Dihydrogen Bonds and Ducks

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

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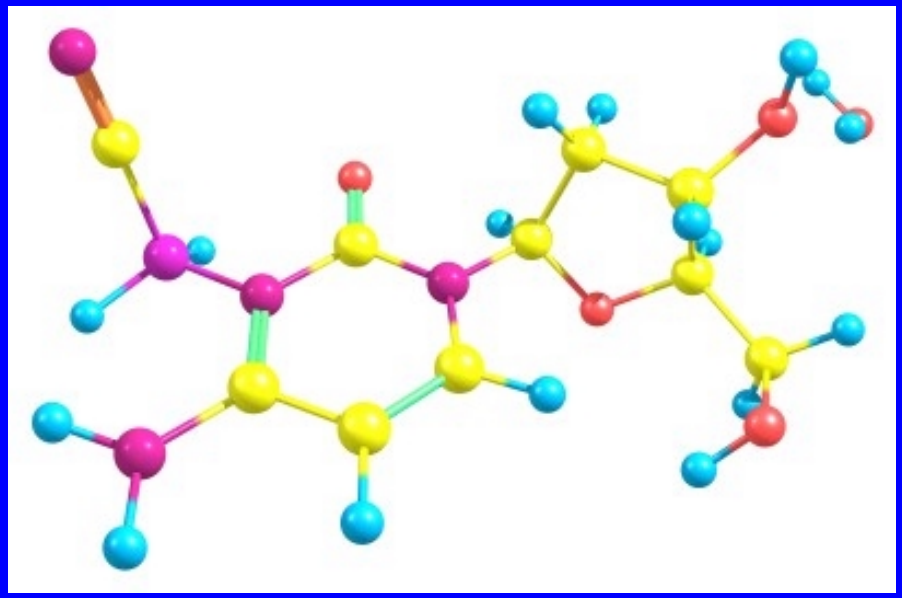
BK1157 – The First Reported Dihydrogen Bond



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

1993 – The Dihydrogen Bond Postulated as a Hydrogen Bond

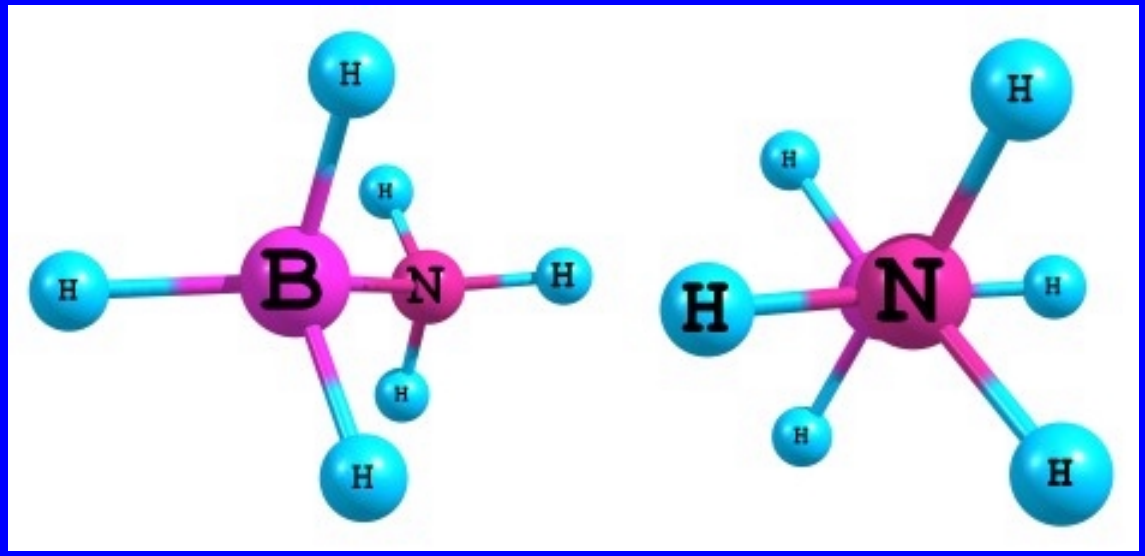
- Calculations at MP2/6-31g**
  - Strength of complexes mirrored Bronsted acidity of hydrogen bond donor
  - Frozen core MP2 calculations implied the dihydrogen interaction preferred to be with one hydrogen

Borazane and the Geometrical Preferences of the Dihydrogen Bond

R2B—— H····H——NR2

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

Borazane and the Dihydrogen Bond



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

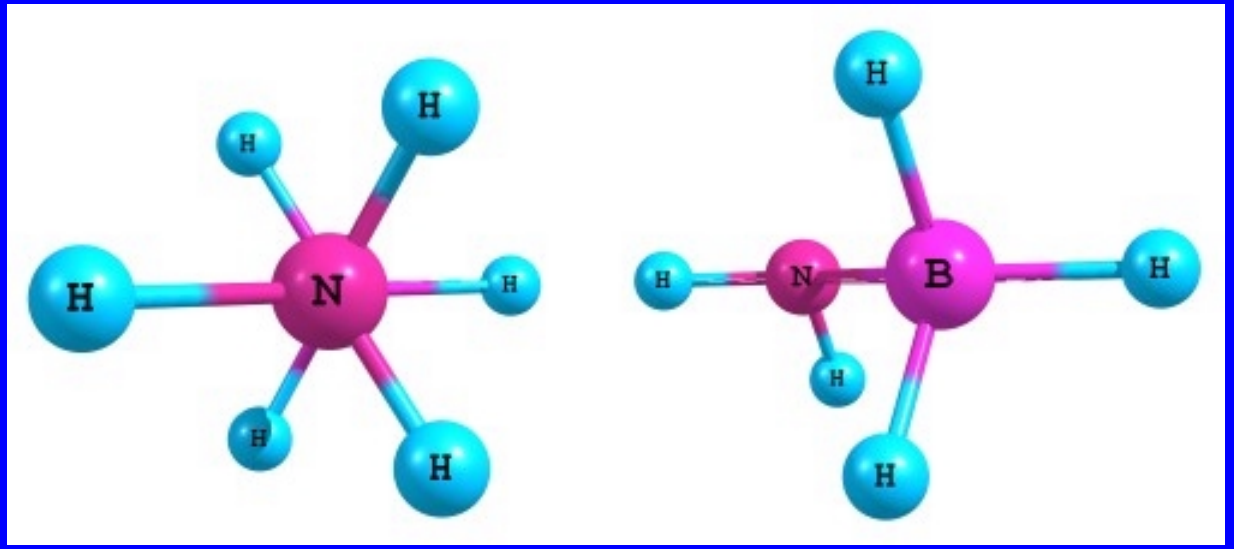
Is The Dihydrogen Bond a Hydrogen Bond?

- Atoms in Molecules (AIM) Theory
  - Developed by Bader
  - Analyzes the electron topology based on QM wavefunction
- Popelier
  - Borrowed concepts developed by Bader
  - Examined Borazane (H3B-NH3) dimer for evidence of hydrogen bonding

Popelier's Criteria For Hydrogen Bonds

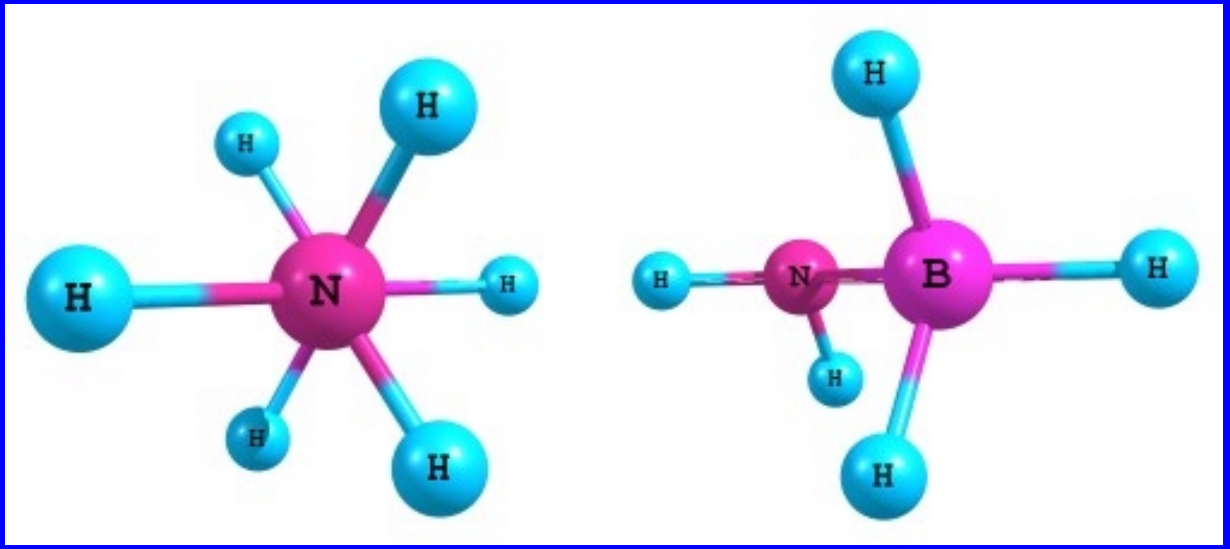
- Bond must have a bond critical point (BCP) and bond path (BP) connecting hydrogen bond donor and acceptor
- Electron density at bcp from 0.002-0.035 au
- Laplacian ranges +0.024 to +0.135 au
- Mutual overlap of donor and acceptor
- Donor should have increased positive charge, decreased dipolar polarization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

Examination of Borazane Dimer by Popelier



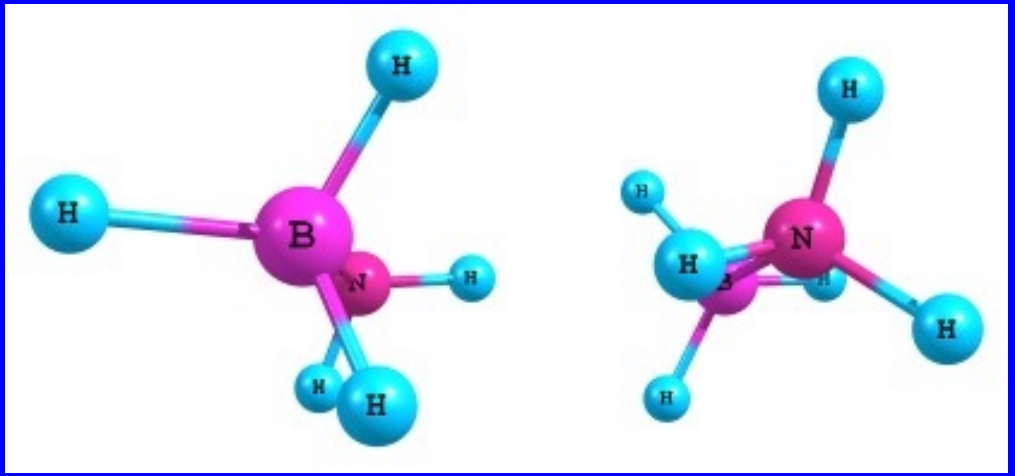
- Calculated structure using mp^2/6-31g**
- The BH – HN interactions met all criteria
- Thus dihydrogen bonds were indeed hydrogen bonds

But Is It?



- Structure is not the ground state but a transition state
- Global minimum depends on whether one uses full or frozen core MP^2!

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 MP^2 (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 MP^2 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 kcals/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

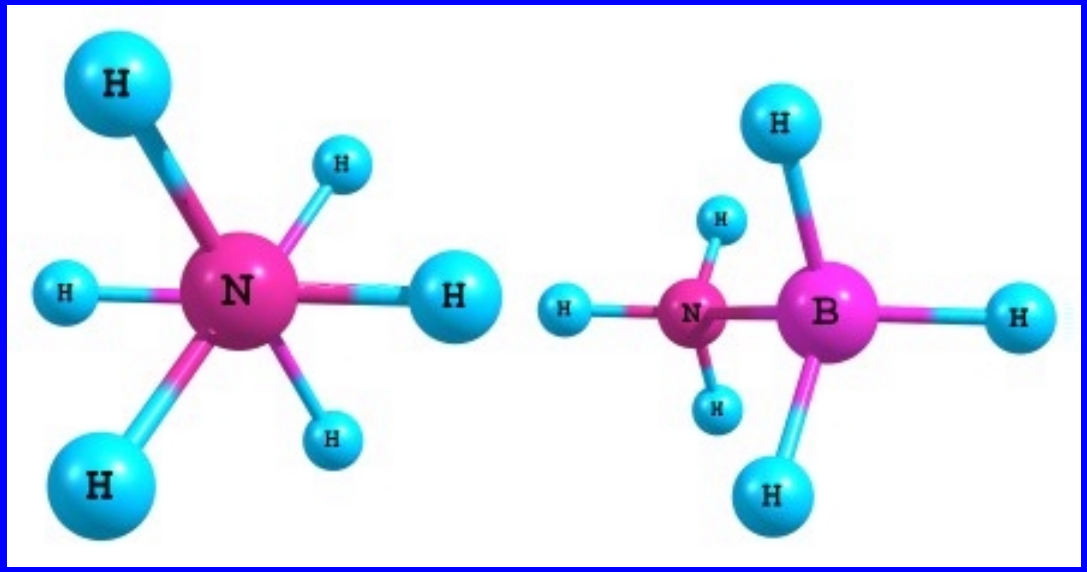
Experimental value 0.7414 (0.0000)

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

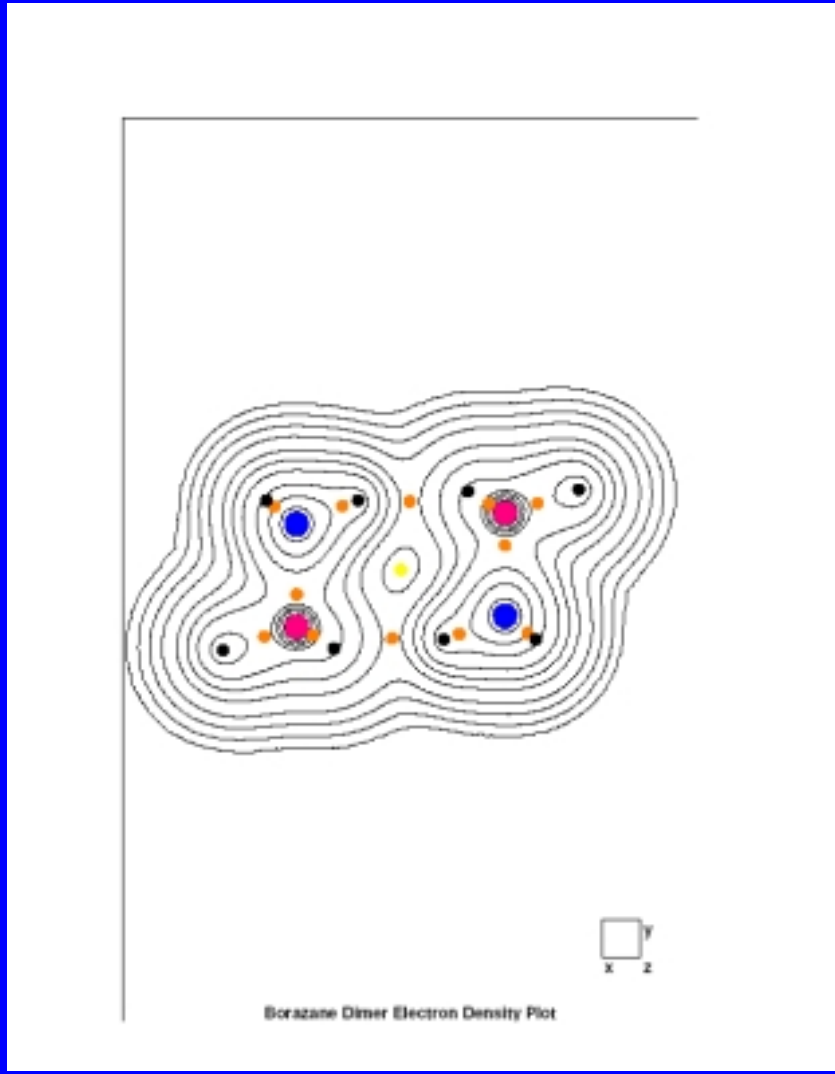
- MP2 calculations with Dunning's double zeta basis sets are inherently unreliable
  - The structures for simple metal hydrides and molecular hydrogen cannot be reliably reproduced
- Pople's triple split basis set a better choice
  - Calculations are less time consuming
  - DFT methods can be superior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

Are Dihydrogen Bonds Possible in The Ground State?



- Borazane dimer with MP^2(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?

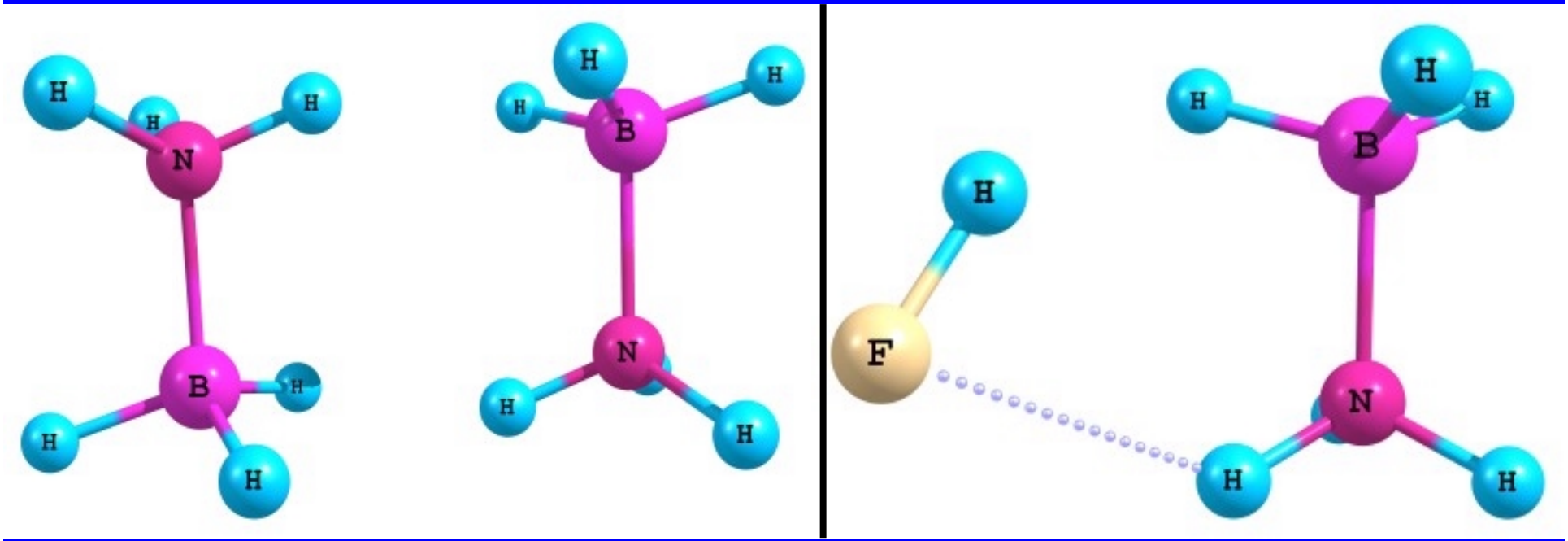
	Dihydrogen Bond Donor	Dihydrogen Bond Acceptor
Charge	0.394	-0.647
Dipole Polarization	-0.00571	-0.1801
Volume	30.20	85.84
ρ (dimer)	0.01726	-0.012 (Laplacian)
Dimer		
Charge	0.439	-0.646
Dipole Polarization	-0.00991	-0.1803
Volume	21.78	81.45
Boron (Qzz/V/q)	-0.0568/24.13/+1.847	0.0564/25.55/+1.842

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

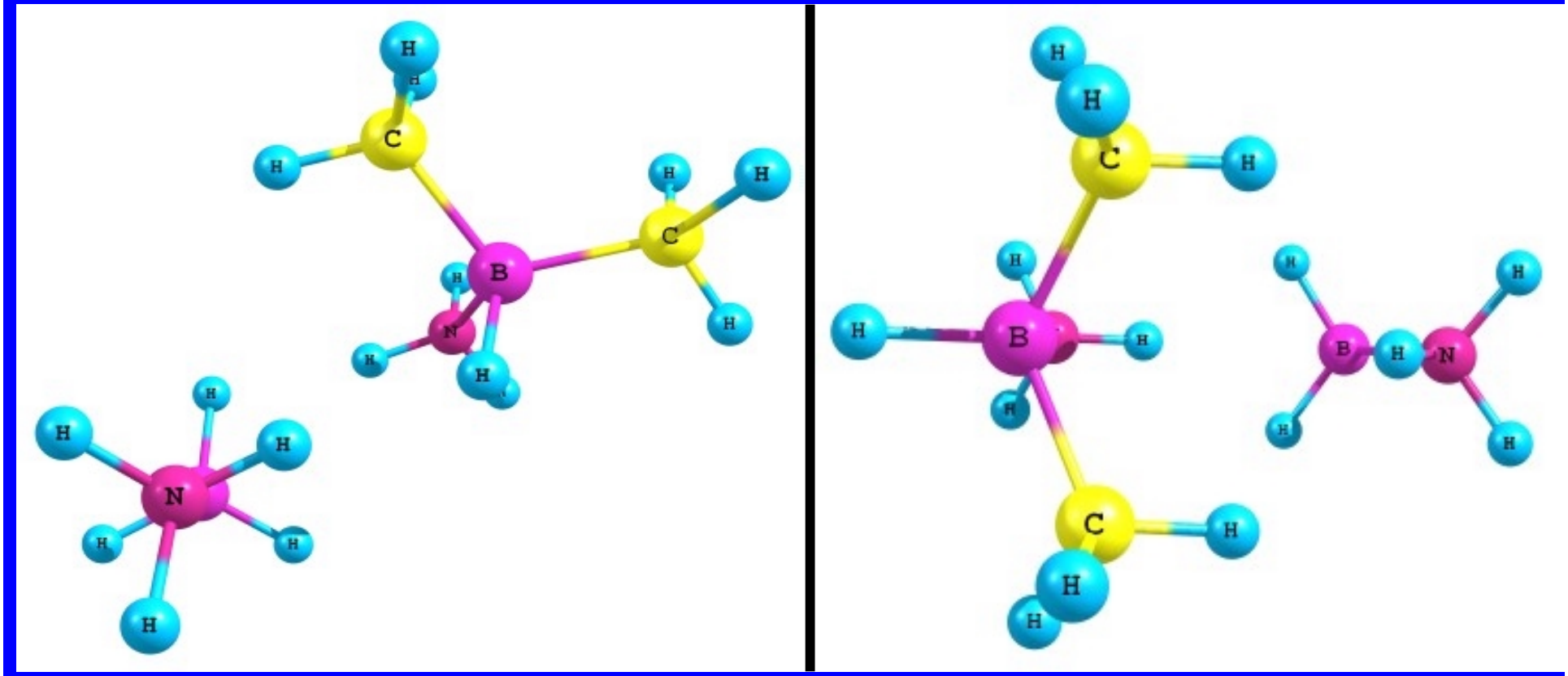
How Strong Are Dihydrogen Bonds?

- Complexes of water or HF with borazane have interaction energies of 6 – 8 kcals/mol
- Crabtree reported a value of 6.1 kcals/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?

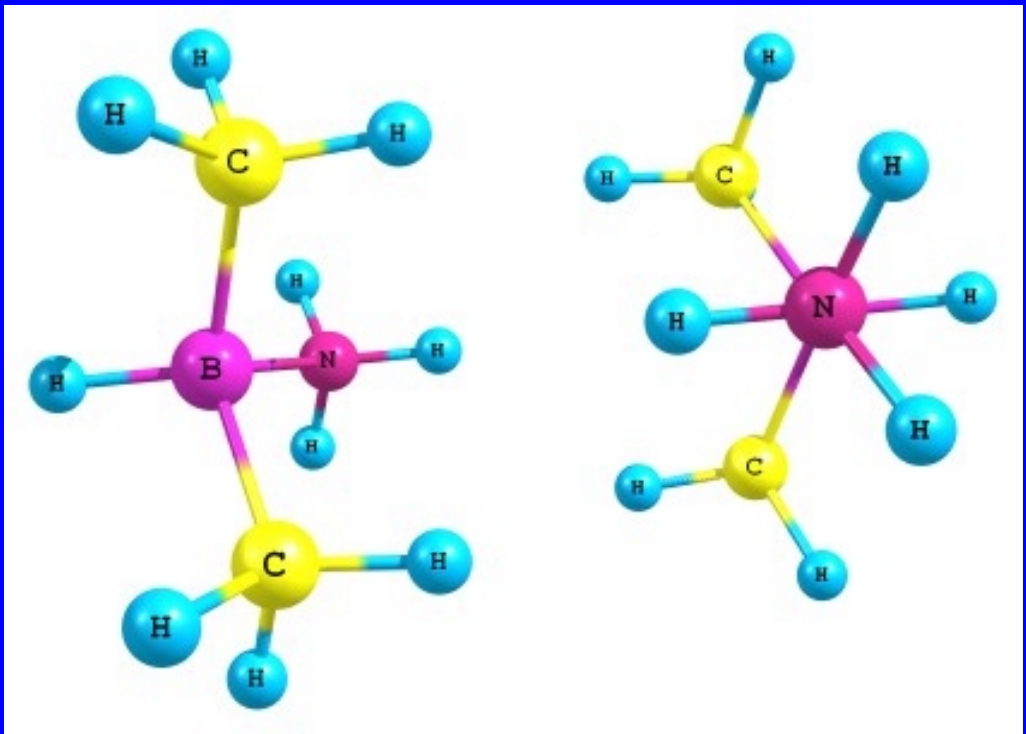
Assessing The Role of Dipolar Interactions



Assessing The Role of Dipolar Interactions



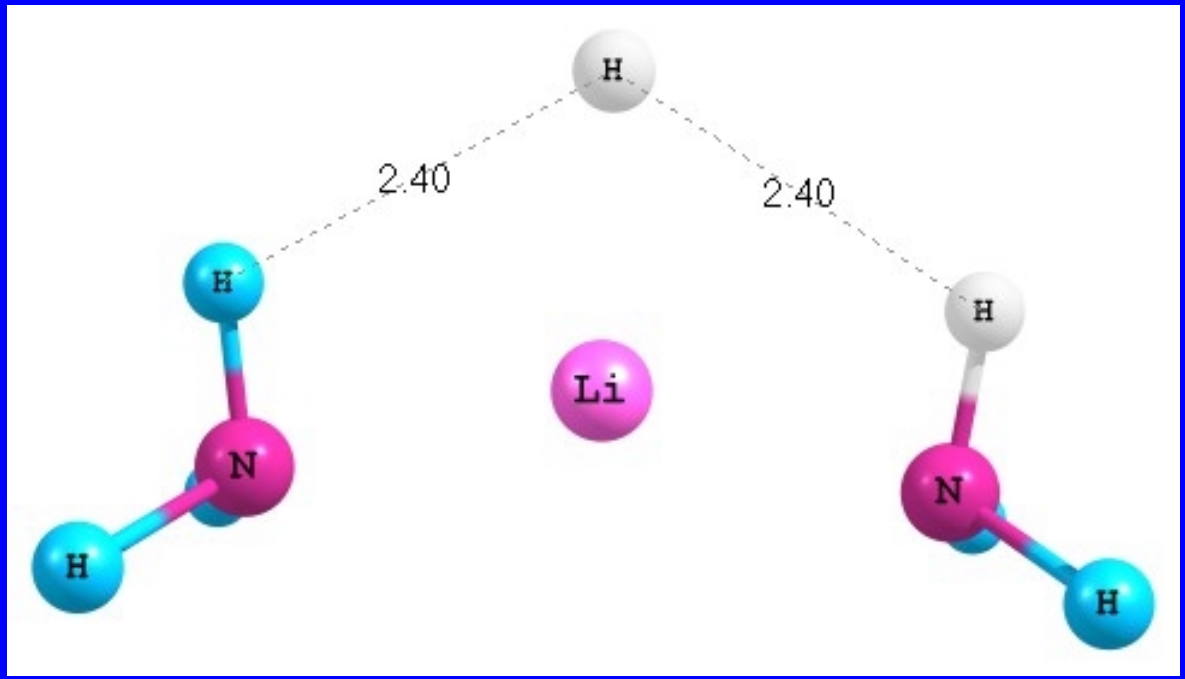
Closing The Circle



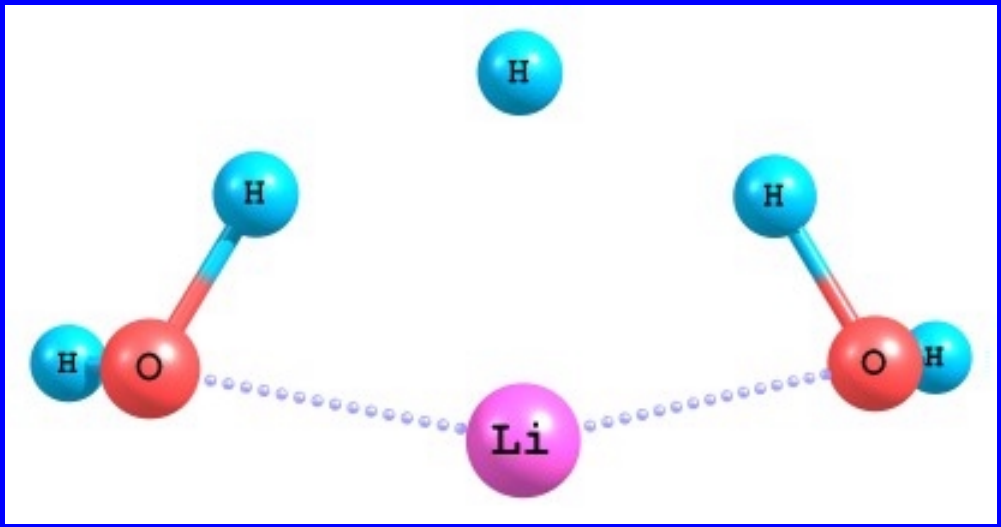
- dE = 3.34 kcals/mol
  - Approximate energy of dihydrogen bond is 4.6 kilocalories
  - Explains Crabtree neutron diffraction structure of borazane

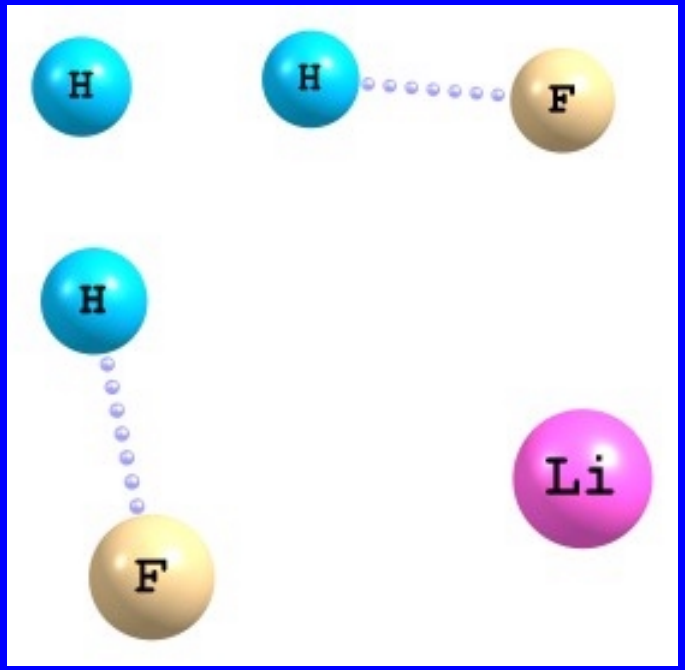
Can Dihydrogen Bonds Be Cooperative?

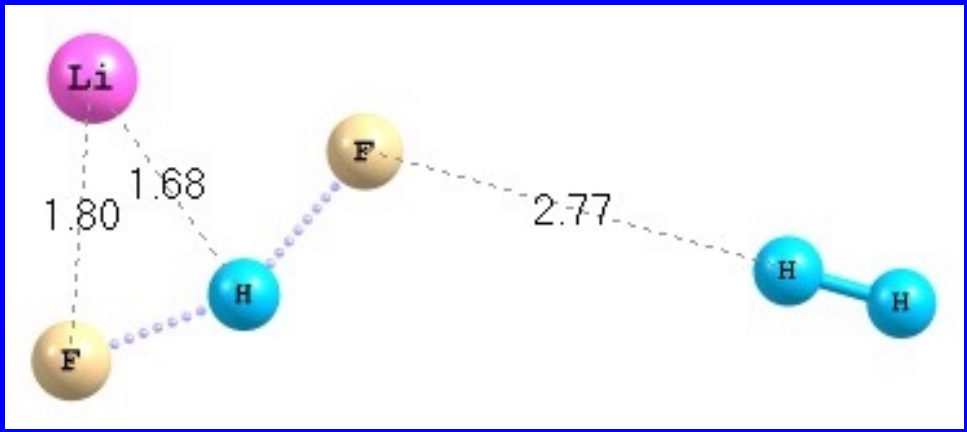
- Examined Structures of $LiH(HF)_2$, $LiH(H_2O)_2$ and $LiH(NH_3)_2$



Cooperative Complexes?







Transition State

Popelier's Criteria For Hydrogen Bonds

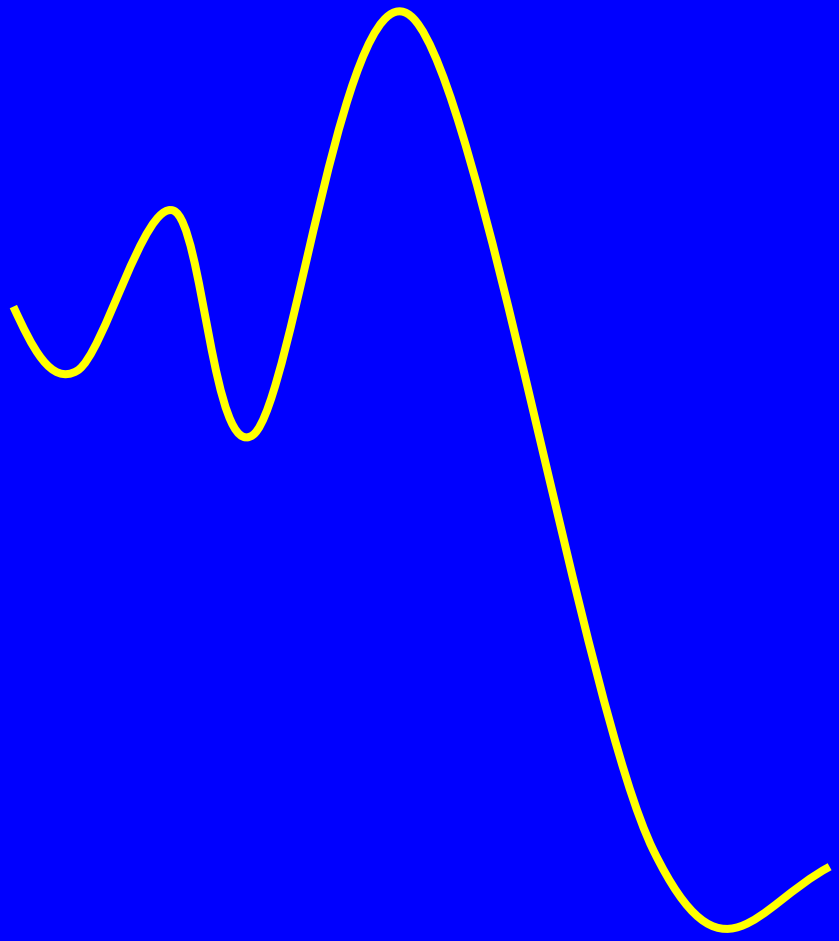
- Bond must have a bond critical point (BCP) and bond path (BP) connecting hydrogen bond donor and acceptor
- Electron density at bcp from 0.002-0.035 au
- Laplacian ranges +0.024 to +0.135 au
- Mutual overlap of donor and acceptor
- Donor should have increased positive charge, decreased dipolar polarization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

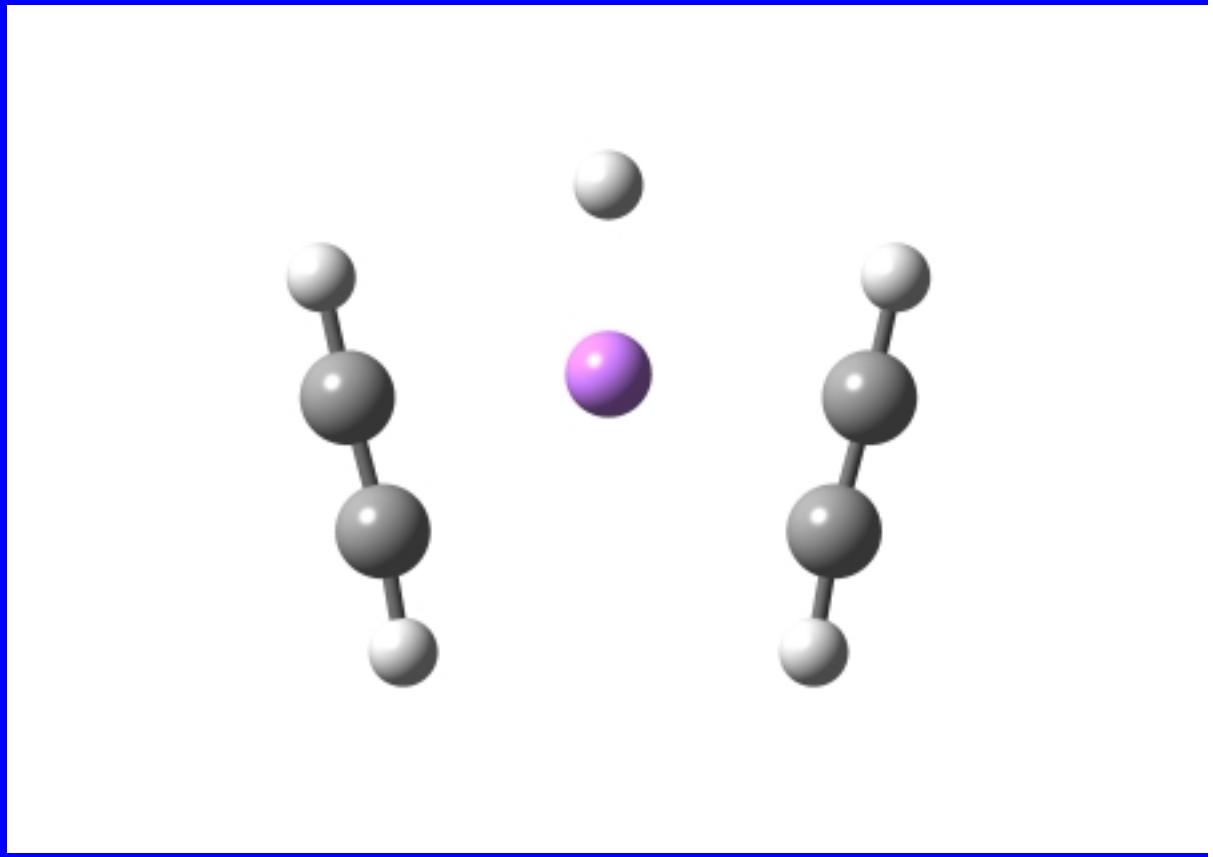
Why Selective Cooperativity?



- 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 Å



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

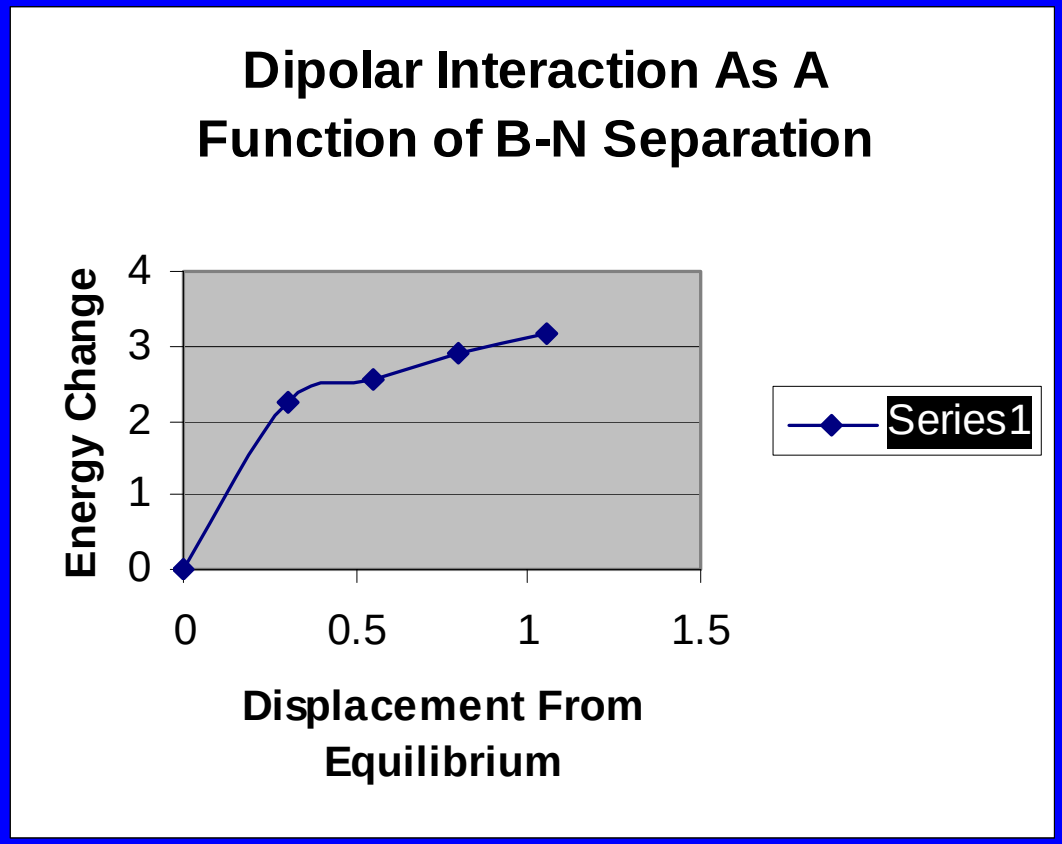
Conclusions

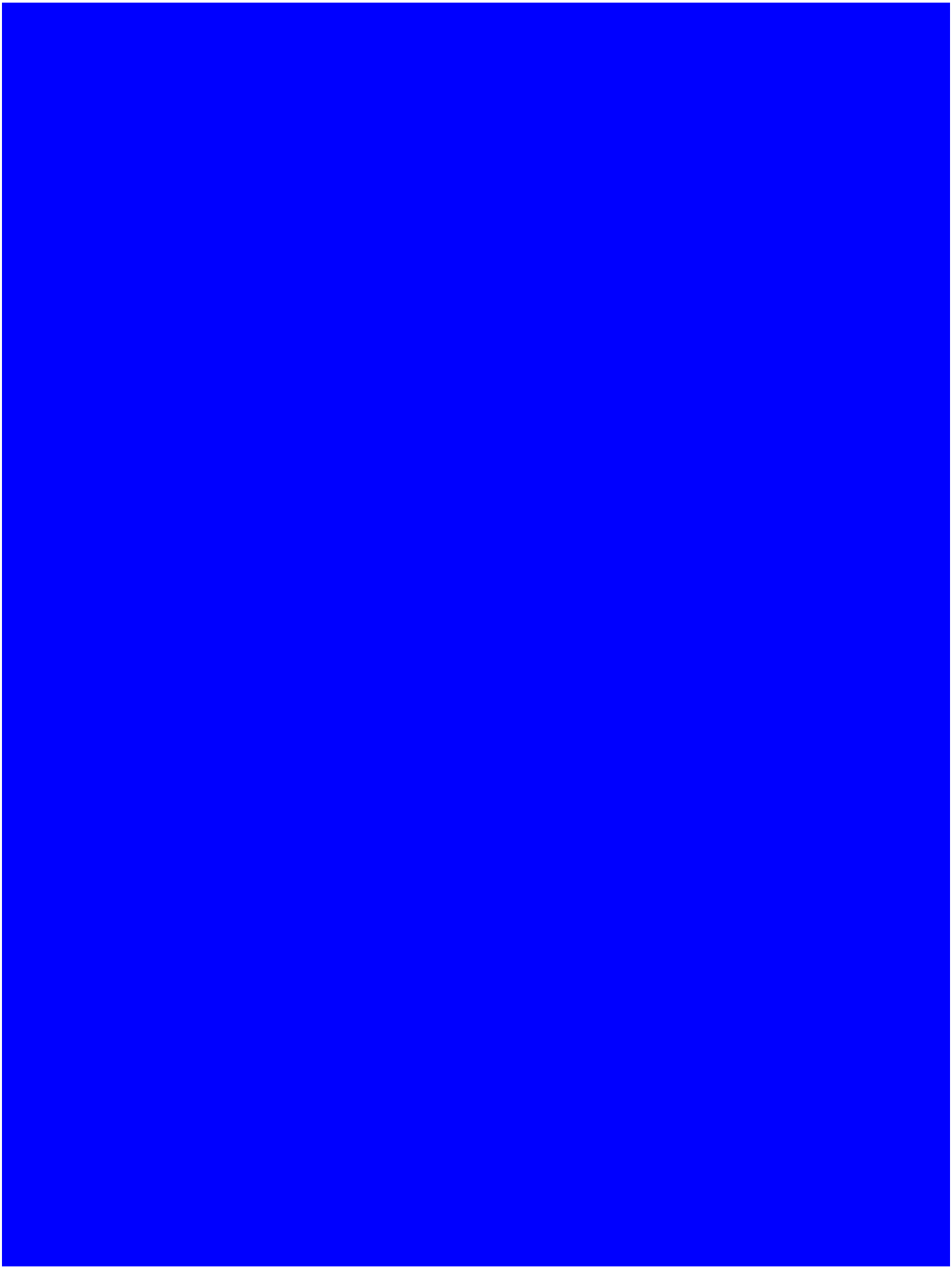
- Dipolar and induced dipolar interactions are important in dihydrogen-bonded structures
- Dihydrogen bonded structures do not connect resonance forms and reflect the ease of dihydrogen formation
- Popelier guidelines are exactly that – and only that
- Despite fulfilling the Popelier criteria, dihydrogen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

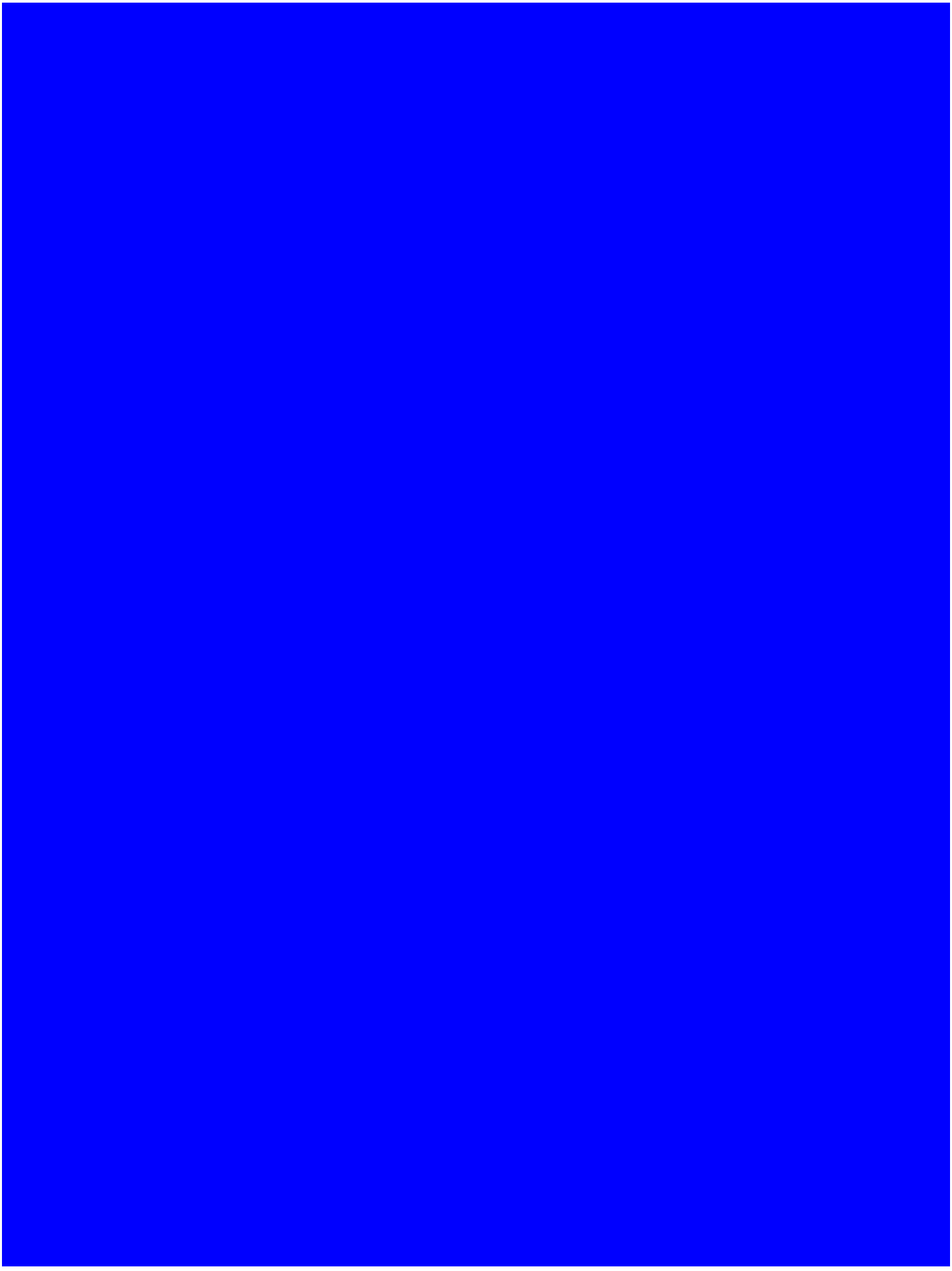
Acknowledgements

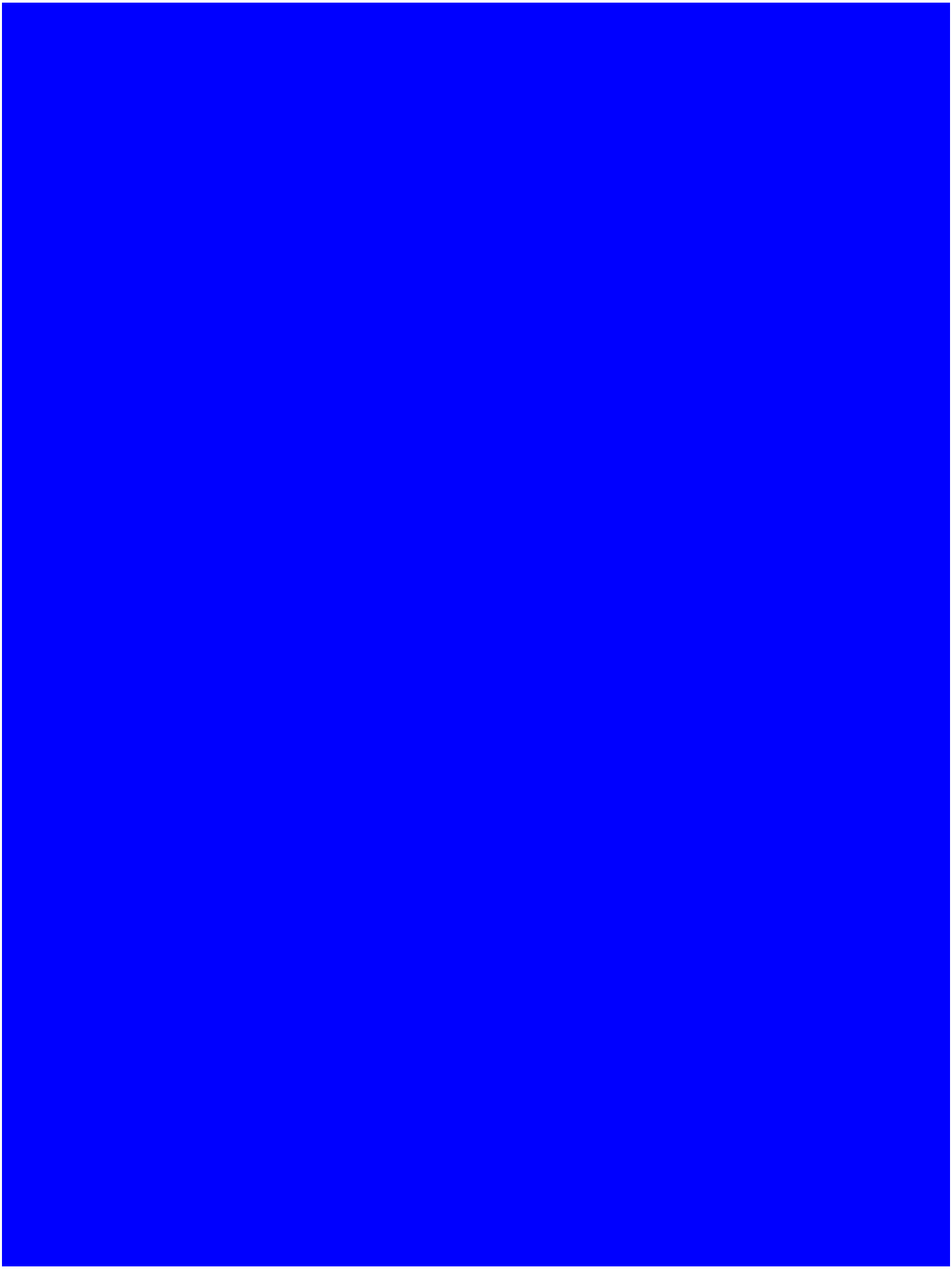
- Alabama Supercomputer Center
- Dr. Roger Klein
- IUPAC

Change In Dipolar Interaction

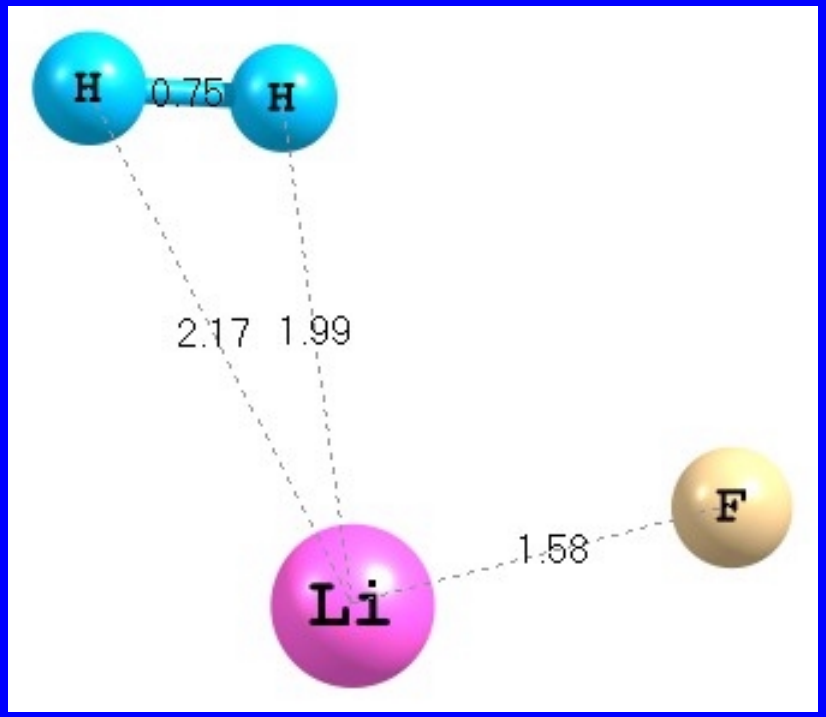


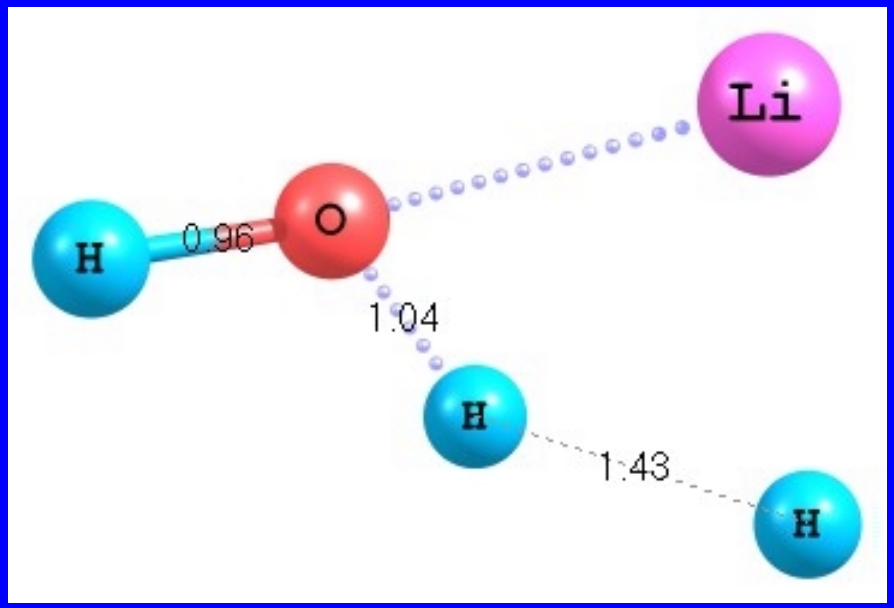


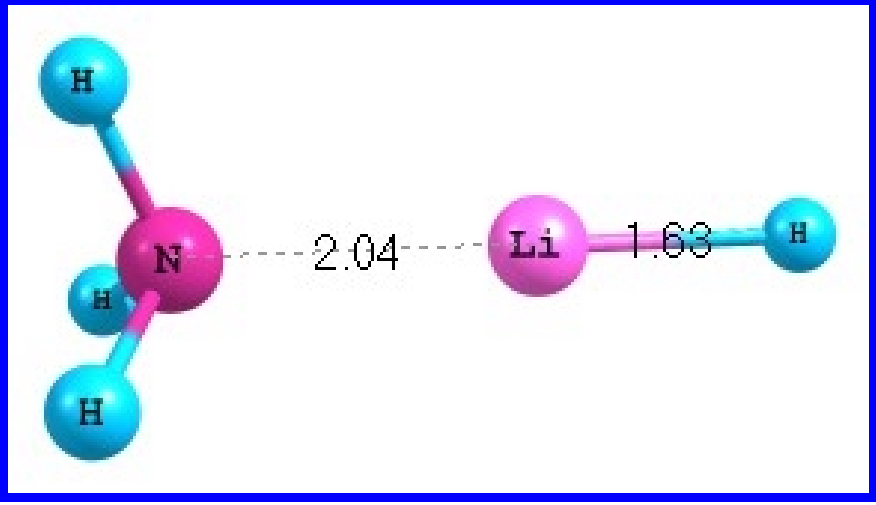




Monomer Structures







Relationship between Charge Density at BCP and Dipole