_{15} are known,^{48,49} no experimental $\Delta_f H^\circ$ values are available. Nevertheless, these $\Delta_f H^\circ$ values have been estimated empirically and calculated *ab initio* many times in the literature.^{6,50–53} The ranges of the theoretical values reported for B_8H_{12} and B_9H_{15} are considerable, spanning from 11.1 to 42.0 and from 26.5 to 49.4 kcal mol⁻¹, respectively. The CCSD(T)//MP2 gives values of 21.5 and 14.7 kcal mol⁻¹, respectively. The $B_{20}H_{16}$

Table 4 The computed gas-phase enthalpy of formation ($\Delta_f H^\circ$) in kcal mol⁻¹

Molecule	$\Delta_f H^\circ$ CCSD(T)//MP2
B_8H_{12}	21.5
B_9H_{15}	14.7
$B_{10}H_{14}$	-2.5
$B_{20}H_{16}$	-33.8

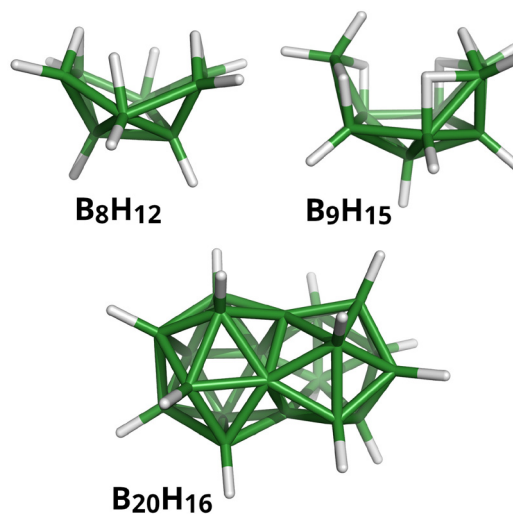


Fig. 5 Molecular diagrams of the B_8H_{12} , B_9H_{15} and $B_{20}H_{16}$ boron hydrides.



molecule is the first synthesized *closo* macropolyhedron.⁵⁴ Whereas the crystal structure of B₂₀H₁₆ is known,⁵⁵ there are no experimental or computational estimates of the $\Delta_f H^\circ$ of B₂₀H₁₆ in the literature. The CCSD(T)//MP2 method yields a $\Delta_f H^\circ$ value of $-33.8 \text{ kcal mol}^{-1}$ for B₂₀H₁₆, which is a highly favorable result even when compared to that of B₁₀H₁₄. In accordance with these findings, the pyrolysis of B₂H₆ at lower temperatures results in the formation of B₁₀H₁₄, while higher temperatures lead to the production of B₂₀H₁₆. This confirms that B₂₀H₁₆ exhibits relatively higher thermodynamic stability.⁵⁶ Additionally, in accordance with these findings, the IBO analysis has shown besides sixteen 2c–2e terminal B–H bonds also thirty multicenter bonds. Specifically, they are fourteen 3c–2e B–B–B and sixteen 4c–2e B–B–B–B bonds, which is approximately three times the number observed in the previously discussed B₁₀H₁₄.

4 Conclusions

This paper investigates the accuracy of various computational methods for reproducing the available experimental $\Delta_f H^\circ$ data for boron compounds. Our findings demonstrate that CCSD(T) yields reliable $\Delta_f H^\circ$ values for boron hydrides only in conjunction with a correlation-consistent basis set optimized for a reliable description of core-valence correlation effects (cc-pwCVQZ) on boron atoms. Additionally, we have demonstrated that empirical dispersion can impair the results of DFT-based methods, particularly when employed in conjunction with the BJ damping function.

The IBO method has been utilized to establish a correlation between quantitative SCF wave functions and a qualitative chemical representation. In addition to confirming the existence of 2c–2e and 3c–2e bonds, our findings have also revealed the existence of 4c–2e and 5c–2e bonds. The 5c–2e bond, a previously reported configuration of a five-centered σ molecular orbital, has been identified in B₅H₉.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

J.F., D.H. and J.H. acknowledge the support of the Czech Science Foundation, project number 23-05083S. J.Ř. acknowledges the support of the Czech Science Foundation, project number 22-17063S.

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