Dalton Transactions

PAPER

Cite this: Dalton Trans., 2013, 42, 701

Received 26th June 2012, Accepted 3rd September 2012 DOI: 10.1039/c2dt31365k

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Introduction

Boranes and borohydrides have recently been intensively studied for hydrogen storage since they contain high hydrogen content and can release hydrogen at relatively low temperatures. Ammonia borane (NH3BH3, denoted as AB) and sodium borohydride (NaBH₄) are arguably the exemplary borane and borohydride, respectively. AB has 19.4 wt% hydrogen and releases 12 wt% hydrogen at moderate temperatures (<120 °C).¹ Solid state decomposition of AB, however, suffers from the release of undesirable volatiles and the lack of costefficient regeneration.² Even though improved performance in these areas has been reported,³ the U.S. Department of Energy (DOE) has shifted the focus from solid state decomposition to AB slurries for vehicular applications, as they offer advantages such as easy spent-fuel transportation and high hydrogen purity.⁴ The high thermal decomposition temperature (>400 °C) has made NaBH4 impractical as a solid state

Thermolysis and solid state NMR studies of NaB₃H₈, NH₃B₃H₇, and NH₄B₃H₈†

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In an effort to broaden the search for high-capacity hydrogen storage materials, three triborane compounds, NaB₃H₈, NH₃B₃H₇, and NH₄B₃H₈, were studied. In addition to hydrogen, thermal decomposition also releases volatile boranes, and the relative amounts and species depend on the cations (Na⁺, NH₄⁺) and the Lewis base (NH₃). Static-sample hydrogen NMR is used to probe molecular motion in the three solids. In each case, the line width decreases from low temperatures to room temperature in accordance with a model of isotropic or nearly isotropic reorientations. Such motions also explain a deep minimum in the relaxation time T_1 . Translational diffusion never appears to be rapid on the 10^{-5} s time scale of NMR.

> hydrogen storage medium.⁵ Therefore, NaBH₄ has been intensively studied for hydrogen release *via* hydrolysis. However, the phase change between the starting material and the products has been a key barrier to its application, which is further complicated by the lack of economical reformation from the hydrolytic products.⁶ Among the other borohydrides, lithium and magnesium borohydrides are still attracting attention, and interesting results have been published, especially on regeneration.^{7,8} Effective hydrogen storage is needed beyond automotive applications, and applications such as portable electronics and stationary energy storage have requirements that are different from those for vehicular applications. In these nonvehicular applications, boranes and borohydrides (including NaBH₄) are promising candidates.

> In addition to studying commercially available compounds, researchers also direct their attention to other compounds, such as AlB_4H_{11} , $^9 NH_3B_3H_7$, 10 and NH_4BH_4 , 11 which have high hydrogen content but lack suitable syntheses. There are actually a variety of boranes and borohydrides. One BH condensation up on the ladder from BH_3 and BH_4^- is diborane (B_2H_6); however, its explosive and toxic nature essentially eliminates it from further consideration. Another BH condensation up is triborane (B_3H_7 and $B_3H_8^-$), which still retains high hydrogen capacity. The synthesis of triborane has been a challenge, however, since it traditionally requires B_2H_6 and its isolation is not satisfactory.¹²

 ${\rm B_3H_8}^-$ has recently been observed during the thermal decomposition of Mg(BH₄)₂.¹³ Dehydrogenation of Mg(BH₄)₂ at 200 °C *in vacuo* results in a highly selective formation of magnesium triborane, Mg(B₃H₈)₂. This process is reversible at 250 °C under 120 atm H₂. As the authors stated, this is the first example of a reversible, solid-state rehydrogenation of a

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 $[\]dagger$ Electronic supplementary information (ESI) available: Hydrogen NMR spectra of NH₄B₃H₈ and NaB₃H₈ at several temperatures (listed in °C). ^{11}B NMR spectra of the solid decomposition products of NH₃B₃H₇ and NH₄B₃H₈. See DOI: 10.1039/c2dt31365k

borohydride occurring below 350 °C. The importance of studying $B_3H_8^-$ manifests itself in two main aspects. First, it leads to more options in the search of hydrogen storage materials beyond BH_3 and BH_4^- based materials. Secondly, it provides a fundamental understanding of the mechanisms of thermal decomposition and regeneration, as evidenced by the case of $Mg(BH_4)_2$.

We have recently reported the syntheses of $NaB_3H_8^{14}$ and $NH_4B_3H_8^{15}$ and their hydrogen release *via* hydrolysis. The new synthetic procedures enable safe and efficient syntheses in a typical laboratory. Our studies have shown that these two compounds outperform $NaBH_4$ and NH_3BH_3 as hydrogen storage materials *via* hydrolysis.^{15,16} This paper presents results on thermal decomposition, structural analysis using density functional theory (DFT) calculations, and the nature of molecular motions *via* static solid-state ¹H nuclear magnetic resonance (NMR) spectrometry. The molecular motions in the solid state, particularly self-diffusion, may be crucial to the rates of the dehydriding and rehydriding reactions, since solid state reactions generally require the transport of atoms from the surface into the bulk.

Experimental

General procedures

All manipulations were carried out on a high-vacuum line or in a glove box filled with high purity nitrogen. $NH_3B_3H_7$, unsolvated NaB_3H_8 , and $NH_4B_3H_8$ were prepared according to the published procedures.^{10,14,15} Due to their hygroscopic nature, all compounds were stored and handled under an inert atmosphere except during measurements. Solution NMR spectra were obtained on a Bruker Avance DPX 250 NMR. ¹¹B NMR spectra were obtained at 80.3 MHz and externally referenced to $BF_3 \cdot OEt_2$ in C_6D_6 at 0.00 ppm.

Thermal decomposition studies

Thermal stability was investigated using a Mettler Toledo highpressure differential scanning calorimeter (DSC27HP) in an argon glove box with a ramp rate of 5 °C min⁻¹. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 analyzer. Powder was loaded onto a quartz crucible and heated to 400 °C at a heating rate of 5 °C min⁻¹ under an Ar flow of 40 cm³ min⁻¹. Mass spectra of the gas released from the thermal decomposition were collected via a Balzer's Quadstar 422 quadrupole mass spectrometer. In a separate experiment, 2 mmol NaB₃H₈ was loaded into a 50 ml flask that was connected to a vacuum line, where another 50 ml flask filled with 10 ml anhydrous tetrahydrofuran (THF) was also attached. The THF was cooled to liquid nitrogen temperature, so was solidified, before the flask was opened to dynamic vacuum. After 10 min dynamic evacuation, the flask with the sample was slowly heated up to 200 °C. The gaseous decomposition products (except for H_2) were condensed into the flask cooled by liquid nitrogen. The condensed products were then analysed using ¹¹B NMR spectroscopy. Similar procedures were

applied in the case of $NH_3B_3H_7$ and $NH_4B_3H_8$. The high sensitivity of ¹¹B allows for an easy and accurate identification of these B containing products. In addition, the relative amounts of the volatile products can be analysed based on NMR signal integration.

Solid state NMR analysis

The solid residue after thermal decomposition was characterized using solid state magic angle spinning (MAS) NMR. This was performed in a field of 6.9 T using 5 mm rotors spinning at 5 kHz. Only ¹¹B was examined, at 94.6 MHz and room temperature. The free induction decays (FIDs) following 3 μ s $\pi/2$ RF pulses were signal averaged over about 30 min (4000 scans), with high-power hydrogen decoupling. The shift reference was liquid BF₃·2H₂O at 0 ppm.

For hydrogen NMR measurements, the borane samples were loaded under N_2 into glass tubes 5 mm in outer diameter (OD) and 16 cm long. The tubes were sealed by flame immediately after being loaded. Hydrogen NMR measurements of the static samples (not spinning) at 85.03 MHz were made in a 2.0 T electromagnet with ¹⁹F NMR stabilization. Temperature control was provided by flowing cold N_2 gas after passing through a thermostatically controlled heater. A thermocouple was placed within 2 cm of the sample. There was no appreciable temperature gradient because of the rapidly flowing gas for both cooling and heating.

Line shapes were generated from Fourier transformation of the FIDs. The decays were generated with short radio frequency (RF) pulses, 1 or 2 μ s, to avoid distortion. The FIDs were extrapolated back to time zero using a Gaussian function, to replace the early signals that were corrupted by probe ringing and receiver recovery.¹⁷ These corrections and precautions are only important for very broad signals (broader than 30 kHz), as observed here at low temperatures.

The hydrogen spin–lattice relaxation time T_1 was measured by the saturate-wait-inspect strategy.¹⁸ Complete saturation was obtained by a train of twenty $\pi/2$ RF pulses spaced at 1 ms each. Inspection used the FID following a final $\pi/2$ pulse (typical duration of 8.5 µs).

Calculation details

The structure of NaB₃H₈ has been solved based on powder X-ray diffraction (XRD) analysis,¹⁴ which is less sensitive to H atom positions than either single-crystal XRD or powder neutron diffraction (on deuterated samples). DFT calculations were carried out to optimize the structure with the aim of obtaining better H positions in the crystal packing. The calculation was executed using CASTEP (Accerlys, Inc; San Diego, California, USA). A norm-conserving non-local pseudopotential generated by the Kerker scheme with an energy cut-off of 400 eV was utilized. An energy change per atom convergence criterion of 0.00002 eV, a root-mean-square displacement of 0.001 Å, and a root-mean-square residual force on movable atoms of 0.05 eV Å⁻¹ were chosen. Electron exchange interactions and correlation were developed by Wu and Cohen *via* a generalized gradient approximation.¹⁹ Starting atomic



Fig. 1 DSC/TGA curves of unsolvated NaB₃H₈ (top) and ¹¹B NMR spectrum of gaseous products dissolved in THF (bottom). B₂H₆ (exists as THF·BH₃, δ 0 ppm), B₆H₁₀ (δ 14.2 ppm) and B₅H₉ (δ –13.9 ppm, δ –53.8 ppm) were detected.

positions for the geometry optimization were obtained from powder XRD analysis for NaB₃H₈.¹⁴ Symmetry was then relaxed to *P*1, where atoms could move freely during geometry optimization *via* the Broyden–Fletcher–Goldfarb–Shanno scheme.

Results and discussion

Thermal decomposition

The DSC scan of NaB₃H₈ shows an endothermic peak at 55 °C upon heating, a sharp exothermic peak at 41 °C during a subsequent cooling at the same rate, and reappearance of the endothermic peak at the same temperature (Fig. 1 (top)). This indicates a phase change in NaB₃H₈ upon heating. XRD analysis carried out under inert atmosphere (due to the hygroscopic nature of the compound) at various temperatures combined with DFT calculations might help elucidate the details of this change in the crystal structure. Combined DSC and TGA results show decomposition starting from 100 °C, resulting in a weight loss of ~30 wt% (Fig. 1 (top)). NMR analysis reveals that B₂H₆, hexaborane (B₆H₁₀), and B₅H₉ coexist in the gaseous products (Fig. 1 (bottom)),²⁰ with the majority of the

 Table 1
 Relative amounts of boron species observed in the decomposition products. (B_5H_9 , $B_3N_3H_6$, and B_2NH_7 are referenced to B_2H_6 , which was set to 1.)

Compound	B_2H_6	B_6H_{10}	B_5H_9	$B_3N_3H_6$	B_2NH_7
NaB ₃ H ₈	1	0.19	3	n/a	n/a
$NH_4B_3H_8$	1	0.05	0.37	0.24	0.49
$NH_3B_3H_7$	1	0.04	0.9	0.4	0.2



Fig. 2 DSC/TGA curves of NH₃B₃H₇ (top) and ¹¹B NMR spectrum of gaseous products dissolved in THF (bottom). B₂H₆ (exists as THF·BH₃, δ 0 ppm), B₅H₉ (δ –13.9 ppm, –53.8 ppm), B₆H₁₀ (δ 14.2 ppm), B₃N₃H₆ (δ 30.8 ppm), and B₂NH₇ (δ –27.5 ppm) were detected.

content being B_5H_9 (Table 1). This is consistent with earlier results. 21

A similar phase change at 70 °C is observed when $NH_3B_3H_7$ was subjected to a DSC scan. Thermal decomposition is exothermic, starting from 100 °C, with a final weight loss of over 70 wt% (Fig. 2 (top)). NMR analysis indicates that not only B_2H_6 , B_6H_{10} , and B_5H_9 , but also borazine ($B_3N_3H_6$) and aminodiborane (B_2NH_7)²⁰ are present in the gaseous decomposition products (Fig. 2 (bottom)). Based on the NMR signal integration ratio, similar amounts of B_2H_6 and B_5H_9 were released (Table 1). The presence of these volatile species leads to the large weight loss, considering that there is only 17.7 wt% H in this compound.



Fig. 3 ¹¹B NMR spectrum of gaseous products from NH₄B₃H₈ dissolved in THF. B₂H₆ (exists as THF.BH₃, δ 0 ppm), B₅H₉ (δ –13.9 ppm, –53.8 ppm), B₆H₁₀ (δ 14.2 ppm), B₃N₃H₆ (δ 30.8 ppm), and B₂NH₇ (δ –27.5 ppm) were detected.

Previous DSC and TGA results on $NH_4B_3H_8$ indicated that melting and decomposition take place simultaneously at 120 °C, leading to ~70 wt% weight loss.¹⁵ Similar to $NH_3B_3H_7$, appreciable amounts of B_2H_6 , B_5H_9 , $B_3N_3H_6$, and B_2NH_7 were identified in the decomposition products by NMR analysis (Fig. 3). Mass spectroscopy did not detect NH_3 in the gaseous product.

During the thermal decomposition of these compounds four common gaseous products were observed: H_2 , B_2H_6 , B_6H_{10} , and B_5H_9 . $B_3N_3H_6$ and B_2NH_7 were observed in the case of $NH_4B_3H_8$ and $NH_3B_3H_7$. These results indicate that upon heating, the boron triangle ruptures and gives off H_2 , B_2H_6 , B_6H_{10} , and B_5H_9 . The volatile borane species then react with NH_4^+ (in the case of $NH_4B_3H_8$) and NH_3 (in the case of $NH_3B_3H_7$), forming $B_3N_3H_6$ and B_2NH_7 .

Our preliminary results have shown that adding porous frameworks such as silica and transition metals such as Co suppress the formation of volatile boranes, but not completely. These compounds are unlikely to be candidates for hydrogen storage through thermolysis.

NMR studies

The solid residue has been characterized using the MAS NMR technique. The ¹¹B NMR spectrum of the solid decomposition products of NaB₃H₈ (Fig. 4) shows a strong peak at –40.6 ppm that is due to BH₄⁻ and a weak peak at –14.0 ppm associated with B₁₂H₁₂^{2-,22} The little broad peak at 1.9 ppm is ascribed to B(OH)₄^{-,23} which is formed *via* reaction with water and oxygen during sample storage and/or thermal decomposition. This finding is consistent with earlier reports that BH₄⁻ and B₁₂H₁₂²⁻ form upon the decomposition of B₃H₈⁻ salts.²¹

In the cases of NH₃B₃H₇ and NH₄B₃H₈, a sharp peak at 1.6 ppm associated with B(OH)₄⁻ is identified. ¹¹B NMR spectra are included in the ESI.[†] The broad peak extending from +30 to -20 ppm is indicative of the formation of amorphous elemental boron.²² B₁₂H₁₂²⁻ (δ -14.0 ppm) is identified in the solid decomposition products of NH₄B₃H₈, but not in those of NH₃B₃H₇. This is likely caused by the differences



Fig. 4 ¹¹B NMR spectrum of the solid decomposition products of NaB₃H₈. The main peaks are identified as BH₄⁻ (δ –40.6 ppm), B₁₂H₁₂²⁻ (δ –14.0 ppm), and B(OH)₄⁻ (1.9 ppm). The most distant little peaks (marked with *) are spinning sidebands.



Fig. 5 Hydrogen NMR spectra of $NH_{3}B_{3}H_{7}$ at several temperatures (listed in $^{\circ}C).$

between $NH_4B_3H_8$ and $NH_3B_3H_7$, such as the ionic interactions between NH_4^+ and $B_3H_8^-$ in comparison with the covalent bonds between NH_3 and B_3H_7 , and the weak dihydrogen interactions in $NH_4B_3H_8$ in contrast to the strong ones in $NH_3B_3H_7$.¹⁰

Static ¹H NMR spectra of NH₃B₃H₇ at several representative temperatures are presented in Fig. 5. ¹H NMR spectra of NH₄B₃H₈ and NaB₃H₈ are provided in the ESI.[†] Each solid undergoes motional narrowing^{24–26} from -135 °C (or -125 °C) to 21 °C. For each sample, a narrow resonance "pip" appears at and above 21 °C off-scale; this signal contains a small



Fig. 6 Hydrogen NMR FWHM line widths as functions of temperature *T*. Dashed lines are guides for the eyes and carry no analytical significance. All line widths carry a $\pm 5\%$ uncertainty.

fraction of the total spectral area and the total ¹H spins. These impurity signals have been attributed to residual solvent from the sample preparation.

Full width at half of maximum (FWHM) line widths were obtained from the experimental spectra and are presented in Fig. 6. None of the solids are at their rigid lattice limit at -135 or -125 °C, but by comparison with organic solids (*e.g.*, cyclohexane)²⁴ with similar densities of ¹H spins, the expected rigid FWHM is approximately 60 kHz. NaB₃H₈ and NH₃B₃H₇ must commence narrowing just below -135 °C, while NH₄B₃H₈ (the narrowest resonance of the three at -135 °C) must begin narrowing well below this temperature. Thus, since NH₄B₃H₈ exhibits reorientation starting from the lowest temperature, one expects the reorientations in NH₄B₃H₈ to have the smallest activation energy.

In the plateau region near 21 °C (see Fig. 6), the line shapes are approximately Gaussian. The second moment M_2 (in units of (rad s⁻¹)²) and the FWHM line width (in Hz units) are related by²⁶

$$FWHM = (2\ln 2M_2)^{1/2} / \pi$$
 (1)

An important theorem holds that one can calculate the M_2 , when the molecular units reorient rapidly, isotropically, and independently, by placing all of the spins in a reorienting molecule or sub-unit at the molecular center.²⁴ For like-spin interactions, the powder-average M_2 is given by²⁶

$$M_2 = 3/5\gamma_1^4 2I(I+1)\Sigma_k 1/r_k^6 \tag{2}$$

where the lattice sum S is well-approximated by 24

$$S = n \ 7.25/V^2$$
 (3)

Here, γ_1 is the magnetogyric ratio of the hydrogen nuclear spin, I = 1/2 for hydrogen, *n* is the number of ¹H spins on each molecular unit, and *V* is the volume per molecular unit.

Provided that the structure is densely packed, the numerical factor in (3) is nearly constant and almost independent of structural details. For all three solids, we have verified that unlike-spin (boron, sodium) contributions to the hydrogen M_2 are small, less than 10% (so a contribution to the FWHM line width of less than 5%).

For NH₃B₃H₇, the reported crystal structure has V = 112.2 Å³ per molecule.¹⁰ The entire molecule was modelled with n = 10 ¹H spins rotating isotropically, yielding $M_2 = 1.47 \times 10^9$ (rad s⁻¹)² and FWHM = 14.4 kHz. In this case, the observed FWHM of 20.5 kHz is sufficiently larger than the calculated value that we suspect the reorientations are not fully isotropic.

For NaB₃H₈, the crystal structure¹⁴ is reported with $V = 109.2 \text{ Å}^3$ per molecule and n = 8 ¹H spins. Letting each B₃H₈ group rotate isotropically gives $M_2 = 1.24 \times 10^9 \text{ (rad s}^{-1})^2$ and FWHM = 13.2 kHz. This is close to the observed 15.5 kHz FWHM at 21 °C, indicating nearly isotropic reorientation at this temperature.

The case of NH₄B₃H₈ is more complicated, as there are 4 ¹H spins on NH₄⁺ and 8 on B₃H₈⁻; cations and anions are modelled to reorient independently of each other. Using the 124 Å³ per NH₄B₃H₈ formula unit from the structure determined from XRD,¹⁵ M₂ = 3.17×10^9 (rad s⁻¹)² and FWHM = 21.1 kHz agrees with the observed 21 kHz FWHM.

Overall, the agreement between the measured FWHM line widths and the calculated values demonstrates that isotropic reorientations occur at 21 $^{\circ}$ C (or, in the case of NH₃B₃H₇, nearly isotropic reorientations).

Above 21 °C, the $NH_3B_3H_7$ and $NH_4B_3H_8$ line widths narrow further; the NaB_3H_8 material was judged to be insufficiently stable for study at elevated temperatures. The additional narrowing *may* signal the onset of translational self-diffusion, although the slope of the observed decrease is too small for the expected, thermally activated behavior.²⁴ In any event, the lines remain broader than 10 kHz at and below 75 °C, so the diffusion motion is never rapid on the 10⁻⁵ s NMR time scale at this temperature.

The spin-lattice relaxation time T_1 is reported in Fig. 7. The T_1 of all three solids passes through a deep minimum near or just below room temperature. First, we examine the temperature of the T_1 minimum. A minimum is expected in standard relaxation theory^{24–26} when $\omega_r \tau$, with ω_r the angular resonance frequency, is approximately one, so τ (the motion correlation time) is about 10^{-9} s; here ω_r is 2π times the resonance frequency of 85.03 MHz. The onset of line narrowing occurs for a τ of approximately 10⁻⁵ s (the reciprocal of the rigid limit line width). Motions (reorientations) here are assumed to be described by the thermal activation expression, $1/\tau = \omega_0$ $\exp(-E/kT)$, with a typical attempt frequency of $\omega_0 = 10^{13} \text{ s}^{-1}$. At the T_1 minimum, the factor $\exp(-E/kT)$ is 10^{-4} , while at the onset of line narrowing this factor is 10⁻⁸. Thus, the absolute temperature at the T_1 minimum should be approximately double that at the onset of narrowing.

For NH₃B₃H₇, the T_1 minimum occurs near 21 °C, predicting the narrowing onset to be near -126 °C, slightly higher than our estimate above based on the line widths. For NaB₃H₈, Paper



Fig. 7 Hydrogen spin–lattice relaxation time T_1 dependence on inverse temperature for the three solids. The dashed curves are guides for the eyes. The T_1 values have a ±10% uncertainty. The dashed horizontal line is the theoretical estimate for the minimum T_1 .

the T_1 minimum appears at -23 °C. The onset of narrowing is thus predicted to be -148 °C, which agrees well with the line width analysis. For $NH_4B_3H_8$, the T_1 minimum occurs at -51 °C, leading to a predicted temperature of -162 °C for the onset of narrowing. Again, this prediction agrees with the line width values. For comparison, in NH_4Cl , the T_1 minimum occurs near -78 °C²⁷ and the onset of narrowing is near -158 °C,²⁸ in the same vicinity as the temperatures reported here for $NH_4B_3H_8$. The T_1 minimum in this sample is particularly broad, suggesting that the reorientation rates of the NH₄⁺ cations and the B₃H₈⁻ anions are somewhat different, but not sufficiently different to yield a resolved double minimum in T_1 . Overall, the observed relationship between the temperatures of the T_1 minima and the narrowing onsets demonstrates that the same thermally activated process (i.e., molecular reorientation) controls both.

Next, we examine the depth of the T_1 minima. All of these solids have approximately the same densities of ¹H spins, so their low-temperature limiting (rigid limit) M_2 values and FWHM rigid line widths should be *approximately* equal.²⁴ The FWHM was set to 60 kHz, and the portion of M_2 (about 89%) that is motionally modulated, $\Delta M_2 = 2.3 \times 10^{10}$ (rad s⁻¹)², was computed using eqn (1). The minimum T_1 is given by (with a very small model dependence):²⁴

$$T_1 \min = (1.0) \omega_0 / \Delta M_2 = 0.023 \text{ s}$$
 (4)

The above estimate is rough, but it applies to all three solids. The agreement in Fig. 7 (see dashed line) with NaB_3H_8 is quite good. The minimum T_1 for $NH_4B_3H_8$ is slightly larger, quite likely due to the extra breadth of the minimum in this solid, due to the separate reorientation rates for the cations and anions. For $NH_3B_3H_7$, the dashed curves (only guides to the eye) in Fig. 7 show a discontinuity in slope near the



Fig. 8 DFT optimized crystal structure of NaB₃H₈. Left: Na⁺ coordinated by six H⁺; right: double stranded structure constraining the movement of $B_3H_8^-$. Purple: Na; grey: H; pink: B.

reported solid–solid phase transition at 24 °C.²⁹ For this sample, the T_1 minimum appears to be pre-empted by the transition, so the true minimum value of T_1 is never obtained.

Overall, the good agreement of the predicted and measured minimum T_1 values confirms that the same motions (molecular reorientations) control T_1 and the line narrowing.

The activation energy of molecular reorientations was calculated using $\tau = 10^{-9}$ s at the T_1 minimum and an assumed attempt rate $\omega_0 = 10^{13} \text{ s}^{-1}$. Thus, at the T_1 minimum, $\exp(-E/kT)$ is approximately 10^{-4} . So, the activation energy *E* in NH₃B₃H₇, NaB₃H₈, and NH₄B₃H₈ is 0.23, 0.20, and 0.18 eV, respectively. While we can trust the relative values of *E* to ±10%, the absolute values depend on the assumed attempt frequency ω_0 and are likely to be reliable only to ±25% (reflecting a ±1 decade uncertainty in ω_0).

DFT geometry optimization

Geometry optimization by DFT indicates that there is no major change in the original structure, but movement of terminal hydrogen on the boron triangle towards the Na⁺ cation indicates a strong Na····H interaction (Fig. 8). Each Na is coordinated by 6 H in a distorted octahedron, with the Na···H distance ~2.3 Å, shorter than those in NaBH₄ (2.44 Å-2.59 Å).³⁰ With all terminal hydrogen atoms on the boron triangle interacting with Na, the movement of $B_3H_8^-$ units will likely be constrained, which results in a high activation energy for reorientation of $B_3H_8^-$.

The crystal structures of $NH_4B_3H_8$ and $NH_3B_3H_7$ have been solved based on single crystal XRD analysis, which affords much better resolution of atomic locations. Separate ion pairs exist in the $NH_4B_3H_8$ crystal structure, where the $N-H^+\cdots H^--B$ dihydrogen interaction is weak.¹⁵ This leads to easy reorientation of NH_4^+ and $B_3H_8^-$. In $NH_3B_3H_7$, the N atom forms a strong bond with one of the B atoms. Additionally, extensive $N-H^+\cdots H^--B$ networks exist in the crystal structure.¹⁰ As a result, the reorientation of the molecule is much constrained. Overall, structural features of the three compounds shed light on the ease of molecular reorientation.

Conclusions

The thermal decomposition of NaB_3H_8 , $NH_4B_3H_8$, and $NH_3B_3H_7$ has been investigated. Hydrogen, diborane,

pentaborane, and hexaborane are the common decomposition products; the presence of $\rm NH_3$ and $\rm NH_4^+$ constituents causes the additional formation of borazine and aminodiborane. These compounds are unlikely candidates for hydrogen storage *via* thermolysis due to these volatile side products. Static solid-state ¹H NMR was used to determine the nature of the molecular motions. In all three, line narrowing is observed from -135 °C to 21 °C and is attributed to reorientations of the molecular sub-units. Translational self-diffusion, which is an important aspect of rapid hydrogen reactions in the solid state, is never rapid on the NMR time scale of 10^{-5} s. The hydrogen spin–lattice relaxation time T_1 passes through a minimum for each of the solids. The temperature and depth of the T_1 minima are in accordance with molecular reorientations being the source of the relaxation.

Acknowledgements

The work at The Ohio State University is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE) under Contract No. DE-FC3605GO15062. M. S. C. at Washington University gratefully acknowledges support from the U.S. Department of Energy, Basic Energy Sciences, from grant DE-FG02-05ER46256. Z. H. is a recipient of an *Australian Research Council's Discovery Early Career Researcher Award* (project number DE120101496). Z. H. thanks Professor L. G. Sneddon for his comments on ¹¹B NMR analysis. We thank S.-J. Hwang for suggestions on the spectral assignment of the ¹¹B MAS-NMR.

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