Hydrogen Storage by Novel CBN Heterocycle Materials

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Detroit, March 19, 2009
In partnership with the Chemical Hydrogen Storage Center of Excellence

STP_16_Liu

Overview

Timeline

start date: September 2008
end date: August 2011
percent complete: 22%

Barriers

A. system weight and volume
C. efficiency
R. regeneration process

Budget

total project funding: $930,855
DOE share: $742,395
UO share: $188,460

FY09 funding: $275,000

Project Collaborators

THE UNIVERSITY OF ALABAMA — Prof. David Dixon

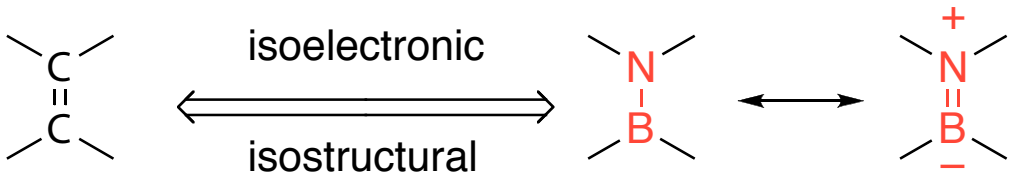
Pacific Northwest NATIONAL LABORATORY — Dr. Tom Autrey

UNIVERSITY OF WASHINGTON — Prof. Karen Goldberg
Prof. Mike Heinekey

Executive Summary

- A new project as part of the CHSCoE
- Focus on cyclic H_2 storage materials containing C, B, and N
- New approach to H_2 storage that complements the materials currently under investigation
- These CBN materials can meet the DOE targets
- Couple *exothermic* H_2 desorption from *BN* with *endothermic* H_2 desorption from *CC* in a *cyclic* system to address reversibility
- Strong collaborative effort with feedback loops between theory, synthesis, catalysis, and charge/discharge characteristics measurements
- Progress: synthesized CBN materials, demonstrated facile H_2 absorption, received attention in general science news media

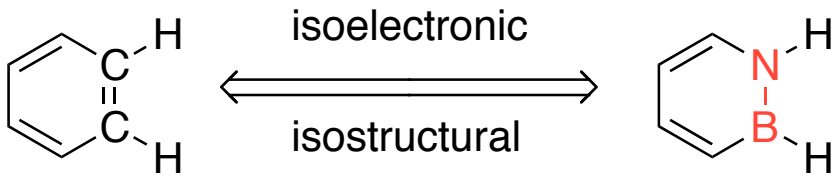
Research in the Liu Group - Relevance



benzene

1,2-dihydro-
1,2-azaborine

- important
- ubiquitous



Scientific Research:

synthesis
structure, bonding
aromaticity
catalysis, mechanism

Applications:

new synthetic methods
biomedical applications
optoelectronic materials
H_2 storage materials

Project Objectives - Relevance

Develop CBN heterocycles as novel hydrogen storage materials:

- liquid-phase
- gravimetric density (> 6 wt. %)
- volumetric density (> 4.5 vol. %)
- thermodynamics (H_2 absorption and desorption)
- regeneration (reversibility)
- 2010 DOE targets

Specific objectives – Phase I (9/1/2008 – 3/31/2010):

- calculate thermodynamic properties of CBN heterocycle materials
- synthesize liquid phase CBN heterocycle materials
- determine thermodynamic properties for CBN heterocycles via experiment
- identify best theoretical model

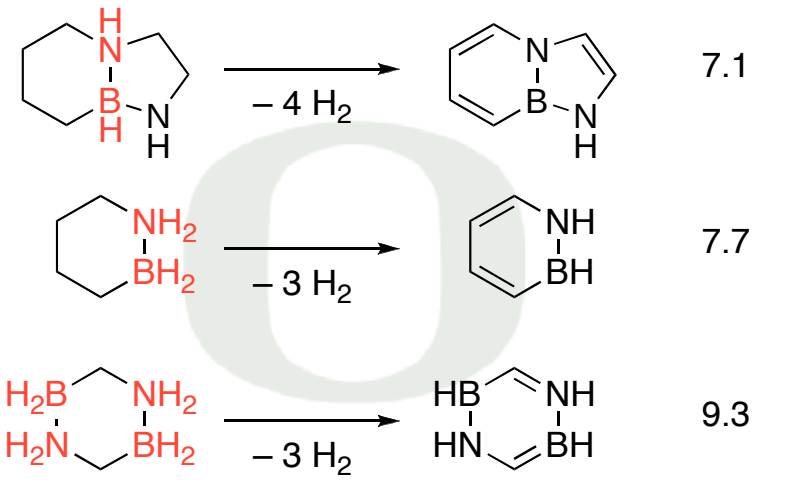
- develop/identify catalysts for H_2 absorption and desorption to/from CBN heterocycles
- demonstrate reversibility

Approach

couple *exothermic* H_2 desorption from *BN* with *endothermic* H_2 desorption from *CC* in a *cyclic* system to achieve optimal thermodynamics for the overall H_2 absorption/desorption process

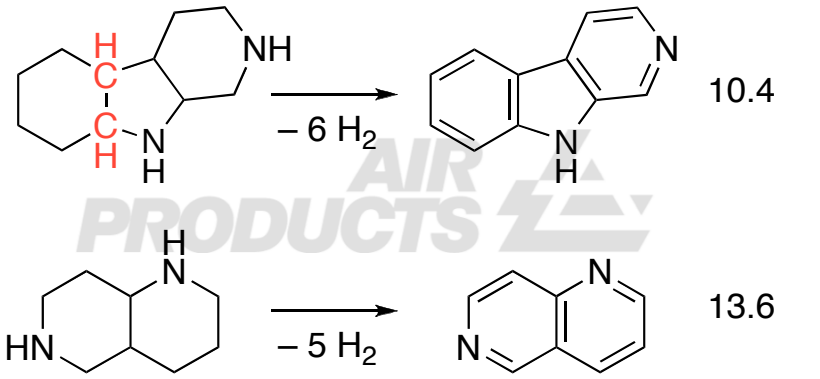
Goal: spent fuel can be directly regenerated on-board with H_2

avg. ΔH (kcal/mol H_2)



Distinct from Air Products approach

- contains boron
- one CC is replaced by BN
- lower activation energy in some of the steps
- synergistically combines features of ammonia borane and cyclic systems



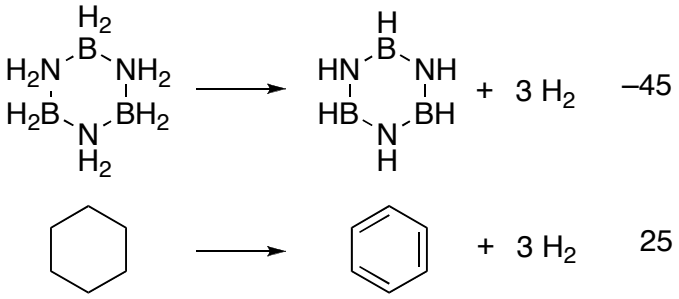
A Collaborative Approach

(calculate, synthesize, measure, optimize)

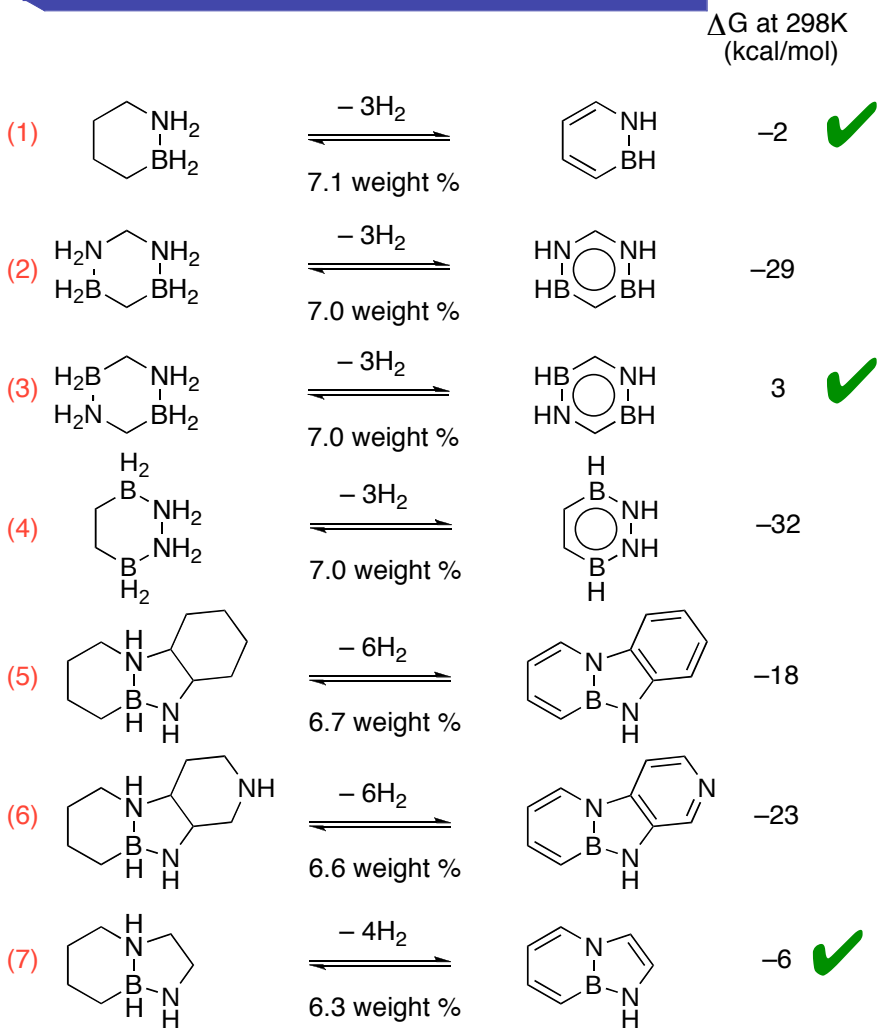
$$\Delta G = \Delta H - T\Delta S$$

reversible H_2 storage: $\Delta G \sim 0$!

@ 298K: ΔG (kcal/mol)



Use theory to help select synthetic candidates



Approach - Summary

- distinct from ammonia borane and cylic systems currently under investigation; complements the current approaches
- addresses technical barriers (system weight and volume, efficiency, regeneration)
- synergistic theoretical and experimental strategy (feedback loop for optimization)
- collaborative effort with CHSCoE partners (UA, PNNL, UW)

Milestones (Phase I)

- computational thermodynamic data of H_2 desorption of CBN heterocycle materials
- availability of CBN heterocycle materials for experimental investigation
- experimental thermodynamic data for CBN materials for comparison with theory
- selection of best theoretical models based on experiment

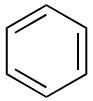
- identification of optimal catalysts/conditions for H_2 desorption from CBN materials and for regeneration of spent fuel

Go/no-go decisions (Phase I)

- go: if materials are synthetically readily available
  no-go: if materials are synthetically not accessible
- go: if materials exhibit appropriate thermodynamic properties (theory + experiment)
  no-go: if materials do not exhibit appropriate thermodynamic properties (theory + experiment)

Developing Synthetic Tools - Progress

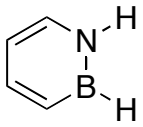
organic



benzene

Faraday
(1825)

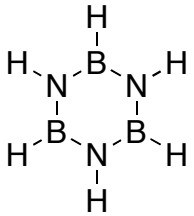
hybrid
organic/inorganic



1,2-dihydro-
1,2-azaborine

(2008)

inorganic



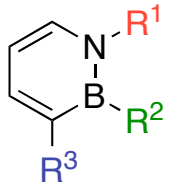
borazine

Stock
(1926)

Adam Marwitz

Myrna Matus

Angew. Chem. Int. Ed.
2009, *48*, 973-7.

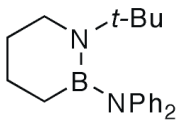


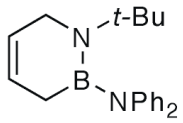
Adam Marwitz

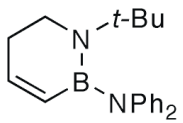
Org. Lett. **2007**, *9*, 4905-8.

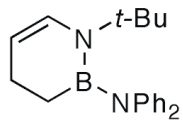
J. Am. Chem. Soc.
2008, *130*, 7250-2.

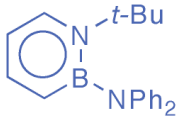
Eric Abbey

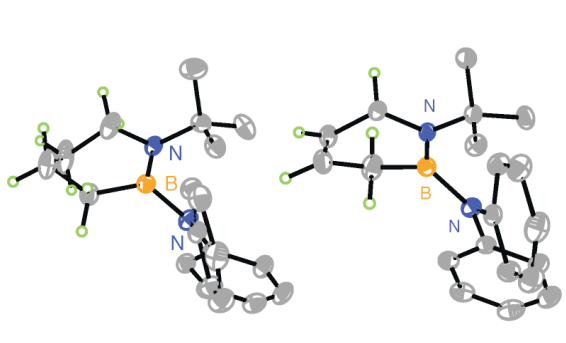








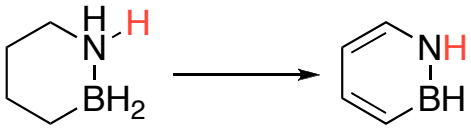




Several new materials have been prepared

Model for C_4BNH_x System - Progress

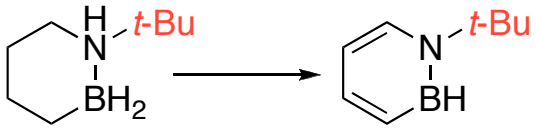
Material (1)



ΔG at 298K (kcal/mol) = –2.3

vs.

more readily available model of (1)

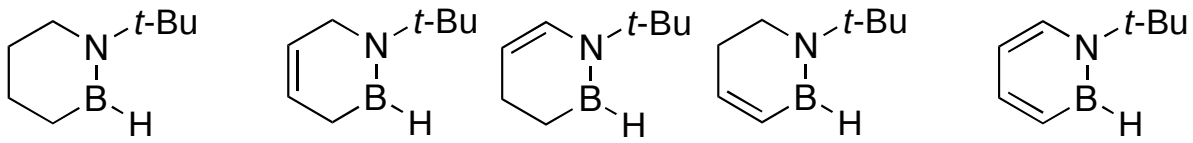


ΔG at 298K (kcal/mol) = –0.4

- similar thermodynamic properties, thus appropriate model

- **successfully prepared all five isomers of the model material**

✔

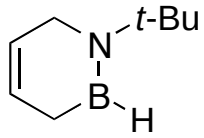


- compounds delivered to UW for H_2 absorption/desorption studies

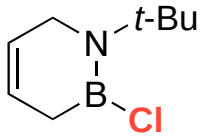
- compounds essential for obtaining experimental thermodynamic data at PNNL

Assessing the Volumetric Density - Progress

- halogenated materials exhibit higher volumetric density



vs.

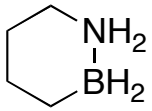


d = 0.849 kg/L

d = 1.005 kg/L

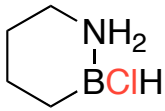
- **CBN materials can meet the 2010 volumetric density targets**

Mw: 85
7.1 wt. %



assuming "d = 0.849"
0.060 kg H_2/L, i.e., 6.0 vol. %

Mw: 119
5.0 wt. %

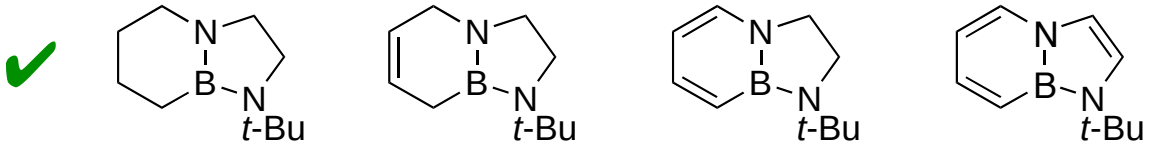


assuming "d = 1.005"
0.050 kg H_2/L, i.e., 5.0 vol. %

- boron substituents might be used to modulate thermodynamic properties without significant loss in volumetric density

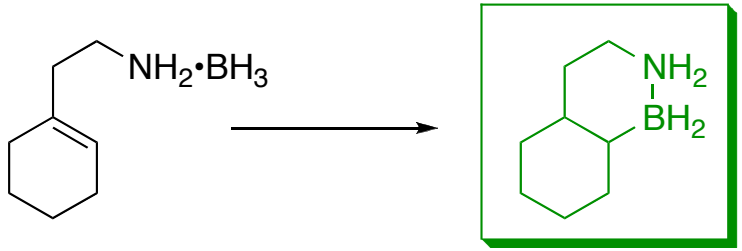
Toward CBN Material (1) and (7) - Progress

- Eric Abbey: *N*-substituted model of CBN Material (7)

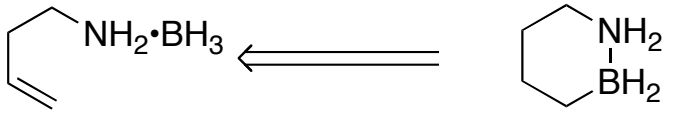


- Kshitij Parab: unsubstituted CBN Material (1)

Vedejs et al., *J. Am. Chem. Soc.* **2003**, *125*, 10502-3.



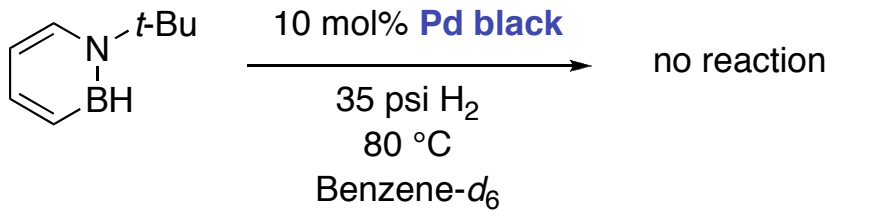
original published procedure not reproducible in our hands; successfully developed new conditions for the synthesis.

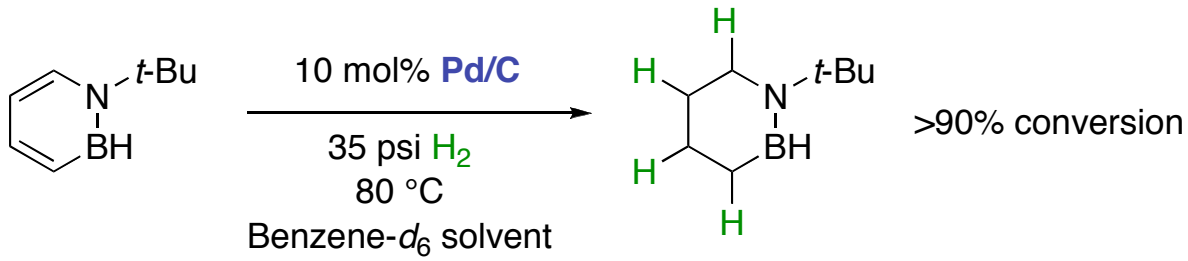


development of unsubstituted CBN Material (1) in progress

More materials are in route

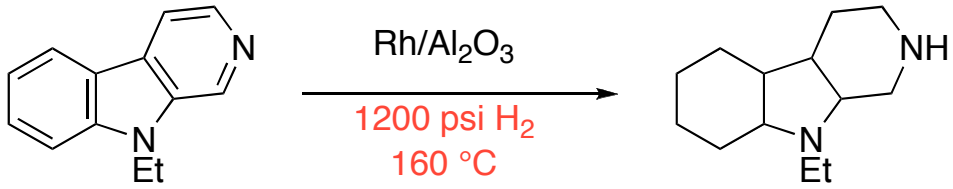
Facile Hydrogen Uptake - Progress





Benzene-d_6 is not hydrogenated!

vs.



Hydrogen uptake has been observed

Collaborations

Project Collaborators

THE UNIVERSITY OF ALABAMA

computational studies of H_2 desorption pathways of cyclic CBN materials, evaluation of thermodynamics and energetics

Pacific Northwest NATIONAL LABORATORY

experimental mechanistic studies of H_2 absorption/desorption to/from cyclic CBN materials, thermodynamic measurements using reaction calorimetry, H_2 charge/discharge characteristics

UNIVERSITY OF WASHINGTON

development/discovery of efficient catalysts for H_2 desorption from CBN materials

Technology Transfer

THE UNIVERSITY OF ALABAMA

obtained computed thermodynamic data and H_2 desorption reaction pathways for CBN heterocycle materials, will provide feedback with experimental data

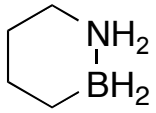
Pacific Northwest NATIONAL LABORATORY

obtained very preliminary thermodynamic data via reaction calorimetry

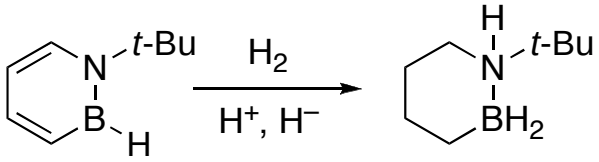
UNIVERSITY OF WASHINGTON

prepared CBN heterocycle materials and delivered to UW for further investigation

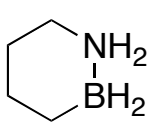
Proposed Future Work

- synthesize 

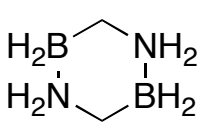
- determine charge/discharge characteristics
- demonstrate regeneration of spent fuel using the model system



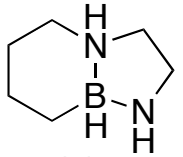
- experimental thermodynamic data for CBN heterocycle materials for comparison with theory, provide feedback loop to optimize theoretical modeling
- focus on developing CBN Materials (1), (3), and (7)



(1)



(3)



(7)

- develop/identify efficient catalysts for H_2 desorption from these CBN materials

The proposed work will be carried out in collaboration with other center partners:

THE UNIVERSITY OF ALABAMA

optimization of theory
thermodynamics
transition states

Pacific Northwest NATIONAL LABORATORY

charge/discharge characteristics
mechanistic studies
thermodynamic data

UNIVERSITY OF WASHINGTON

catalyst development
couple exothermic H_2 desorption from BN
with endothermic H_2 desorption from CC

Project Summary

Relevance:	development of novel liquid phase hydrogen storage materials with desirable storage capacity and thermodynamics for reversible H_2 absorption and desorption
Approach:	coupling of exothermic H_2 desorption from BN with endothermic H_2 desorption from CC in a cyclic system to achieve optimal thermodynamics for H_2 absorption/desorption; distinct from amine-borane and cyclic materials currently under investigation
Progress:	**• developed synthetic tools for CBN heterocycle materials** **• prepared set of heterocycle CBN materials for H_2 absorption/ desorption studies, delivered to partners within the CHSCoE** **• demonstrated facile H_2 absorption by CBN heterocycle materials**
Collaborations:	active partnership with CHSCoE members (UA, PNNL, UW)
Future Work:	• further develop the synthesis of CBN Heterocycle Materials (1), (3), and (7) • obtain experimental thermodynamic data for CBN materials • determine/optimize H_2 charge/discharge characteristics