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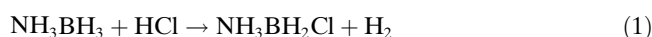
Hima K. Lingam,^[a] Xuenian Chen,^{*,[a, b]} Ji-Cheng Zhao,^{*,[b]} and Sheldon G. Shore^{*,[a]}

Hydrogen storage is defined by the US Department of Energy as a “grand challenge” to the implementation of hydrogen-powered-fuel-cell vehicles.^[1] Ammonia borane (AB) is one of the most widely studied compounds for chemical hydrogen storage because of the high gravimetric hydrogen content (19.6%), the good stability at room temperature, and the general availability.^[2] In contrast, the diammoniate of diborane (DADB), an ionic dimer of AB that has the same gravimetric hydrogen-storage capacity as AB and better/lower hydrogen-release temperature, has attracted very little attention^[3] as a potential hydrogen-storage material, mostly due to the difficulty in obtaining the pure compound. Although it has been recognized as a key intermediate in the dehydrogenation and oligomerization of AB,^[3b] reports on DADB have essentially declined due to issues regarding the synthesis. Furthermore, the instability of the diammoniate of diborane in organic solvents at ambient temperature leads to confusion about the purity of the sample.

DADB, which was first reported by Stock in 1923 in a reaction between B₂H₆ and NH₃,^[4] is a colorless, nonvolatile, saltlike compound. Although several structures have been proposed for DADB over the years, it remained a matter of debate until Parry's group identified the correct structural formula [H₂B(NH₃)₂][BH₄] in 1958 by using classical analytical techniques.^[5] The structure has since been verified by NMR spectroscopy^[6] and XRD analysis.^[7] DADB is an undesirable byproduct in the preparation of AB in displacement reactions between ammonia and either THF·BH₃ or (CH₃)₂S·BH₃. The DADB formation mechanism in these reactions remained unclear until a recent study characterized the long-postulated intermediate ammonia diborane (NH₃BH₂(μ-H)BH₃) by boron NMR spectroscopy to account for the presence of DADB and also revealed the important role of dihydrogen bonds in the formation of

DADB.^[8] Interestingly, the anion of a proposed DADB structure, [NH₄][H₃BNH₂BH₃], that proved to be incorrect, was recently synthesized by the group of Girolami.^[9]

A few attempts were made in the past to find a large-scale synthesis of DADB. Reactions that lead to DADB include ammonia and B₂H₆,^[4,10,11] solid-state decomposition of NH₄BH₄,^[12] and ball milling NaBH₄ and NH₄F.^[3] Herein we report a sequence of quantitative reactions [reactions (1)–(3)] for the synthesis of DADB in large scale.



This convenient preparative method for DADB takes advantage of a modified synthesis of the cationic borane complex [H₂B(NH₃)₂]⁺Cl[−], which was first synthesized by Shore and Parry in a reaction of DADB and NH₄Cl.^[5c] Cationic borane complexes can also be prepared by a reaction of amines with halogen-substituted boranes.^[13] Reactions (1) and (2) represent a new route to the cationic borane complex [H₂B(NH₃)₂]⁺Cl[−]. When ammonia monochloroborane (NH₃BH₂Cl), formed readily as gaseous HCl is added to a solution of AB in diethyl ether,^[14] is dissolved in liquid ammonia it is converted quantitatively to [H₂B(NH₃)₂]⁺Cl[−], formation of which was verified by ¹¹B NMR spectroscopy (Figure S1b in the Supporting Information) and confirmed by XRD (Figure S4 in the Supporting Information).^[7]

A synthesis was successfully scaled to yield 10 g of DADB by converting NH₃BH₂Cl to [H₂B(NH₃)₂]⁺Cl[−] in liquid ammonia followed by the addition of KBH₄ (1:1 mol ratio). DADB was isolated in a high yield (98%) after filtration of KCl and removal of liquid ammonia under dynamic vacuum at −78 °C. NMR spectra (¹¹B and ¹H) indicate a high-purity DADB synthesis. We report for the first time ¹H, ¹H{¹¹B}, ¹¹B, and ¹¹B{¹H} NMR spectra of DADB in [D₈]THF at −40 °C. The ¹H NMR spectrum contains a quartet at δ = −0.10 ppm for BH₄[−] hydrogen atoms and a very broad signal at around δ = −2.08 ppm for BH₂ hydrogen atoms coupled with boron (Figure 1a). Both signals are converted to sharp singlets at the corresponding positions in the boron-decoupled ¹H NMR spectrum (Figure 1b). The ¹¹B NMR spectrum of DADB contains a quintet at δ = −38.5 ppm corresponding to borohydride and a broad signal at δ = −15.2 ppm related to BH₂ (Figure 2, −40 °C spec-

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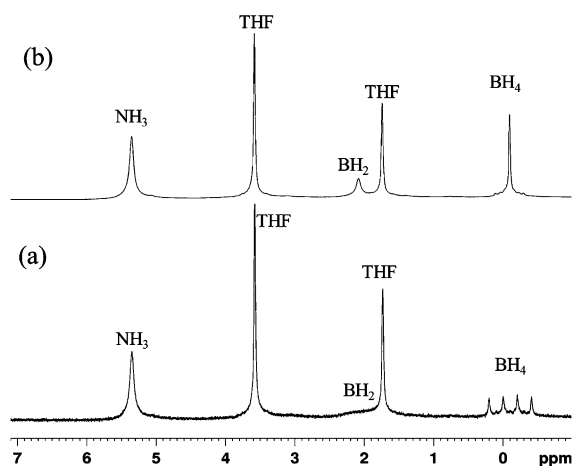


Figure 1. a) ^1H and b) $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of DADB in $[\text{D}_8]\text{THF}$ at -40°C .

trum). The broad signal for BH_2 , believed to be due to quadrupole interactions of boron at low temperatures, resolved into a triplet above 0°C as shown in Figure 2.^[15] A clear triplet for BH_2 was also observed in liquid ammonia (Figure S2a in the Supporting Information).^[6a]

DADB is stable in liquid ammonia,^[5] but decomposes in organic solvents at room temperature. The instability in THF has been demonstrated by variable-temperature ^{11}B NMR experiments carried out between -40°C and 27°C

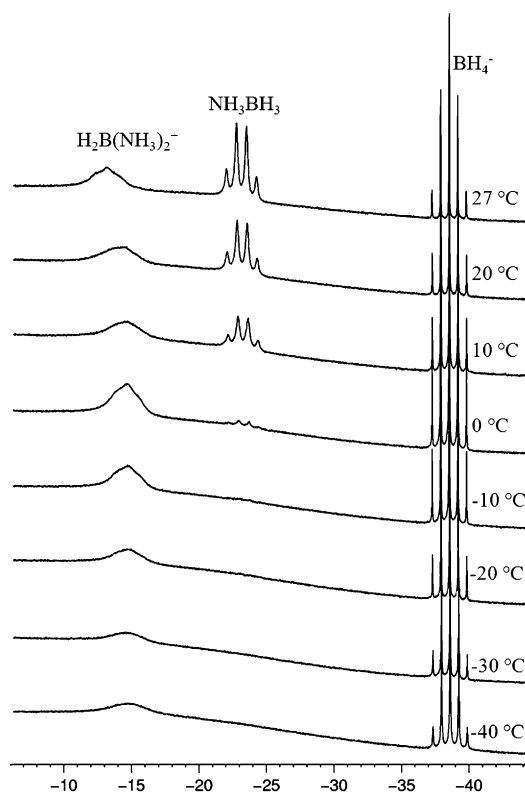


Figure 2. Variable-temperature ^{11}B NMR spectra of DADB from -40°C to 27°C with 10°C intervals.

(Figure 2). DADB was stable at lower temperatures, slowly converting irreversibly to AB as the temperature was raised (-10°C). Once AB was formed, it did not revert back to DADB when the temperature was lowered (Figure S6 in the Supporting Information).

Attempts to avoid the use of liquid ammonia by synthesizing DADB in THF at low temperatures were unsuccessful. Consistent with literature reports, a mixture of DADB, AB, and a variety of other products was observed.^[5c] DADB was converted to a mixture of cyclotriborazane and AB when kept at room temperature in THF for two days (Figure S7 in the Supporting Information). In summary, by improving the synthesis of $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Cl}$, a convenient synthesis of DADB has been developed based on the metathesis reaction between $[\text{H}_2\text{B}(\text{NH}_3)_2]\text{Cl}$ and KBH_4 in liquid ammonia. DADB is stable in THF at temperatures below -30°C and is partially converted into ammonia borane at higher temperatures.

Experimental Section

In a typical synthesis $[(\text{NH}_3)_2\text{BH}_2]\text{Cl}$ (1.23 g, 14.9 mmol) and KBH_4 (0.805 g, 14.9 mmol) were placed in a 150 mL flask, which was connected to a vacuum line, and liquid NH_3 (60 mL) was condensed into the flask. The solution was stirred for 90 min at -78°C . KCl was filtered from the solution and ammonia was removed slowly from the filtrate under vacuum to yield DADB (0.90 g, 14.5 mmol; 97% yield), for which the XRD pattern matches previously reported structures.^[7] ^{11}B NMR (128.7 MHz, liquid NH_3): $\delta = -14.8$ (t, BH_2), -38.8 ppm (q, BH_4); ^{11}B NMR (128.7 MHz, $[\text{D}_8]\text{THF}$): $\delta = -15.2$ ppm (t), -38.5 ppm (q) (Figure S2 in the Supporting Information); ^1H NMR (400.17 MHz, $[\text{D}_8]\text{THF}$): $\delta = 5.35$ (br, 6H of NH_3), 2.08 (br, 2H of BH_2), 0.10 ppm (q, 4H of BH_4 ; Figure S3 in the Supporting Information); elemental analysis (%) calculated for $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4]$: H 19.59, N 45.38; found: H 19.33, N 43.30.

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Keywords: boron • diammoniate of diborane • hydrogen storage • metathesis • NMR spectroscopy

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