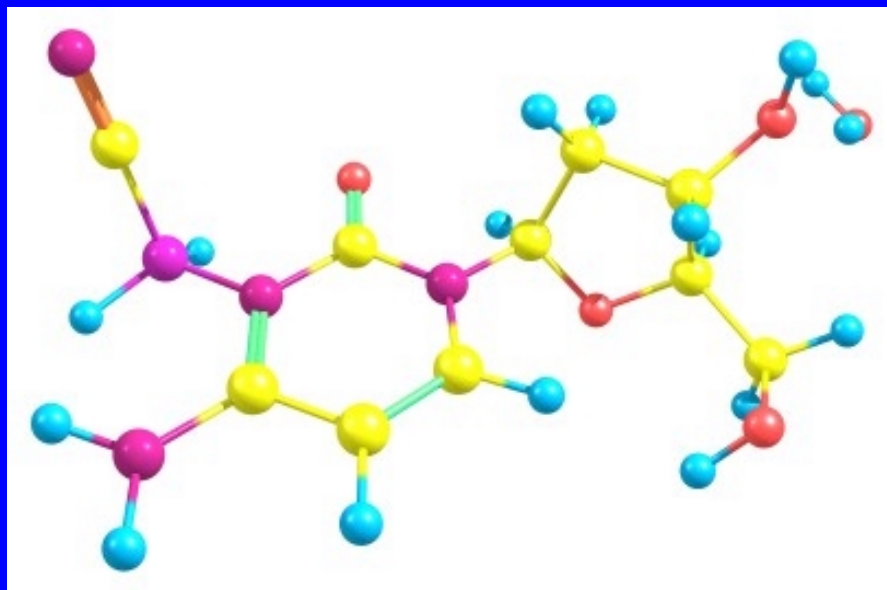


Dihydrogen Bonds and Ducks

If It Walks Like a Duck and
Quacks Like a Duck,
Is It a Duck?

Mark A. Zottola
University of
Alabama-Birmingham

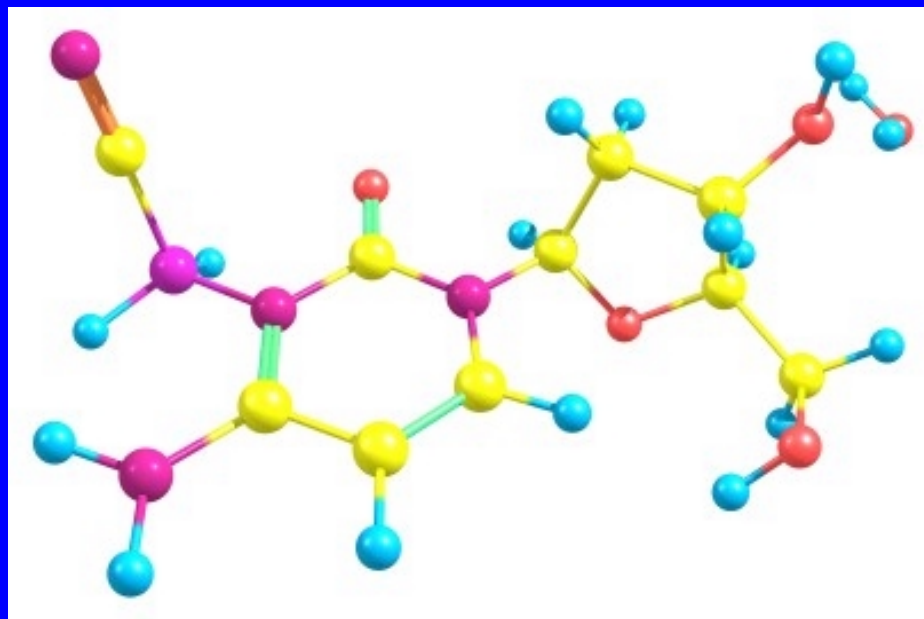
BK1157 – The First Reported Dihydrogen Bond



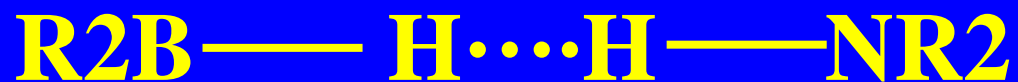
- Hydrogen positions were refined, not assigned
- Contacts between BH HN and BH HO (H2O)

1993 – The Dihydrogen Bond Postulated as a Hydrogen Bond

- Calculations at MP2/6-31g**
 - Strength of complexes mirrored Bronsted acidity of hydrogen bond donor
 - Frozen core MP2 calculations implied the dihydrogen interaction preferred to be with one hydrogen

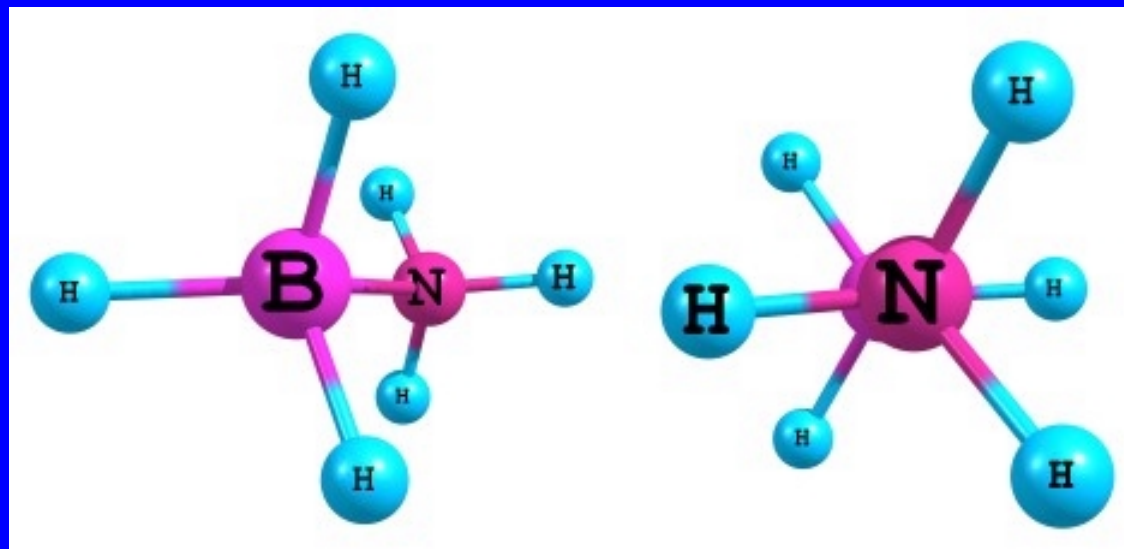


Borazane and the Geometrical Preferences of the Dihydrogen Bond



- CSD search revealed wide range of (B)HHN and (N)HHB angles
 - $D_{\text{H-H}}$ Avg. 1.96 Å, 1.7 – 2.2 Å, 0.13 Å
 - **NH**··**HB** (Ψ) Avg. 149°, 117 – 171°, 17°
 - **BH**··**HN** (θ) Avg. 120°, 90-171°, 26°

Borazane and the Dihydrogen Bond



- Calculations (parameterized CI) reveal
 - $D_{\text{H-H}}$ 1.82 Å, $\Psi = 158.7^\circ$, $\theta = 98.8^\circ$
 - $\Delta E(\text{H-H}) = 6.1$ Kcals per interaction

Dihydrogen Bonds Follow Classical Definition of Hydrogen Bonds

- Directionality
 - High level calculations show dihydrogen interactions prefer one hydrogen over another
 - Spherical symmetry of 1s orbitals mean wide range of acceptable geometries
 - Crystallographic database work bears this out
- Strength
 - Strength of dihydrogen bonds follows Bronsted acidity of donor hydrogen

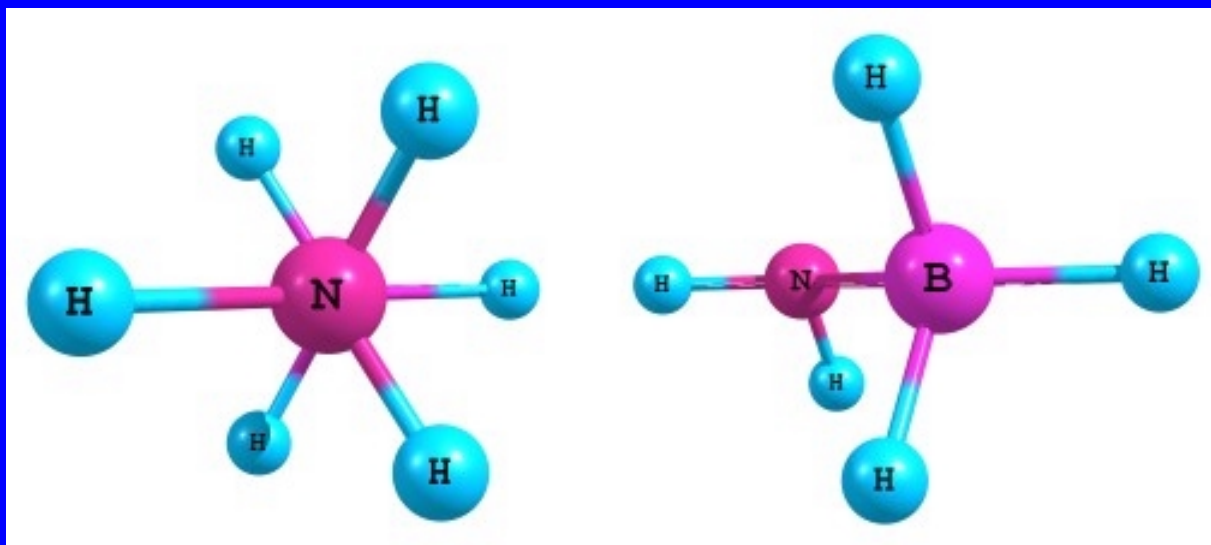
Is The Dihydrogen Bond a Hydrogen Bond?

- Atoms in Molecules (AIM) Theory
 - Developed by Bader
 - Analyzes the electron topology based on QM wavefunction
- Popelier
 - Borrowed concepts developed by Bader
 - Examined Borazane ($\text{H}_3\text{B}-\text{NH}_3$) dimer for evidence of hydrogen bonding

Popelier's Criteria For Hydrogen Bonds

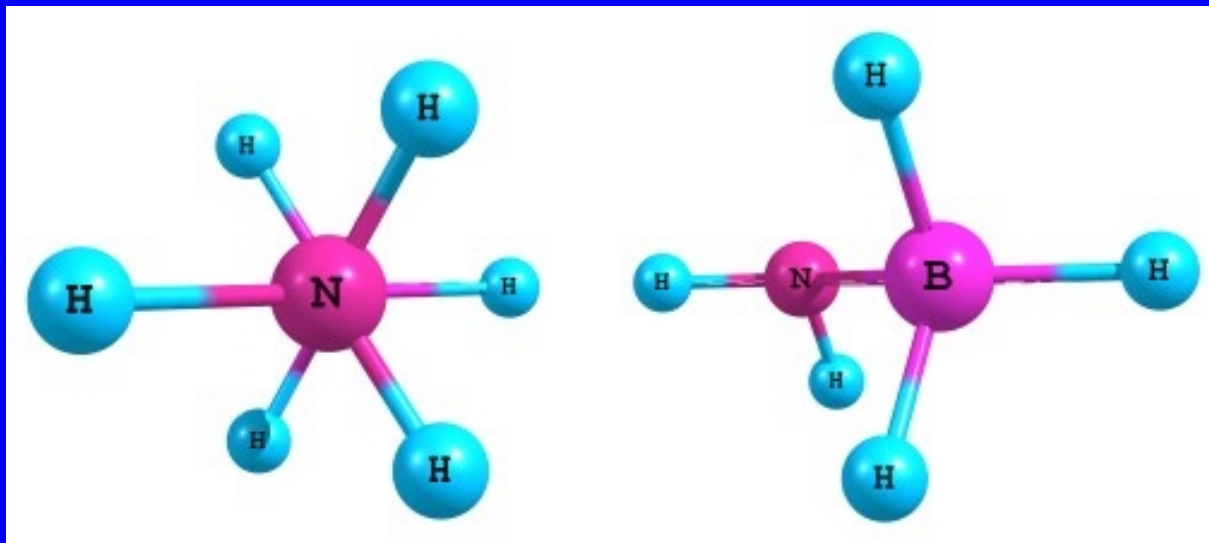
- Bond must have a bond critical point (BCP) and bond path (BP) connecting hydrogen bond donor and acceptor
- Electron density at bcp from 0.002-0.035 au
- Laplacian ranges +0.024 to +0.135 au
- Mutual overlap of donor and acceptor
- Donor should have increased positive charge, decreased dipolar polarization and a decrease in the atomic volume

Examination of Borazane Dimer by Popelier



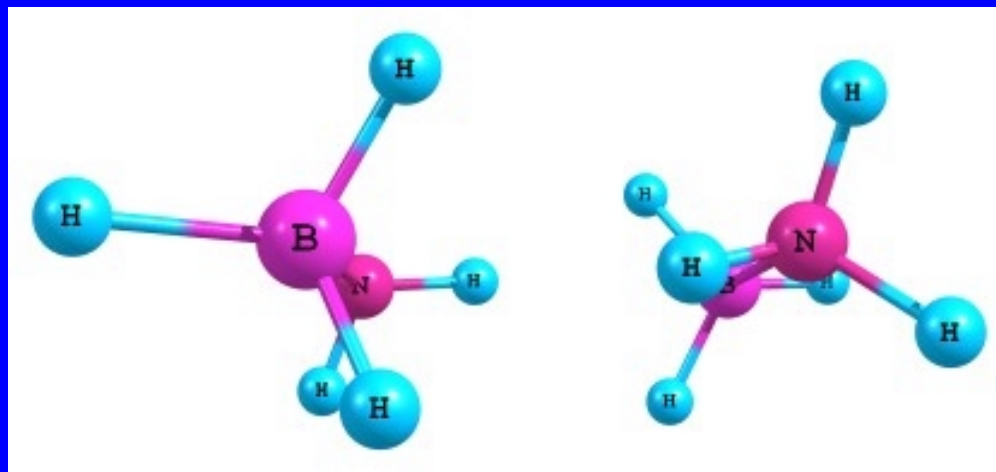
- Calculated structure using mp²/6-31g**
- The BH – HN interactions met all criteria
- Thus dihydrogen bonds were indeed hydrogen bonds

But Is It?



- Structure is not the ground state but a transition state
- Global minimum depends on whether one uses full or frozen core MP²!

Questioning The Calculations On Dihydrogen Bonds



- Is this interaction real?
 - Are ground state molecules seeing this effect?
- What is the appropriate level of theory for studying this?
 - Is MP² (frozen core) appropriate?

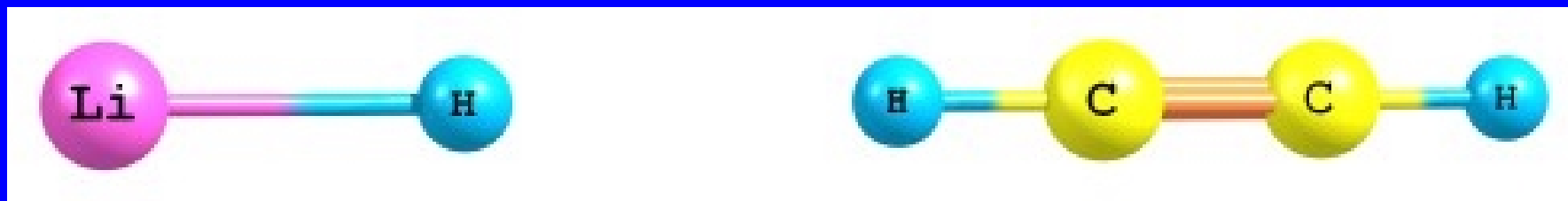
More Questions on Dihydrogen Bonds in Borazane Dimer

- How strong is the interaction?
 - What role do dipolar interactions play
- How similar is this to a “normal” hydrogen-bonded system?
 - Can this interaction be tuned to acceptor strength
 - Is this as reversible as a hydrogen bond?
 - Can dihydrogen bonds exhibit cooperativity?

Re-Examination of The Borazane Dimer

- Frozen core vs. Full
 - Frozen core calculations result in asymmetric structures
 - No obvious rationale for this result
 - Full MP² calculations including core orbitals give perfectly symmetric structures
 - Therefore gold-standard MP2(full) with an augmented Dunning correlation consistent double zeta basis set should work well

Death of The Gold Standard



- Examination of a paper by Grabowski et al on Metal hydrides with mildly acidic hydrogens
 - “Gold Standard” calculations performed
 - Interaction energy of ~ 4 kcal/mol
 - Bond lengths for metal hydrides seemed off

Metal Hydrides as a Function of Basis Set and Method

Hydride	Li-H	Na-H	K-H
experimental	1.5949	1.8873	2.2440
6-311++G(2d,p)			
B3LYP	1.5949	1.8873	2.2444
B3PW91	1.5992	1.8946	2.2440
MPW1PW91	1.5983	1.8923	2.2423
MP2(fc)	1.5976	1.9050	2.2454
MP2(full)	1.5948	1.8883	2.2444
CCSD	1.5991	1.9102	2.2654
aug-cc-pVDZ			
MP2(fc)	1.6197	1.9199	2.2440
MP2(full)	1.5957	1.9008	2.2440
CCSD	1.6252	1.9288	na

Dihydrogen As a Function of Basis Set and Method

Experimental value 0.7414 (0.0000)

aug-cc-pVDZ

6-311++G(2d,p)

B3LYP 0.7608 0.0194

B3LYP 0.7442 0.0028

MPW1PW91 0.7588 0.0174

MPW1PW91 0.7444 0.0030

MP2(fc/full) 0.7549 0.0135

MP2(fc/full) 0.7383 -0.0031

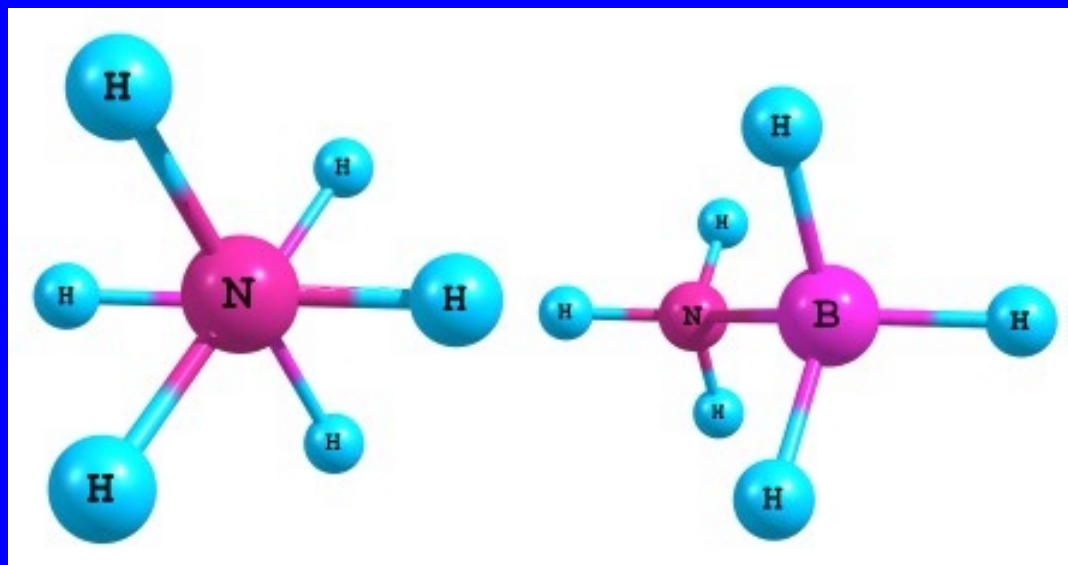
CCSD 0.7617 0.0203

CCSD 0.7435 0.0021

Conclusions On Calculations

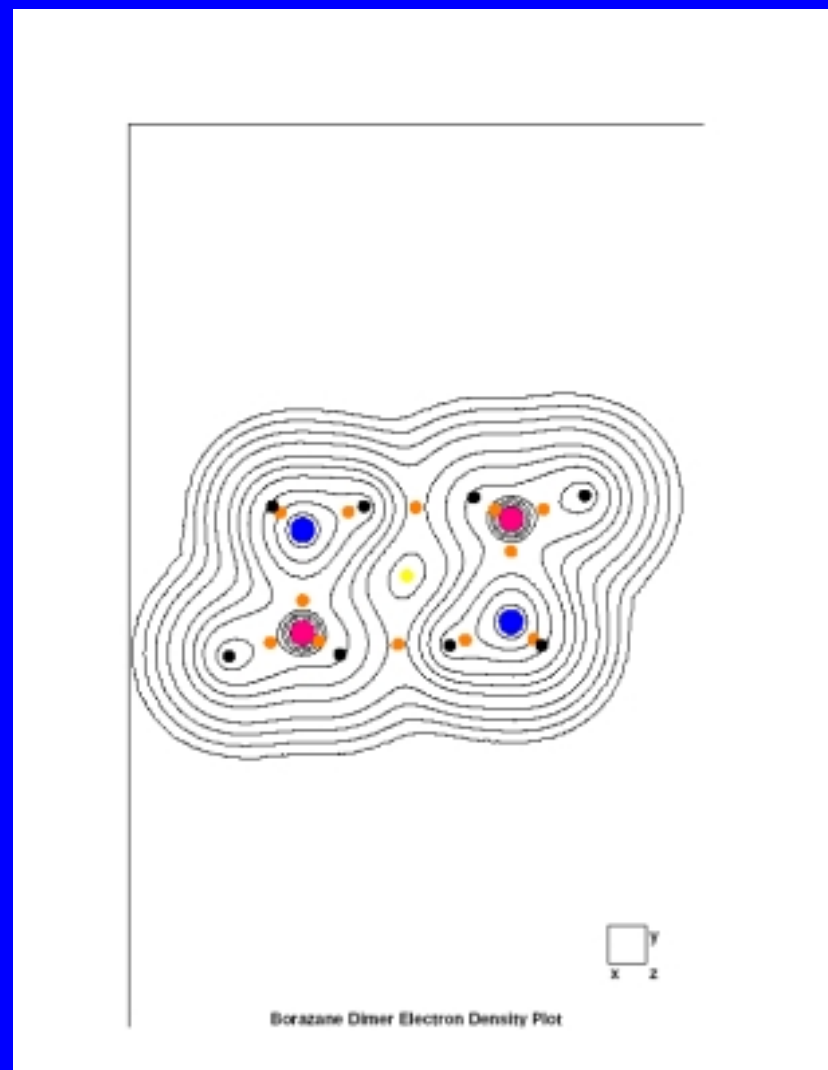
- MP2 calculations with Dunning's double zeta basis sets are inherently unreliable
 - The structures for simple metal hydrides and molecular hydrogen cannot be reliably reproduced
- Pople's triple split basis set a better choice
 - Calculations are less time consuming
 - DFT methods can be superior to higher order methods

Are Dihydrogen Bonds Possible in The Ground State?



- Borazane dimer with MP²(full) or MPW1PW91 with 6-311+g(2d,p) symmetric
- Structures still meet Popelier criteria for hydrogen bonds
- This is a ground state interaction

Electron Density Plot For Borazane Dimer



Ground State Dihydrogen Bonds?

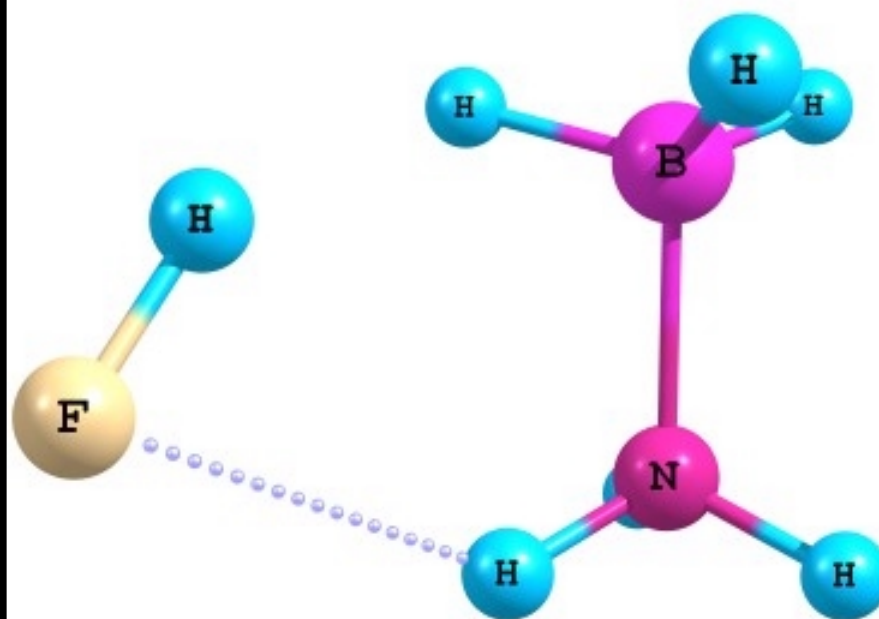
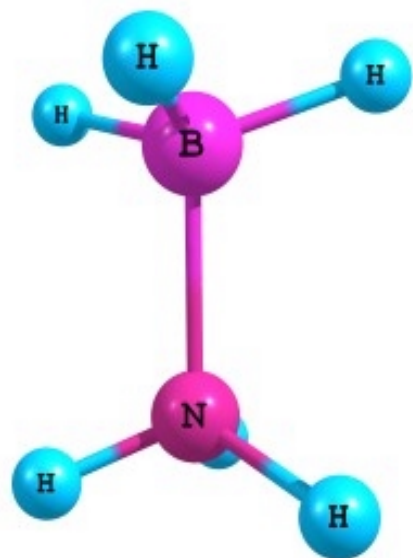
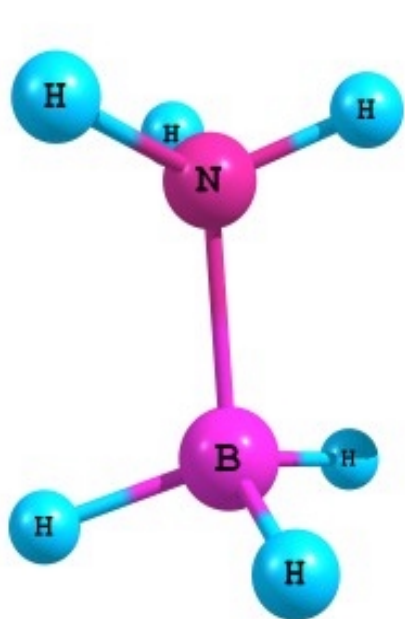
	Dihydrogen Bond Donor	Dihydrogen Bond Acceptor
Charge	0.394	-0.647
Dipole Polarization	-0.00571	-0.1801
Volume	30.20	85.84
ρ (dimer)	0.01726	-0.012 (Laplacian)
Dimer		
Charge	0.439	-0.646
Dipole Polarization	-0.00991	-0.1803
Volume	21.78	81.45
Boron ($Q_{zz}/V/q$)	-0.0568/24.13/+1.847	0.0564/25.55/+1.842

- Borazane dimer has locative dihydrogen interaction
- Evidence barely supports dihydrogen interaction

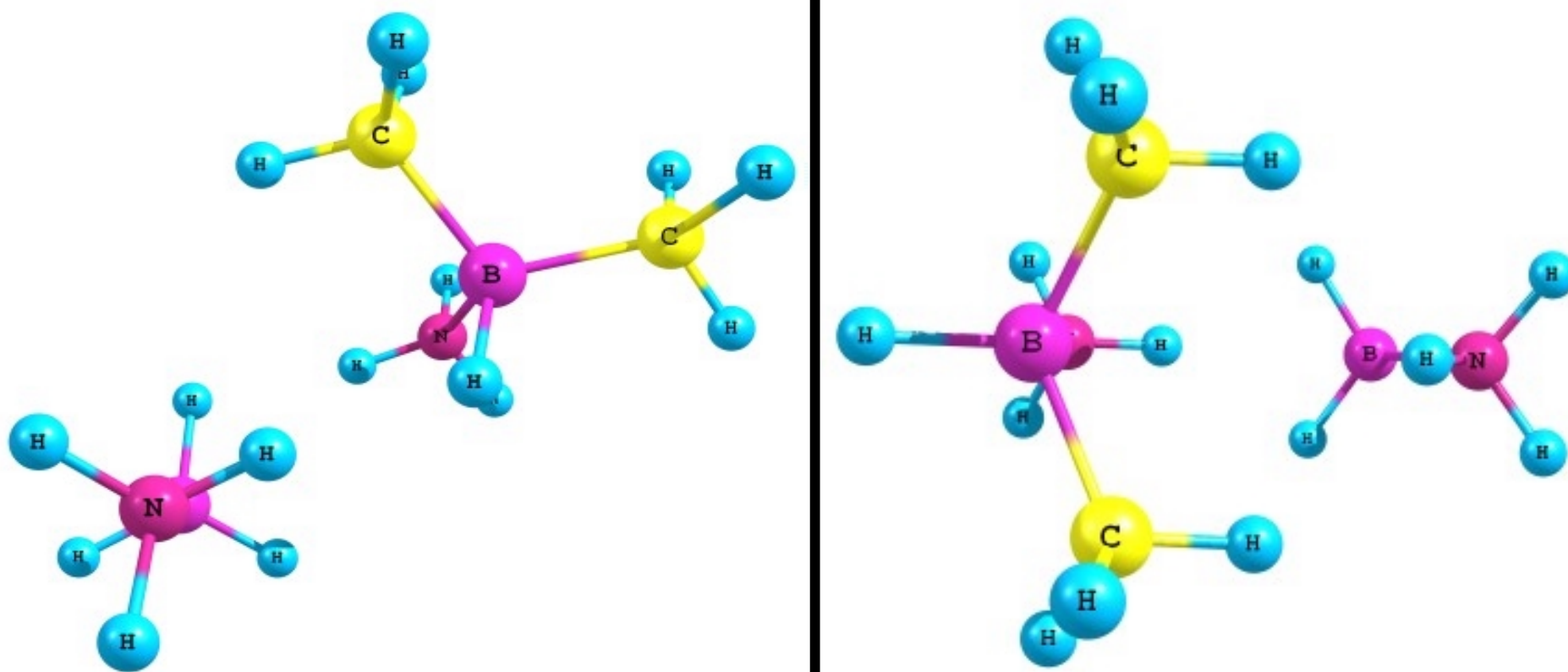
How Strong Are Dihydrogen Bonds?

- Complexes of water or HF with borazane have interaction energies of 6 – 8 kcal/mol
- Crabtree reported a value of 6.1 kcal/mol from borazane dimer
- What is role of dipole stabilization in these systems?
 - How much do electrostatics dominate the dihydrogen bond?
 - Which is stronger – dipolar interaction or the dihydrogen bond?

Assessing The Role of Dipolar Interactions

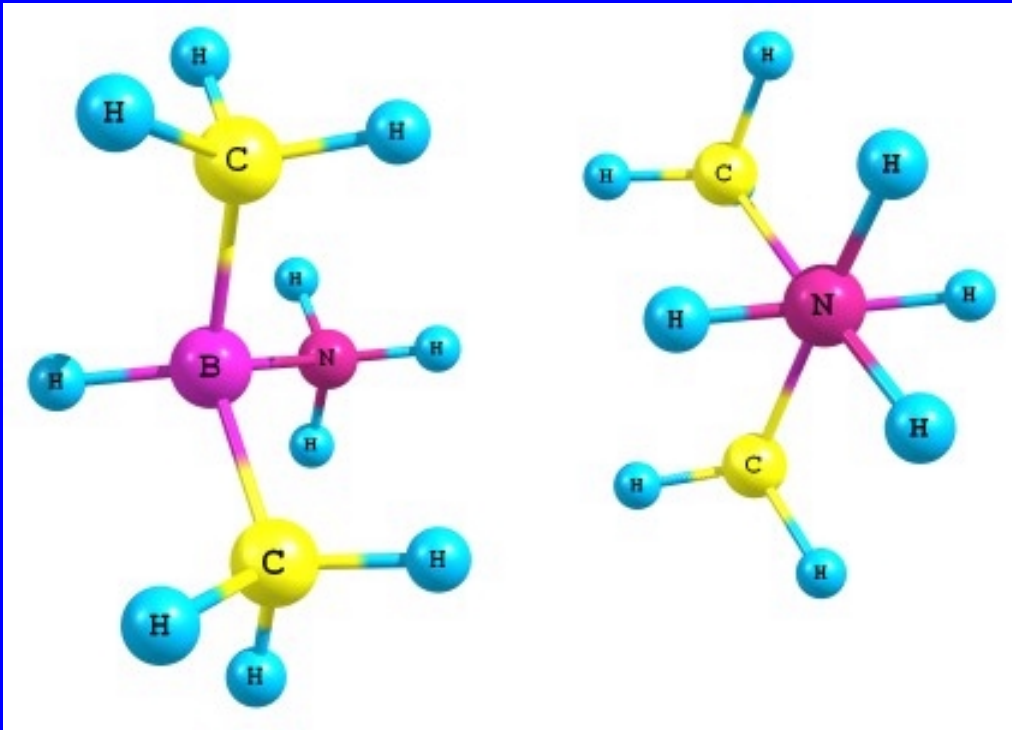


Assessing The Role of Dipolar Interactions



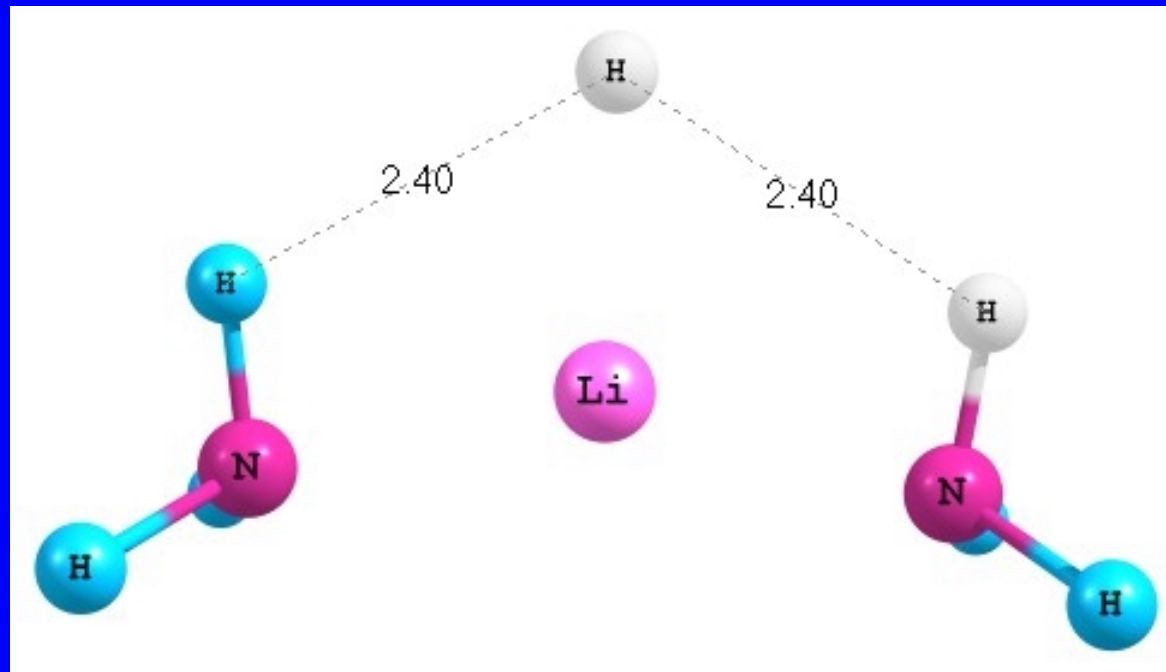
Closing The Circle

- $dE = 3.34$ kcal/mol
 - Approximate energy of dihydrogen bond is 4.6 kilocalories
 - Explains Crabtree neutron diffraction structure of borazane

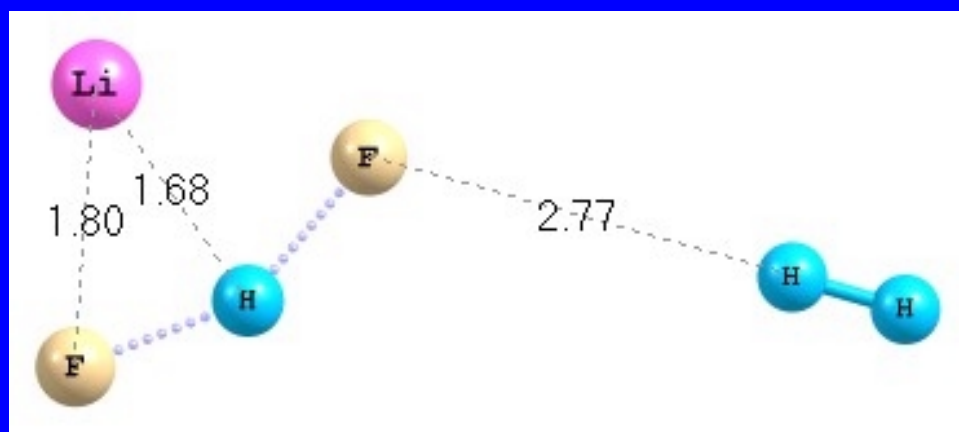
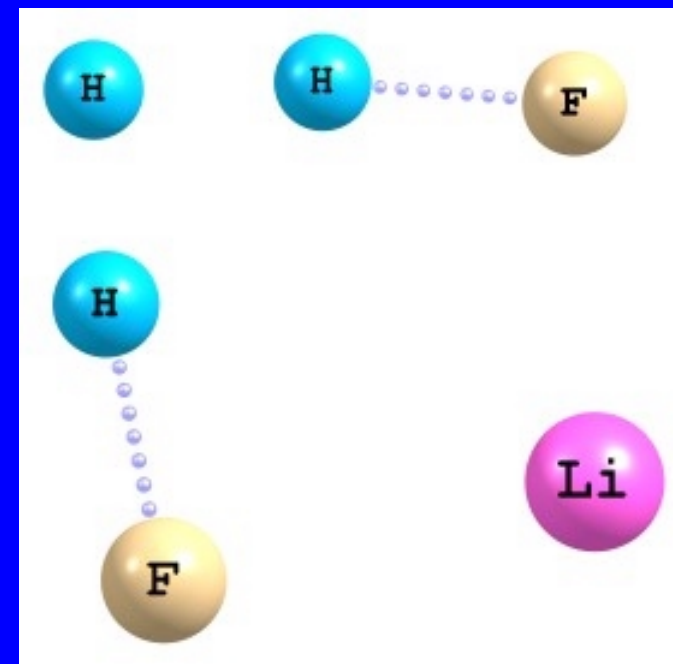
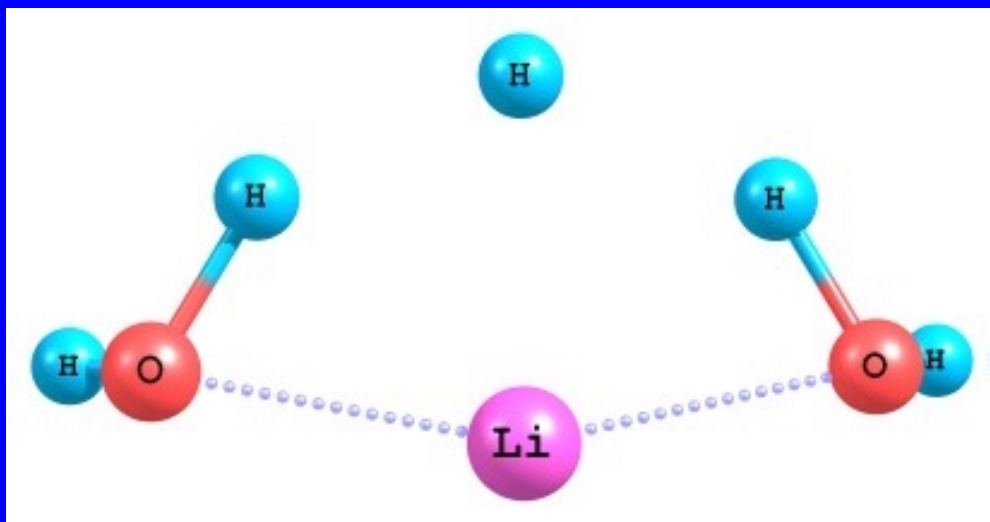


Can Dihydrogen Bonds Be Cooperative?

- Examined Structures of $\text{LiH}(\text{HF})_2$, $\text{LiH}(\text{H}_2\text{O})_2$ and $\text{LiH}(\text{NH}_3)_2$



Cooperative Complexes?



Transition State

Popelier's Criteria For Hydrogen Bonds

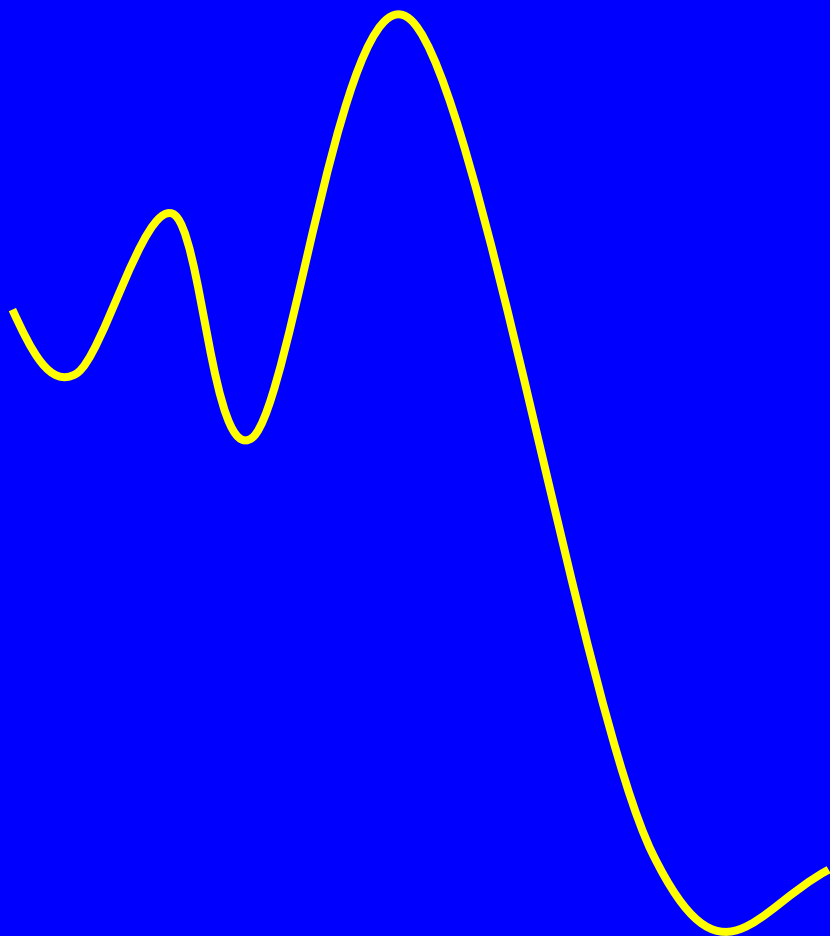
- Bond must have a bond critical point (BCP) and bond path (BP) connecting hydrogen bond donor and acceptor
- Electron density at bcp from 0.002-0.035 au
- Laplacian ranges +0.024 to +0.135 au
- Mutual overlap of donor and acceptor
- Donor should have increased positive charge, decreased dipolar polarization and a decrease in the atomic volume

Cooperative Dihydrogen Bonds?

	Dihydrogen Bond Donor	Dihydrogen Bond Acceptor
Charge	0.532	-0.743
Dipole Polarization	-1.606	-1.165
Volume	20.41	146.8
ρ	0.0452	
Dimer		
Charge	0.556	-0.656
Dipole Polarization	-0.118	-0.146
Volume	19.48	119.1
ρ	0.0554	

- Water complex shows cooperativity
- Geometry dependent on Brønsted acidity of donor and charge on hydridic hydrogen

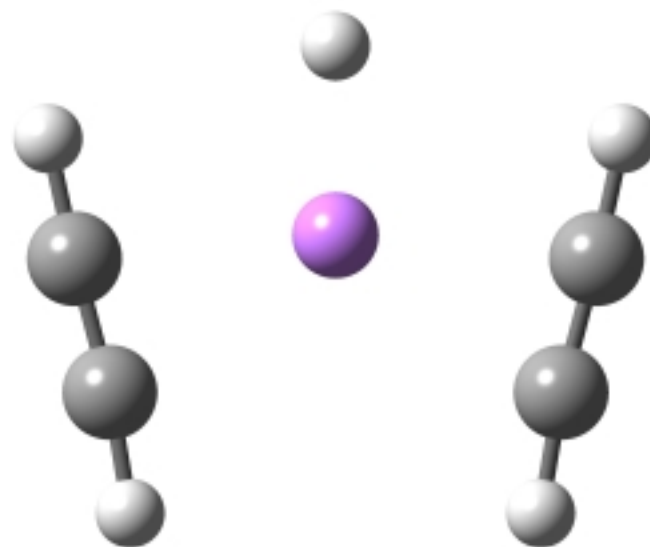
Why Selective Cooperativity?



- Unlike hydrogen bonds, dihydrogen bonds do not connect tautomers
- Dihydrogen bonds stabilize intermediates on path to produce dihydrogen

Cooperativity in Other Systems

- Li - π electron interaction more important
- Interproton distance of 2.67 \AA



Observations

- Dihydrogen bonds are relatively weak
- Calculations on dihydrogen-bonded systems are sensitive to the level of calculation
- Cooperativity seen only in special circumstances
- Dihydrogen bonds rarely show cooperativity

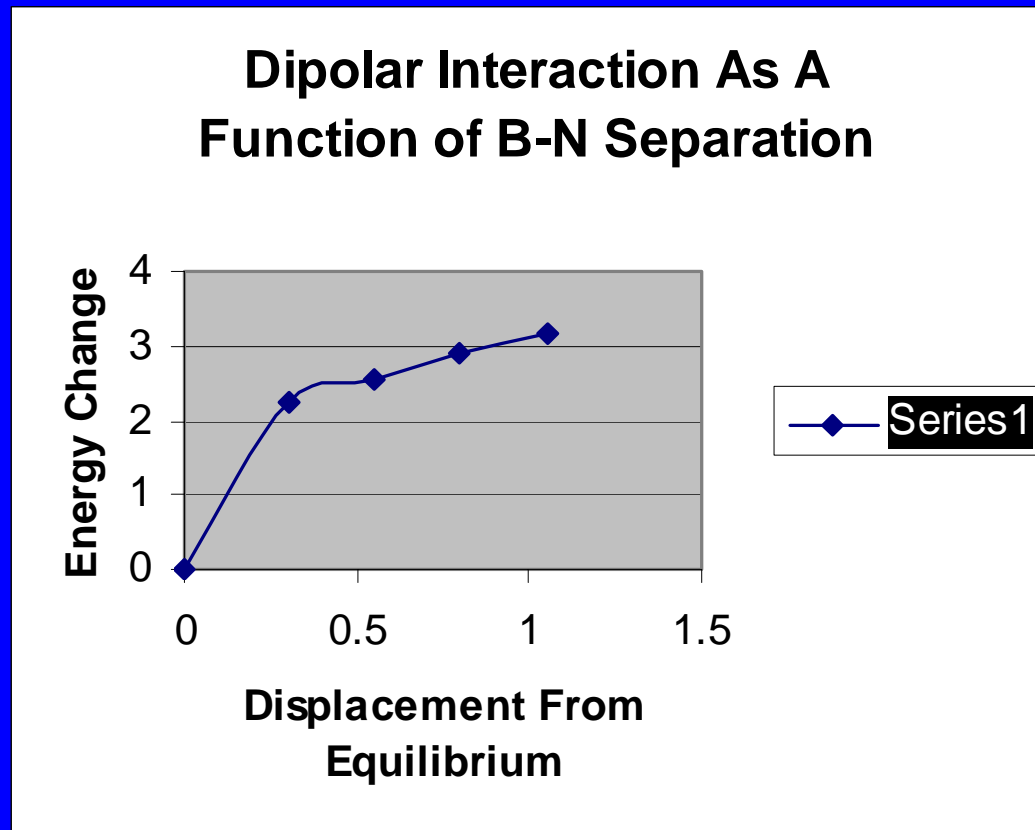
Conclusions

- Dipolar and induced dipolar interactions are important in dihydrogen-bonded structures
- Dihydrogen bonded structures do not connect resonance forms and reflect the ease of dihydrogen formation
- Popelier guidelines are exactly that – and only that
- Despite fulfilling the Popelier criteria, dihydrogen bonds are not true hydrogen bonds

Acknowledgements

- Alabama Supercomputer Center
- Dr. Roger Klein
- IUPAC

Change In Dipolar Interaction



the 1990s, the number of people in the world who are poor has increased from 1.1 billion to 1.5 billion. The number of people who are extremely poor has increased from 600 million to 800 million.

There are a number of reasons for this. One is that the world population has increased from 5 billion to 6 billion. Another is that the world economy has not grown fast enough to keep pace with the population increase.

There are also a number of reasons why the world economy has not grown fast enough. One is that the world is not using its resources efficiently. Another is that the world is not investing enough in education and health care.

There are also a number of reasons why the world is not using its resources efficiently. One is that the world is not using its land and water resources wisely. Another is that the world is not using its energy resources wisely.

There are also a number of reasons why the world is not investing enough in education and health care. One is that the world is not spending enough on education. Another is that the world is not spending enough on health care.

There are also a number of reasons why the world is not spending enough on education and health care. One is that the world is not spending enough on research and development. Another is that the world is not spending enough on infrastructure.

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of the information system. The second part of the model is the 'information system' which is defined as 'the set of components that are used to collect, store, process, disseminate and control information, and that facilitate communication and decision making' [1, p. 16]. The third part of the model is the 'information system environment' which is defined as 'the set of external factors that affect the information system' [1, p. 16].

The model is based on the idea that the information system is the central element of the information system environment. The information system is the core of the information system environment. The information system environment is the context in which the information system operates. The information system environment is the set of external factors that affect the information system. The information system environment is the set of external factors that affect the information system.

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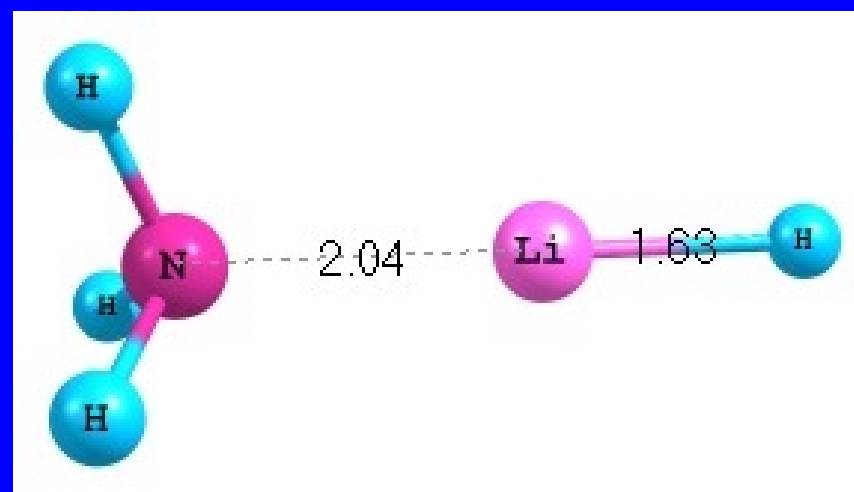
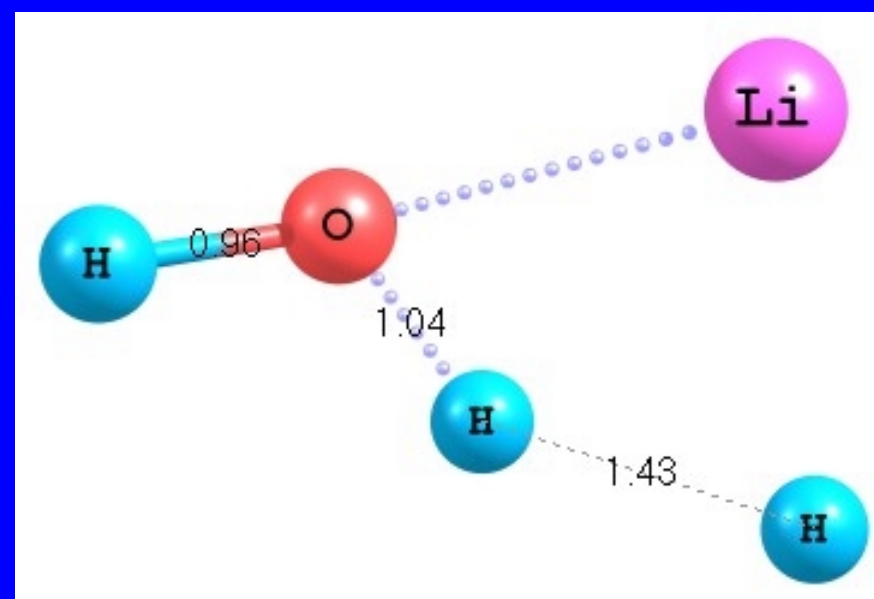
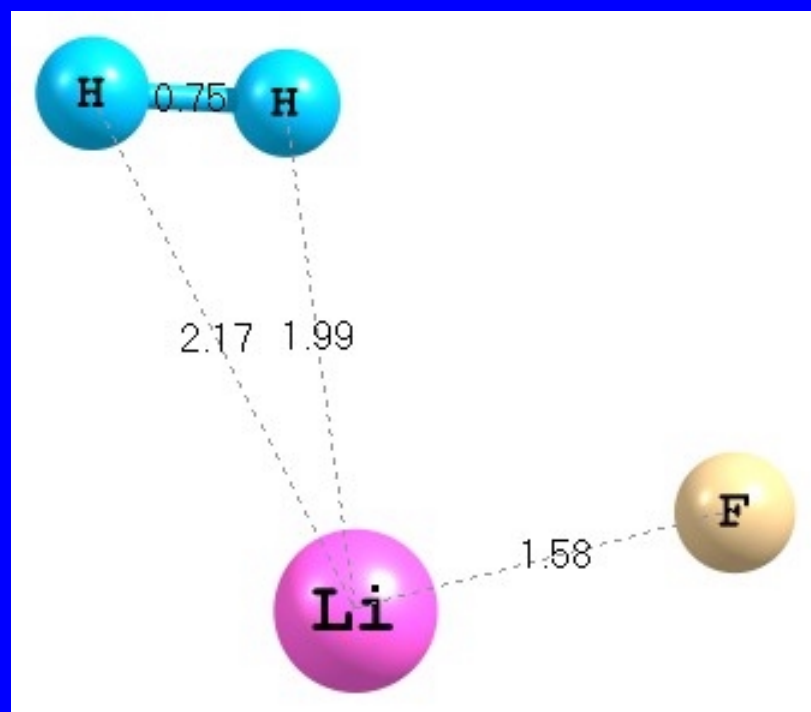
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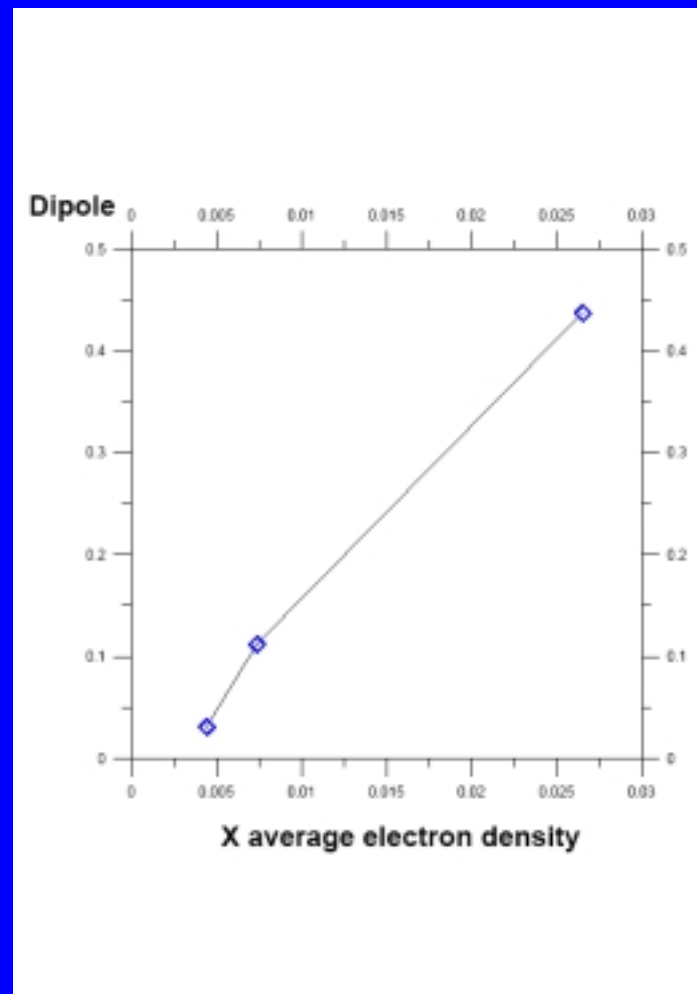
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Monomer Structures



Relationship between Charge Density at BCP and Dipole



the 1990s. The 1990s have been a decade of change for the UK, with the country moving from a traditional manufacturing economy to a service economy. The 1990s have also been a decade of change for the world, with the end of the Cold War and the emergence of a new global order. The 1990s have been a decade of change for the UK, with the country moving from a traditional manufacturing economy to a service economy. The 1990s have also been a decade of change for the world, with the end of the Cold War and the emergence of a new global order.

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