Non-additive effects of H-bond: a quantum chemical topology perspective.

Tomás Rocha Rinza
Institute of Chemistry, National Autonomous University of Mexico

September 26, 2016

Outline

- Introduction. Quantum chemical topology: the Quantum Theory of Atoms in Molecules (QTAIM) and the Interacting Quantum Atoms (IQA) energy partition.

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- Introduction. Quantum chemical topology: the Quantum Theory of Atoms in Molecules (QTAIM) and the Interacting Quantum Atoms (IQA) energy partition.

- Some applications:

  - Cooperative effects of hydrogen bonding in small water clusters (Guevara-Vela *et al.*, *Chem. Eur. J. 19*, 14304, **2013**).

  - Hydrogen bond cooperativity and anticooperativity within the water hexamer (Guevara-Vela *et al. Phys. Chem. Chem. Phys. 18*, 19557, **2016**).

  - Cooperative and anticooperative effects in resonance assisted hydrogen bonds in merged structures of malondialdehyde (Guevara-Vela *et al.*, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/c6cp04386, Romero-Montalvo *et al. Phys. Chem. Chem. Phys.*, DOI: 10.1039/c6cp04877c).

Quantum Chemical Topology

$$\varrho(\mathbf{r}) = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \right\rangle = N \sum_{\omega} \overbrace{\int \ldots \int}^{N-1 \text{ times}} |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N$$

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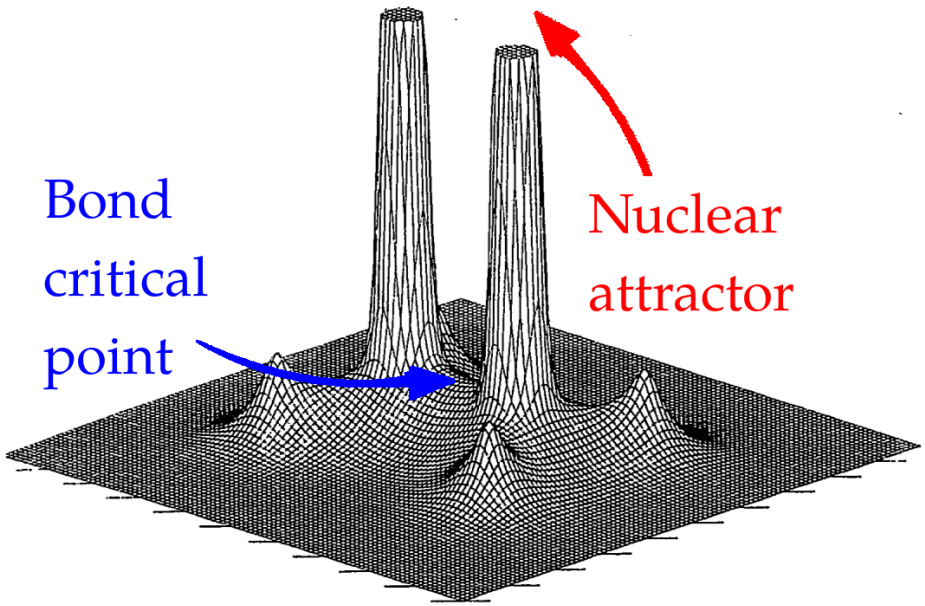
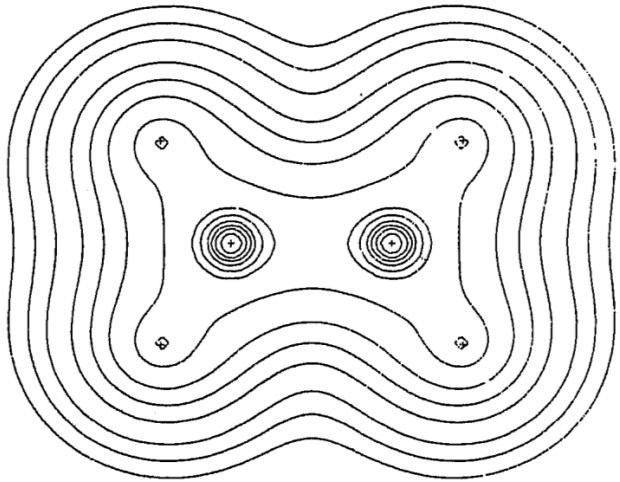
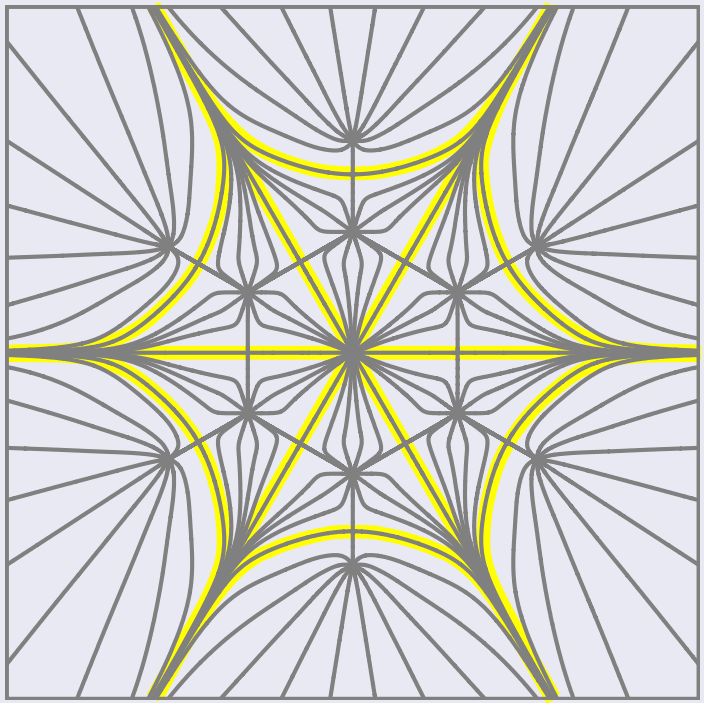




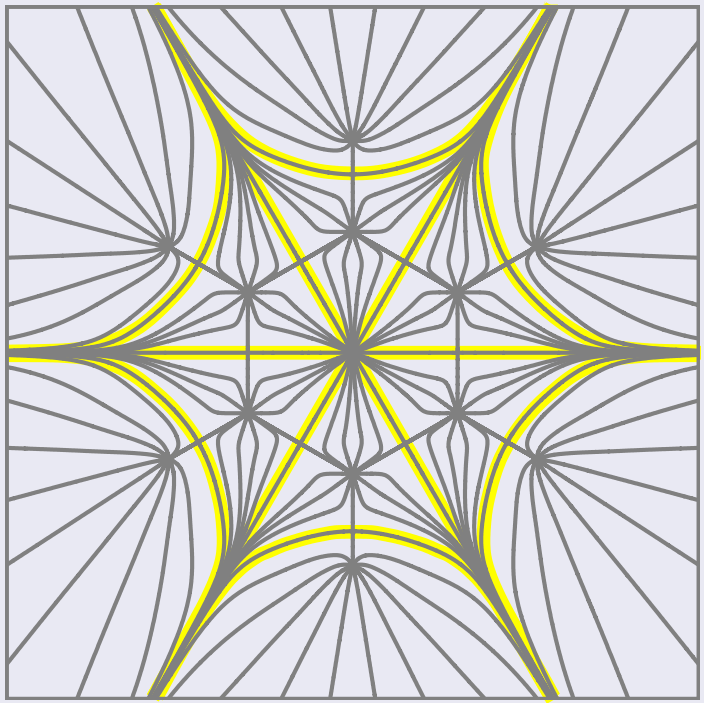
QTAIM and IQA



$\varrho(\mathbf{r}) \rightarrow i)$ theory of molecular structure and $ii)$ division of molecular space in open subsystems.

R. F. W. Bader, *Atoms in molecules: a quantum theory*, Clarendon Press, 1994.

QTAIM and IQA



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- Local properties of $\varrho(\mathbf{r})$:
  - $\varrho(\mathbf{r})$,
  - $\nabla^2\varrho(\mathbf{r})$,
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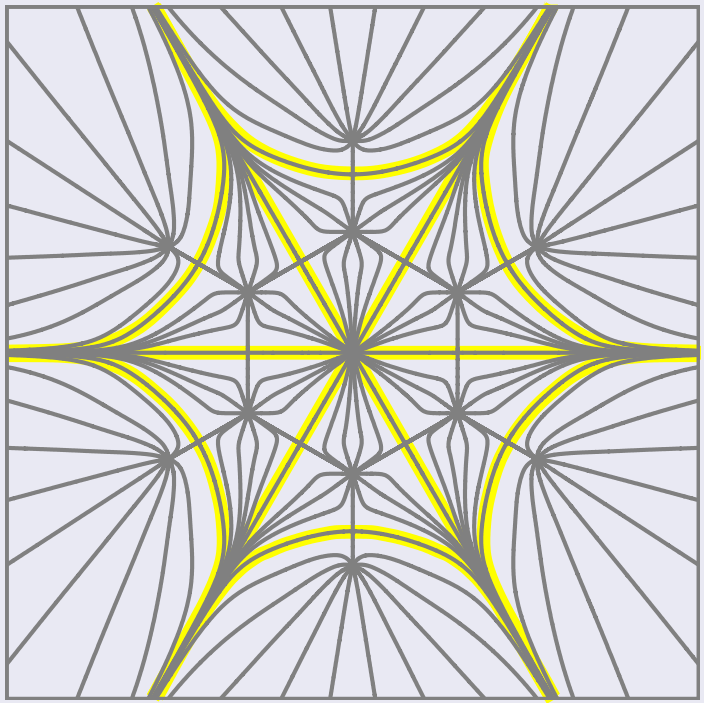
QTAIM and IQA



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  - $H(\mathbf{r})$,
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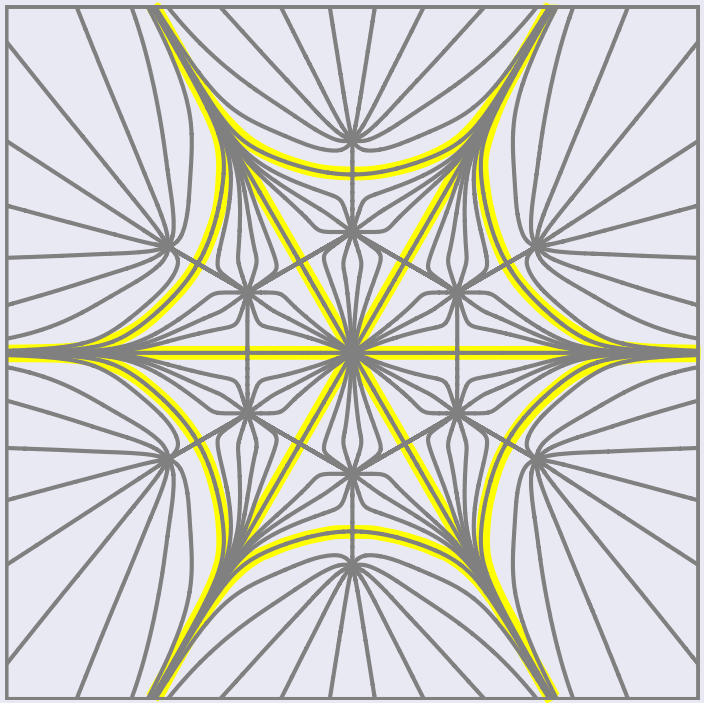
- Integrated properties of $\varrho(\mathbf{r})$
  - $N(\Omega)$,
  - $E(\Omega)$,
  - $\lambda(\Omega, \Omega)$,
  - $\delta(\Omega, \Omega')$

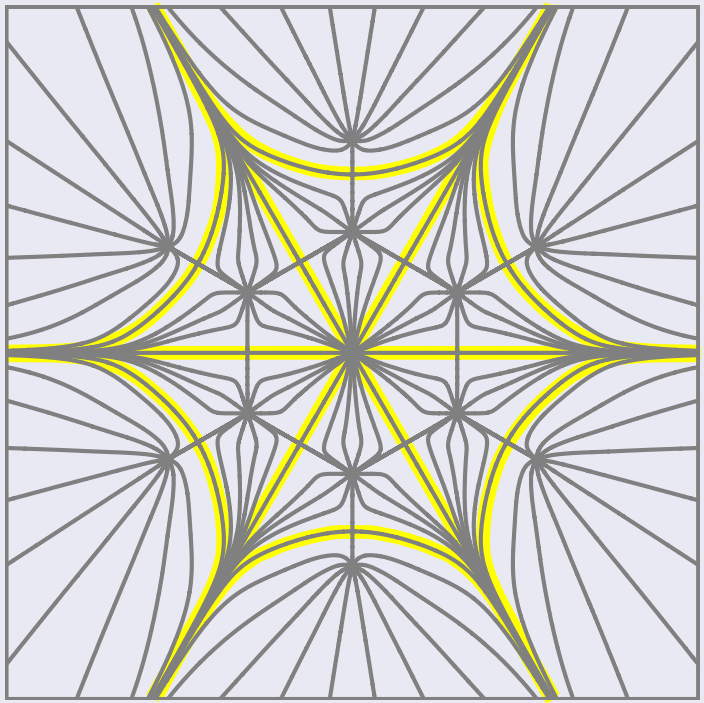
QTAIM and IQA



$$E = \sum_{\mathrm{A}} E^{\mathrm{A}}_{\mathrm{net}} + \sum_{\mathrm{A>B}} E^{\mathrm{AB}}_{\mathrm{int}}$$

Salvador *et al*, *J. Chem. Phys.*, *115*, 1153, **2001**
Blanco *et al*, *J. Chem. Theor. Comput.* , *1*, 1096, **2005**

QTAIM and IQA



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- We have

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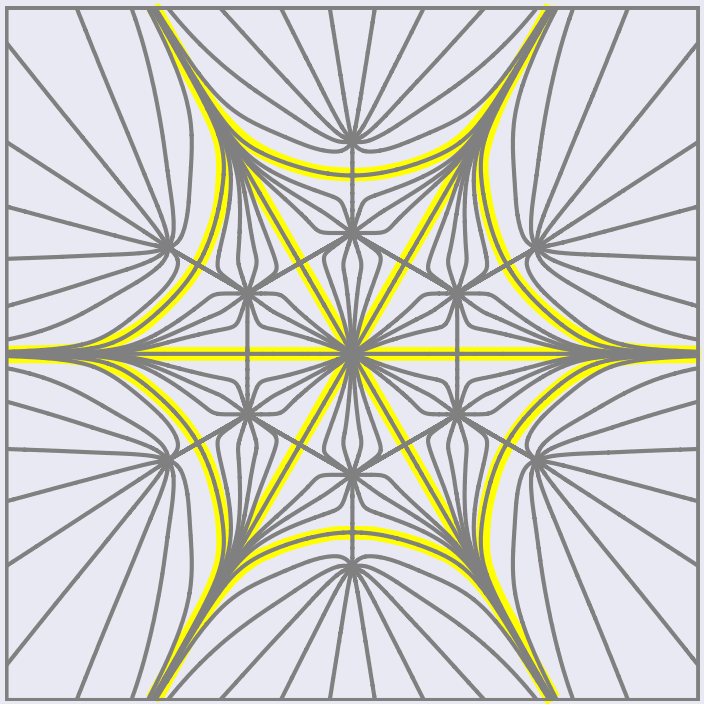
QTAIM and IQA



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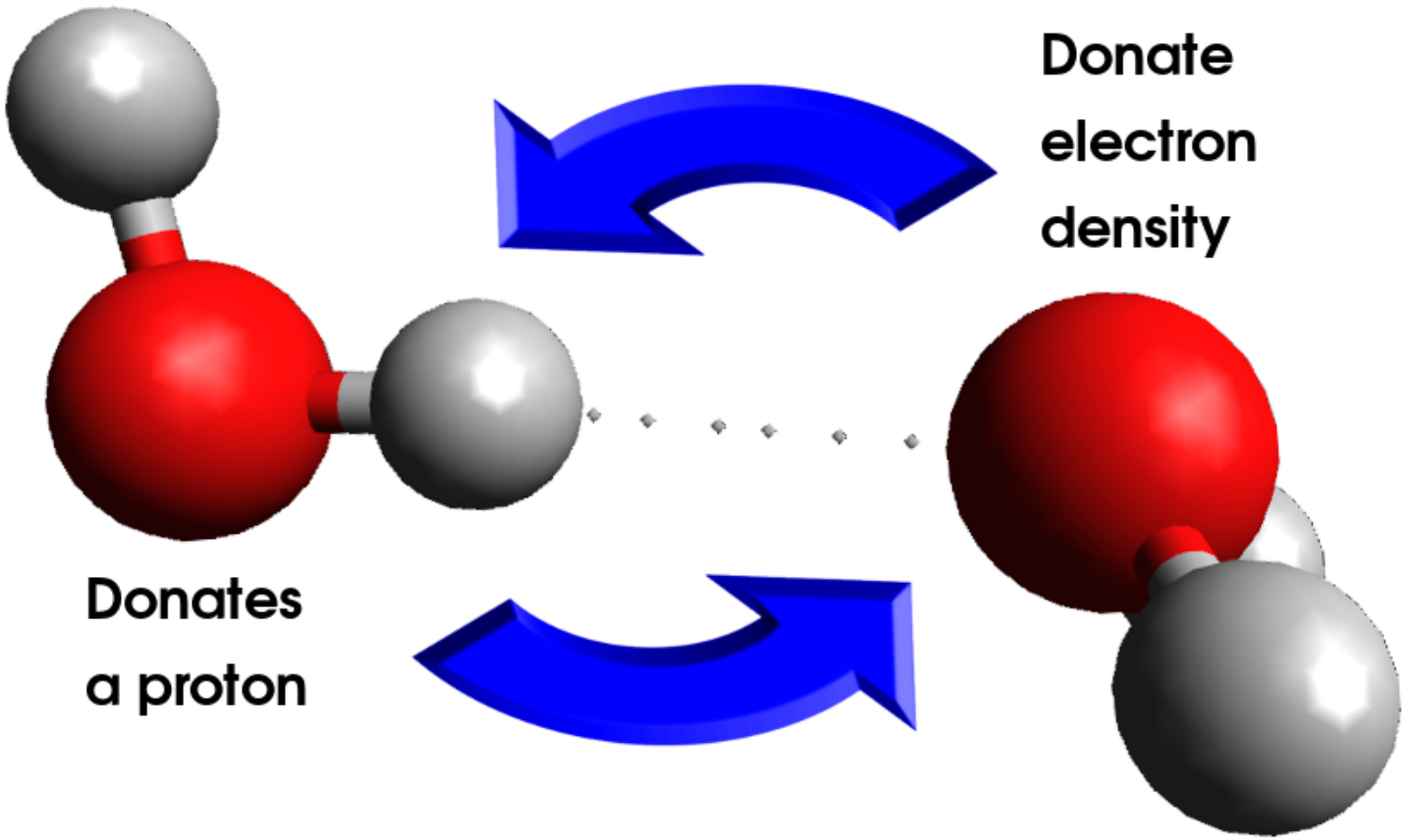
- with

$$E^{\mathrm{AB}}_{\mathrm{int}} = V^{\mathrm{AB}}_{\mathrm{coul}} + V^{\mathrm{AB}}_{\mathrm{X}} + V^{\mathrm{AB}}_{\mathrm{corr}}$$

H-bond cooperative effects analyzed through IQA

(Guevara-Vela *et al. Chem. Eur. J.*, *19*, 14304, **2013**).



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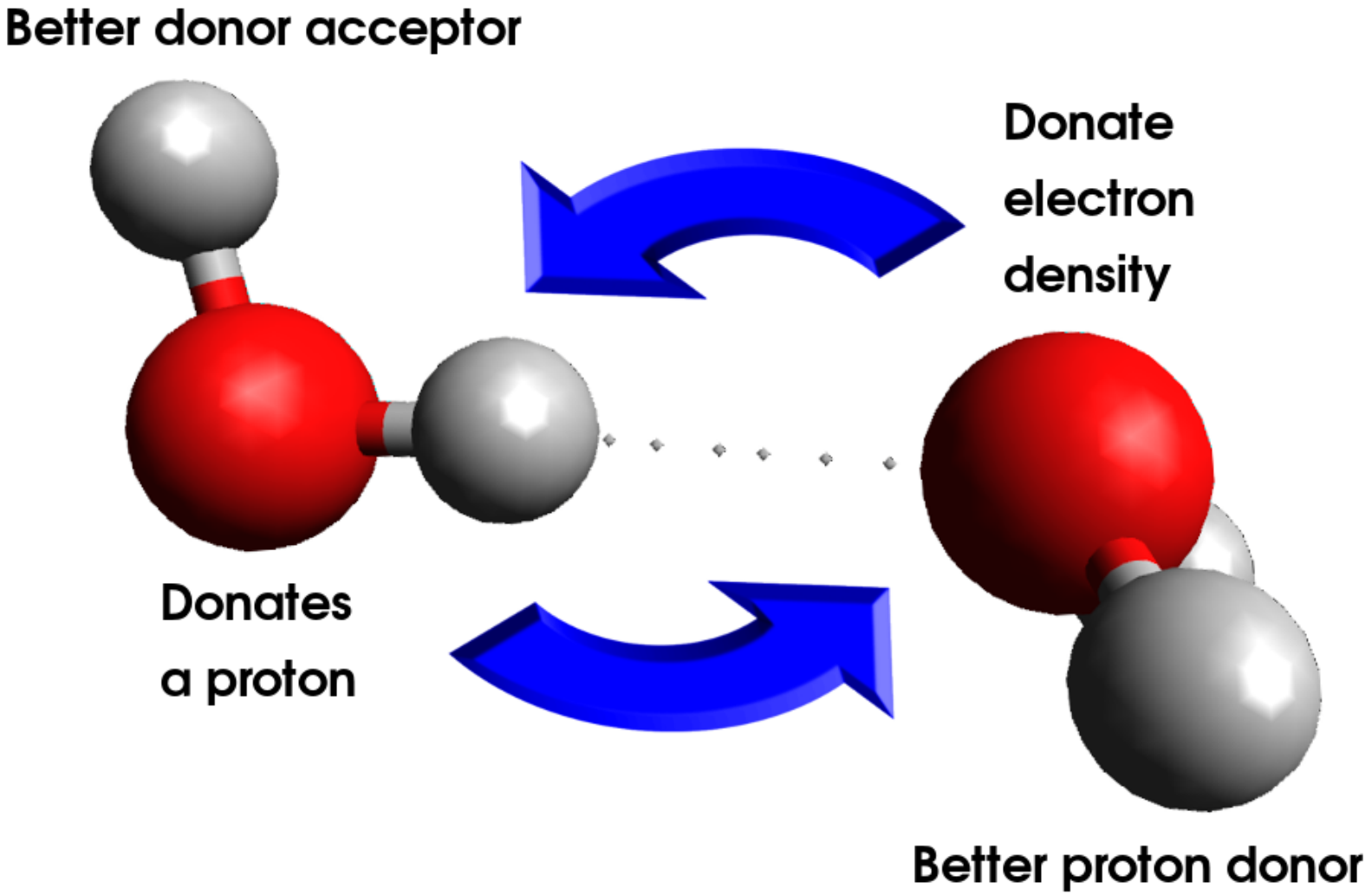

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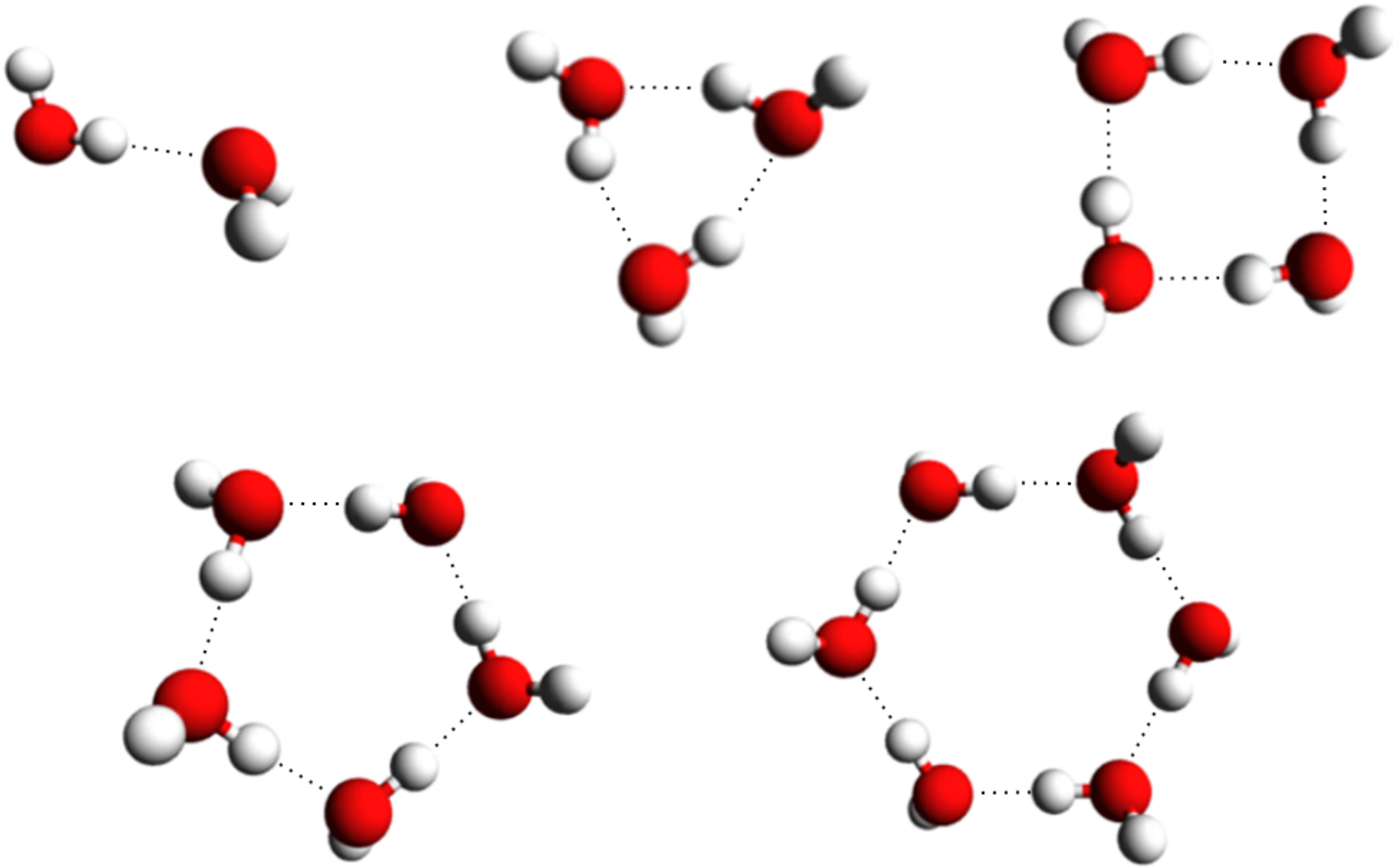

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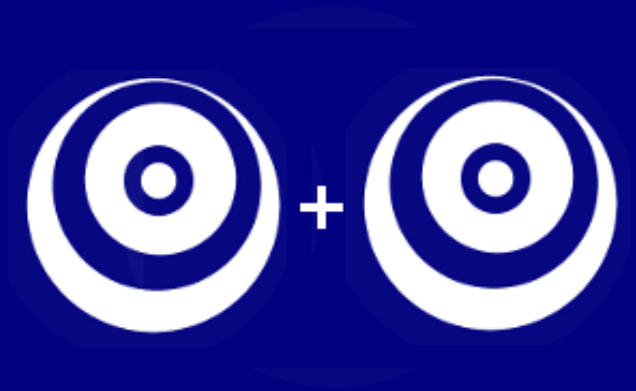
Energías de deformación e interacción



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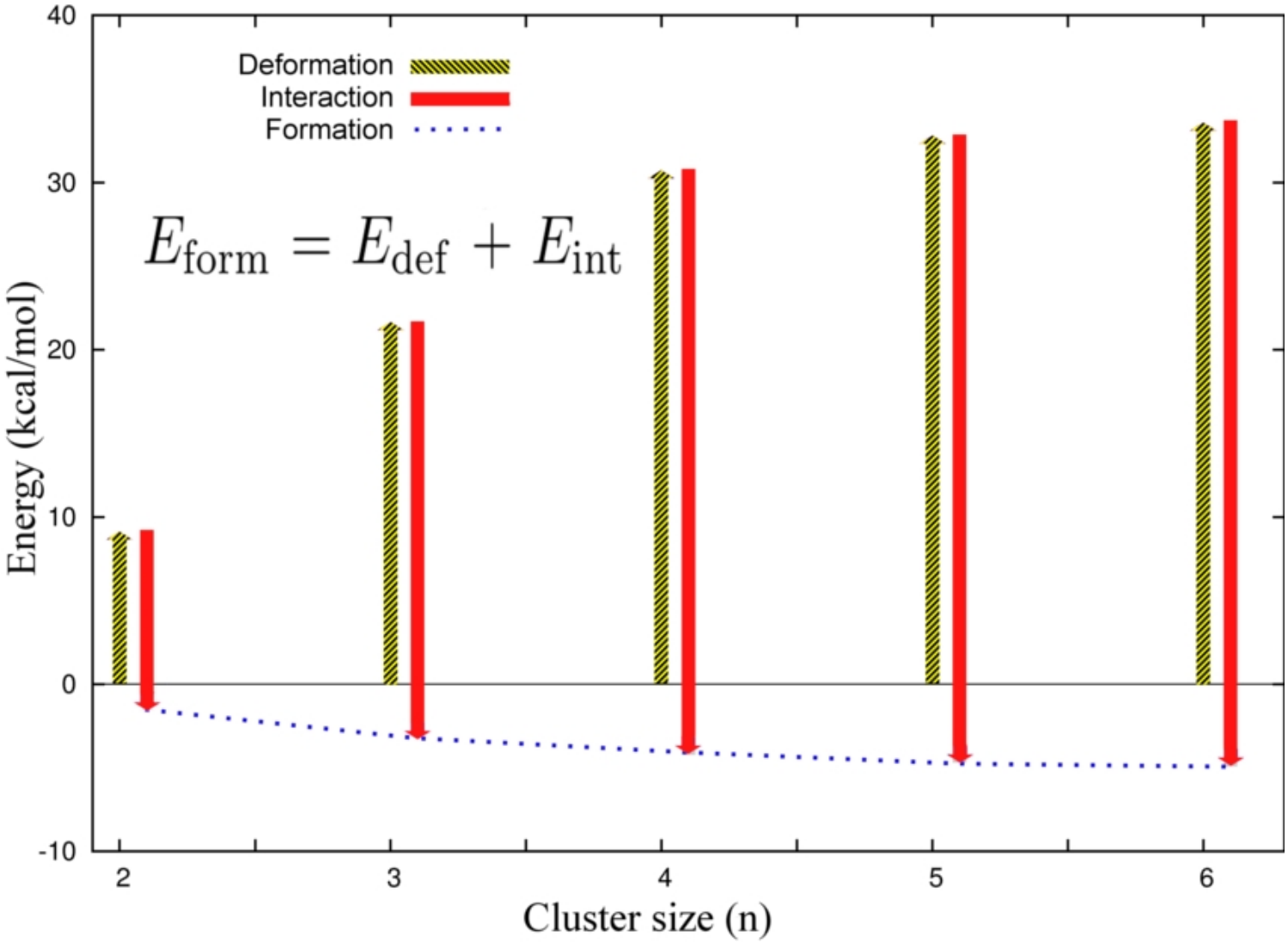

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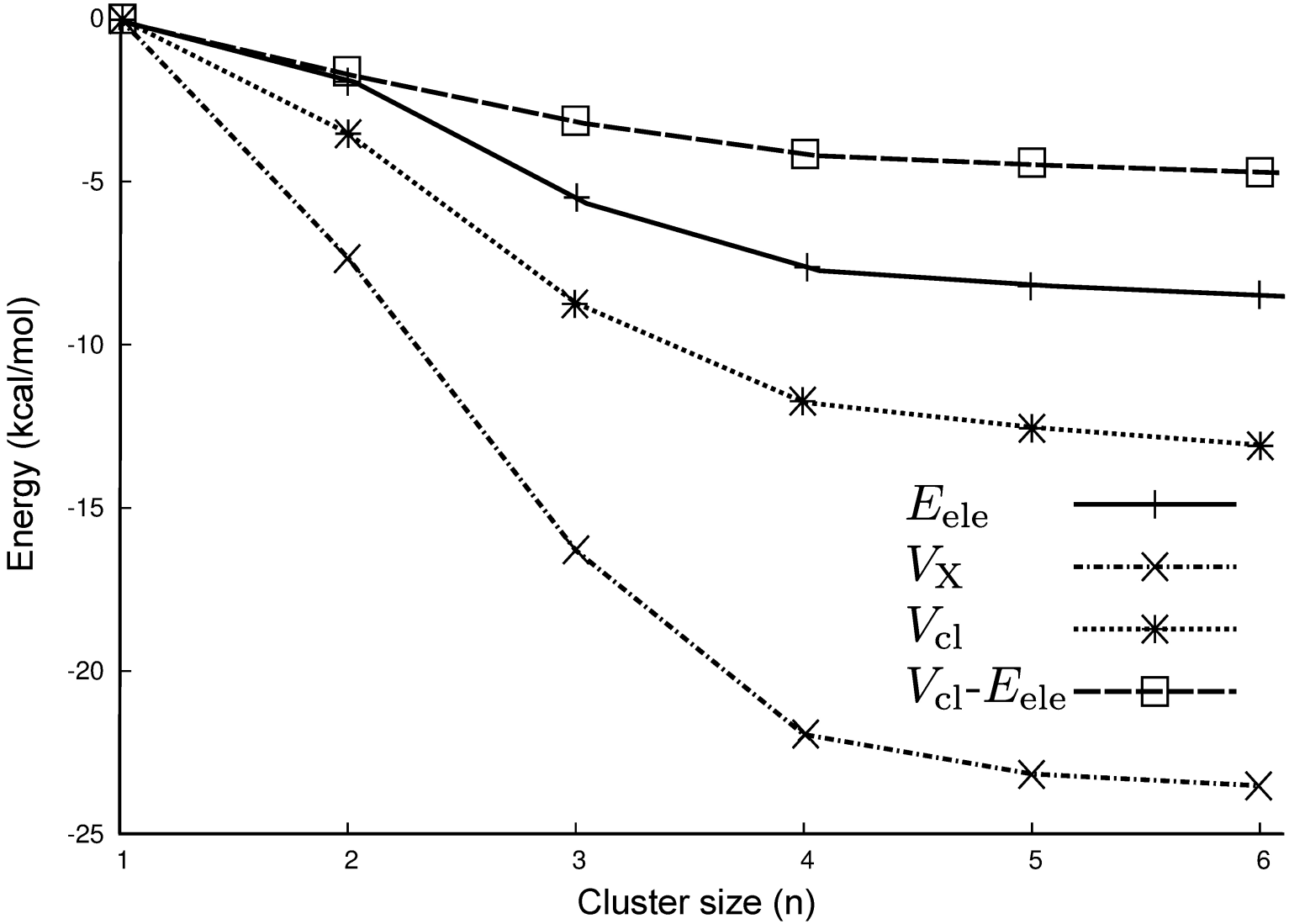
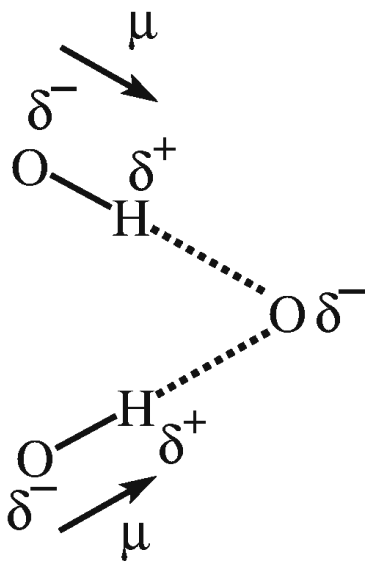
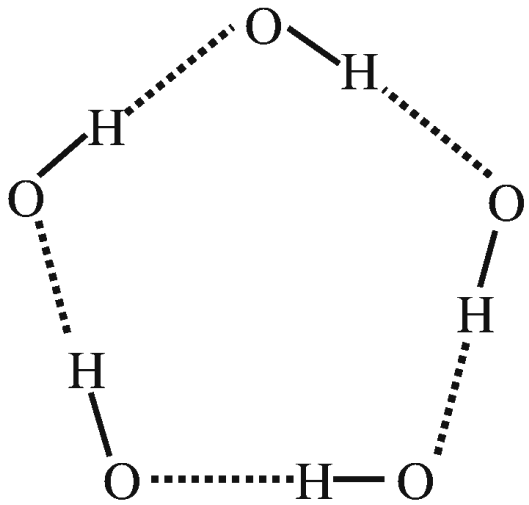


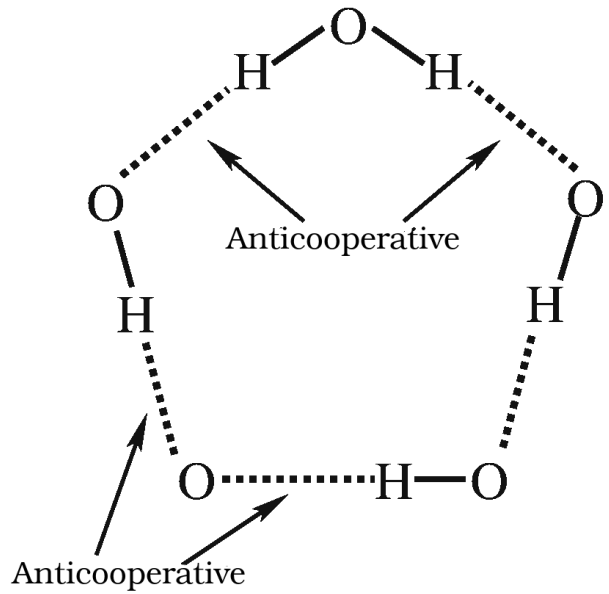
Hydrogen bonding anticooperative effects



Double acceptor



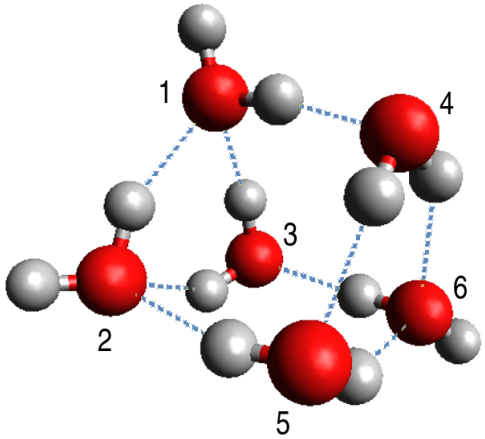
Homodromic cylce



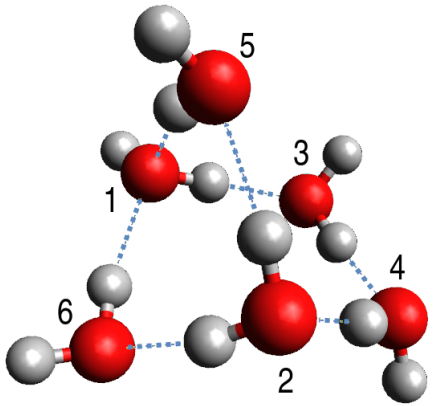
Antidromic cycle

H-bond cooperativity and anticooperativity within the water hexamer

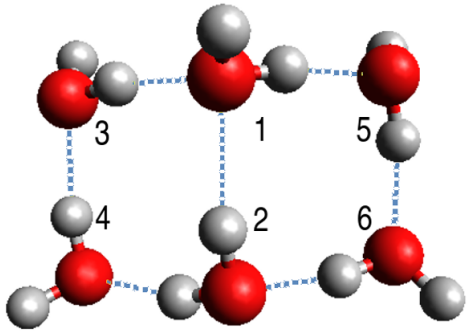
(Guevara-Vela *et al.* *Phys. Chem. Chem. Phys.* Phys. *18*, 19557, **2016**).



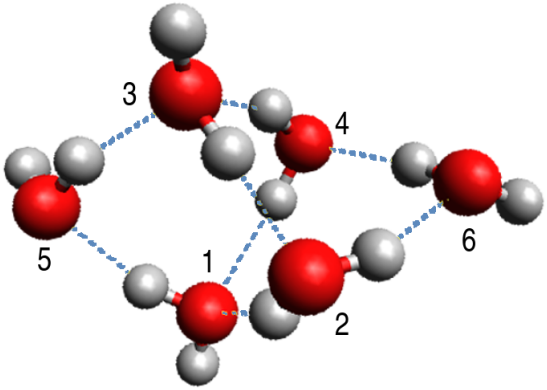
Prism



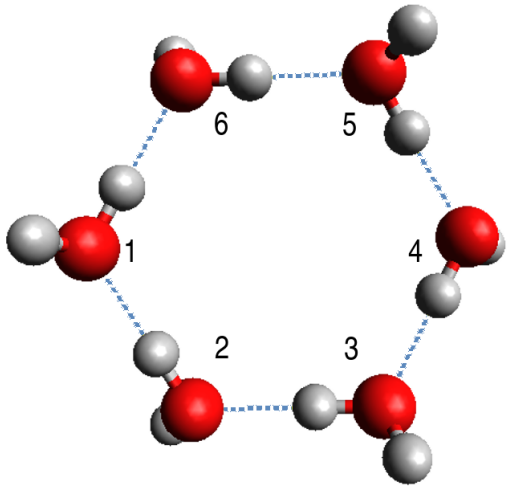
Bag



Book



Cage



Ring

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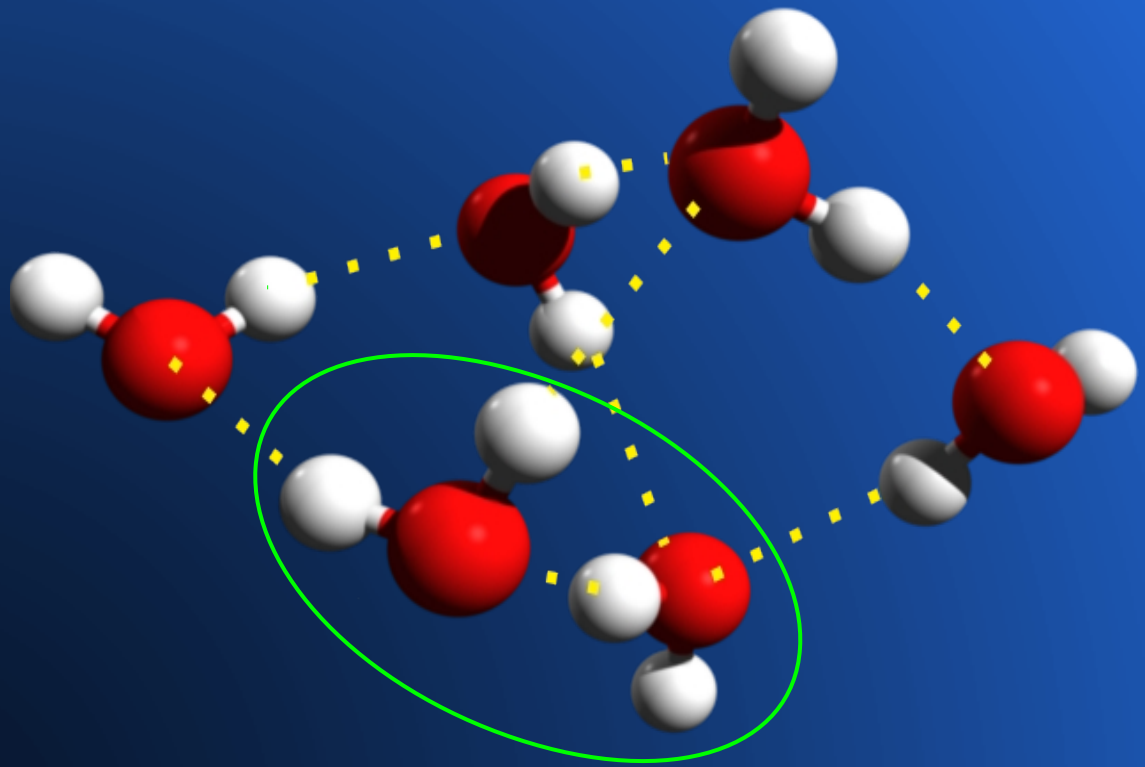
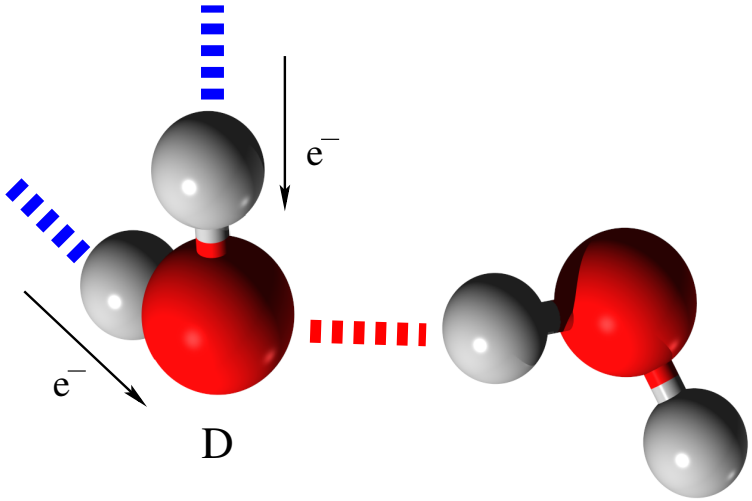


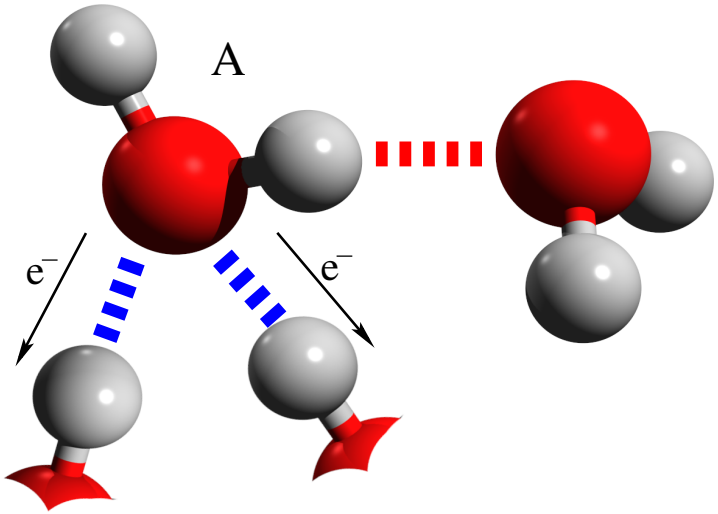
A particularly strong type of H-bond within the water hexamer.

H-bond cooperativity and anticooperativity within the water hexamer

(Guevara-Vela *et al.* *Phys. Chem. Chem. Phys.* Phys. *18*, 19557, **2016**).



(a)



(b)

H-bond cooperativity and anticooperativity within the water hexamer

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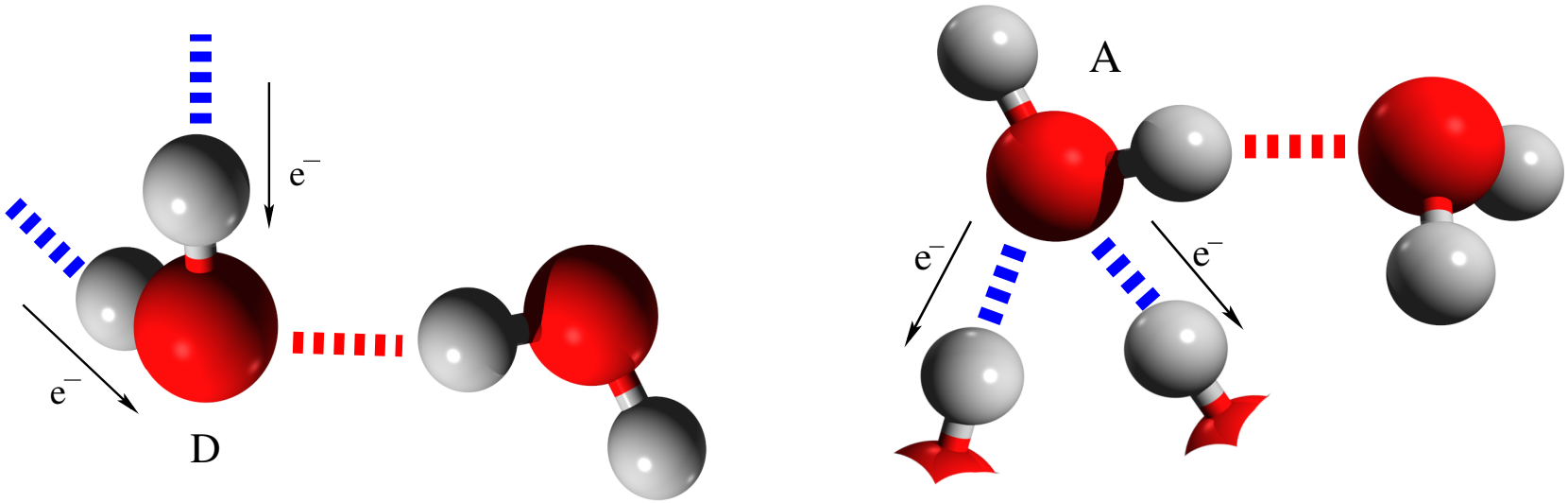

(a) (b)

Double donors are bad donors but good acceptors.
Double acceptors are bad acceptors but good donors.

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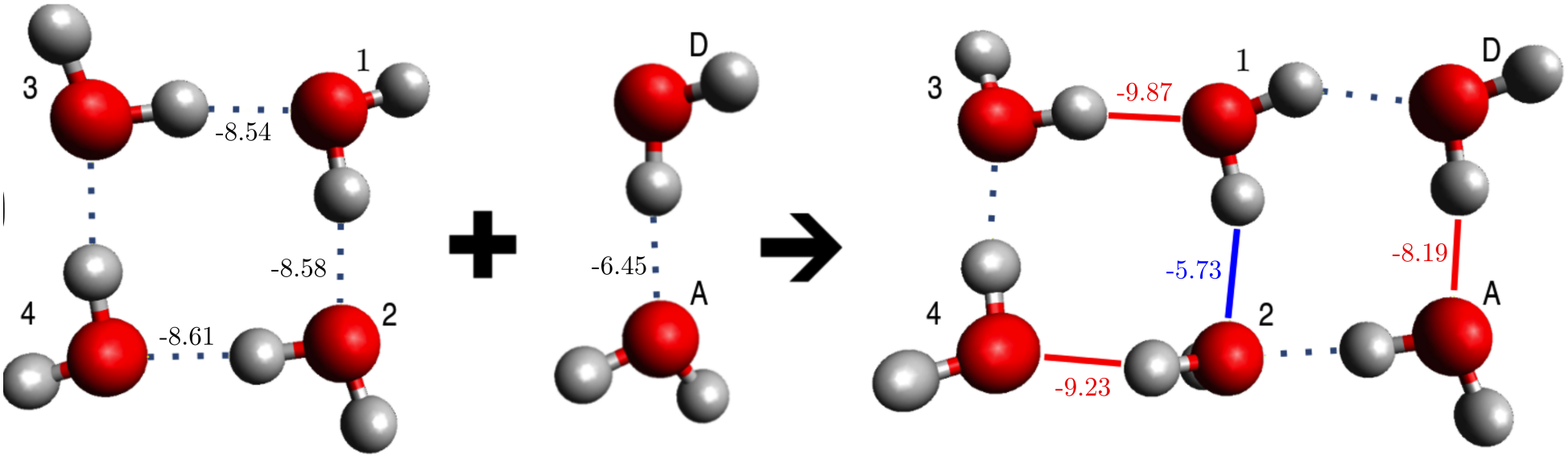

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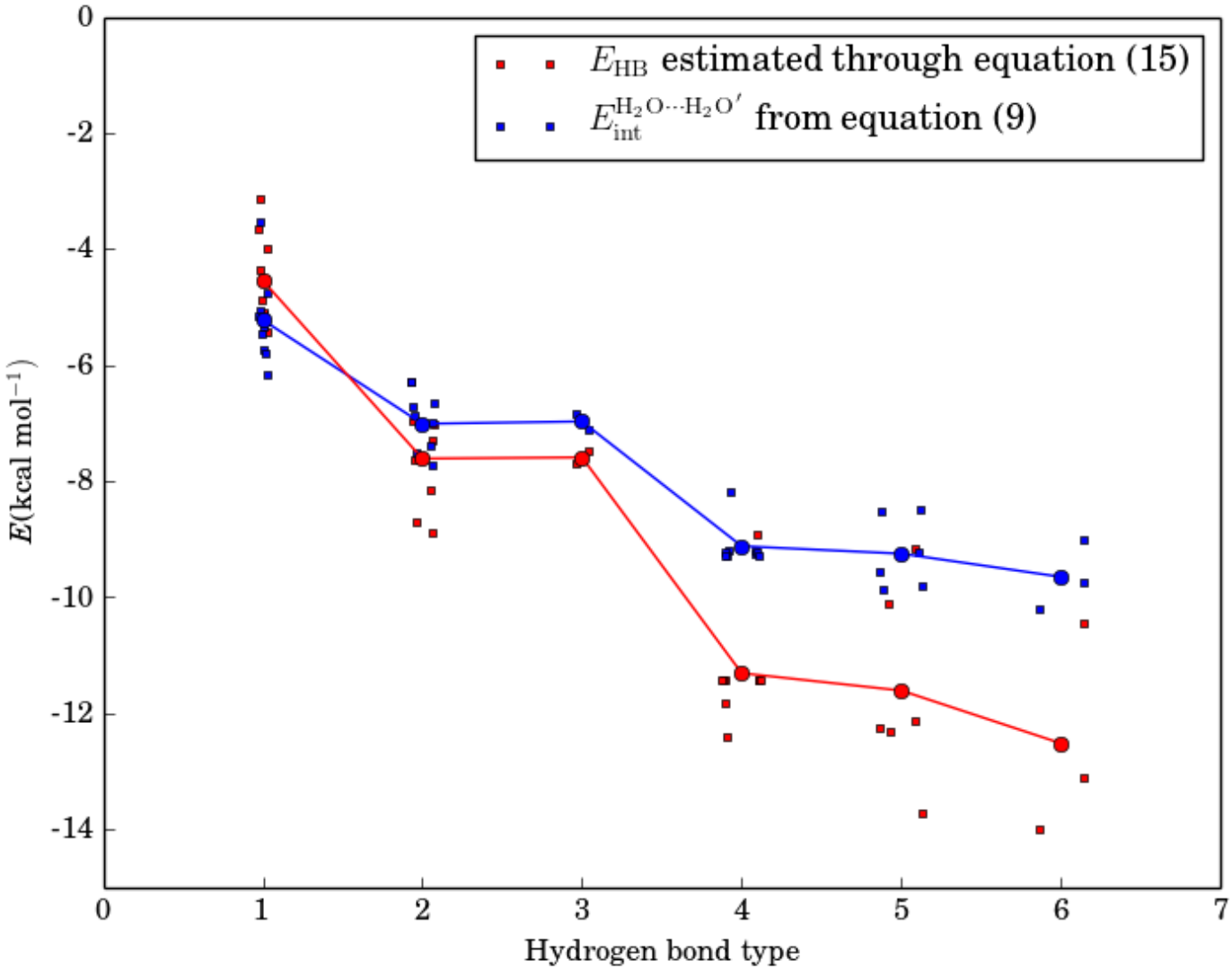

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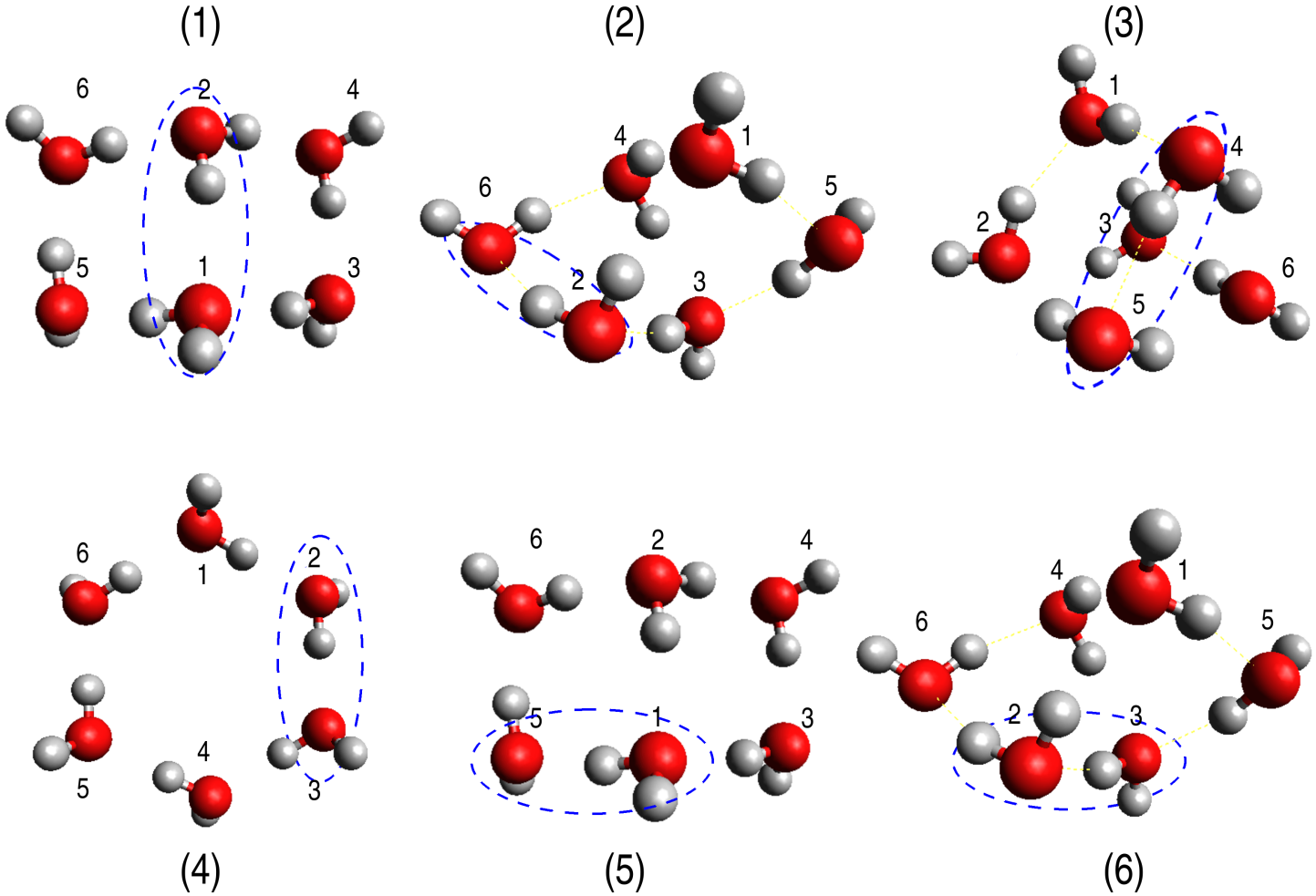
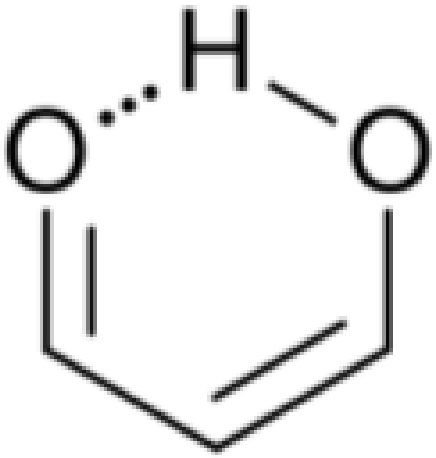
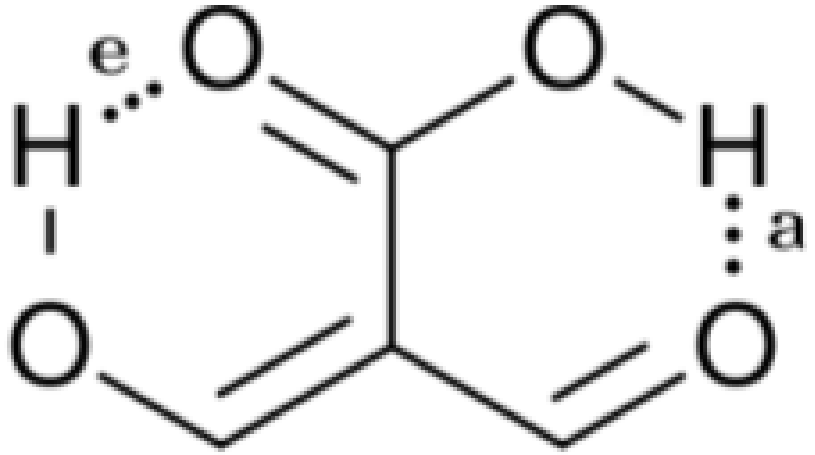


Cooperative and anticooperative effects in resonance assisted hydrogen bonds

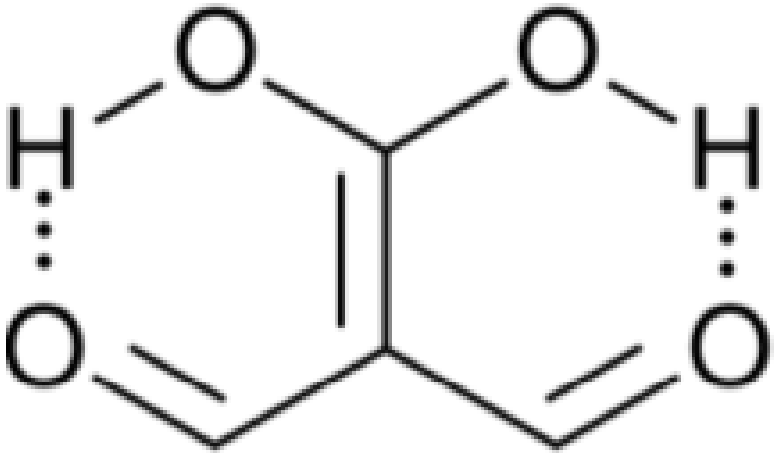
(*PCCP* DOI: 10.1039/c6cp04877c., *PCCP* DOI: 10.1039/c6cp04386k)



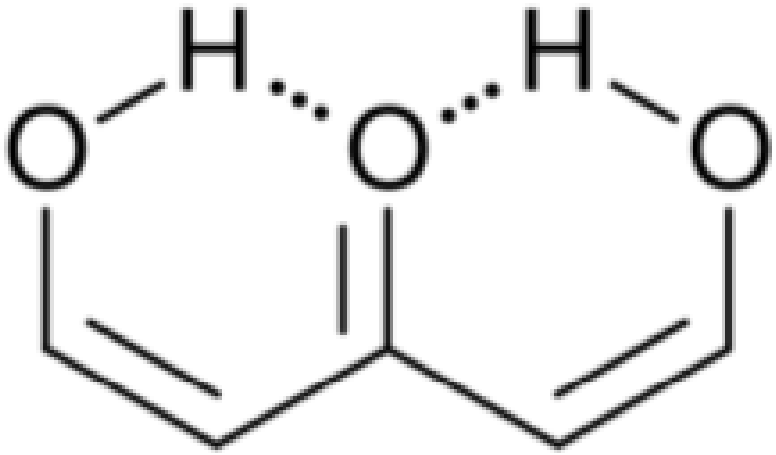
(a) 1



(b) 2



(c) 3



(d) 4

Cooperative and anticooperative effects in resonance assisted hydrogen bonds

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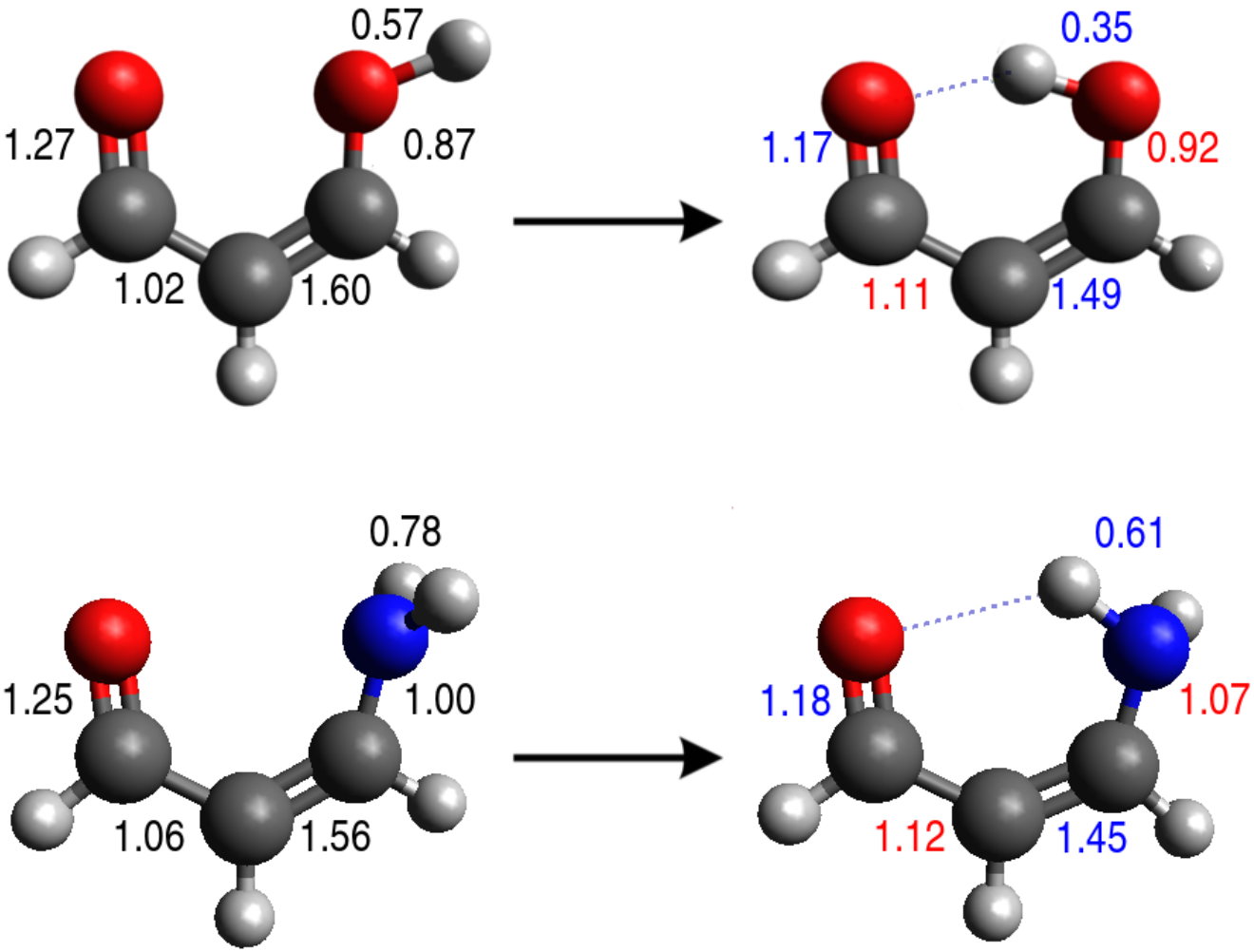

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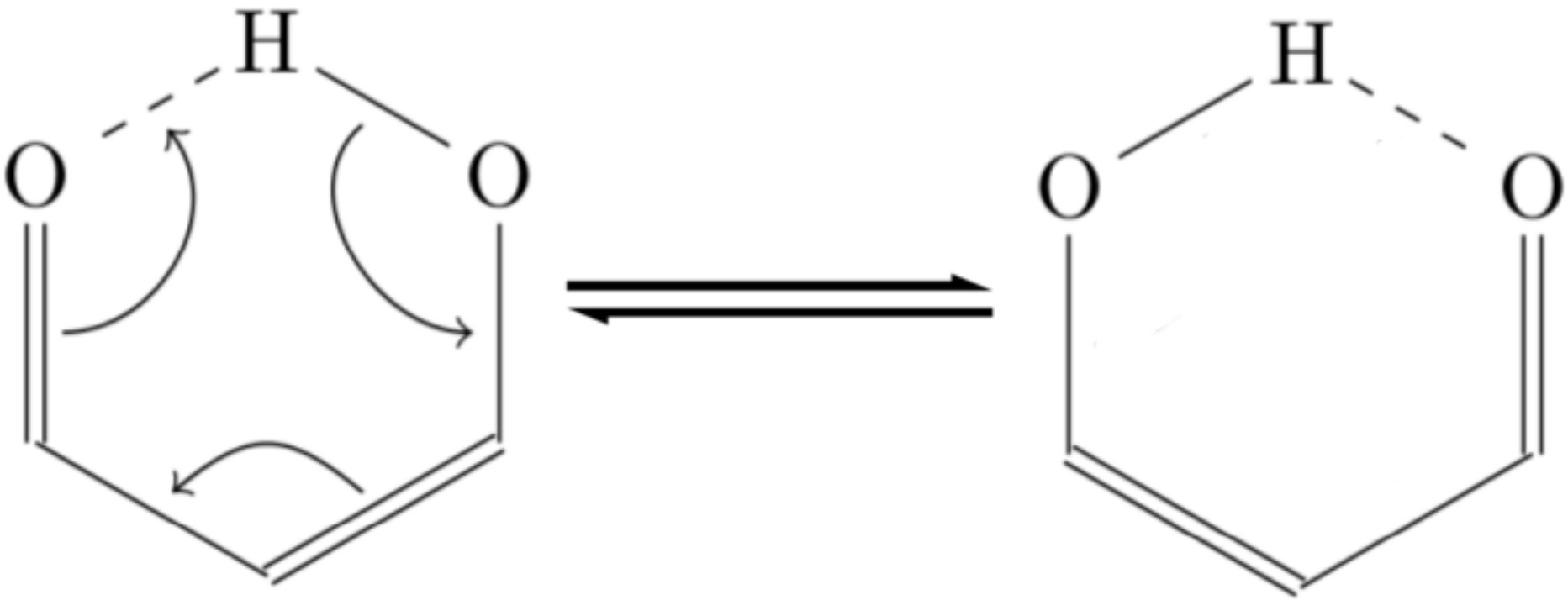

$$N = \sum_{\mathrm{A}} \lambda(\mathrm{A}) + \frac{1}{2} \sum_{\mathrm{A} \neq \mathrm{B}} \delta(\mathrm{A}, \mathrm{B})$$

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System	$\frac{1}{2} \sum_{\mathrm{A} \neq \mathrm{B}} \Delta\delta^{\mathrm{AB}}$	$\sum_{\mathrm{A}} \Delta V_{\mathrm{x}}^{\mathrm{A}}$	$\frac{1}{2} \sum_{\mathrm{A} \neq \mathrm{B}} \Delta V_{\mathrm{x}}^{\mathrm{AB}}$
CHO-CH=CH–OH	−0.10	−31.77	16.81
CHO-CH=CH–NH_2	−0.07	−23.71	17.00
CHO-CH_2–CH_2–OH	−0.03	−10.37	6.62
CHO-CH_2–CH_2–NH_2	−0.01	−3.19	2.07

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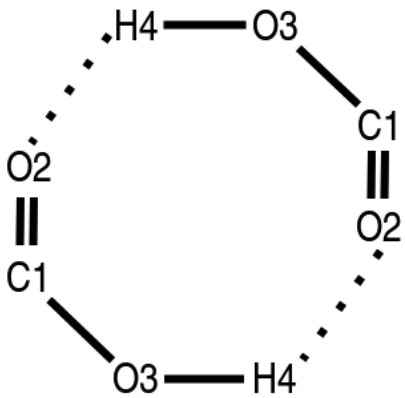

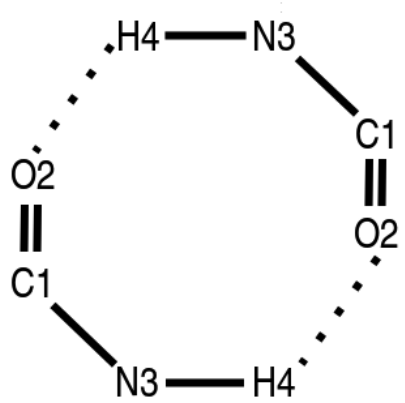

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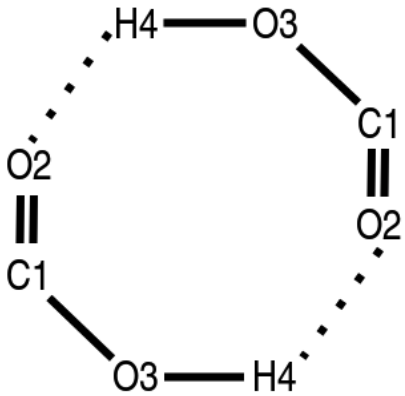

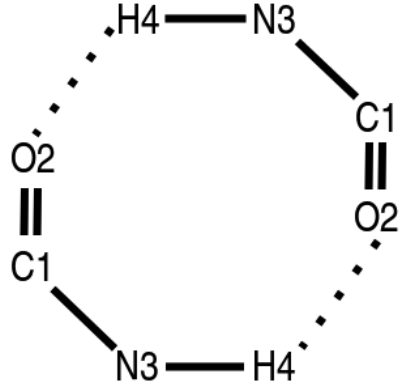

System	E_{int}^{AB}	V_{cl}^{AB}	V_{x}^{AB}	E_{def}^{A}
Formic acid	−41.61	−16.52	−25.09	33.64
Formamide	−32.17	−12.99	−19.17	26.21
Water	−19.86	−6.68	−13.17	8.17

Cooperative and anticooperative effects in resonance assisted hydrogen bonds

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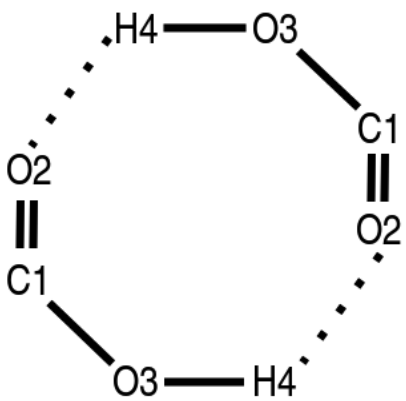

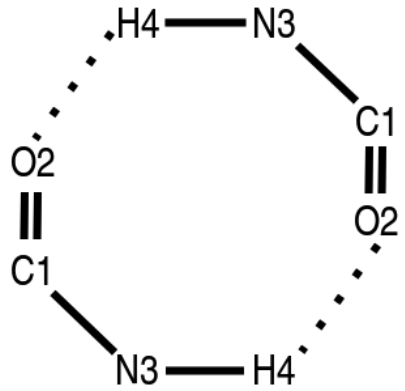

System	E_{int}^{AB}	V_{cl}^{AB}	V_{x}^{AB}	E_{def}^{A}
Formic acid	−41.61	−16.52	−25.09	33.64
Formamide	−32.17	−12.99	−19.17	26.21
Water	−19.86	−6.68	−13.17	8.17

$$\frac{|V_{\text{x}}^{\text{HCOOH}\cdots\text{OC(H)OH}}|}{|E_{\text{int}}^{\text{HCOOH}\cdots\text{OC(H)OH}}|} < \frac{|V_{\text{x}}^{\text{H}_2\text{O}\cdots\text{H}_2\text{O}}|}{|E_{\text{int}}^{\text{H}_2\text{O}\cdots\text{H}_2\text{O}}|}$$

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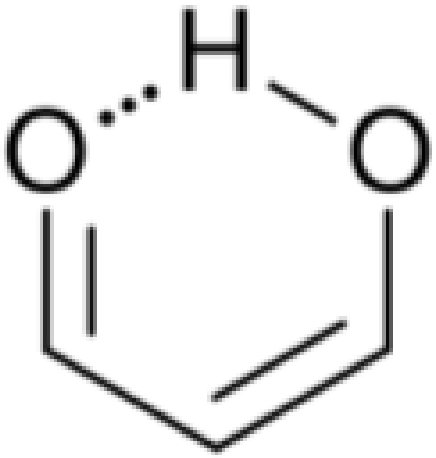
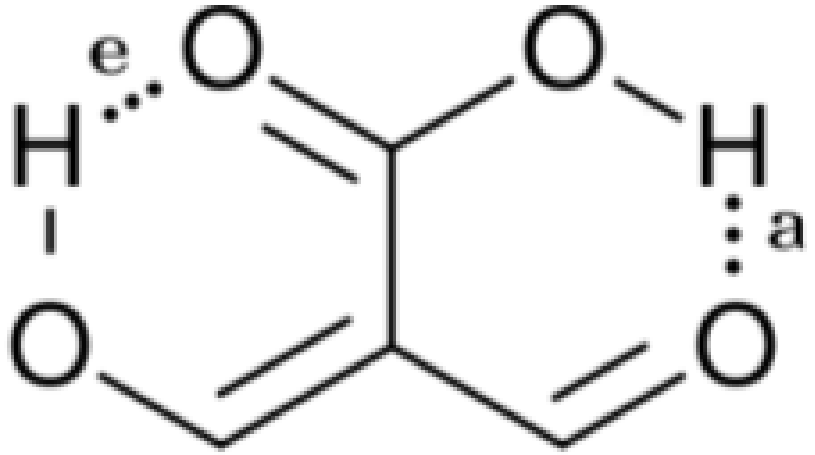
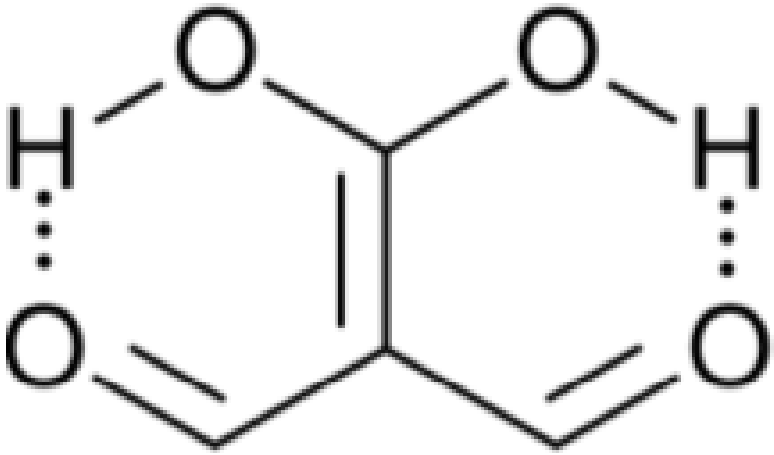


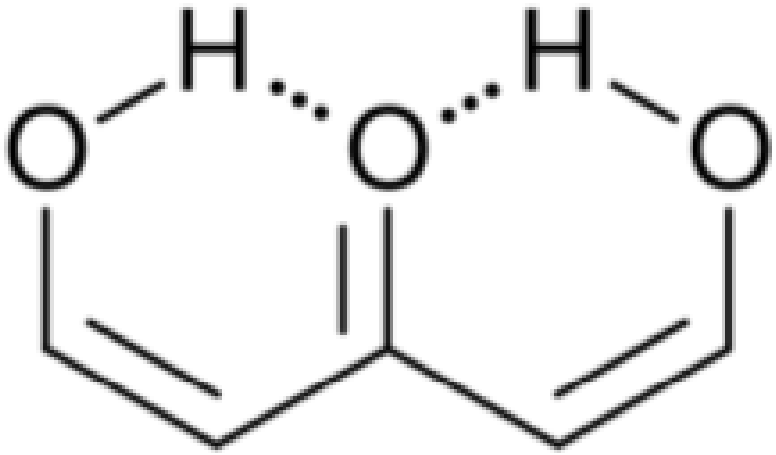
(a) 1



(b) 2



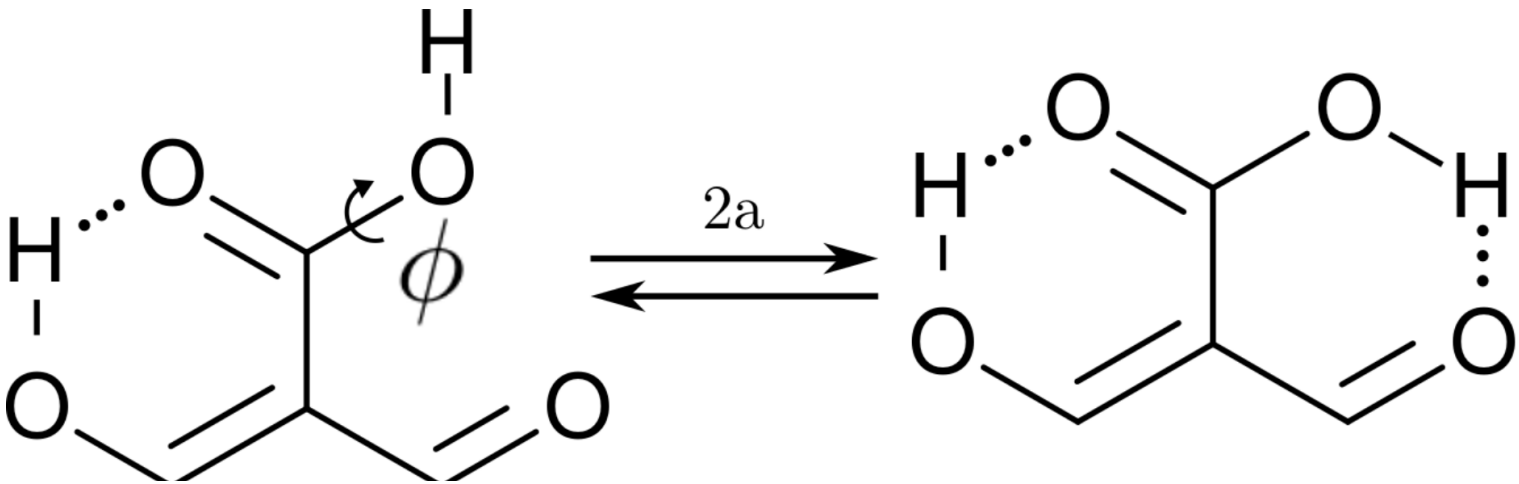
(c) 3



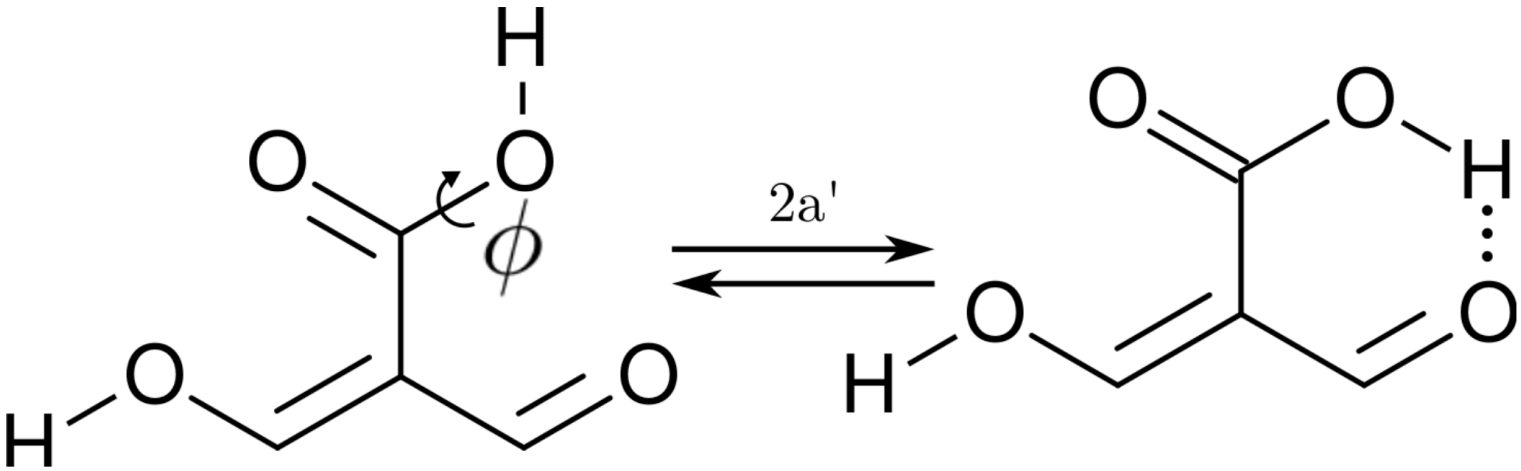
(d) 4

Cooperative and anticooperative effects in resonance assisted hydrogen bonds

(*PCCP* DOI: 10.1039/c6cp04877c., *PCCP* DOI: 10.1039/c6cp04386k)



$\Delta E_{\text{form}}(\mathbf{2a})$,

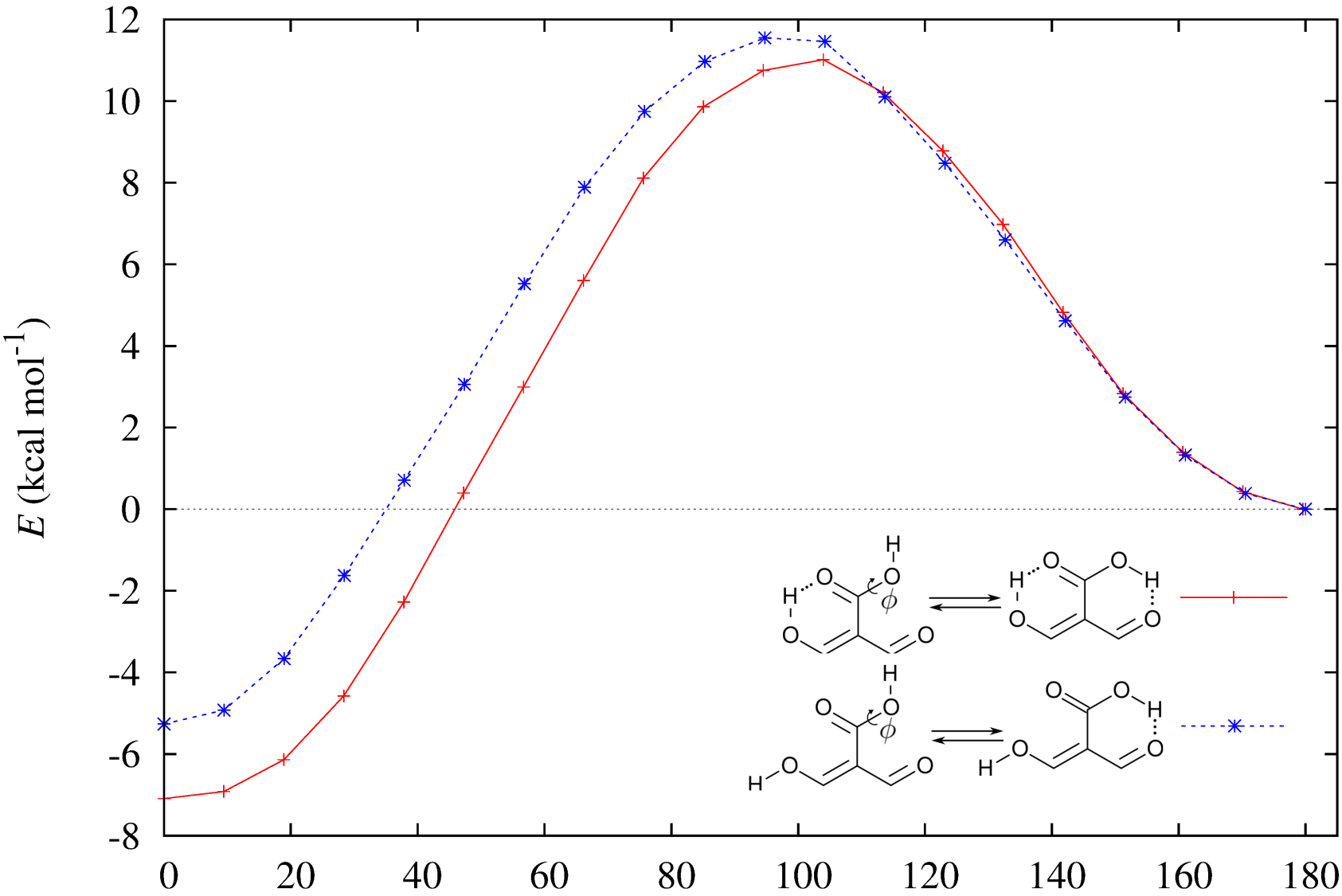


$\Delta E'_{\text{form}}(\mathbf{2a})$,

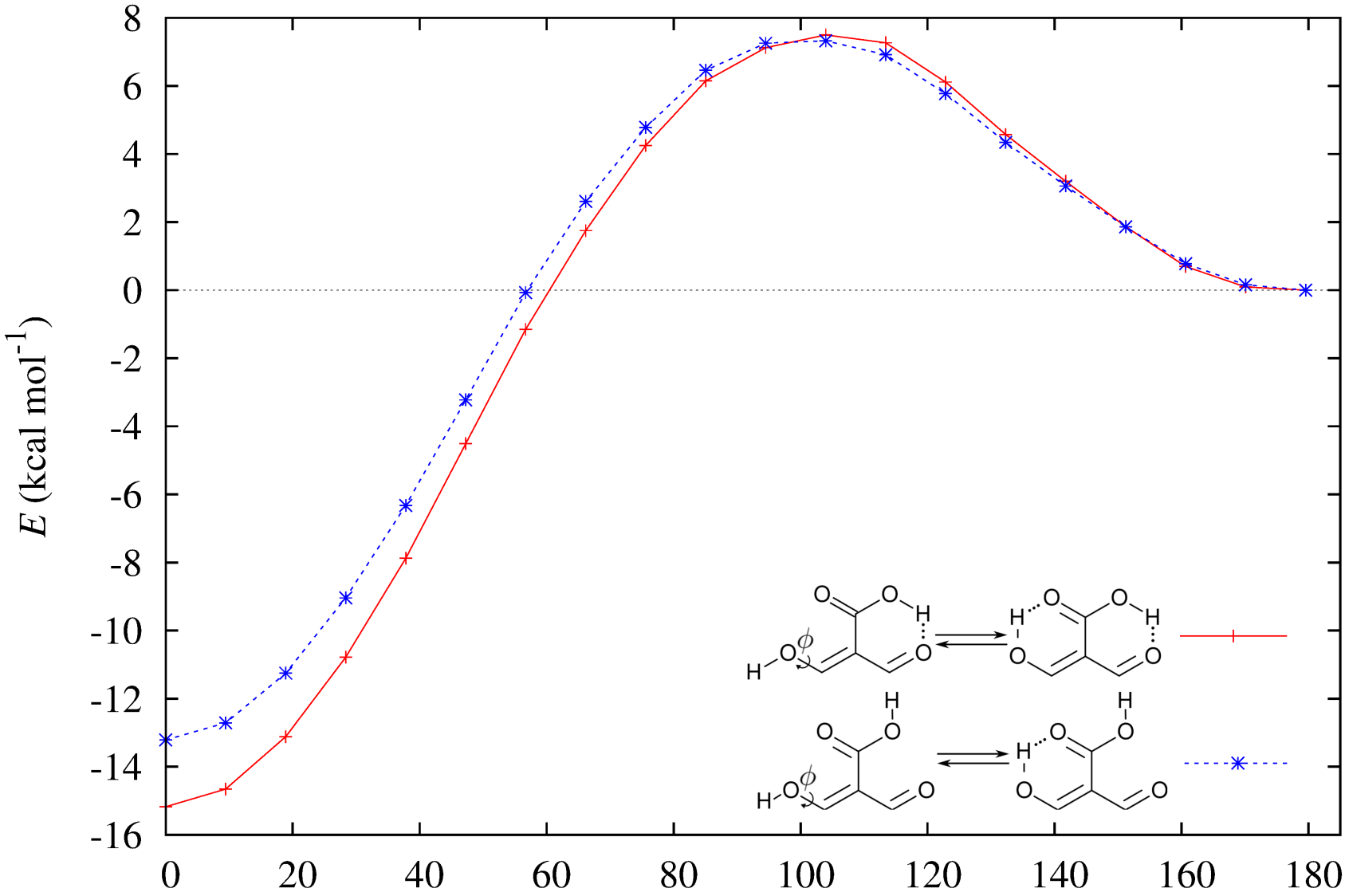
Cooperative and anticooperative effects in resonance assisted hydrogen bonds

(*PCCP* DOI: 10.1039/c6cp04877c., *PCCP* DOI: 10.1039/c6cp04386k)

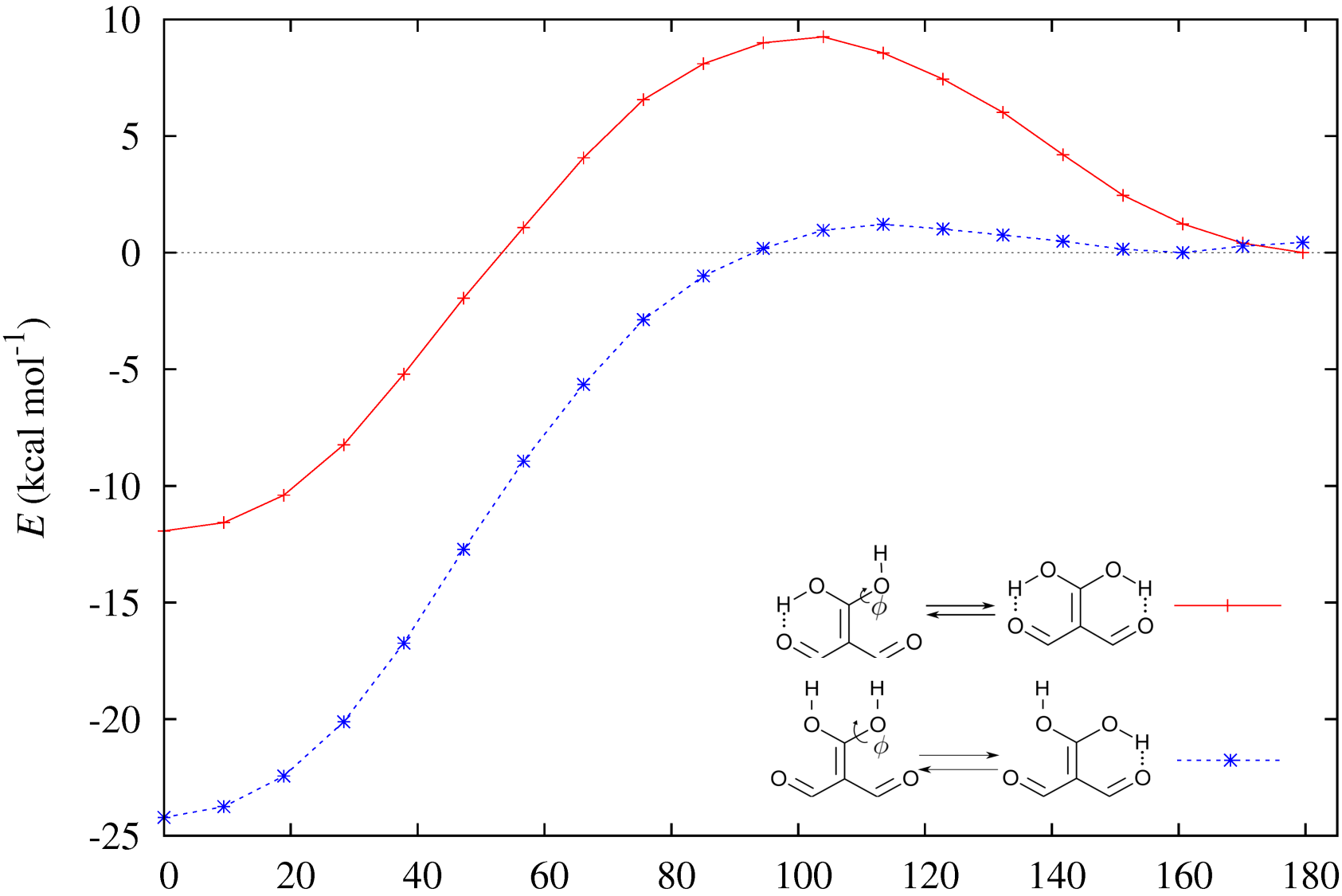
2a



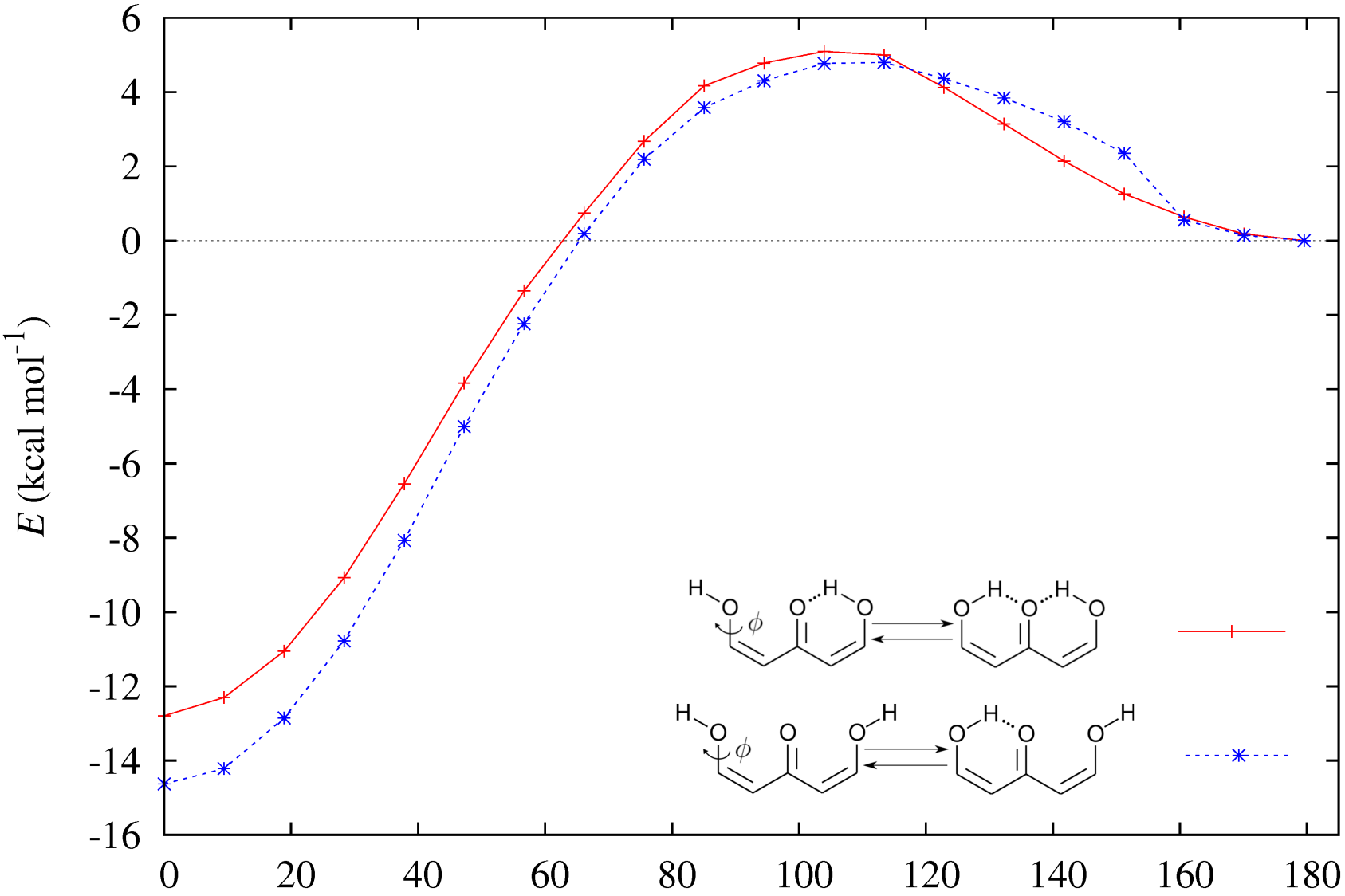
2e


8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
E (kcal mol-1)
0
20
40
60
80
100
120
140
160
180
ϕ
ϕ

3



4


6
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-6
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-12
-14
-16
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60
80
100
120
140
160
180
E (kcal mol-1)
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H
O
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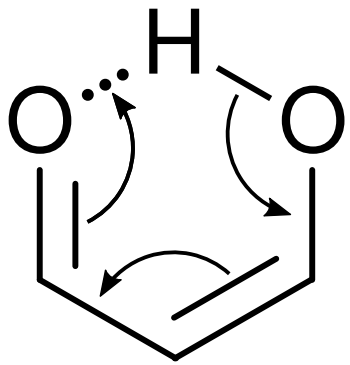
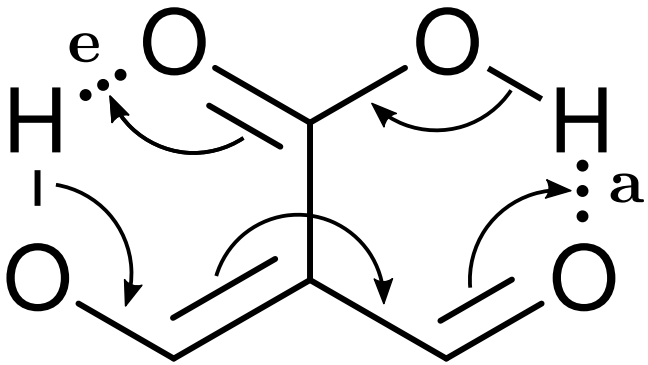
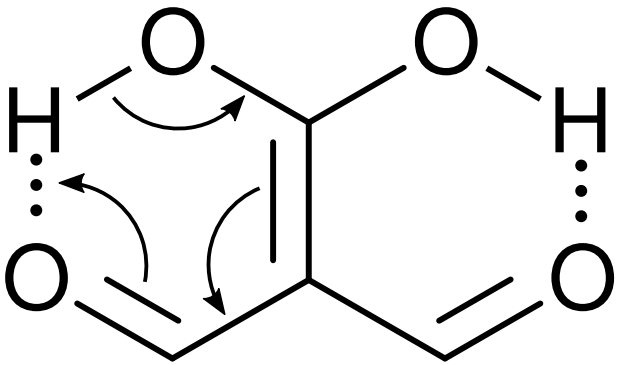


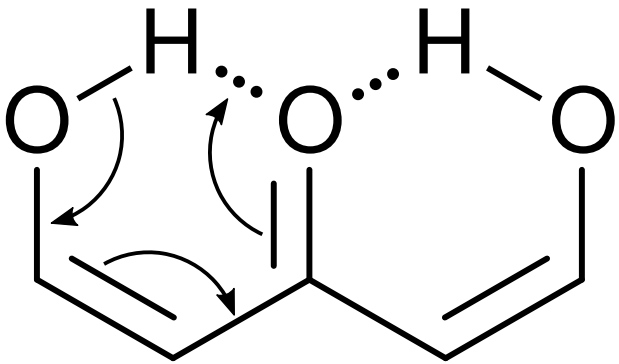
(a) 1



(b) 2



(c) 3



(d) 4

$$\Delta E_{\text{coop}}(\mathbf{2a}) = \Delta E_{\text{form}}(\mathbf{2a}) - \Delta E'_{\text{form}}(\mathbf{2a})$$
$$\Delta E_{\text{coop}}(\mathbf{2e}) = \Delta E_{\text{form}}(\mathbf{2e}) - \Delta E'_{\text{form}}(\mathbf{2e})$$
$$\Delta E_{\text{coop}}(\mathbf{3}) = \Delta E_{\text{form}}(\mathbf{3}) - \Delta E'_{\text{form}}(\mathbf{3})$$
$$\Delta E_{\text{coop}}(\mathbf{4}) = \Delta E_{\text{form}}(\mathbf{4}) - \Delta E'_{\text{form}}(\mathbf{4})$$

HB	$\Delta E_{\mathrm{coop}}(\mathbf{N})$	$\Delta E_{\mathrm{form}}(\mathbf{N})$	$\Delta E'_{\mathrm{form}}(\mathbf{N})$
2a	−1.82	−7.09	−5.27
2e	−1.97	−15.18	−13.21
3	12.29	−11.93	−24.22
4	1.84	−12.79	−14.63

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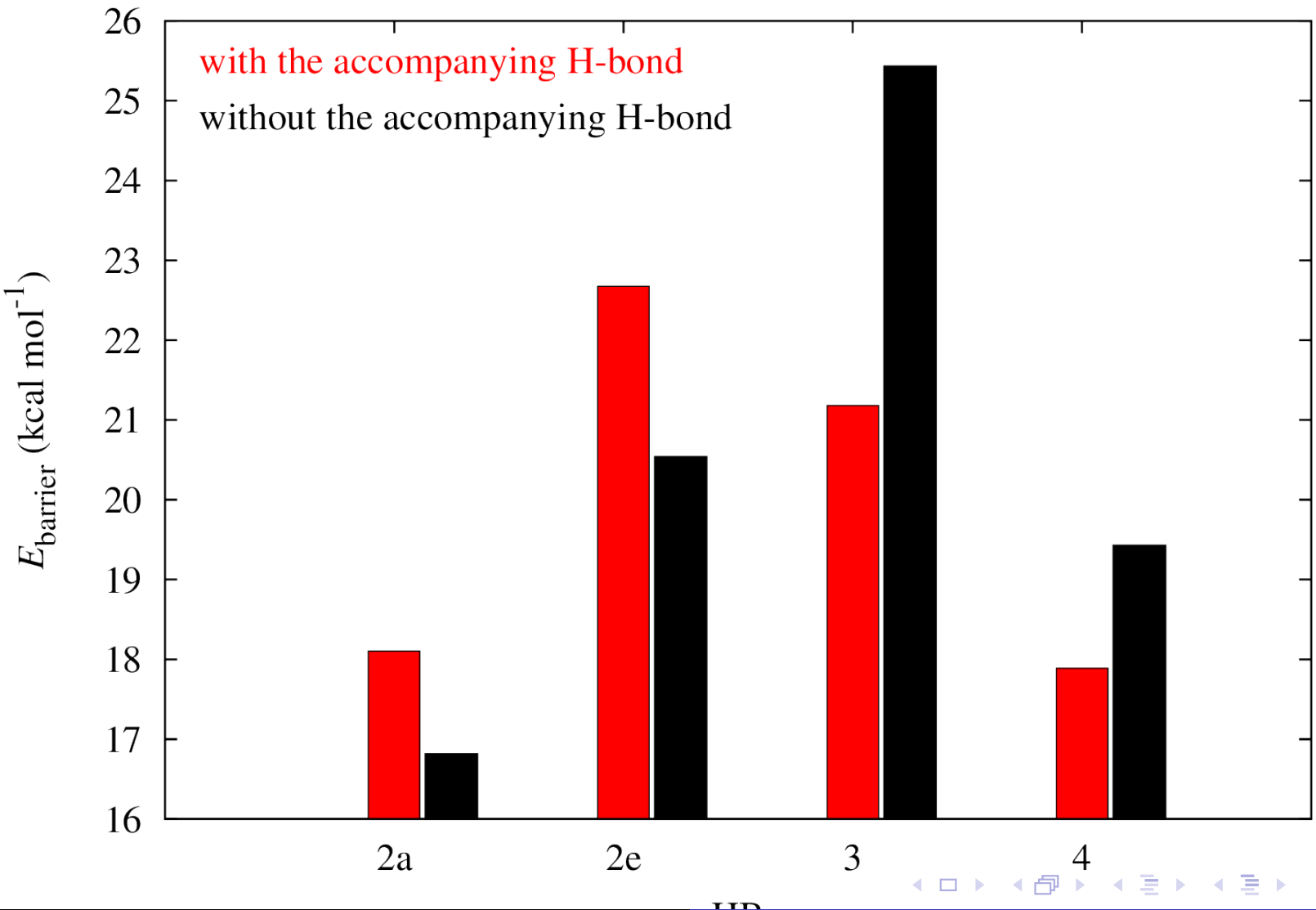


IQA additive energies

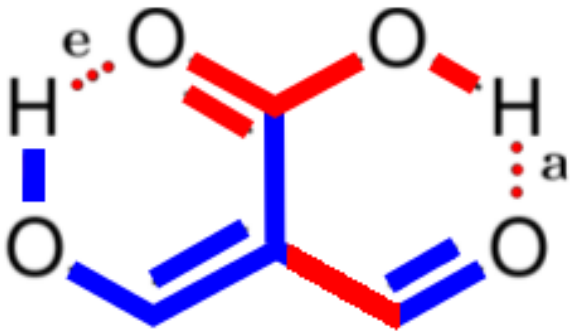
HB	$\Delta E_{\text{add}}^{\text{O}-\text{H}\cdots\text{O}}$	$\Delta E_{\text{add}}^{\cdots\text{CH}=\text{CH}-\text{C}\cdots}$	ΔE
1	−22.27	12.99	−9.28
2a (2e present)	−20.33	16.38	−3.96
2a (2e absent)	−15.48	13.29	−2.19
2e (2a present)	−24.25	11.10	−13.15
2e (2a absent)	−20.64	9.25	−11.38
3 (accompanying HB present)	−21.86	12.91	−8.96
3 (accompanying HB absent)	−28.43	7.62	−20.80
4 (accompanying HB present)	−18.21	6.74	−11.47
4 (accompanying HB absent)	−20.93	9.27	−11.66

$$\Delta E_{\mathrm{coop}}(\mathbf{M}) = \sum_{\mathrm{A}} \Delta E^{\mathrm{A}}_{\mathrm{net/coop}}(\mathbf{M}) + \frac{1}{2} \sum_{\mathrm{A}\neq\mathrm{B}} \Delta E^{\mathrm{AB}}_{\mathrm{int/coop}}(\mathbf{M}) \quad \mathbf{M} = \mathbf{2},\ \mathbf{3}, \mathbf{4}$$

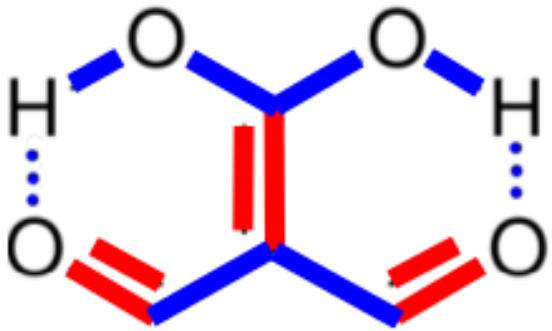
$$\Delta E_{\mathrm{coop}}(\mathbf{M}) = \sum_{\mathrm{A}} \Delta E^{\mathrm{A}}_{\mathrm{net/coop}}(\mathbf{M}) + \frac{1}{2} \sum_{\mathrm{A}\neq\mathrm{B}} \Delta E^{\mathrm{AB}}_{\mathrm{int/coop}}(\mathbf{M}) \quad \mathbf{M} = \mathbf{2},\ \mathbf{3}, \mathbf{4}$$

System	$\sum_{\text{bicyclic}} \Delta E^{\mathrm{AB}}_{\mathrm{int/coop}}$	$\sum_{\text{bicyclic}} \Delta V^{\mathrm{AB}}_{\mathrm{cl/coop}}$	$\sum_{\text{bicyclic}} \Delta V^{\mathrm{AB}}_{\mathrm{xc/coop}}$
2	−10.70	−7.48	−3.22
3	64.66	85.98	−21.31
4	26.39	27.77	−1.38

Cooperative and anticooperative effects in resonance assisted hydrogen bonds (*PCCP* DOI: 10.1039/c6cp04877c., *PCCP* DOI: 10.1039/c6cp04386k)



2



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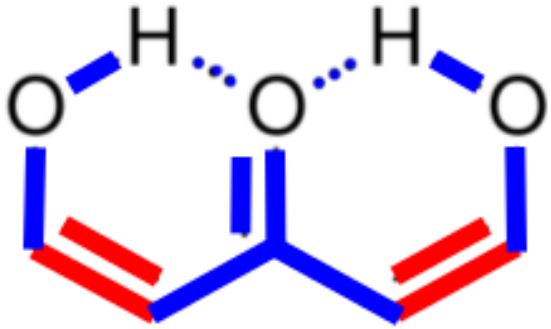

4

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