

IV.B.1b Hydrogen Storage by Novel CBN Heterocycle Materials

Shih-Yuan Liu

University of Oregon
Department of Chemistry
1253 University of Oregon
Eugene, OR 97403-1253
Phone: (541) 346-5573
E-mail: lsy@uoregon.edu

DOE Technology Development Manager:
Grace Ordaz

Phone: (202) 586-8350
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire

Phone: (303) 275-4795
E-mail: James.Alkire@go.doe.gov

Contract Number: DE-FG36-08GO18143

Project Start Date: September 1, 2008
Project End Date: March 31, 2012

Objectives

The objective of this project is to develop novel boron-nitrogen heterocycles as liquid-phase hydrogen storage materials with storage capacities and thermodynamic properties that have the potential to lead to rechargeable systems capable of meeting DOE targets. We seek to:

- Develop new materials that:
 - (a) are structurally well-defined along the desorption/absorption processes
 - (b) exhibit appropriate enthalpy of H₂ desorption
 - (c) are liquids at operating temperatures
 - (d) possess high H₂ storage capacities
- Identify catalysts that will release hydrogen from these materials at temperatures <200°C.
- Develop conditions that will readily recharge the spent fuel.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates
- (R) Regeneration Processes

Technical Targets

This project is developing new liquid phase materials for hydrogen storage that can be readily regenerated. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2015 hydrogen storage targets:

- Specific energy: 1.8 kWh/kg (5.5 wt%)
- Energy density: 1.3 kWh/L (4.0 vol%)

Accomplishments

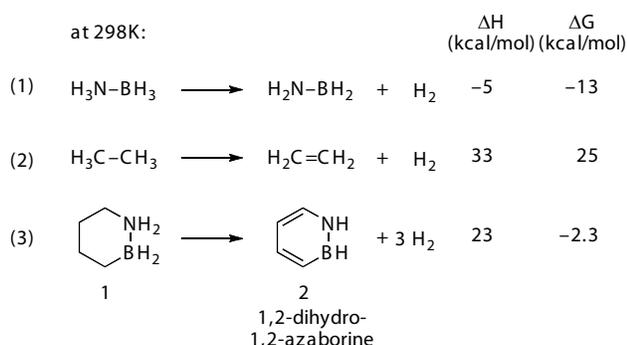
- Selected two materials with favorable thermodynamics to move forward.
- Synthesized all intermediates along the proposed desorption pathway for Material (1).
- Developed a first-fill synthesis of fully charged fuel for Material (1).
- Demonstrated a pathway for regeneration of the spent fuel for Material (1).
- Performed preliminary thermodynamic measurements that corroborate computational predictions for Material (1).



Introduction

Hydrogen storage is a vital component in the development of a hydrogen-based energy infrastructure. Boron-nitrogen containing compounds, e.g., ammonia-borane (H₃N-BH₃ or AB), have attracted much attention as chemical H₂ storage materials because of their high gravimetric hydrogen densities and fast kinetics of H₂ release. This project is developing structurally well-defined liquid carbon-boron-nitrogen (CBN) hydrogen storage materials (i.e., heterocycles containing carbon, boron, and nitrogen) that have the potential to be reversibly regenerated using molecular hydrogen. A liquid phase, hydrogen storage system that can be regenerated using molecular hydrogen is highly desired for many reasons, including versatility, lower cost and improved efficiency, and durability. Such a storage material will allow on-board hydrogen storage. It can also be applied as an off-board energy carrier for vehicle and stationary applications that takes advantage of the existing liquid fuels infrastructure.

Approach



In order to accomplish reversibility, neutrality in free energy of the hydrogen release process (i.e., $\Delta G \sim 0$ kcal/mol) at the operating temperature is pivotal. The dehydrogenation of AB is exergonic by -13 kcal/mol at 298 K (eq. 1). In contrast to AB, the dehydrogenation of its isoelectronic organic counterpart, ethane (CH_3-CH_3), is endergonic by $+25$ kcal/mol (eq. 2). The coupling of endothermic dehydrogenation from BN in a cyclic six-membered framework could lead to a reversible H₂ storage system. Indeed, high-level computational analysis indicates that the release of H₂ from CBN heterocycles such as **1** has favorable overall thermodynamics conducive to reversibility, (e.g., see eq. 3). The potential for reversible hydrogen release/uptake and the relatively high gravimetric hydrogen density of CBN heterocycle materials (e.g. 7.1 wt% for **1**) render their preparation and development an important goal. In a collaborative effort with the Chemical Hydrogen Storage Center of Excellence, this project is investigating several CBN heterocycle materials for H₂ storage applications using a synergistic theoretical and experimental approach. Synthesis will be a crucial

component of this project given the relatively unexplored nature of these CBN heterocycles. The structurally well-defined nature of these CBN heterocycle materials will facilitate their characterization and mechanistic investigation of the proposed desorption/absorption processes.

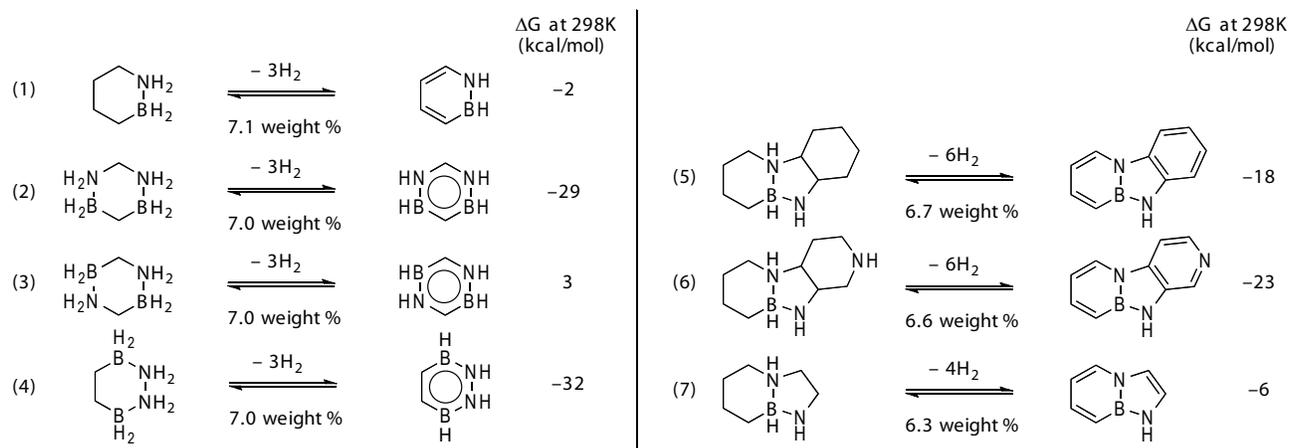
Results

Thermodynamic Analysis of CBN Heterocycle Materials

We used theory to guide our initial target selection for synthesis. Scheme 1 illustrates the calculated thermodynamic data for H₂ desorption for seven proposed CBN materials. Theory predicts that Materials (1), (3), and (7) have the potential for reversibility ($\Delta G \sim 0$ kcal/mol). With the help of theory, and based on availability of synthetic methods, we conclude that our synthetic efforts should be initially directed toward Materials (1) and (7).

Synthesis of Model CBN Heterocycle Materials

The hydrogen release from heterocycle **1** can potentially involve partially spent-fuel intermediates **3-6** (Scheme 2, top). Synthetic access to all compounds on the pathway from the fully charged material **1** to the discharged fuel **2** will be essential to understand and improve the H₂ release and uptake properties of this particular storage system. We pursued the preparation of *N*-protected derivatives **2'-6'** (R = *t*-Bu, Scheme 2, bottom) as models for **2-6** due to their ready availability. High-level calculations show that the thermodynamic properties of CBN Material (1) do not change significantly when the nitrogen is protected with a *t*-Bu group (Scheme 2).



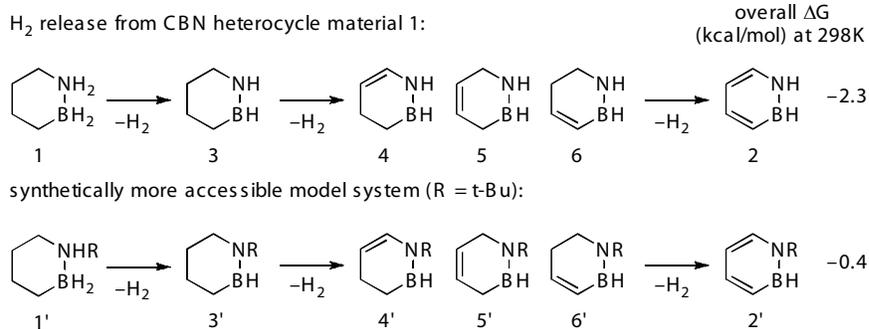
SCHEME 1. Calculated Thermodynamic Properties of CBN Heterocycles

Scheme 3 illustrates the synthesis of 2'-6'. We previously reported the preparation of heterocycle 7, which ultimately serves as the universal precursor to 2'-6'. The yields described in Scheme 3 have not been optimized. Compounds 2'-6' are all liquids with melting points below -30°C.

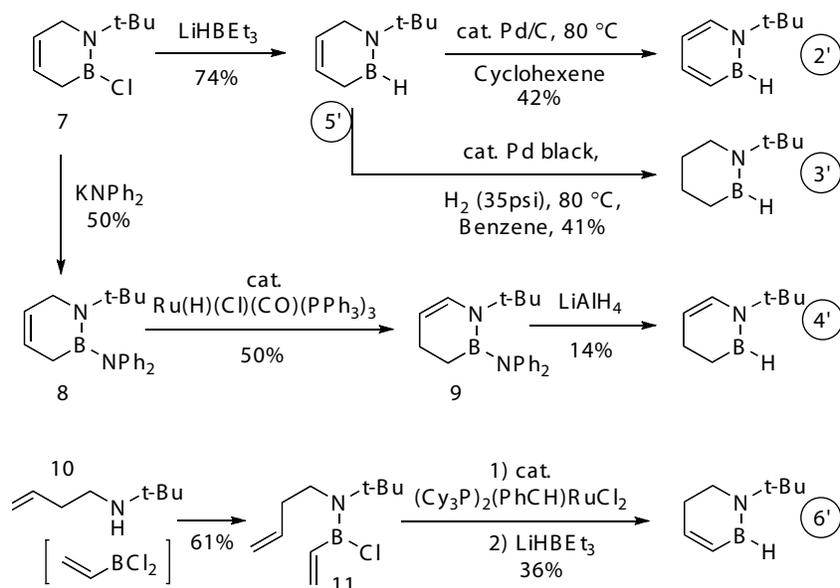
We also developed a first-fill synthesis of the fully charged model fuel 1', thus making all the materials/intermediates along the proposed dehydrogenation pathway synthetically available for further experimental investigation. Scheme 4 describes our synthesis. Reaction of homoallyl bromide 12' with *t*-butylamine produced homoallylamine 13'. Treatment of this amine with BH₃·THF furnished the amine-borane complex 14'. Subsequent intramolecular hydroboration yielded the desired model charged fuel 1' (R = *t*-Bu) with a storage capacity of 4.3 wt%. Replacement of the *t*-butylamine with methylamine gave a material with 6.1 wt% storage capacity, an increase of 42%. The yields described in Scheme 4 have not been optimized.

Development of Conditions/ Catalysts that will Recharge the Spent Fuel

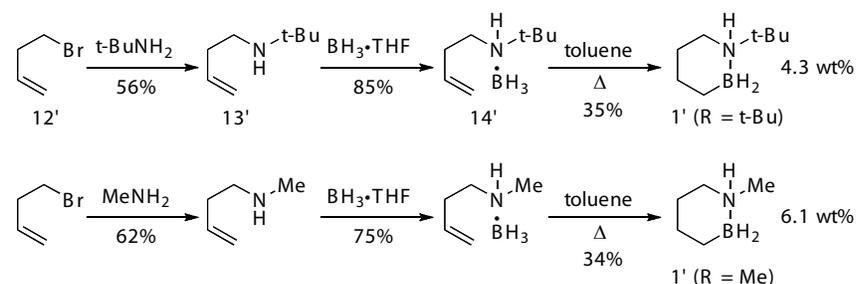
We investigated the regeneration of spent-fuel material 2' using a combination of molecular H₂ and hydride/proton sources. We determined that the spent-fuel material 2' readily takes up two equivalents of molecular H₂ to furnish 3' under mild conditions (Scheme 5). We also established that addition of potassium hydride (KH) to 3' followed by protonation with hydrochloric acid in a single pot gave the desired product 1' in 71% isolated yield. The regeneration route illustrated in Scheme 5 represents a simple and atom economic way to regenerate our spent fuel, with potassium chloride salt being the only byproduct from the regeneration sequence. However,



SCHEME 2. CBN Heterocycle Material (1) and its Model System

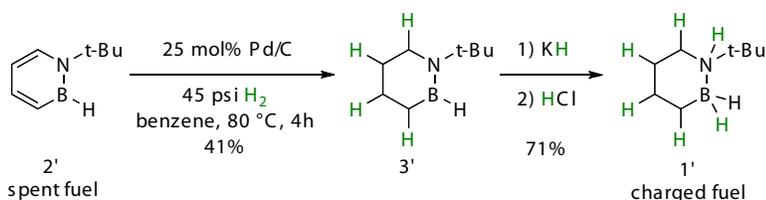


SCHEME 3. Synthesis of Model Compounds of CBN Material (1)

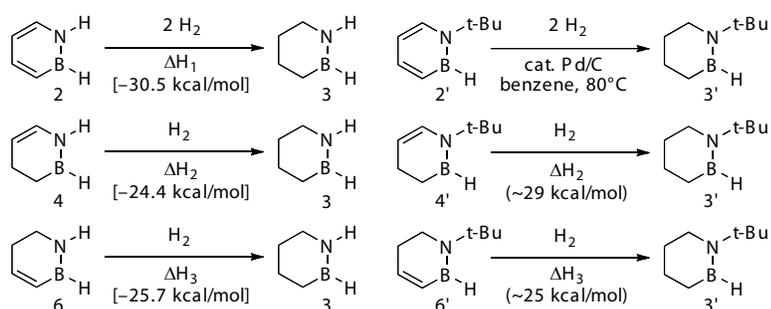


SCHEME 4. First-Fill Synthesis of Model CBN Material (1)

the use of KH needs to be avoided to improve the energy efficiency of the process. The yields described in Scheme 5 have not been optimized.



SCHEME 5. Regeneration of Model Spent Fuel 2'



SCHEME 6. Preliminary Experimental Thermodynamic Data

Preliminary Experimental Thermodynamic Measurements

The availability of **2'**, **4'**, and **6'** allowed us to experimentally assess the thermodynamic properties of CBN material system (1). Scheme 6 shows the calculated hydrogenation enthalpies [in brackets] versus the experimentally determined values (in parenthesis). These hydrogenations were carried out using a homogeneous catalyst $\text{RuCl}_2(\text{PPh}_3)_3$. Thus, calorimetric measurements in general support the computationally determined reaction enthalpy values. We determined that compound **2'** can be readily hydrogenated using Pd/C as a catalyst. However, we were unable to measure the hydrogenation enthalpy of this reaction due to the heterogeneous reaction conditions. $\text{RuCl}_2(\text{PPh}_3)_3$ did not promote the hydrogen uptake of **2'**.

Conclusions and Future Directions

In summary, we developed a versatile synthetic toolbox for the preparation of novel CBN heterocycle H_2 storage materials, including a first-fill synthesis of the charged fuel, the synthesis of the spent fuel, and all proposed partially spent fuel along the desorption pathway. The synthetic availability of CBN heterocycle materials enabled us to 1) determine preliminary thermodynamic data and 2) demonstrate a pathway for regeneration of the spent fuel. In Fiscal Year 2011, we will:

- Optimize our current synthetic toolbox with regard to yields.
- Complete experimental thermodynamic properties for model CBN heterocycles using appropriate homogeneous catalysts.
- Improve energy efficiency for recharging the spent fuel.
- Develop conditions/catalysts for H_2 desorption for CBN materials.
- Formulate the charged fuels as liquids.

FY 2010 Publications/ Presentations

1. "Dehydrogenation Reactions of Cyclic $\text{C}_2\text{B}_2\text{N}_2\text{H}_{12}$ and $\text{C}_4\text{BNH}_{12}$ Isomers"; Matus, M.; Liu, S.-Y.; Dixon, D.A. *J. Phys. Chem. A* **2010**, *114*, 2644-2654.
2. Hydrogen Storage by Boron-Nitrogen Heterocycles: A Simple Route for Spent Fuel Regeneration"; Campbell, P.; Zakharov, L.; Grant, D.; Dixon, D.A.; Liu, S.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 3289-3291.
3. "Microwave Spectrum, Structural Parameters, and Quadrupole Coupling for 1,2-Dihydro-1,2-azaborine"; Daly, A.M.; Tanjaroan, C.; Marwitz, A.J.C.; Liu, S.-Y.; Kukulich S.G. *J. Am. Chem. Soc.* **2010**, *132*, 5501-5506.
4. "Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles"; Liu, S.-Y.; *Boron in the Americas XII Meeting*, East Lansing, MI, June 2010.
5. "Hydrogen Storage by Novel CBN Heterocycle Materials"; Liu, S.-Y.; oral presentation at the *D.O.E. Hydrogen Annual Review*, Washington, D.C., June 2010.
6. "Hydrogen Storage by Novel CBN Heterocycle Materials"; Liu, S.-Y. International Energy Agency, Hydrogen Implementing Agreement *Task 22 Expert Meeting*, Death Valley, NV, April 2010.
7. "BN Heterocycles for Hydrogen Storage"; Patrick G. Campbell, Shih-Yuan Liu; *Materials Science Institute Conference*, Gleneden Beach, OR, December 2009.
8. "Hydrogen Storage by CBN Heterocycle Materials"; Liu, S.-Y.; *Seminar at San Francisco State University*, San Francisco, CA, October 2009.
9. "Hydrogen Storage by CBN Heterocycle Materials"; Liu, S.-Y.; Washington, DC, *American Chemical Society National Meeting 238 Symposium "Advances in Experimental and Computational Studies of Materials for Hydrogen Storage"* (FUEL 297), August 2009.