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Facile Synthesis of Aminodiborane and Inorganic Butane Analogue $NH_3BH_2NH_2BH_3$

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Abstract: A new ambient-temperature, catalyst-free reaction between ammonia borane and tetrahydrofuran borane produces aminodiborane via the formation of a dihydrogen bond and subsequent molecular hydrogen elimination. The facile synthesis of aminodiborane will make this long-sought active chemical reagent readily available for both inorganic and organic reactions. From aminodiborane, an inorganic butane analogue, $NH_3BH_2NH_2BH_3$, was prepared, and its single-crystal structure displayed a gauche rather than an anti form conformation.

Aminodiborane ($NH_2B_2H_5$, **1**), one of the oldest members of the borane family, was first found serendipitously in 1938 and then prepared through a tedious procedure using diborane gas at −130 °C with a low yield.[1] Except for its structure determination,[2] no further studies of its reactions or properties have been reported in the past 70 years, mostly because of its unavailability. It has been a challenging and long-sought goal to find a convenient preparation of **1** so this active chemical reagent can be applied in both organic and inorganic syntheses. Here we report a facile synthesis method for **1** that takes advantage of the formation of a dihydrogen bond and subsequent dihydrogen elimination between a protonic hydrogen of amine and a hydridic hydrogen of borane (BH_3) in a reaction between ammonia borane (NH_3BH_3, **2**) and THF borane ($THFBH_3$, **3**) (reaction 1).

$$NH_3BH_3 + THFBH_3 \rightarrow NH_2B_2H_5 + H_2 + THF \qquad (1)$$

This reaction was inspired by the considerable strength and flexibility of dihydrogen bonds that has been revealed by ongoing research over the last two decades[3] and several examples where dihydrogen elimination between amine and borane with[4] or without[5] a transition-metal catalyst has led to new B−N bonds. Electronic structure calculations also predicted that **1** is the most stable product in the reaction of **2** and BH_3 proceeding via different transition states.[6]

The synthesis of organic molecules through C−X (X = C, N, O) bond formation using transition-metal catalysts is a thoroughly developed area in chemistry. In contrast, preparation of inorganic chain molecules is still in its infancy. To our knowledge, there are only a few reported unsubstituted boron−nitrogen inorganic polymeric compounds[5] and a few substituted boron−nitrogen four-membered chain molecules.[4b,c,7] Here we report the synthesis and structure of $NH_3BH_2NH_2BH_3$ (**4**), an inorganic butane analogue, by reaction of **1** with ammonia gas.

Solid **2** was added to an equimolar borane THF solution (1 M) at room temperature. Gas bubbles (presumably H_2, not measured) appeared immediately while the mixture was stirring at room temperature. A new signal at −27.0 ppm characteristic of **1** was monitored by ^{11}B NMR analysis of the reaction mixture. As the reaction proceeded, the intensity of reactant boron signals decreased and the product signal increased until the reaction ceased. The yield was 90% on the basis of the resonance intensities of boron signals in the ^{11}B NMR spectra of the reaction mixture. The formation of trace amounts of unidentified impurities was detected by ^{11}B NMR analysis. After reaction, the mixture was filtered to remove a small amount of white precipitate produced during the reaction. Most of the THF was fractionally condensed from the filtrate under a dynamic vacuum to produce a concentrated aminodiborane THF solution. When the solution was cooled to −78 °C, a crystalline substance was formed and collected with an isolated yield of 70%. The crystals melted when warmed to room temperature and were shown to consist of **1** and THF in a 1:1 ratio (**1-THF**) based upon the integration of the hydrogen signals in the ^1H NMR spectra of **1-THF** in toluene-d_8.

The structure of **1** was determined with large uncertainties using electron diffraction[2a,b] and redetermined more accurately from microwave spectroscopic data.[2c] No single-crystal X-ray structure has been reported to date. As **1** is a liquid at ambient temperature, we utilized 18-crown-6 ether to bind **1** by weak hydrogen bonds in order to obtain a solid suitable for X-ray analysis.[8] Single-crystal X-ray diffraction analysis showed that the crystalline adduct of 18-crown-6 and aminodiborane, $C_{12}H_{24}O_6 \cdot 2NH_2B_2H_5$ (**5**), is triclinic and belongs to the $P\bar{1}$ space group. The molecular structure of the $NH_2B_2H_5$ moiety in **5** obtained from X-ray structural analysis is depicted in Figure 1.

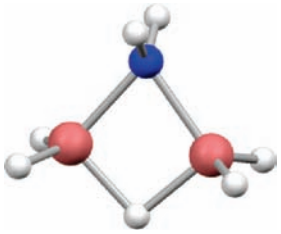

Figure 1. Structure of $NH_2B_2H_5$ (**1**). N, blue; B, orange; H, light-gray.

Two obvious structural changes occur when **2** and **3** react to form **1**: two new bonds form (a B−H−B bridge hydrogen bond and a N−B bond) as THF and molecular dihydrogen are eliminated. There is insufficient theoretical or experimental work at this point to delineate the reaction mechanism. However, we believe the most plausible pathway of the reaction involves the formation of a dihydrogen bond and subsequent elimination of molecular hydrogen. This reaction is different from more common reactions between amine and borane in which a dative B−N bond is formed by donation of an electron pair of the amine into the empty orbital of boron.

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With structural features such as a bridge hydrogen bond and a four-membered ring, **1** can be expected to be highly reactive. The new facile synthesis of **1** reported here will make this chemical reagent readily available as a starting material for the synthesis of new boron-containing compounds or as a powerful reducing agent to be applied in organic reduction reactions. As an example, we synthesized $NH_3BH_2NH_2BH_3$ (**4**) from **1**. Ammonia gas was bubbled into a solution of **1** to produce **4** by breaking of the bridge hydrogen bond and opening of the four-membered ring (reaction 2).

$$NH_2B_2H_5 + NH_3 \rightarrow NH_3BH_2NH_2BH_3 \qquad (2)$$

Both boron and proton NMR analyses clearly showed the signals associated with various amine and borane groups in **4** (Figure 2).

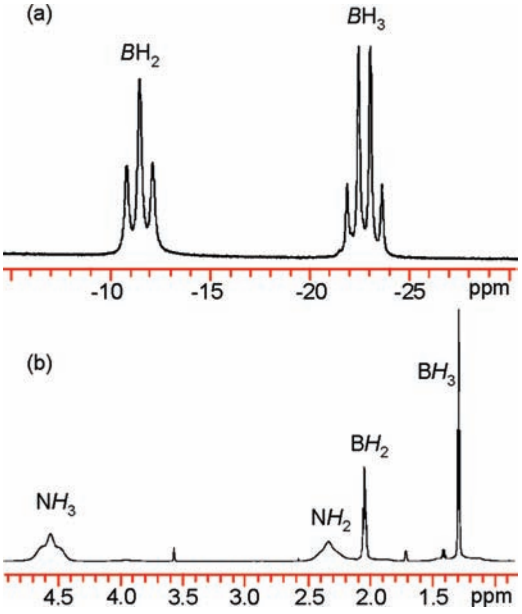

Figure 2. (a) ^{11}B and (b) $^{1}H\{^{11}B\}$ NMR spectra of $NH_3BH_2NH_2BH_3$ (**4**) in THF-d_8.

Although **4** and butane are isoelectronic, **4** is a white crystalline solid powder at room temperature with a melting point of 62 °C. To facilitate the crystal structure determination, we prepared single crystals of an adduct of **4** with 18-crown-6 ether, $C_{12}H_{24}O_6 \cdot N_2B_2H_{10}$ (**6**). Single-crystal X-ray diffraction analysis showed that the molecular structure of the **4** moiety in **6** exhibits the gauche form (Figure 3) rather than the anti form, which is the most stable conformation for butane.

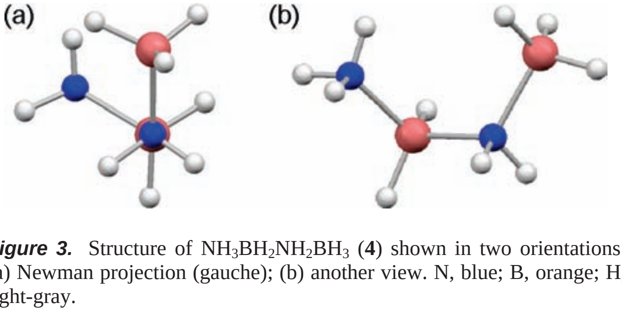

Figure 3. Structure of $NH_3BH_2NH_2BH_3$ (**4**) shown in two orientations: (a) Newman projection (gauche); (b) another view. N, blue; B, orange; H, light-gray.

The gauche form of **4** can be attributed to a weak dihydrogen bond between N−H and B−H that prevents the B−N bonds from rotating freely (Figure S6 in the Supporting Information). The observed crystal structure is consistent with electronic structure calculations that predicted a negative enthalpy of formation for the gauche form and a positive enthalpy for the anti form of **4**.[9]

Compound **4** is a potential hydrogen storage material with 16.9 wt % hydrogen. It has been predicted as an intermediate during thermal decomposition of NH_3BH_3.[10] Thus, its properties are relevant to NH_3BH_3 studies as well as hydrogen storage research. It can also be applied to the reduction of carbonyls to alcohols. Further study of **4** is in progress.

In conclusion, we have developed a practical synthesis of aminodiborane using a new ambient-temperature, catalyst-free reaction between ammonia borane and tetrahydrofuran borane. The facile synthesis of aminodiborane will make this long-sought active chemical reagent readily available for both inorganic and organic reactions. From aminodiborane, we successfully synthesized the inorganic butane analogue $NH_3BH_2NH_2BH_3$ (**4**). Its successful synthesis calls for more exploration of inorganic chain compounds, which can be a potentially rich field in chemistry.

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Supporting Information Available: Crystallographic data for **5** and **6** (CIF); experimental preparations and proton and boron NMR spectra for **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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