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Hydrogen Storage by Boron−Nitrogen Heterocycles: A Simple Route for Spent Fuel Regeneration

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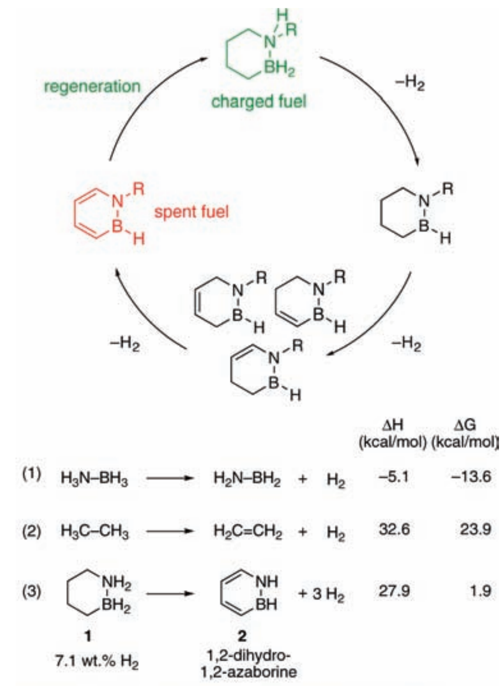
The efficient and safe storage of hydrogen is a crucial component for the development of a hydrogen-based energy infrastructure.[1] Consequently, various hydrogen storage approaches are currently being investigated, including metal hydrides,[2] sorbent materials,[3] and chemical hydride systems.[4,5] Boron- and nitrogen-containing chemical hydrides have attracted much attention because of their high gravimetric hydrogen densities and fast kinetics of hydrogen release. Ammonia borane ($H_3N{-}BH_3$ or AB) is a very promising candidate among the chemical hydride materials, exhibiting a gravimetric density of 19.6 wt % H_2.[6] While the release of H_2 from AB and its derivatives has been extensively investigated in the recent past,[7–15] the issue of spent fuel regeneration has received less attention.[16,17] This is arguably due to the complicated and ill-defined nature of the various spent fuel products from AB dehydrogenation. It has been reported that depending on dehydrogenation conditions, monomeric BN heterocycles (e.g., cyclotriborazene, cyclopentaborazane, and borazine), polymeric amino- or iminoboranes, and/or polyborazylene materials can be generated.[4] In recent reports, Gordon, Dixon, and co-workers[18] elegantly demonstrated that polyborazylene spent fuel can be converted back to AB in a three-step protocol using benzenedithiol as the digestion reagent and $(n\text{-Bu})_3SnH$ and $(n\text{-Bu})_2SnH_2$ as reductants.

Recyclability (i.e., spent fuel regeneration) is critical to the success of any hydrogen storage system. The ideal reductant for regenerating any spent fuel would be molecular hydrogen itself. Our research group has been focusing on developing new chemical hydrogen storage materials that (a) are well-defined molecular species throughout the entire fuel lifecycle, (b) possess high H_2 storage capacities, (c) exhibit an appropriate enthalpy of H_2 desorption conducive to regeneration by H_2, and (d) are liquids at operating temperatures.

Scheme 1 illustrates the proposed fuel cycle of our material. The charged fuel (highlighted in green) is a BN-heterocyclic analogue of cyclohexane, which upon release of 3 equiv of H_2 produces the spent fuel material, an aromatic BN heterocycle analogous to benzene (highlighted in red). As can be seen from Scheme 1, the charged and spent fuel and the potential intermediates are well-defined molecular compounds. Furthermore, we have determined that the spent fuel and partially dehydrogenated intermediates are low-melting liquids (for R = *t*-Bu, the melting points are below −30 °C; see the Supporting Information). With regard to the thermodynamics of hydrogen release/uptake, we have predicted that the coupling of exothermic dehydrogenation from B−N bonds [e.g., dehydrogenation of AB is exergonic by −13.6 kcal/mol at 298 K (eq 1 in Scheme 1)][19] with endothermic dehydrogenation from C−C bonds [e.g., dehydrogenation of ethane is endergonic by +23.9 kcal/mol (eq 2 in Scheme 1)] in a cyclic six-membered framework (taking advantage of the aromatic stabilization energy) should lead to a reversible H_2 storage system (i.e., $\Delta G \approx 0$ kcal/mol).[19] Indeed, electronic structure calculations at the CCSD(T) level indicate that the release of three H_2 molecules from BN heterocycle **1** exhibits overall thermodynamics conducive to reversible H_2 uptake/release (eq 3 in Scheme 1).[20] These features and the relatively high gravimetric density (up to 7.1 wt % H_2 for compound **1**) render BN heterocycle materials a potentially viable H_2 storage platform.

Scheme 1. Hydrogen Storage by BN Heterocycle Materials



Electronic structure calculations at the CCSD(T) level (298K).

For our initial contribution in this area, we chose to focus on the issue of spent fuel regeneration. In this communication, we demonstrate that the BN spent fuel heterocycle can be converted to the fully charged material with molecular H_2 and H^+/H^- equivalents under mild temperatures and pressures. Furthermore, we provide the first crystallographic characterization of the reaction intermediates along the pathway from the spent fuel to the charged material, allowing direct observation of the structural changes associated with increasing hydrogen saturation.

The spent fuel material illustrated in Scheme 1 belongs to the family of 1,2-dihydro-1,2-azaborines, a class of aromatic heterocycles that was initially explored by Dewar in the 1960s[21] and subsequently further developed by Ashe[22–24] and our group.[25–31] We recently reported the synthesis and characterization of the parent

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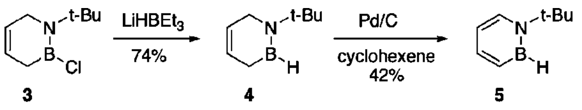
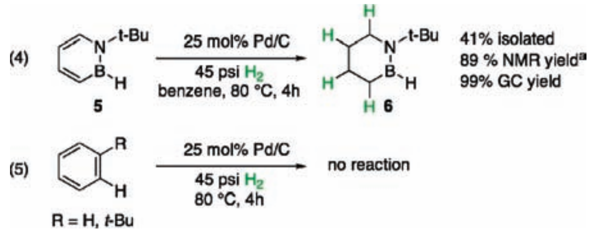
spent fuel material, 1,2-dihydro-1,2-azaborine **2** (see eq 3 in Scheme 1).[27] In this study, we chose to investigate the regeneration of the N-substituted analogue (Scheme 1, R = *t*-Bu) because of its ready synthetic availability. Scheme 2 describes the preparation of *N*-*t*-Bu-1,2-dihydro-1,2-azaborine (**5**). Treatment of the known precursor **3**[26] with $LiHBEt_3$ furnished partially spent fuel material **4** as a clear colorless liquid in 74% isolated yield. Subsequent dehydrogenation over catalytic amounts of Pd/C[25] produced the desired model spent fuel material **5**, also as a low-melting liquid.

Scheme 2. Synthesis of Model Spent Fuel Material **5**



We determined that the **5** readily takes up 2 equiv of molecular H_2 to furnish **6** under mild conditions (eq 4 in Scheme 3). Full conversion was achieved in 4 h at a hydrogen pressure of 45 psi (~3 atm) at 80 °C in the presence of catalytic amounts of Pd/C. Heterocycle **6** was isolated as a clear low-melting liquid in 41% yield after distillation. In separate experiments, we determined by NMR and GC analysis that the actual hydrogenation reaction is a high-yield process. Thus, we believe that the moderate isolated yield of **6** is likely caused by the volatility of the product and loss through distillation. The NMR experiment (performed in C_6D_6) indicated no formation of cyclohexane derivatives (i.e., benzene is not hydrogenated). To provide further support for this observation, we treated benzene and *tert*-butylbenzene under the same conditions as shown in eq 4 and observed only unreacted starting materials (eq 5 in Scheme 3).[32] Equations 4 and 5 in Scheme 3 suggest that the activation barrier for hydrogen uptake is substantially lower for BN heterocycle material **5** than for the corresponding aromatic carbocycles.

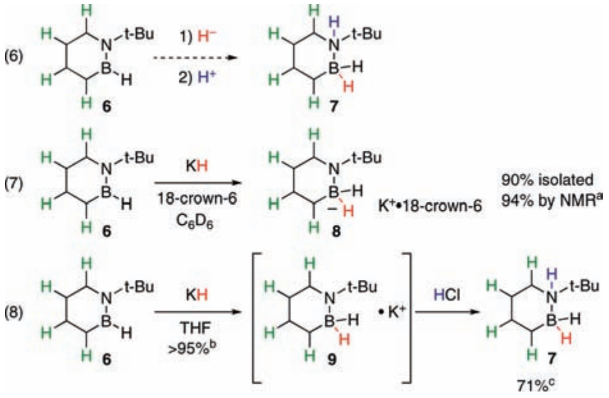
Scheme 3. Partial Regeneration of Spent Fuel Material **5** by Molecular H_2



[a] Determined in C_6D_6 against a calibrated internal standard.

Scheme 3 also reveals that hydrogenation across the BN bond did not proceed with molecular H_2 to furnish the fully charged fuel. To the best of our knowledge, the isolation and characterization of monocyclic BN cyclohexane derivatives (e.g., **7** in Scheme 4) has remained elusive to date.[33] Inspired by Piers' work on Lewis amphoteric *o*-phenylene-bridged aminoboranes,[34] we envisioned that **7** could be prepared from **6** via sequential addition of hydride and proton equivalents (eq 6 in Scheme 4). Gratifyingly, we determined that treatment of **6** with KH in the presence of a crown ether furnished the desired adduct **8** in 90% isolated yield (eq 7 in Scheme 4). The isolated yield is in good agreement with the observed NMR yield. Subsequent protonation of **8** produced the fully charged material **7**, as observed by NMR spectroscopy. However the desired product **7** proved difficult to separate from the remaining crown ether byproduct. We were therefore delighted to discover that the use of 18-crown-6 is unnecessary. Addition of KH to **6** in THF followed by protonation with HCl in a single pot produced the charged fuel **7** in 71% isolated yield over two steps (eq 8 in Scheme 4). Intermediate **9** was formed in high yield as measured by NMR analysis but was not isolated. The regeneration route described by eqs 4 and 8 represents a simple, atom-economical way to regenerate the spent BN heterocycle fuel. We also believe that the synthetic availability of BN cyclohexane derivatives (i.e., fully charged fuel) will now enable studies geared toward hydrogen desorption from these materials. BN cyclohexane **7** is a crystalline solid that has a melting point of 96−98 °C. It does not appear to decompose during melting and freezing cycles.

Scheme 4



[a] Determined in C_6D_6 against a calibrated internal standard. [b] Determined in THF-d_8 against a calibrated internal standard. [c] Isolated yield from **6** over two steps.

We determined the X-ray structures of compounds **7** and **8** (Figure 1), thus unambiguously confirming our structural assignments.[35] Changes in the bond lengths occur upon hydride addition and protonation. We used the previously determined crystal structure of compound **6′**[26] as a model for **6** because **6** is a low-melting liquid. The B−N bond length of 1.403(2) Å in **6′** has substantial double-bond character.[36] Upon addition of a hydride (see compound **8**), the B−N bond distance is significantly lengthened to 1.547(5) Å, which is more typical of a single B−N bond. Protonation on nitrogen leads to further lengthening of the B−N distance to 1.646(2) Å in compound **7**. This is consistent with the more dative rather than covalent bonding between the nitrogen and boron in **7** relative to **8**. The B−N bond distances in AB and Me_2HN-BH_3 in the solid state are 1.564(6) and 1.5965(13) Å, respectively.[37] The increased B−N distance in **7** versus AB and Me_2HN-BH_3 may be due to the steric bulk imposed by the *N*-*t*-Bu group. Also interesting are the changes associated with the B−C distance. The B−C bond lengthens substantially upon hydride addition [1.584(3) Å in **6′** and 1.643(6) Å in **8**]. This is consistent with the change in hybridization of boron from sp^2 to sp^3 and a substantial increase in negative charge at boron. However, upon protonation at nitrogen, the B−C bond distance shortens to 1.615(2) Å in **7**. This contraction is consistent with the decrease in negative charge at boron in **7** relative to **8**. Also apparent from Figure 1 is the pyramidalization of boron and nitrogen upon hydride addition. The sums of the bond angles around boron and nitrogen in **6′** are 359.9(2) and 360.0(2)°, respectively. On the other hand, the corresponding values in **8** are 332.3(3)° for boron and 340.1(4)° for nitrogen, which are much closer to the 328.5° value for a perfect tetrahedron. Protonation at nitrogen results only in minor changes in the pyramidalization of B and N. The sums of the equatorial bond angles around boron and nitrogen in **7** are 329.2(8) and 339.7(1)°, respectively.

We performed a high-level [G3(MP2)] computational analysis of the overall dehydrogenation reaction for selected N-substituted

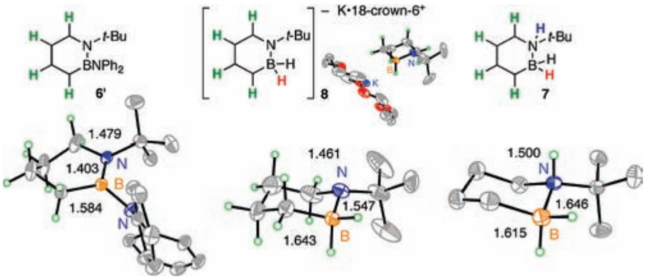
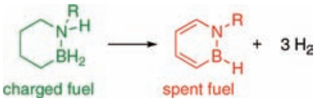


Figure 1. ORTEP illustrations, with thermal ellipsoids drawn at the 35% probability level, of BN heterocycles **6′**, **8**, and **7**.

BN cyclohexane fuels.[38] Table 1 shows that hydrogen release from the charged fuel to produce the spent fuel is endothermic on the enthalpy scale but is essentially thermoneutral at 298 K on the free-energy scale for N-substituted BN cyclohexanes. The thermodynamic properties of these BN heterocycles are relatively independent of the nitrogen substituent, indicating that the results for our model system (R = *t*-Bu) should be applicable to materials with higher storage capacities (e.g., R = H, Me).

Table 1. Electronic Structure Calculations at the G3(MP2) Level (298 K)



entry	R	Δ*H* (kcal/mol)	Δ*G* (kcal/mol)
1	H	23.5	−2.3
2	Me	26.0	−0.3
3	*t*-Bu	25.2	−0.4

In summary, we have described a potentially viable hydrogen storage platform based on well-defined BN heterocycle materials and demonstrated a simple route for the regeneration of model spent fuel material **5** to the charged fuel **7** using H_2 and H^-/H^+ sources. Crystallographic characterization of intermediates along the regeneration pathway established the correct structural assignments, revealing unique bonding changes associated with increasing hydrogen content on boron and nitrogen. While the described regeneration scheme is not yet optimal from an energetic point of view (i.e., the use of highly energetic KH needs to be avoided),[39] the synthetic access to the fully charged BN cyclohexane fuels made possible by this work should enable investigations of these materials in hydrogen desorption studies.

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Supporting Information Available: Experimental procedures, compound characterization data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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