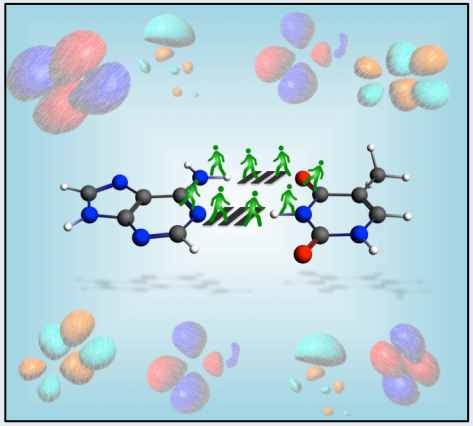
Understanding hydrogen bonding with Kohn-Sham MO theory and Energy Decomposition Analysis.



Célia Fonseca Guerra

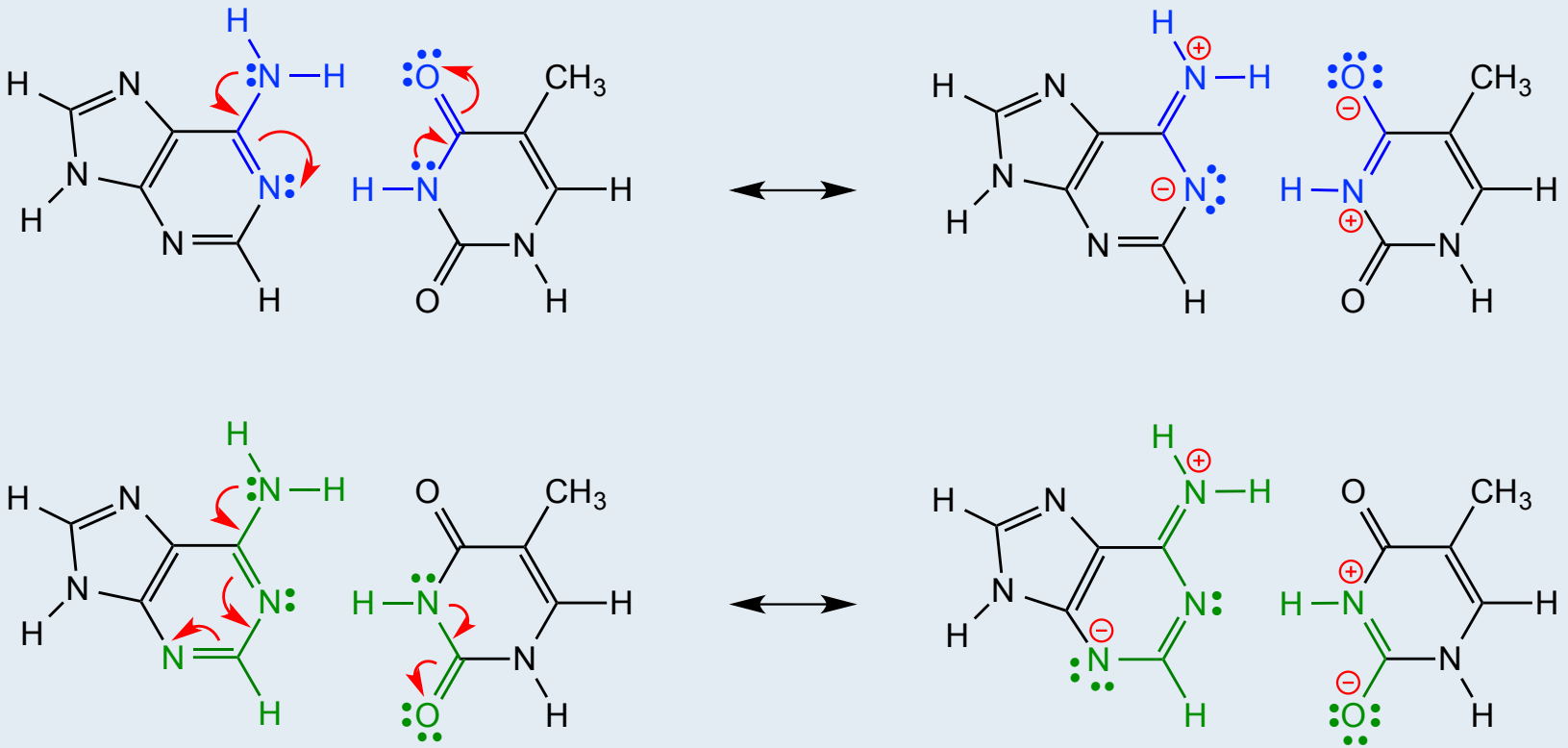
TCCM ADF Tutorial

ACMM

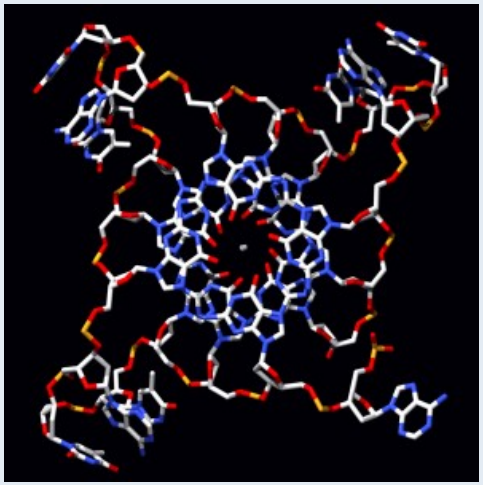
VU UNIVERSITY AMSTERDAM

Importance of Resonance-Assistance

In Watson-Crick Base Pair AT



Outline



1. B-DNA: Hydrogen bonds in Watson Crick base pairs

2. G-DNA: Cooperativity in Guanine Quartets

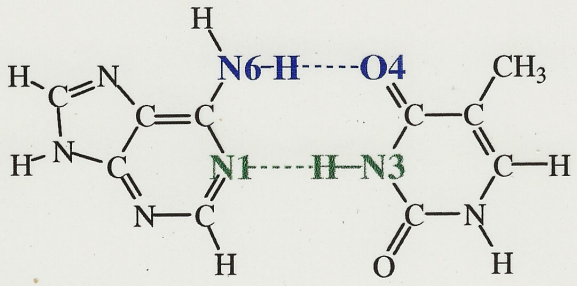
3. Importance of aromaticity for hydrogen bonds

Kohn-Sham DFT Approach

DFT with ADF:

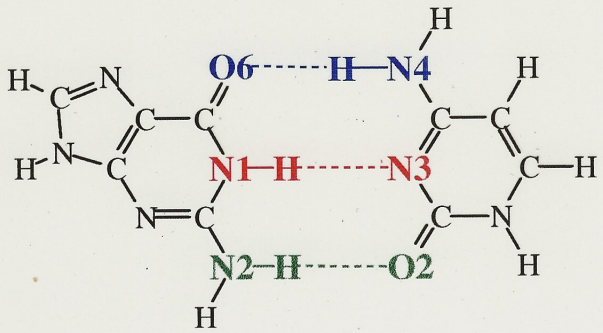
- Level → BP86/TZ2P &BLYP-D3(BJ)/TZ2P
- Accuracy → ca. kcal/mol, trends better

Adenine - Thymine



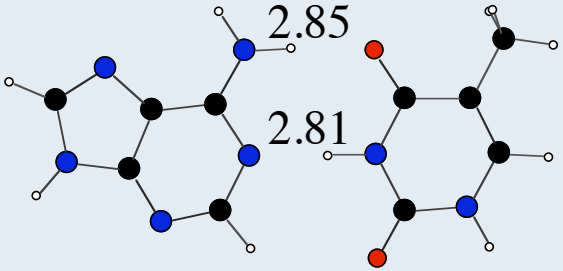
Method	N6-H···O4 (Å)	N1···H-N3 (Å)	ΔH_{298} (kcal/mol)
HF/6-31G**	3.09	2.99	-10.5
HF/cc-pVTZ(-f)	3.06	2.92	-10.5
B3LYP/6-31G**	2.94	2.84	-10.9
BP86/TZ2P	2.85	2.81	-11.8
experiment	2.95	2.82	-12.0

Guanine – Cytosine



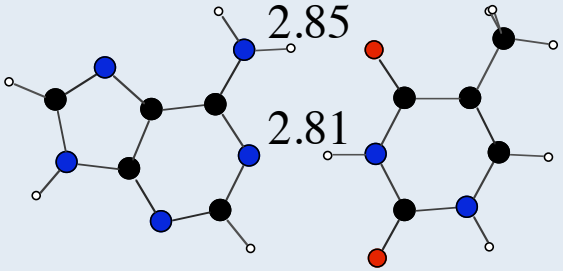
Method	N2-H···O2 (Å)	N1-H···N3 (Å)	O6···H-N4 (Å)	ΔH_{298} (kcal/mol)
HF/6-31G**	3.02	3.04	2.92	-21.9
HF/cc-pVTZ(-f)	2.92	2.95	2.83	-21.2
B3LYP/6-31G**	2.92	2.93	2.79	-24.0
BP86/TZ2P	2.87	2.88	2.73	-23.8
experiment	2.86	2.95	2.91	-21.0

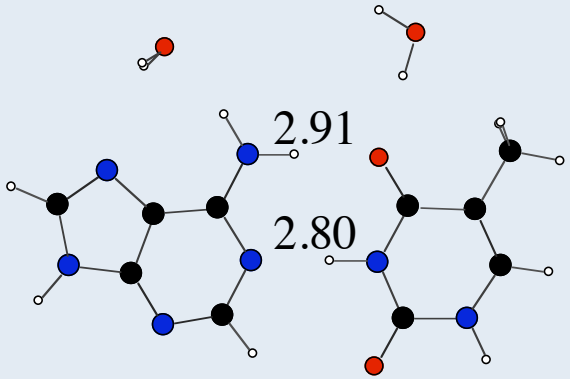
Adenine-Thymine with H_2O and Na^+

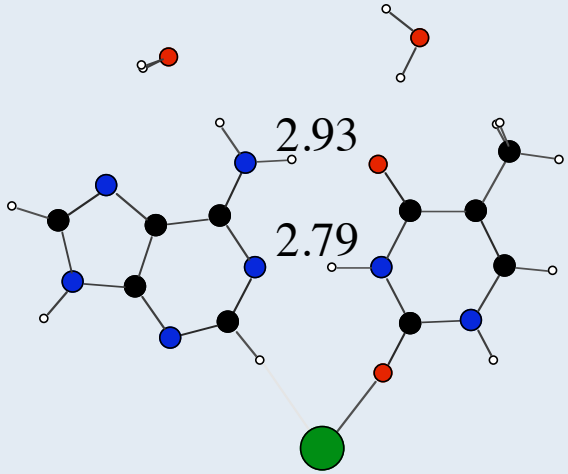


Experimental values: 2.95 Å
2.82 Å

Adenine-Thymine with H_2O and Na^+

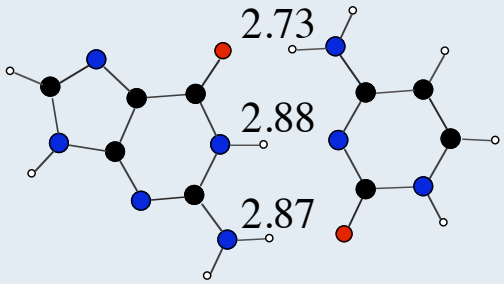






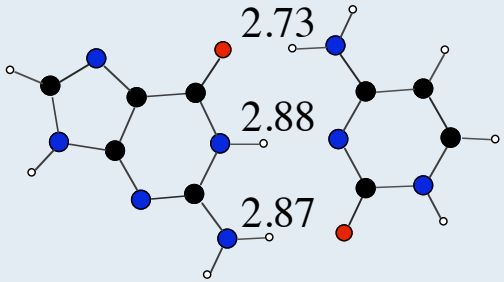
Experimental values: 2.95 Å
2.82 Å

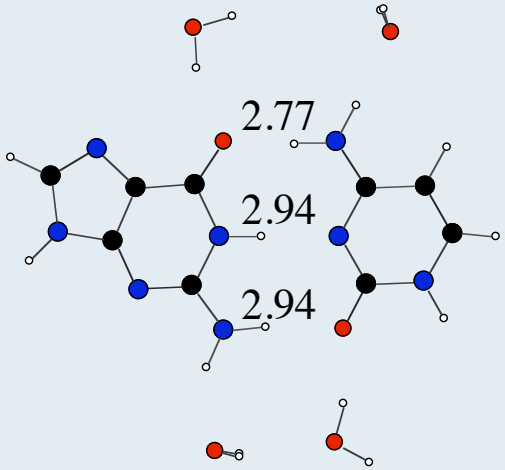
Guanine-Cytosine with H_2O and Na^+



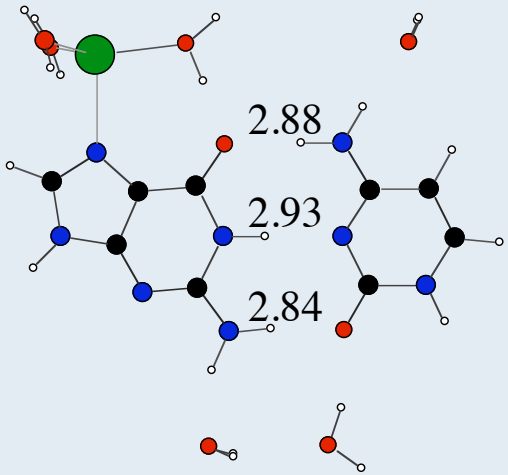
Experimental values: 2.91 Å
2.95 Å
2.86 Å

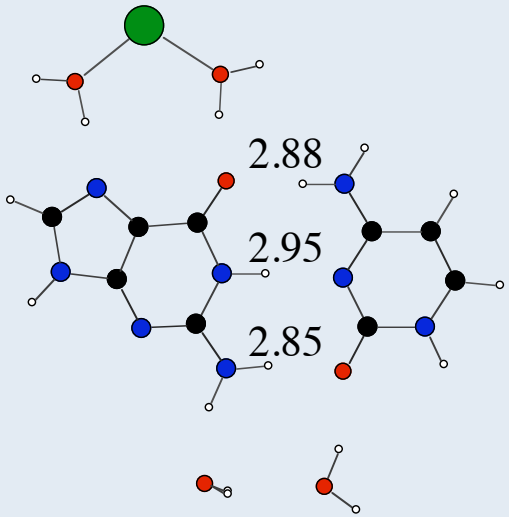
Guanine-Cytosine with H_2O and Na^+





Experimental values: 2.91 Å
2.95 Å
2.86 Å



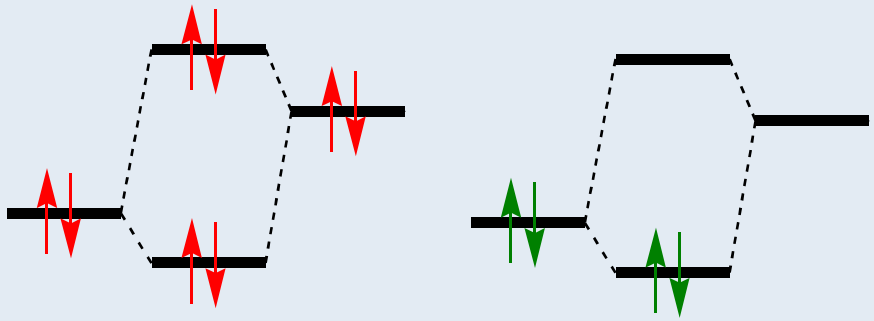


Energy Decomposition Analysis: Closed-Shell Fragments

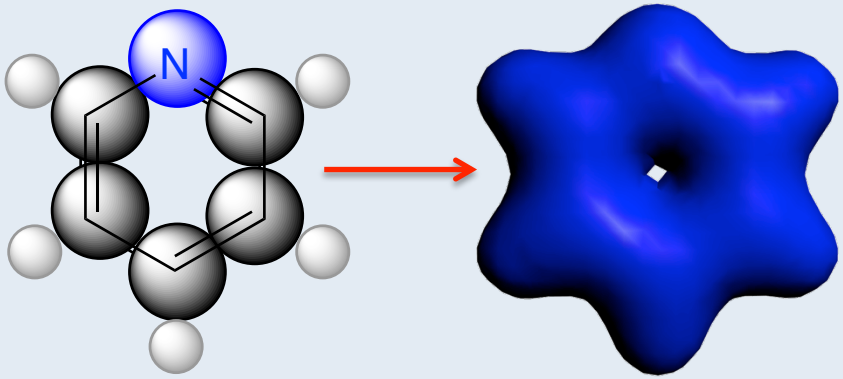
$$\Delta E = \Delta E_{\text{strain}} + \Delta E_{\text{int}}$$

$$\Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$$

$\delta+ \Rightarrow \Leftarrow \delta-$



Voronoi Deformation Density



$$\sum_B \rho_B(\mathbf{r}) \text{ to } \rho^{molecule}(\mathbf{r})$$

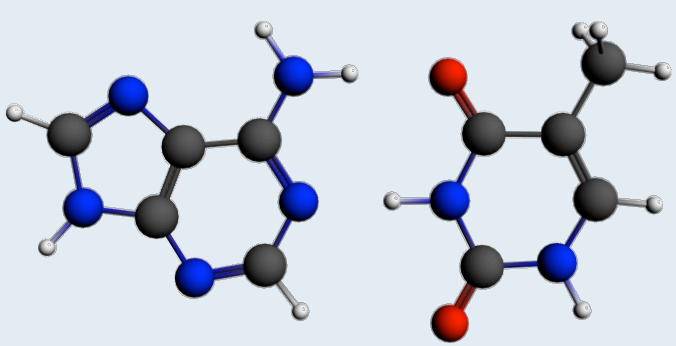
$Q_A^{VDD} < 0 \rightarrow$ A **gains** electrons

$Q_A^{VDD} > 0 \rightarrow$ A **loses** electrons

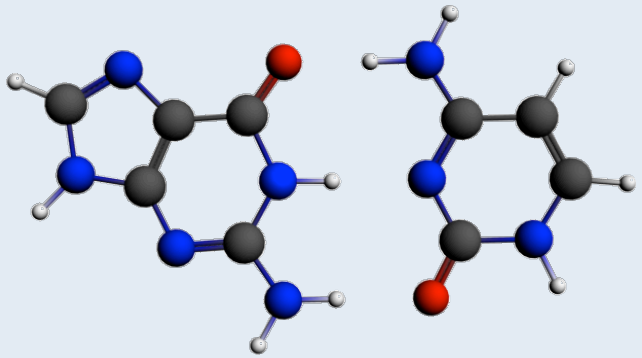
$$Q_A^{VDD} = -\int_{\text{Voronoi cell of A}} \left(\rho^{molecule}(\mathbf{r}) - \sum_B \rho_B(\mathbf{r}) \right) d\mathbf{r}$$

J. Comput. Chem **2004**, 25, 189

1. Watson-Crick Base Pairs



Adenine – Thymine



Guanine – Cytosine

donor-acceptor interactions as important as electrostatic interactions

C. Fonseca Guerra et al., *Chem. Eur. J* **1999**, *5*, 3581
and *Angew. Chem. Int. Ed.* **1999**, *38*, 2942

1. B-DNA: Energy Decomposition Analysis

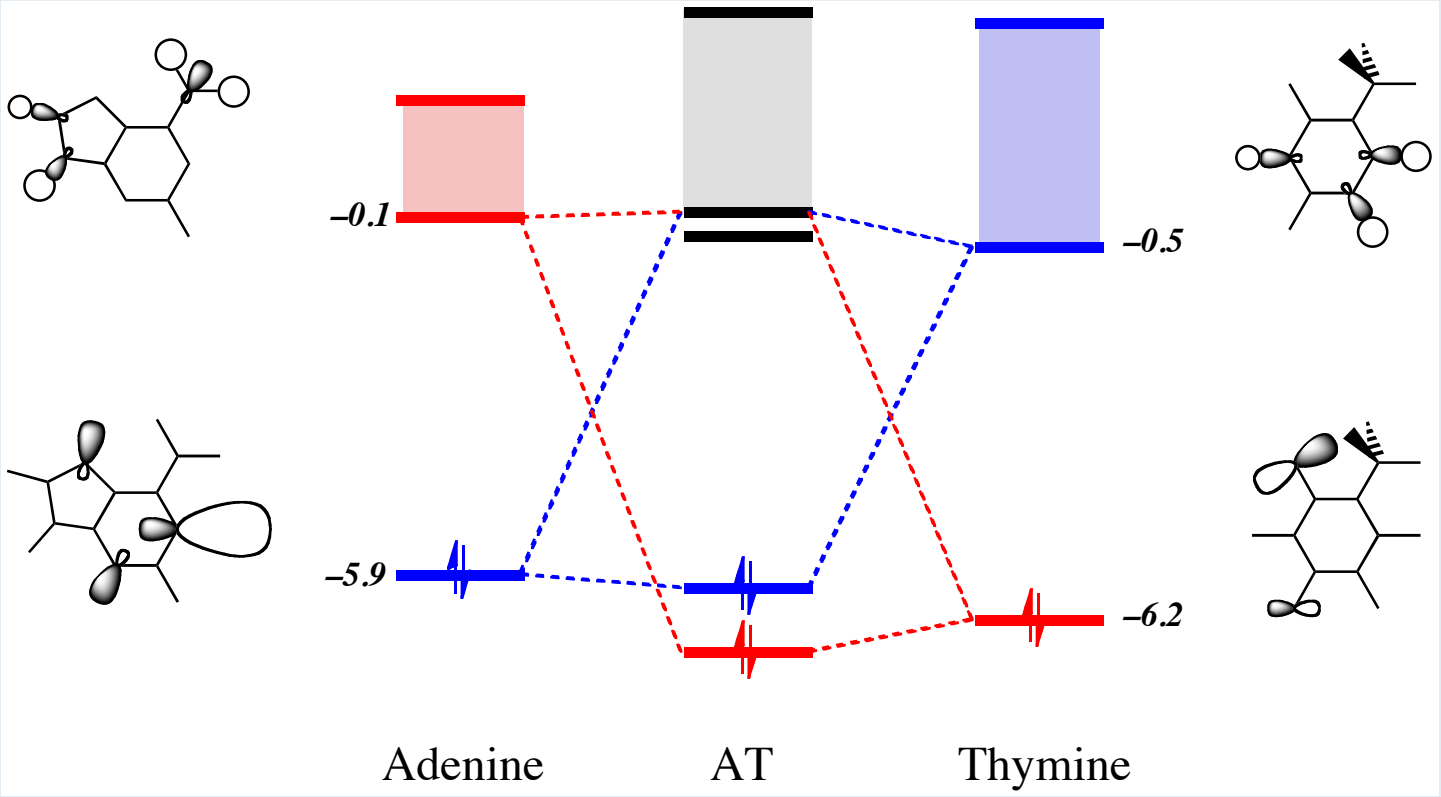
	AT	GC
ΔE_{Bond}	–13.0	–26.5
ΔE_{prep}	2.3	4.1
ΔE_{int}	–15.3	–30.6
ΔE_{Pauli}	39.2	52.1
ΔV_{elstat}	–32.1	–48.6
ΔE_{oi}	–22.4	–34.1

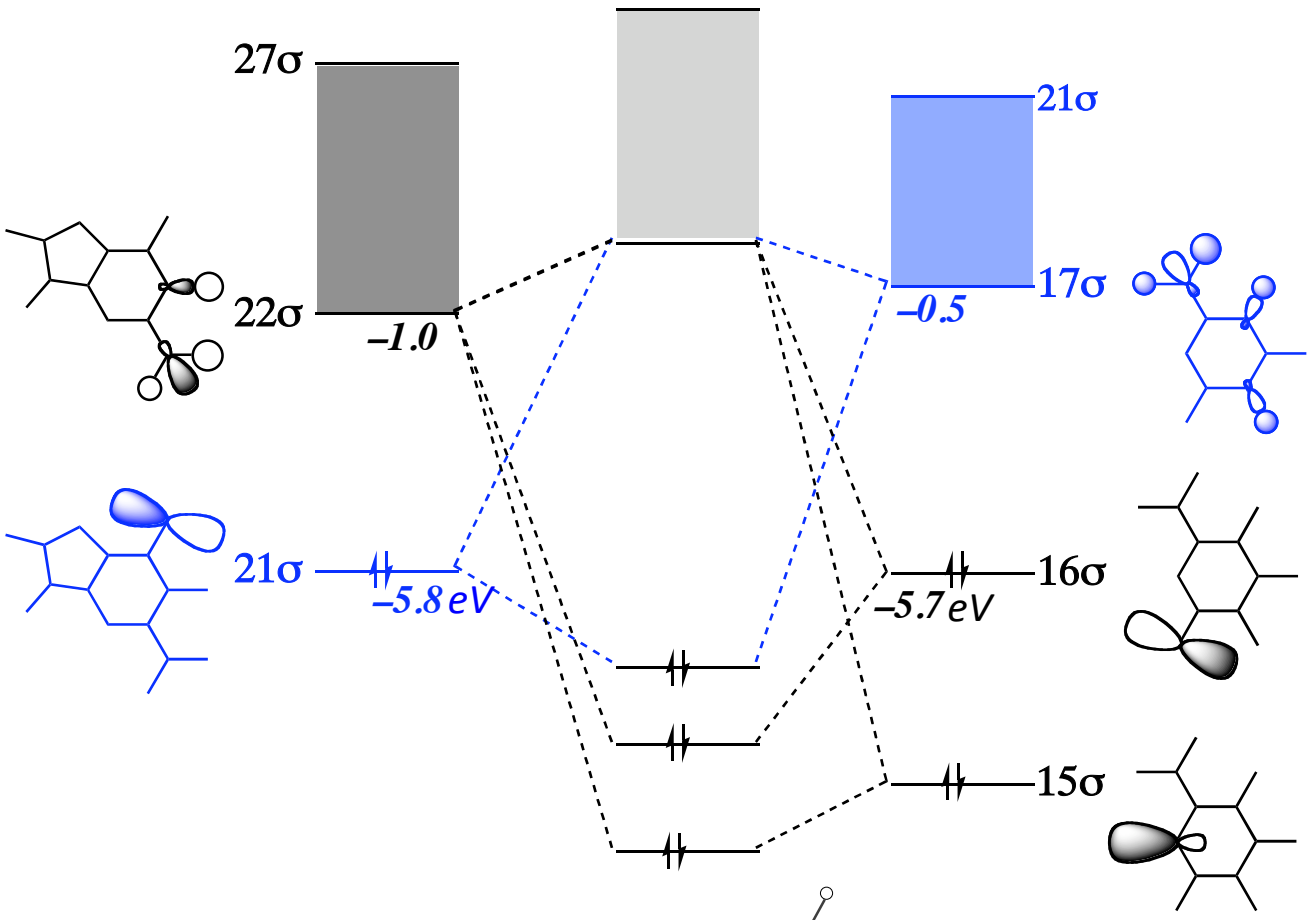
I. B-DNA: Energy Decomposition Analysis

	AT	GC
ΔE_{Bond}	–13.0	–26.5
ΔE_{prep}	2.3	4.1
ΔE_{int}	–15.3	–30.6
ΔE_{Pauli}	39.2	52.1
ΔV_{elstat}	–32.1	–48.6
ΔE_{oi}	–22.4	–34.1
ΔE_{σ}	–20.7	–29.3
ΔE_{π}	–1.7	–4.8

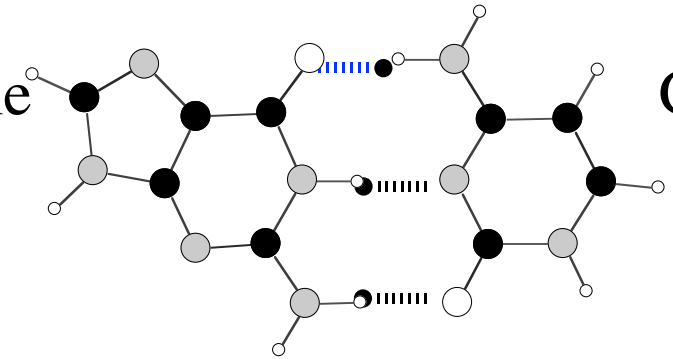
RAHB

I. B-DNA: MO diagrams of AT and GC





Guanine



Cytosine

C. Fonseca Guerra et al.,
Chem. Eur. J **1999**, *5*, 3581

Voronoi Deformation Density Method

$$\Delta Q_A = -\int_{\substack{\text{Voronoi}\\ \text{cell of A}}} \left[\rho_{pair}(\mathbf{r}) - \rho_{base1}(\mathbf{r}) - \rho_{base2}(\mathbf{r})\right] d\mathbf{r}$$

Separation of VDD in σ and π:

$$\Delta Q_A = \Delta Q_A^{\sigma} + \Delta Q_A^{\pi}$$

For each irreducible representation:

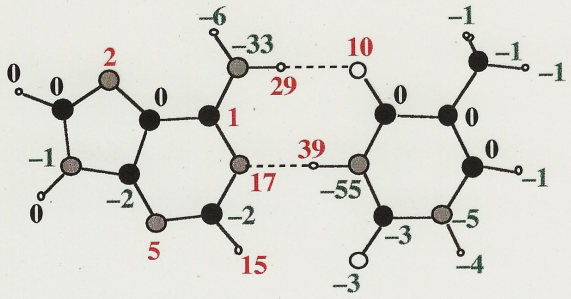
$$\Delta Q_A^{\Gamma} = -\int_{\substack{\text{Voronoi}\\ \text{cell of A}}} \left[\rho_{pair}^{\Gamma}(\mathbf{r}) - \rho_{base1}^{\Gamma}(\mathbf{r}) - \rho_{base2}^{\Gamma}(\mathbf{r})\right] d\mathbf{r}$$

where $\rho^{\Gamma} = \sum_{i\in\Gamma}^{occ} \left|\psi_i^{\Gamma}\right|^2$

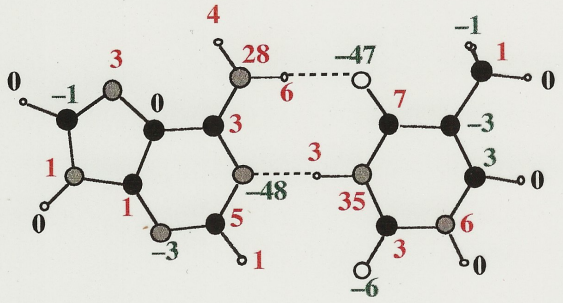
Charge rearrangements with VDD

(in milli-electron)

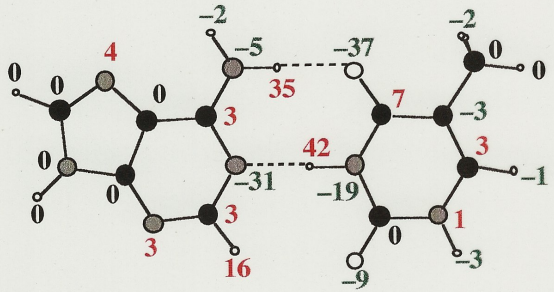
ΔQ_A^{σ}



ΔQ_A^{π}



ΔQ_A

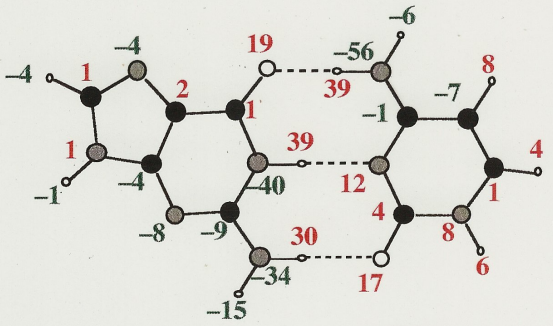


	Adenine	Thymine	
ΔQ_{Base}	.03	-.03	electron

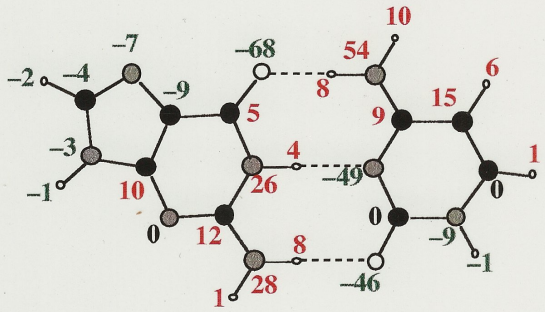
Charge rearrangements with VDD

(in milli-electron)

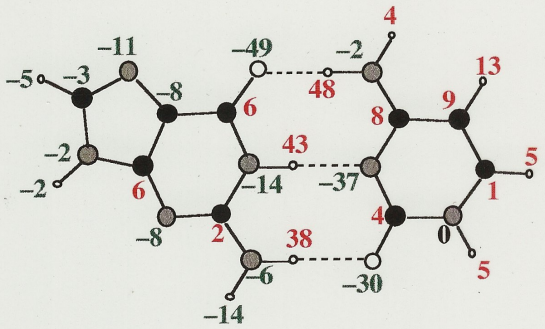
ΔQ_A^{σ}



ΔQ_A^{π}



ΔQ_A



ΔQ_{Base}	Guanine	Cytosine	
	-.03	.03	electron

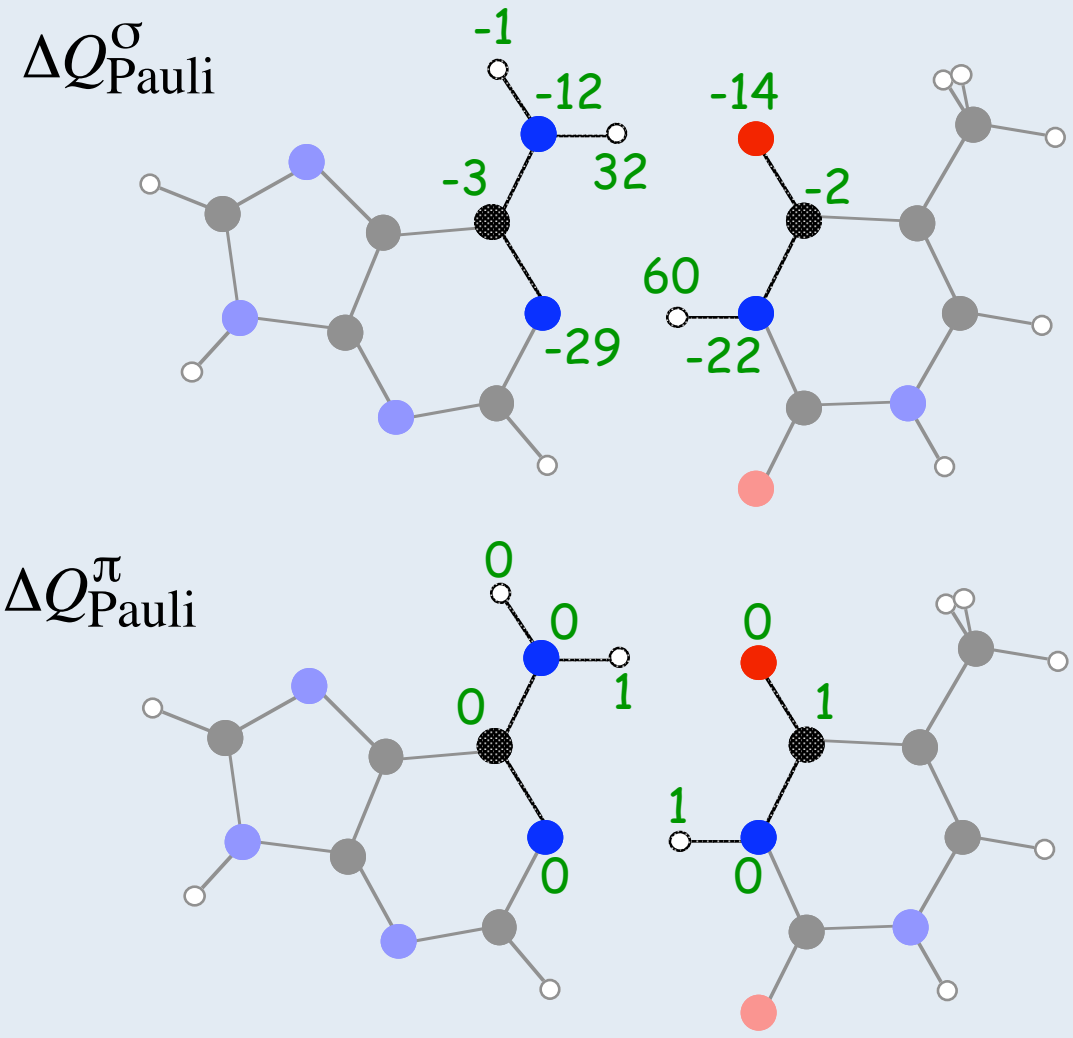
Charge rearrangements

$$\Delta Q_{\mathrm{Pauli,A}} = -\int_{\substack{\text{Voronoi cell}\\ \text{of A in molecule}}} \left(\rho^{0}_{\mathrm{complex}}(\mathbf{r}) - \sum_{\text{subsystems}} \rho_i(\mathbf{r}) \right) d\mathbf{r}$$

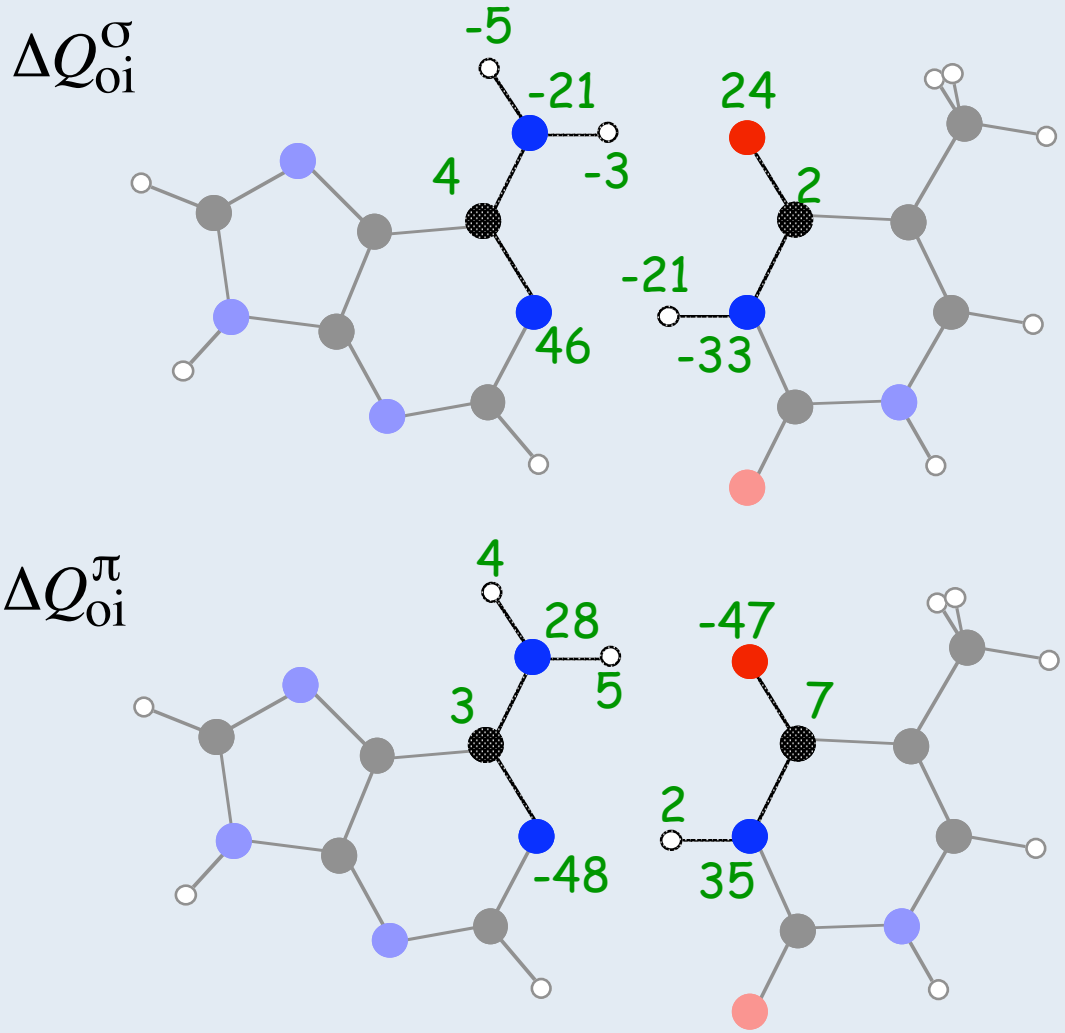
$$\Delta Q_{\mathrm{oi,A}} = -\int_{\substack{\text{Voronoi cell}\\ \text{of A in molecule}}} \left(\rho_{\mathrm{complex}}(\mathbf{r}) - \rho^{0}_{\mathrm{complex}}(\mathbf{r}) \right) d\mathbf{r}$$

$\Delta Q_{\mathrm{Pauli,A}}$ and $\Delta Q_{\mathrm{oi,A}}$ can also be decomposed into contributions of different irreducible representations Γ

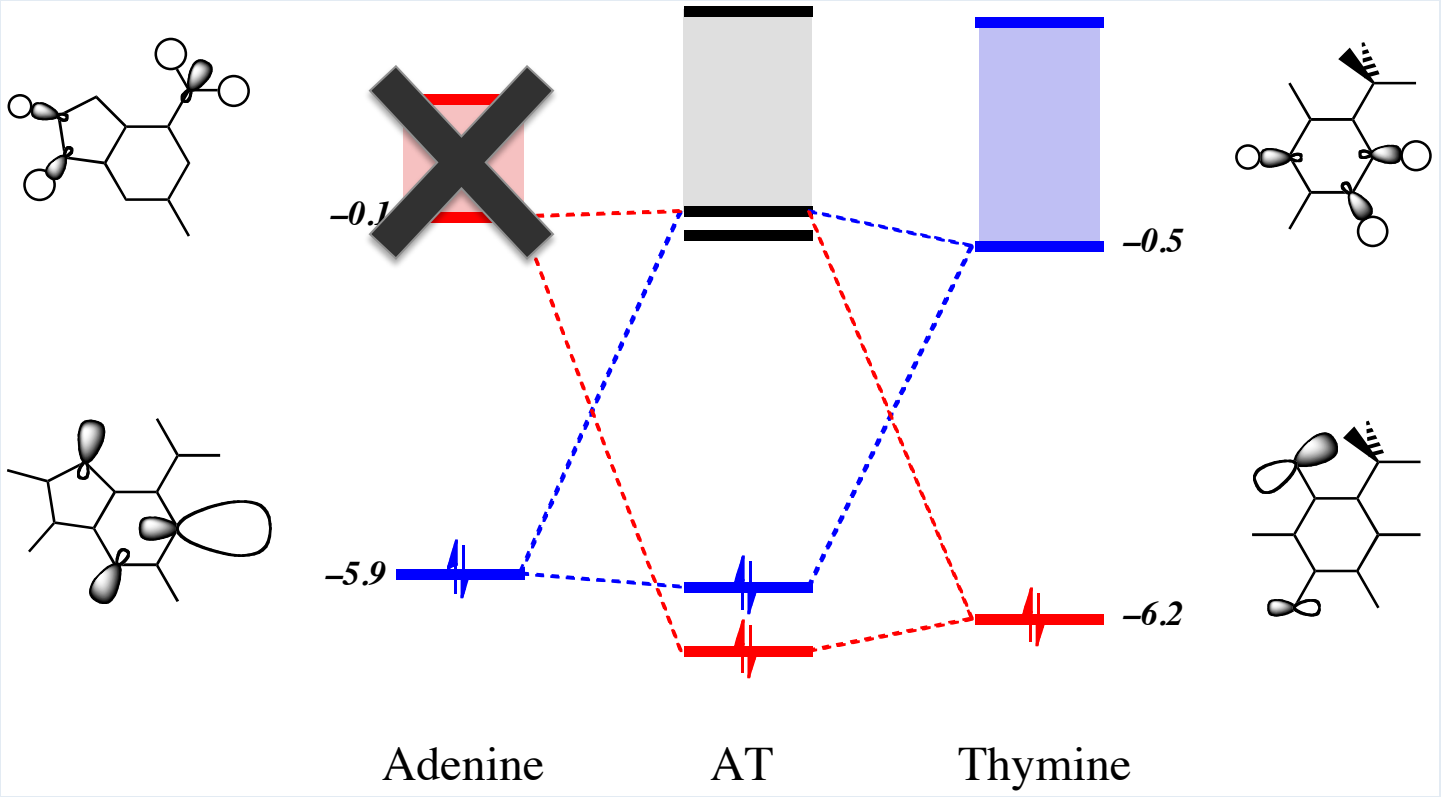
1. B-DNA: charge flow due to Pauli repulsion from VDD



1. B-DNA: charge flow due to orbital interactions from VDD



1. B-DNA: Synergy in hydrogen bonds



RemoveFragOrbitals

1. B-DNA: Synergy in hydrogen bonds

A(σ,–)T(–,–) ⟶ charge flow from **T** to ***A***

A(–,–)T(σ,–) ⟶ charge flow from ***A*** to **T**

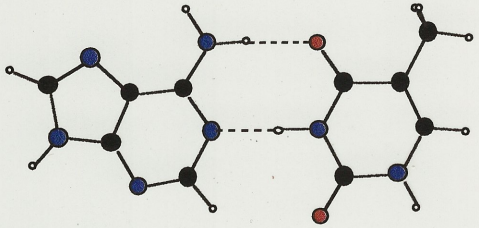
A(–,π)T(–,–) ⟶ polarization on ***A***

A(–,–)T(–,π) ⟶ polarization on **T**

A(σ,–)T(σ,–) ⟶ only charge transfer

A(–,π)T(–,π) ⟶ only polarization

Synergy in hydrogen bonds

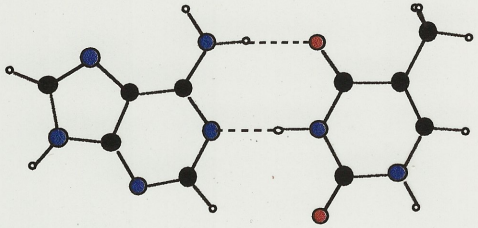


Adenine - Thymine

	ΔE_σ	ΔE_π	ΔE_{oi}
A(σ,–)T(–,–) A(–,–)T(σ,–)			
A(–,π)T(–,–) A(–,–)T(–,π)			
A(σ,–)T(σ,–) A(–,π)T(–,π)	–20.4	–1.3	–21.7
A(σ,π)T(σ,π)	–20.7	–1.7	–22.4

(in kcal/mol)

Synergy in hydrogen bonds

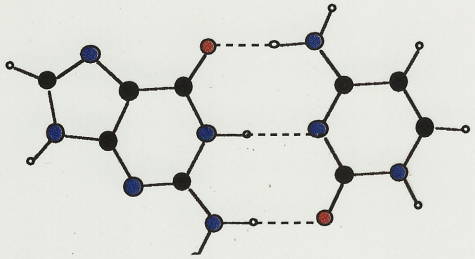


Adenine - Thymine

	ΔE_σ	ΔE_π	ΔE_{oi}
A(σ,–)T(–,–) A(–,–)T(σ,–)	–21.2		
A(–,π)T(–,–) A(–,–)T(–,π)		–1.4	
			–22.6
A(σ,–)T(σ,–) A(–,π)T(–,π)	–20.4	–1.3	–21.7
A(σ,π)T(σ,π)	–20.7	–1.7	–22.4

(in kcal/mol)

Synergy in hydrogen bonds

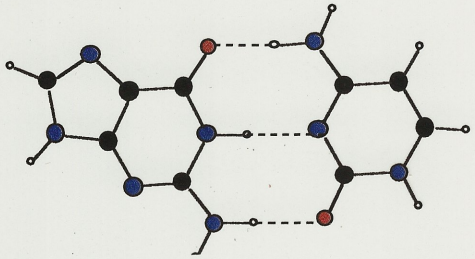


Guanine – Cytosine

	ΔE_σ	ΔE_π	ΔE_{oi}
G(σ,–)C(–,–) G(–,–)C(σ,–)			
G(–,π)C(–,–) G(–,–)C(–,π)			
G(σ,–)C(σ,–)	–28.9		–32.7
G(–,π)C(–,π)		–3.8	
G(σ,π)C(σ,π)	–29.3	–4.8	–34.1

(in kcal/mol)

Synergy in hydrogen bonds

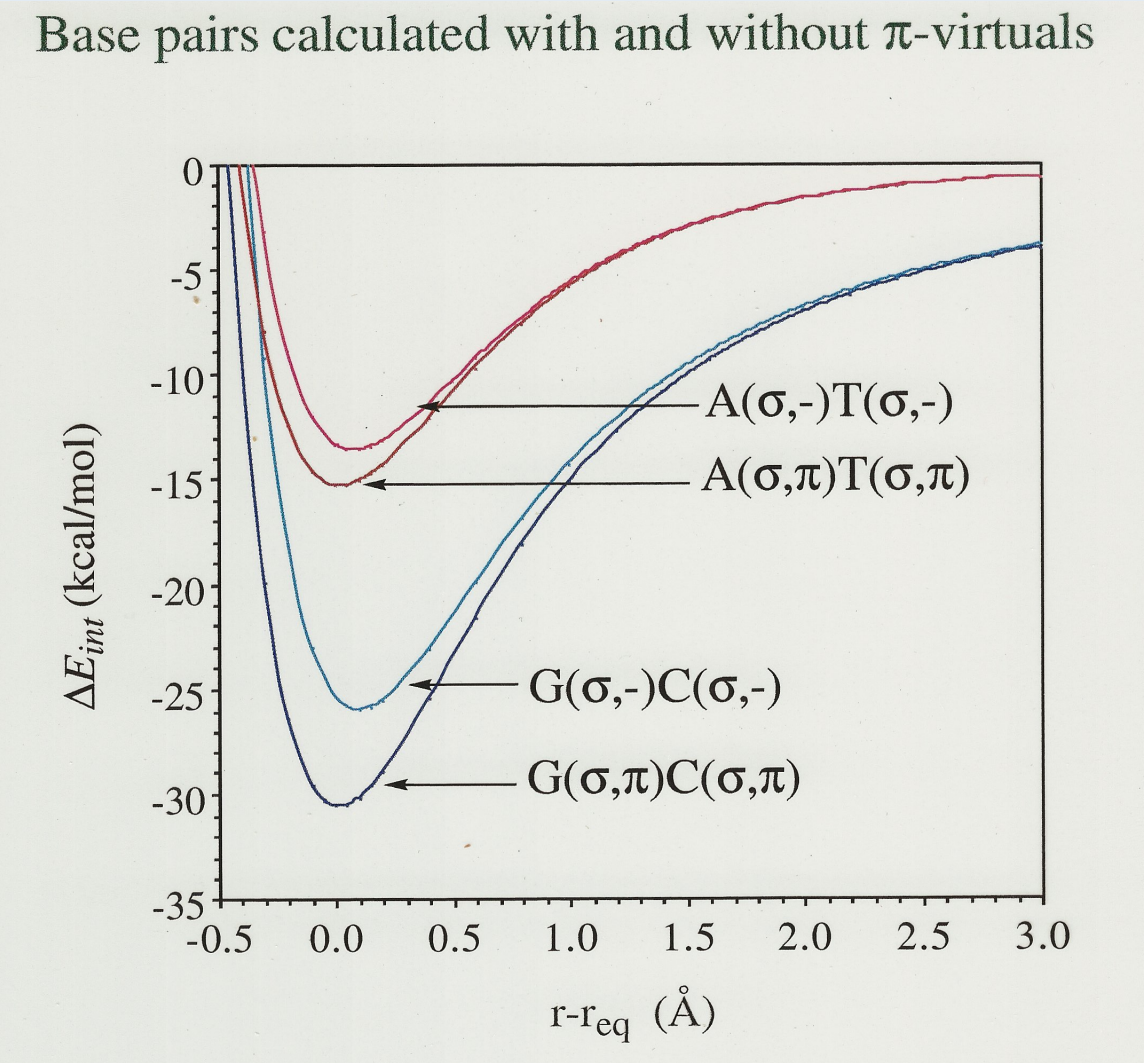


Guanine – Cytosine

	ΔE_σ	ΔE_π	ΔE_{oi}
G(σ,–)C(–,–) G(–,–)C(σ,–)	–30.0		–33.6
G(–,π)C(–,–) G(–,–)C(–,π)		–3.6	
G(σ,–)C(σ,–) G(–,π)C(–,π)	–28.9	–3.8	–32.7
G(σ,π)C(σ,π)	–29.3	–4.8	–34.1

(in kcal/mol)

I. B-DNA: Role of π electrons

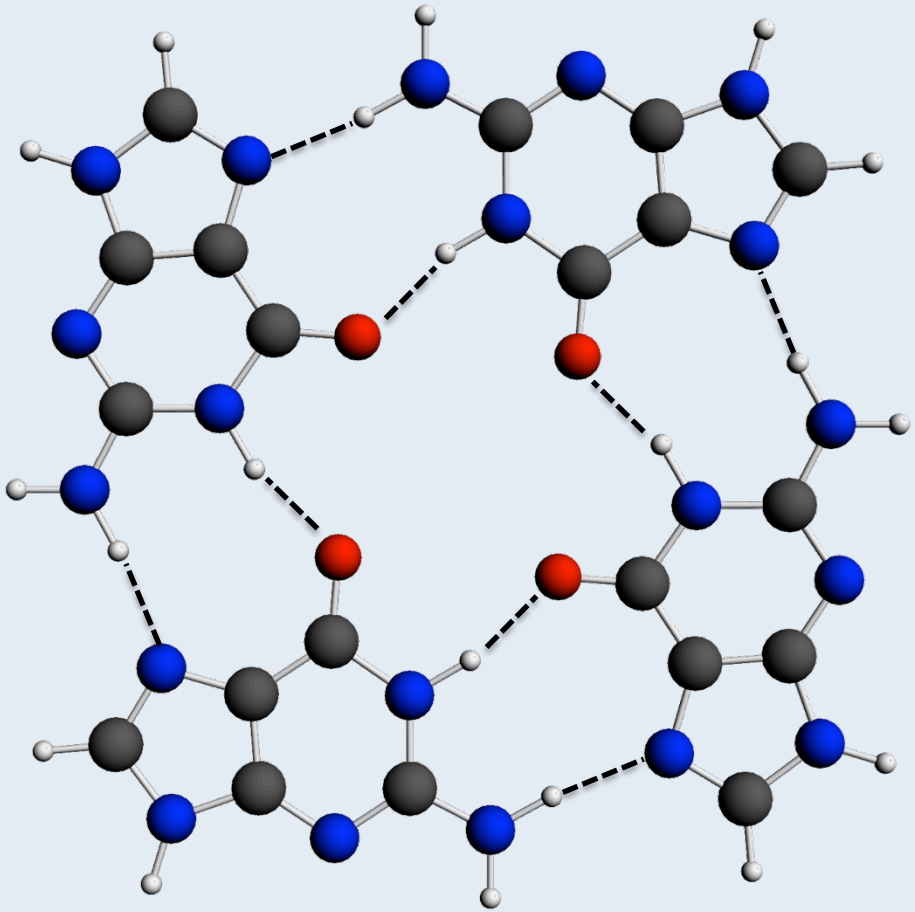


1. B-DNA: Conclusions on RAHB

- Electrostatic interaction
- Orbital interaction
  - Charge transfer in σ system
  - Some assistance by π delocalisation

But also in G-DNA

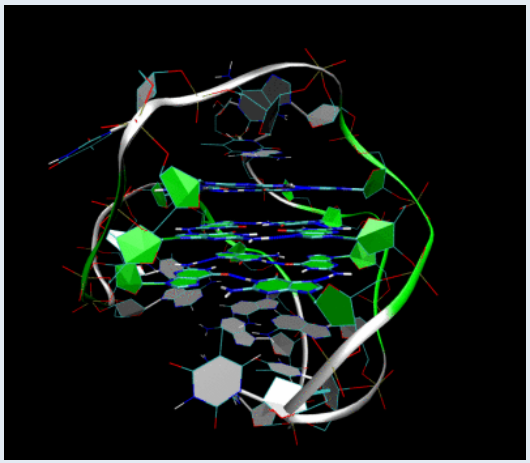
2. G-DNA: Guanine quartet



2. G-DNA: In Telomeres

Nobel Prize in Medicine 2009

for the discovery of how chromosomes are protected by telomeres and the enzyme telomerase

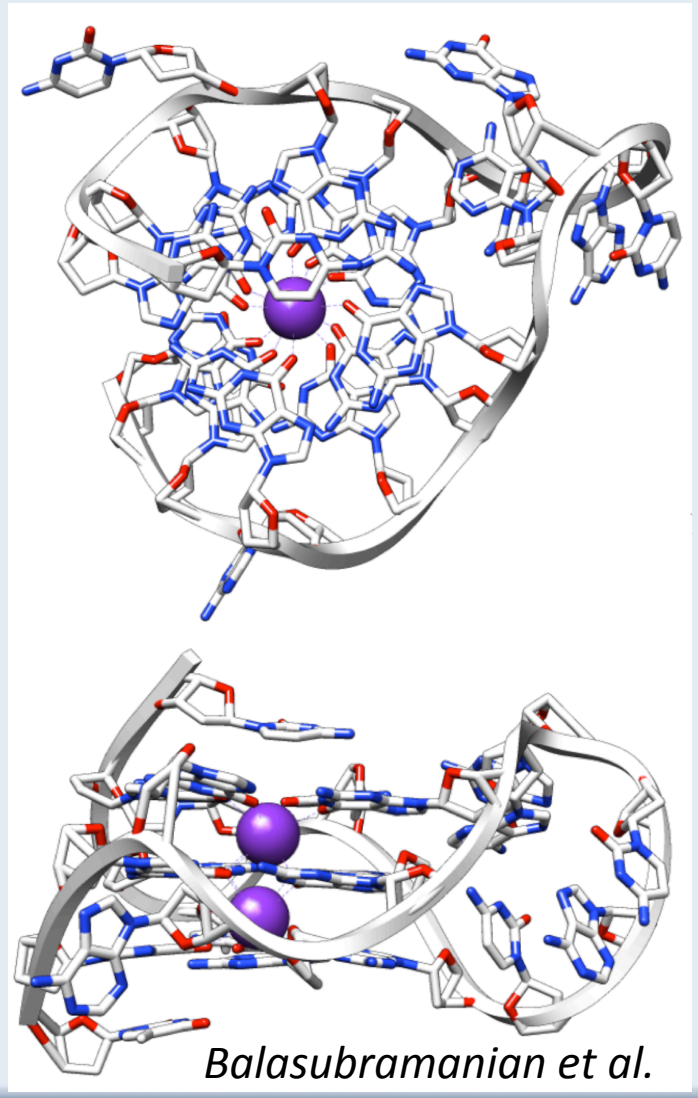


Blackburn

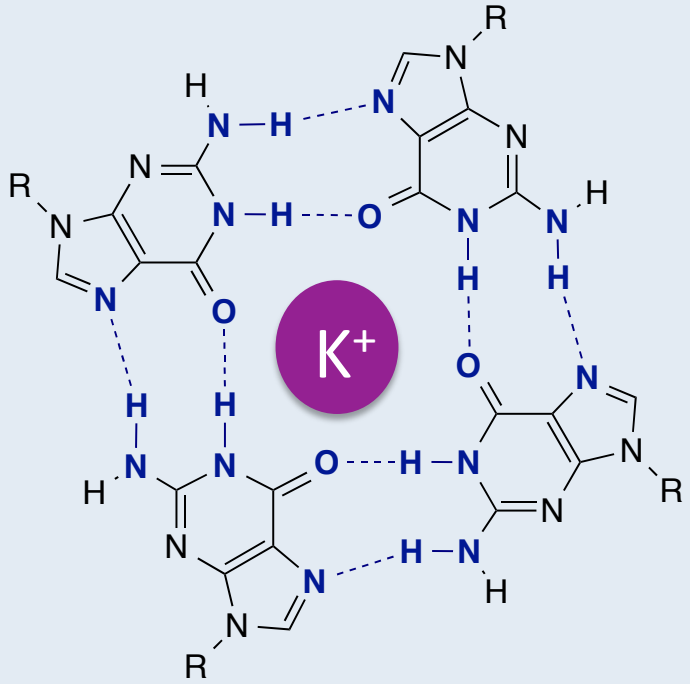
Greider

Szostak

2. G-DNA: In Telomeres

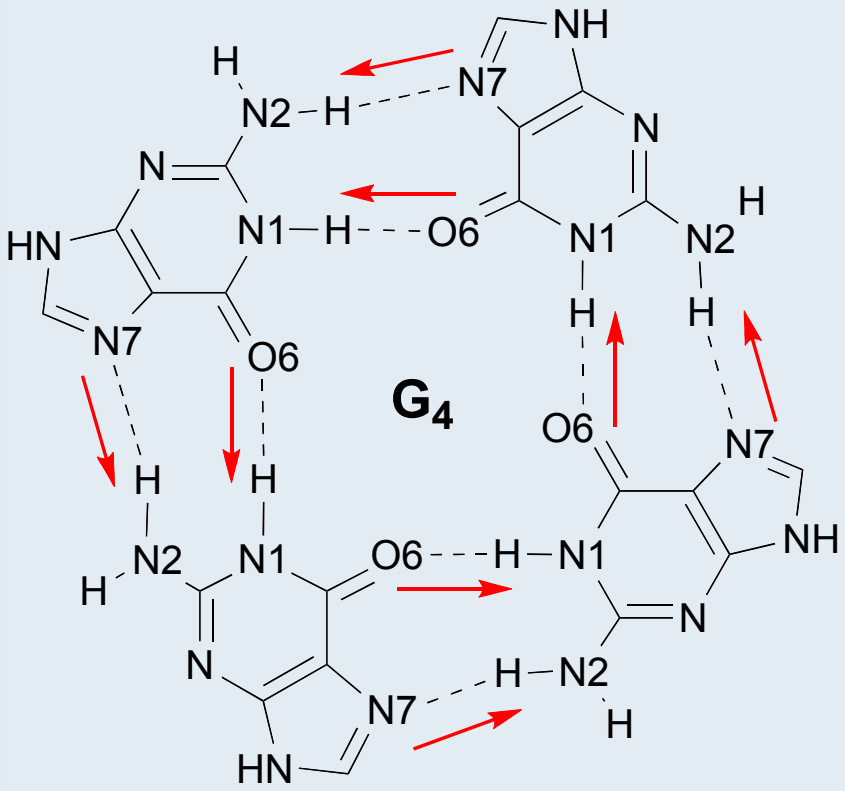


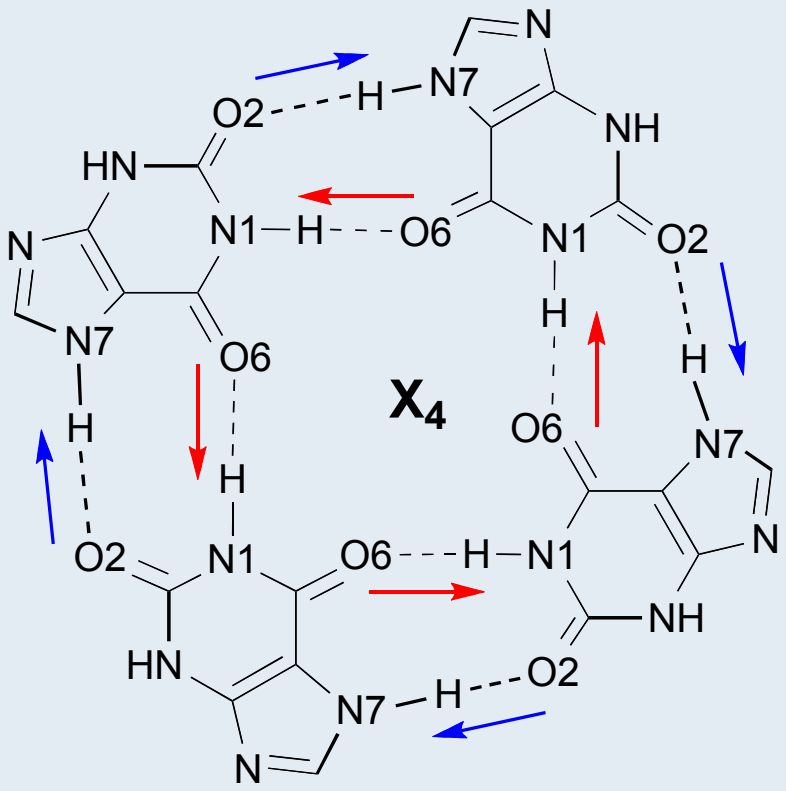
Balasubramanian et al.



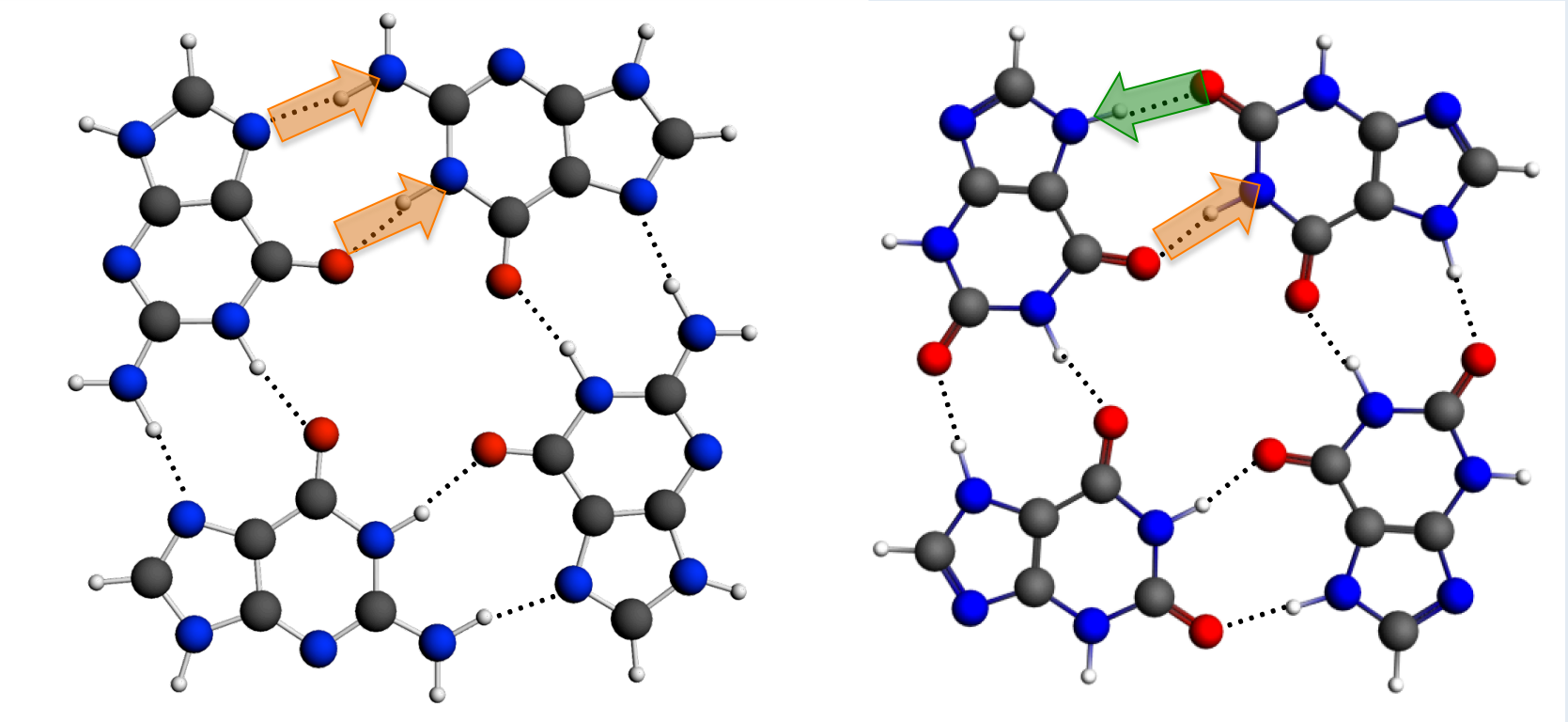
$$4*\Delta E(G_2) < \Delta E(G_4)$$

2. G-DNA: Guanine and Xanthine





2. G-DNA: Guanine and Xanthine

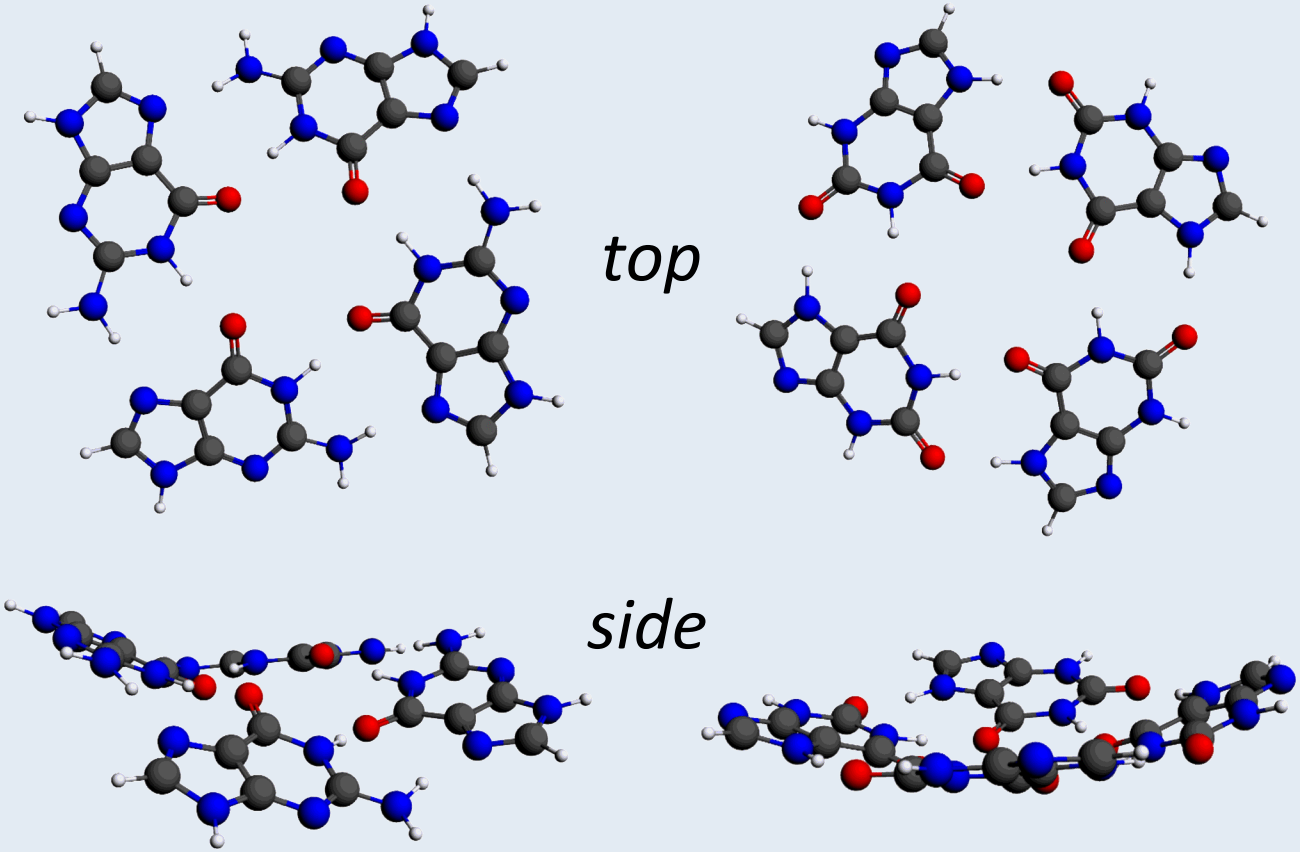


$4 \bullet \Delta E(G_2) < \Delta E(G_4)$

$4 \bullet \Delta E(Xan_2) = \Delta E(Xan_4)$

Chem. Eur. J. **2011**, *17*, 12612

2. G-DNA: Guanine and Xanthine



G_4 (in S_4)

X_4 (in C_4)

Chem. Eur. J. **2011**, *17*, 12612

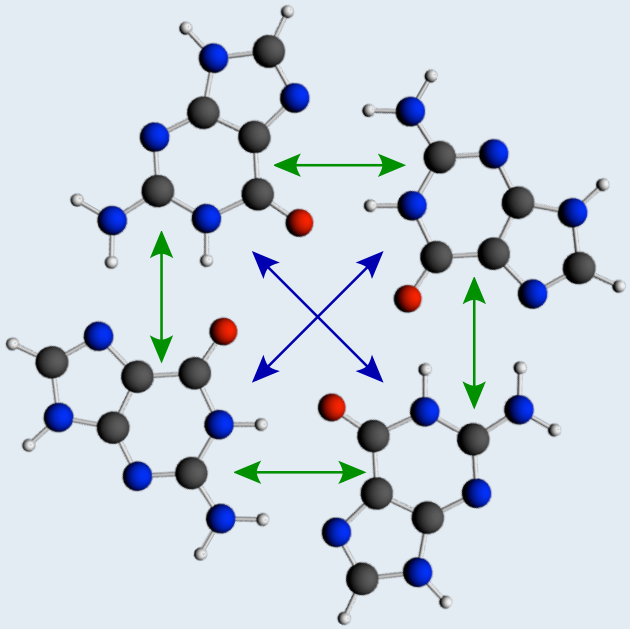
2. G-DNA: Guanine and Xanthine

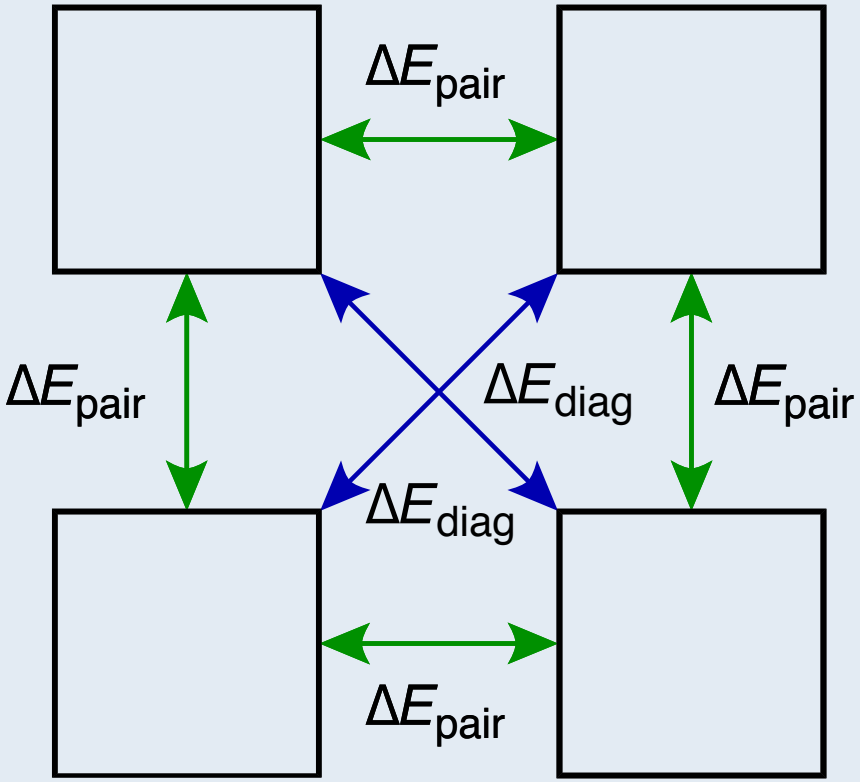
Quartet	Symmetry	ΔE_{bond}
G_4	S_4	**–79.8**
	C_{4h}	–79.1
X_4	C_4	**–66.5**
	C_{4h}	–65.5

- *G_4 stronger bound than X_4*
- *C_{4h} symmetry applicable*

Chem. Eur. J. **2011**, *17*, 12612

2. G-DNA: Cooperativity





$$\text{Synergy} = \Delta E_{int} - (4*\Delta E_{pair} + 2*\Delta E_{diag})$$

2. G-DNA: Cooperativity

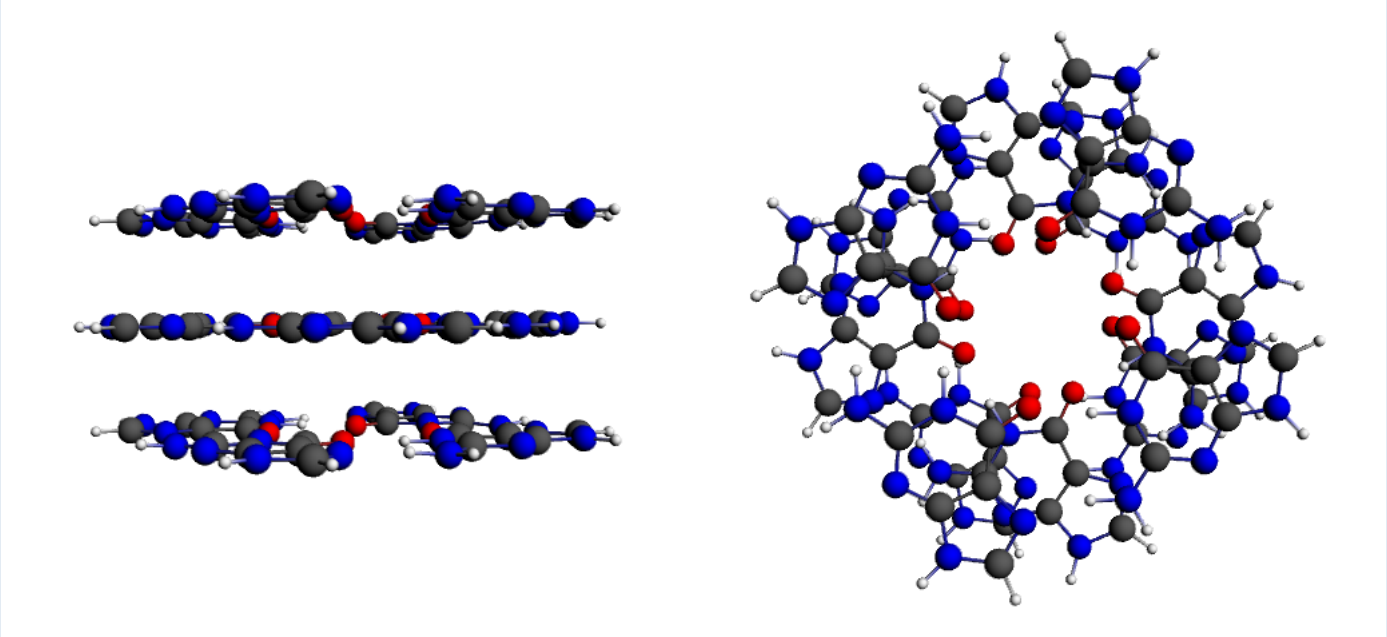
Quartet	ΔE_{int}	ΔE_{sum}	$\Delta E_{int} - \Delta E_{sum}$
G_4	–89.1	–68.3	
G_4 no π	–75.4	–61.2	
X_4	–72.6	–71.1	
X_4 no π	–64.6	–62.2	

2. G-DNA: Cooperativity

Quartet	ΔE_{int}	ΔE_{sum}	$\Delta E_{int} - \Delta E_{sum}$
G_4	–89.1	–68.3	**–20.8**
G_4 no π	–75.4	–61.2	**–14.3**
X_4	–72.6	–71.1	–1.5
X_4 no π	–64.6	–62.2	–2.4

- *cooperativity*
- *even when **π** electrons do **NOT** cooperate!*

2. G-DNA: G_4-[B_4]-G_4



$$\Delta E_{int} = \underbrace{[\Delta E(G_{12}) - \Delta E(G_8)]}_{\text{Quartet}} - \underbrace{4*[\Delta E(G_9) - \Delta E(G_8)]}_{\text{Base}}$$

2. G-DNA: G_4–[B_4]-G_4

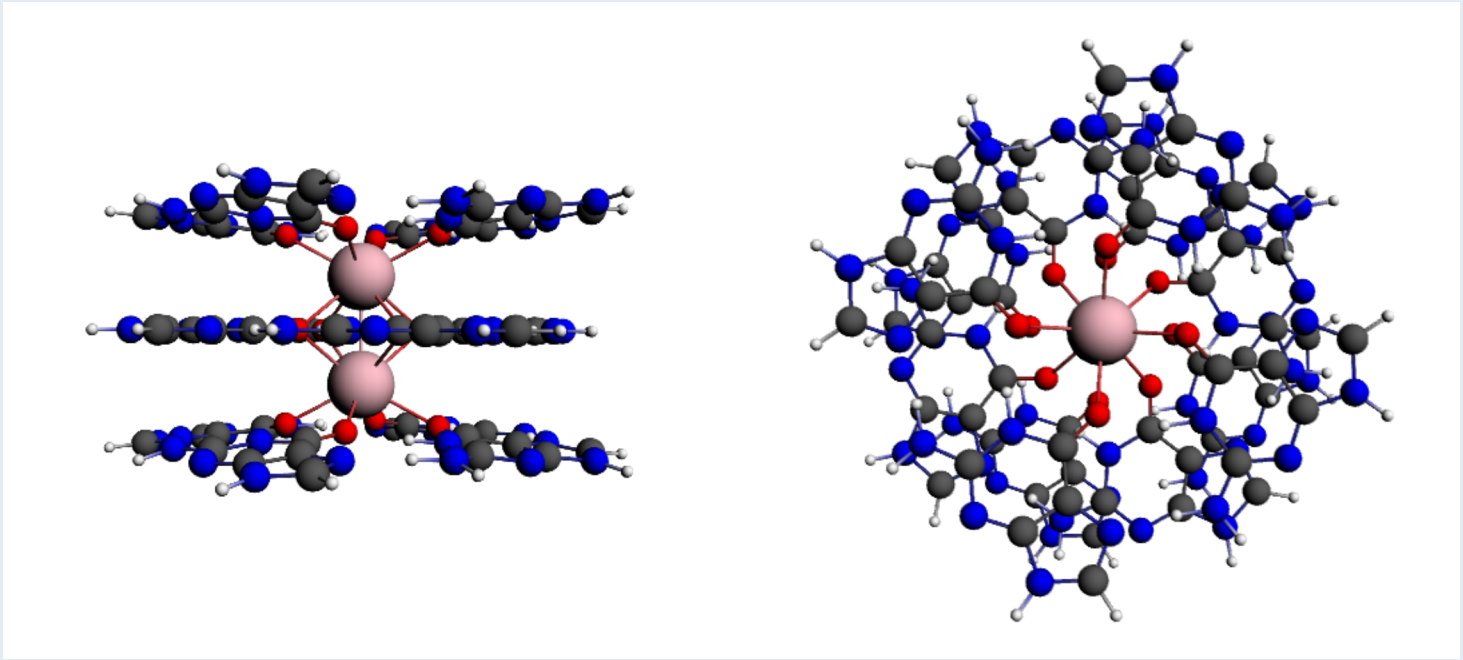
Quartet	ΔE_{int}	ΔE_{sum}	$\Delta E_{int} - \Delta E_{sum}$
G_4	–87.0	–71.6	
X_4	–73.4	–72.3	

2. G-DNA: G_4–[B_4]–G_4

Quartet	ΔE_{int}	ΔE_{sum}	$\Delta E_{int} - \Delta E_{sum}$
G_4	–87.0	–71.6	**–15.3**
X_4	–73.4	–72.3	–1.1

Cooperativity between H-bonds in stack!

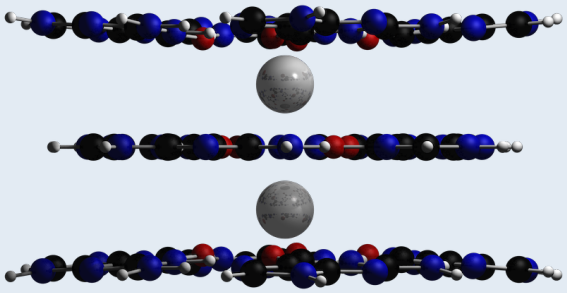
2. G-DNA: G_4–K^+–[B_4]–K^+–G_4



$$\Delta E_{int} = [\Delta E(G_{12}K_2^{2+}) - \Delta E(G_8K_2^{2+})] - 4*[\Delta E(G_9K_2^{2+}) - \Delta E(G_8K_2^{2+})]$$

Quartet **Base**

2. G-DNA: G_4–K^+–[B_4]–K^+–G_4

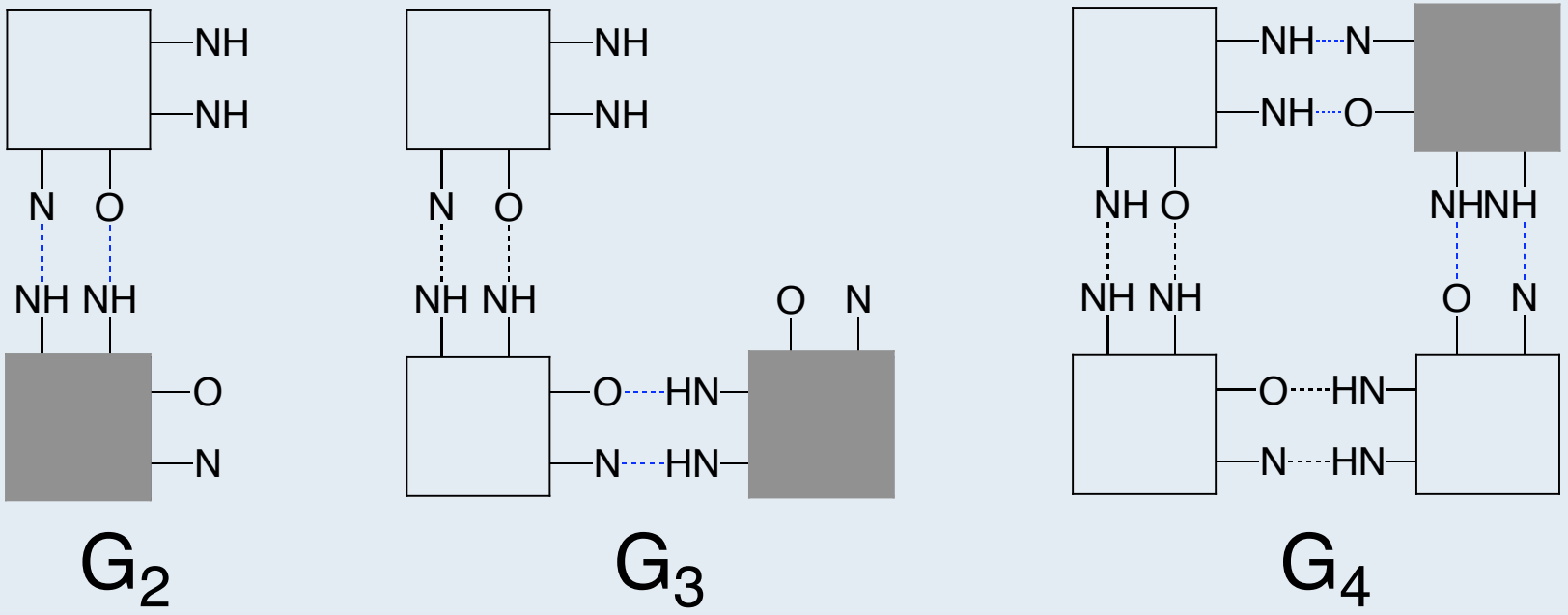


$G_4K^+[G_4]K^+G_4$

	Quartet	ΔE_{int}	ΔE_{sum}	Synergy
$G_4 – K^+ – [G_4\ ] – K^+ – G_4$	G_4	–72.7	–54.8	–17.9

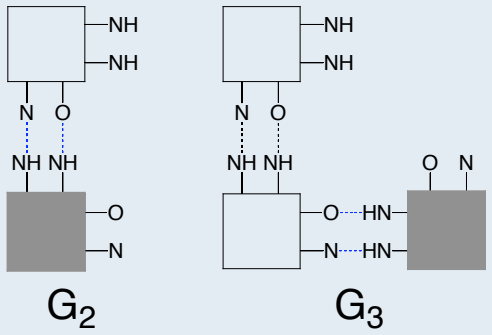
Cooperativity under "natural" conditions

2. G-DNA: Building up G_4



2. G-DNA: Building up G_4

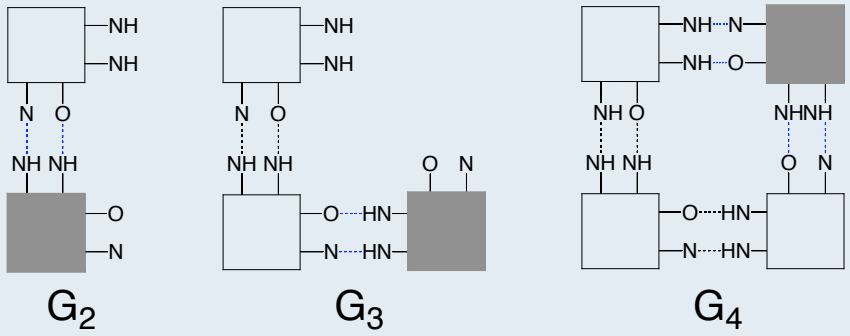
	G_2 (G+G)	G_3 (G_2+G)
ΔE_{oi}	–16.4	–18.3
ΔE_{Pauli}	30.7	30.0
ΔV_{elstat}	–26.2	–29.9
ΔE_{disp}	–4.2	–4.4
ΔE_{int}	–16.1	–22.7



G_2 G_3

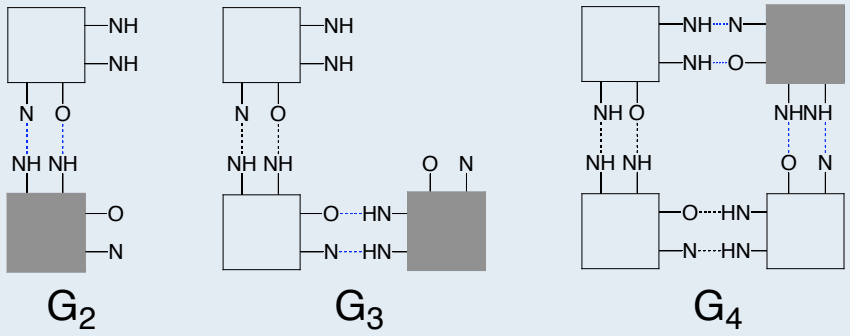
2. G-DNA: Building up G_4

	G_2 (G+G)	G_3 (G_2+G)	G_4 (G_3+G)
ΔE_{oi}	–16.4	–18.3	–42.1
ΔE_{Pauli}	30.7	30.0	60.9
ΔV_{elstat}	–26.2	–29.9	–60.6
ΔE_{disp}	–4.2	–4.4	–8.6
ΔE_{int}	–16.1	–22.7	–50.3



2. G-DNA: Building up G_4

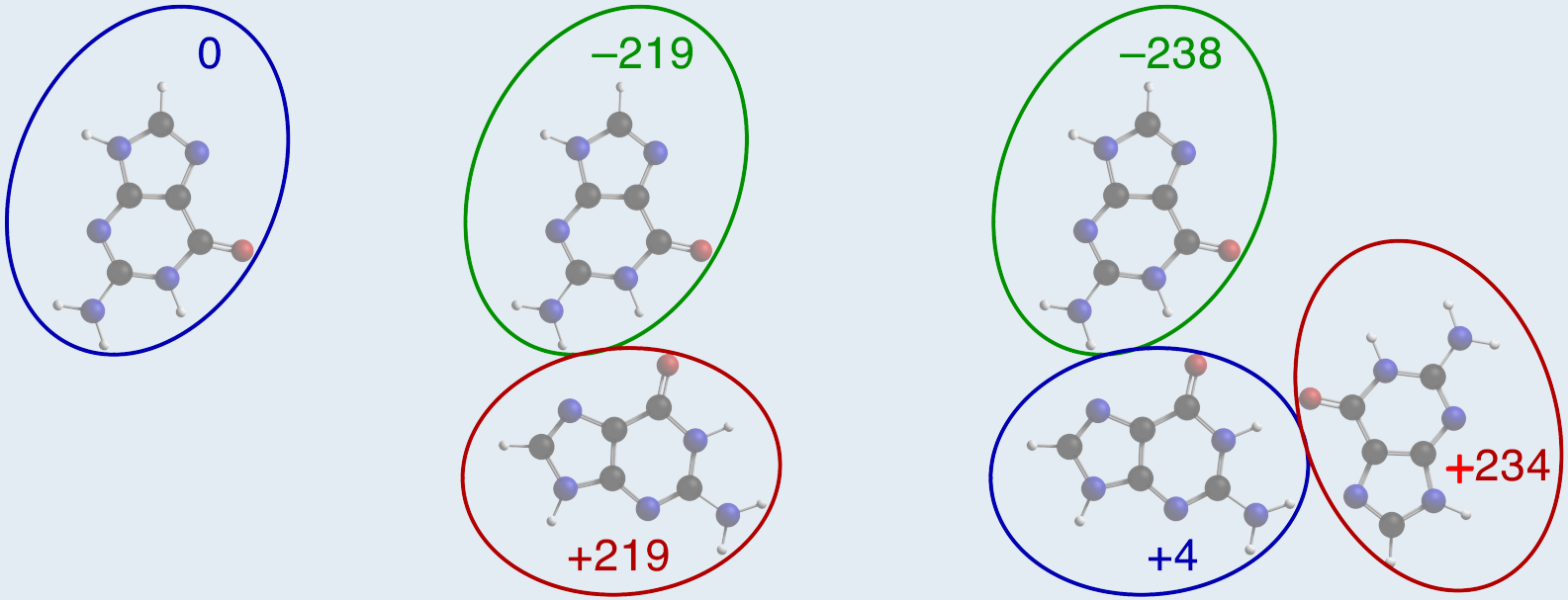
	G_2 (G+G)	G_3 (G_2+G)	G_4 (G_3+G)	$[G_2 + G_3 + G_4] - 4G_2 - 2G_{2diag}$
ΔE_{oi}	–16.4	–18.3	–42.1	–10.8
ΔE_{Pauli}	30.7	30.0	60.9	–1.4
ΔV_{elstat}	–26.2	–29.9	–60.6	–8.6
ΔE_{disp}	–4.2	–4.4	–8.6	0.0
ΔE_{int}	–16.1	–22.7	–50.3	–20.8



2. G-DNA: Building up G_4

	G_2 (G+G)	G_3 (G_2+G)	G_4 (G_3+G)	$[G_2 + G_3 + G_4] - 4G_2 - 2G_{2diag}$
ΔE_{oi}	–16.4	–18.3	–42.1	–10.8
ΔE_{Pauli}	30.7	30.0	60.9	–1.4
ΔV_{elstat}	–26.2	–29.9	–60.6	–8.6
ΔE_{disp}	–4.2	–4.4	–8.6	0.0
ΔE_{int}	–16.1	–22.7	–50.3	–20.8
ΔE_{σ}	–14.6	–16.0	–35.9	–7.8
ΔE_{π}	–1.8	–2.3	–6.2	–3.0

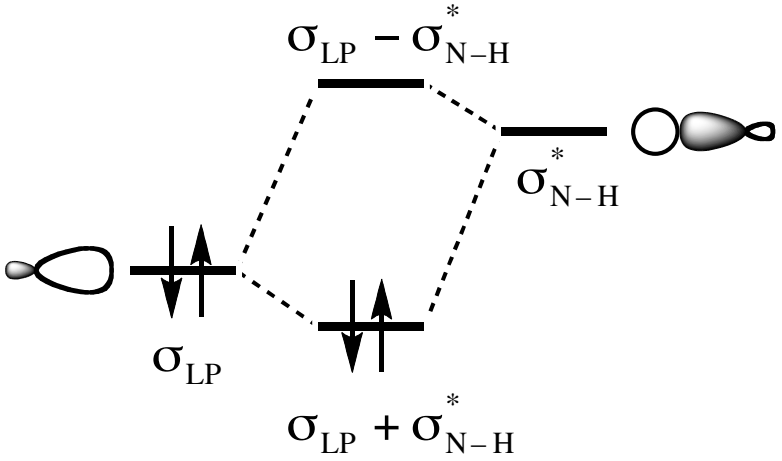
2. G-DNA: Electrostatic interaction

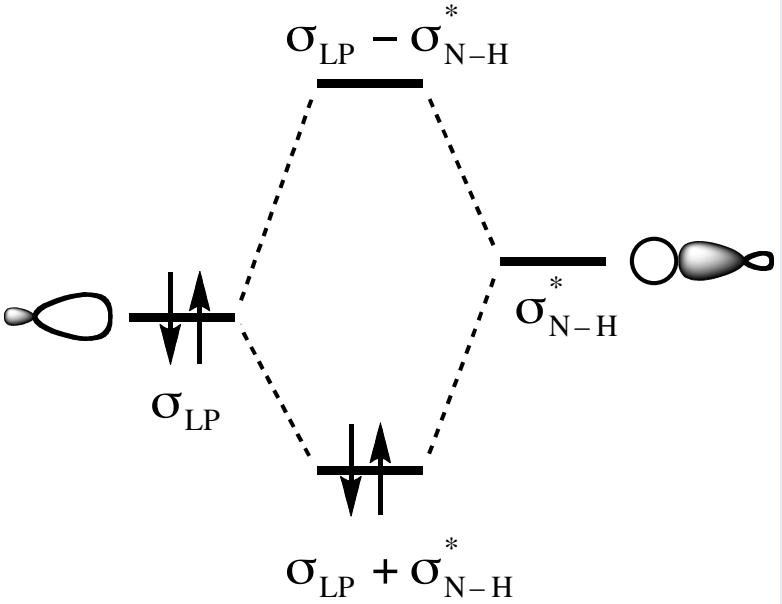


G G_2 G_3

In mili-electrons

2. G-DNA: MO-diagram





Weaker

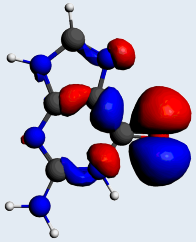
$$\frac{\left\langle \sigma_{LP} \middle| \sigma^*_{N-H} \right\rangle^2}{E_{\sigma_{LP}} - E_{\sigma^*_{N-H}}}$$

Stronger

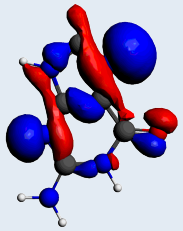
2. G-DNA: Donor orbitals G_4 (eV)

G

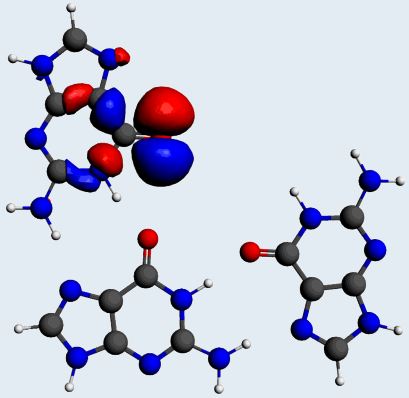
σ_{HOMO} **–5.7**



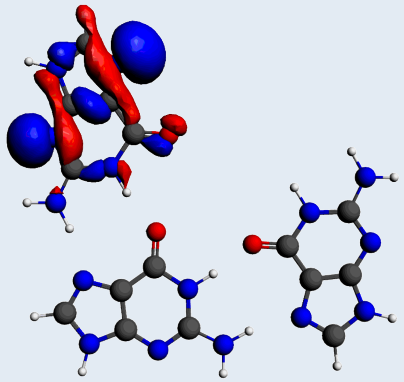
σ_{HOMO-1} **–6.1**



G_3



σ_{HOMO} **–4.4**

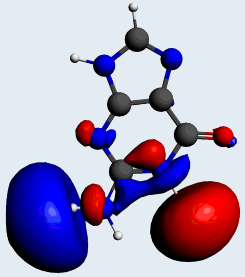


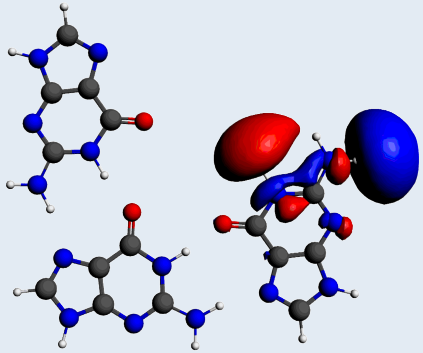
σ_{HOMO-1} **–5.0**

2. G-DNA: Acceptor orbitals G_4 (eV)

σ_{LUMO+2}

0.1



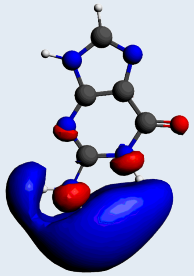


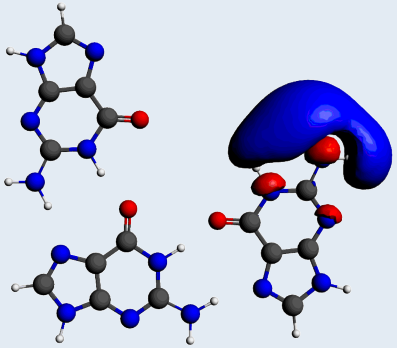
σ_{LUMO+3}

–0.1

σ_{LUMO}

–1.1





σ_{LUMO}

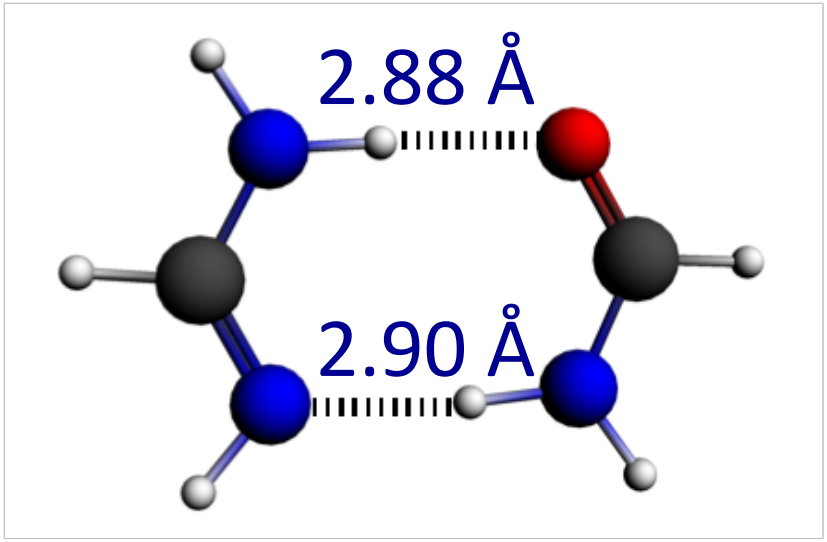
–1.2

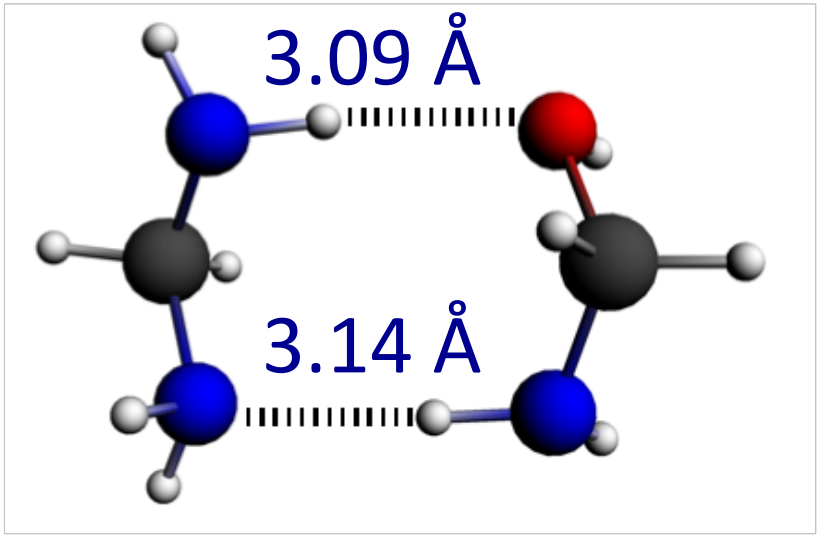
2. G-DNA: Cooperativity G_4

- about 20 kcal/mol
- in gas phase, stack and telomere
- not due to RAHB!
- due charge separation in σ system

due to covalent component in hydrogen bonds

3. Aromaticity: Why sp^2 beats sp^3?



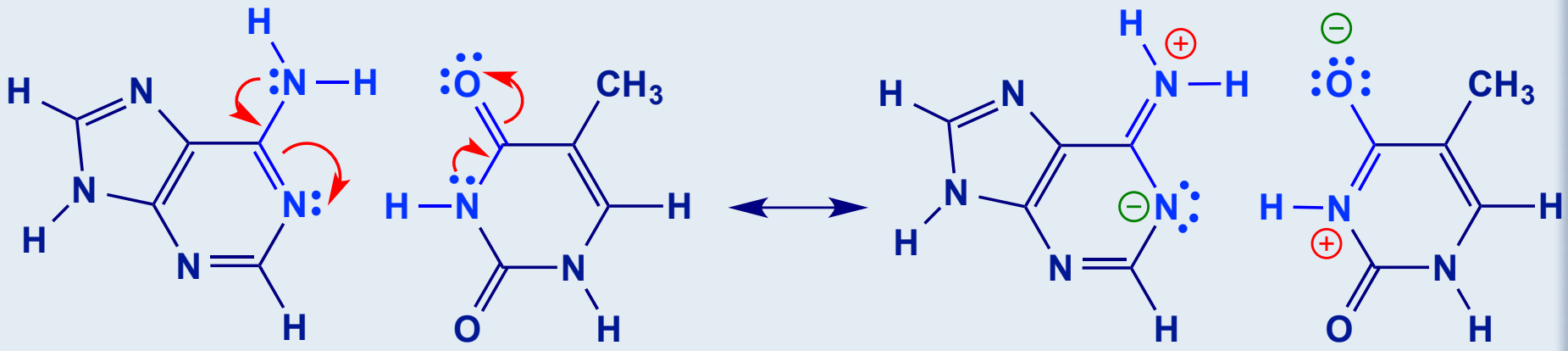


–17.9 kcal/mol

–8.9 kcal/mol

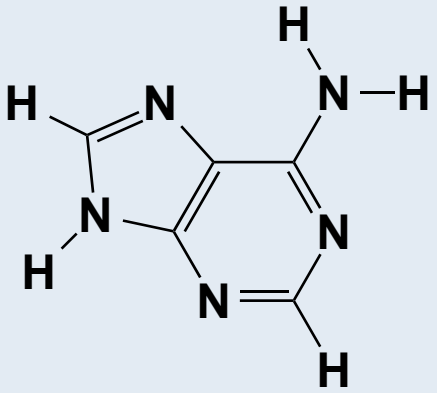
3. Aromaticity: Resonance-Assisted Hydrogen Bonding

In Watson-Crick Base Pair AT

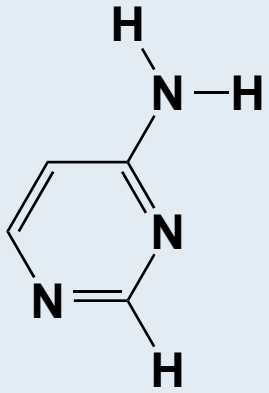


π electrons "assist" the hydrogen bonds

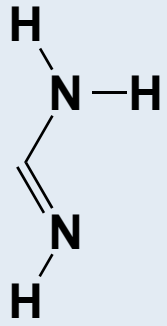
3. Aromaticity: Importance



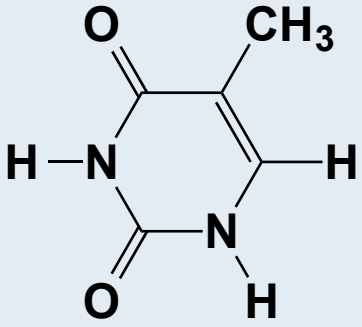
A



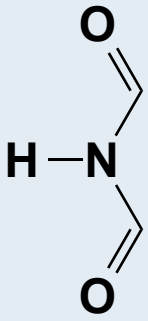
A'



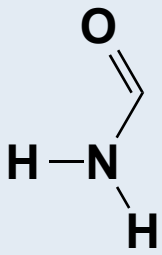
A''



T

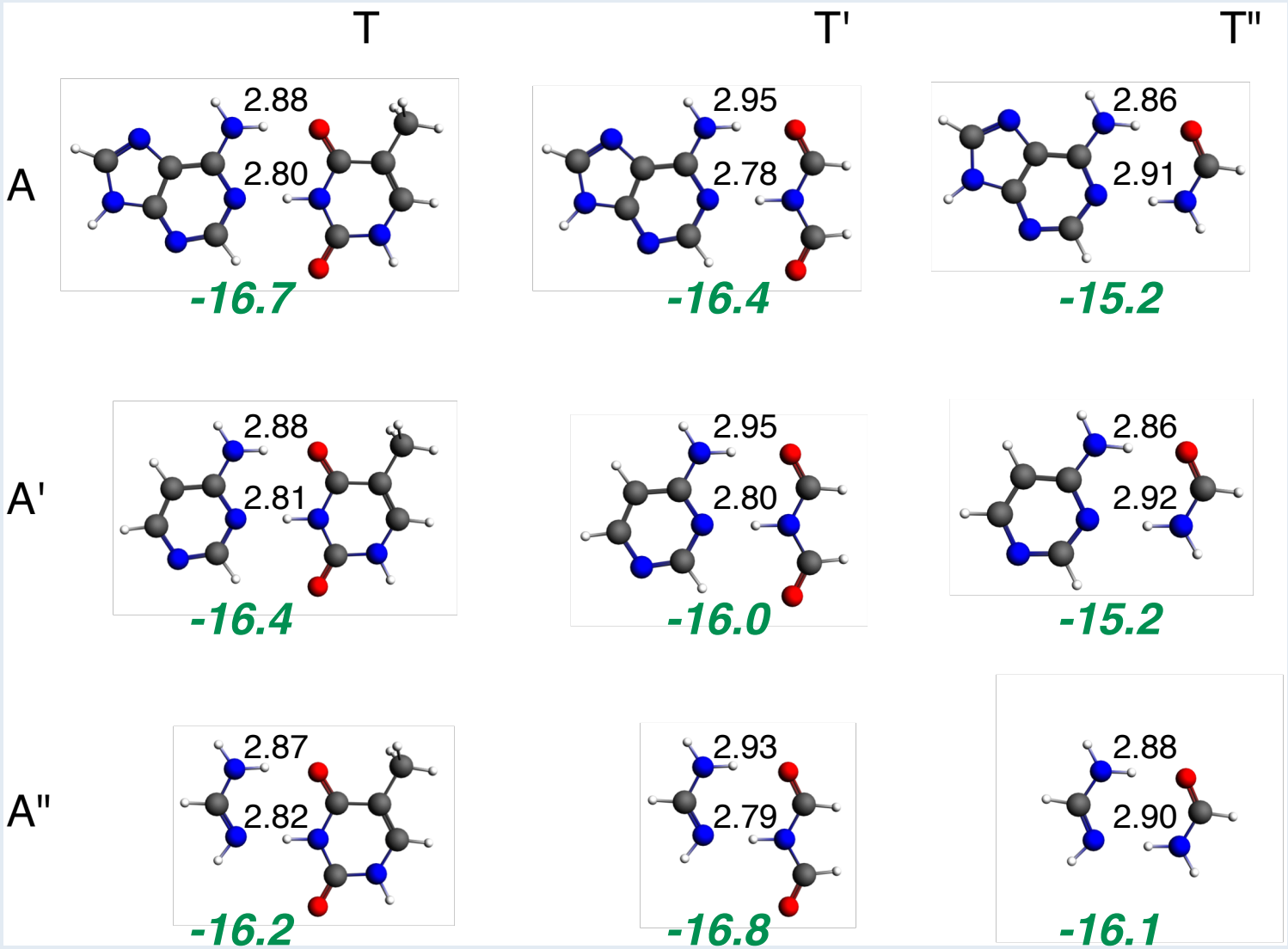


T'

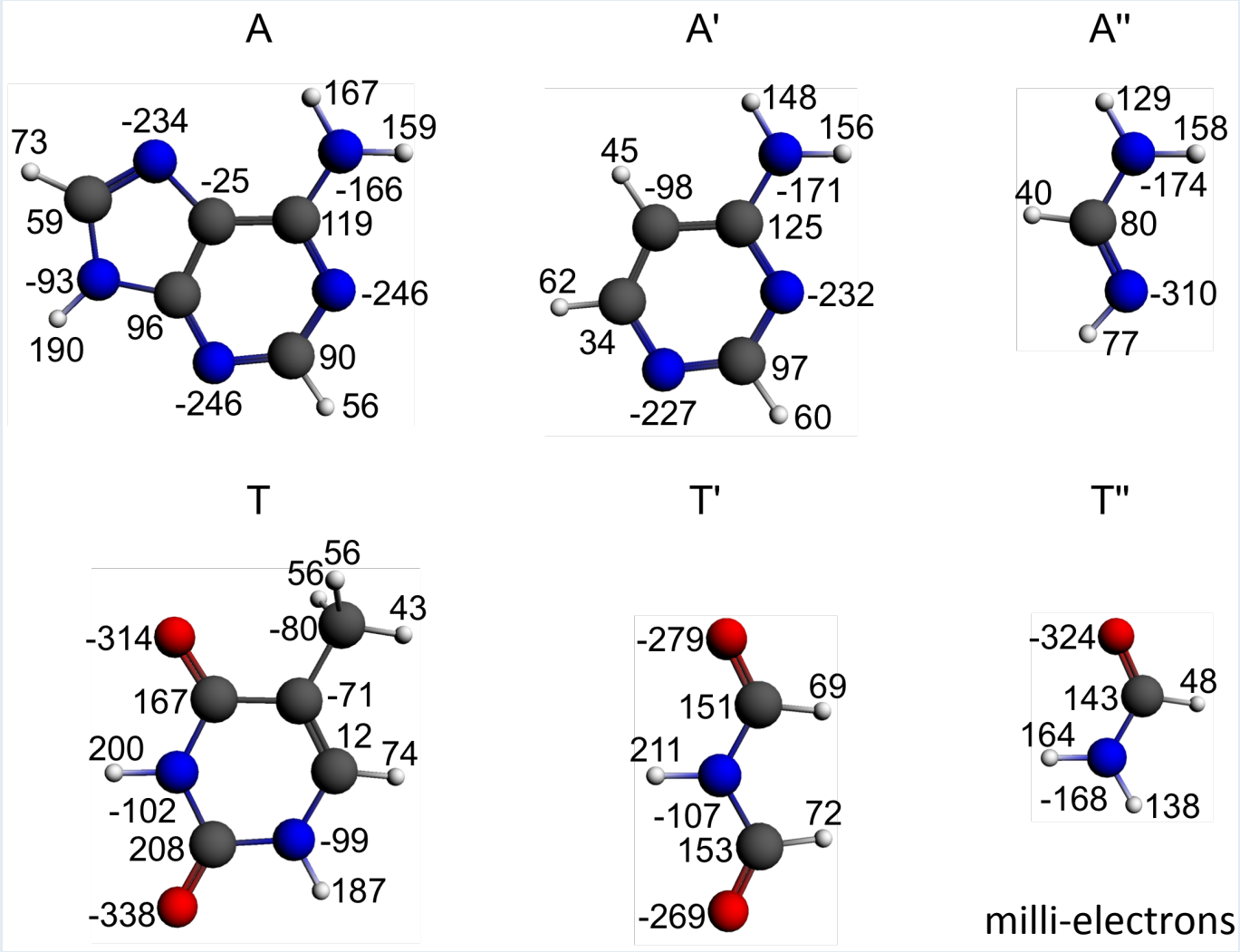


T''

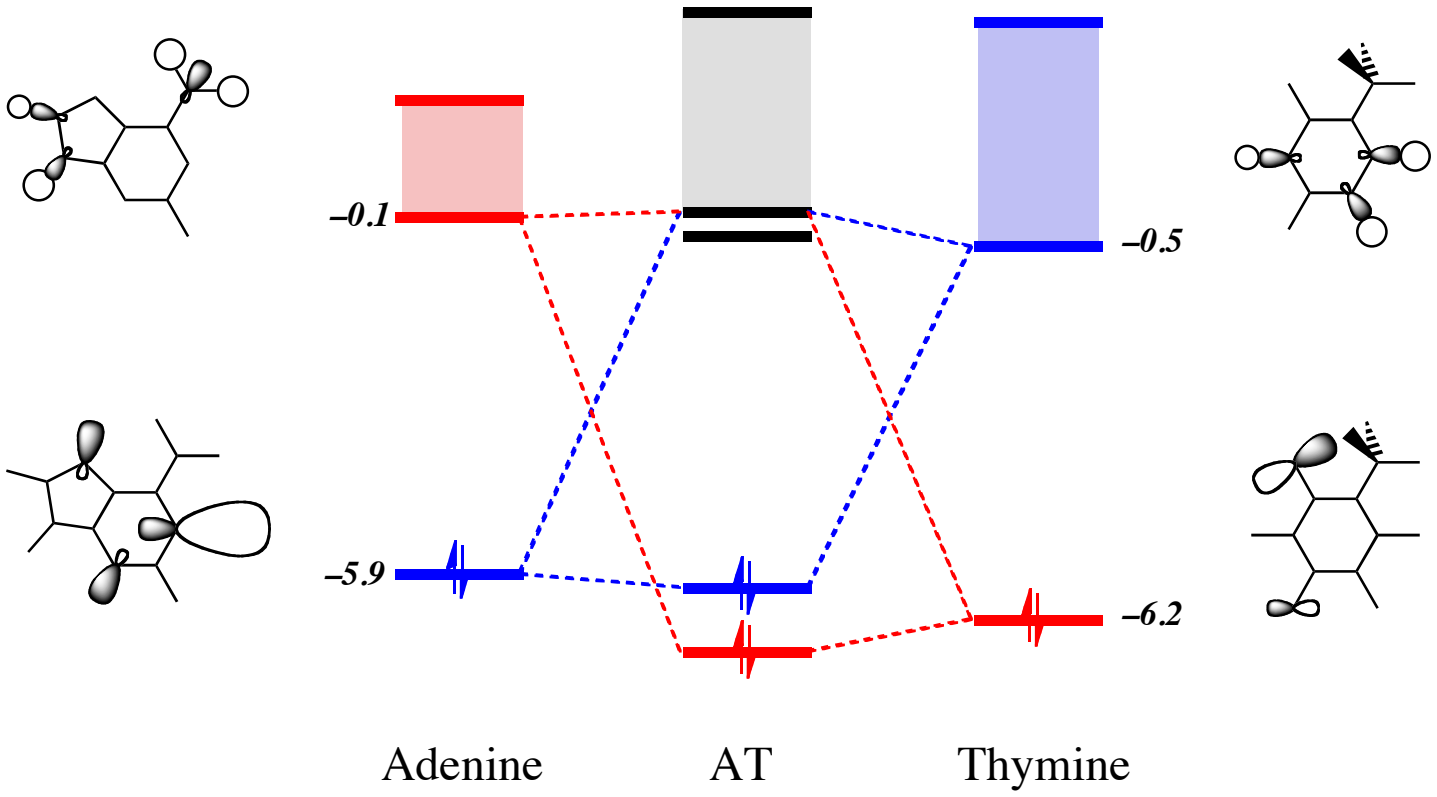
3. Aromaticity: H-bond distances and energies



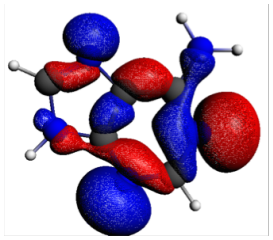
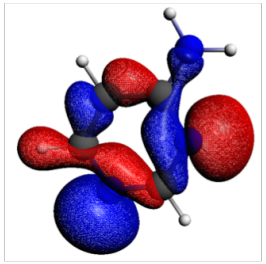
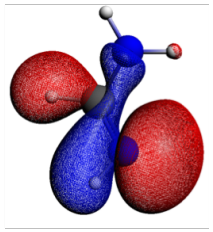
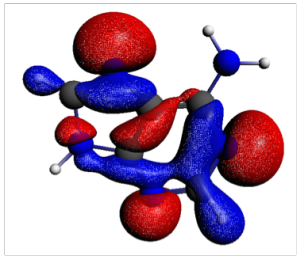
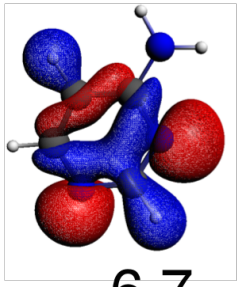
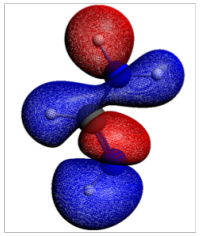
3. Aromaticity: Electronic structure of A, T & mimics



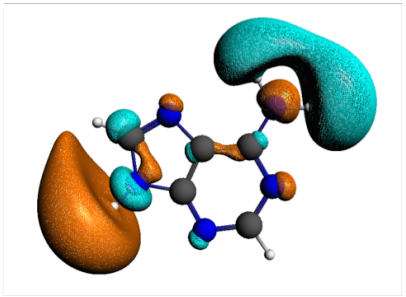
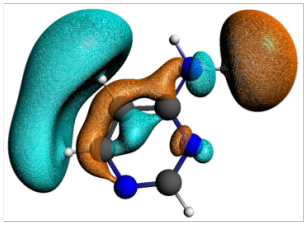
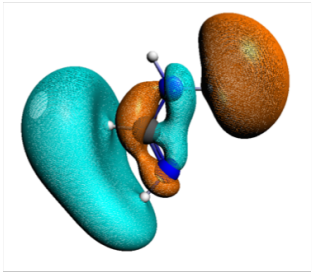
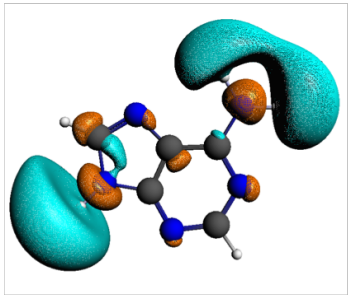
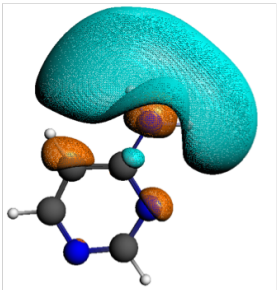
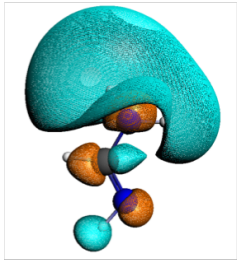
3. Aromaticity: MO diagram for AT



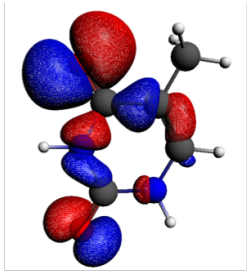
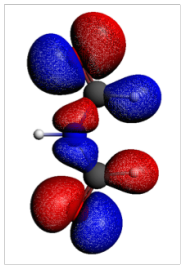
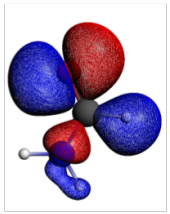
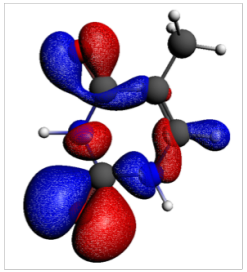
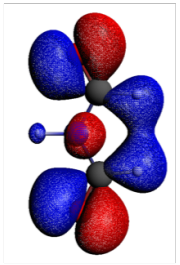
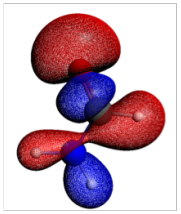
3. Aromaticity: Occupied orbitals of A

A	A’	A”	
			σ_{HOMO}
-5.7	-5.6	-5.8	
			σ_{HOMO-1}
eV -6.5	-6.7	-10.9	

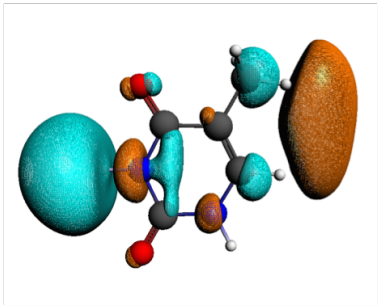
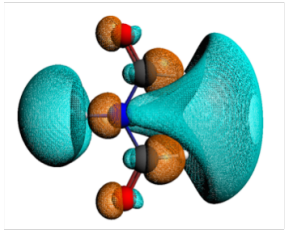
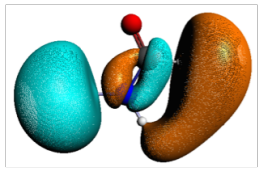
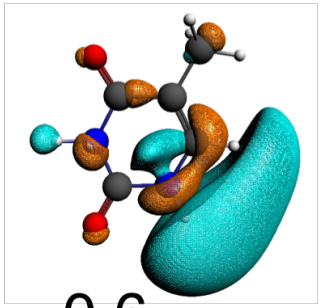
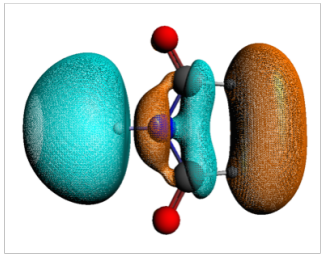
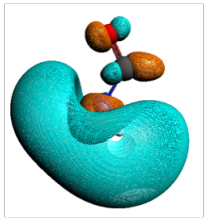
3. Aromaticity: Unoccupied orbitals of A

A	A’	A”	
			σ_{LUMO+1}
-0.1	0.4	0.3	
			σ_{LUMO}
-0.3	-0.5	-0.4	

3. Aromaticity: Occupied orbitals of T

	T	T’	T”
σ_{HOMO}	 -6.0	 -6.5	 -5.9
σ_{HOMO-1}	 -6.8	 -7.3	 -9.8

3. Aromaticity: Unoccupied orbitals of T

	T	T’	T”
σ_{LUMO+1}	 0.1	 0.1	 0.2
σ_{LUMO}	 -0.6	 -0.5	 -0.6

3. Energy Decomposition Analysis

		ΔE	ΔE_{prep}	ΔE_{int}	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{σ}	ΔE_{π}	ΔE_{disp}
A	T	-16.7							
A	T’	-16.4							
A	T”	-15.2							
A’	T	-16.4							
A’	T’	-16.0							
A’	T”	-15.2							
A”	T	-16.2							
A”	T’	-16.8							
A”	T”	-16.1							

3. Energy Decomposition Analysis

		ΔE	ΔE_{prep}	ΔE_{int}	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{σ}	ΔE_{π}	ΔE_{disp}
A	T	-16.7	1.8	-18.5					
A	T’	-16.4	2.0	-18.4					
A	T”	-15.2	1.4	-16.7					
A’	T	-16.4	1.8	-18.3					
A’	T’	-16.0	1.9	-17.9					
A’	T”	-15.2	1.5	-16.7					
A”	T	-16.2	2.3	-18.5					
A”	T’	-16.8	2.5	-19.4					
A”	T”	-16.1	1.8	-17.9					

3. Energy Decomposition Analysis

		ΔE	ΔE_{prep}	ΔE_{int}	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{σ}	ΔE_{π}	ΔE_{disp}
A	T	-16.7	1.8	-18.5	-31.9	39.9			
A	T’	-16.4	2.0	-18.4	-31.2	39.4			
A	T”	-15.2	1.4	-16.7	-27.3	32.0			
A’	T	-16.4	1.8	-18.3	-31.0	38.6			
A’	T’	-16.0	1.9	-17.9	-30.0	37.9			
A’	T”	-15.2	1.5	-16.7	-26.8	31.3			
A”	T	-16.2	2.3	-18.5	-31.2	38.2			
A”	T’	-16.8	2.5	-19.4	-31.5	38.2			
A”	T”	-16.1	1.8	-17.9	-28.4	32.3			

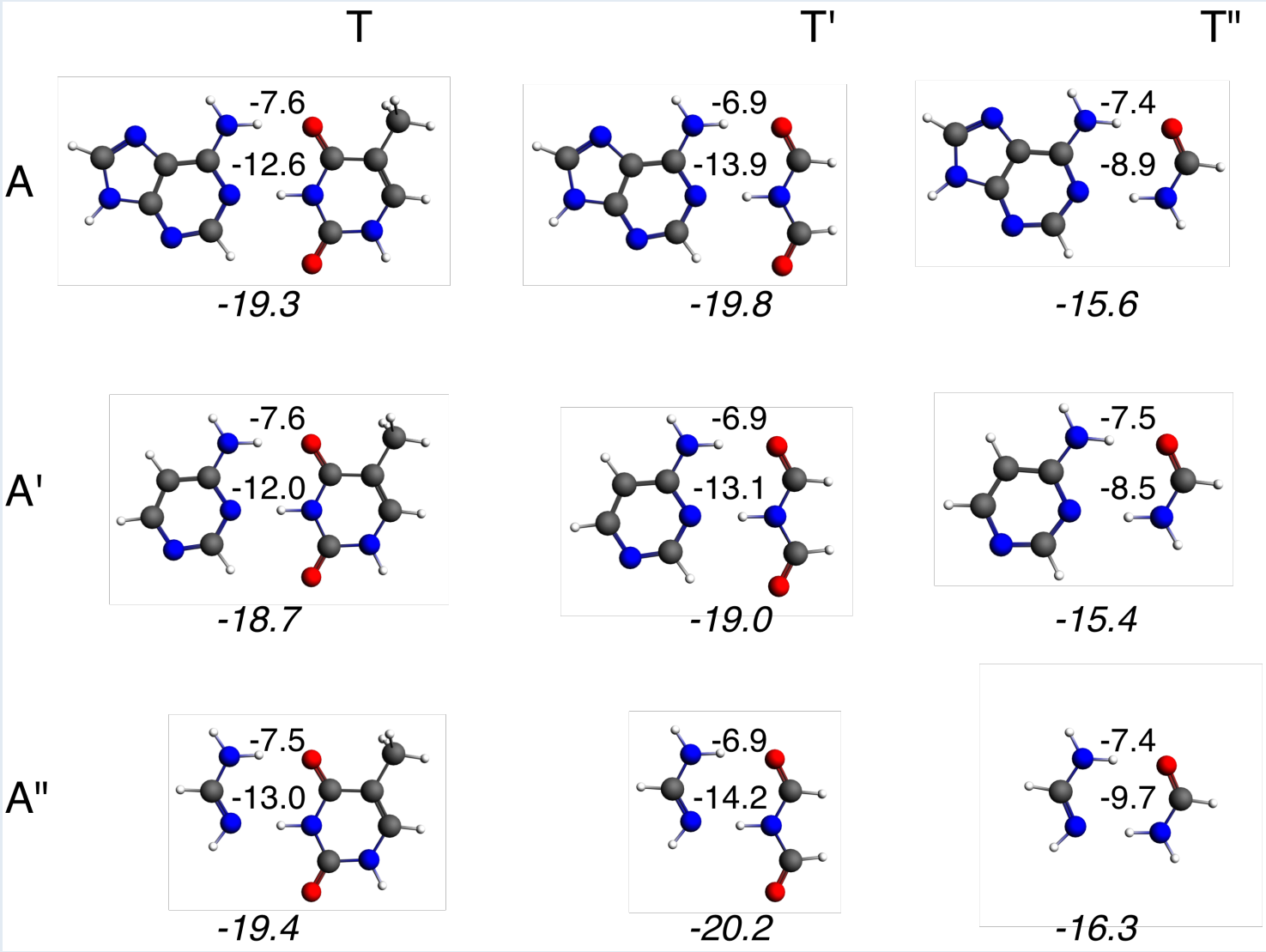
3. Energy Decomposition Analysis

		ΔE	ΔE_{prep}	ΔE_{int}	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{σ}	ΔE_{π}	ΔE_{disp}
A	T	-16.7	1.8	-18.5	-31.9	39.9	-19.5	-1.6	
A	T’	-16.4	2.0	-18.4	-31.2	39.4	-20.0	-1.6	
A	T”	-15.2	1.4	-16.7	-27.3	32.0	-15.9	-1.6	
A’	T	-16.4	1.8	-18.3	-31.0	38.6	-19.0	-1.5	
A’	T’	-16.0	1.9	-17.9	-30.0	37.9	-19.3	-1.6	
A’	T”	-15.2	1.5	-16.7	-26.8	31.3	-15.6	-1.6	
A”	T	-16.2	2.3	-18.5	-31.2	38.2	-19.7	-1.8	
A”	T’	-16.8	2.5	-19.4	-31.5	38.2	-20.4	-1.9	
A”	T”	-16.1	1.8	-17.9	-28.4	32.3	-16.6	-1.9	

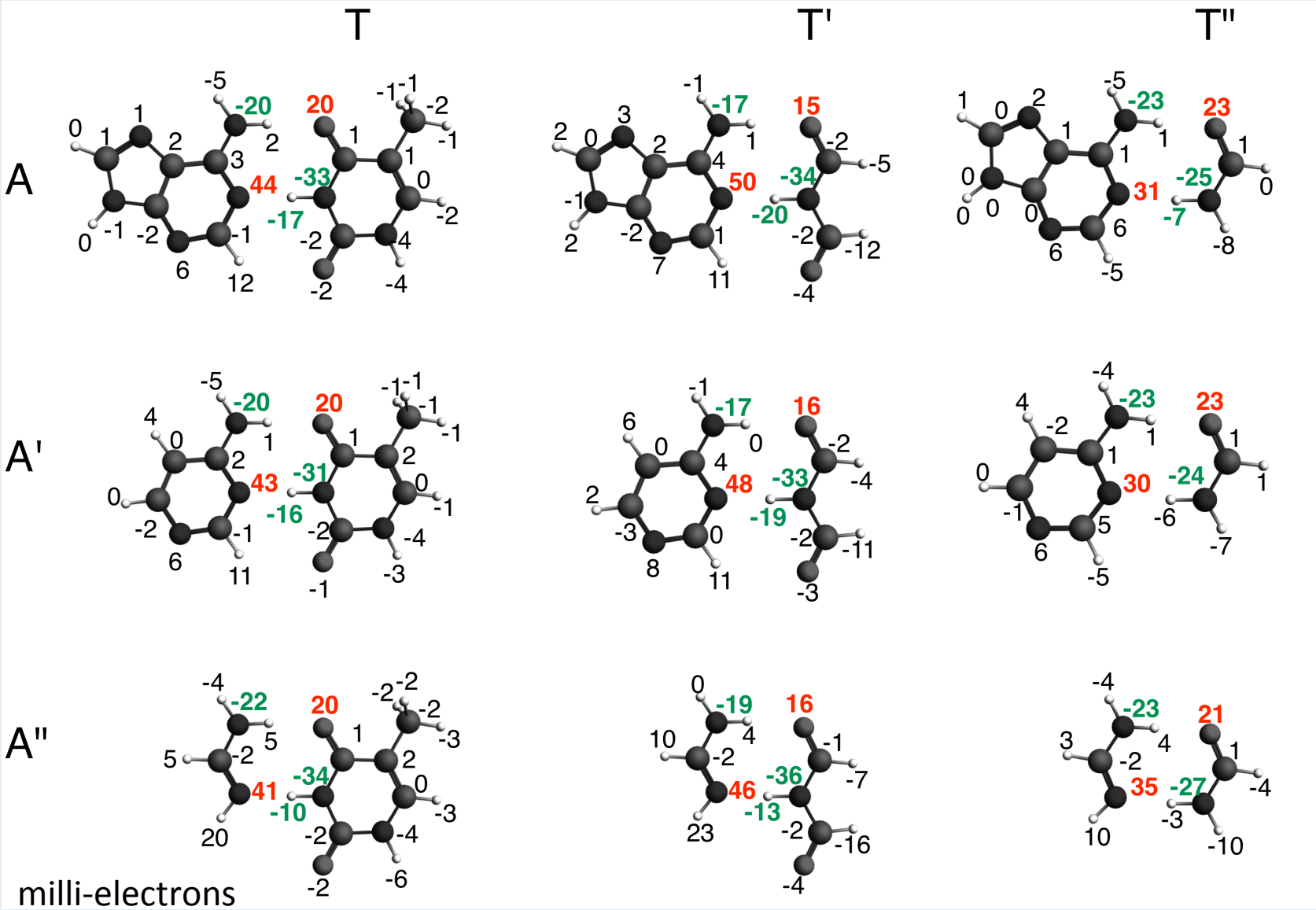
3. Energy Decomposition Analysis

		ΔE	ΔE_{prep}	ΔE_{int}	ΔE_{elstat}	ΔE_{Pauli}	ΔE_{σ}	ΔE_{π}	ΔE_{disp}
A	T	-16.7	1.8	-18.5	-31.9	39.9	-19.5	-1.6	-5.4
A	T’	-16.4	2.0	-18.4	-31.2	39.4	-20.0	-1.6	-5.0
A	T”	-15.2	1.4	-16.7	-27.3	32.0	-15.9	-1.6	-3.9
A’	T	-16.4	1.8	-18.3	-31.0	38.6	-19.0	-1.5	-5.3
A’	T’	-16.0	1.9	-17.9	-30.0	37.9	-19.3	-1.6	-4.9
A’	T”	-15.2	1.5	-16.7	-26.8	31.3	-15.6	-1.6	-3.9
A”	T	-16.2	2.3	-18.5	-31.2	38.2	-19.7	-1.8	-4.1
A”	T’	-16.8	2.5	-19.4	-31.5	38.2	-20.4	-1.9	-3.8
A”	T”	-16.1	1.8	-17.9	-28.4	32.3	-16.6	-1.9	-3.4

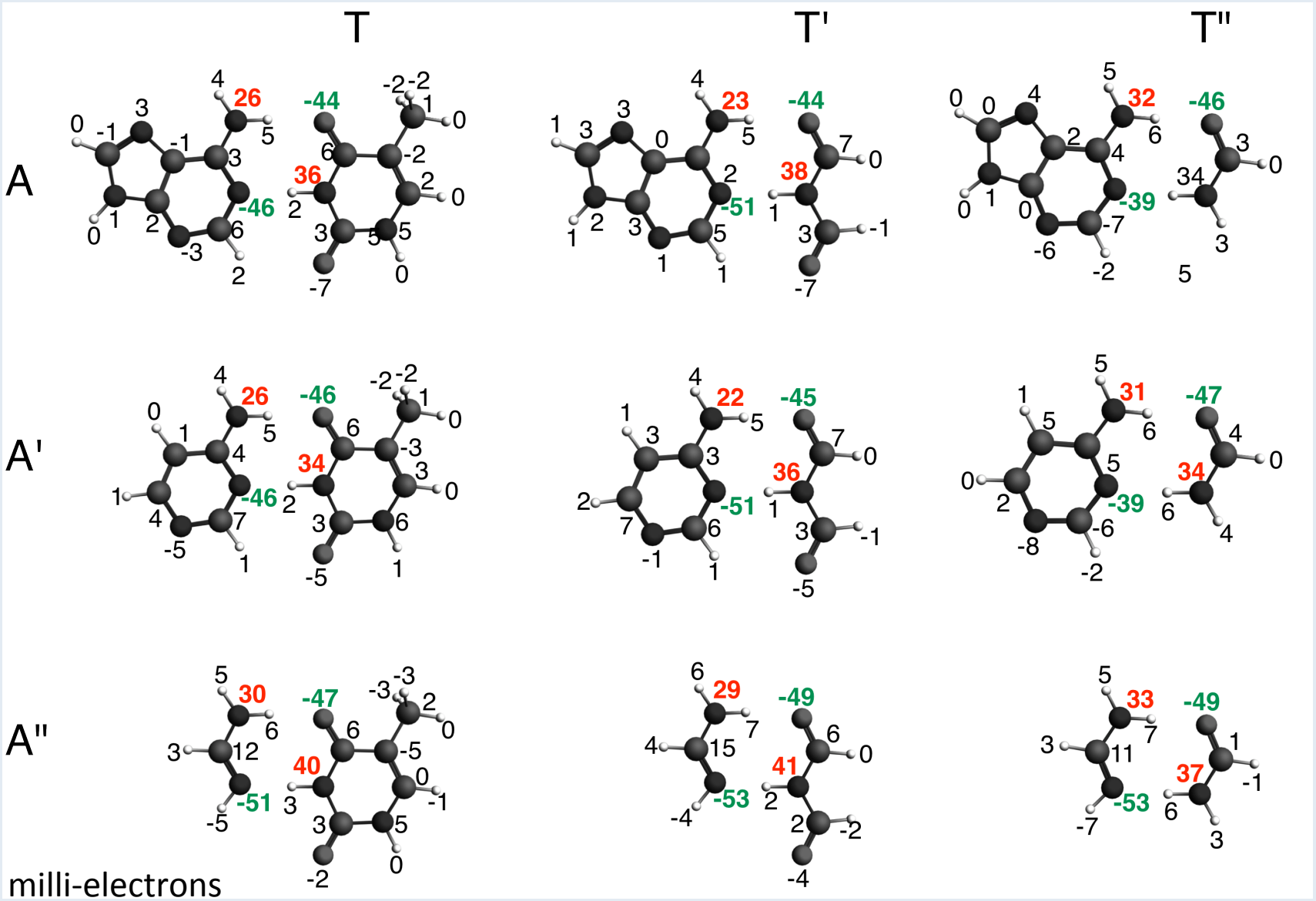
3. Aromaticity: Donor-acceptor interactions



3. Aromaticity: σ component of $\Delta Q_{A,oi}$

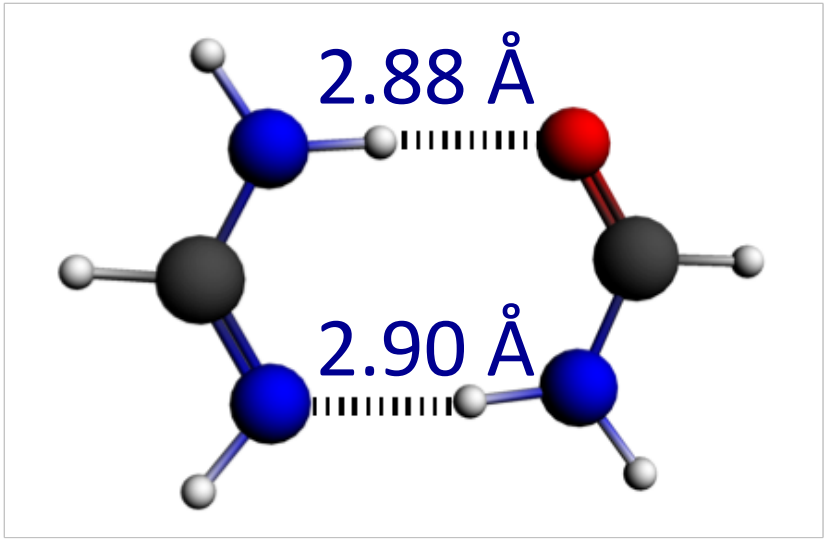


3. Aromaticity: π component of $\Delta Q_{A,oi}$



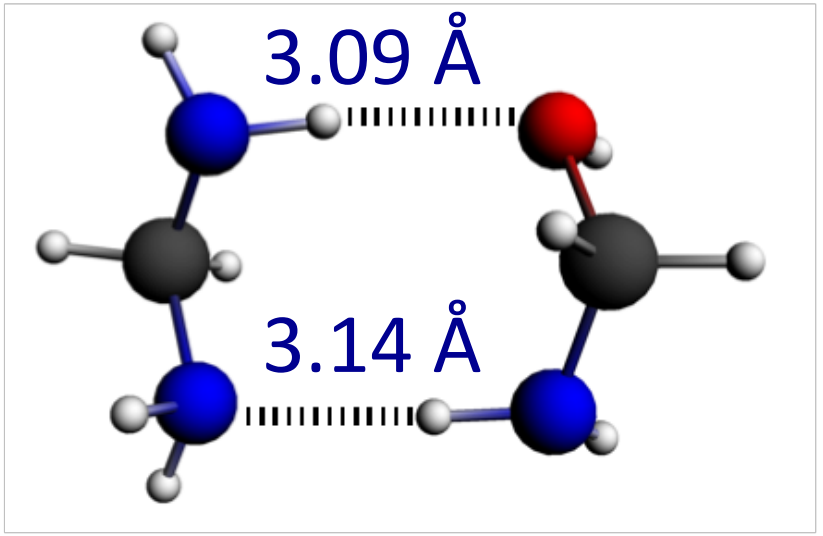
3. sp^2 versus sp^3

A”T”



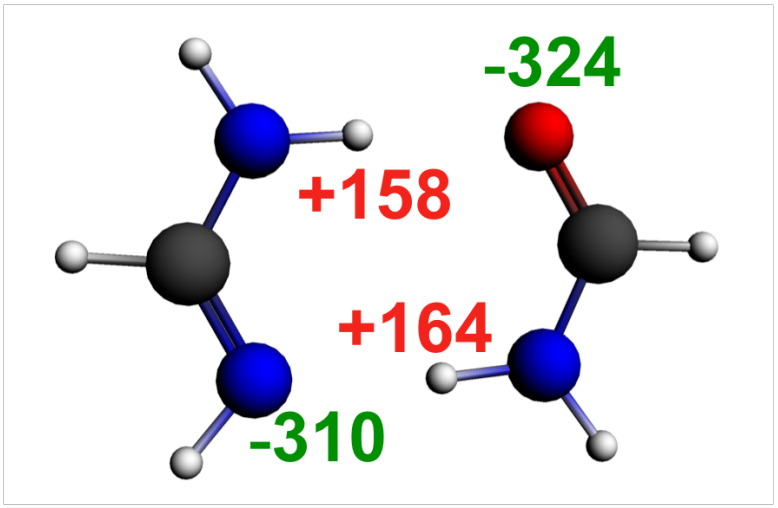
–17.9 kcal/mol

a”t”

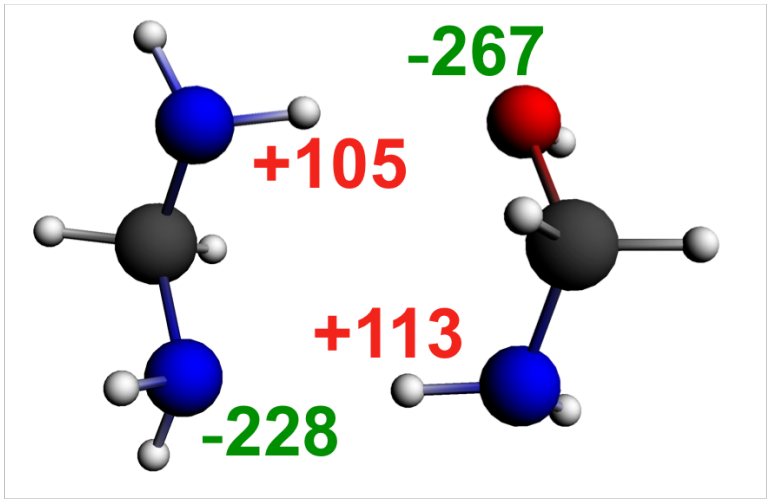


–8.9 kcal/mol

3. sp^2 versus sp^3: electrostatics

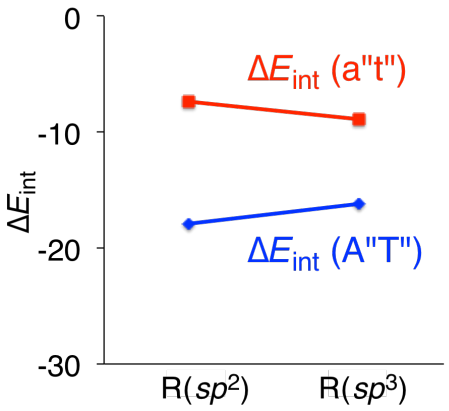


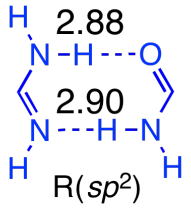
A"T"

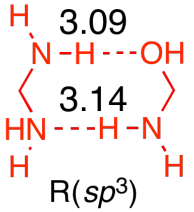


a"t"

3. Energy Decomposition Analysis

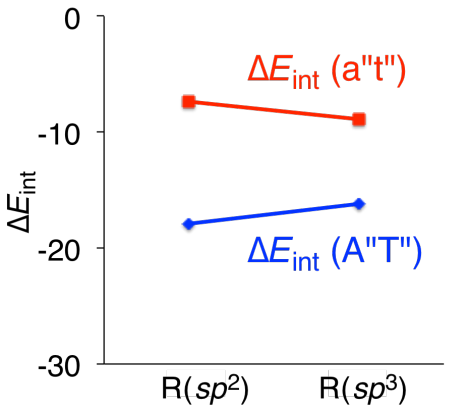


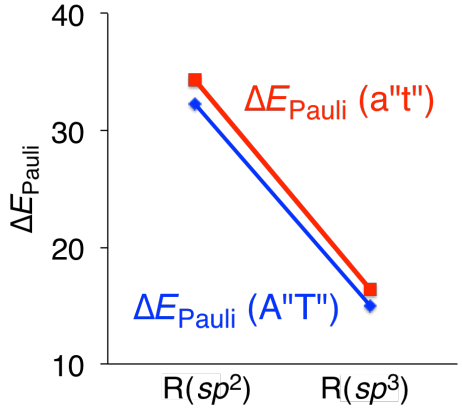


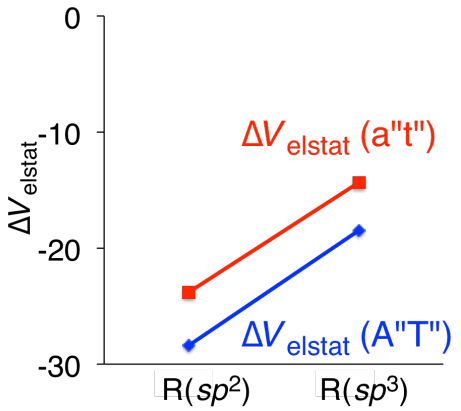


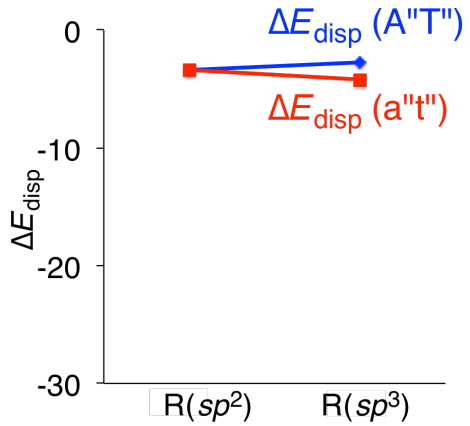
Overlap **<A”|T”> increases more than overlap <a”|t”>**

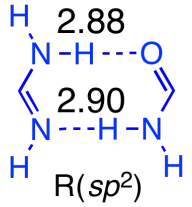
3. Energy Decomposition Analysis

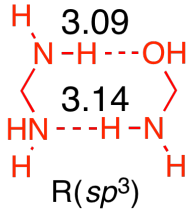






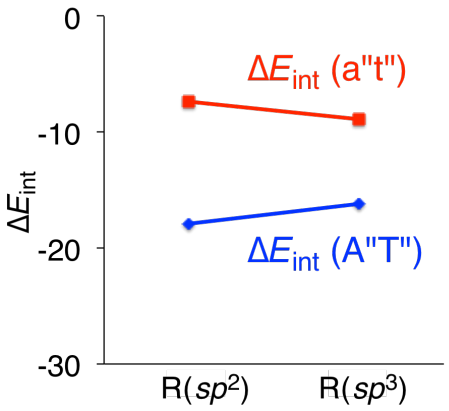


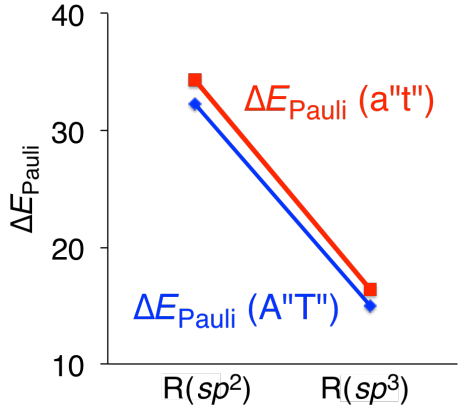


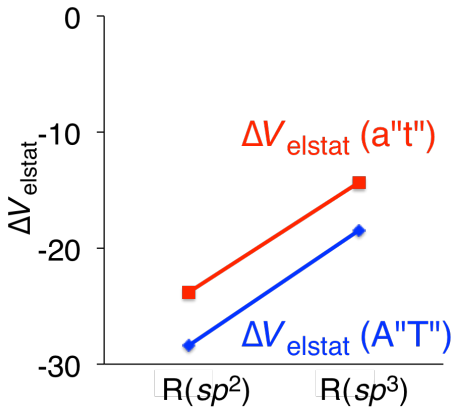


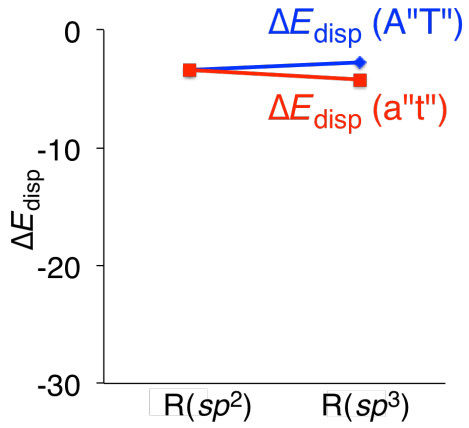
Overlap **<A”|T”> increases more than overlap <a”|t”>**

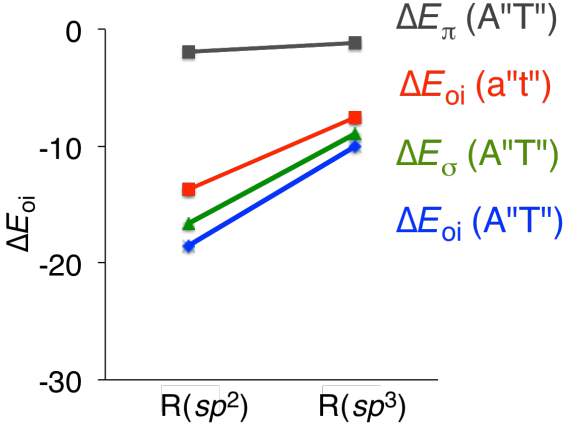
3. Energy Decomposition Analysis

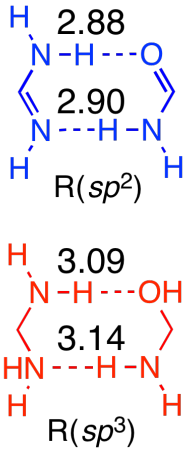






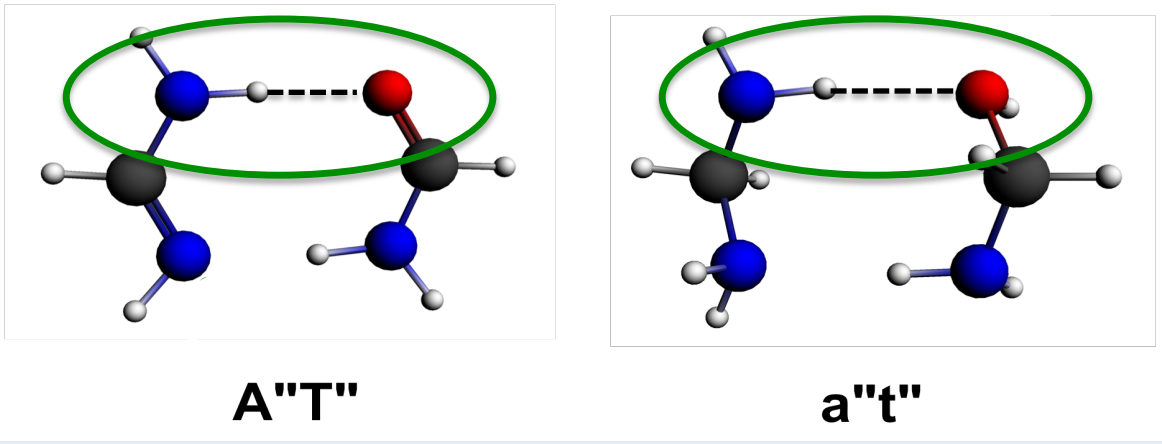






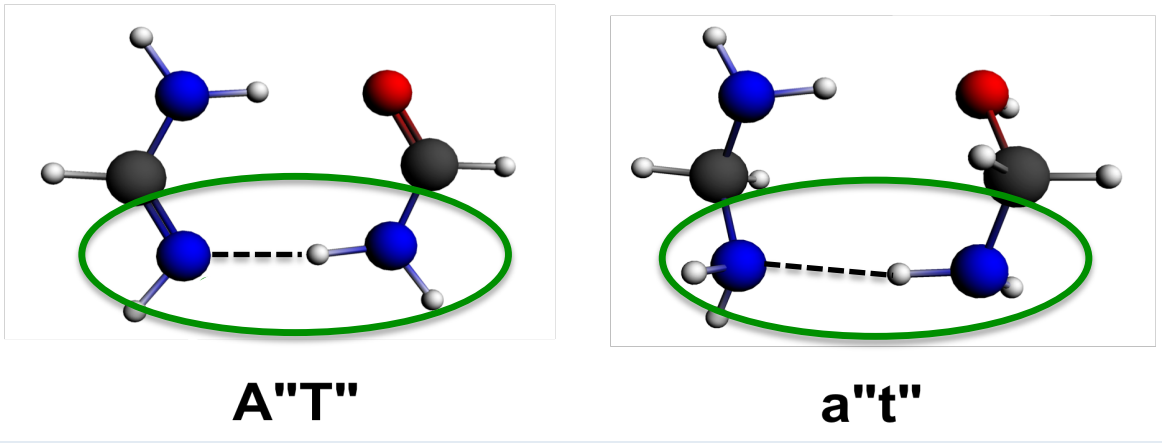
3. MO analysis at R(sp^2)

***Gross populations:* N–H•••O**	**A"T"**		**a"t" at R(sp^2)**
σ_{LUMO+1} of A"	0.02	LUMO+1 of a"	0.01
σ_{LUMO} of A"	0.01	LUMO of a"	0.02
σ_{HOMO} of T"	**1.95**	HOMO of t"	2.00
σ_{HOMO-1} of T"	2.00	**HOMO-1 of t"**	**1.96**
σ_{HOMO} of T"	**-5.85 eV**	**HOMO-1 of t"**	**-6.54 eV**



3. MO analysis at R(sp^2)

***Gross populations:* N•••H–N**	**A"T"**		**a"t" at R(sp^2)**
σ_{LUMO+1} of T"	0.04	LUMO+1 of t"	0.02
σ_{LUMO} of T"	0.03	LUMO of t"	0.01
σ_{HOMO} of A"	**1.91**	**HOMO of a"**	**1.93**
σ_{HOMO-1} of A"	2.00	HOMO-1 of a"	1.99
σ_{HOMO} of A"	-5.80 eV	HOMO of a"	-6.31 eV
$< \sigma_{HOMO} \mid \sigma_{LUMO} >$	**0.23**	**< HOMO | LUMO >**	**0.10**



3. sp^2 and sp^3: Conclusions

- **π assistance is not exclusively due to aromaticity**

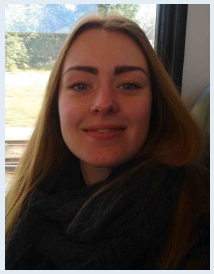
- sp^2 systems have stronger hydrogen bonds than sp^3:

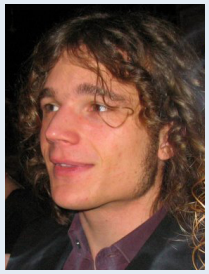
  due to enhanced electrostatic interactions and also better covalent interactions.

Acknowledgements


G. Paragi


H. Zijlstra


N. Smits


L. Wolters


L. Guillaumes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Further reading on RAHB

- *CEJ* **1999**, *5*, 3581
- *JACS* **2000**, *17*, 12612
- *CEJ* **2011**, *17*, 12612
- *CEJ* **2014**, *20*, 9494
- *PCCP*, **2015**, *17*, 1585
- *ChemOpen*, **2015**, *4*, 318

http://www.few.vu.nl/~guerra/