Hydrogen bond without borders

- N. Sathyamurthy
- Department of Chemistry, Indian Institute of Technology Kanpur
- Collaborators: V. Subramanian,
  R. Parthasarathi, M. Elango,
  Central Leather Research Institute, Chennai
  B. K. Mishra, IIT Kanpur
- Funded by: CSIR, New Delhi

Importance of Hydrogen Bonding

- Hydrogen bonding is an intensely studied interaction in physics, chemistry and biology and its significance is conspicuous in various real life examples
    - liquid water, solution structure and hydration shell - ionic and non-ionic solutes
    - protein folding
    - purine/pyrimidine (GC/AT(U)) base-pairing in nucleic acids
- H-bond is a key interaction in molecular recognition - chemical and enzymatic reactions

Hydrogen Bond

- Definition: a proton/hydrogen atom covalently bonded to one electronegative atom(X) interacting with another electronegative atom (Y):

  $X^{\delta-}–H^{\delta+}\ldots Y^{\delta-}$

- The 'simple' Pauling definition
  - partially electrostatic
  - partially covalent
  - geometry dependent
- Characteristics of Hydrogen Bonding
  - Strength: 5-10 kcal/mol, compared to 50-100 kcal/mol for a covalent bond and 0.5-1 kcal/mol for van der Waals interaction
  - Directionality: within a few degrees deviation from collinearity
  - H…O length: 1.6 – 2.6Å (compared to 0.96Å for O-H)
  - Stretching frequency: red shift on hydrogen bond formation

Experimental Evidence

- Heat of vaporization for strength

  Example: ΔH_{vap} = 9.72 kcal/mol for water Two hydrogen bonds around each oxygen atom. So, ~ 5 kcal/mol for each hydrogen bond

- X-ray and neutron diffraction for geometry
- IR and Raman spectra for stretching frequencies

How about theory?

- Supermolecule approach: $\Delta E = E_{supermolecule} - E_{molecules}$
- Hartree-Fock, large basis set including polarization and diffused functions 6-311++g**
- Density functional theory, but not really satisfactory because it does not include dynamic correlation
- (second order) Møller-Plesset perturbation theory (MP2) works out better
- AIM theory (R F W Bader)

Atoms In Molecules (AIM)

- The concept of AIM was evolved to define the molecular properties as an average of atomic properties
  - Electron density $\rho(r_c)$,
  - Gradient vector field of electron density ($\nabla\rho$),
  - Critical points (at which $\nabla\rho$ vanishes) and
  - Second derivative of electron density or Laplacian ($\nabla^2\rho(r_c)$)

$$\rho(r) = N\sum_{\sigma}\int |\psi(x, x_2, \ldots, x_N)|^2 \, d^3r_2 \ldots d^3r_N$$

$$\nabla^2\rho = \nabla.\nabla\rho = \frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2}$$

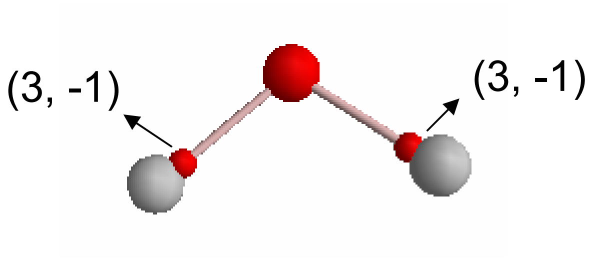
Critical Points

- (3, –3) CP ρ is the local maximum at r_c
- (3, –1) CP ρ is maximum at r_c in the plane defined by their corresponding axes – bond critical point
- (3, +1) CP ρ is minimum at r_c in the plane defined by their corresponding axes – ring critical point
- (3, +3) CP ρ is the local minimum at r_c –cage critical point

Characterization of atomic interactions

- In covalent interactions, $\rho(r_c)$ is high at BCP ($>10^{-1}$ a.u.). The $\nabla^2\rho(r_c)$ is usually large with negative Laplacian.
- In nonbonding interactions $\rho(r_c)$ is quite small and $\nabla^2\rho(r_c)$ is positive ($\sim10^{-2}$ a.u. or 10^{-3} a.u.).

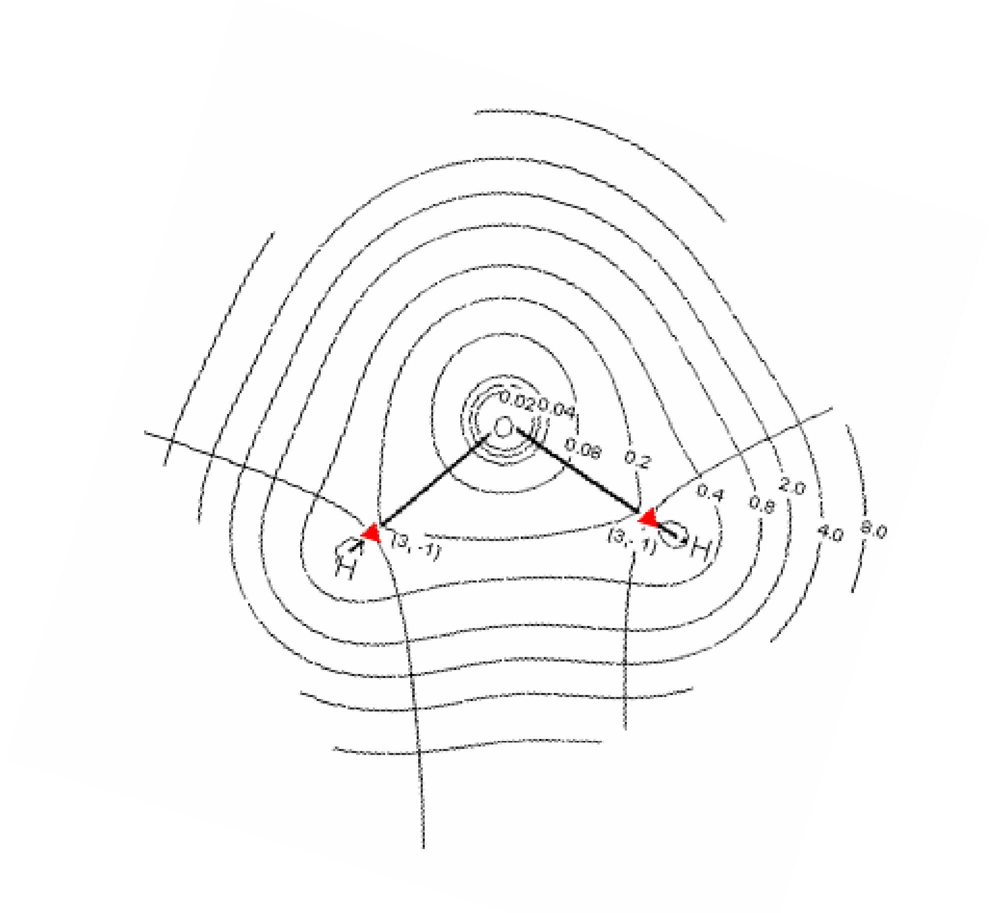
Water monomer : AIM Analysis



Covalent bond

$\rho_c = 0.391\ (e/a_o^3)$

$\nabla^2 \rho_c = -0.611\ (e/a_o^5)$



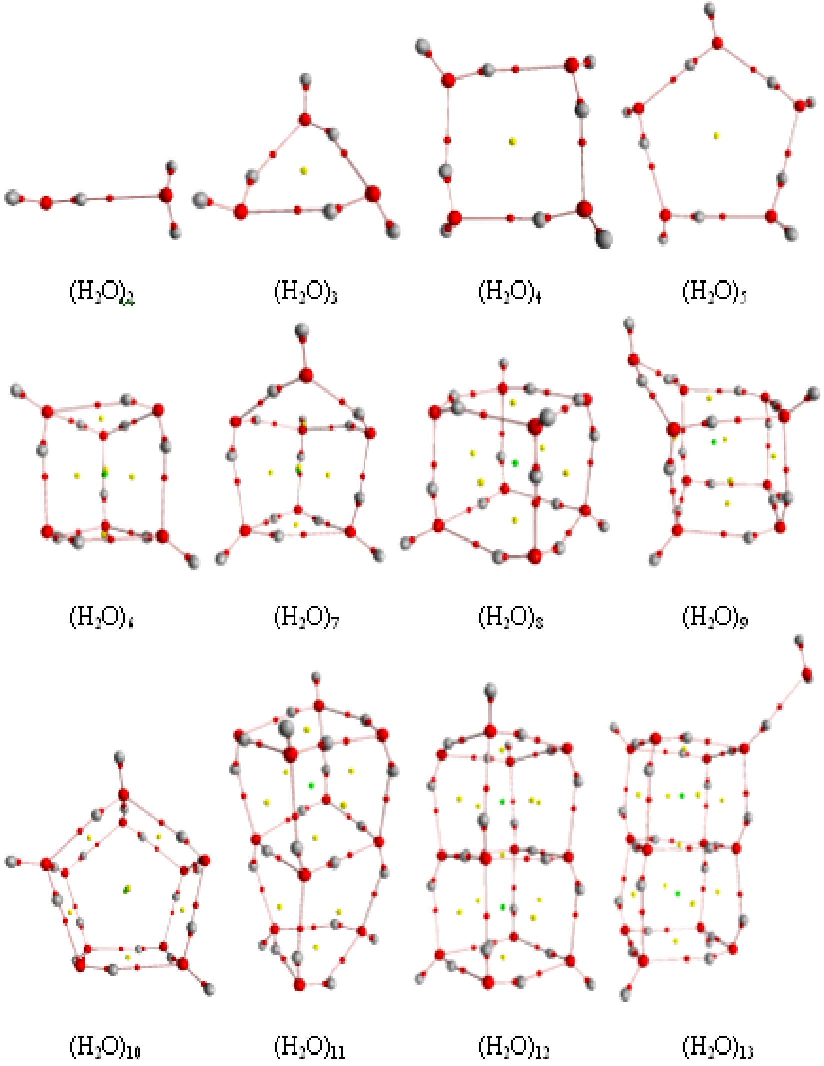
Contour plots of ρ(r)

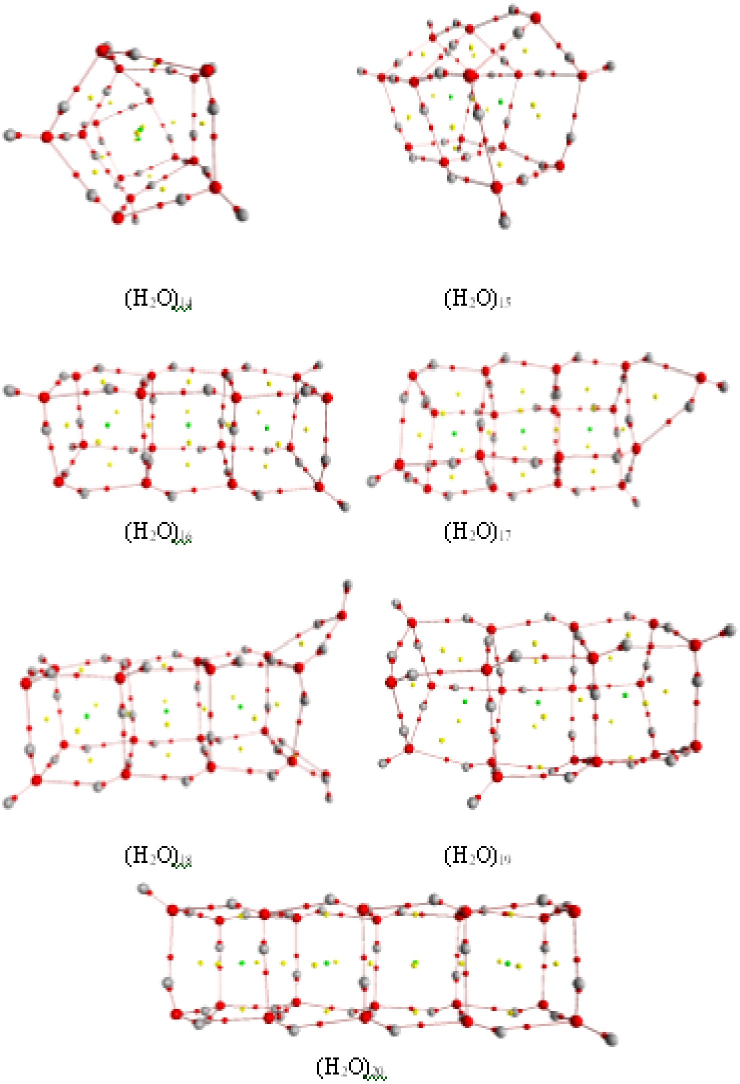
Electron Density Topography Analysis of Hydrogen bonding in water clusters

- Hydrogen bonding between water molecules is a classical example
- Only the most stable conformation obtained by *ab initio* calculations selected for electron density analysis
- All AIM calculations have been made using the AIM 2000 software

R. Parthasarathi and V. Subramanian, Characterization of Hydrogen Bonding: From van der Waals interactions to Covalency, In *Hydrogen Bonding-New Insight, (Challenges and Advances in Computational Chemistry and Physics Series)*; Grabowski, S. J, Ed.; Kluwer: 1-58, 2006.

Molecular electron density topography of water clusters



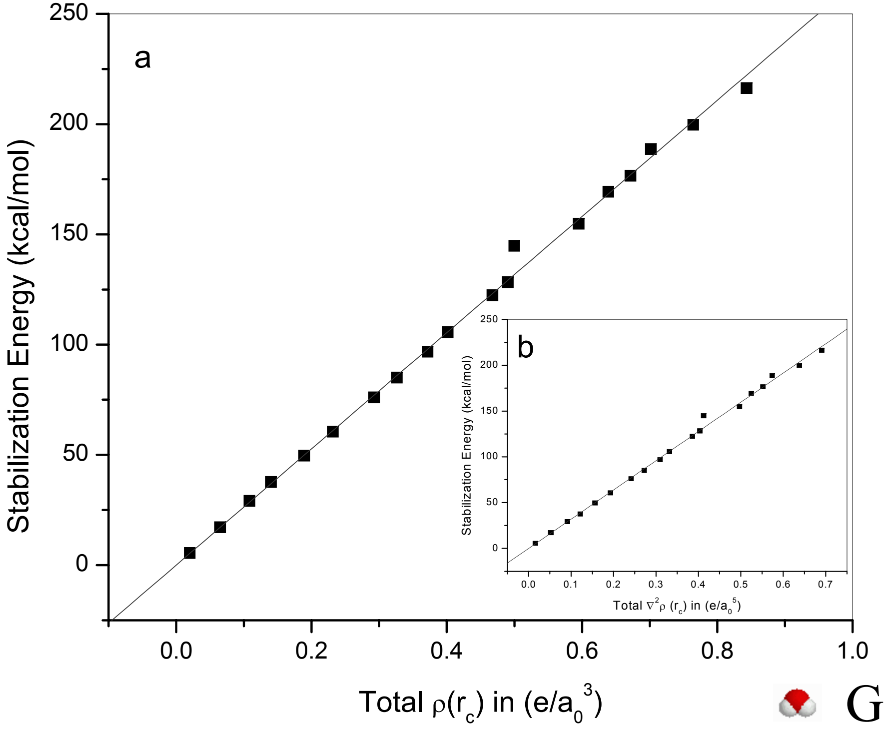


Bond critical points are denoted by red dots and yellow dots denotes the ring critical points

Density and the Laplacian at the bond critical points for hydrogen bonds in water clusters

	$\rho_c/(e/a_o^3)$	$\nabla^2\rho_c/(e/a_o^5)$
Dimer	0.02	0.016
Trimer	0.021	0.017 per H bond
Tetramer	0.026	0.023
covalent bond	0.39	-0.611 for comparison

Linear Relationship between stabilization energy and (a) total $\rho(r_c)$ and (b) total $\nabla^2\rho(r_c)$ (inset) for water clusters.



$$SE = 263.50 \sum \rho(r_c)$$

$$SE = 319.28 \sum \nabla^2 \rho(r_c)$$

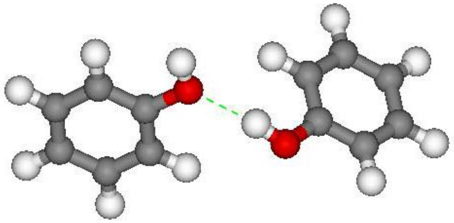
- Greater the electron density and the Laplacian at the bond critical point, larger is the stabilization energy

Interaction of water molecules with other molecules

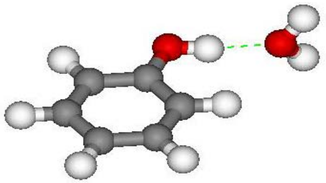
- Phenol, for example
- $PhOH\ldots OH_2$ mixed dimer
- $PhOH\ldots OH_2\ldots OH_2$ or $(PhOH)_2\ldots OH_2$ cyclic mixed trimer
- mixed tetramer

Parthasarathi, R.; Subramanian, V.; Sathyamurthy, N.
Hydrogen Bonding in Phenol, Water, and Phenol-Water Clusters
J. Phys. Chem. A. 2005,*109*, 843-850.

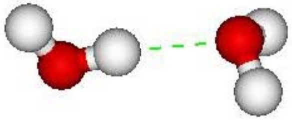
Optimized molecular structure of various phenol, water and phenol-water clusters



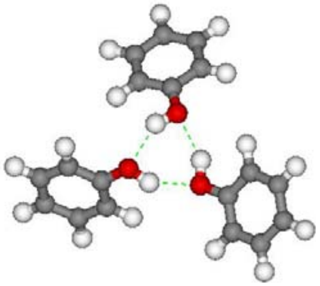
P_2



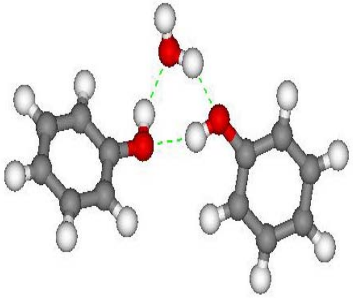
PW



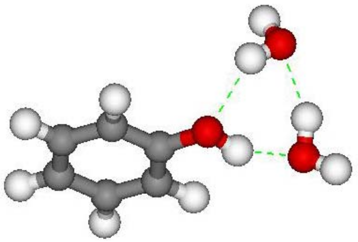
W_2



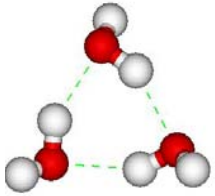
P_3



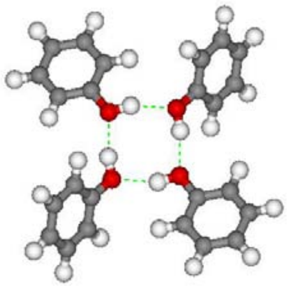
P_2W



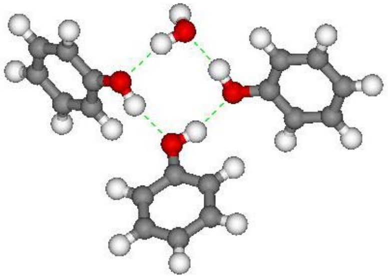
PW_2



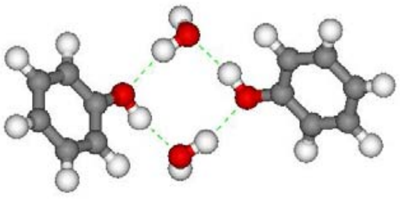
W_3



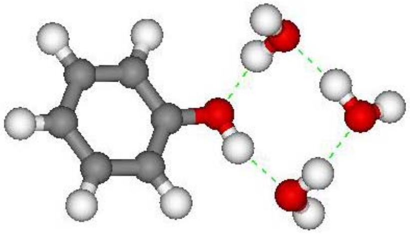
P_4



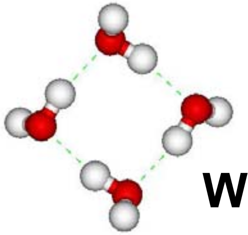
P_3W



P_2W_2

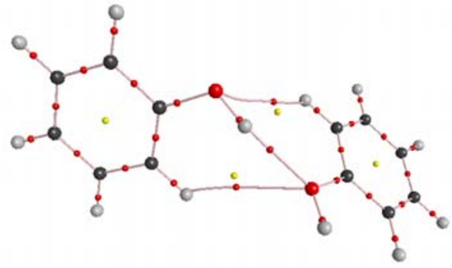


PW_3

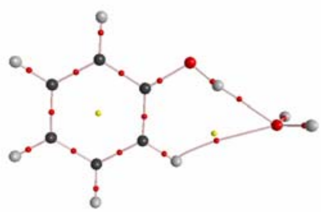


W_4

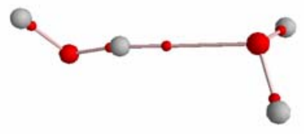
Molecular topography of phenol, water and phenol-water clusters



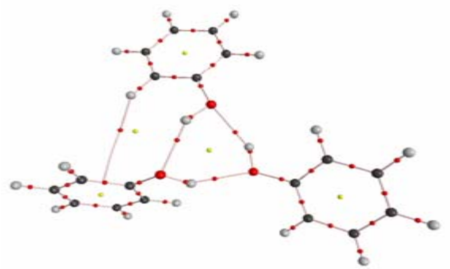
P_2



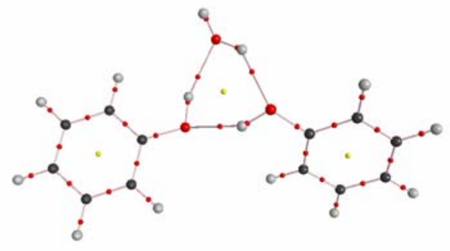
PW



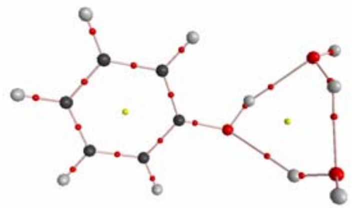
W_2



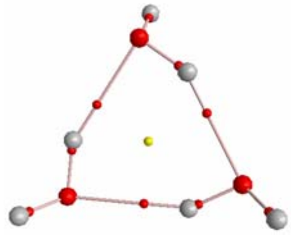
P_3



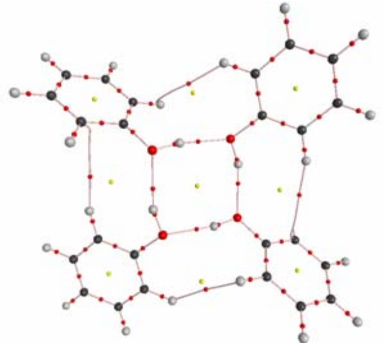
P_2W



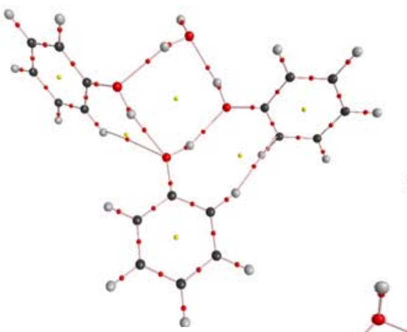
PW_2



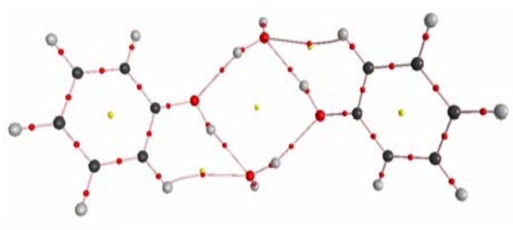
W_3



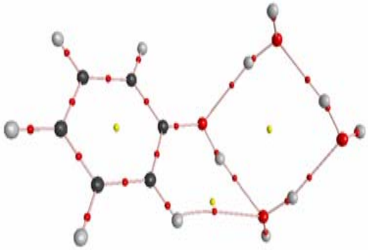
P_4



P_3W



P_2W_2



PW_3

W_4

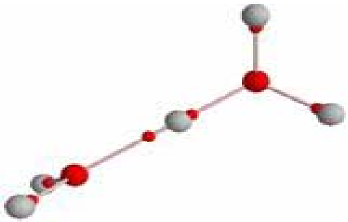
Electron density $\rho(r_c)$ and Laplacian of Electron density ($\nabla^2\rho(r_c)$) for various phenol-water clusters

Clusters	Electron density (e/a_o^3)	Laplacian of electron density (e/a_o^5)	Electron density (e/a_o^3)	Laplacian of electron density (e/a_o^5)
	Primary (strong) hydrogen bond		Secondary (weak) hydrogen bond	
P_2	0.021	0.019	0.003 – 0.004	0.004 – 0.005
W_2	0.021	0.018	-	
PW	0.025	0.022	0.004	0.005
P_3	0.021 – 0.022	0.019 – 0.020	0.002	0.002
W_3	0.022 – 0.024	0.019 – 0.020	-	-
PW_2	0.017 – 0.028	0.015 – 0.024	-	-
P_2W	0.018 – 0.027	0.016 – 0.023	-	-
P_4	0.025 – 0.028	0.022 – 0.024	0.002 – 0.003	0.002 – 0.003
W_4	0.029	0.025	-	-
PW_3	0.024 – 0.033	0.020 – 0.028	0.005	0.005
P_2W_2	0.025 – 0.032	0.022 – 0.027	0.005	0.005
P_3W	0.024 – 0.033	0.021 – 0.028	0.003 – 0.004	0.002 – 0.005

Interaction of Water with Ionic Species

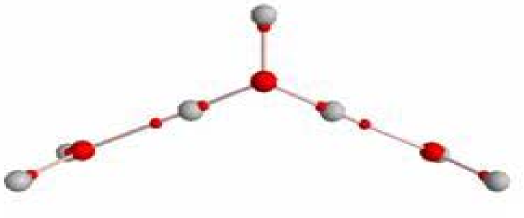
- In addition to its fundamental importance to aqueous chemistry, these strong interactions are implicated in ionic crystals and clusters, ion solvation, electrolytes and acid-base chemistry.
- The importance of this interaction in proton solvation, surface phenomenon, self-assembly process in supramolecular chemistry and biomolecular structure and function has also been recognized.
- $H_3O^+ \ldots(H_2O)_{1\text{-}6,}$
- $OH^- \ldots(H_2O)_{1\text{-}4}$
- To predict the structure and strength of ionic hydrogen bonds in the clusters of $H_3O^+ W_n$ and OH^-W_m where n =1-6 and m =1-4.
- To probe the power of AIM method to differentiate hydrogen bonding in the first and second solvation shells in ionic clusters and quantification of H-bonding.

*Molecular topography of protonated water clusters (Calculated stabilization energies (kcal/mol) (MP2/6-311++G** level))*



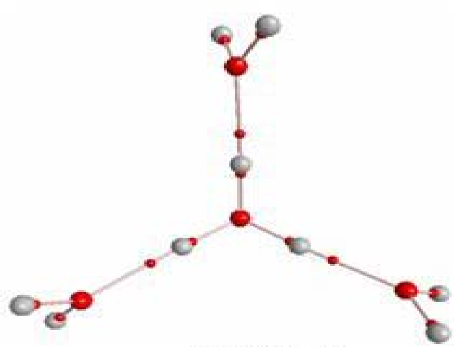
$H_3O^+W_1$

49.99



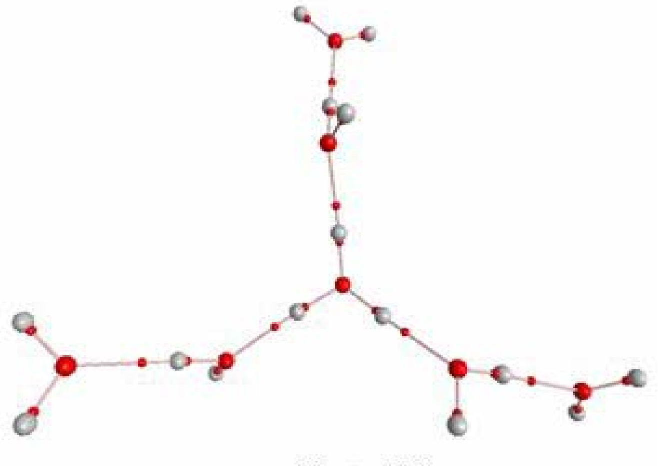
$H_3O^+W_2$

58.27



$H_3O^+W_3$

75.23



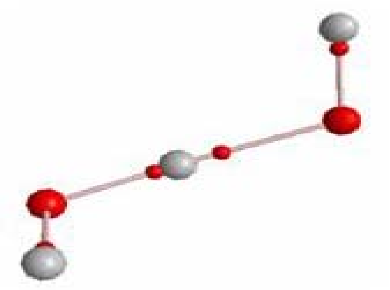
$H_3O^+W_6$

111.1

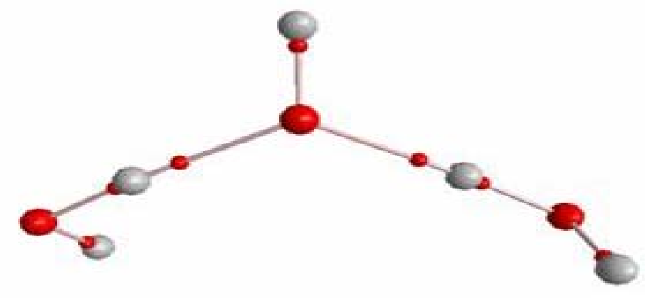
Electron density ($\rho(r_c)$) and Laplacian of Electron density ($\nabla^2\rho(r_c)$) at HBCP for various protonated water clusters in first and second solvation shells

Cluster	Solvation shell	$\rho(r_c)$ (e/a_o^3)	$\nabla^2\rho(r_c)$ (e/a_o^5)
H_3O^+W	First	0.1607	-0.1077
$H_3O^+W_2$	First	0.0739	0.0467
		0.0739	0.0467
$H_3O^+W_3$	First	0.0575	0.0456
		0.0575	0.0456
		0.0575	0.0456
$H_3O^+W_6$	First	0.0644	0.0467
		0.0641	0.0468
		0.0641	0.0467
	Second	0.0335	0.0352
		0.0337	0.0356
		0.0335	0.0356

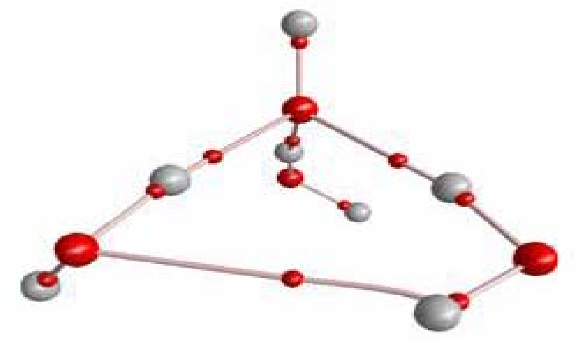
Molecular topography of $OH^{-}W_{n=1-4}$ *clusters*



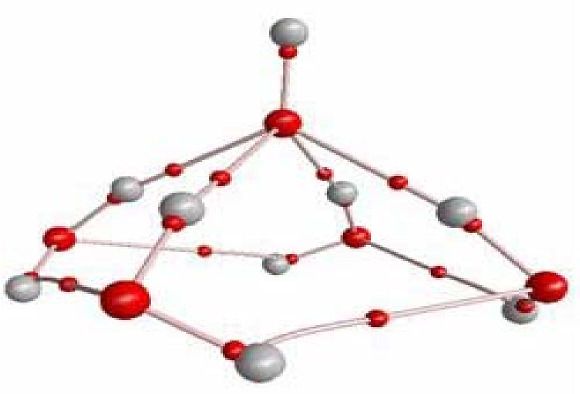
$OH^{-}W_1$



$OH^{-}W_2$



$OH^{-}W_3$



$OH^{-}W_4$

*Calculated stabilization energies (SE) (MP2/6-311++G** level)*

Cluster	Number of H-bonds (distances in Å)		SE kcal/mol
	$OH^{-}\cdots W$	$W\cdots W$	
$OH^{-}W_1$	1(1.38)		32.18
$OH^{-}W_2$	2(1.54)		49.30
$OH^{-}W_3$	3(1.5-1.7)	1(2.5)	65.52
$OH^{-}W_4$	4(1.73)	4(2.47)	222.12

Electron density ($\rho(r_c)$) and Laplacian of Electron density ($\nabla^2\rho(r_c)$) at HBCP

Cluster	Electron density (e/a_o^3)	Laplacian of Electron density (e/a_o^5)	Electron density (e/a_o^3)	Laplacian of Electron density (e/a_o^5)
	$OH^-\cdots W$		$W\cdots W$	
OH^-W_1	0.1003	0.0287		
OH^-W_2	0.0648	0.0427		
	0.0648	0.0427		
OH^-W_3	0.057	0.0422	0.00797	0.0075
	0.0424	0.0368		
	0.0548	0.0419		
OH^-W_4	0.0401	0.0356	0.00896	0.0084
	0.04	0.0355	0.00903	0.0085
	0.0401	0.0356	0.00896	0.0084
	0.04	0.0355	0.00904	0.0085

Stronger the hydrogen bond

- Larger is the value of the density and its Laplacian at the hydrogen bond critical point.
- How strong can a hydrogen bond get?
- How weak can a hydrogen bond get?
- Will the strength be still reflected in the density and the Laplacian at the HBCPs?

Hydrogen bonding without borders

- In continuation of our efforts to understand the hydrogen bonded complexes and clusters, a diverse class of intermolecular complexes ranging from van der Waals interaction to covalent bonding was examined
- Strength of some H-bond is nearly that of a covalent bond
- A variety of weak H-bonds has also been observed
- Hence, an attempt has been made to understand the concept of hydrogen bonding without borders using the topological properties of electron density and also to quantify the transition from weak to moderate to strong H-bonding to develop a unified picture of the nature of H-bond

Stabilization energy (SE) (MP2/aug-cc-pVDZ) and Electron density ($\rho(r_c)$) for various H-bonded complexes

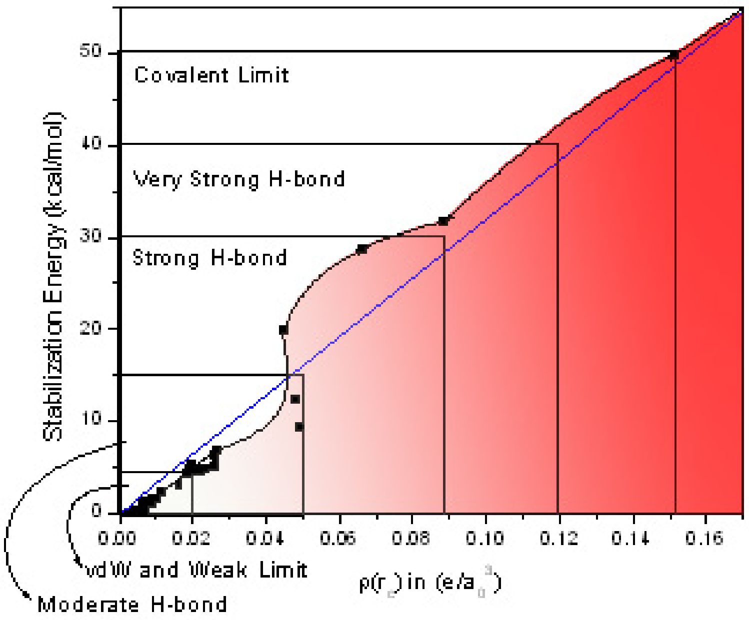
H-bonded Complexes	SE (kcal/mol)	$\rho(r_c)$ (e/a_o^3)
$H_3O^+ \ldots H_2O$	49.7	0.1517
$OH^- \ldots H_2O$	**31.7**	**0.0883**
$NH_3 \ldots NH_4$	28.6	0.0667
$NH_4 \ldots H_2O$	19.8	0.0453
$NH_3 \ldots HF$	12.4	0.0482
$NH_3 \ldots HCl$	9.33	0.0497
HCN…HF	6.88	0.0266
$C_6H_5OH \ldots H_2O$	**6.28**	**0.0262**
$CH_3OH \ldots CH_3OH$	5.22	0.0264
$CH_3OH \ldots H_2O$	5.16	0.0198
$HCl \ldots H_2O$	5.09	0.0258
$NH2COH \ldots H_2O$	4.85	0.0193
$CHOH \ldots H_2O$	4.81	0.0234
HCN…HCl	4.68	0.0211

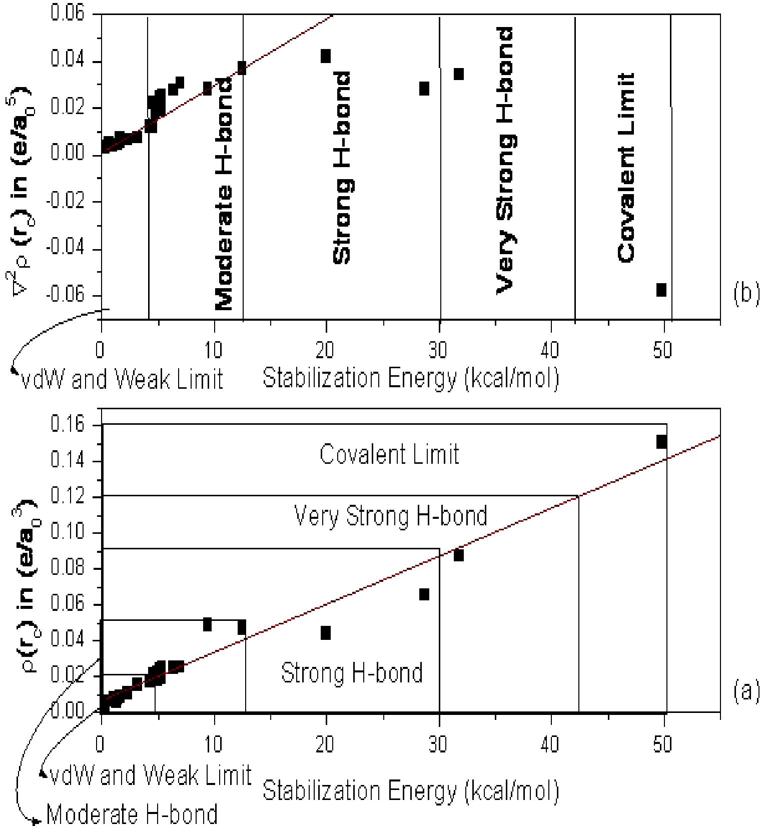
H-bonded Complexes	SE (kcal/mol)	$\rho(r_c)$ (e/a_o^3)
$PH_3 \ldots HF$	4.48	0.0196
$H_2O \ldots H_2O$	**4.46**	**0.022**
$C_2H_4 \ldots HF$	4.16	0.0183
$PH_3 \ldots HCl$	3.08	0.0163
$PH_3 \ldots H_2O$	2.17	0.0119
$H_2S \ldots H_2S$	1.55	0.0102
$SH_2 \ldots HF$	1.54	0.0093
$H_2S \ldots PH_3$	1.37	0.0091
HCl..HCl	1.22	0.0068
$SeH_2 \ldots HF$	0.91	0.0093
$CH_4 \ldots NH_3$	0.54	0.0073
$CH_4 \ldots HF$	0.25	0.0047
$CH_4 \ldots SH_2$	0.23	0.0045
$CH_4 \ldots Ar$	0.11	0.0038

The electron density at the bond critical point varies smoothly over the entire range

There is a gradual change in the magnitude of the Laplacian also – until one goes over to the covalent bond, at which stage the Laplacian changes sign!

Classification of various types of hydrogen bonded interactions based on stabilization energy and $\rho(r_c)$





$\rho(r_c)$ in covalent limit > $\rho(r_c)$ in strong > $\rho(r_c)$ in medium > $\rho(r_c)$ in weak

R. Parthasarathi, V. Subramanian, and N. Sathyamurthy, Hydrogen Bonding Without Borders: An Atoms-In-Molecules Perspective, J. Phys. Chem. A 110 (2006) 3349.

Summary

- There is a linear relationship between the electron density and the Laplacian of the electron density at the HBCP and the strength of the H-bond; the variation is smooth in going from van der Waals to classical H-bonding to strong H-bonding.

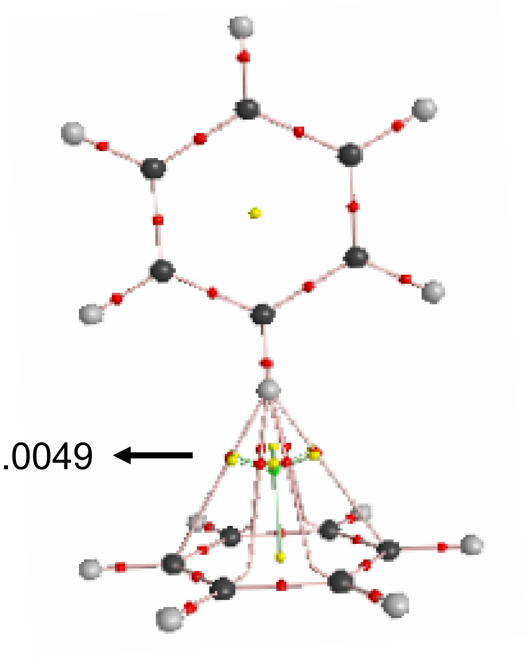
π-π Stacking in Aromatic Systems

Benzene-Benzene

- How do they interact?
- Is stacking preferred?
- Look at graphite sheets. They are stacked with about 3.5 Å between them
- Do they (benzene molecules) behave like closed shell systems?
- No dipole moment, but they have quadrupole moment. Do they matter?
- Experiment and theory: stacking and T-shaped are comparable in energy
- For a recent review see M.O. Sinnokrot and C. D. Sherrill, J. Phys. Chem. A2006, 110, 10656

Benzene dimer

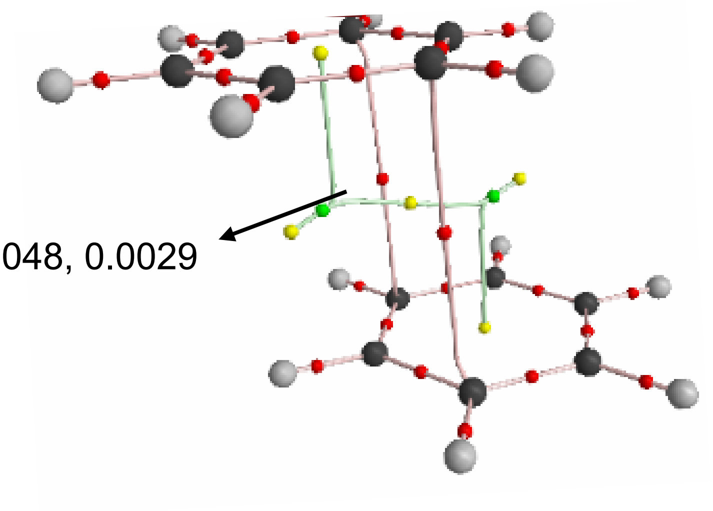
T-shaped



0.0061, 0.0049

Six (3, -1) critical points

parallel-displaced orientation



0.0048, 0.0029

Two (3, -1) critical points

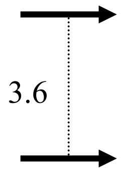
Interaction energy: 2-3 kcal/mol

Pyridine Dimer and Trimer
Pyridine has permanent dipole moment!

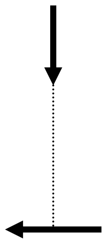
Brijesh Kumar Mishra and N. Sathyamurthy ***J. Phys. Chem. A*****, 109, 6, (2005)**

Dipole-Dipole Interaction

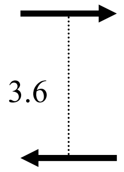
$$E = -\mu_A \mu_B (2 \cos \theta_A \cos \theta_B - \sin \theta_A \sin \theta_B \cos \Phi) / 4\pi\varepsilon_o R^3$$



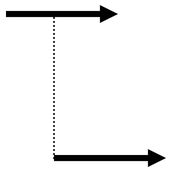
E = **1.84 kcal/mol**



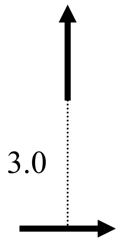
E = **0**



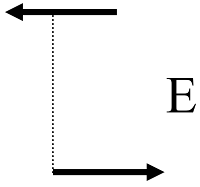
E = **-1.84 kcal/mol**



E = **0.92 kcal/mol**

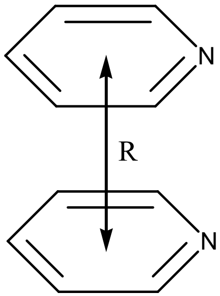


E = **0**

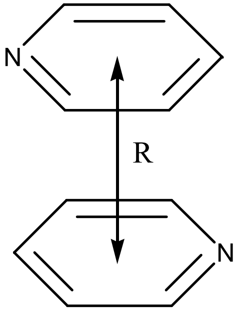


E = **-1.11 kcal/mol**

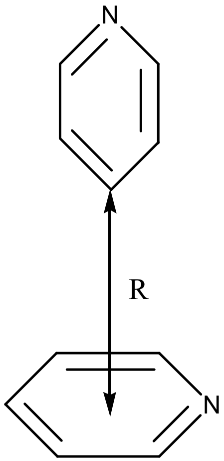
MP2/6-311++G** (BSSE corrected)



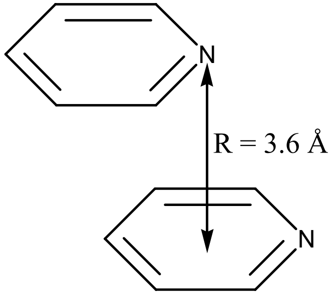
-1.53 kcal/mol



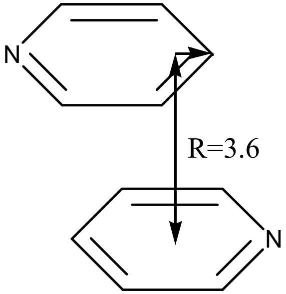
-3.05 kcal/mol



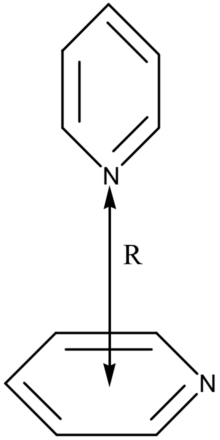
-1.91 kcal/mol



-2.39 kcal/mol

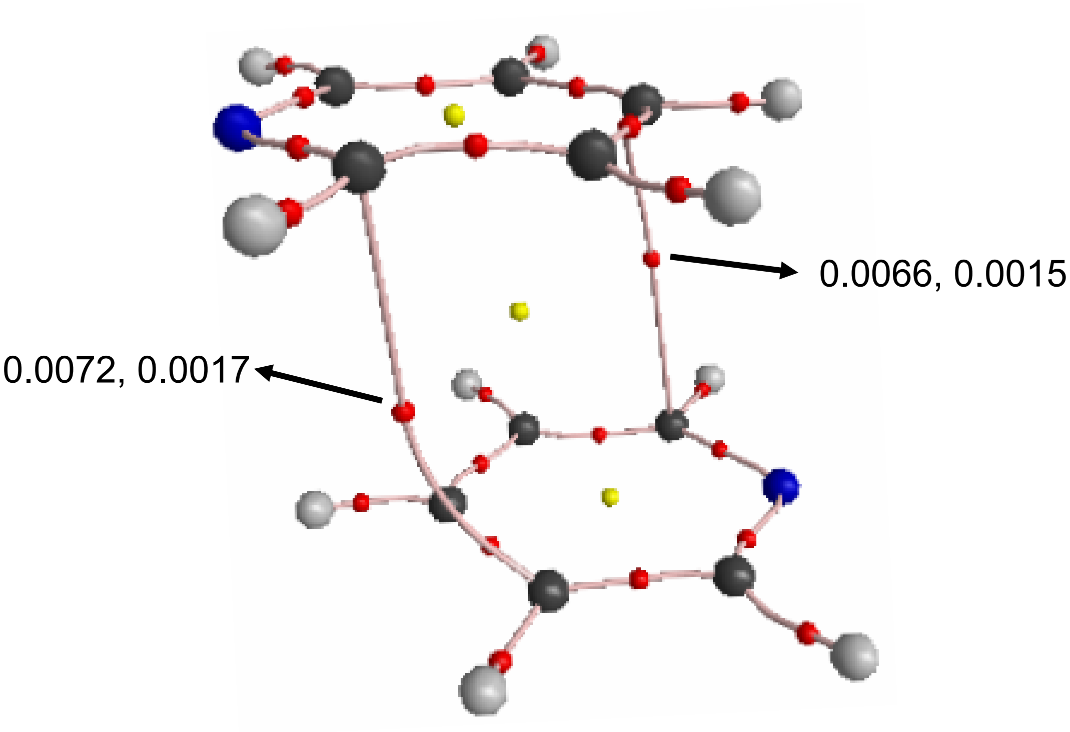


-3.97 kcal/mol



-1.47 kcal/mol

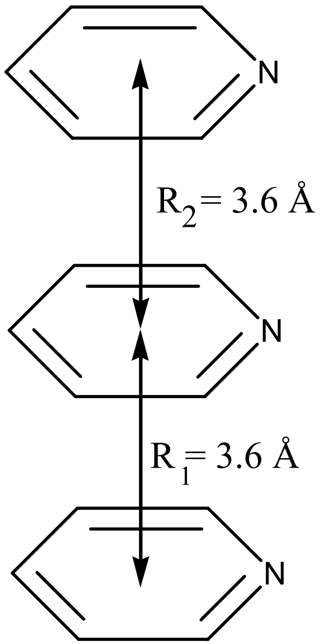
The most stable geometry of pyridine dimer (antiparallel-displaced orientation)



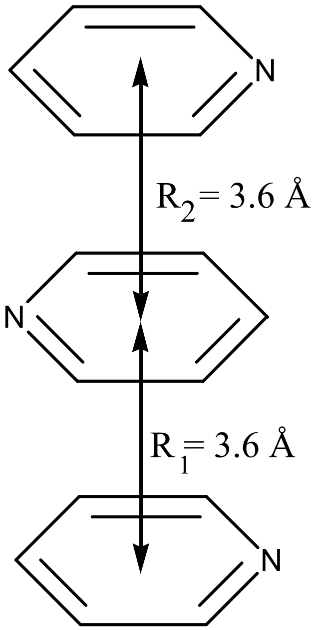
Most stable

- Stacking, anti-parallel, displaced!
- Same is true for the trimer

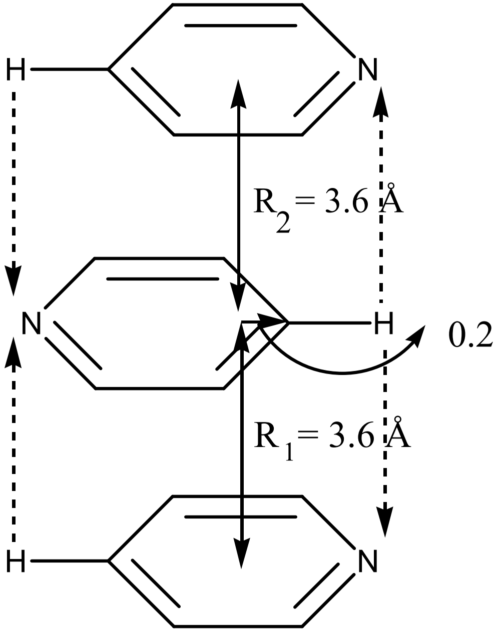
MP2/6-311++G** (BSSE corrected)



-3.18 kcal/mol



-6.14 kcal/mol

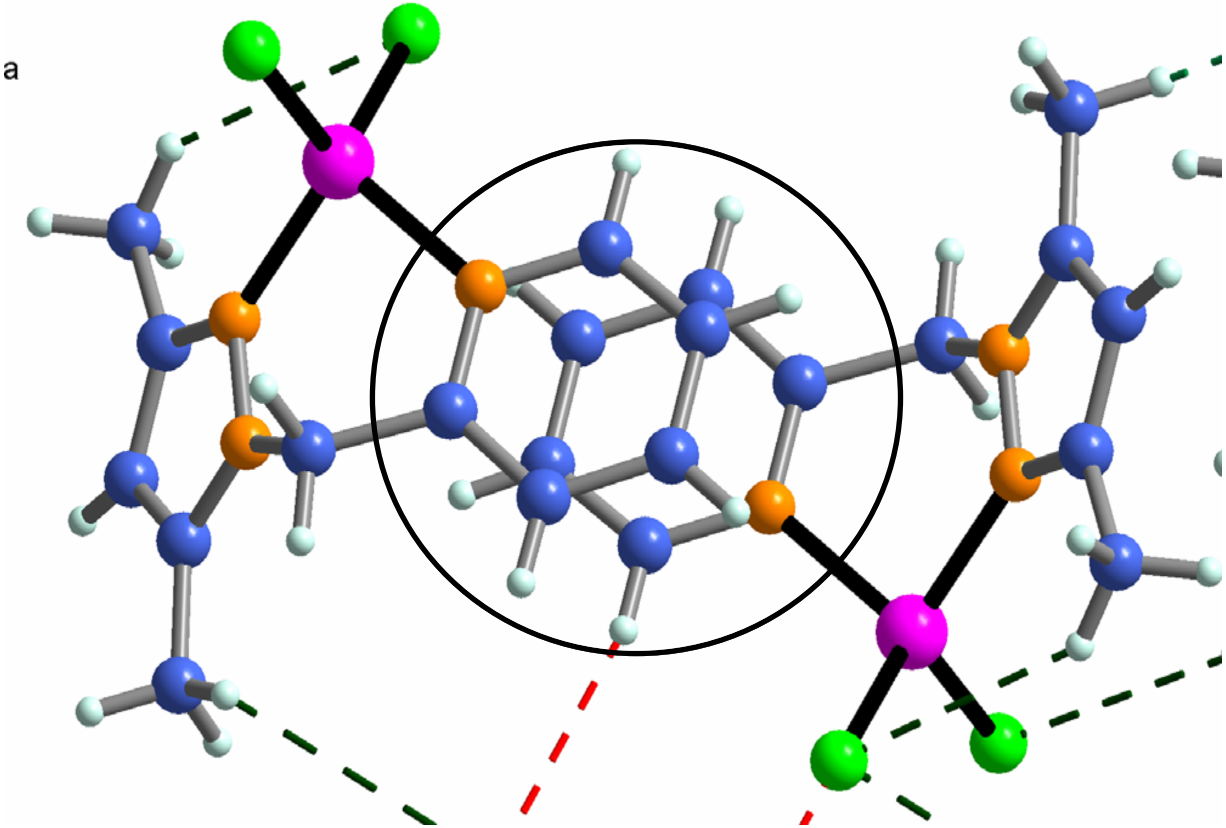


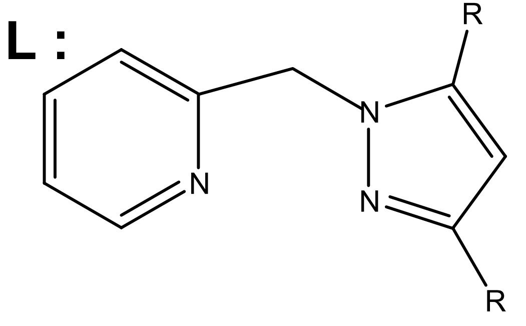
-8.04 kcal/mol

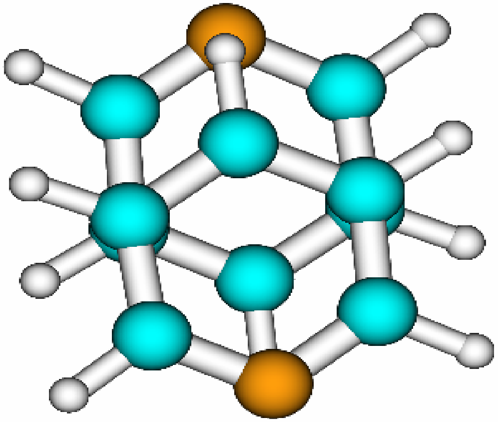
Experimental evidence?

- Yes, from the lab of Dr. R.N. Mukherjee

$[(L^2)CoCl_2]$



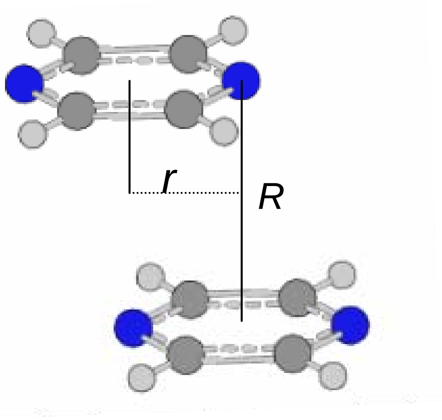




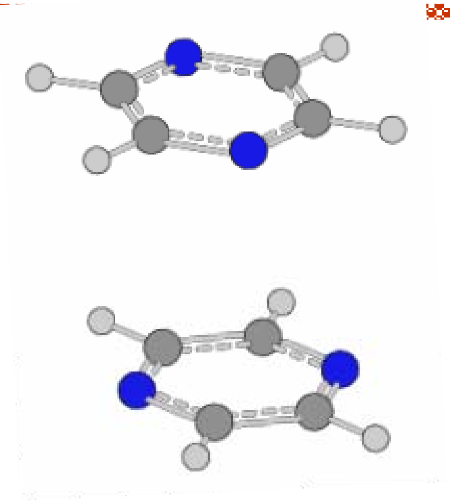
V. Balamurugan et al. Chem. Eur. J. 2004, 10, 1683-1690

Pyrazine Dimer:

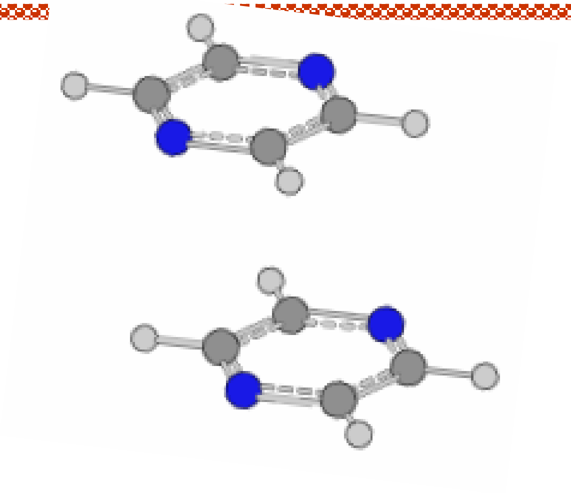
Pyrazine has no dipole moment,
but it has quadrupole moment.
It should prefer T-shape or
parallel displaced



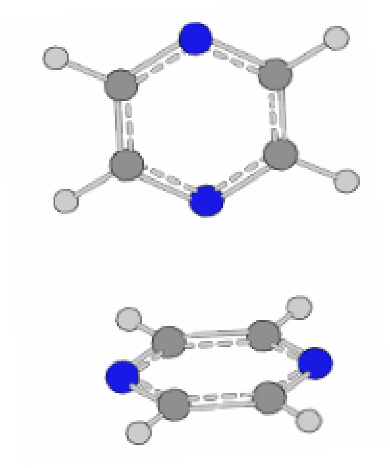
N-N-axial-displaced



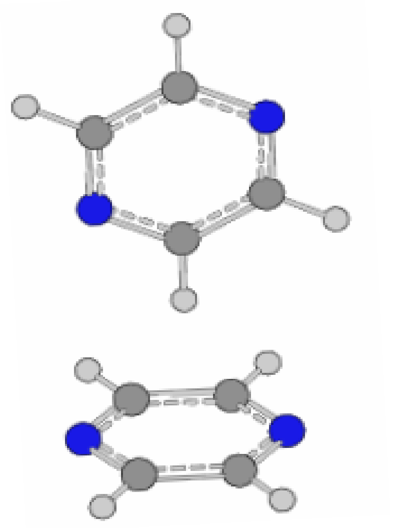
Cross-displaced



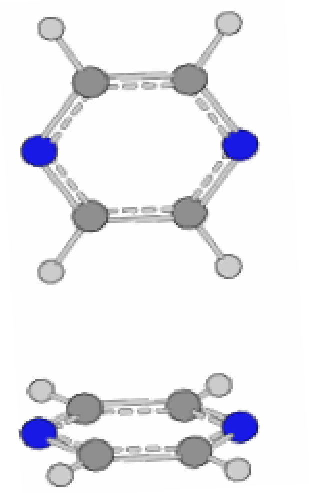
Lateral-displaced



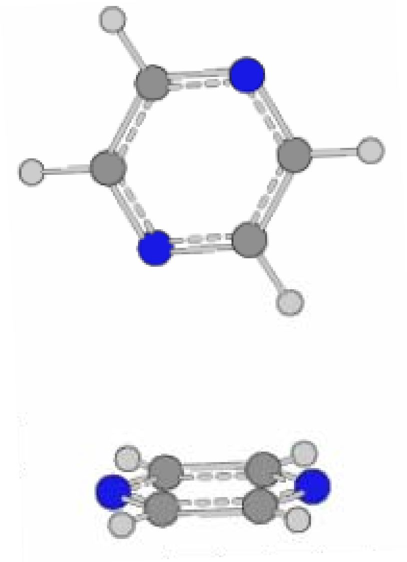
$T_{\text{N-ring}}$



$T_{\text{H-ring}}$

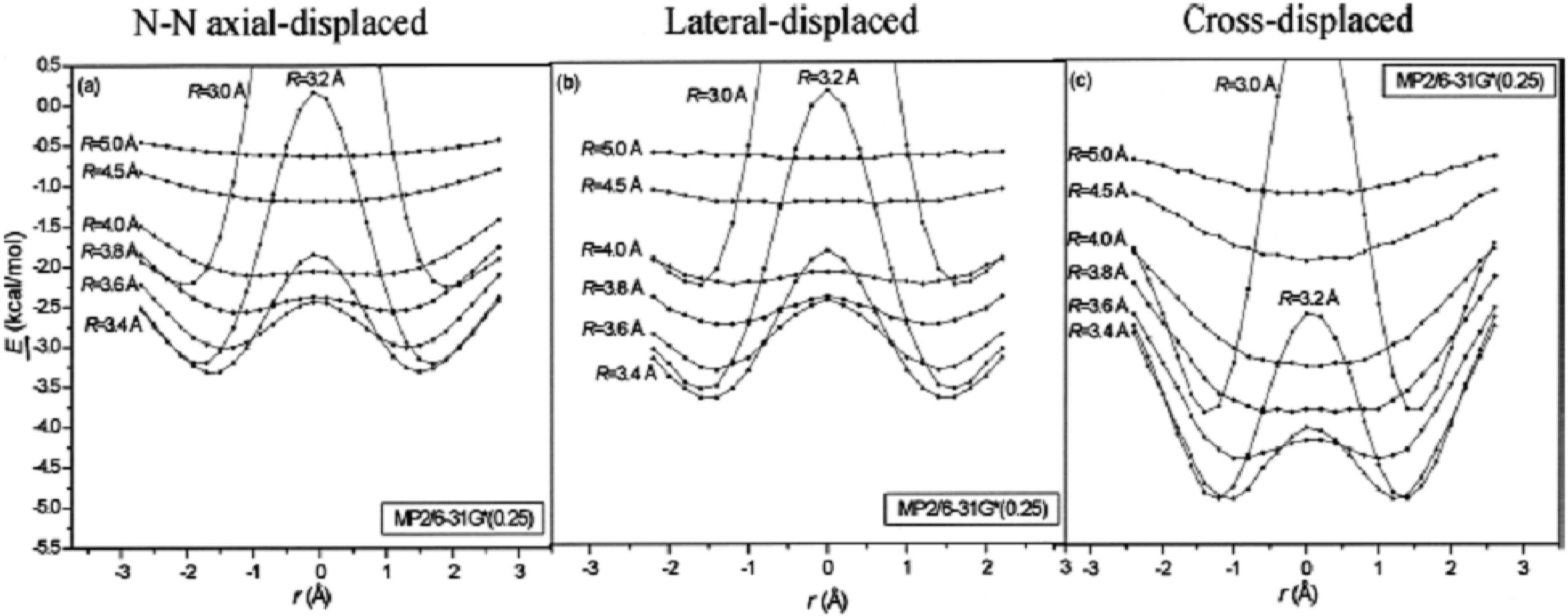


$W_{\text{C-C}}$



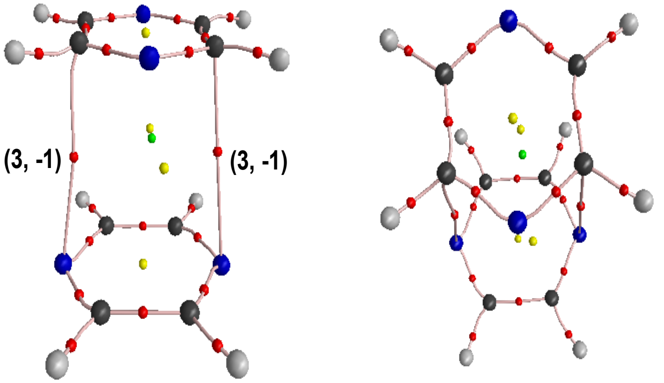
$W_{\text{C-N}}$

Brijesh K. Mishra and N. Sathyamurthy *J.T.C.C.* 5, 2006, 1-11

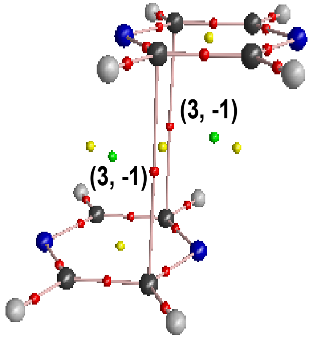

N-N axial-displaced
Lateral-displaced
Cross-displaced
(a)
(b)
(c)
R=3.0 Å
R=3.2 Å
R=5.0 Å
R=4.5 Å
R=4.0 Å
R=3.8 Å
R=3.6 Å
R=3.4 Å
MP2/6-31G*(0.25)
E (kcal/mol)
r (Å)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-3
-2
-1
0
1
2
3

Interaction energies for different geometries of pyrazine dimer using cc-pVDZ basis set

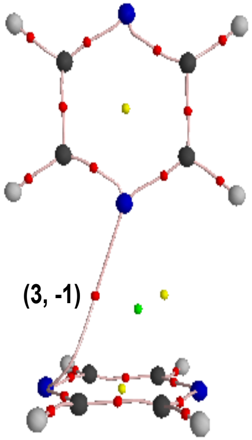
Geometries	*R* (Å)	*r* (Å)	MP2 (kcal/mol)	MP4 (kcal/mol)	CCSD(T) (kcal/mol)
N-N-axial-displaced	3.1	1.2	-4.54	-1.19	-2.24
Cross-displaced	3.1	1.6	-6.56	-2.57	-3.78
$T_{\text{N-ring}}$	4.2	-	-5.48	-3.21	-3.98
$W_{\text{C-C}}$	4.8	-	-3.51	-2.24	-2.78



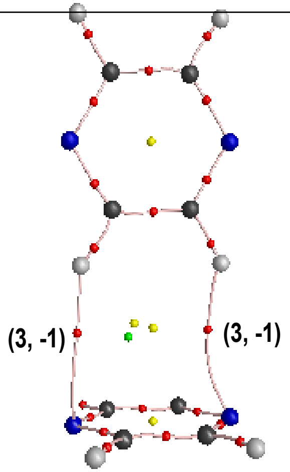
Parallel-displaced-rotated **Top view**



N-N axial-displaced



T-shape



Wedge Shape

Molecular topography of pyrazine dimers obtained from theoretical charge density.

Summary

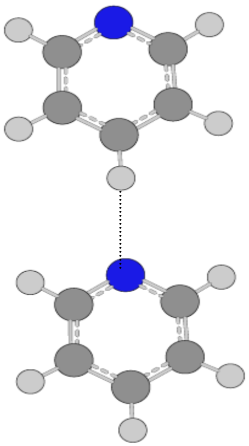
- Stacking interaction in benzenoid systems influenced by multipole (dipole and quadrupole) moments of the molecules.
- Electron density and the Laplacian at the bond critical points are comparable to those obtained for hydrogen bonding and follow the same linear relation between the strength and density

Spreading in N-Heterocyclic Aromatic Ring: Weak Hydrogen Bonding

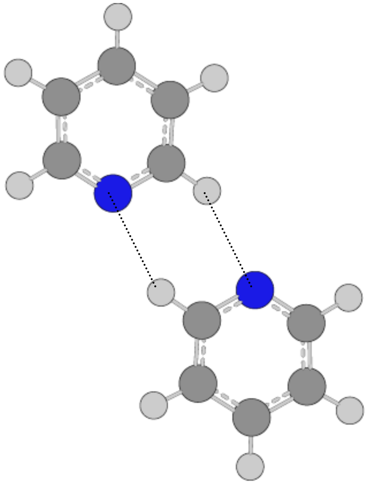
Method : MP2/6-311G**
BSSE correction
AIM Analysis

Pyridine dimers and trimers

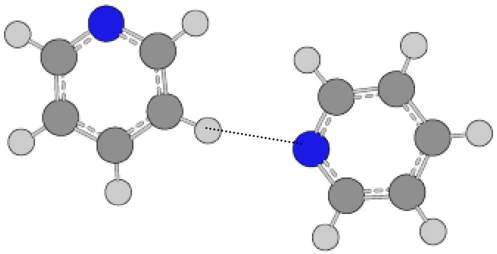
* Stabilization energies in kcal/mol



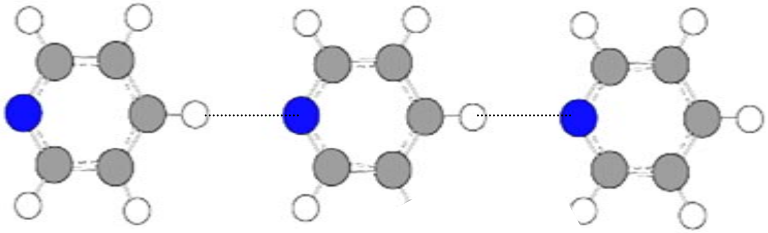
Dimer-1
-2.25



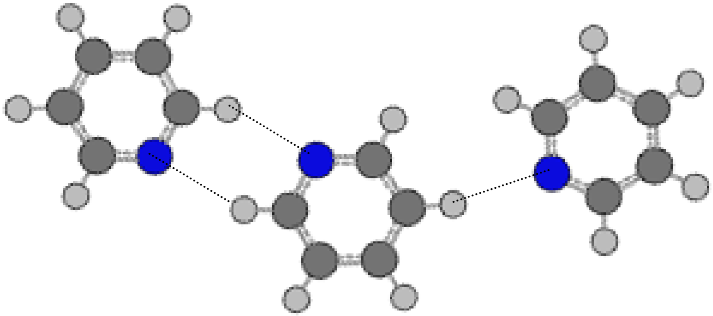
Dimer-2
-3.25



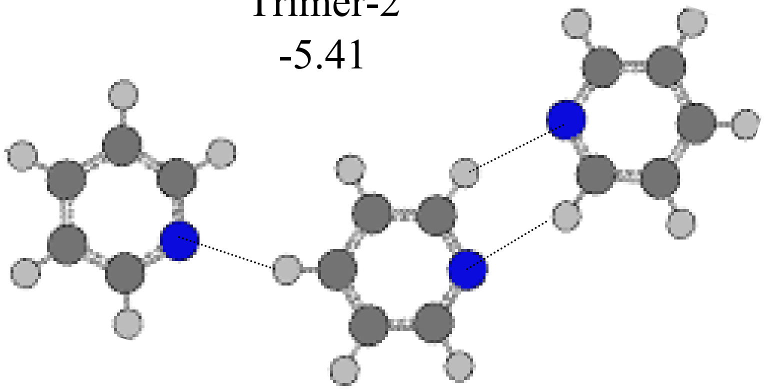
Dimer-3
-2.30



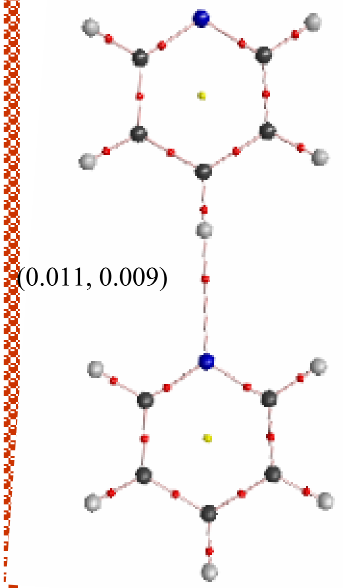
Trimer-1
-4.79



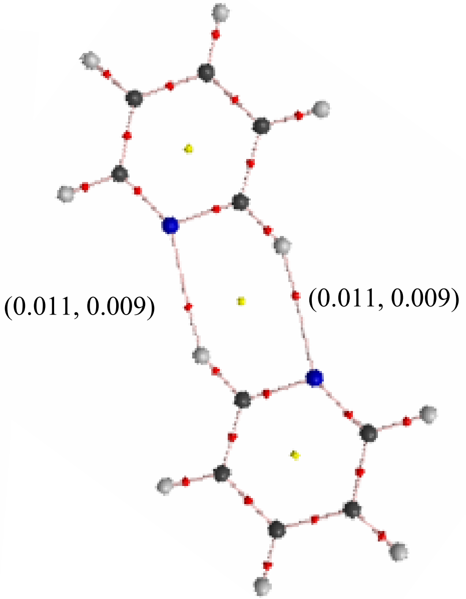
Trimer-2
-5.41



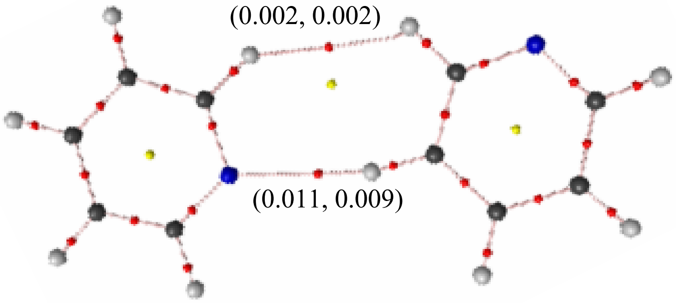
Trimer-3 (-5.38)



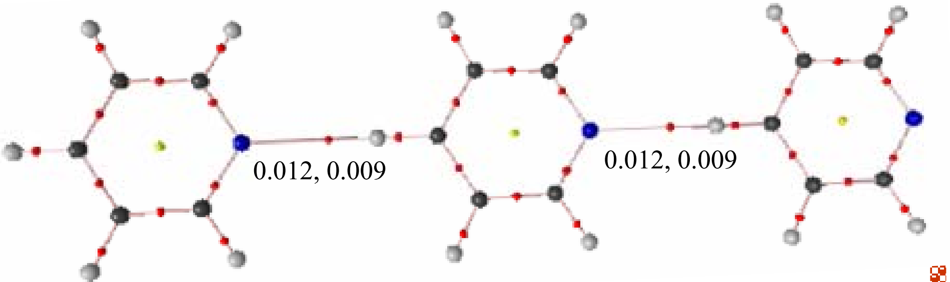
Dimer-1



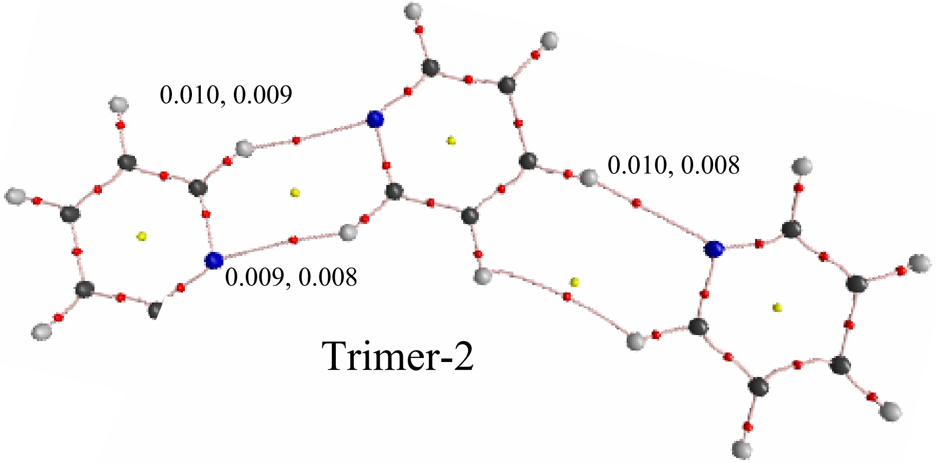
Dimer-2



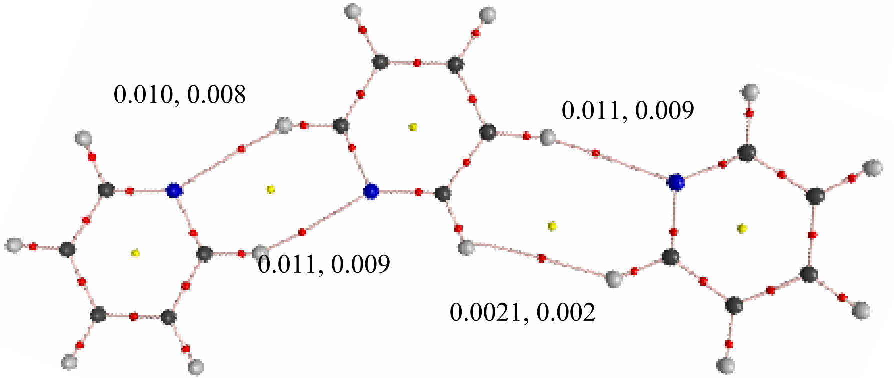
Dimer-3



Trimer-1

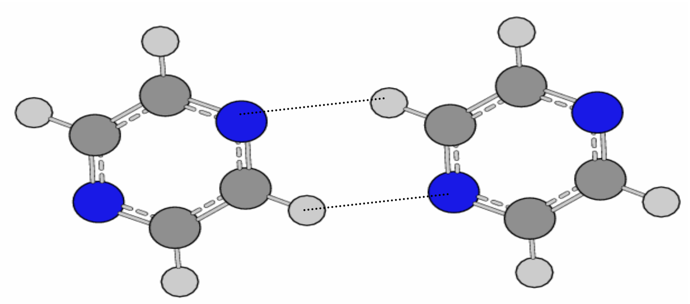


Trimer-2

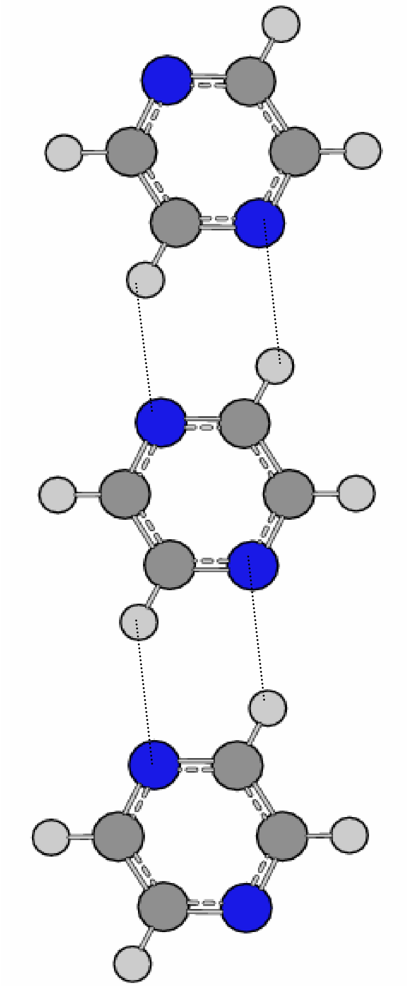


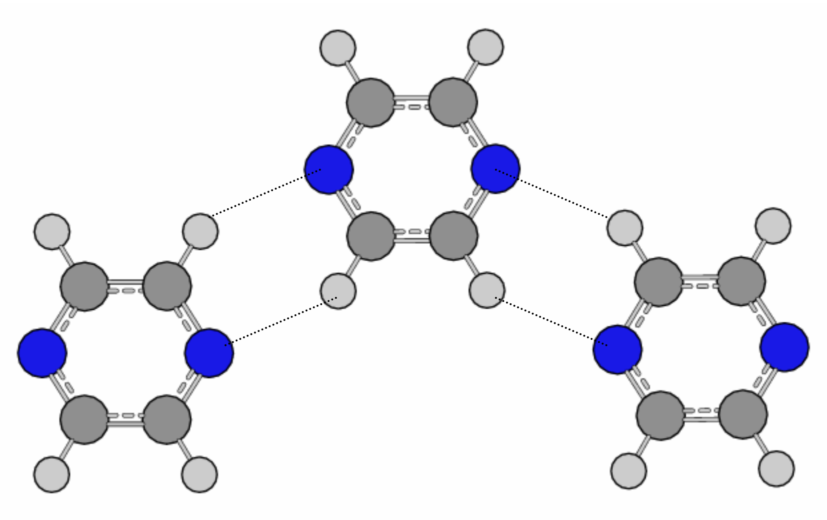
Trimer-3

Pyrazine dimer and trimer: stabilization energy in kcal/mol



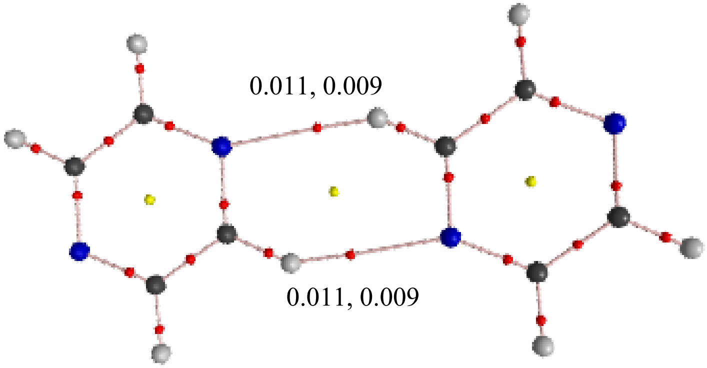
Dimer
-3.64



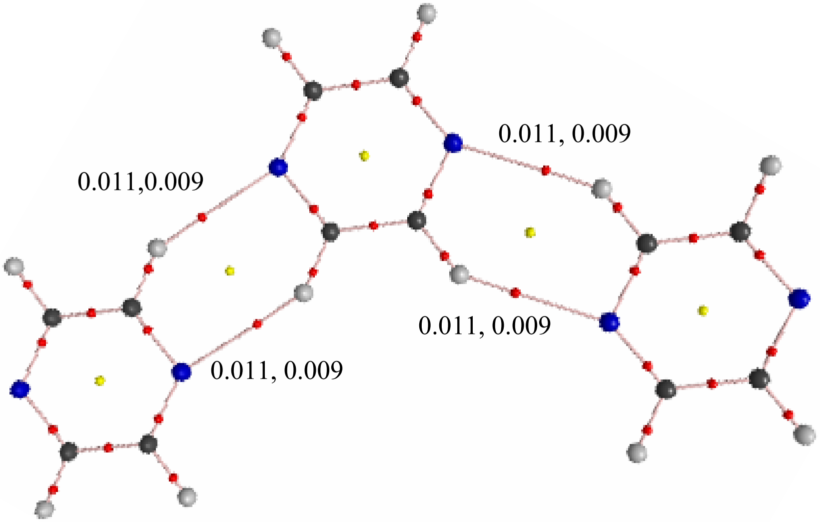


Trimer-1
-7.32

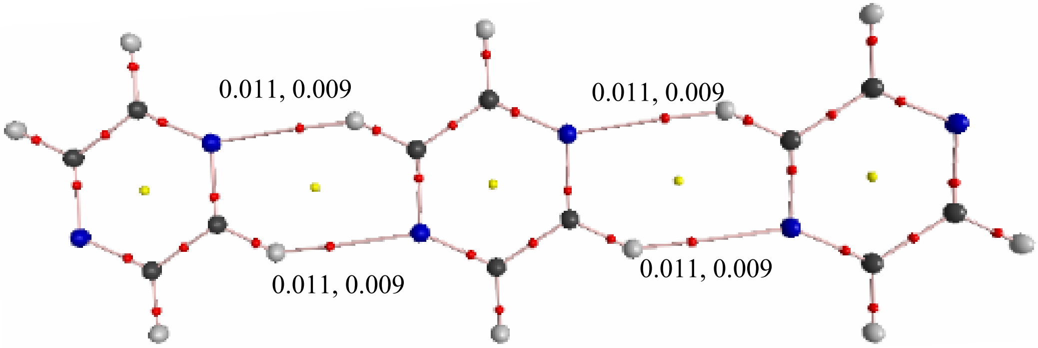
Trimer-2
-7.19



Dimer

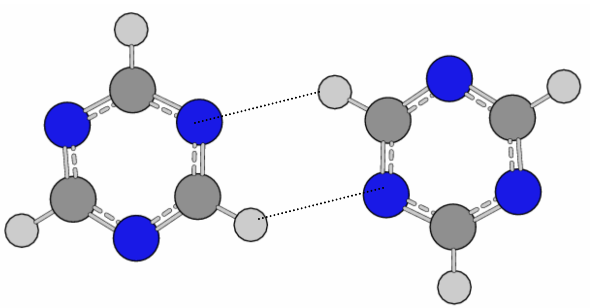


Trimer-1



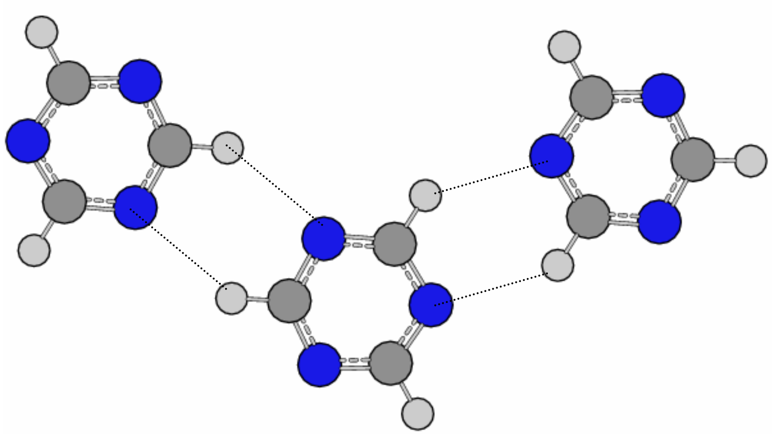
Trimer-2

1,3,5-Triazine dimer, trimer and tetramer



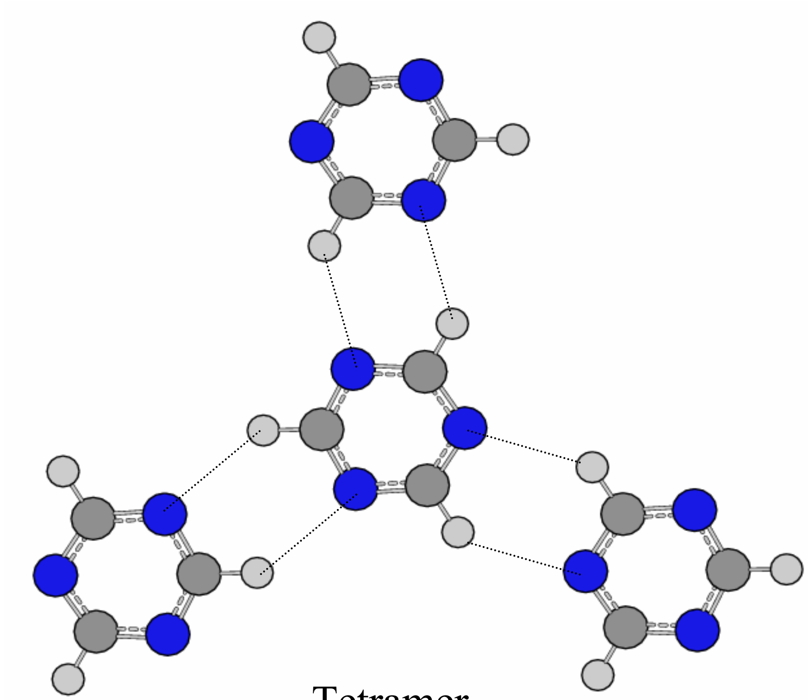
Dimer

-3.07



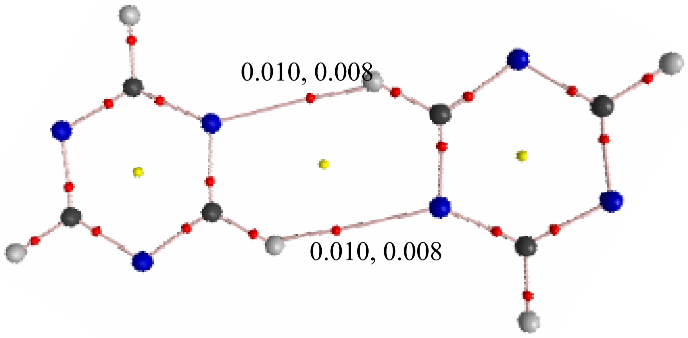
Trimer

-6.22

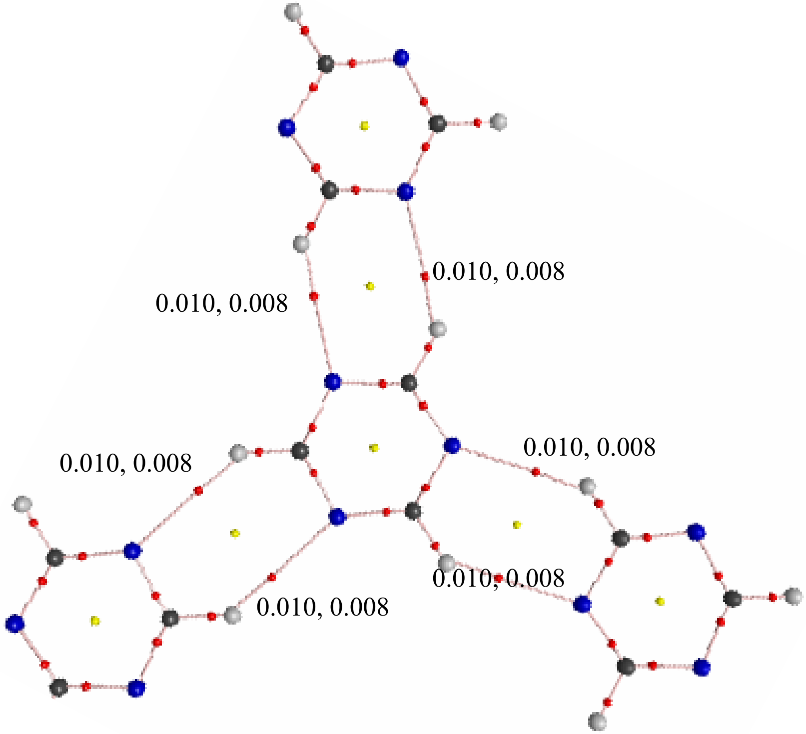


Tetramer

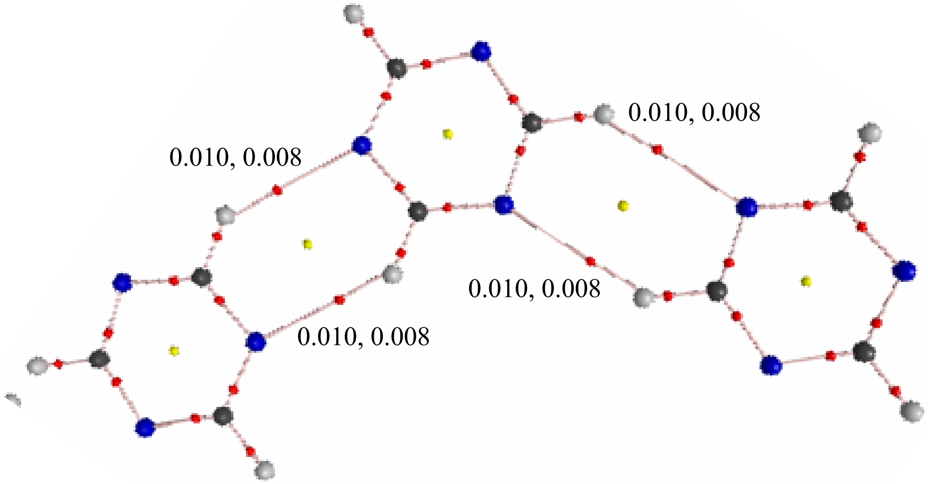
-9.44



Dimer

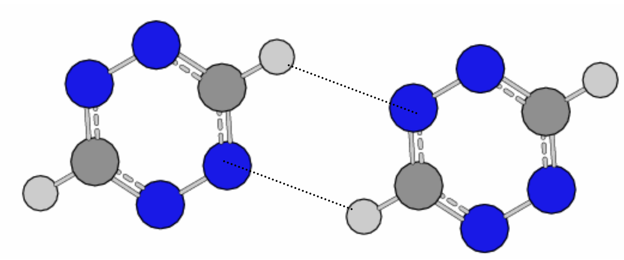


Tetramer

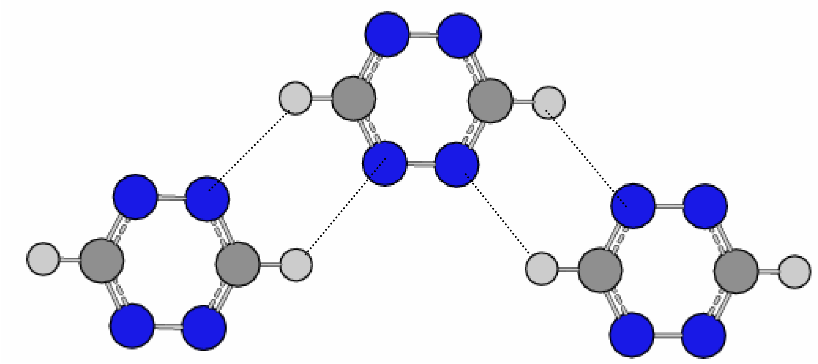


Trimer

Tetrazine dimer and trimers

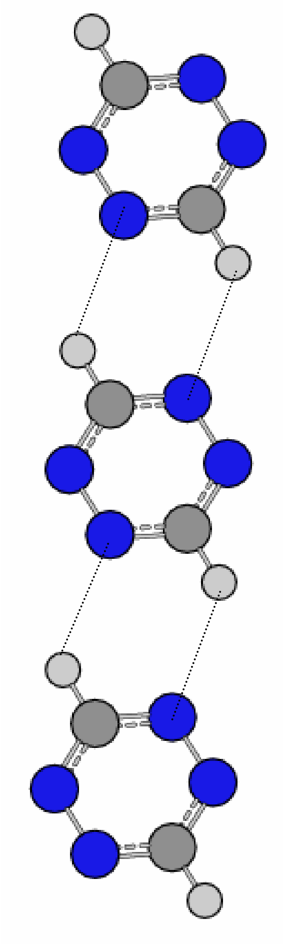


Dimer
-4.26



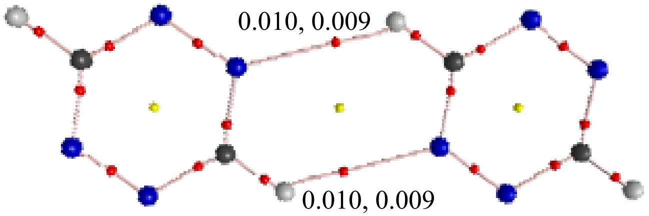
Trimer-1

-8.39

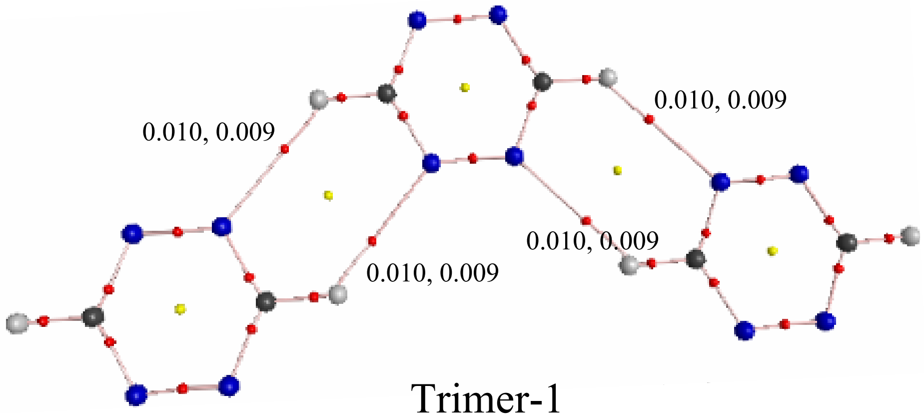


Trimer-2

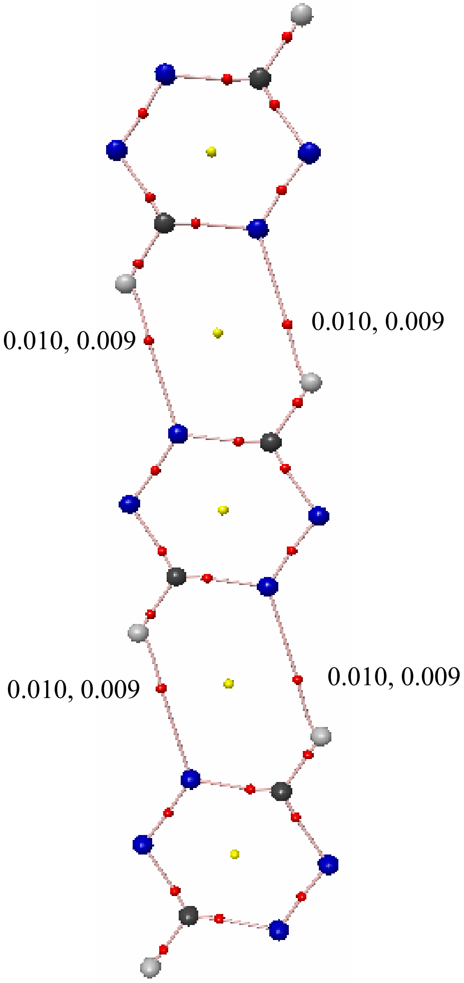
-8.60



Dimer



Trimer-1



Trimer-2

Same story

- Electron density at the BCPs in spreading and stacking interaction is comparable to that for hydrogen bond
- Its magnitude and Laplacian reflect the strength

THANK YOU

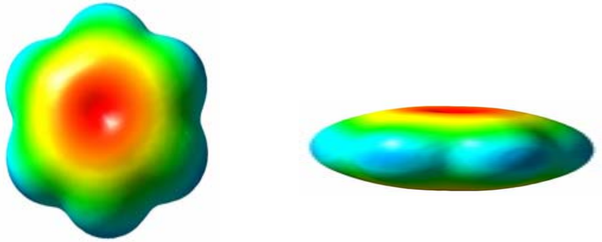
Preference of Orientation in Van der Waals Complexes

Method

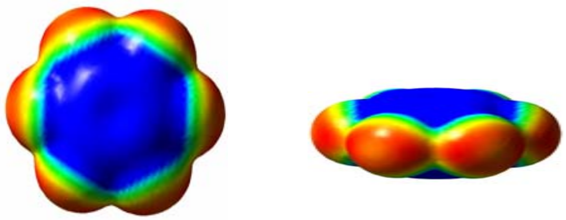
- MP2/6-311++G**
- BSSE correction using counterpoise method
- Packages:
- Gaussian 03
- CADPAC
- Orient 3.2

Quadrupole moment :

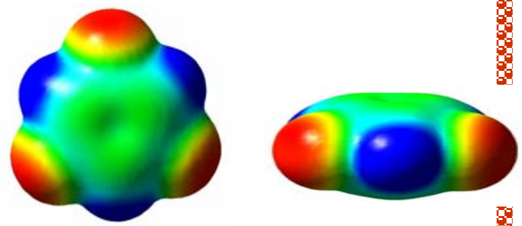
Benzene	Hexafluorobenzene	1,3,5 trifluorobenzene
-8.38 debye Ǻ	**+9.24 debye Ǻ**	**0.81 debye Ǻ**



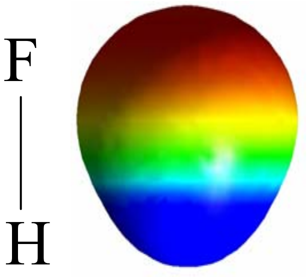
Benzene



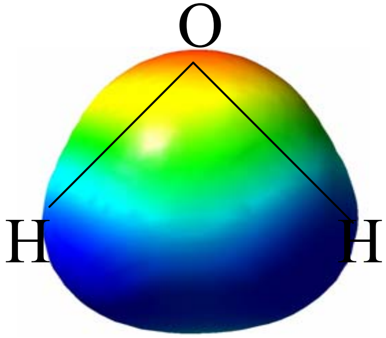
Hexafluorobenzene



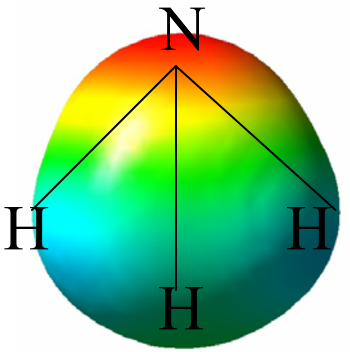
1,3,5-trifluorobenzene



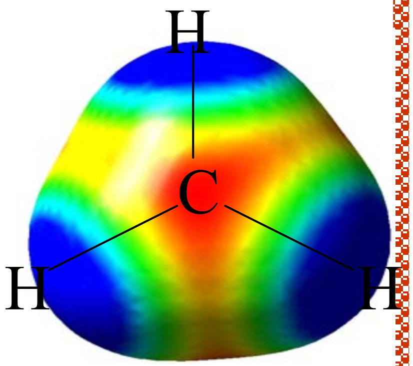
HF



H_2O

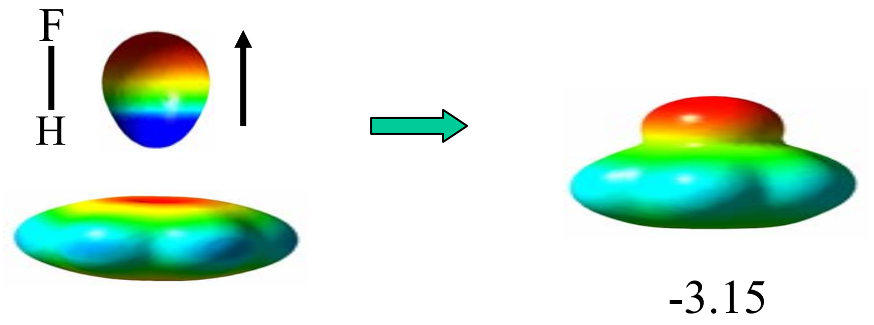
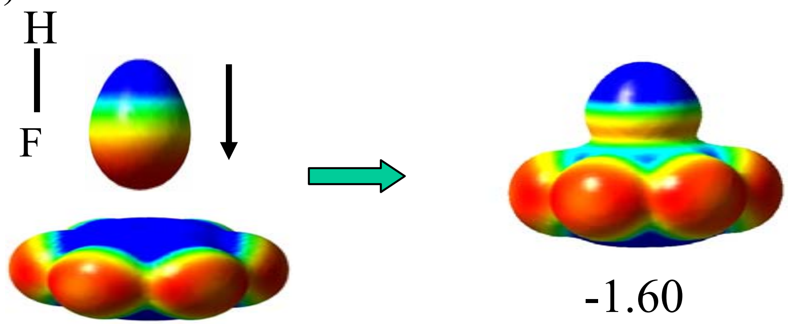
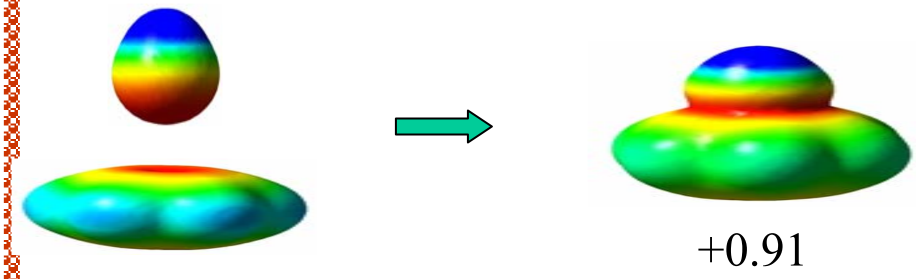
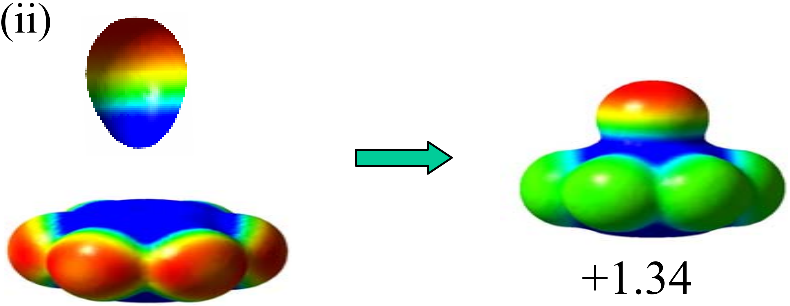
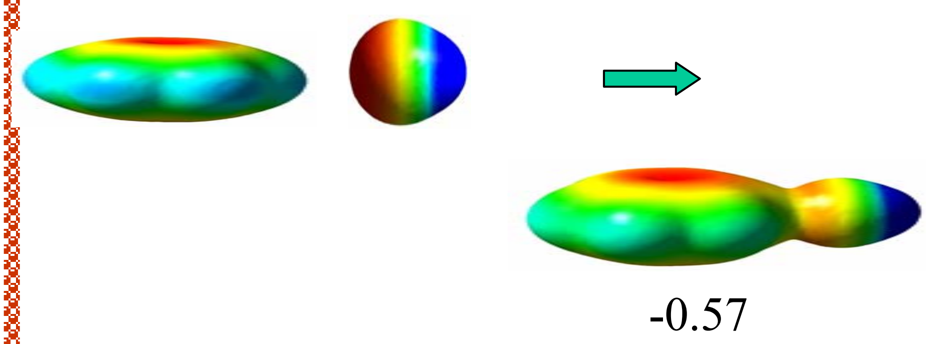
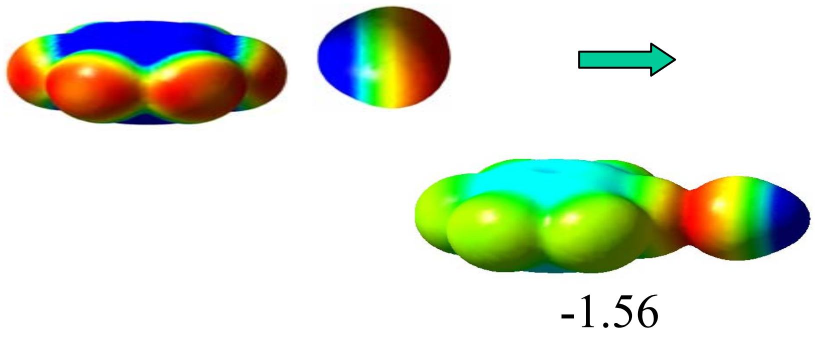


NH_3



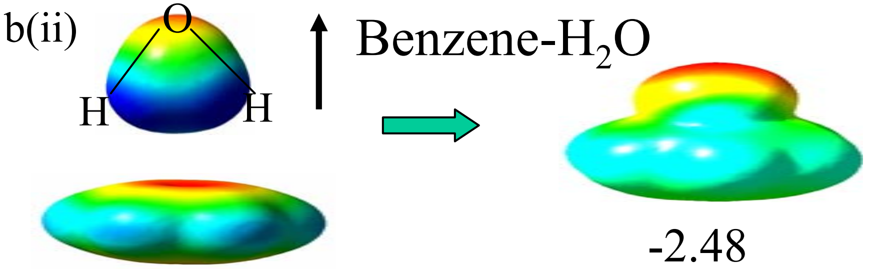
CH_4

Blue: positive Red: negative

Benzene-HF	Hexafluorobenzene-HF
1a(i)  	2a(i) 
1a(ii)  	2a(ii) 
1a(iii)  	2a(iii) 

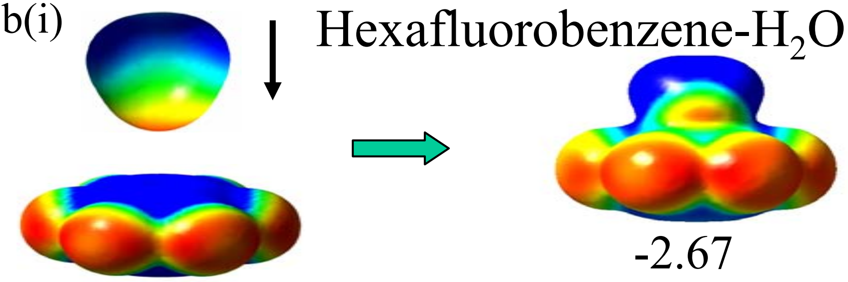
Benzene-H_2O

1b(ii)

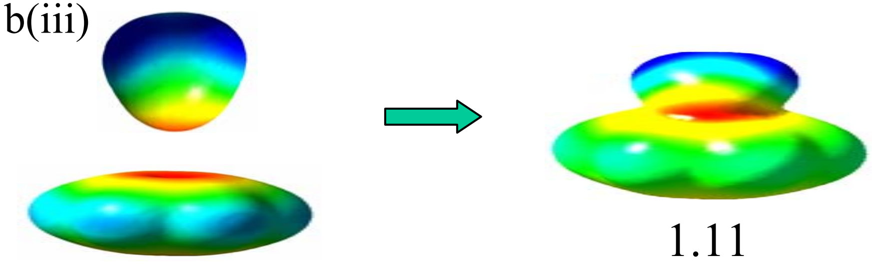


Hexafluorobenzene-H_2O

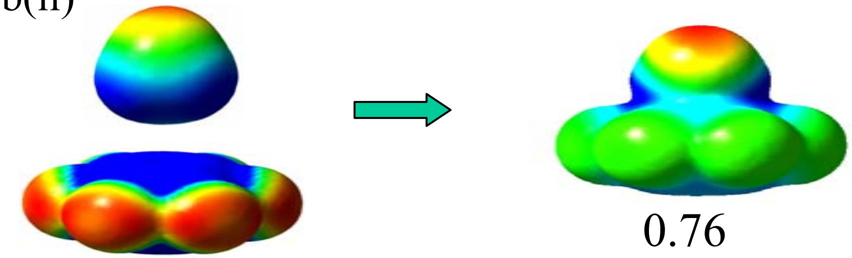
2b(i)



1b(iii)



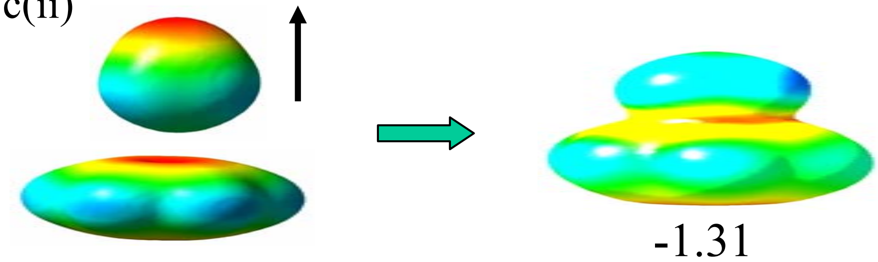
2b(ii)



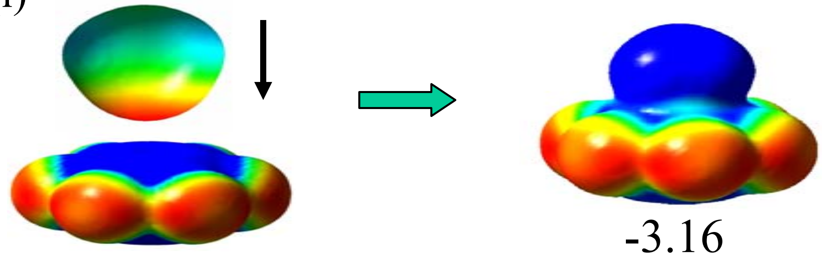
Benzene-NH_3

Hexafluorobenzene-NH_3

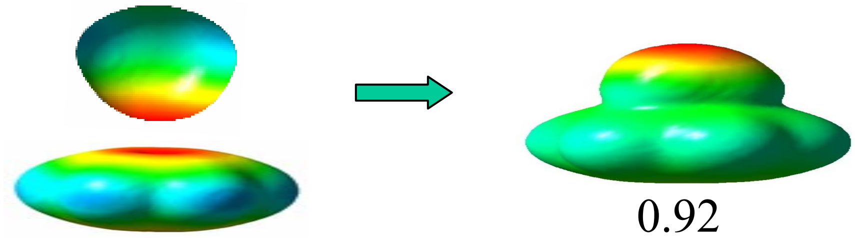
1c(ii)



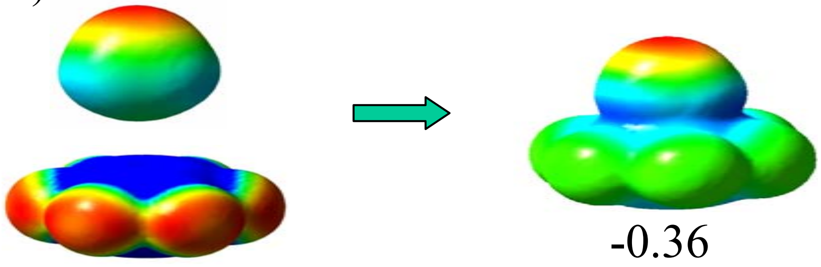
2c(i)

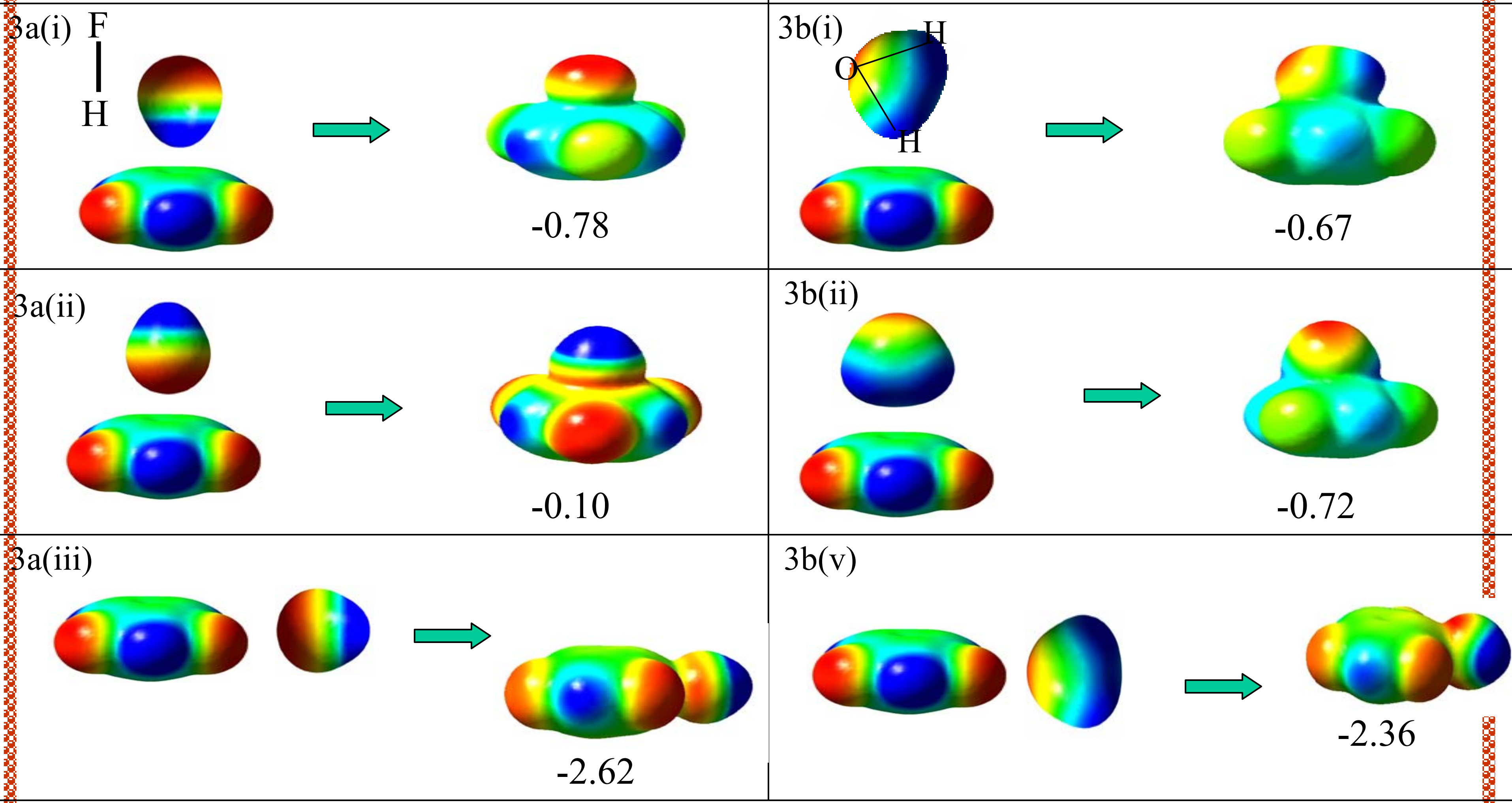


1c(iii)



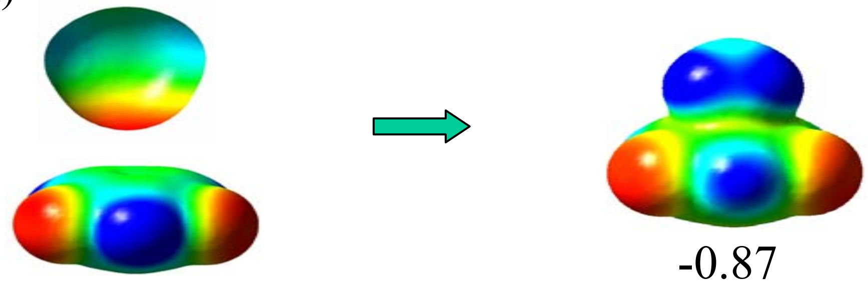
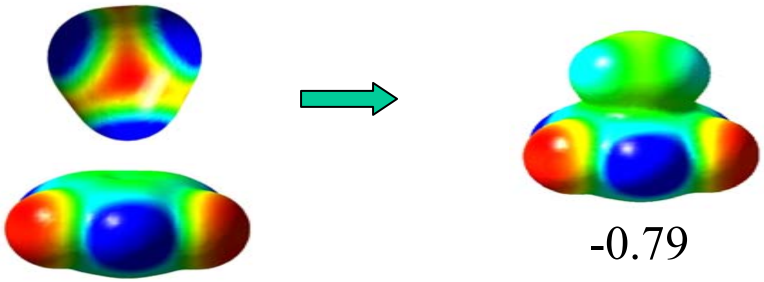
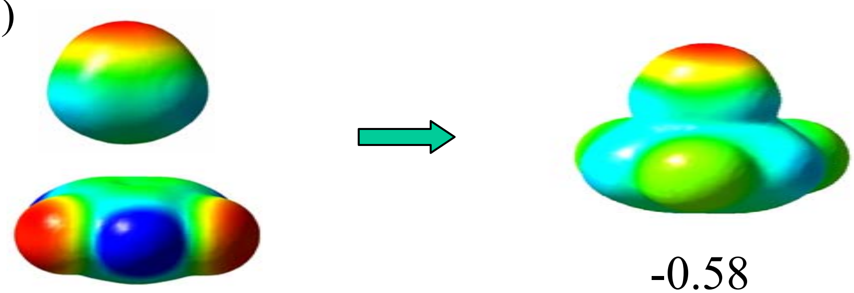
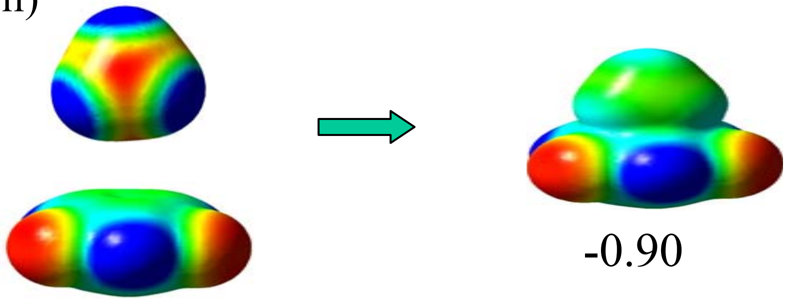
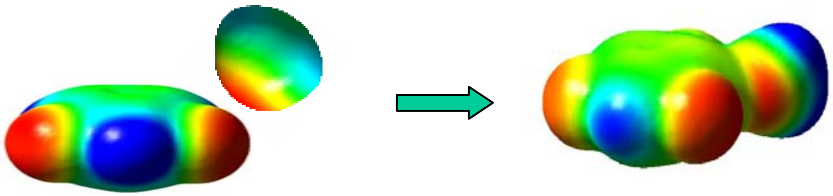
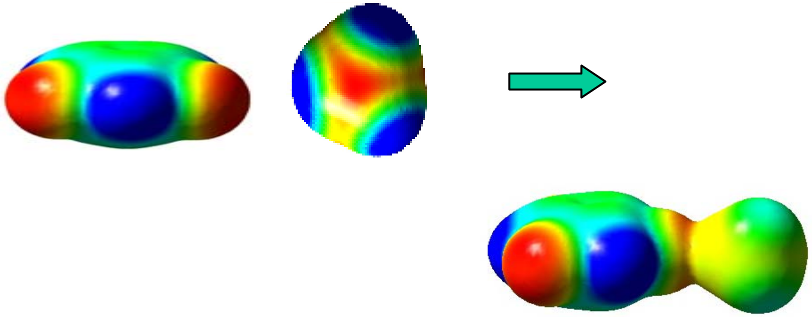
2c(iii)

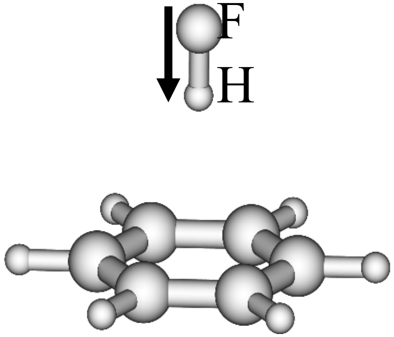




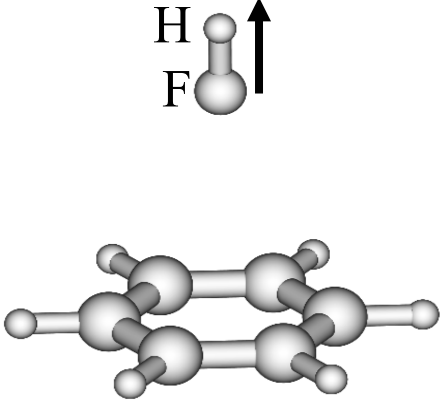
1,3,5-trifluorobenzene-HF

1,3,5-trifluorobenzene-H_2O

3c(i)  -0.87	4d(i)  -0.79
3c(ii)  -0.58	4d(ii)  -0.90
3c(iv)  -2.87	4d(iii)  -0.20
1,3,5-trifluorobenzene-NH_3	1,3,5-trifluorobenzene-CH_4

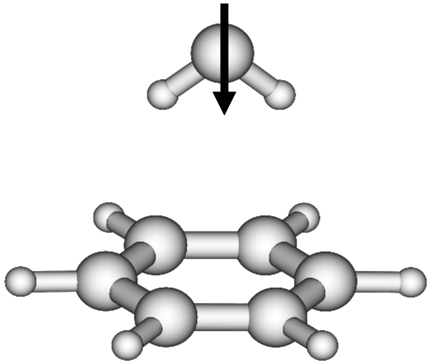


-3.15 kcal/mol (-5.42)

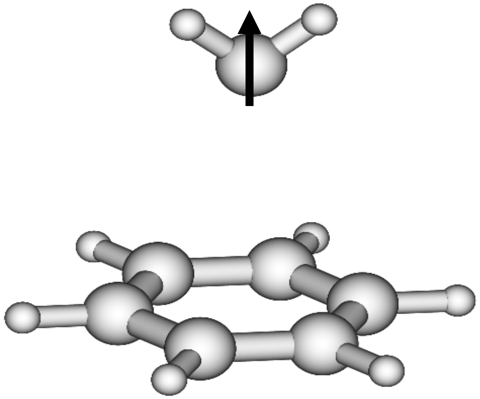


+0.91 kcal/mol (-0.14)

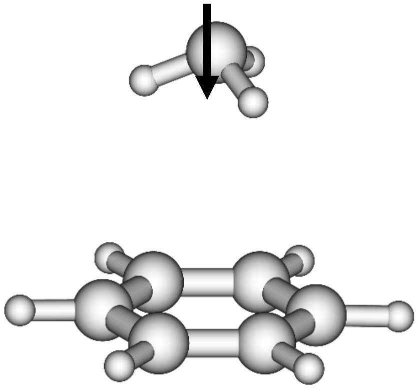
Benzene-molecule interaction



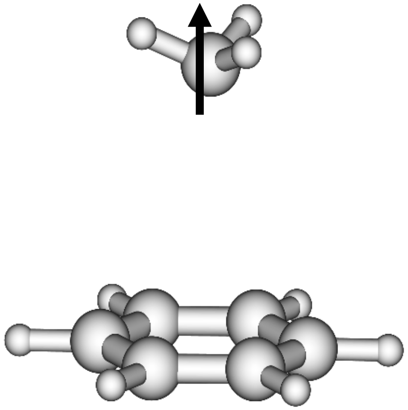
-2.48 kcal/mol (-4.30)



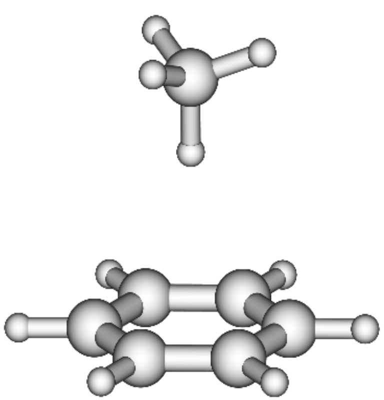
+1.11 kcal/mol (-0.17)



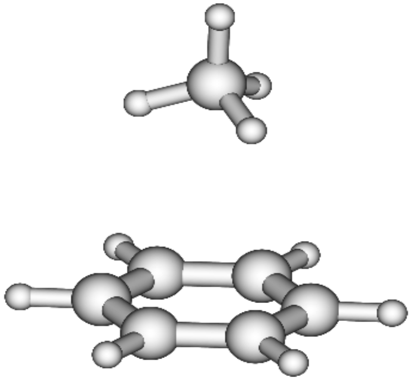
-1.31 (-2.89)



+0.92 (-0.31)



-0.85 (-2.66)



-0.94 (-2.55)

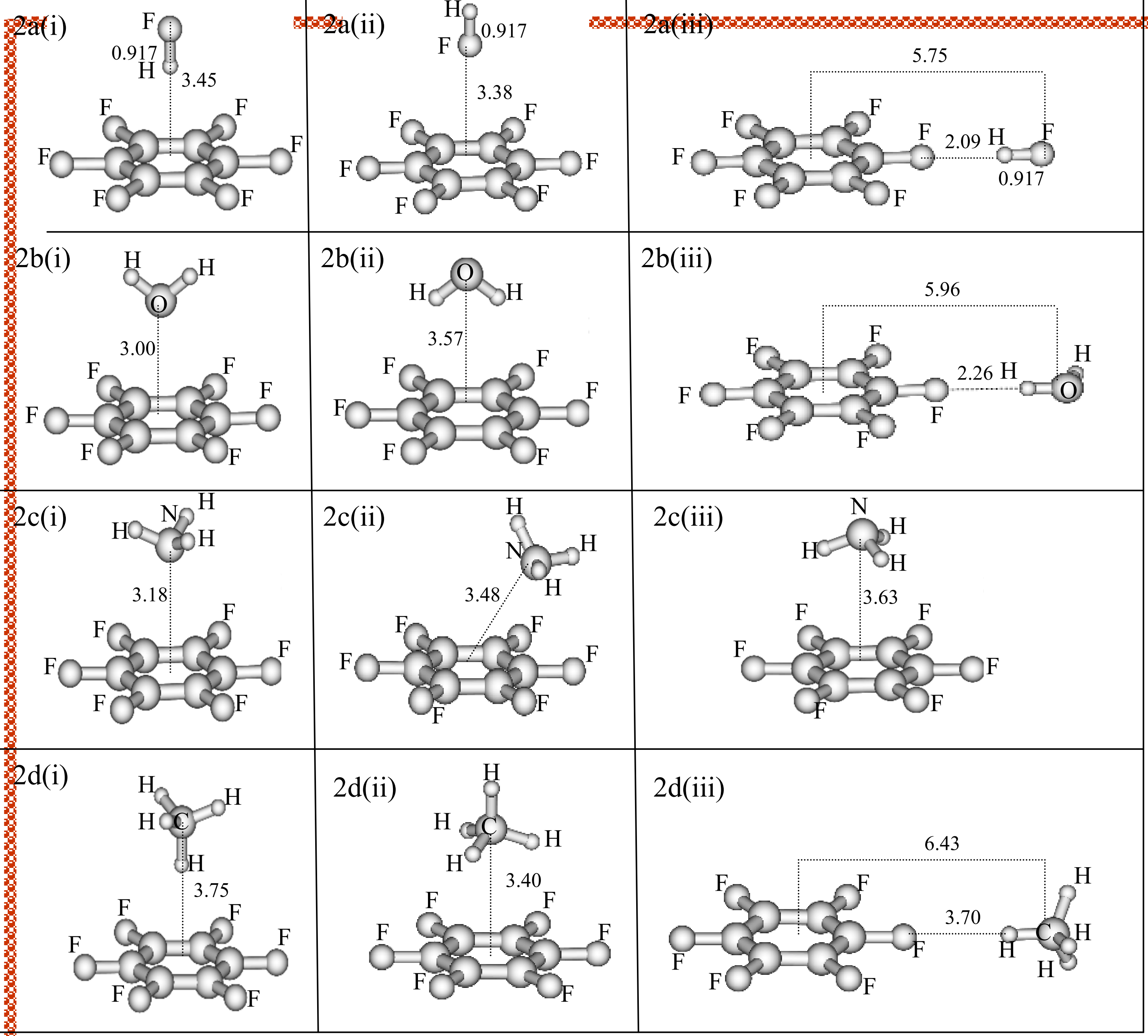
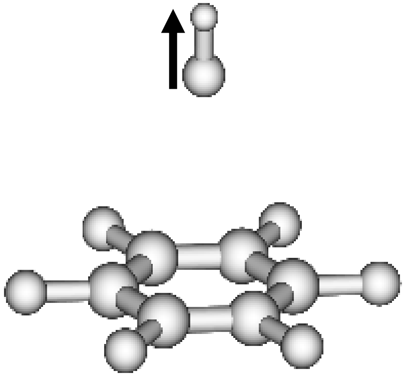
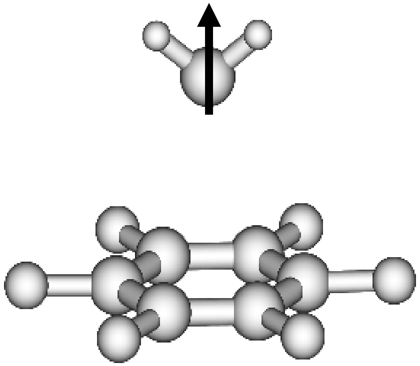

2a(i)
F
0.917
H
3.45
2a(ii)
H
0.917
F
3.38
2a(iii)
5.75
F
2.09 H
F
0.917
2b(i)
H
H
O
3.00
2b(ii)
O
H
H
3.57
2b(iii)
5.96
H
2.26 H
O
F
2c(i)
N
H
H
H
3.18
2c(ii)
H
N
H
H
3.48
2c(iii)
N
H
H
H
3.63
2d(i)
H
H
H
C
H
3.75
2d(ii)
H
H
C
H
H
3.40
2d(iii)
6.43
H
3.70
C
H
H
H
F

Fig 2.

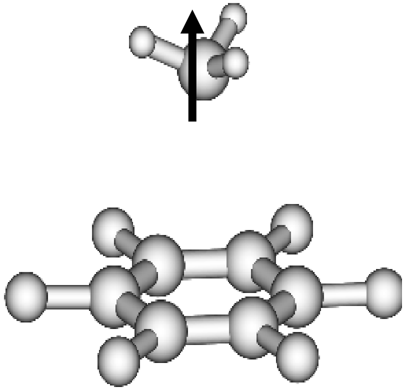


-1.60

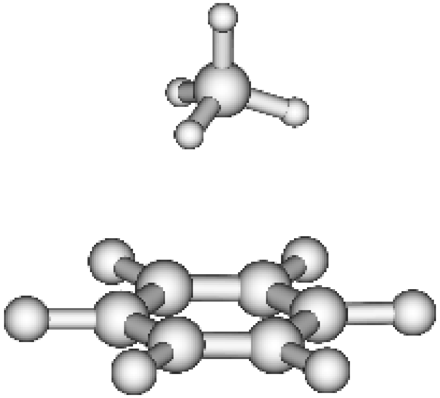


-2.70

Hexafluorobenzene-molecule interaction



-3.14



-1.25

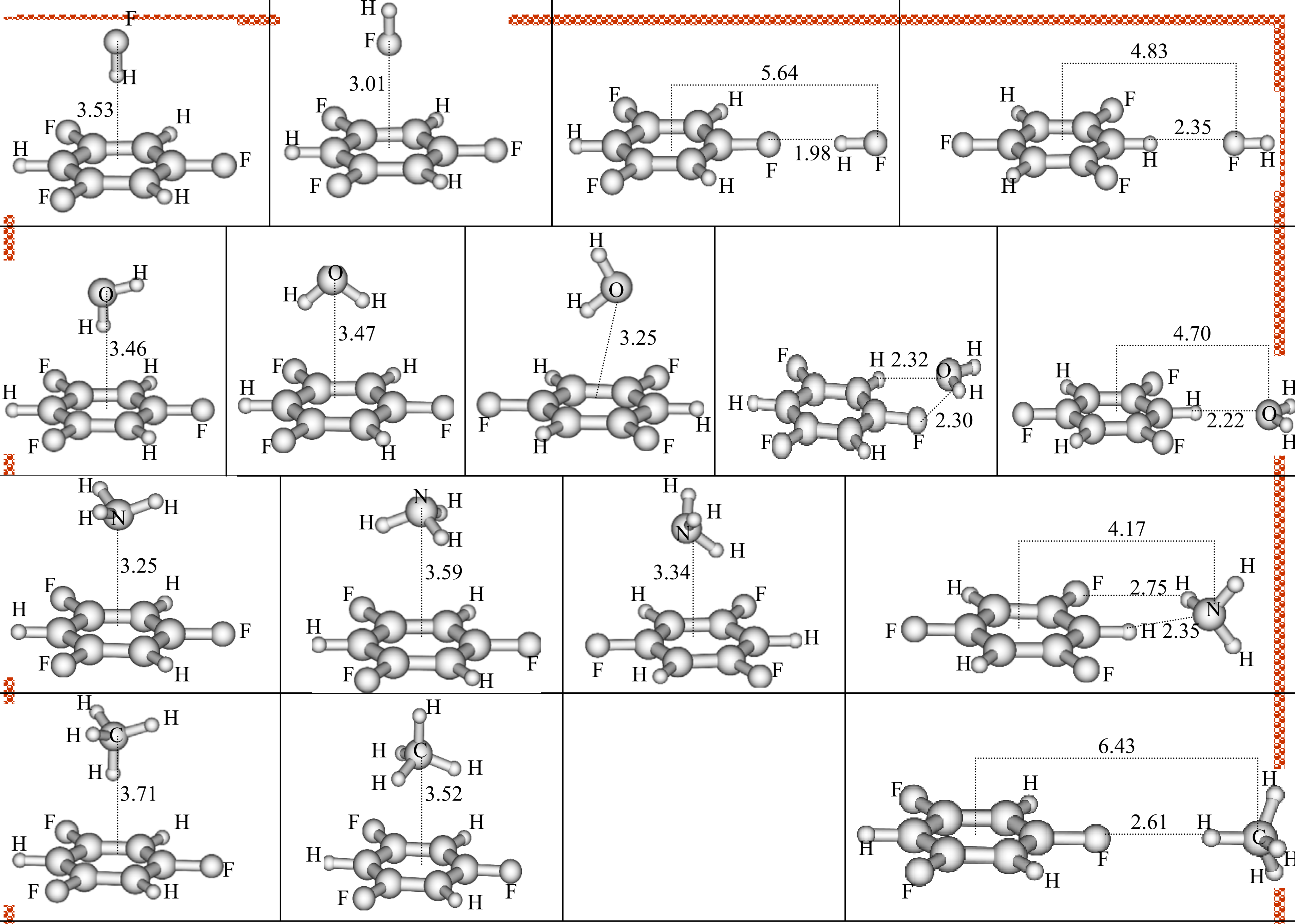
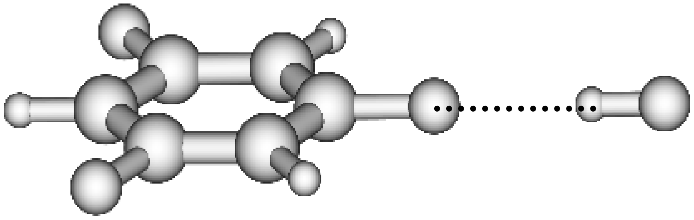
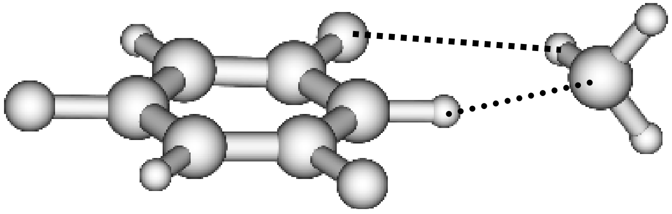

F
H
3.53
F
H
3.01
5.64
1.98
4.83
2.35
O
3.46
O
3.47
O
3.25
2.32
O
2.30
4.70
O
2.22
N
3.25
N
3.59
N
3.34
4.17
2.75
N
2.35
C
3.71
C
3.52
6.43
2.61
C

Fig 3

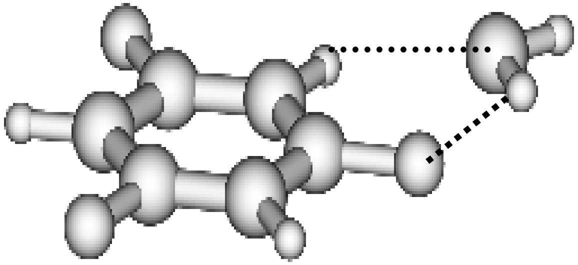


-2.62 (-3.06)

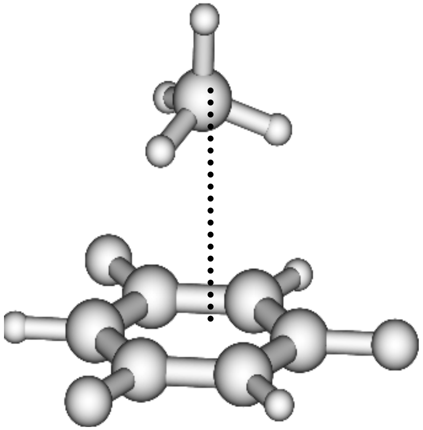


-2.87 (-4.44)

Sym-trifluorobenzene-molecule interaction



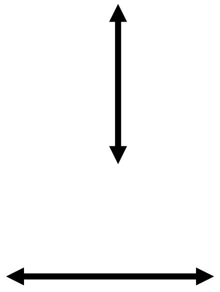
-2.93 (-4.16)



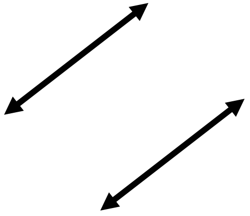
-0.90 (-2.64)

Quadrupole-Quadrupole Interaction

$$E = -3\Theta^{A}\Theta^{B}\ /\ 4\pi\varepsilon_{o}\mathrm{R}^{5}$$



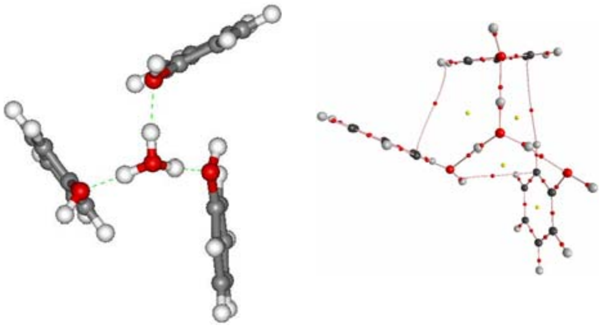
$$E = -2.4\Theta^{A}\Theta^{B}\ /\ 4\pi\varepsilon_{o}\mathrm{R}^{5}$$



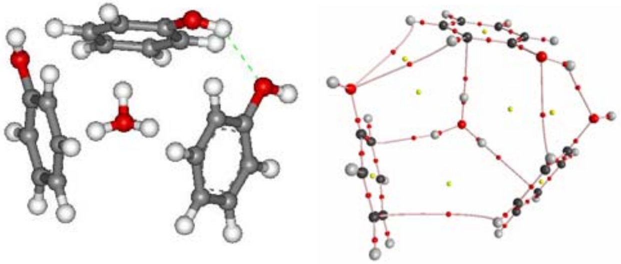
$$E = +2.25\Theta^{A}\Theta^{B}\ /\ 4\pi\varepsilon_{o}\mathrm{R}^{5}$$

A. J. Stone

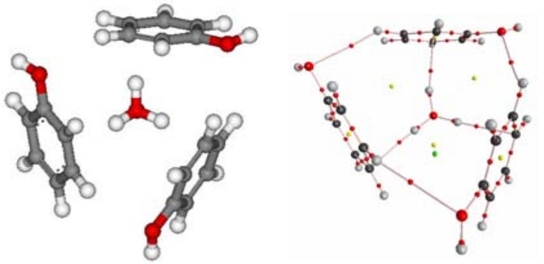
The Solvation of H_3O^+ by phenol: Hydrogen bonding **vs** *π complexation*



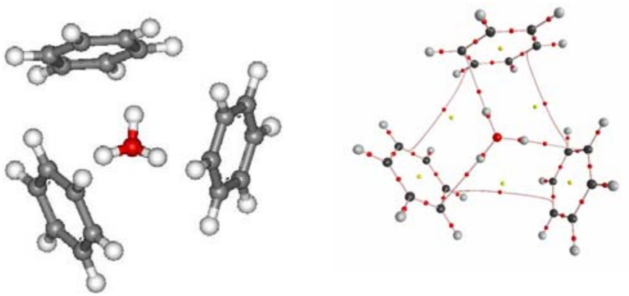
C1→-72.99



C2 →-55.35

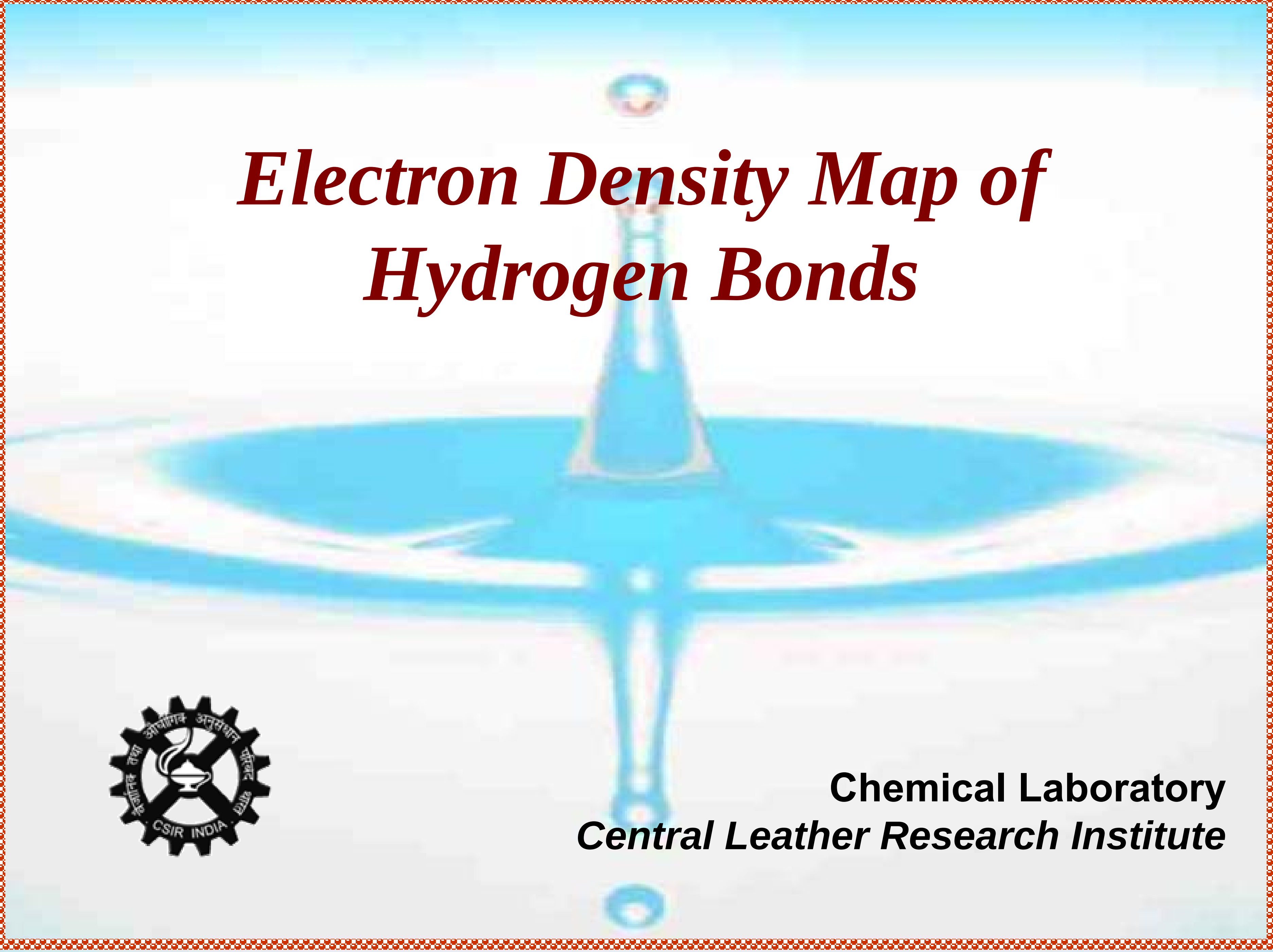


C3 → -53.74



C4 →-49.73

- Noncovalent Bonding: anything other than covalent!
- We are considering hydrogen bonds and other weak interactions stacking,π-OH and π- π between neutral and ionic atoms/molecules



Electron Density Map of Hydrogen Bonds

Chemical Laboratory
Central Leather Research Institute

SCHEMATICS

- Introduction
  - Hydrogen bonding
  - State-of-the-art computational approaches and AIM theory
- The usefulness of electron density topography in eliciting the strength of H-bonding interaction in a variety of systems

Number of Hydrogen Bonds (nH), Hydrogen Bonded Critical Points(nHBCP), Ring Critical Points(nRCP), Cage Critical Points(nCCP), Stabilization Energies (SE, kcal/mol), Sum of Electron density $\rho(r_c)$ and Laplacian of Electron density ($\nabla 2\rho(r_c)$) for the Most Stable Water Clusters

molecule		n_H	nHBCP	nRCP	nCCP	SE	$\rho(r_c)$ (e/a_o^3)	$\nabla^2\rho(r_c)(e/a_o^5)$
$(H_2O)_2$		1	1			5.5	0.02	0.0157
$(H_2O)_3$		3	3	1		17.1	0.065	0.0524
$(H_2O)_4$		4	4	1		29.1	0.1083	0.0916
$(H_2O)_5$		5	5	1		37.7	0.1401	0.1216
$(H_2O)_6$	prism	9	9	5	1	49.6	0.1892	0.1566
$(H_2O)_7$	7A	10	10	5	1	60.53	0.2317	0.1927
$(H_2O)_8$	8A	12	12	6	1	76.01	0.2925	0.2416
$(H_2O)_9$	9A	13	13	6	1	85.05	0.3262	0.2724
$(H_2O)_{10}$	10A	15	15	7	1	96.75	0.3718	0.3097
$(H_2O)_{11}$	11A	16	18	8	1	105.69	0.4014	0.3318
$(H_2O)_{12}$	12A	20	20	11	2	122.39	0.4677	0.3857
$(H_2O)_{13}$	13A	21	21	11	2	128.33	0.4903	0.4034
$(H_2O)_{14}$	14A	23	23	12	2	144.78	0.4998	0.4124
$(H_2O)_{15}$	15A	25	25	13	2	154.82	0.595	0.4968
$(H_2O)_{16}$	16A	28	28	16	3	169.33	0.6389	0.5245
$(H_2O)_{17}$	17A	29	30	17	3	176.51	0.6717	0.5517
$(H_2O)_{18}$	18A	31	32	18	3	188.64	0.7018	0.5735
$(H_2O)_{19}$	19A	33	33	18	3	199.69	0.7645	0.6381
$(H_2O)_{20}$	20A	36	36	21	4	216.28	0.8433	0.6905

Number of hydrogen bonds (N_{HB}) and stabilization energies (|SE|) for P_m, W_n and P_mW_n clusters as obtained from different levels of calculation using 6-31G basis set*

Clusters	N_{HB}		|SE| (kcal/mol)		
	Primary	Secondary	HF	MP2	DFT/B3LYP
P_2	1	2	4.3	5.7	4.8
W_2	1	-	4.7	5.2	5.4
PW	1	1	6.3	7.3	7.7
P_3	3	1	12.8	17.7	15.6
W_3	3	-	14.1	16.6	18.9
PW_2	3	-	14.5	17.1	18.9
P_2W	3	-	13.5	16.8	17.0
P_4	4	4	22.2	31.6	27.9
W_4	4	-	25.3	30.7	35.2
PW_3	4	1	25.0	30.1	33.6
P_2W_2	4	2	24.9	31.1	32.7
P_3W	4	2	23.6	30.9	30.4