Delocalization Indices for Non-Covalent Interaction Hydrogen Bond

Sílvia Simon

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Outline

1. Introduction
2. Computational Details
3. Results
    1. Dihydrogen bond (DHB)
    2. Resonance Assistance HB : Substituent effect (RAHB)
    3. 3D atomic partition schemes
4. Conclusion

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X-H···Y-Z

Geometric and Spectroscopic criteria

H···Y distance is found to be less than the sum of their van der Waals radii
The shorter the stronger

X-H···Y linearity. The more closely to 180º the stronger the bond is

X-H red shift (in general) and **new H···Y vibrational** mode.

NMR – proton deshielding for H in X-H

E. Arunan, G.R. Desiraju, R.A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D.C. Clary, R.H. Crabtree, J.J. Dannenberg, P. Hobza, Pure Appl. Chem. 83 (2011) 1619.

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X-H···Y-Z

Energetic criteria

The forces involved in the formation of a hydrogen bond include those of an electrostatic origin, those arising from charge transfer between the donor and acceptor leading to partial covalent bond formation between H and Y, and those originating from dispersion.

eg. - EDA Energy Decomposition Analysis (ADF)

$$\Delta E_{bond} = \Delta E_{prep} + \Delta E_{int}$$

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi}$$

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Topological criteria

QTAIM

Analysis of the electron density topology of hydrogen-bonded systems usually shows a bond path connecting H and Y and a (3,–1) bond critical point between H and Y.

Some Popelier's criteria

$$r(bcp) = 0.02 - 0.04 ua$$

$$\nabla^2 r(bcp) = 0.02 - 0.15 ua$$

P. L. A. Popelier, Characterization of a dihydrogen bond on the basis of the electron density, J. Phys. Chem. A, 102 , 1873–1878 (1998)

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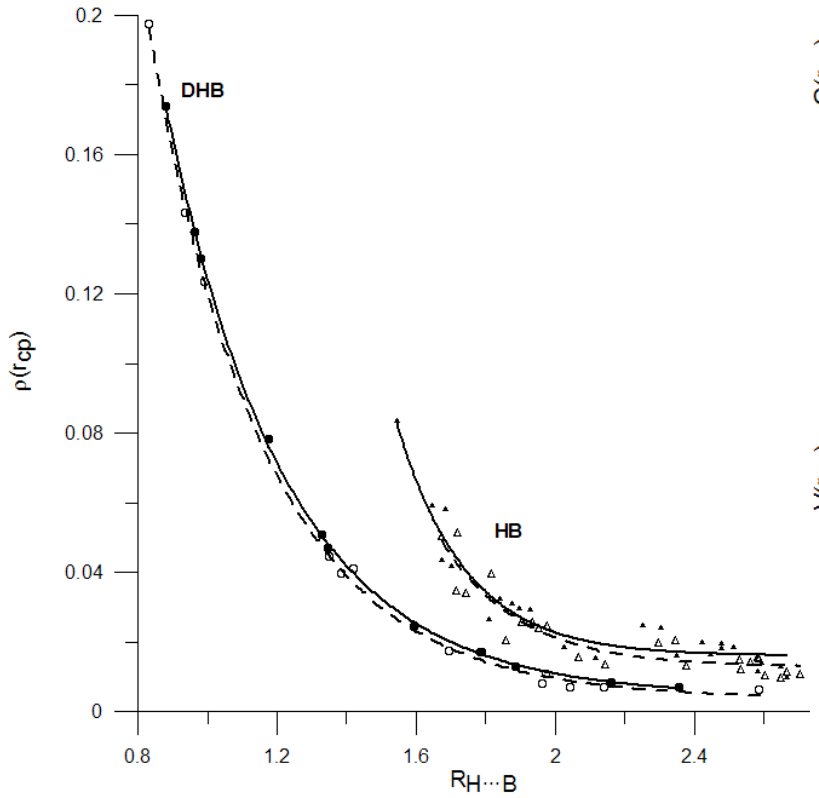
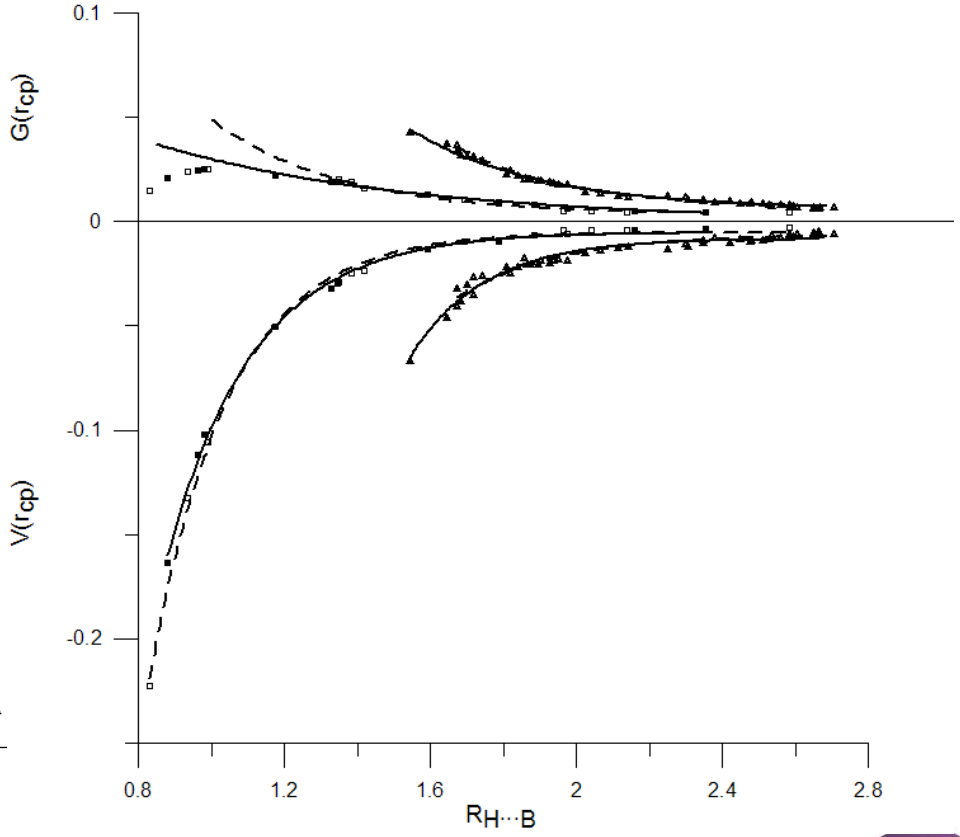
1. Introduction

Density at the bcp



Energy density at the bcp



D. Hugas, S. Simon, M. Duran, The Journal of Physical Chemistry A 111 (2007) 4506

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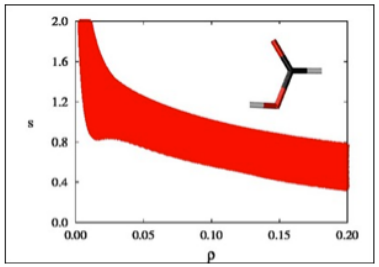
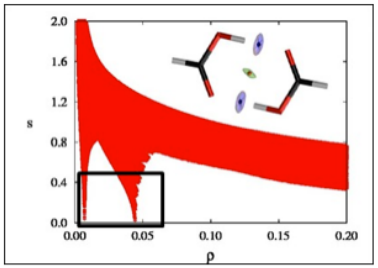
NCI (Non-Convalent Interaction)

Reduce Density Gradient (RDG) in front of density



a) Formic acid



b) Formic acid dimer

ELF (Electron Localization Function)

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Delocalization Indices (DI)

Number of electrons delocalize or share between A and B

$$\delta(A,B) = -2\int_A\int_B \Gamma_{XC}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

For monodeterminantal closed-shell wavefunctions one obtains:

$$\delta(A,B) = 4\sum_{i,j}^{N/2} S_{ij}(A)S_{ij}(B)$$

J Poater, M Sola, M Duran, X Fradera Theoretical Chemistry Accounts 107 (6), 362-371

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Objectives

- ✓ How DI can be used to characterize non-covalent interaction – HB

  - Dihydrogen-Bonded complexes
  - Substituent effect on Tautomerization in RAHB

- ✓ 3D-scheme for atomic basin calculation: how to lower the computational cost

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Computational Details

METHOD

- ✓ DFT/B3LYP
- ✓ 6-31G++(d,p), 6-311G++(d,p) and 6-311G++(3df,2dp)

PROGRAMS

Gaussian03
ADF (EDA – energy decomposition analysis)
ESI-3D (in general within QTAIM atomic basin definition)
AIM2000
Afuzzy

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3.1 DiHydrogen Bond

Correlation with other HB descriptors in order to assess if DI will help us to classify the HB (DHB) by means of different strength

How DI will help to define closed or shared shell complexes, is there a unique value?

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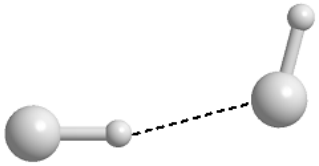
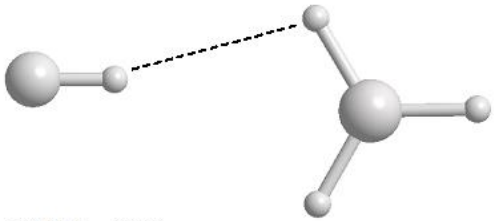
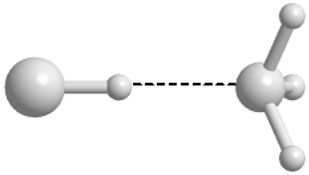


1, 2, 3 XH···YH (Y=F,Cl,Br)

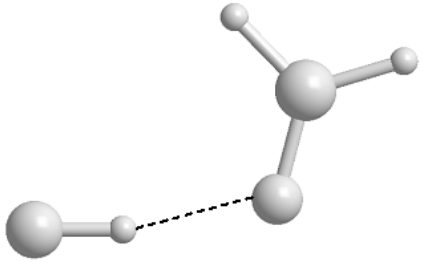
4, 5 XH···YH_2 (Y=O,S)



12 XH···HBH_2

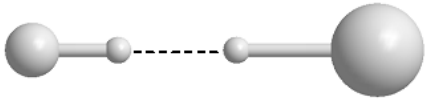


6, 7 XH···YH_3 (Y=N,P)

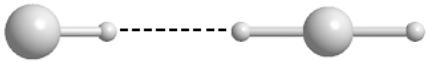


8 XH···OCH_2

X = F, Cl and Br



9, 10 XH···HM (M=Li,Na)



11 XH···HBeH

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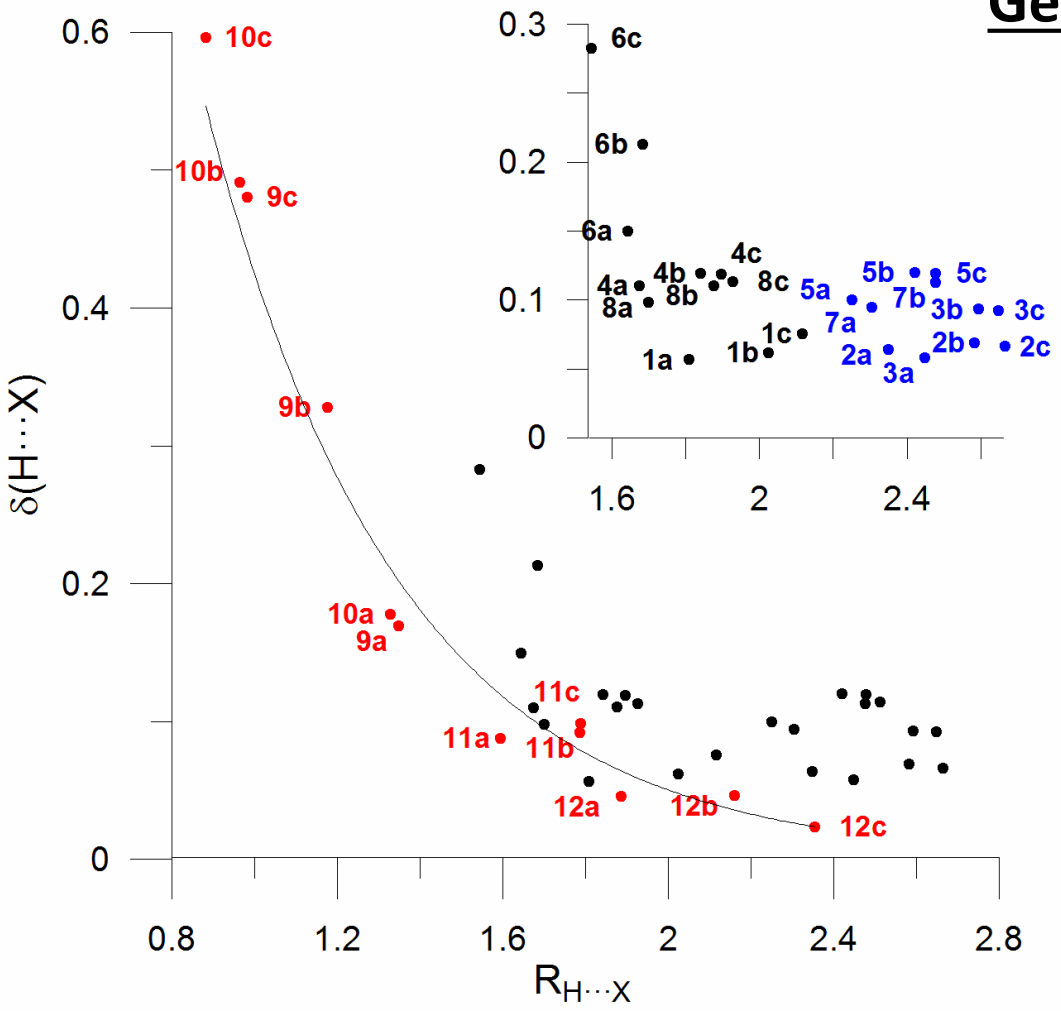
$\delta(H\cdots X)$ vs $R_{H\cdots X}$



Geometrical parameters

X-H···Y-Z

Number – Y
Letter - X

- Dependence on polarity H-X
- Dependence on Y periode

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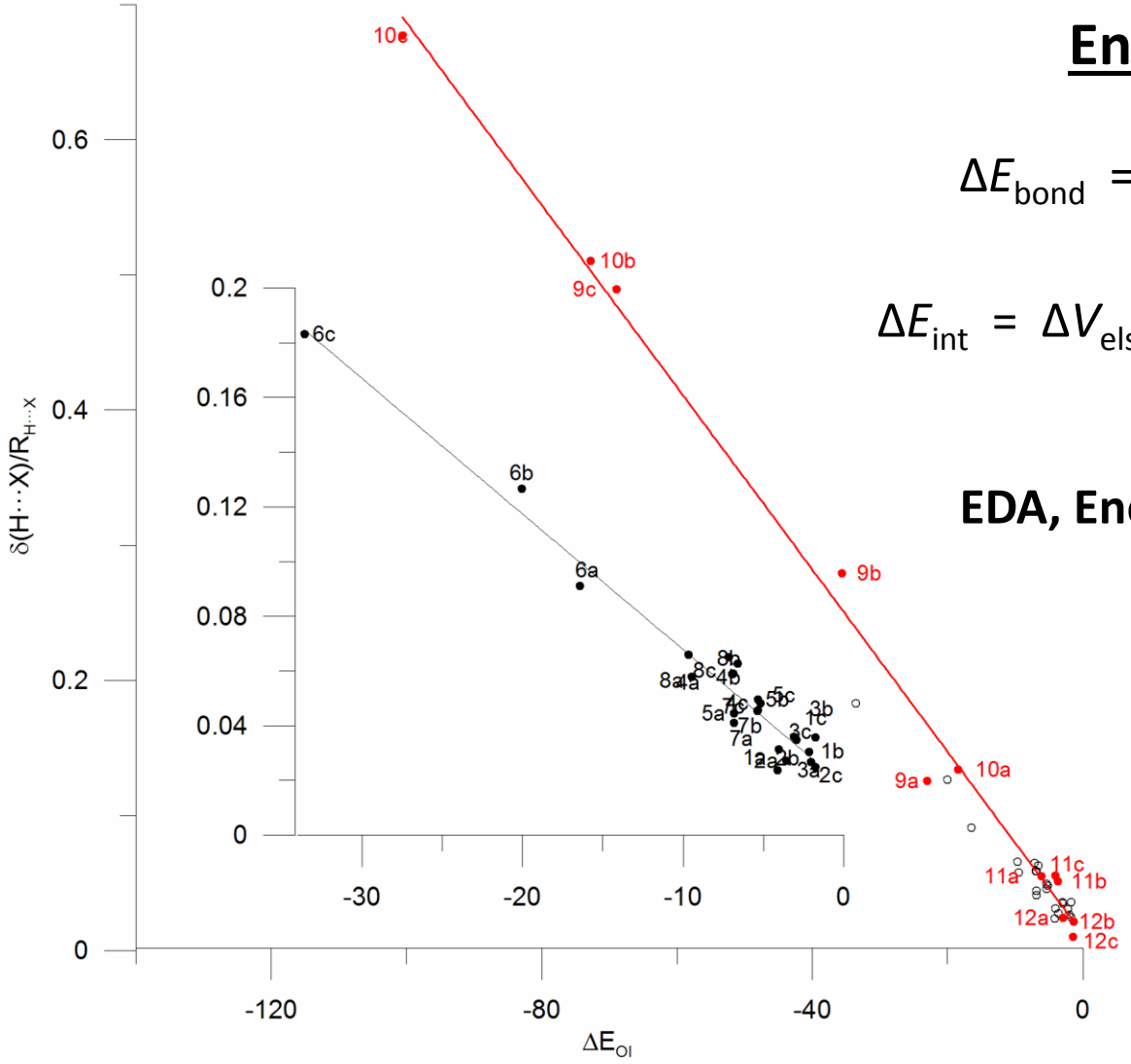
δ(H···X) vs E_{OI}



Energetics

$$\Delta E_{bond} = \Delta E_{prep} + \Delta E_{int}$$

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi}$$

EDA, Energy Decomposition Analysis

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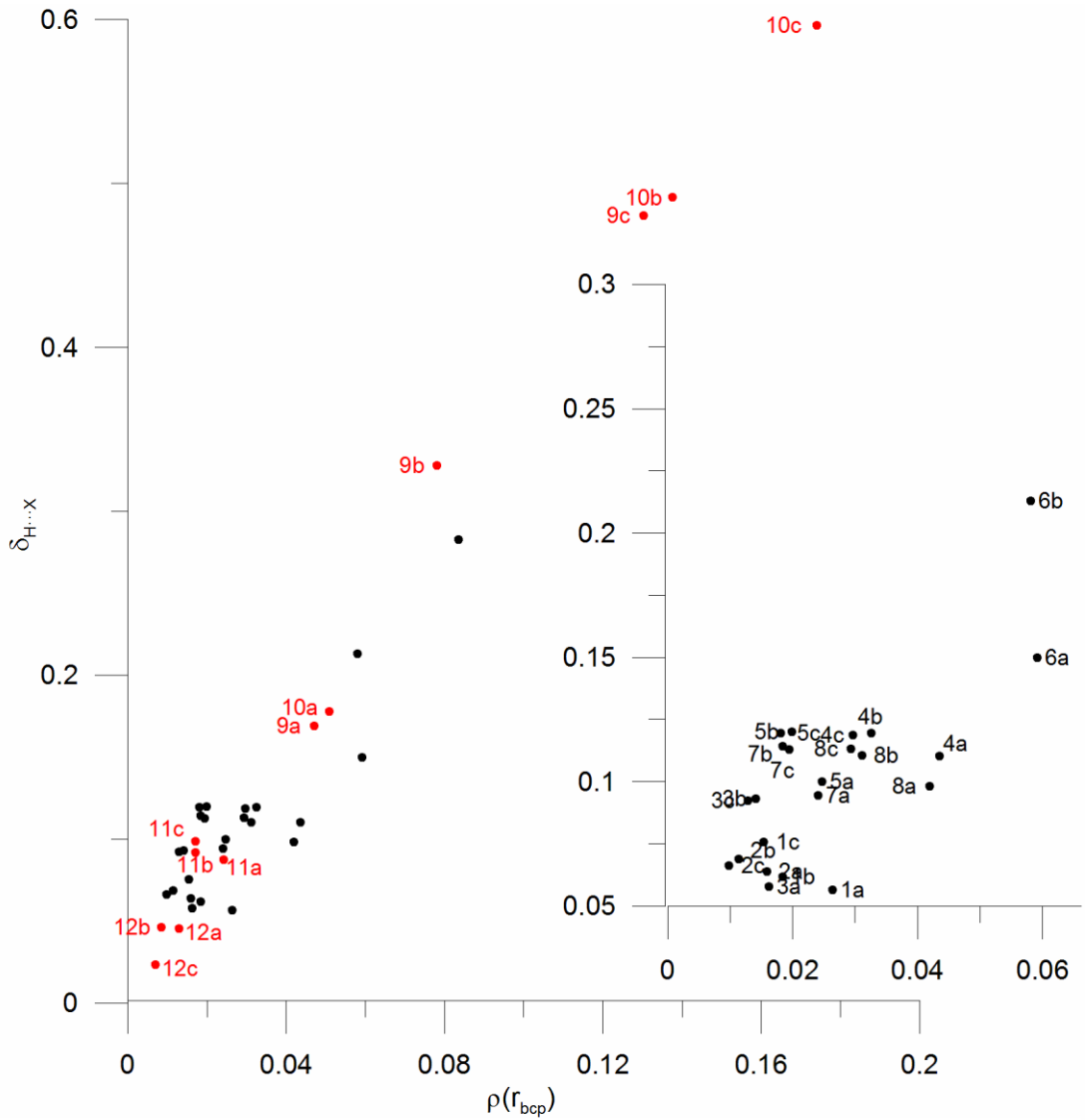

Topological Parameters

ρ(bcp)

- Dependence on polarity H-X

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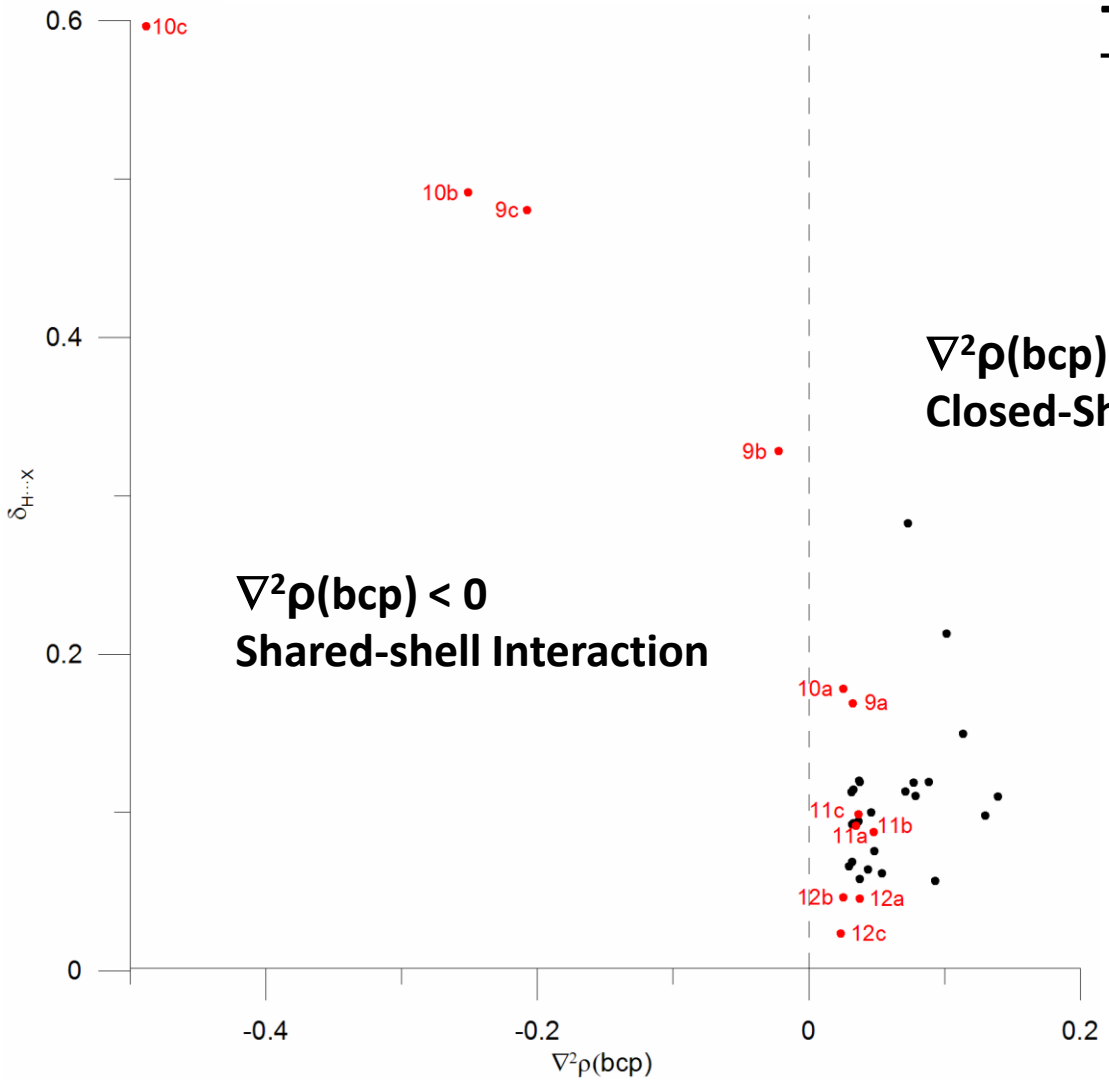
δ(H···X) vs $\nabla^2\rho$(bcp)



Topological Parameters

$\nabla^2\rho$(bcp) > 0
Closed-Shell interaction

$\nabla^2\rho$(bcp) < 0
Shared-shell Interaction

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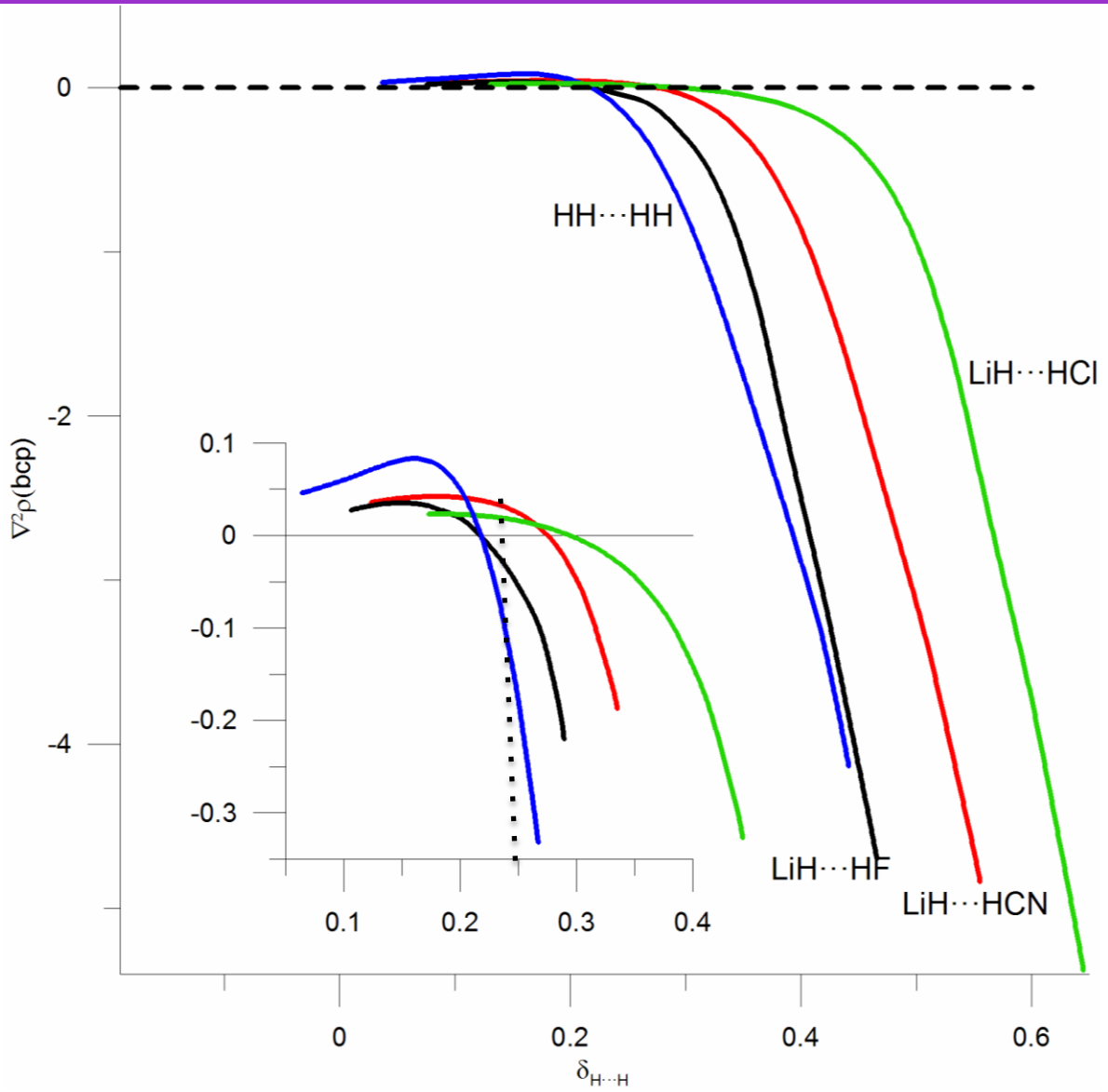
$\nabla^2\rho$(bcp) vs δ(H···X)



Linear transit

LiH···HF

LiH···HCN

LIH···HCl

HH···HH

No unique value of δ(H···X) will serve to define the nature of DHB.

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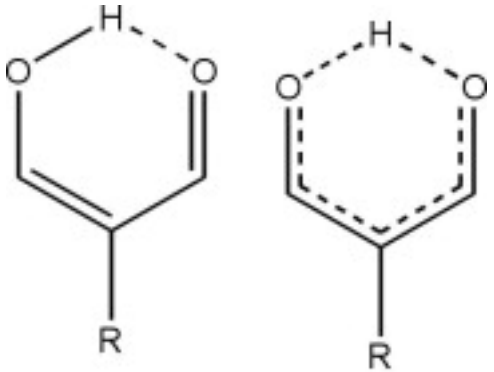
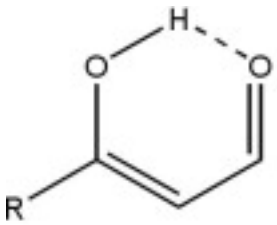
RAHB: Effect of Substituents

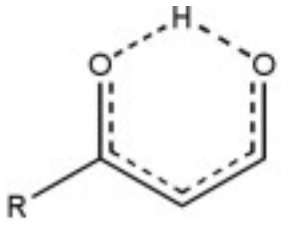


GS

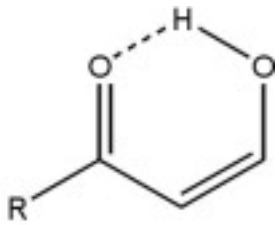
TS



GS1



TS



GS2

R = OH, NH_2, F, CH_3, CN, NO_2, CHO, NO

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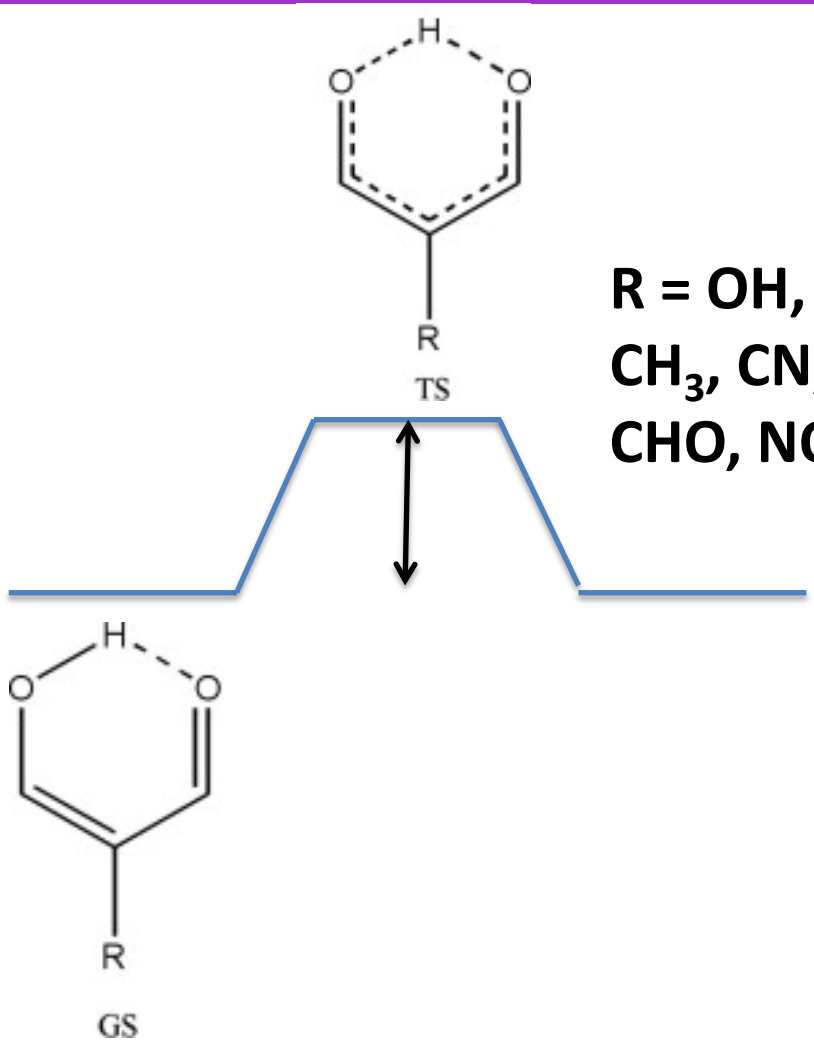
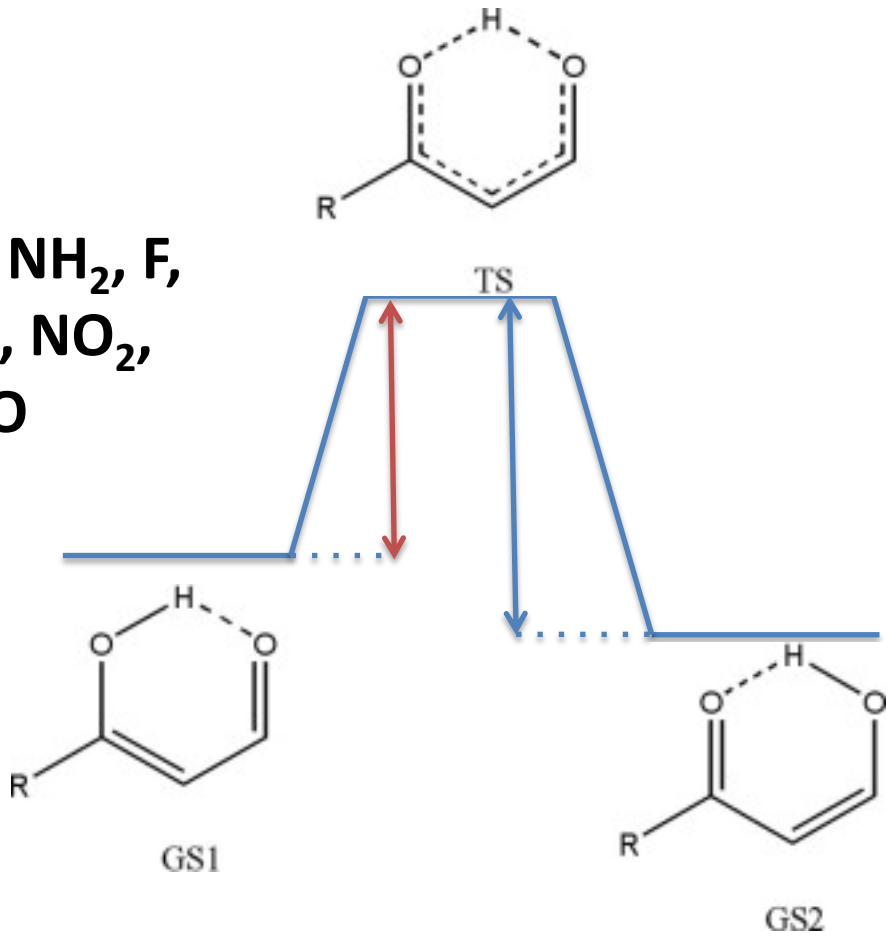
3. RESULTS



R = OH, NH_2, F,
CH_3, CN, NO_2,
CHO, NO



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- Do DI help in Activation energy prediction?

- How to account for different substituent effect? Resonance Assisted versus Inductive/field Effect.

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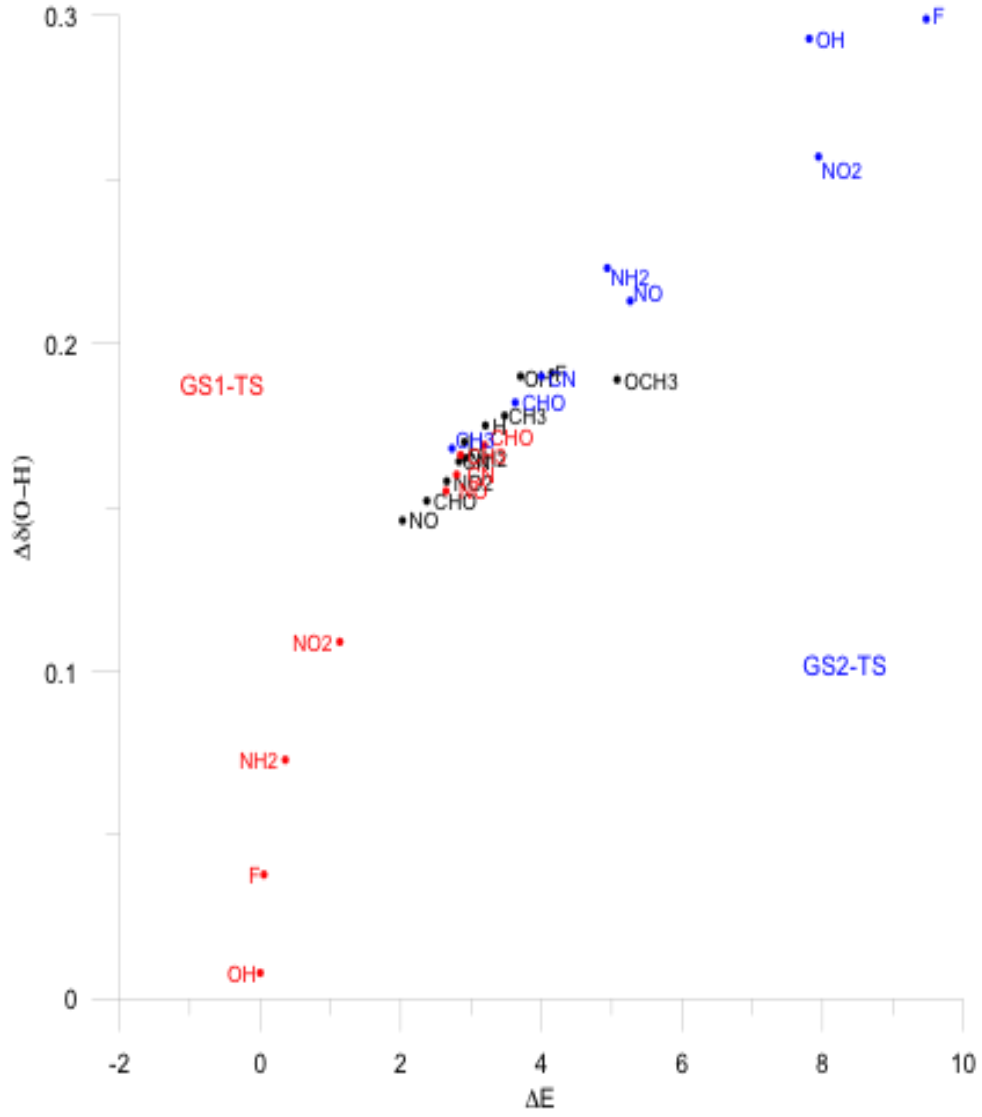
Δδ(O···X) vs ΔE



Direct relationship between change in DI with activation energy.

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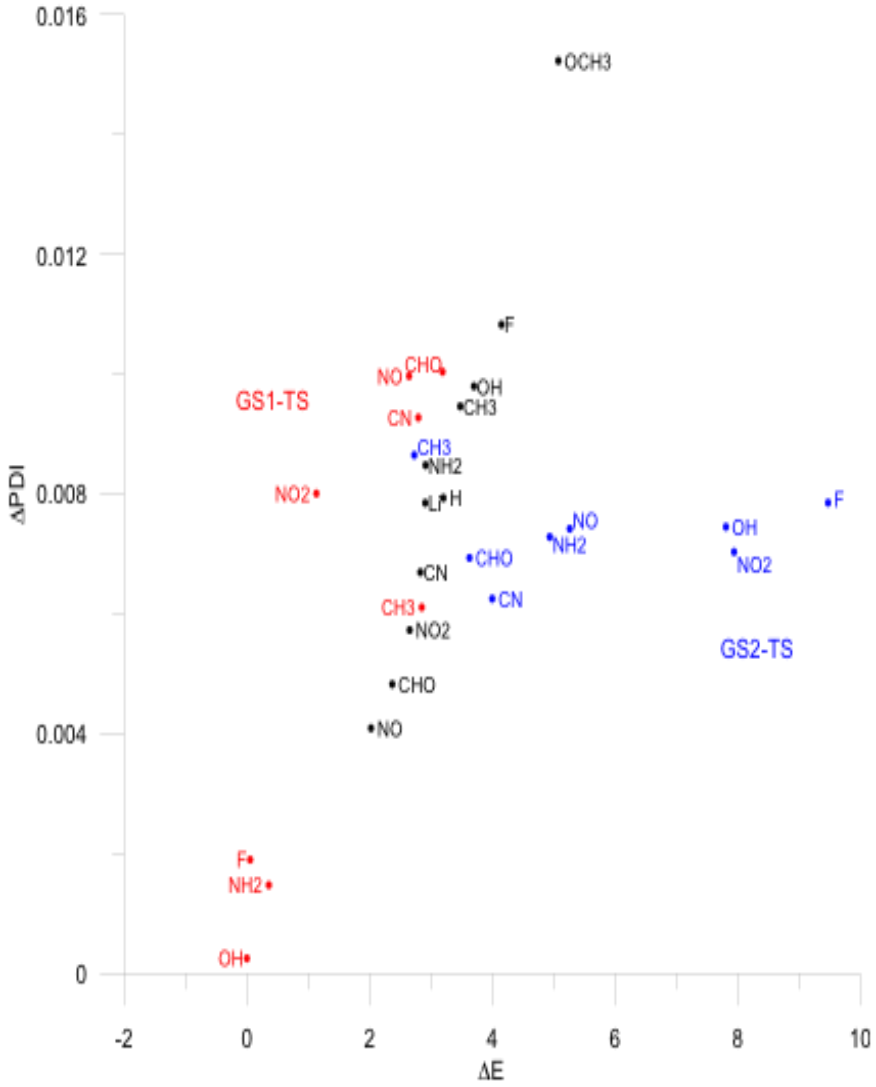
3.2 RAHB



Substituent effect?

para-delocalization (**PDI**) – *Average of all DIs of para-related carbon atoms in a given 6-MR*

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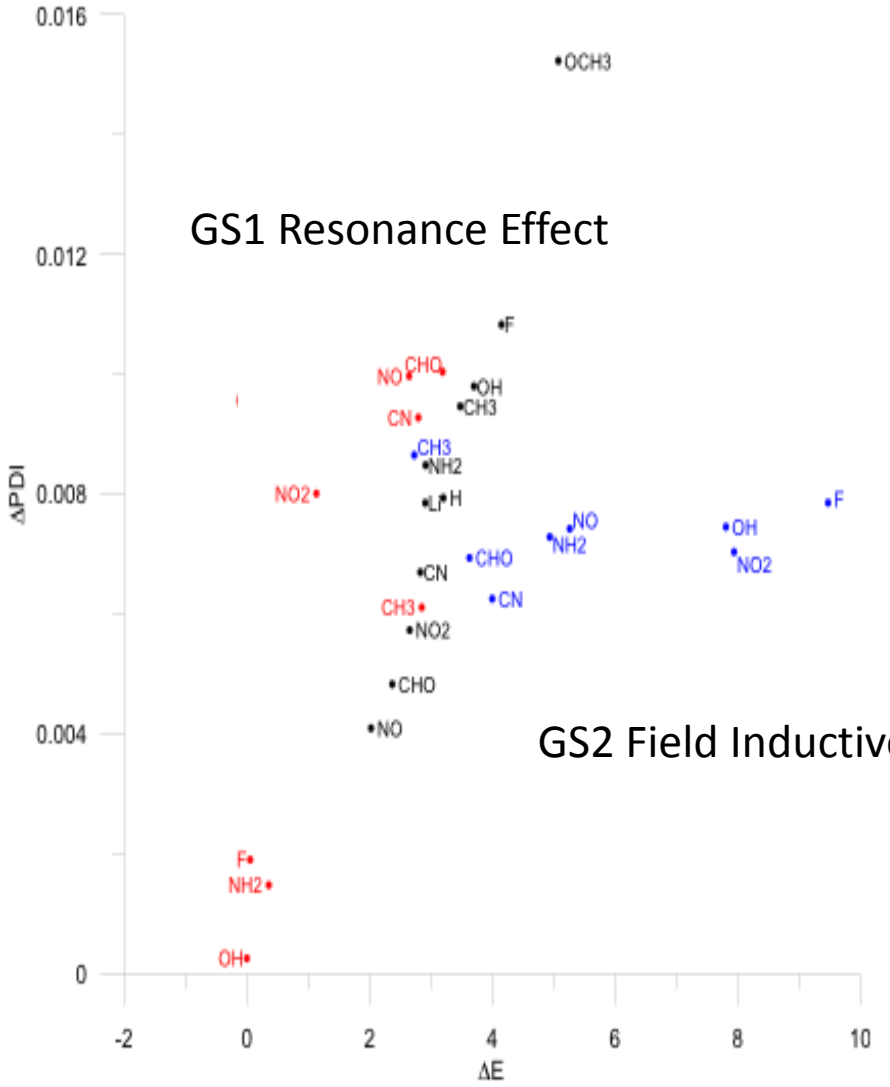
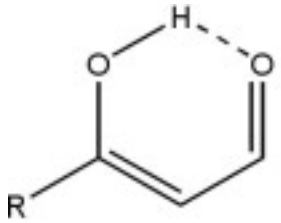
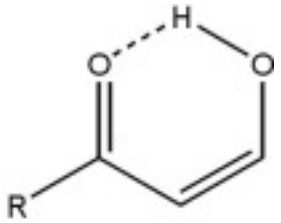
3.2 RAHB



GS1 Resonance Effect



GS1



GS2

GS2 Field Inductive

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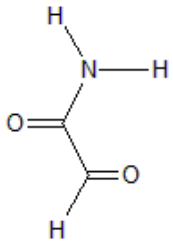
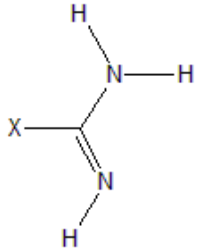
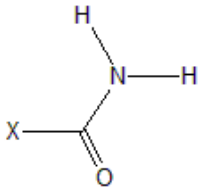
3.2 RAHB



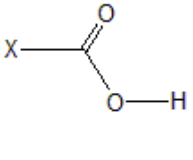
FOR



FI_X



FA_X



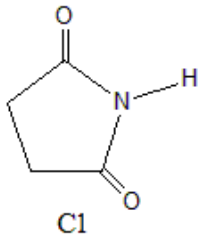
FO_X

X= H, Br, CCH, CN, Cl, F, NH_2, OH

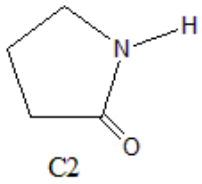
OH···O

OH···N

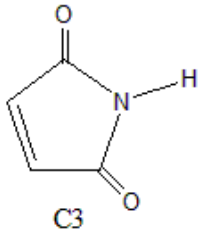
NH···N



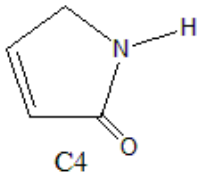
C1



C2



C3



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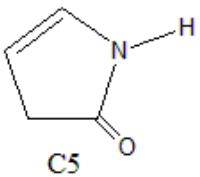

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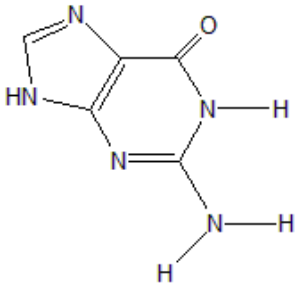

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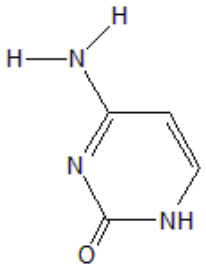

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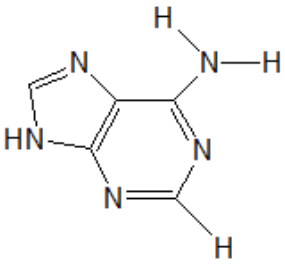
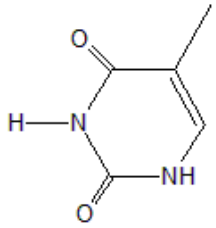


A



T

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QTAIM vs Fuzzy-atom

$$\delta(A,B) = -2\int_A\int_B \Gamma_{XC}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

QTAIM - atomic boundaries are determined from the zero-flux surface conditions of the gradient of the one-electron density.

Fuzzy-atom assign a non-negative atomic weight functions $w_A(r)$ to define the atomic basin in all the 3D space

Becke atoms, where the atomic radii are used to determine the weight function

Becke_ρ – bcp as atomic radii

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QTAIM vs Fuzzy-atom

Fuzzy-atom assign a non-negative atomic weight functions $w_A(r)$ to define the atomic basin in all the 3D space

Becke atoms, where the atomic radii are used to determine the weight function

Becke_ρ – bcp as atomic radii

Hirshfeld -based on promolecular densities

$$w_A(\vec{r}) = \frac{\rho_A^0(\vec{r})}{\sum_B \rho_B^0(\vec{r})}$$

Hirshfeld_I - the density of the isolated atoms must integrate the same population as the atom in the actual molecule

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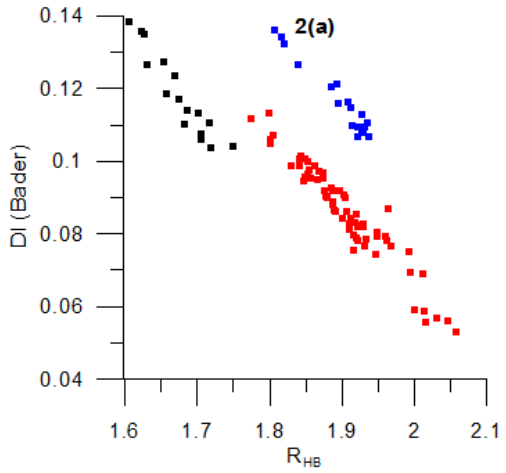
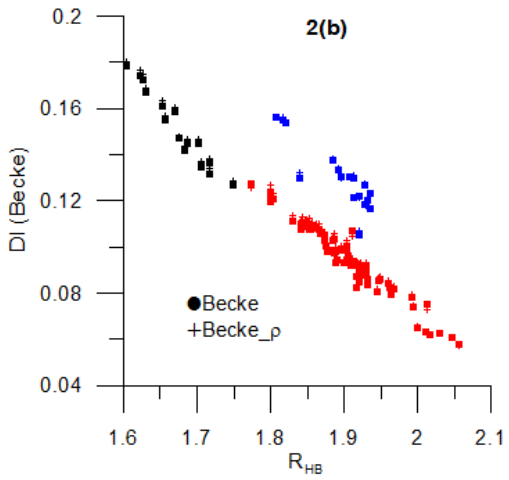
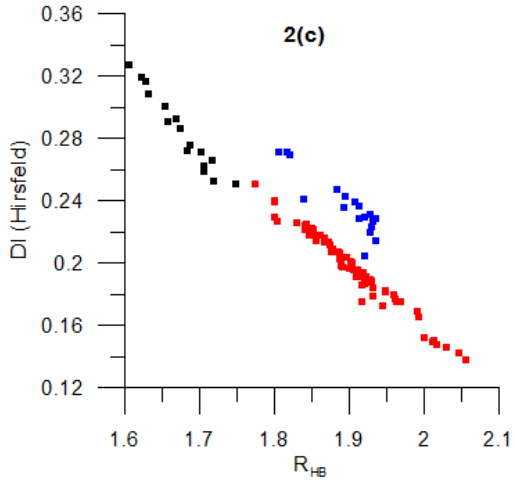
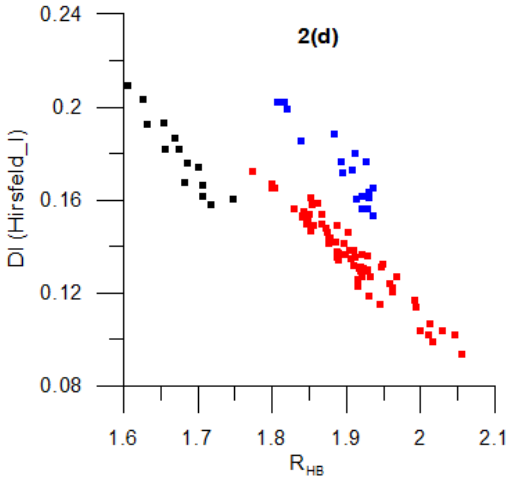
DI vs $R_{H\cdots X}$

3D-Schemes









OH···O

OH···N

NH···N

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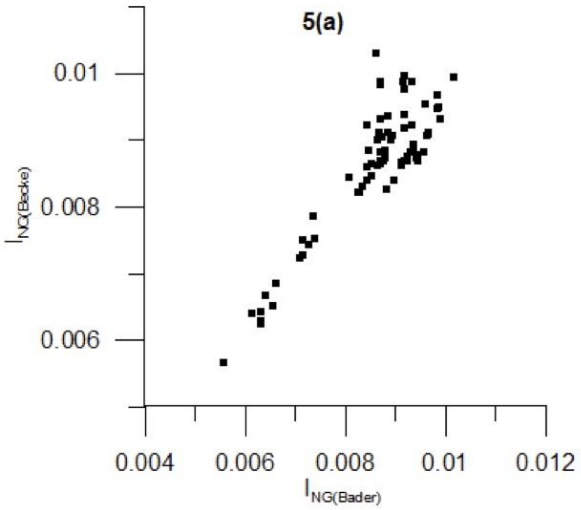
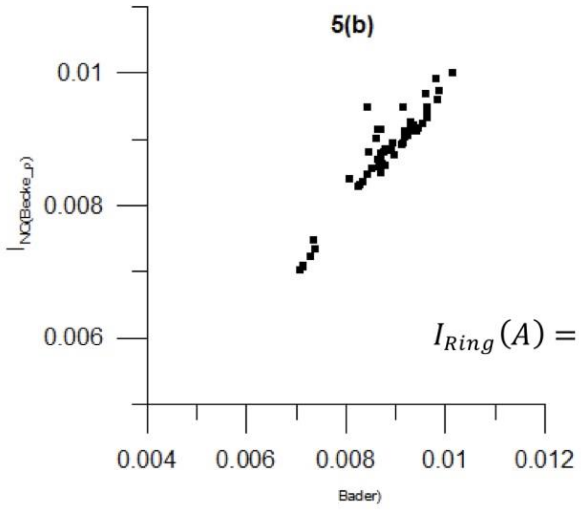
I_{NG} Fuzzy vs Bader

3D-Schemes

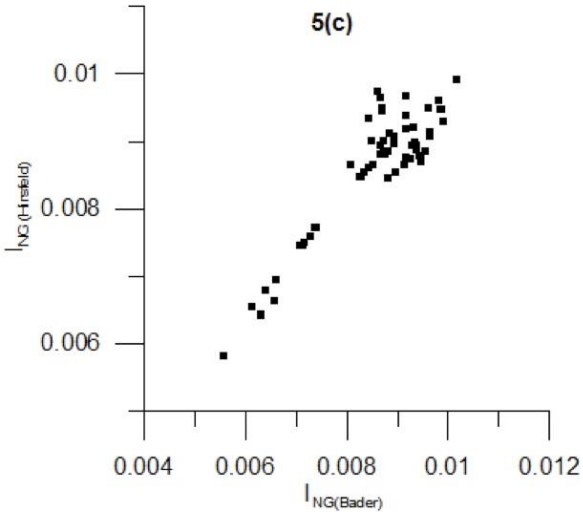


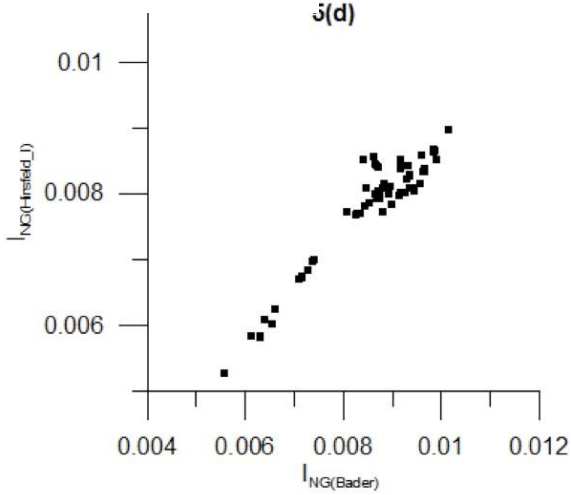


Fuzzy vs QTAIM

I_{NG}

$$I_{Ring}(A) = \sum_{i_1,i_2,\ldots,i_n}^{occ} S_{i_1,i_2}(A_1) S_{i_2,i_3}(A_2) \cdots S_{i_n,i_1}(A_n)$$





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Paris 2013

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4. Conclusion

- ✓ δ(H···X) (DI) will help to characterize HB.
- ✓ No unique value of δ(H···X) will serve to define the nature of HB.
- ✓ δ(H···X) can be related to activation energy for malonaldehyde tautomerization but aromaticity indices will help to learn substituents effect.
- ✓ Fuzzy-atoms 3D-scheme can help to lower DI computational cost calculation.

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3D-Schemes

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