ACCOUNTS
of chemical research

The Roles of Dihydrogen Bonds in Amine Borane Chemistry

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RECEIVED ON APRIL 5, 2013

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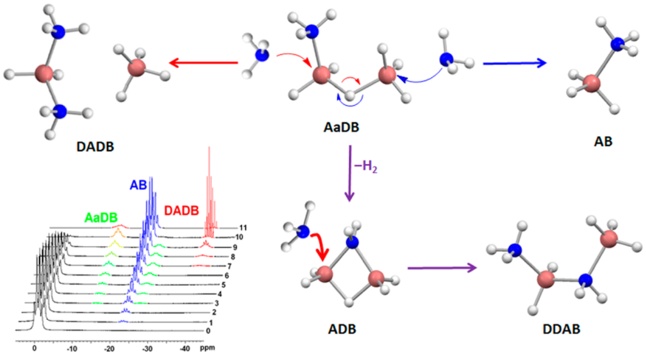

A dihydrogen bond (DHB) is an electrostatic interaction between a protonic hydrogen and a hydridic hydrogen. Over the past two decades, researchers have made significant progress in the identification and characterization of DHBs and their properties. In comparison with conventional hydrogen bonds (HBs), which have been widely used in catalysis, molecular recognition, crystal engineering, and supramolecular synthesis, chemists have only applied DHBs in very limited ways. Considering that DHBs and conventional HBs have comparable strength, DHBs could be more widely applied in chemistry.

Over the past several years, we have explored the impact of DHBs on amine borane chemistry and the syntheses and characterization of amine boranes and ammoniated metal borohydrides for hydrogen storage. Through systematic computational and experimental investigations, we found that DHBs play a dominant role in dictating the reaction pathways (and thus different products) of amine boranes where oppositely charged hydrogens coexist for DHB formation. Through careful experiments, we observed, for the first time, a long-postulated reaction intermediate, ammonia diborane (AaDB), whose behavior is essential to mechanistic understanding of the formation of the diammoniate of diborane (DADB) in the reaction of ammonia (NH_3) with tetrahydrofuran borane ($THF\cdot BH_3$).

The formation of DADB has puzzled the boron chemistry community for decades. Mechanistic insight enabled us to develop facile syntheses of aminodiborane (ADB), ammonia borane (AB), DADB, and an inorganic butane analog $NH_3BH_2NH_2BH_3$ (DDAB). Our examples, together with those in the literature, reinforce the fact that DHB formation and subsequent molecular hydrogen elimination are a viable approach for creating new covalent bonds and synthesizing new materials. We also review the strong effects of DHBs on the stability of conformers and the hydrogen desorption temperatures of boron−nitrogen compounds. We hope that this Account will encourage further applications of DHBs in molecular recognition, host−guest chemistry, crystal engineering, supramolecular chemistry, molecular self-assembly, chemical kinetics, and the syntheses of new advanced materials.

1. Introduction

The dihydrogen bond (DHB) is gaining recognition as an important unconventional hydrogen bond (HB). It is characterized as the interaction between a protonic hydrogen of a conventional HB donor HX (X = F, O, and N) and a hydridic hydrogen, a σ bonding pair of electrons that serves as an alternative to a conventional HB acceptor, a basic lone pair of electrons of an electronegative atom.[1] Conventional HBs, important examples of noncovalent bonding, have broad impact on the physical properties of substances and are often a factor in the design of catalysts, molecular recognition, crystal engineering, and supramolecular synthesis.[2]

Brown recognized interaction between oppositely charged hydrogens in solution IR spectra in the late 1960s,[3] but

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significant progress in the study of dihydrogen bonding was only achieved in the past two decades.[4] Neutron and X-ray single crystal diffraction are the most reliable techniques among a variety of methods used to identify and characterize DHBs, providing the distance between two hydrogen atoms and the geometry of the X–H···H–Y moiety. Neutron diffraction is the preferred method. A DHB is considered to be present when the $H^+\cdots H^-$ distance is less than 2.4 Å.[4] DHBs exhibit a nearly linear X–H···H fragment and a bent H···H–Y arm. NMR chemical shifts of protonic and hydridic hydrogens and IR absorption bands of N–H and B–H stretching vibrations have also been used as evidence for the presence of DHBs.[4] DHB and HB strengths are comparable, ranging from 5 to 30 kJ/mol.[4] Most DHBs arise from electrostatic interaction between oppositely charged hydrogen atoms with a small covalent contribution, but theoretical and experimental studies have also identified homopolar DHBs involving hydride–hydride or proton–proton interactions,[5] which are capable of stabilizing solids and promoting elimination of molecular hydrogen.

Although DHBs and their fundamental properties have been extensively studied, examples of DHBs as mediators in synthetic chemistry are relatively rare. Except for initial explorations in supramolecular and crystal engineering,[6] most efforts have been concerned with the potential catalytic role of metal hydrides.[1,4] The comparable strengths of DHBs and HBs and the wide impact of conventional HBs suggest an expanding role for DHBs in structure, catalysis, and reaction mechanism.

In this Account, we focus on the impact of DHBs on chemistry of amine boranes, a research program we have followed over the past several years, whose accomplishments include development of large scale syntheses of ammonia borane (NH_3BH_3, AB),[7] aminodiborane ($NH_2B_2H_5$, ADB),[8] and the diammoniate of diborane ($[H_2B(NH_3)_2][BH_4]$, DADB)[9] and characterization of DHB influence on the relative rates of formation of AB and DADB in the reaction of ammonia (NH_3) and $THF\cdot BH_3$.[10] Not only do DHBs influence system stability, structure, reaction mechanism, and catalysis, but in reactions not available to hydrogen bonding systems, $H^{\delta+}\cdots H^{\delta-}$ interactions promote proton/hydride exchange and elimination of molecular hydrogen (Figure 1).

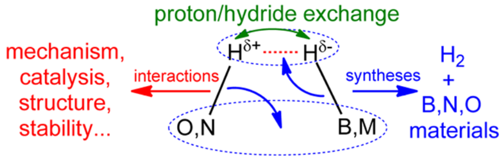


FIGURE 1. Influences of dihydrogen bonds on borane chemistry (M refers to metallic elements).

2. The Influence of DHB Interactions on Reaction Pathways

2.1. The Story of the Diammoniate of Diborane (DADB).

Amine borane chemistry spans nearly a century,[11] beginning with a report by Stock in 1923.[12a]

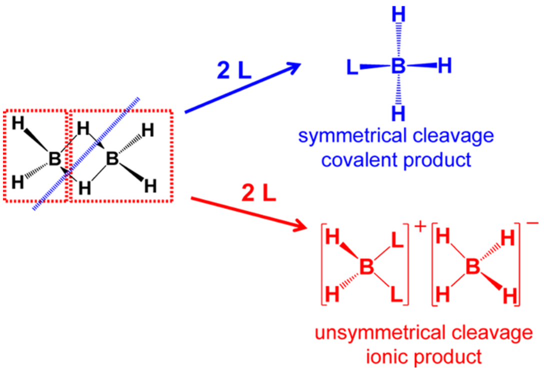


FIGURE 2. The two cleavage patterns of diborane.

> *When B_2H_6 is treated with excess ammonia at room temperature, precisely two molecules of ammonia combine with it [one molecule of B_2H_6] to form the colorless, nonvolatile, salt-like compound $B_2H_6\cdot 2NH_3$.*[12b]

The precise quantitative result justified Stock's nomenclature, the diammoniate of diborane,[13] but the structural formula of DADB remained an open question until the correct structure, $[H_2B(NH_3)_2][BH_4]$, was reported in a classic series of papers by Parry and co-workers in 1958.[14] DADB's ion pair structure, a boronium cation and a borohydride anion, has been confirmed by ^{11}B NMR[15] and by Autrey and co-workers in 2010 using X-ray diffraction (XRD).[16] Among the proposed structures for DADB, $[NH_4]_2[B_2H_4]$ in 1933,[12b] $[NH_4][BH_3NH_2BH_3]$ in 1938,[17] and $[(NH_4)(BH_2NH_2)(BH_4)]$ in 1956,[18] $[NH_4][BH_3NH_2BH_3]$ was the inspiration for a 2010 synthesis of a compound containing the $[BH_3NH_2BH_3]^-$ anion by the reaction of $NaNH_2$ with AB.[19] While of interest, this compound is not the one obtained from the reaction of B_2H_6 with NH_3.

Knowledge of the correct structure of DADB increased interest in accounting for its formation. In contrast to the formation of ionic DADB when NH_3 reacts with B_2H_6 (reaction 1),[20] the reaction of trimethylamine (Me_3N) with B_2H_6 produces covalent trimethylamine borane, Me_3NBH_3 (reaction 2).[21] A similar covalent adduct forms in the addition of carbon monoxide to B_2H_6 (reaction 3).[21] Formation of covalent and ionic products seems linked to an apparent cleavage reaction of B_2H_6 (Figure 2), induced by either

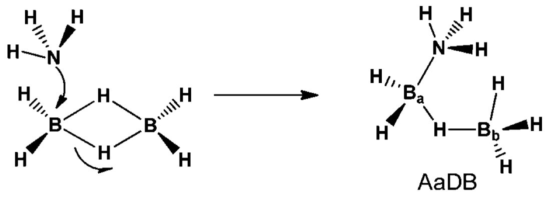


FIGURE 3. Reaction of NH_3 and B_2H_6.

symmetrical (blue) or unsymmetrical (red) addition of base, with symmetrical and unsymmetrical (nonsymmetrical) cleavage products described in the literature.[14b]

$$B_2H_6 + 2NH_3 \rightarrow [H_2B(NH_3)_2][BH_4] \qquad (1)$$

$$B_2H_6 + 2Me_3N \rightarrow 2Me_3N \cdot BH_3 \qquad (2)$$

$$B_2H_6 + 2CO \rightarrow 2CO \cdot BH_3 \qquad (3)$$

It was proposed that as B_2H_6 added a Lewis base, represented in Figure 3 by NH_3 as an example of Lewis bases such as Me_3N, Me_2NH, $MeNH_2$, or CO, an intermediate, ammonia diborane ($NH_3BH_2(\mu\text{-H})BH_3$, AaDB), formed as a bridge hydrogen bond was broken. The equivalent boron atoms in diborane are nonequivalent B_a and B_b in AaDB. Addition of NH_3 to AaDB yields two products: addition at B_a produces ionic DADB while addition at B_b produces covalent AB.[14c]

Recently we have confirmed the existence of AaDB,[10] more than 50 years after it was initially proposed[14c] and can now also account for the selectivity of Lewis base addition to AaDB. Historically, accounting for this selectivity drew on inductive effects, inherent donor character of the ligand, steric effects, and solvent polarity, with steric effects and solvent polarity receiving the greatest attention.[11a,22,23] Sterically demanding Me_3N clearly adds to less hindered B_b of AaDB while the smaller base, NH_3, adds to more hindered B_a. Between these two limiting cases, NH_3 addition yielding ionic DADB and Me_3N addition yielding covalent Me_3NBH_3 (reactions 1 and 2), mixtures of covalent and ionic products were obtained in the reactions of $MeNH_2$ or Me_2NH, and the proportion of the covalent product increased with increased methyl substitution (increased steric requirements).[22b] However, since amine dielectric constants decrease with increasing methyl substitution, it was argued that the high dielectric constant of NH_3 promotes formation of the ionic product, and the low dielectric constant of Me_3N promotes formation of the covalent product.[22a]

Steric and solvent polarity arguments yield a consistent explanation[22,23] that fails when a wider range of Lewis bases are examined. For example, covalent products (base addition at B_b of AaDB) are obtained when B_2H_6 reacts with CO,[21] $(CH_3)_2S$,[24] THF,[25] or $C_6H_5N(CH_3)_2$.[25] Unhindered CO and NH_3 yield different products. While THF, $(CH_3)_2S$, and Me_2NH have similar steric requirements and the dielectric constants of $(CH_3)_2S$ and Me_2NH are similar, they form very different products. The apparent complexity of selectivity was acknowledged in the literature with comments such as "It is not yet possible to predict the course of such reactions with certainty",[23a] "The factors governing the course of these reactions are not fully understood",[23b] and "However, more subtle factors are probably involved also."[22b] The limited confidence in the steric/solvent polarity explanation was further undermined by the thermodynamic stability of $[H_2B(\text{base})_2]^+$ cations in which "base" is a bulky base such as a tertiary amine, phosphine, arsine, or dialkyl sulfide.[26]

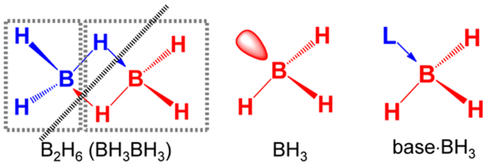


FIGURE 4. Bonding analysis of B_2H_6 and $L \cdot BH_3$.

2.2. Comparison of Reactions of a Lewis Base with Diborane and Also with a Borane Adduct. Reactions of B_2H_6 with Lewis bases reported in the early literature were performed under difficult circumstances. Diborane is a flammable gas, many of the bases are corrosive gases, and the reactions required cryogenic conditions and high vacuum techniques. Such extreme reaction conditions make it difficult to study the reaction extensively to obtain detailed mechanistic information. To explore the mechanism of DADB formation, we have used $THF \cdot BH_3$ as a proxy for more reactive B_2H_6, which can be considered a homogeneous Lewis acid base adduct (Figure 4) compared with $THF \cdot BH_3$, a heterogeneous adduct. We found that reactions of a Lewis base with either B_2H_6 or $L \cdot BH_3$ yield the same types of products when the base is stronger than THF (Table 1).[7]

2.3. Mechanism for the Formation of DADB. Mild conditions for NH_3 adding to $THF \cdot BH_3$ made it possible to use ^{11}B NMR to monitor reaction progress, the results of which we interpreted in terms of the mechanism shown in Figure 5. All signals of AB (steps 1 and 3II), DADB (step 3I), and intermediate AaDB (step 2) were observed over time in the ^{11}B NMR (Figure 6). Initially NH_3 displaces THF from $THF \cdot BH_3$ to produce AB. Intermediate AaDB forms as AB reacts with $THF \cdot BH_3$, displacing THF. That AaDB is an intermediate common to the reactions of both B_2H_6 (Figure 3) and $THF \cdot BH_3$ (Figure 5) accounts for the similarity of products described in Table 1. In reactions of either B_2H_6 or $THF \cdot BH_3$, base adds to internal boron (B_a) of AaDB to yield the ionic

TABLE 1. Comparison of the Products between Reactions of a Lewis Base with B_2H_6 and also with $THF \cdot BH_3$

$L + B_2H_6$	products	refs	$L + THF \cdot BH_3$	products[b]
$THF + B_2H_6$	$THF \cdot BH_3$	25		
$(CH_3)_2S + B_2H_6$	$(CH_3)_2SBH_3$	24	$(CH_3)_2S + THF \cdot BH_3$	$(CH_3)_2SBH_3$
$C_6H_5(CH_3)_2N + B_2H_6$	$C_6H_5(CH_3)_2NBH_3$	25	$C_6H_5(CH_3)_2N + THF \cdot BH_3$	$C_6H_5(CH_3)_2NBH_3$
$NH_3 + B_2H_6$	$NH_3BH_3 + [H_2B(NH_3)_2][BH_4]$[a]	20	$NH_3 + THF \cdot BH_3$	$NH_3BH_3 + [H_2B(NH_3)_2][BH_4]$
$MeNH_2 + B_2H_6$	$MeNH_2BH_3 + [H_2B(MeNH_2)_2][BH_4]$	22b	$MeNH_2 + THF \cdot BH_3$	$MeNH_2BH_3 + [H_2B(MeNH_2)_2][BH_4]$
$Me_2NH + B_2H_6$	$Me_2NHBH_3 + [H_2B(Me_2NH)_2][BH_4]$	22b	$Me_2NH + THF \cdot BH_3$	$Me_2NHBH_3 + [H_2B(Me_2NH)_2][BH_4]$
$Me_3N + B_2H_6$	Me_3NBH_3	21	$Me_3N + THF \cdot BH_3$	Me_3NBH_3

[a] The formation of trace amount of DADB in this reaction is confirmed by ^{11}B NMR spectra of liquid solution after reaction. [b] Results obtained from our lab.

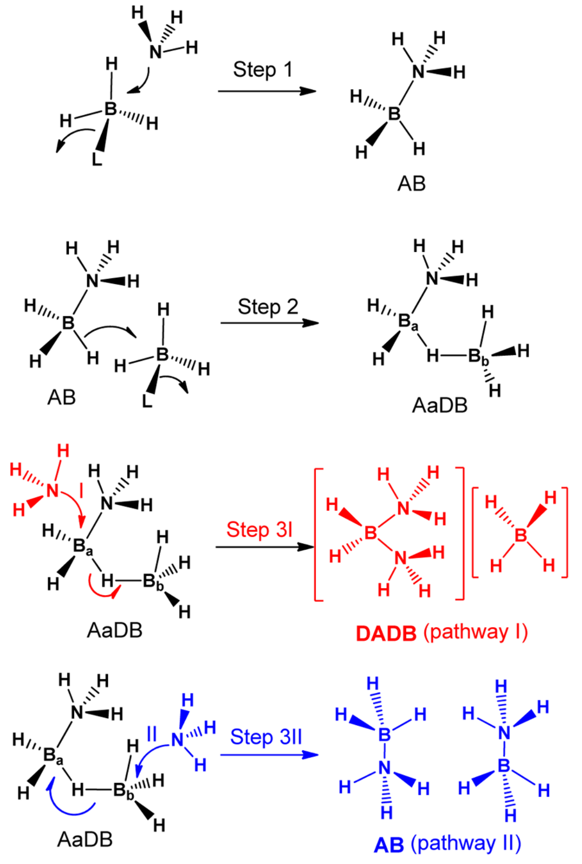


FIGURE 5. Mechanism of NH_3 reacting with $THF \cdot BH_3$.

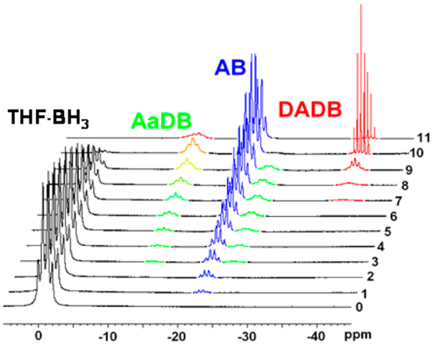


FIGURE 6. ^{11}B NMR evidence for AaDB (green) in a THF solution of AB and $THF \cdot BH_3$.

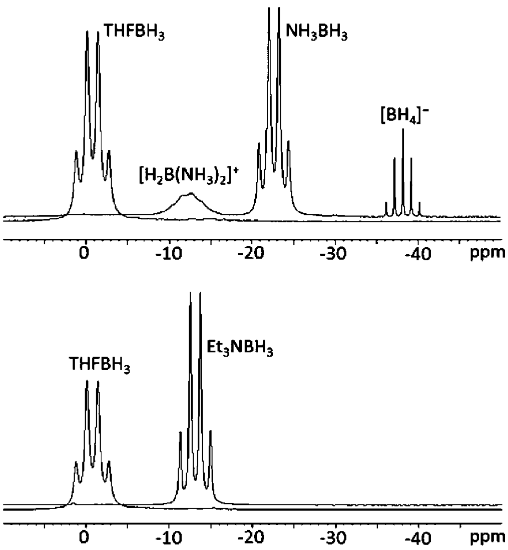


FIGURE 7. Comparison of ^{11}B NMR spectra of reactions of $THF \cdot BH_3$ with NH_3 (top) or Et_3N (bottom).

product (pathway I) or to terminal boron (B_b) to yield the covalent product (pathway II).[10] Triplet and quartet signals corresponding to BH_2 and BH_3 in $NH_3BH_2(\mu\text{-}H)BH_3$ were the first evidence for the existence of AaDB (Figure 6).[27,28] When a large excess of NH_3 was reacted with $THF \cdot BH_3$, only AB was detected in both solution and solid because the reaction stops at step 1 in this case since $THF \cdot BH_3$ is unavailable to produce AaDB in step 2.

To confirm that DHBs rather than a solvent effect control reaction selectivity, a control experiment was performed in which the solvent effect of THF was constant as equimolar bases were added to a THF solution of $THF \cdot BH_3$ in a manner that the bases did not influence solution polarity. The NH_3 reaction produced a mixture (Figure 7, top), but only pure triethylamine borane (Et_3NBH_3) was produced with triethylamine (Figure 7, bottom). An ionic product formed only when dihydrogen bonds could form between protonic hydrogens of NH_3 and hydridic hydrogens of BH_3.

Both AaDB and formed AB are factors in the formation of DADB, their roles now confirmed by our experiments and further clarified by theoretical analysis. Computational

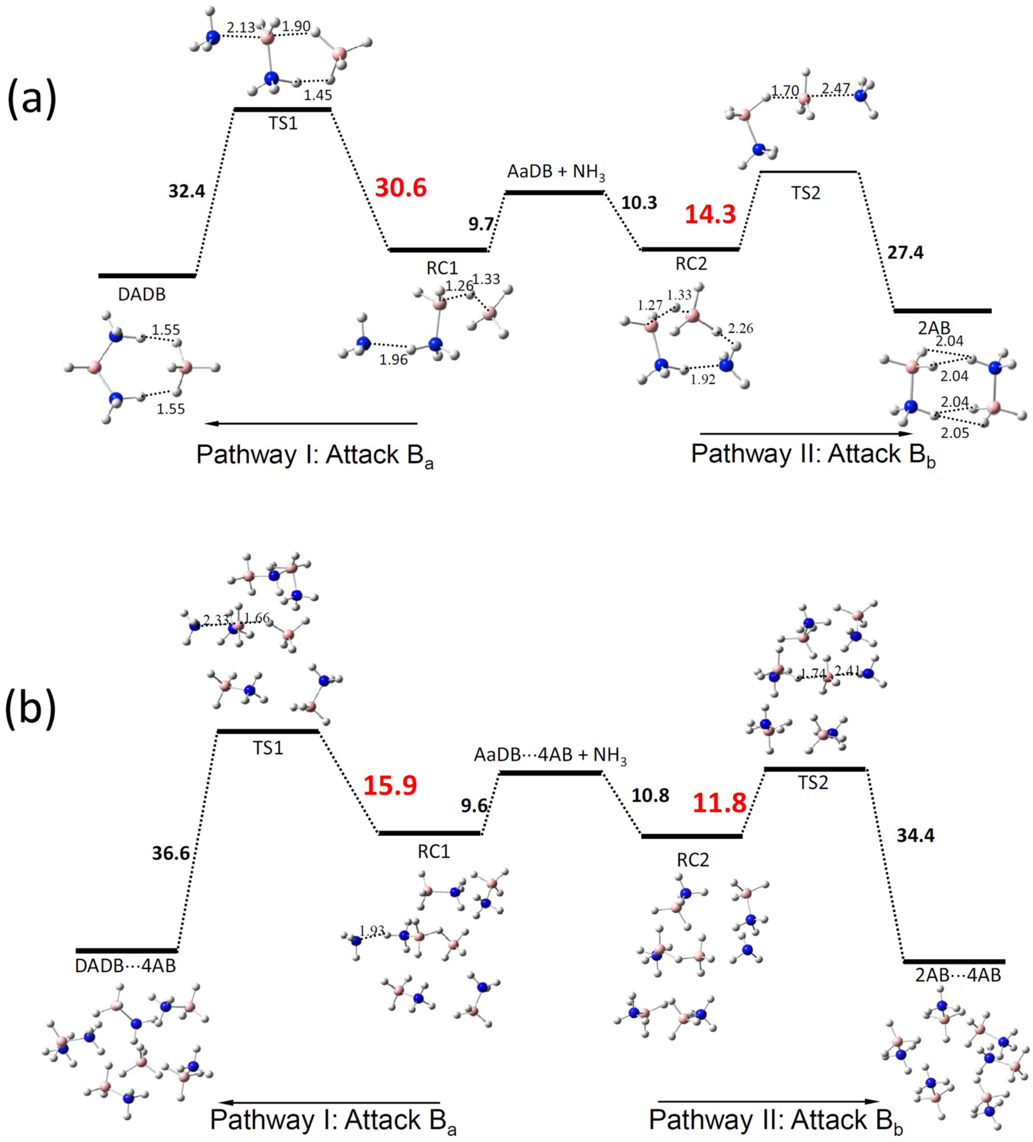


FIGURE 8. Energy profile for both reaction pathways (in kcal/mol) and optimized reaction complexes (RC), transition states (TS), and products for both reaction pathways of NH_3 attacking the AaDB intermediate without AB molecular interaction (a) and with four AB molecular interactions (b) (H white, N blue, B pink). Bond lengths are shown in Å. Reprinted with permission from ref 10. Copyright 2011 American Chemical Society.

results predict significantly lower activation energy for formation of covalent compared with ionic product (Figure 8). Pathway II (Figure 8a) is favored by 16.3 kcal/mol. However, upon introduction of DHBs into the model system, interactions between formed AB and transition states, TS1 and TS2, dramatically decreased the predicted activation energy of pathway I with little change in the activation energy of pathway II. When the DHB interactions with four AB molecules are considered, the difference in activation energies between competitive pathways decreases to only 4.1 kcal/mol (Figure 8b), a result more consistent with experiment.[10] A mixture of covalent and ionic products can be expected when DHBs are present to promote formation of the ionic product.

Theoretical analysis only considered DHB interaction of transition states with formed AB[10] although DHBs can form between the transition state and any species in the system, such as NH_3 and formed DADB. All DHB interactions will influence the relative activation energies of pathways I and II. A mixture of covalent and ionic products in the reaction of NH_3 with $THF \cdot BH_3$ occurs because DHBs dramatically reduce the activation energy of pathway I and the reaction to produce DADB becomes competitive with formation of AB. Steric and dielectric constant factors are important but not dominant.

The formation of DADB is not the only example of which DHB interactions influence reaction mechanism. Another such example is the reduction of ketone by sodium borohydride.[29] The DHB interactions between the hydroxyl group and BH_4^- lead the hydride to attack the carbonyl group from one side such that the *cis* isomer is the major product.

In the case of DADB formation, formed AB acts as a "catalyst" through DHB interactions with the transition states to reduce the activation energy of pathway I, leading to a change in the reaction product. In the ketone reduction case, BH_4^- anion was located on one side through DHB interactions to favor the *cis* isomer.

2.4. Large-Scale Synthesis of Ammonia Borane. AB is the most studied compound for hydrogen storage,[7] however, as discussed above, its synthesis is an important exception to the pattern that Lewis base borane adducts are prepared in displacement reactions.[30] Our mechanism (Figure 5) predicts that pure AB can be produced if formation of the intermediate AaDB can be minimized. Two strategies are successfully employed: (1) THF in $THF \cdot BH_3$ is replaced with a stronger Lewis base to slow substitution that leads to AaDB (step 2) and (2) formed AB precipitates when a suitable nonpolar reaction solvent is used. AB is unavailable for reaction in step 2. Applying these strategies by bubbling NH_3 into a toluene solution of dimethylaniline borane ($C_6H_5Me_2N \cdot BH_3$, $DMA \cdot BH_3$) yields pure AB.[7] This procedure is suitable for a continuous process to produce AB on large-scale, which will dramatically decrease the production cost of AB.

3. Dihydrogen Bond Effects on Conformation

Both protonic and hydridic hydrogens can be present in amine boranes, creating the possibility for significant structural consequences from intra- or intermolecular DHBs. The inorganic B/N analog of butane, 1,3-diaza-2,4-diborabutane ($NH_3BH_2NH_2BH_3$, a dehydro-dimer of ammonia borane, DDAB), was prepared for the first time in our lab.[8] DDAB is isoelectronic with butane but structurally quite distinct. It is well-known that the anti conformer of butane is more stable than its gauche conformer. In contrast, computations predict that the gauche conformer of DDAB, stabilized by an intramolecular DHB, is about 11.2 kcal/mol more stable than the anti conformer.[31] Single-crystal X-ray diffraction analysis clearly shows the opposite: the anti conformer is favored in the solid, stabilized by 24 intermolecular DHBs (Figure 9)[32] which were not considered in the computations.

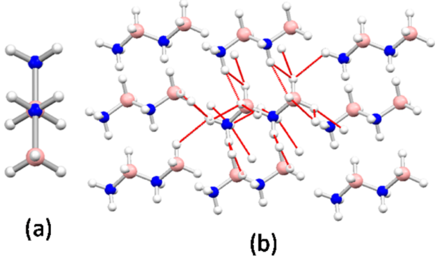


FIGURE 9. Anti-conformer of DDAB: (a) Newman projection down the N−B bond; (b) intermolecular DHBs (N blue, B pink, and H white).

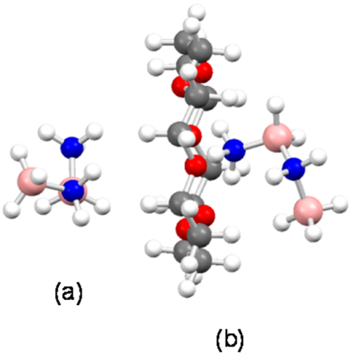


FIGURE 10. Crystal structure of 18-crown-6 adducts with DDAB: (a) Newman projections down the N2−B1 bond; (b) side views of the adducts of DDAB with crown ether (N blue, B pink, H white, O red, C dark gray).

Intermolecular DHBs were eliminated by adding a crown ether to a DDAB solution to form an 18-crown-6 adduct with DDAB in which its terminal $-NH_3$ interacts with the crown ether through classical HBs (Figure 10). The bulky crown ether at the end of DDAB prevents the formation of intermolecular DHBs, allowing the hydride of the terminal $-BH_3$ at the other end of DDAB to bend back to interact with a proton of the terminal $-NH_3$ to form the gauche conformer.[32]

Similar influence of inter- and intramolecular DHBs on conformation has been observed in linear ammonia borane oligomers and ammonia triborane by the Sneddon group[33] and in the B−N cyclohexane analogue, $N_3B_3H_{12}$, by the Shore group.[34] In the crystal structure of $N_3B_3H_{12}$ redetermined recently, its "chair" conformer was found to be stabilized by intermolecular DHBs. Blocking the intermolecular DHBs would probably lead to a "boat" conformer stabilized by intramolecular DHBs.

4. Reactions Promoted by Dihydrogen Bond Interactions

Elimination of molecular hydrogen as oppositely charged hydrogens combine and a new covalent bond is formed (reaction 4) has been known for a long time. Parry and Shore's 1955 synthesis of AB by metathesis of an ammonium salt and a borohydride salt[35] and synthesis of scorpionate ligands provide examples of the formation of new B−N compounds.[36] Both reactions were developed before the recognition of DHBs. More recently an expanding array of compounds, X−Y, have been synthesized according to reaction 4, for example, ammonia borane chloride, alkali or alkaline earth metal aminoboranes, and boron nitrogen polymeric materials.[37] Such reactions may have far more potential than previously recognized.

$$X—H + H—Y \rightarrow H_2 + X—Y \qquad (4)$$

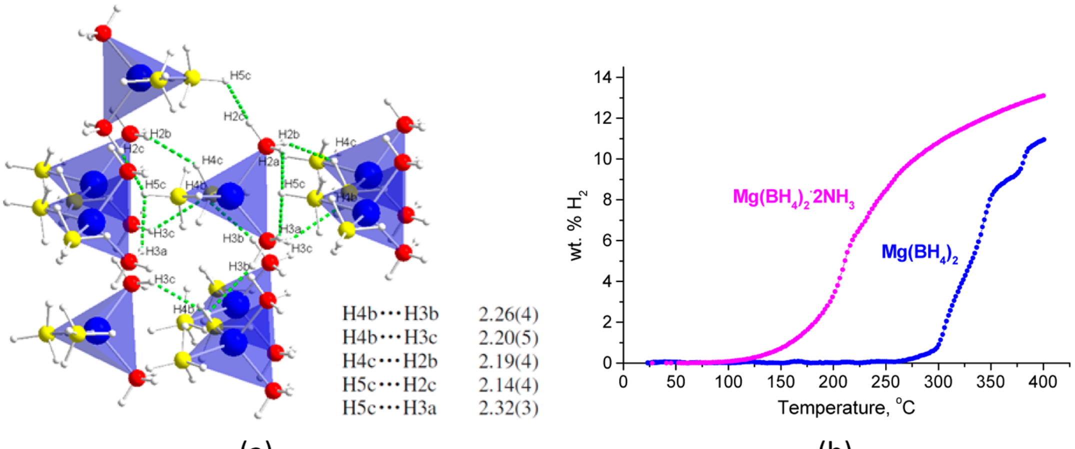
4.1. Synthesis of Aminodiborane. Aminodiborane ($NH_2B_2H_5$, ADB),[8] a small, cyclic derivative of B_2H_6 in which a bridge H has been replaced by an NH_2 group, was synthesized in 1938 through a tedious procedure involving gaseous B_2H_6 at −130 °C that produced only a less than 10% yield of ADB.[38] Our recent report is the first alternative synthesis of ADB offered since that initial discovery.[8,38] In the new synthesis AB and $THF\cdot BH_3$ react at ambient temperature to form AaDB (step 2, Figure 5), which in the absence of base loses molecular hydrogen and closes to form a four-membered ring, ADB. Loss of molecular hydrogen likely is promoted by the formation of a DHB, which also promotes formation of the new B−N bond.

4.2. Design of Hydrogen Storage Materials. Since DHB formation promotes the release of molecular hydrogen, oppositely charged hydrogens in close proximity represent a straightforward strategy in the design of solids as potential hydrogen storage materials or the improvement of the hydrogen release properties of existing solids.[39] Ammoniated metal borohydrides, as a related system of amine borane, represent an application of this strategy. Hydrogen release temperatures of alkali and alkaline earth metal borohydrides are either too high or too low for these materials to be useful for hydrogen storage. Introduction of NH_3 into metal borohydrides creates DHBs between NH_3 and BH_4^-, changing metal borohydride structure, and improving hydrogen release properties.[39] For example, dehydrogenation of $Mg(BH_4)_2$ starts at about 250 °C, while dehydrogenation of diammoniated magnesium borohydride, $Mg(BH_4)_2\cdot 2NH_3$, starts much lower at 150 °C (Figure 11). The difference in behavior is attributed to DHBs in $Mg(BH_4)_2\cdot 2NH_3$, which were confirmed by structural analysis of $Mg(BH_4)_2\cdot 2NH_3$ (Figure 11).[39b] We have also confirmed the relationship of DHBs to hydrogen release in the ammonium salts of deca- and dodecahydrodecaborates, $(NH_4)_2B_{10}H_{10}$ and $(NH_4)_2B_{12}H_{12}$.[40]

4.3. Syntheses of New Materials. According to reaction 4, an X—Y bond formation is facilitated by DHB promotion of hydrogen release, which can be used to synthesize new materials containing B−O or B−N covalent bonds. Dehydropolymerization of borazine gives polyborazylene.[41a] This reaction has recently been used to synthesize a new class of hydrogen storage material, highly porous borazine-linked polymers (BLPs) (Figure 12).[41b] Polarizable π-electron centers in BLPs promote hydrogen-framework interactions, which are thought to account for the high hydrogen storage capacities reported.

5. Proton Hydride Exchange Reaction of Boron Hydrides

DHBs can lead to proton and hydride exchange reactions, which have been observed in proton transfer reactions of metal hydrides. According to a well-accepted mechanism, two oppositely charged hydrogens form a molecular hydrogen coordination complex, an ionic pair intermediate from which molecular H_2 is released or proton and hydride exchange reactions take place. Transition metal molecular hydrogen coordination complexes have been well characterized in which a back-donating bond is believed to play an important role in stabilizing the species. In contrast to transition metals, boron does not accommodate back-donation. It is thus not surprising that little is known of molecular



(a) (b)

FIGURE 11. Structure (a) and thermal desorption behavior (b) of diammoniated magnesium borohydride. Reprinted with permission from reference 39b. Copyright 2008 American Chemical Society.

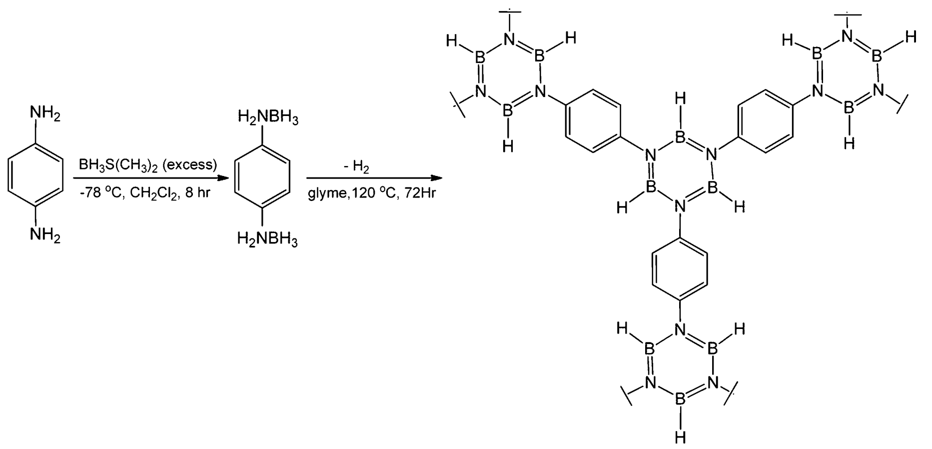


FIGURE 12. Synthesis of BLPs through hydrogen elimination.

hydrogen coordination complexes in boron hydrides. The only example of such complexes is BH_5, which was observed by IR spectroscopy under cryogenic conditions.[42] Very recently, boron as a strong Lewis acidic center was observed to bond to molecular hydrogen and activate it.[43]

Boron molecular hydrogen coordination complexes are very unstable, and for this reason they have not been fully characterized. However, the proton/hydride exchange reaction has been observed in the boron hydride system. Such exchange reactions imply two possibilities: (1) the proton and hydride exchange in boron hydride systems has a different mechanism from that of transition metal hydrides, or (2) if the same mechanism operates in the boron hydride systems, the boron molecular hydrogen coordination complexes should be present under certain conditions even though they are very transient. It would be both interesting and significant to explore new examples of proton and hydride exchange in boron hydride systems.

6. Conclusion and Outlook

Application of the DHB concept has not only led to new syntheses of ammonia borane, aminodiborane, and diammoniate of diborane, as well as mechanistic understanding for reactions that have puzzled chemists for decades, but also created new porous materials and potential hydrogen storage materials. These advances demonstrate that hydrogen elimination promoted by DHBs can be applied to the design and synthesis of advanced materials. Studies can be performed in the future to explore the application of DHBs in molecular recognition, host–guest chemistry, crystal engineering, and supramolecular chemistry, molecular self-assembly, chemical kinetics through interactions of $H^{\delta+}\cdots H^{\delta-}$, and synthesis of new advanced materials with unusual structures and properties through reactions promoted by strong DHBs. Considering the comparable strength of DHBs and conventional HBs and the wide application of the conventional HBs, one can expect that application of DHBs can be a rich field of chemistry.

The work that was published in recent years was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), under Contract No. DE-FC3605GO15062 with Prof. J.-C. Zhao as the principal investigator. Earlier work was supported by the National Science Foundation through several decades' continuous support to Prof. Sheldon Shore as the principal investigator. The authors are grateful to Prof. Thomas Evans for very valuable comments in manuscript preparation. Prof. X. Chen acknowledges the financial support from the National Natural Science Foundation of China under grant number 21371051.

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FOOTNOTES

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