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Electronic structure study of H_3BXH_3 (X=B, N and P) as hydrogen storage materials using calculated NMR and XPS spectra

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ABSTRACT

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Boron-based materials have been used for hydrogen storage applications owing to their high volumetric and gravimetric hydrogen density. The present study quantum mechanically investigates the electronic structures of three compounds: diborane (DB, B₂H₆), ammonia borane (AB, H_3BNH_3) and phosphine borane (PB, H_3BPH_3). The exploration is facilitated using calculated nuclear magnetic resonance (NMR) chemical shifts, together with outer valence ionisation potentials (IP) and core electron binding energy (CEBE). The findings show a distinct electronic structure for diborane, differing notably from AB and PB, which exhibit certain similarities. Noteworthy dissimilarities are observed in the chemical environments of the bridge hydrogens and terminal hydrogens in diborane, resulting in a substantial chemical shift difference of up to 5.31 ppm. Conversely, in AB and PB, two distinct sets of hydrogens emerge: protic hydrogens $(H_p-N \text{ and } H_p-P)$ and hydridic hydrogens (H_h-B) . This leads to chemical shifts as small as 0.42 ppm in AB and as significant as 3.0 ppm in PB. The absolute isotropic NMR shielding constant $(\sigma_{\rm B})$ of ¹¹B in DB is 85.40 ppm, in contrast to 126.21 ppm in AB and 151.46 ppm in PB. This discrepancy indicates that boron in PB has the most robust chemical environment among the boranes. This assertion finds support in the calculated CEBE for B Is of 196.53, 194.01 and 193.93 eV for DB, AB and PB respectively. It is clear that boron in PB is the most reactive atom. Ultimately, understanding the chemical environment of the boranes is pivotal in the context of dehydrogenation processes for boron-based hydrogen storage materials.

Keywords: borane compounds, CEBE, core electron binding energy, DFT calculations, ¹H proton and ¹¹B NMR chemical shift-shielding constant, role of hydrogens and boron in boranes, valence ionisation energy spectrum.

Introduction

New momentum has emerged globally in the study of energy storage materials, catalysed by two decades of intensive research and development across both academic and industrial domains.¹ Despite these advances, there remains a need to address persisting scientific, technological and economic hurdles associated with the hydrogen life cycle. This includes production, storage, transportation, distribution and utilisation of hydrogen. Hydrogen storage and transportation have become significant for hydrogen energy export countries such as Australia.² As a result, the processes of dehydrogenation and hydrogenation are important in chemical hydrogen storage using hydrogen carriers. The storage issue is particularly challenging,¹ given its implications in transportation such as on board shipping. Among hydrogen storage techniques, chemical hydrogen storage, using chemical binding (chemisorption), has been more attractive than conventional physical techniques, including the cryogenic liquefaction of hydrogen at -253° C. Hydrogen carriers such as ammonia borane (AB) exhibit notable advantages. AB boasts a high hydrogen content of 19.6 wt-%, remarkable stability under ambient conditions, non-toxicity, and high solubility in common solvents.^{2,3} AB holds potential as both a liquid-state hydrogen carrier and a solid-state hydrogen storage material.¹ When dissolved, AB functions as a liquid-state hydrogen carrier (LHC).³ This property aligns well with preexisting energy infrastructure, allowing reuse with minimum modification.² Nevertheless, challenges persist with AB, primarily revolving around the dehydrogenation–hydrogenation process and the establishment of economically viable chemical pathways for these operations. Compounds like B–N and P–B adducts, such as AB and phosphine borane (PB, H₃BPH₃), stand out as efficient and lightweight materials for hydrogen storage.

Ammonia borane may be the simplest amine borane, yet its history has been anything but simple.⁴ As a solid hydrogen storage material that is both efficient and safe, AB has gained significant attention in recent years. In a comprehensive review by Demirci¹ summarising the literature up to June 2020, a range of hydrogen chemical storage compounds containing boron were examined. These include borohydride, lithium borohydride, sodium borohydride, potassium borohydride, borane, AB, diborane (DB), amidoboranes, hydrazine borane, triborane and dodecaborane. The hydrogen generating capacity of AB, essentially its role as a hydrogen carrier, has been recognised for a considerable period.¹ Although AB possesses characteristics associated with propellant and energetic materials, its primary identity remains that of a hydrogen carrier. The hydrogen released from AB is used for electricity generation through conversion in fuel cells.¹

Phosphine borane, which can dissolve in liquid ammonia, has been comparatively less explored as an LHC. The behaviour or property of PB involves the thermal or catalytical elimination of H_2 , yielding cyclic and polymeric phosphinoboranes.⁵ Mechanistic insights into the reversible activation of H_2 in this context indicate an interaction with the Lewis acidic boron centre, followed by intramolecular proton migration to phoshorus.⁵ Notably, the arrangement of cations and anions

positions the BH and PH units facing each other, with a BH····HP proximity of 2.75 Å, significantly surpassing typical intermolecular H-bonding distances. In the domain of synthesis and industry, PB plays a pivotal role in facilitating efficient dehydrocoupling of secondary PB adducts, leading to the formation of the corresponding polymers.⁶ Although discussions touch on the nature of the coordinate bond between phosphines and the borane group, comprehensive and definitive information concerning the precise nature of the P–B bond remains to be firmly established.⁷

Diborane stands out as a clear precursor for AB and PB; however, it poses challenges due to its pyrophoric and toxic nature.⁸ The amine and phosphine adducts of borane exhibit improved stability and diminished reactivity compared with B_2H_6 , thereby reducing safety concerns. AB and PB both offer substantial promise as pivotal elements in hydrogen storage fuels, primarily owing to their stability and high gravimetric hydrogen content. Fig. 1 illustrates that DB has undergone considerable investigation,¹ not only for its applications in energy materials but also owing to its fundamental chemical bonding, notably the unique B–H–B three-centre–two-electron (3c–2e) bonding character.⁹ An extensive overview encompassing several decades of research in the application of AB in chemical hydrogen storage can be found in Demirci.^{1,10}

PB, the simplest adduct of its kind, was synthesised as 'diborane diphosphine' and later was found to be the monomer H_3BPH_3 ,^{11,12}

$$B_2H_6 + PH_3 \rightarrow H_3BPH_3 + BH_3$$

Phosphine borane tends to undergo substantial dissociation, resulting in the formation of B_2H_6 and the corresponding phosphorus ligand.¹³

The direct addition of H_2 to unsaturated bonds is typically symmetry-forbidden, necessitating the involvement of



Fig. 1. Number of articles from a search on the Web of Science for boron-containing hydrogen chemical storage materials to June 2020.¹ Grey bars are borohydrides and derivatives, and orange bars are borane and its derivatives.

catalysts, which can be either heterogeneous or homogeneous transition metal catalysts, for hydrogenation reactions. However, the activation of hydrogen by main group compounds under mild conditions remained unexplored until a significant breakthrough was reported in 2005.¹⁴ Power and co-workers, particularly through their work on digermyne, achieved the first directed addition of hydrogen to a closedshell unsaturated main group compound under ambient conditions.¹⁴ This transition metal-like behaviour is demonstrated by a variety of main group element species, offering intriguing possibilities for applications in homogeneous catalysis. The emergence of transition metal-free reactions highlights the potential of reactive main group compounds and underscores the significance of molecular design, particularly the strategic selection of substituents at the main group element, for both isolation and practical applications.¹⁵ This avenue not only holds the promise of cost reduction but also addresses environmental concerns, which are of great importance to the industry.

Crucial to this achievement is an understanding of kinetic stabilisation, thermodynamic stabilisation and the use of ligands possessing the requisite electronic properties for the reactive species.¹⁵ To stabilise low-valent and electrondeficient compounds, strong s- and p-donors have proved to be suitable, with examples encompassing N-heterocyclic imines and their carbon and phosphorus derivatives.¹⁵ The hydrogen release of AB is exothermic and thus nonreversible.¹⁶ Consequently, understanding the electronic properties of boranes, including ionisation potentials, becomes pivotal for gaining deeper insights into the thermodynamics of hydrogen storage materials.¹⁷ The study of suppressing the thermal dehydrogenation of AB^{11,18} involves an exploration of the added nucleophile's role in inhibiting dehydrogenation. This aspect is further supported by the observation of facile phosphine-ammonia exchanges.¹⁰

The consideration of B-N and B-P adducts as hydrogen storage materials stems from their potential to influence hydrogen storage capacity and release characteristics. Their structural properties can significantly affect their performance in this regard. For example, AB displays a high theoretical hydrogen capacity of 19.6 wt-%, releasing hydrogen at ~6.5 wt-% below 385 K but up to 15.4 wt-% under certain conditions.¹⁶ By contrast, PB boasts a moderate theoretical hydrogen capacity of 14.5 wt-% and can release hydrogen in the range of 8-10 wt-%. Diborane, with a theoretical hydrogen capacity of 18.5 wt-%, can release hydrogen up to 6.3 wt-%.¹⁹ AB and PB represent examples of Lewis acid-Lewis base adducts, where the stability of the central dative bond plays a significant role. Describing the factors influencing the strength of B–N and B–P bonds is instrumental in understanding this phenomenon.²⁰ Although this approach provides a general estimate of the dative bond's strength, the dissociation energy of the dative bond is not solely linked to the strengths of the Lewis acid or Lewis base. As a result, the Lewis acidity of boron is primarily influenced by substituent size and electronegativity.²⁰

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The investigation of the electronic structures of compounds involving BH₃ bonding with BH₃, NH₃, and PH₃ is significant when studying the release of hydrogen. Numerous theoretical studies have been conducted on AB and its dehvdrogenated products, as well as small boron-nitrogen hydrides, vielding insights into the hydrogen release process.^{21,22} This understanding of B-N and B-P adducts electronic structures in the gas phase is crucial for understanding their behaviour in hydrogenation and dehydrogenation processes. Although various gas-phase studies for DB, AB and PB are available, including our recent research on AB and its dehydrogenated borane hydrides,^{22,23} fewer investigations have delved into the nature of protic N-H and hydridic B-H hydrogen in AB and PB. Furthermore, these studies rarely explore how the electronic structures, especially chemical bonding characterised by valence ionisation energies, influence the behaviour of protic and hydridic hydrogens in AB and PB compared with DB. In an ongoing study, well-established quantum mechanical methods were employed to elucidate the roles of hydrogens in AB, PB and DB. We recently combined O 1s X-ray photoelectron spectroscopy (XPS) and ¹H NMR chemical shifts to study the intramolecular hydrogen bonding of salicylic acid.²⁴ The present analysis incorporates ¹H NMR spectroscopy with valence ionisation potentials (IP) as well as B 1s XPS to shed light on the functions of protic and hydridic hydrogens in these borane compounds. By combining these techniques, a comprehensive understanding of the interplay between electronic structure, chemical bonding and hydrogen behaviour within these compounds can be obtained.

Computational details

The details of the quantum mechanical calculations are the same as mentioned in our previous study.²² Briefly, the geometries of DB, AB and PB are optimised in the gas phase, based on coupled-cluster theory (CCSD(T)) with the cc-pVTZ basis set, i.e. the CCSD(T)/aug-cc-pVQZ level of theory. NMR calculations are conducted using density functional theory (DFT) B3PW91/aug-cc-pVTZ level of theory, and the valence vertical ionisation energies (VIEs) are calculated using the Δ PBE0(SAOP)/et-pVQZ method developed by Segala and Chong.²⁵ The CEBE calculations use the Δ (PW86-PW91/et-pVQZ) + C_{rel} method.²⁶ All calculations were performed using the Gaussian 16 computational chemistry package²⁷ and Amsterdam Density Functional (ADF) suites of programs.²⁸

Results and discussion

Major structural differences among the boranes

The primary distinguishing structural feature among DB, AB and PB compounds lies in the types of atoms and groups attached to the central boron atom. DB only has hydrogen atoms bonded to the boron atoms, whereas AB and PB respectively have nitrogen and phosphorus atoms connected to the boron atom.9 These distinct bonding arrangements and molecular architectures lead to variations in the physical and chemical characteristics of these compounds, including their hydrogen storage capacity and reactivity. In Fig. 2, the structural differences are evident. Diborane has two boron atoms linked by two bridging hydrogen atoms (H_b), with each boron atom forming bonds with two additional hydrogen atoms. In AB, the boron atom is connected to an amino (NH₃) group and three boron-hydrogen (B-H) bonds. Similarly, in PB, the boron atom is attached to a phosphine (PH₃) group and three B–H bonds. Each of these compounds harbours two categories of hydrogen atoms: bridge (H_b) and terminal (H_t) hydrogens in diborane (DB),⁹ and protic (H_p) hydrogens in AB and PB originating from the N-H and P-H bonds. These hydrogens possess partial positive charges (δ^+) . Additionally, there are hydridic (H_b) hydrogens in AB and PB within B-H bonds, carrying partial negative charges (δ^{-}) .³ This intricate arrangement of atoms and hydrogen groups forms the foundation for the distinctive properties and behaviours of these compounds.

The structural differences between DB and both AB and PB are quite pronounced. In DB, two boron atoms are linked through bridge hydrogens, presenting a unique arrangement. By contrast, AB and PB feature a single B-X bond (where X=N or P), which allows rotations around this bond. The energy barriers associated with these rotations are defined as the energy difference between eclipsed and staggered conformers, analogous to the behaviour observed in molecules like ethane.²⁹ Specifically, the calculated rotational energy barriers around the B-X bond for H₃B-NH₃ and H₃B-PH₃ have been reported as 2.48 and 2.62 kcal mol^{-1} (1 kcal mol⁻¹ = 4.186 kJ mol⁻¹) for AB and 2.47 and $2.55 \text{ kcal mol}^{-1}$ for PB, calculated using the MP2/6-31 + +G(d,p) and DFT-based B3LYP/6-31 + +G(d,p) levels of theory respectively.²⁹ For comparison, the rotational energy barrier of ethane (CH₃–CH₃) is $2.875 \text{ kcal mol}^{-1}$.³⁰ As a result, the present study focused solely on eclipsed AB and PB for the C_{3v} point group symmetry. This choice aligns with the low-temperature dynamics study of AB, which also adopted the eclipsed structure.³¹ Importantly, the energy



Diborane (DB), D_{2h} Ammonia borane (AB), C_{3v} Phosphine borane (PB), C_{3v}

Fig. 2. Chemical structures of diborane (DB), ammonia borane (AB) and phosphine borane (PB) and their point group symmetry. In DB, the hydrogens are labelled as bridge hydrogens (H_b) and terminal hydrogens (H_t); in AB and PH, the hydrogens are labelled as protic (N–H and P–H) hydrogens (H_p) and hydridic (B–H) hydrogens (H_b).

barriers observed for AB and PB are approximately half of the earlier estimated 4–6 kcal mol⁻¹ barrier that restricts internal rotation in DB.³² This difference underscores the varying rotational dynamics between these compounds.

Table 1 compares properties among the three compounds DB, AB and PB. Notably, the B-X bond lengths shows different values: 1.762 Å for B–B (or B…B distance) in DB. 1.655 Å for B–N in AB and 1.949 Å for B–P in PB. This trend in bond lengths aligns with expectations, as the van der Waals radii³³ for B, N, and P are 1.92, 1.55 and 1.80 Å respectively. The reported complexation energy (E_c) reveals that the stability of PB is $-21.10 \text{ kcal mol}^{-1}$, comparatively less stable than AB with an E_c of -25.97 kcal mol⁻¹.³³ Examining the structural parameters of H₃BXH₃ in Table 1, it is evident that the HBN angle in AB (104.88°) increases to 117.82° for the HBP angle in PB, whereas the bond lengths of hydridic hydrogens (H_h-B) in the boranes remain quite similar (1.188 Å for H–B in DB, 1.210 Å for H–B in AB and 1.207 Å for H–B in PB). The lengths of protic hydrogen bonds (H_p-N and H_p-P) exhibit significant differences. Specifically, the H_p-N bond length in AB is notably shorter at 1.015 Å, whereas the H_p-P bond length in PB is significantly longer at 1.405 Å compared with their corresponding hydridic bonds (H_h–B). The H–X bond lengths in AB and PB closely resemble the bond lengths of H-N in ammonia (NH₃), at 1.017 Å, and H–P in phosphine (PH₃),

 Table I. Selected electronic properties of diborane, ammonia borane and phosphine borane.

Property H ₂ B ₂ H ₄		H ₃ BNH ₃	H ₃ BPH ₃		
Symmetry	D _{2h}	C _{3v}	C _{3v}		
E_{tot} (E_h)	-53.143253	-83.063511	-369.267118		
E _c (kcal mol ⁻¹)	-	-25.97 ^A	-21.10 ^A		
R_{B-X} (Å)	1.762	1.655 (1.66) ^{10,35}	1.949		
∠HXB (°)	t, 122.24 (121.5) ^B	111.06	7.82 (6.9) ³⁶		
∠HBX (°)	b, 95.85 (95.8)	104.88	103.42 (103.6)38		
R _{H-X} (Å)	1.315 (1.314),b ^B	1.015 (1.020) ^A	1.405 (1.399, ³⁶ 1.404 ^A)		
R _{H-B} (Å)	1.188 (1.184),t ^B	1.210	1.207 (1.212) ³⁶		
μ (D)	0	5.40 (5.64) ^C	4.35 (4.36) ^C		
A (MHz)	80 404 (79 6 I 6) ^D	73 821	57 188		
B (MHz)	8 344 (8 8) ^D	17713	10 476 (10 591) ^E		
C (MHz)	6 848 (6 707) ^D	17713	10 476 (10 591) ^E		

All the data except for those in parentheses are calculated using the method in CCSD(T)/cc-pVTZ level of theory. E_{tot} , total electronic energy of the compound; A, B and C, rotational constants; μ , dipole moment; b, bridge H; t, terminal H in DB. ^AObserved = 79616, 18181, and 16707 MHz (average absolute deviation = 271 MHz).

^BMP2(full)/6-31G(d).³³

^CCalculated using calculated using MP2/6-31++G(d,p).²⁹

^DDiborane, t for H_t–B-H_t and b for H_b–B–H.⁹

^EObserved = 10 591 MHz (deviation = 115 MHz).

at 1.421 Å.³⁴ In DB, the bridge H_b –B bond length (1.315 Å) is significantly longer than the terminal H_t –B bond length (1.188 Å), indicating a distinct bonding nature. This set of structural parameters contributes to the unique characteristics and behaviours of these boron compounds.

The nature of the N-B bond in AB and P-B bond in PB is predominantly polar. The interaction between the electron lone pair of phosphines and boranes leads to increased acidity of the P-H bond, whereas the P-B bond decreases electron density on the phosphorus atom. As a result, PB displays a longer P–B bond length of 1.949 Å and exhibits a weaker adjacent P-H bond in comparison with AB. In PB, the bond length of P–H_b is 1.416 Å, considerably longer than the N–H_h bond length of 1.015 Å. Owing to its high symmetry (D_{2h}) , DB is a non-polar compound with no permanent dipole moment. By contrast, the dipole moment of AB is 5.40 D, surpassing PB's dipole moment of 4.35 D. This divergence in dipole moments can be attributed to the larger dipole moment of the Lewis base NH₃ (1.55 D for NH₃ using MP2/6-311 + G(3df,2p) in comparison with PH_3 (0.58 D).³⁷ Furthermore, the interaction energy within the bond formed by PH₃ must result from the distortion of the PH₃ electron pair due to the positive field of the Lewis acid (BH₃). This intricate interplay of polarities and interactions contributes to the varied characteristics and behaviours observed in these compounds.

NMR chemical shifts of the boranes

Further advances in understanding the structure and reactivity of these borane compounds will not only contribute to tackling challenges in the field of hydrogen storage but also to other domains of boron chemistry.³⁸ NMR spectroscopy is a powerful tool for unravelling molecular structures. The structural information provided by the NMR technique is multifaceted, site-specific, remarkably stable and reliably reproducible over time.³⁹ Our investigation looked into the role of hydrogen atoms within DB, AB and PB through the lens of ¹H NMR chemical shifts. To accomplish this, the NMR absolute isotropic shielding constants (chemical shifts)⁷ for the boranes were calculated. The absolute isotropic shielding constants (σ , ppm)⁷ were calculated using the gauge-independent atomic orbital (GIAO) method^{40–43} in conjunction with the B3PW91 functional. This functional has demonstrated accuracy in predicting NMR shield tensor (chemical shifts) for molecules⁴³ and compounds containing boron.⁴⁴

The chemical shift (δ_A , ppm) of atom A in the boranes is given by:

$$\delta_{\rm A} = \sigma_{\rm A} - \sigma_{\rm A}^{\rm C}$$

where σ_A^{0} is the absolute isotropic shielding constant of same atom A in a reference compound. Usually, the reference standards for σ_H^{0} and σ_C^{0} are the shielding constants of ¹H and ¹³C in tetramethylsilane (TMS) respectively, whereas the reference standard for σ_N^{0} is ¹⁵N in NH₃ and for σ_B^{0} is ¹¹B in BF₃·OEt₂ (boron trifluoride diethyl etherate).⁴³ In the G16 computational chemistry package, $\sigma_H^{0} = 31.8821$ ppm in TMS, $\sigma_B^{0} = 83.6$ ppm in B₂H₆, $\sigma_N^{0} = 258.4$ ppm in NH₃, all calculated using B3LYP/6-311 + G(2d,p) (GIAO).

Table 2 reports the calculated absolute isotropic shielding constants (σ_B) for DB, AB and PB. The marked differences in these σ_B constants arise from the diverse chemical

Table 2. The calculated absolute isotropic shielding constant (σ) of DB, AB and PB.

Molecules	Structure	σ(⁺⁺ B) (δ _B) (ppm)	σ(X) (δ _X) (ppm)	σ(H _b (H _B)) (δ _{H,h}) (ppm)	σ(H _t (H _X)) (δ _{H,p}) (ppm)	Δδ (ppm)
B ₂ H ₆ (DB)	$\begin{array}{c} H_{t} \\ H_{t} \\ H_{t} \end{array} = \begin{array}{c} H_{b} \\ H_{b} \\ H_{b} \end{array} = \begin{array}{c} H_{t} \\ H_{t} \\ H_{t} \end{array}$	85.40 (53.32) ^A	85.4 ^{A,B}	32.32 (-0.44) ^B	27.01 (4.87) ^B	5.31
H₃BNH₃ (AB)	$\begin{array}{ccc} H_p & H_h \\ V & / \\ H_p & H_h \\ H_p & H_h \end{array}$	126.21 (94.13) ^A	231.39 (249.122) ^{ABC}	29.47 (2.41) ^B	29.05 (2.83) ^B	0.42
H ₃ BPH ₃ (PB)	H _p H _h ↓ / H _p IIII→ PBII H _h ↓ H _p ↓ H _p H _h	151.46 (119.38) ^A	454.37 ^{ABD}	30.59 (1.28) ^B	27.60 (4.28) ^B	3.0

The experimental chemical shifts of ¹¹B in BH₃ and H₃BNH₃ are 86 and -16.6 ppm.⁴⁴ Unless results are associated with a reference citation, data are calculated using the method in B3PW91/aug-cc-pVTZ (ppm). No reference – absolute shielding (σ).

^{A11}B chemical shifts relative to the IUPAC standard BF3·OEt₂(δ = 0 ppm) at 20°C (σ_B = 32.08 ppm).⁴⁷

^BChemical shift (δ_{H}) with respect to σ_{H} = 31.8821 ppm of H in TMS.

^CExperimental $\sigma_N^0_N = 264.5$ ppm in NH₃⁴⁸ and calculated $\sigma_N^0 = 261.3$ ppm in NH₃ using B3PW91/6-31G*.⁴³

^DCalculated $\sigma_P^0 = 606.110 \text{ ppm}$ in PH₃ in gas phase using CCSD(T)/aug-pVQZ⁴⁹ and $\sigma_p = 357.6 \text{ ppm}$ for (CH₃)₃PBH₃. δ (free P) is reported to be 246 ppm.⁷

environments of these compounds. Specifically, boron in DB features the smallest shielding constant ($\sigma_{\rm B} = 85.40$ ppm), whereas boron in PB exhibits the largest shielding constant ($\sigma_{\rm B} = 151.46$ ppm). AB falls between DB and PB, with a shielding constant of $\sigma_{\rm B} = 126.21$ ppm. The shielding constants of hydrogens ($\sigma_{\rm H}$) within DB, AB and PB are reported in Fig. 2. A standardised absolute shielding scale for boron is established with reference to the shielding constant in liquid BF₃·OEt₂, which is 110.9 ppm for ¹¹B.⁴⁵ In the present study, utilising the absolute isotropic shielding constant (σ) directly rather than the chemical shift (δ) serves to minimise discrepancies stemming from different methods. For example, $\sigma_{\rm B}^{0} = 83.6$ ppm of B₂H₆ is calculated using the B3LYP/ 6-311 + G(2d,p) (GIAO) and 85.40 ppm using B3PW91/augcc-pVTZ. It is important to acknowledge that, although the accuracy of an atom's absolute isotropic shielding constant in a specific chemical environment hinges on the chosen level of theory,⁴³ employing the same level of theory across a series of compounds can help mitigate certain systematic errors. NMR techniques have been leveraged to investigate B-N and B-P coupling for AB⁴⁶ and PB.⁷

The calculated chemical shifts $\delta(^{11}B)$ of AB and PB are referenced against $\delta(^{11}B)$ of DB, which is 85.40 ppm. Experimentally, $\delta(^{11}B)$ for AB is observed at -21.6 ppm relative to the IUPAC standard BF₃·OEt₂ ($\delta = 0$ ppm) at 20°C. Calculated δ ⁽¹¹B) values for AB show some variability depending on the methods employed, yielding values of -24.7, -23.7 and -27.1 ppm with respect to the IUPAC standard BF₃·OEt₂.⁵⁰ As reported in Table 2, the distinct chemical environments of boron in DB, AB and PB are clearly apparent, as evidenced by their NMR chemical shifts of $\delta(^{11}B)$. The shifts in $\delta(^{11}B)$ across the boranes are quite significant. Specifically, $\delta(^{11}B)$ for AB and PB shifts by 40.80 and 66.06 ppm respectively, relative to δ ⁽¹¹B) of DB. The trend is $\delta(^{11}B)$ (PB) > $\delta(^{11}B)$ (AB) > $\delta(^{11}B)$ (DB). This order reveals the principle that the stronger the chemical environment of boron, the larger its chemical shift.

The hydrogens within the Lewis acid BH₃ and Lewis base XH₃ (X=N and P) of AB and PB exhibit notable differences from the hydrogens in DB. In the staggered configurations, the chemical shifts of the three-fold degenerate protic hydrogens (H_p –X) are 2.83 ppm in AB and 4.28 ppm in PB. Conversely, the chemical shift of three-fold degenerate hydridic hydrogens (H_b-B) in the BH₃ fragment follows the reverse order: 2.47 ppm in AB and 1.28 ppm in PB. Moving to DB, the chemical shifts of the bridge hydrogens (H_{bs}) and terminal hydrogens (H_{ts}) are -0.44 and 4.87 ppm respectively. As a result, the two distinct groups of hydrogens in DB, AB and PB exhibit chemical shifts of 5.31, 0.42 and 3.0 ppm respectively. The most substantial difference is observed in the H_bs and H_ts of DB, followed by the H_bs and H_ps of PB. By contrast, the differences between the H_bs and H_ps of AB are the smallest. However, both AB and PB show the same trend: protic hydrogens have a stronger chemical environment than hydridic hydrogens. Importantly, the calculated chemical shifts align with findings from other NMR studies of AB in diverse mediums, including solutions.⁴⁶ This consensus indicates the robustness and validity of the trends obtained in chemical shifts, which reflect the distinct chemical environments and bonding characteristics within these borane compounds.

Fig. 3 compares the NMR hydrogen shielding constants ($\sigma_{\rm H}$) of the boranes. The boranes studied here feature two distinct groups of hydrogen atoms, each with markedly different roles and bonding characteristics. The hydrogen chemical shifts ($\delta_{\rm H}$) of the boranes are relatively modest when compared with the reference methyl hydrogens (–CH₃). The $\sigma_{\rm H}$ value for TMS is 31.88 ppm, indicating that $\sigma_{\rm H}$ (TMS). The borane compounds host two distinct types of hydrogen atoms, H_b and H_t in DB, and H_p and H_h in AB and PB. As shown in Fig. 3, the difference between hydrogen groups is most pronounced ($\delta_{\rm H} = 5.31$ ppm) in DB, whereas the difference is least marked ($\delta_{\rm H} = 0.42$ ppm) in AB. In PB,



Fig. 3. Comparison of the NMR absolute isotropic hydrogen and boron shielding constants σ for DB, AB and PB calculated using B3PW91/aug-cc-pVTZ (ppm). The hydrogen chemical shifts of the boranes are in blue for hydridic hydrogens (H_hs), red for protic hydrogens (H_ps) and green for hydrogens in DB.

the hydrogen shielding constant difference is substantial, with a large splitting of 3.0 ppm.

A notable point is the nuanced role of the hydrogens in DB. It can be argued that DB may be more appropriately represented as $H_2B_2H_4$, rather than B_2H_6 , as the six hydrogens in DB do not all play identical roles. Specifically, the bridge H_bs in DB, formed through three-centre-two-electron bonds, exhibit stronger chemical characteristics compared with the terminal H_ts in DB.⁹ For both AB and PB, the hydridic hydrogens (H_hs) (represented in blue in Fig. 3) within the hydrogens in the H–B bonds demonstrate larger shielding constants than their protic hydrogen (H_ps) counterparts (in red) within the same compound.

Ionisation potentials of the boranes

To further understand the borane compounds, we calculated their IPs.²³ It is important to note that the IP of a compound includes both the valence IP and core IP, which are measured using photoelectron spectroscopy (PES) and XPS respectively. The complete valence IP of DB is readily available,⁹ whereas the availability of data on the experimental valence IPs for AB and PB are quite limited. The first (valence) IP of AB was measured as 10.58 eV for the VIP and 9.44 eV for the adiabatic ionisation potential (AIP) using mass spectrometry.⁵¹ The AIP value agrees with 9.26 ± 0.03 eV determined by a recent photo-electron–photoion coincidence (PEPICO) spectroscopic measurement.²³ The measured IP value of a compound depends on experimental conditions, spectroscopic techniques, resolution and the spectral analyses, and the measurement process.⁵²

Accurate theoretical calculations are essential for molecular spectroscopy, guiding the interpretation of experimental results and enabling more accurate determination of key properties.^{52,53} Table 3 compares the calculated valence IPs for the three borane compounds. The agreement between calculated valence IPs and measurements⁹ for DB suggests that the Δ PBE0(SAOP)/et-pVQZ method in the present study is accurate. Therefore, the same method was used to

calculated the valence IPs for both AB²² and PB. The complete valence IPs of AB were confirmed by recent gas-phase measurements at the Elettra synchrotron in Italy (please see 'In proof' section at the end of this article). This recent measurement of AB increases our confidence in the calculated valence IPs of PB, although no available IPs for PB exist.

The IPs of DB diverge significantly from those of AB and PB complexes, which can be attributed to DB's distinct D_{2h} point group symmetry and different structural characteristics. AB and PB share the C_{3v} point group symmetry in the form of Lewis acid–Lewis base complexes. This commonality allows AB and PB to share the same character table and irreducible representations with orbitals of a_1 and e_1 symmetries. However, the ground state configurations of AB and PB diverge owing to the variations in the valence electronic structures stemming from the nitrogen and phosphorus atoms within the complexes.

Fig. 4 compares the simulated valence IP spectra of AB and PB in the energy region of 5-35 eV. Four major IP bands in PB (top) but five major bands in AB (bottom) appear in the spectra. Although some similarities exist between the spectra of PB and AB, there are notable differences. The lowest five valence IPs of AB span a wider energy range $(\sim 11-30 \text{ eV})$ compared with PB $(\sim 11-22 \text{ eV})$. The valence IPs and their assignment exhibit an interesting pattern for the a_1 orbitals and the doubly degenerate e_1 orbitals in both AB and PB. There is a small energy gap (Δ IP 0.22 eV) in PB between the outer valence highest occupied molecular orbital (HOMO), 3e₁, a doubly degenerate orbital and the next HOMO, HOMO-1, 7a₁. As a result, the first IP band at approximately 11 eV, which consists of three closely lying states, leads to a single band so that there are four distinct IP bands in the outer valence IP spectrum of PB. However, the IP energy gap between HOMO and HOMO-1 of AB is larger, measuring 2.01 eV, which is likely sufficient for spectrometer resolution, resulting in five IP bands in the spectrum of AB. The IPs of AB agree with a previous calculation using the B3LYP/6-31 + + G(d,p)//MP/6-31 + + G(d,p) method,²⁹ which however, does not include orbital 3a1 at 29.88 eV.

l able 3.	Valence vertical	ionisation	potentials	(VIPs)	of DB,	AB and	PB (eV)	•

Molecule	Valence configuration	First	Second	Third	Fourth	Fifth	Sixth
$B_2H_6 D_{2h}$	$(2a_g)^2(2b_{3u})^2(1b_{1u})^2(1b_{2u})^2(3a_g)^2$ (1b _{1g}) ²	lb _{1g} 11.80 (11.89) ^A	3a _g 13.01 (13.30) ^A	lb _{2u} 13.49 (13.91) ^A	lb _{1u} 14.69 (14.75) ^A	2b _{3u} 15.52 (16.11) ^A	2a _g 21.56 (22.33) ^B
$H_3BNH_3 C_{3v}$	$(3a_1)^2 (\underline{1e_1})^4 (\underline{4a_1})^2 (5a_1)^2 (2e_1)^4$	2e _{1:} 10.57 [⊂] (10.58) ^{D,E}	5a ₁ : 12.58 ^C	4a ₁ : 16.95 ^C	le ₁ : 18.56 ^C	3a ₁ : 29.88 ^C	
H ₃ BPH ₃ _{C3v}	$(5a_1)^2 (\underline{6a_1})^2 (\underline{2e_1})^4 (7a_1)^2 (\mathbf{3e_1})^4$	3e _{1:} 11.06	7a ₁ : 11.28	2e ₁ : 14.96	6a ₁ : 16.54	5a ₁ : 22.33	

The HOMO is highlighted in bold. The symmetries of orbitals underlined are swapped positions in AB and PB.

^AExperimental (Hel photoelectron spectra).⁵⁴

^BCalculated using green function (GF).⁵⁵

^CCalculated using Δ PBE0(SAOP)/et-pVQZ.²²

^DExperimental mass spectrometry vertical ionisation energy (VIE) for 10.58 eV and adiabatic ionisation energy (AIE) for 9.44 eV.⁵¹ Theory to method CCSD(T)/CBS, 9.29 eV,²¹ 896.4 kJ mol⁻¹ (9.29 eV)³⁵ and 997.7 kJ mol⁻¹ (10.61 eV).⁵⁶

^EPEPICO spectroscopy²³ (synchrotron light) determined the AIE of AB as 9.26 ± 0.03 eV.



Fig. 4. Calculated valence ionisation spectra of AB (bottom) and PB (top). The ionisation energies (degeneracy is considered) in Table 3 are convoluted using a Gaussian broadening function with full width at half maximum (FWHM) at 0.05 eV. The related valence states (orbitals) are also indicated in the spectra. Purple spectrum (top) is for PB and blue spectrum (bottom) is for AB.

Fig. 5. Comparison of the CEBE of B Is of DB, AB and PB. The order of CEBE is B Is (PB) < B Is (AB) < B Is (DB).

Further information using energy decomposition analysis (EDA) reveals that in AB,²⁹ the charge transfer (CT) is largely governed by the π (HOMO) orbital with an N \rightarrow B CT profile. Mallajosyula *et al.*²⁹ suggested that in PB, the dominant contribution is from the $\sigma(6a_1)$ orbital with a marginal contribution from the HOMO (3e₁). However, the present study reveals that the outer valence orbitals, such as $\pi(3e_1, 2e_1)$ and $\sigma(7a_1)$, do not exhibit distinct CT character, whereas the $\sigma(6a_1)$ orbital displays a B \leftarrow P CT character, and the $\sigma(5a_1)$ orbital exhibits a B \rightarrow P CT character. As a result, the IP spectra of AB and PB exhibit similarities in their $\sigma(a_1)$ states with CT characteristics, but their $\pi(e_1)$ orbitals are notably different. The $\pi(e_1)$ orbitals of AB displays CT character, whereas the $\pi(e_1)$ orbitals of PB exhibit a more covalent character.

Core electron binding energies provide valuable information about the chemical environments of atoms within compounds.⁵⁷ The comparison of calculated CEBE for boron (B 1s) in the different borane compounds – DB, AB, and PB – can reveal important insights into their local electronic structures. As shown in Fig. 5, B 1s CEBE values for DB, AB and PB are 196.53, 194.01 and 193.93 eV respectively. The B 1s CEBE values for DB and AB agree well with available experimental values of 196.5 eV for DB⁵⁸ and 193.73(4) eV for AB,⁵⁹ whereas no experimental B 1s CEBE for PB is available. The trend of B 1s CEBE values among the compounds is as follows: B 1s (PB) < B 1s (AB) < B 1s (DB). This implies that the core electrons of boron in PB require less energy to be ionised (oxidised) compared with those in AB, whereas the core electrons of boron in DB require more energy to be ionised. Lower CEBE values indicate a more chemically reactive environment, which corresponds to a more active chemical environment. This trend aligns with the larger ¹¹B NMR chemical shifts reported in Fig. 3. It is important to note that whereas XPS and NMR techniques have different mechanisms, they both provide valuable information about the chemical and electronic properties of a compound, local to a specific atom.

Conclusion

The present study elucidates the electronic structures of two sets of hydrogens in diborane ($H_2B_2H_4$), ammonia borane (H_3B – NH_3) and phosphine borane (H_3B – PH_3). The electronic structure and bonding nature of DB markedly differ from the donor–acceptor borane complexes of AB and PB. Although all three boranes process two distinct hydrogen groups, the bridge hydrogens (H_bs) and terminal hydrogens (H_ts) in diborane exhibit a significant chemical shift difference of up to 5.31 ppm in the ¹H NMR spectra. AB and PB share a common bonding pattern involving protic hydrogens (H–N and H–P) (H_ps) and hydridic hydrogens (H–B) (H_bs), linked by the $B \leftarrow X$ (X=N and P) bond. However, the chemical shift difference between H_ps and H_bs in AB is small at $\Delta \delta_{\rm H} = 0.42$ ppm, and it increases to 3.0 ppm for PB. The NMR chemical environment of ¹¹B was calculated as 85.40 ppm in diborane, 126.21 ppm in AB, and 151.46 ppm in PB, consistent with the calculated B 1s CEBE of 196.53, 194.01 and 193.93 eV for DB, AB and PB respectively. Both ¹¹B NMR and B 1s XPS spectroscopy clearly reveal that the chemical environments of boron in AB and PB are more similar compared with that in DB. It is always worth considering novel approaches and combining existing techniques to obtain a more profound understanding of systems under investigation, despite the significantly different mechanisms of NMR and XPS. Exploring the interplay between NMR and XPS could represent an interesting and potentially valuable research avenue for investigating novel compounds, including those relevant to energy storage materials. Finally, the outer valence orbitals of AB and PB reflect their differing bonding characteristics, with AB exhibiting slightly greater susceptibility to oxidation due to its slightly lower first ionisation potential (10.57 eV) compared with PB (11.07 eV).

Confirmation

We are pleased to announce the successful completion of gas-phase synchrotron-sourced photoemission and X-ray absorption measurements for ammonia borane at Elettra Sincrotrone Trieste in Italy. The outcomes of these experiments show exceptional agreement with our valence IP and CEBE calculations. Specifically, we precisely determined the complete valence IP spectrum, which encompasses the calculated band at 29.99 eV ($3a_1$). The calculated B 1s energy, at 194.01 eV, has been confirmed. We are currently in the final stages of manuscript preparation, describing these compelling findings resulting from a decade collaboration between theoretical and experimental approaches.

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