Playing around with Beryllium Bonds and other Closed-shell Interactions

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NCI Workshop
Paris, June 27, 2013

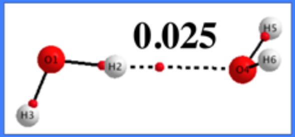
Most of the non-covalent interactions involve closed-shell systems: van der Waals complexes, hydrogen bonds, halogen bonds, …..

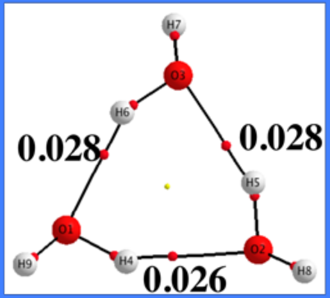
They share (with the only exception of van der Waals interactions) four (somehow inter-related) common characteristics:

- **Cooperativity**
- **Polarization effects or charge transfer**
- **Deformation**
- **Change in the intrinsic properties of the interacting systems**

All this is well known and Hydrogen Bonds are a paradigmatic example in which we can find these four common characteristics.

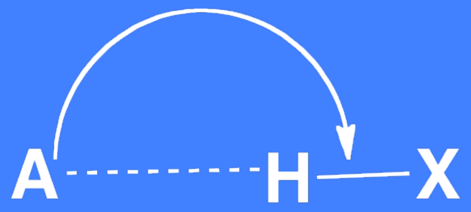
Cooperativity: is evident when one compares the water dimer and the water trimer.

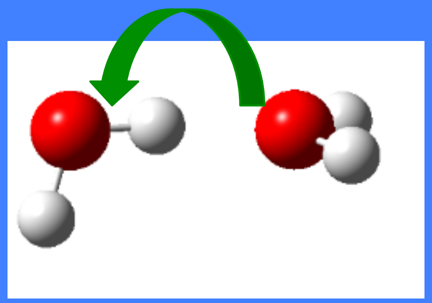




Polarization effects or charge transfer

Indeed, in a hydrogen bond, besides the electrostatic interaction it can be viewed as the result of a charge transfer from the lone pairs of the HB acceptor (A) to the σ_{XH}* antibonding orbital of the HB donor (XH)



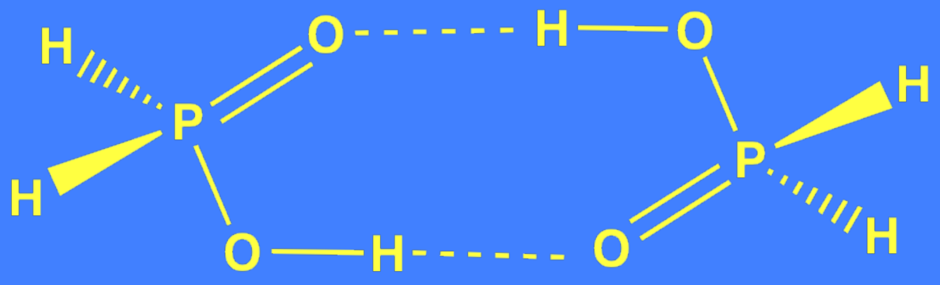


This charge transfer is reflected in a weakening of the X-H covalent bond, which accordingly lengthens, whereas its stretching frequency is red-shifted (signature of HBs used to measure the strength of the interaction)

This electron density re-distribution is behind cooperativity and deformation.

Cooperativity, because it changes the intrinsic properties of the monomers
Deformation because density is transfer to antibonding empty orbitals

But this charge transfer, which is usually small in conventional HBs, can become very large in strong HBs.



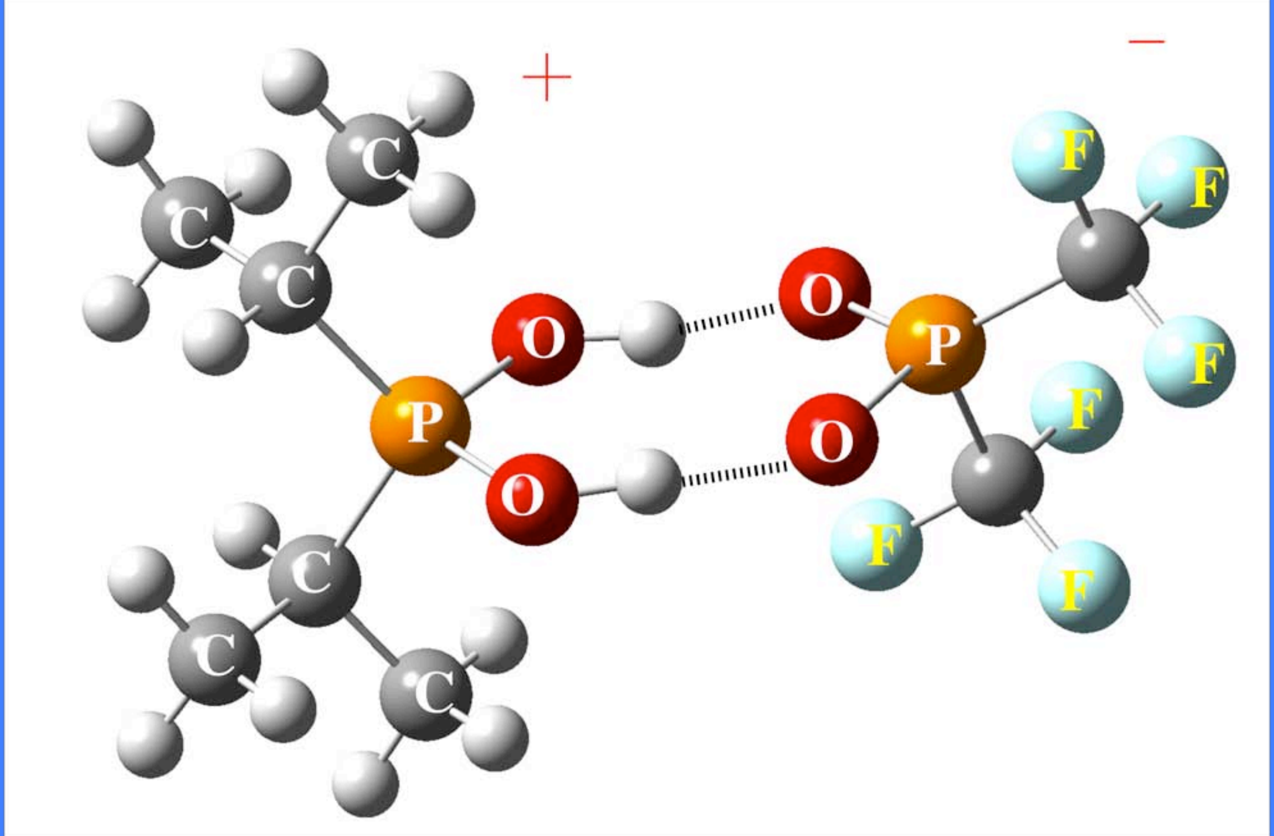
Dimerization energy: 98 kJ mol^{-1} (more than twice that of carboxylic acids)

The OH elongates from 0.968 Å to 1.023 Å

The O-H stretching frequency is red-shifted by 800 cm^{-1} !!!
Explains Fermi resonance

JCP 1998, 109, 2685

When the HB is very strong the charge transfer from the HB acceptor to the σ_{XH}* antibonding orbital of the HB donor (XH) is so large that the X-H bond cleaves and a spontaneous proton transfer takes place.

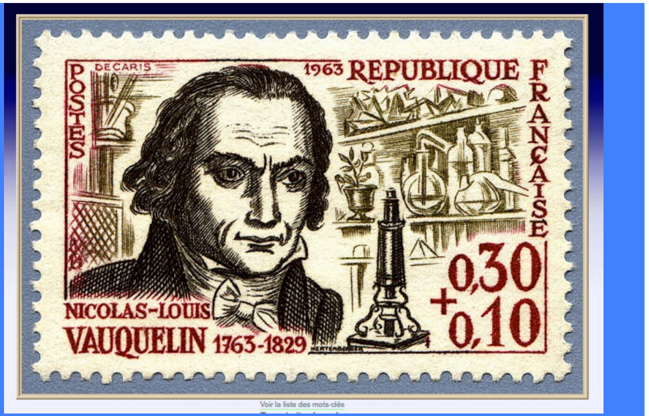


ChemPhysChem 2001, 7, 466

But these characteristics are not necessarily exclusive of hydrogen bonds. They could be found whenever an element, not very electronegative, is covalently bonded to a more electronegative one, and at the same time has low-lying empty orbitals which allow it to behave as a good electron acceptor.

Be derivatives are one of those cases, in which the Be atom presents low-lying empty *p* orbitals, even if the *2s-2p* energy gap is significant

Be was discovered by Nicolas-Louis Vauquelin


POSTES
DECARIS
1963 REPUBLIQUE FRANÇAISE
NICOLAS-LOUIS
VAUQUELIN 1763-1829
0,30
+0,10
Voir la liste des mots-clés

Although it is extremely toxic, Be itself and some of its derivatives are heavily used in Industry:

- to produce age-hardening alloys such as BeCu
- useful material for heat dissipation
- to fabricate lightweight mirrors with good dimensional stability
- as moderator in nuclear reactors
- Its oxide is a very good heat conductor, but at the same time is an excellent electrical insulator

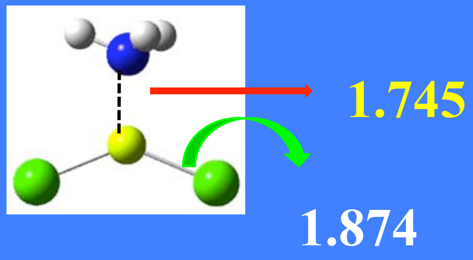
-Its chloride derivative catalyzes the Friedel-Crafts reaction and forms many interesting complexes (Dressel et al., *Z. Naturforsch.* 2002, *58b*, 173 – 182.)

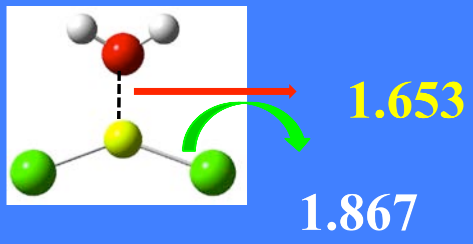
-“tetrahedral proton”

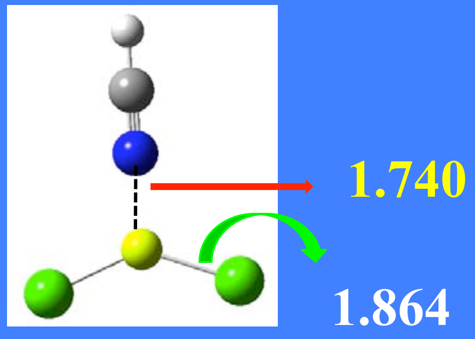
BeX_2 (X = H, F, Cl, OH)

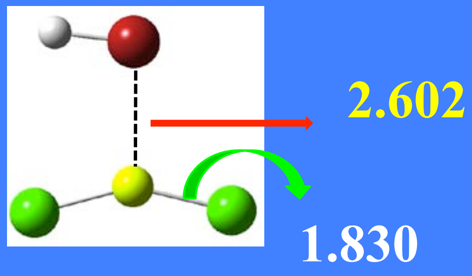
NH_3, H_2O, FH, PH_3, SH_2, ClH, BrH, CO, HCN, LiCN, HN=CH_2, OCH_2, CH_3NH_2

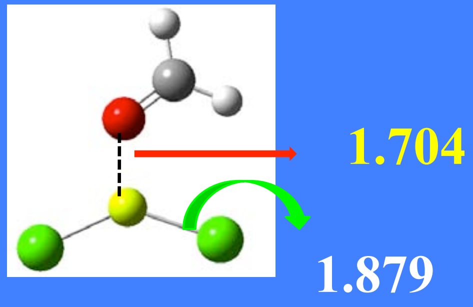
J. Chem. Theor. Comput. 5, 2763 (2009)

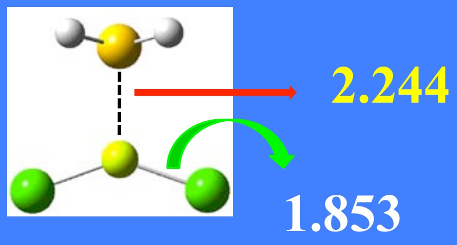


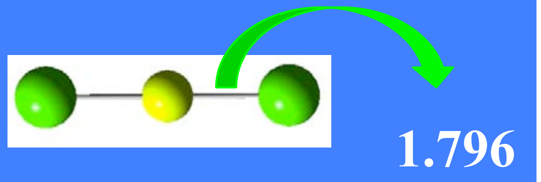












Bond distances smaller than the sum of the van der Waals radii.

Significant deformation of the Lewis acid.

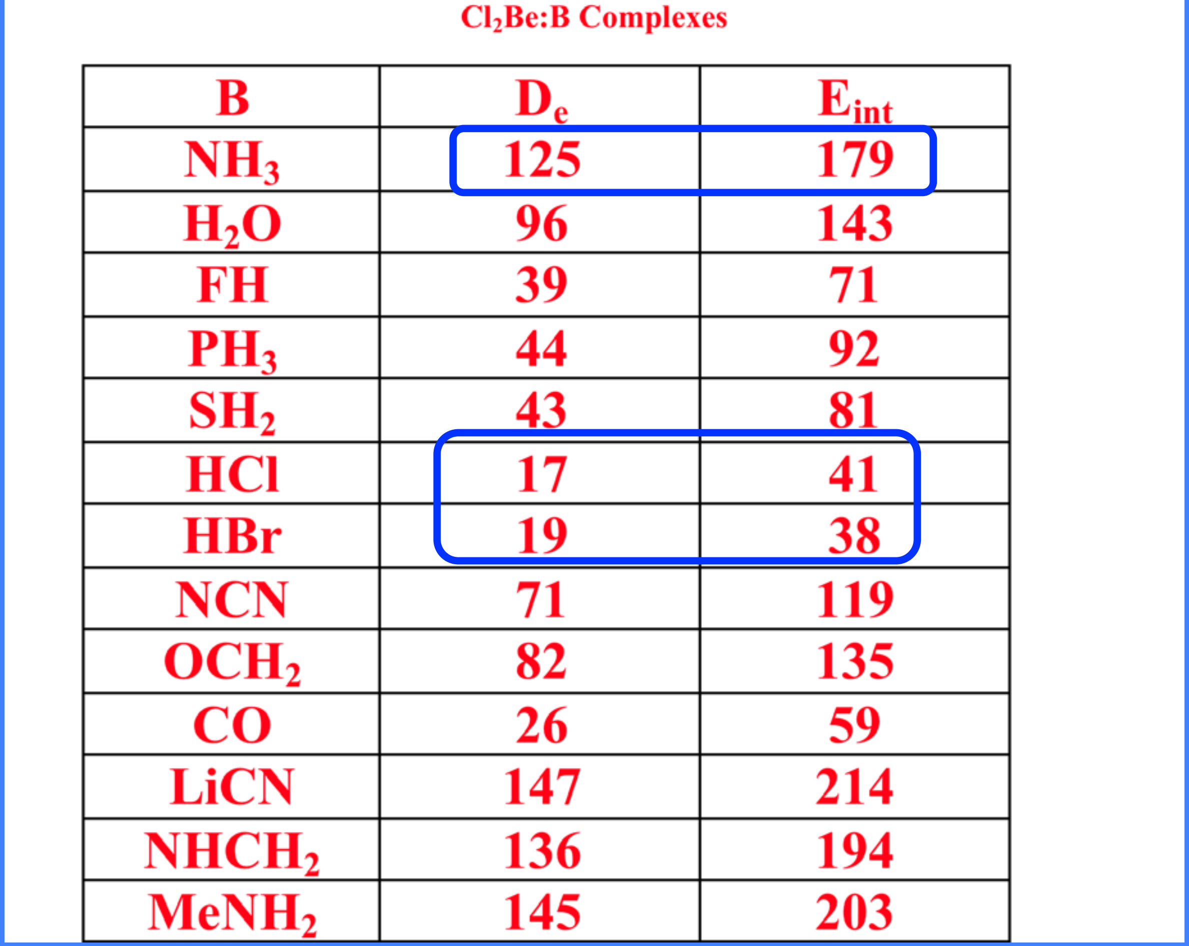
Due to the deformation:

D_e = E (complex) – E (monomers)$_{equilibrium}$

not a good measure of the strength of the interaction

Better the interaction energy:

E_{int} = E(complex) – E(monomers)$_{complex}$

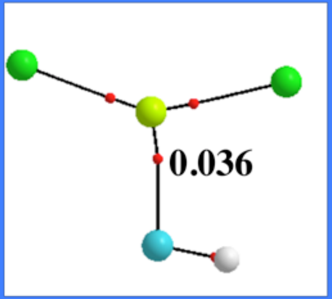


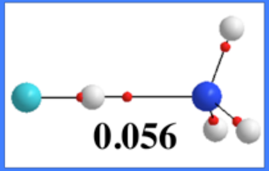
Cl_2Be:B Complexes

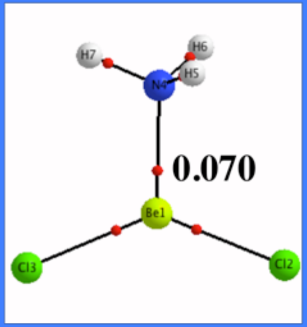
B	D_e	E_{int}
NH_3	125	179
H_2O	96	143
FH	39	71
PH_3	44	92
SH_2	43	81
HCl	17	41
HBr	19	38
NCN	71	119
OCH_2	82	135
CO	26	59
LiCN	147	214
$NHCH_2$	136	194
$MeNH_2$	145	203

Some interaction energies up to five times those in conventional hydrogen bonds (values in kJ mol^{-1})

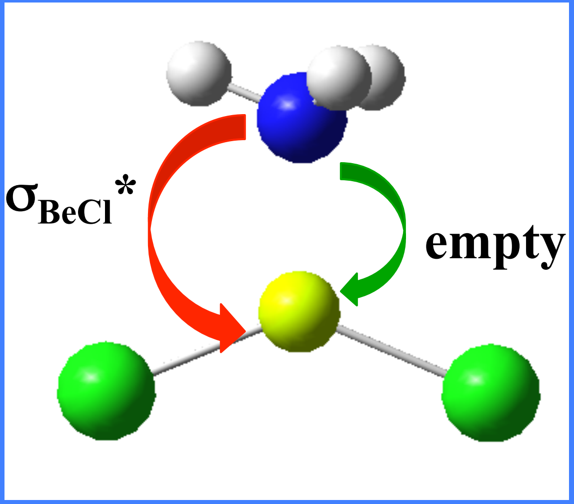
The topology of these two closed-shell interactions, HBs and Beryllium bonds, is similar






H7
H6
H5
N4
0.070
Be1
Cl3
Cl2

NBO second order perturbation analysis:



Antibonding σ_{BeCl}^* orbital

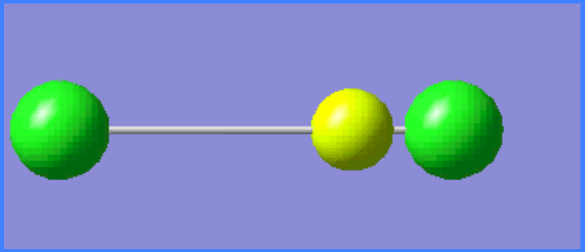
empty p orbital of Be

J. Chem. Theor. Comput. 5, 2763 (2009)

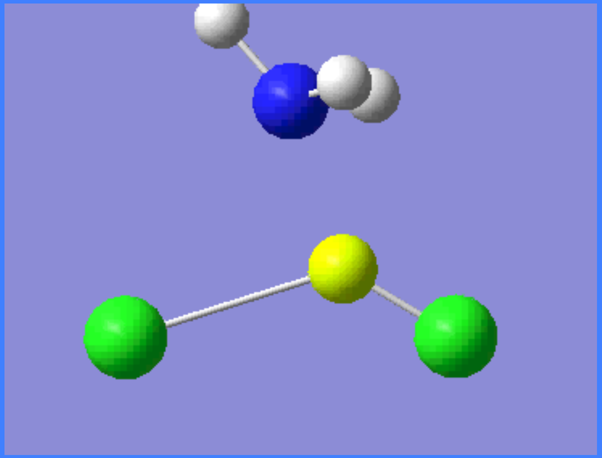
The participation of Be *p* orbital results in a bending of XBeX ($sp \rightarrow sp^2$)

The population of the σ_{BeCl}* antibonding orbital in a significant lengthening of the Be-Cl bond (about 0.08 Å)

Consistently the antisymmetric stretching appears blue shifted



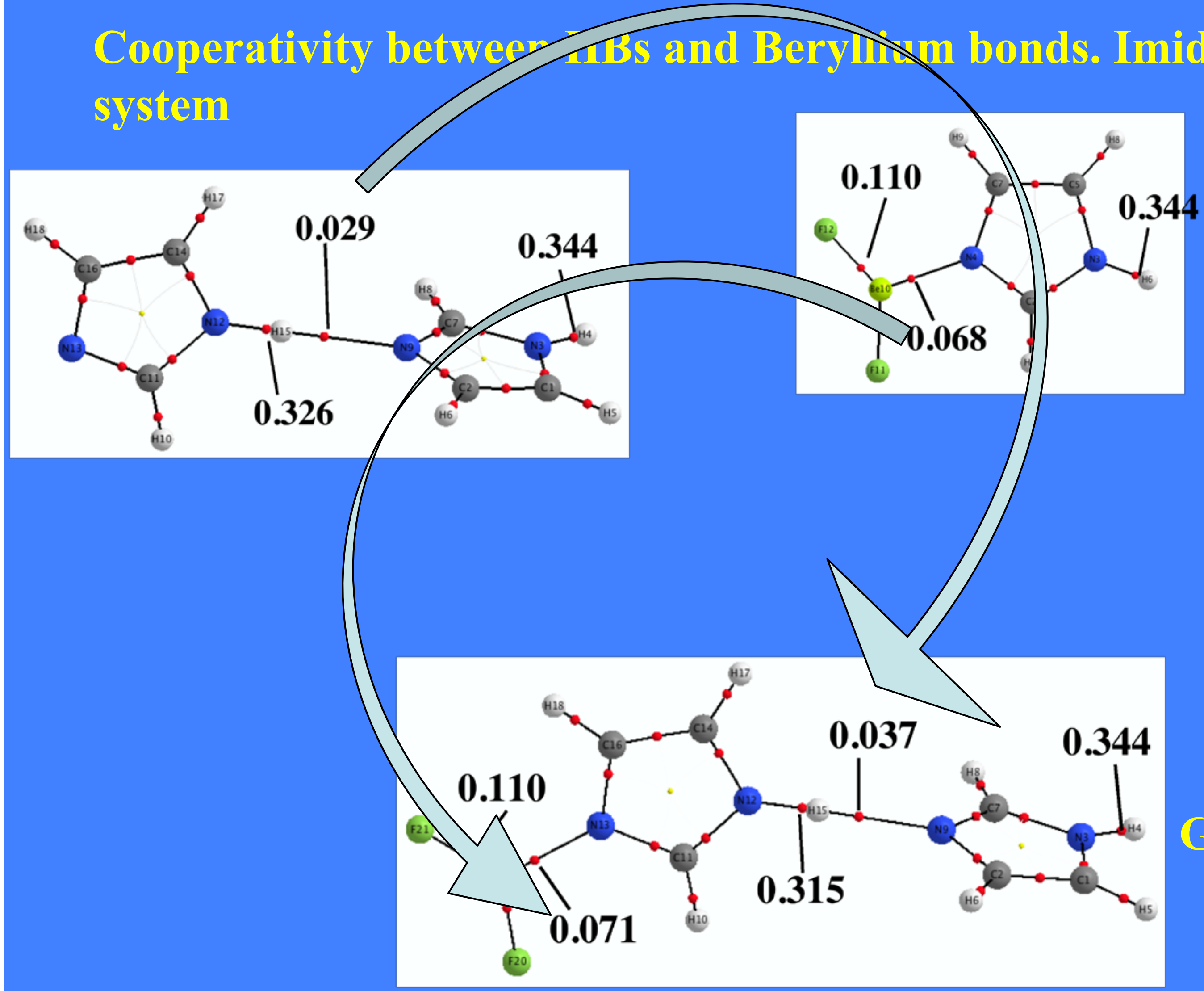
1131 cm^{-1}



928 cm^{-1}

COOPERATIVITY

Cooperativity between HBs and Beryllium bonds. Imidazole as model system

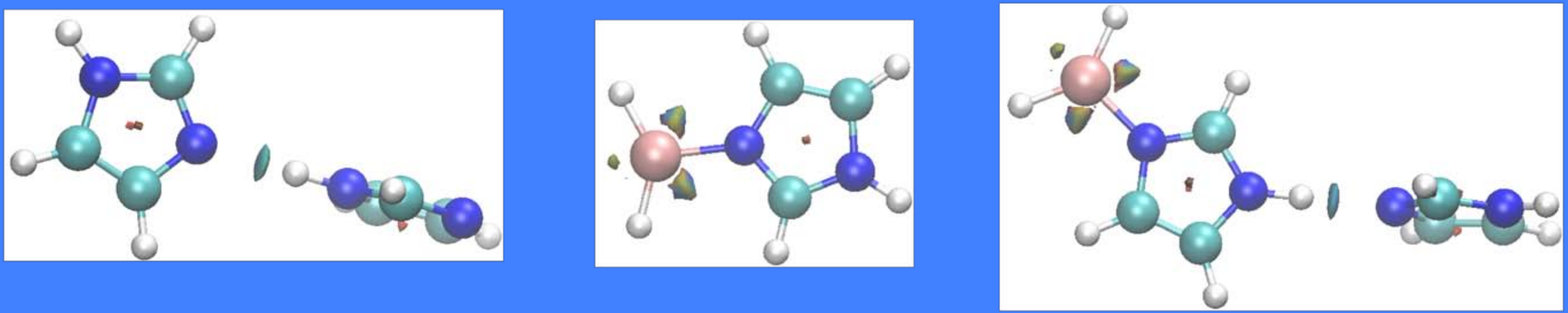

0.029
0.344
0.326
0.110
0.344
0.068
0.037
0.344
0.110
0.315
0.071
H17
H18
C16
C14
N12
H15
N13
C11
H10
H8
C7
N9
N3
H4
C2
C1
H6
H5
H9
H8
C7
C5
F12
Be10
N4
N3
H6
F11
F21
F20

Global minimum

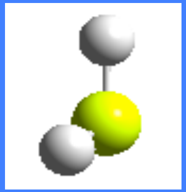
Both become reinforced

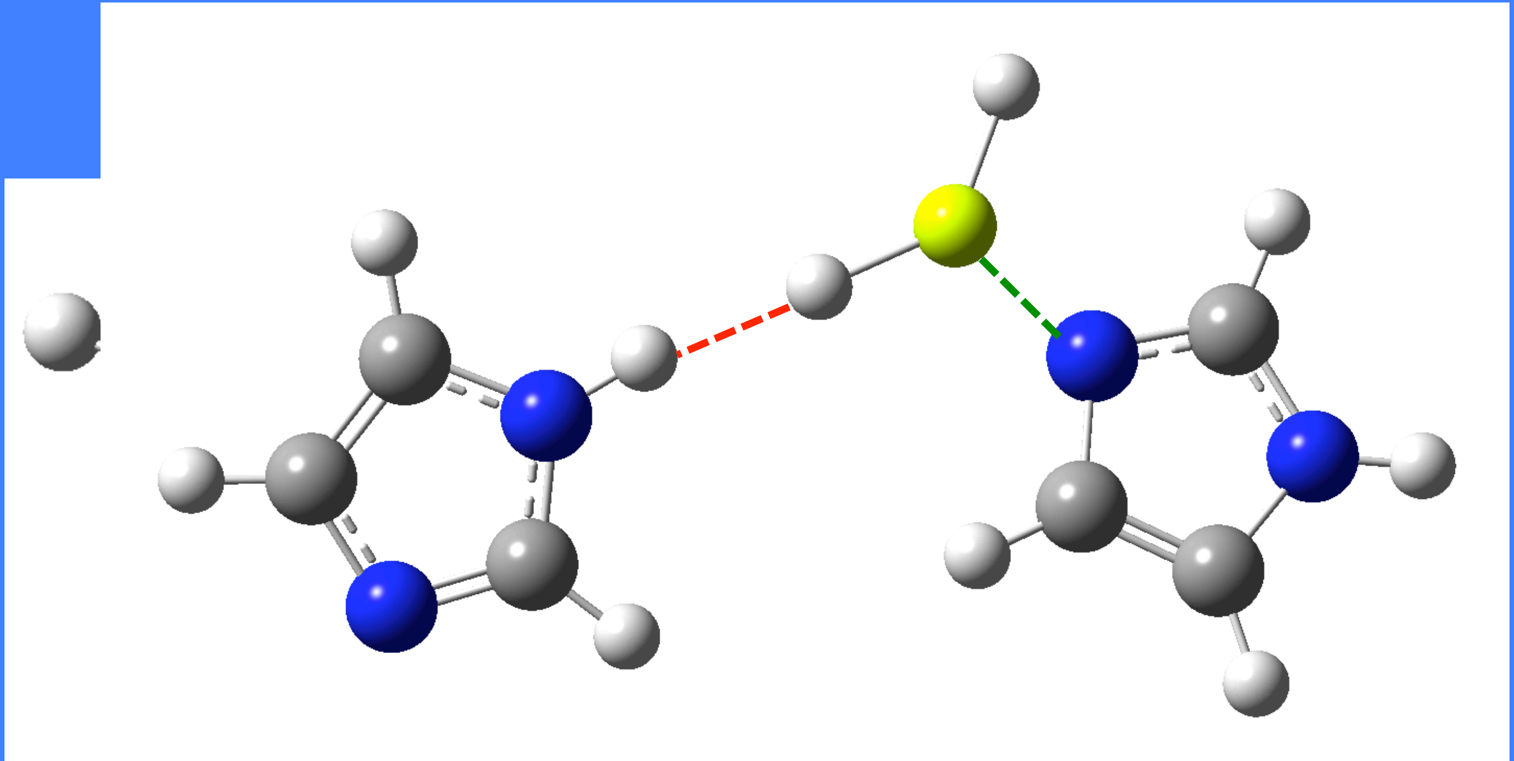
J. Chem. Theor. Comput. 2012 , 2, 2293-2300

The description in terms of the Non-Covalent index is similar, with greater absolute values of λ_2 in the complex with BeH_2



What happen when they compete?



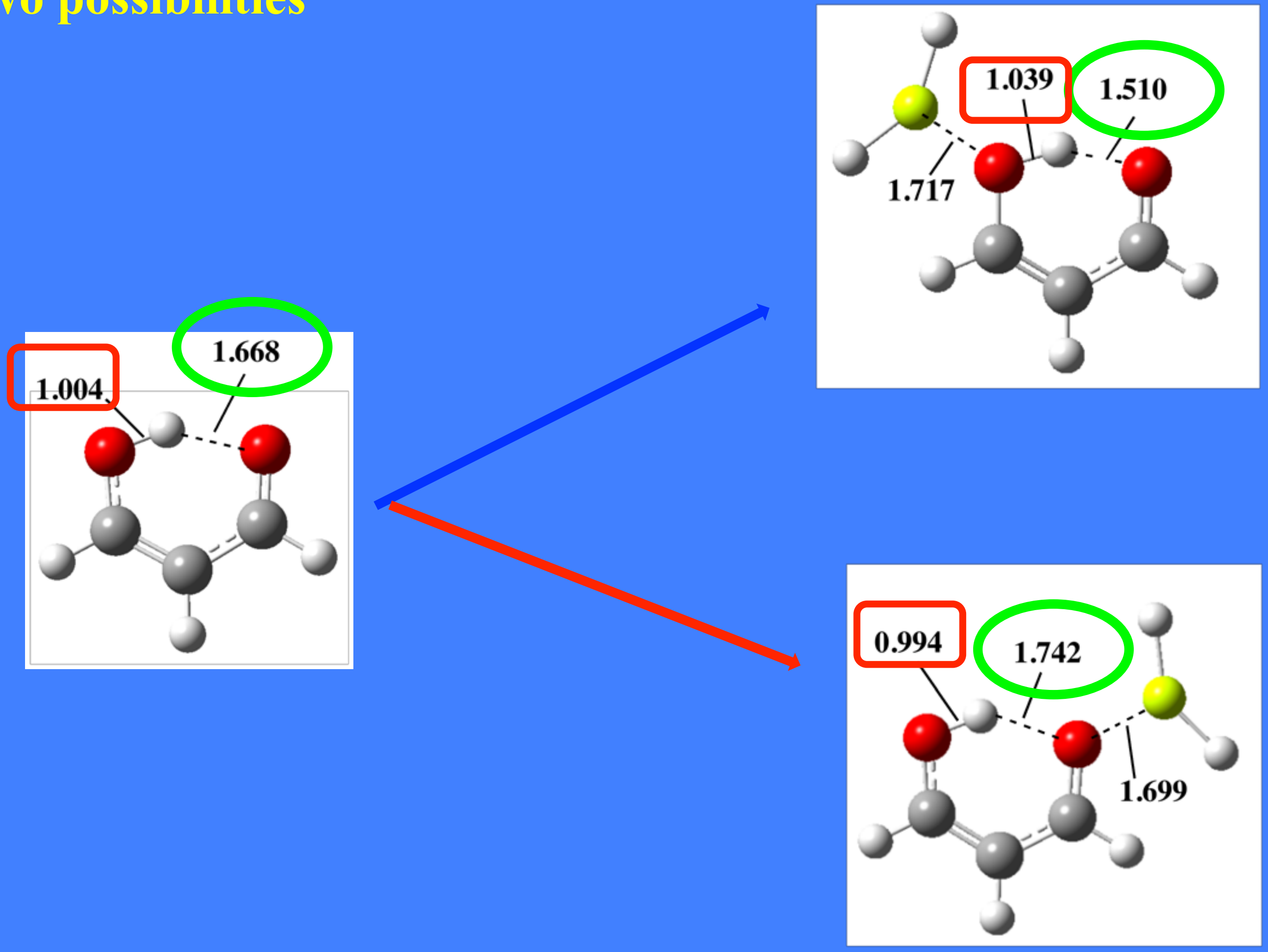


Which is still 4 kJ mol^{-1} higher in energy than the global minimum

J. Chem. Theor. Comput. 2012 , 2, 2293-2300

They can also modulate the strength of intramolecular hydrogen bonds.
Malonaldehyde

Two possibilities

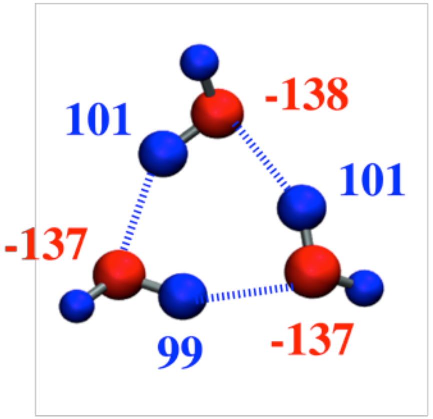

1.004
1.668
1.039
1.510
1.717
0.994
1.742
1.699

It would be possible to get a direct energetic information about cooperativity through the evaluation of atomic energy components?

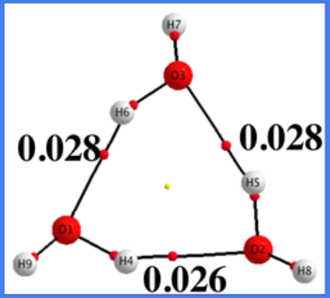
Method proposed by Boyd et al. for the study of the Guanine Quadruplex formation. J. Phys. Chem. B 114, 9833 (20109

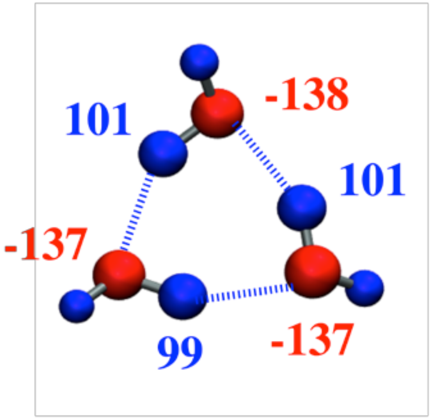
We decompose the total interaction energy into atomic energy components, so we represent the change in the atomic energies in the complex with respect to the energy of each atom as it exists in the non-interaction monomers.

Blue: Positive (destabilizing) energy change
Red: Negative (Stabilizing) energy change
The size of the spheres is proportional to the energy change



Interaction of water clusters with BeX_2 derivatives as model systems





In water trimer the H atoms become destabilized: Contribute to mitigate the electron density redistributions.

Consistent with:

Ring strain energy decreases dramatically on going from the perfluorinated cyclopropane to unsubstituted cyclopropane

P. v. R. Schleyer, *NATO Adv. Study Inst. Ser. C, 1986, 189, 69-73.*

J. G. Hamilton and W. E. Palke, *J. Am. Chem. Soc., 1993, 115, 4159-4164.*

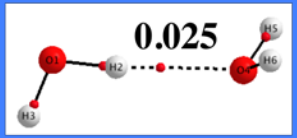
M. Alcamí, O. Mó and M. Yáñez, *J. Comput. Chem., 1998, 19, 1072-1086.*

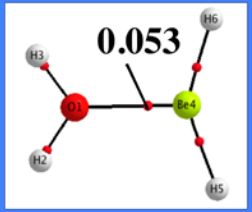
***Ring Strain Energy.* Ciclopropane: 105 kJ mol^{-1}**

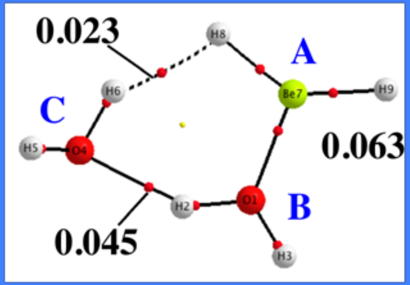
its perfluoro derivative: 350 kJ mol^{-1}

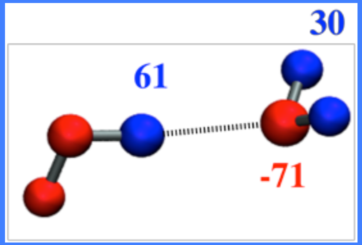
Stability of carbocations and caboanions decreases with their degree of substitutionK. B. Wiberg, P. v. R. Schleyer and A. Streitwieser, *Can. J. Chem., 1996, 74,* 892-900.

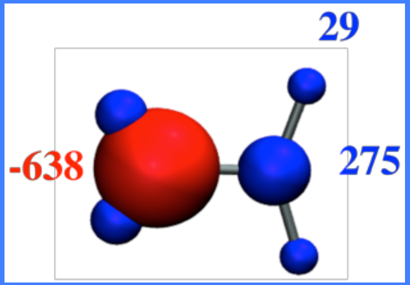
But, do they describe cooperativity?

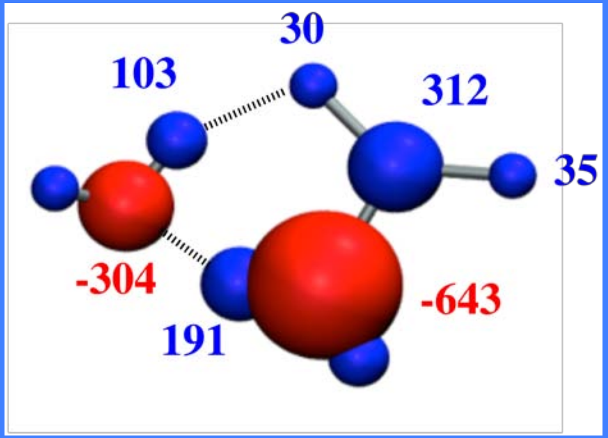

0.025
O1
H2
H3
O4
H5
H6

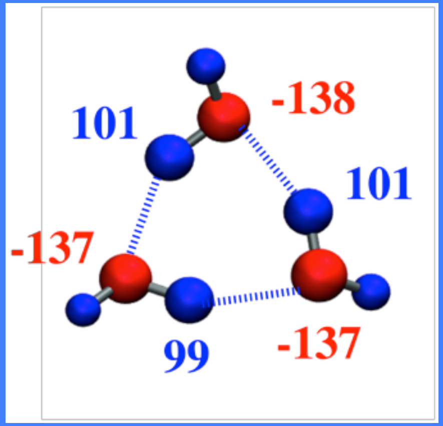

0.053
H3
O1
H2
Be4
H6
H5


0.023
H8
A
Be7
H9
C
H6
H5
O4
0.063
0.045
H2
O1
B
H3






30
103
312
35
-304
-643
191

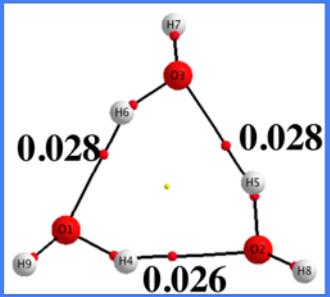

-138
101
101
-137
99
-137

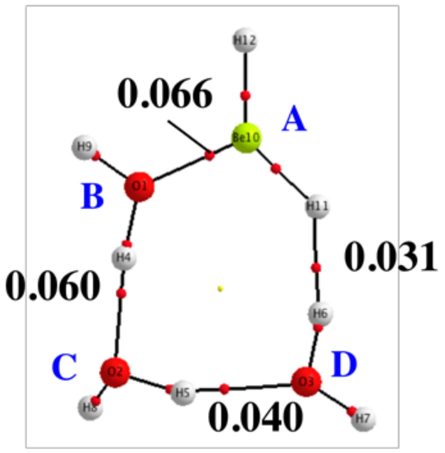
The larger the destabilization of the H the stronger the HB

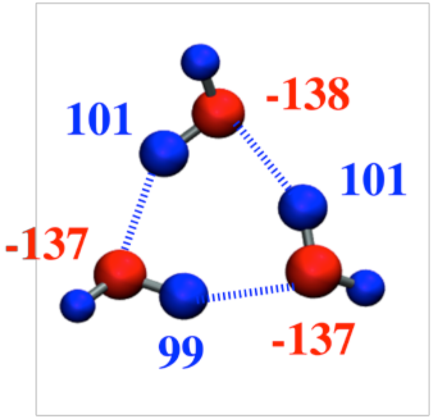
The same applies to beryllium bonds

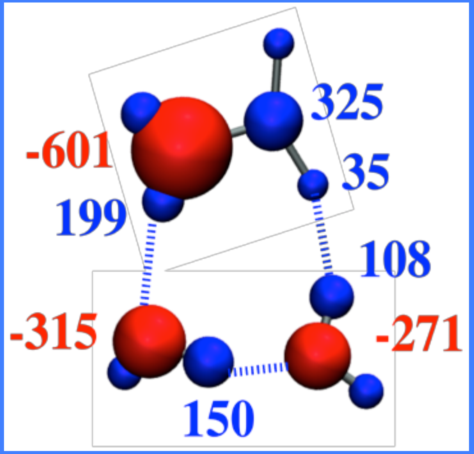
Phys Chem Chem Phys 2012, 14(42), 14540

Relative energies in kJ mol^{-1}


H7
O3
H6
0.028
0.028
H5
O1
O2
H9
H4
H8
0.026


H12
0.066
A
Be10
H9
O1
B
H11
0.031
H4
0.060
H6
C
O2
D
O3
H5
H8
H7
0.040


101
-138
101
-137
99
-137


325
-601
35
199
108
-315
-271
150

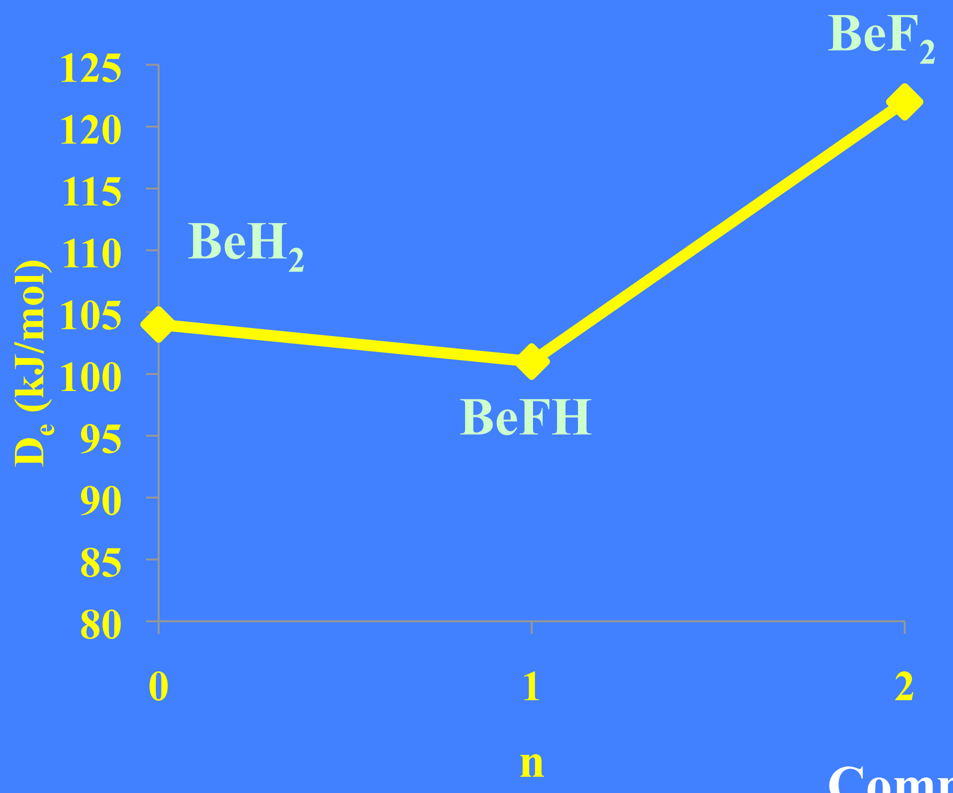
Phys Chem Chem Phys 2012, 14(42), 14540

Relative energies in kJ mol^{-1}

The important role of deformation

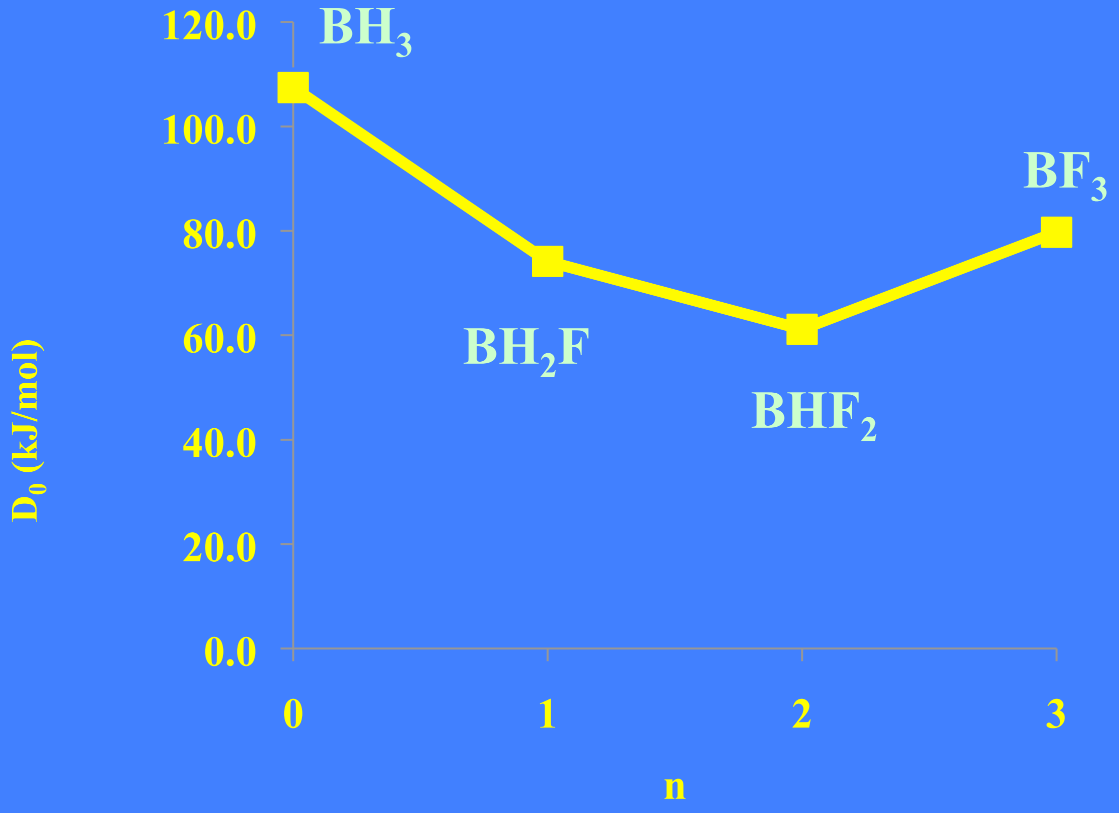
There are surprising results that can only be explained by the effects that the deformation produces in the properties of the Be derivative

The dissociation energy of FHBe-NH_3 complex is smaller than that of H_2Be-NH_3!



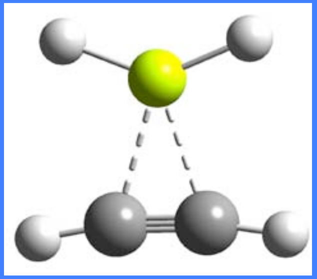
Comput Theor Chem 2012, 998, 74-79.

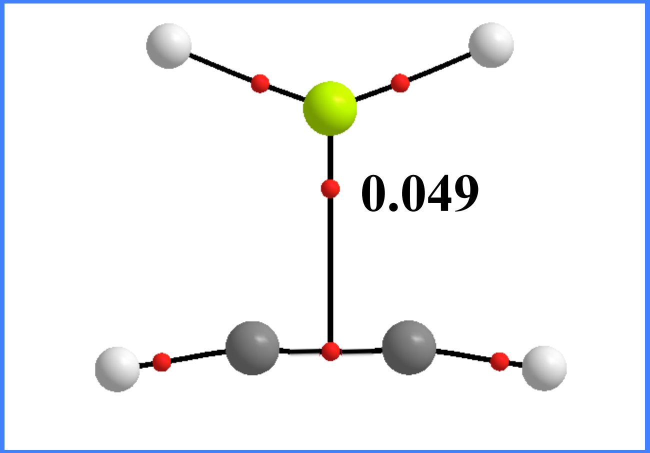
The same behavior reported before for $H_{3-n}F_nB\text{-}NH_3$ complexes the dissociation energy varies “anomalously” with the number of halogen atoms attached to B

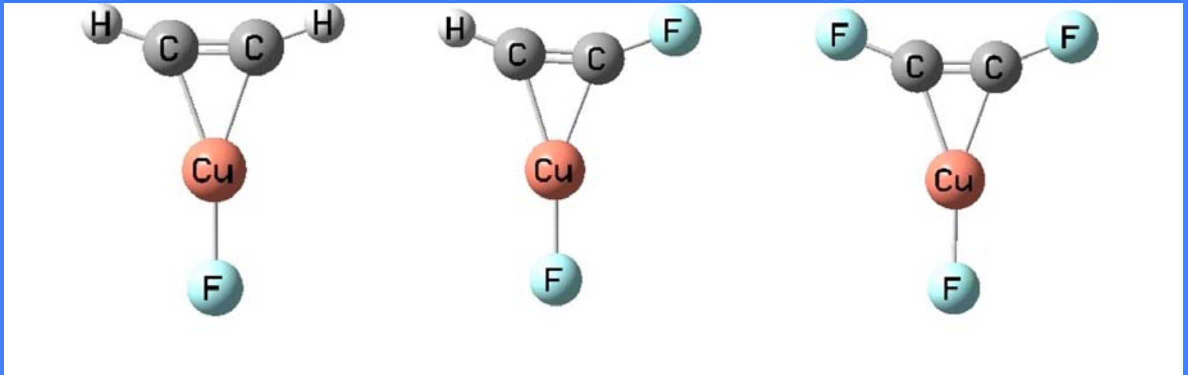


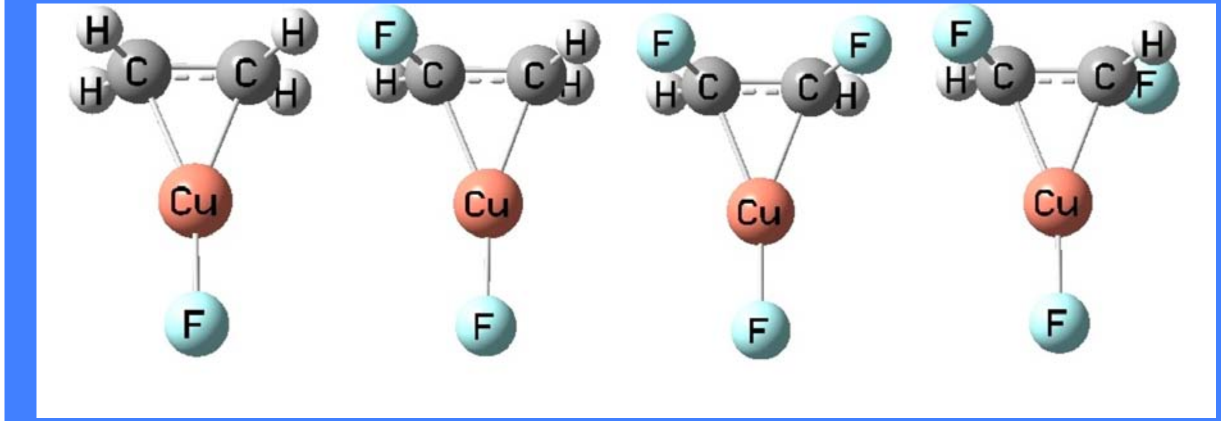
Chem. Eur. J. 2010, 16(39), 11897-11905

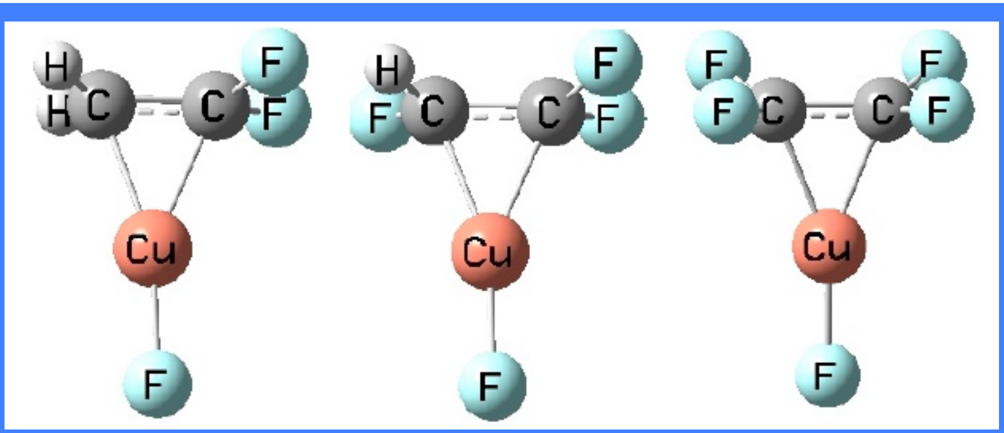
These distortions are also significant in π-complexes, and the effects on the binding energies unexpected!






H C C H Cu F
H C C F Cu F
F C C F Cu F

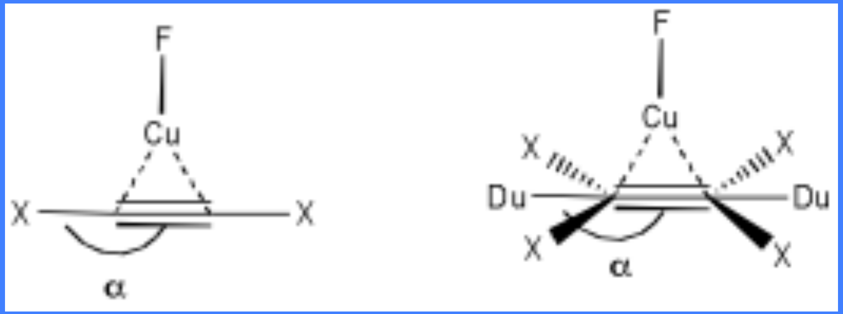

H H C C H H Cu F
F H C C H H Cu F
F H C C F H Cu F
F H C C H F Cu F


H H C C F F Cu F
H F C C F F Cu F
F F C C F F Cu F

Geometry optimizations:
MP2/aug-cc-pVTZ
CCSD(T)/aug-cc-pVTZ (few selected cases)

PCCP 14, 11468 (2012)

Significant distortion of the unsaturated organic moiety



$\alpha \approx 160^o$

But some unexpected results are found!

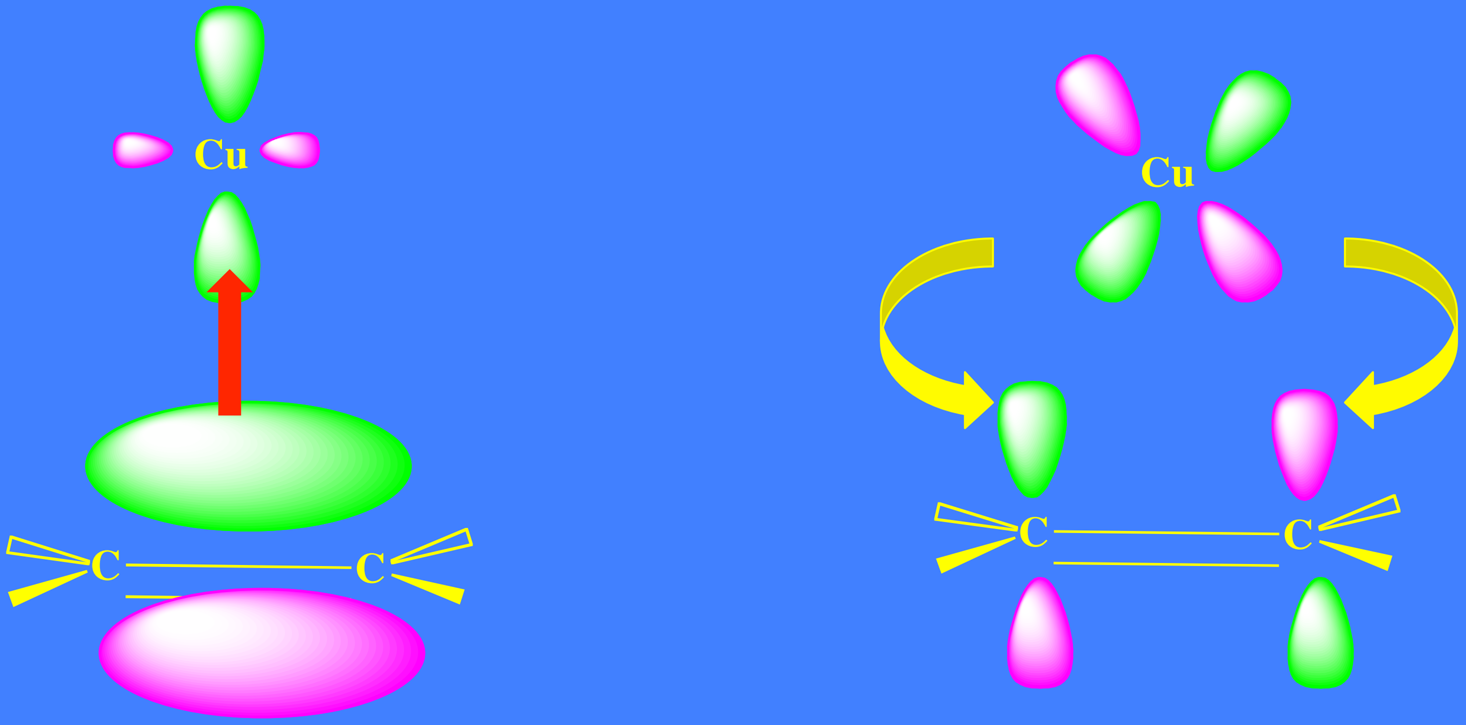
X	E_{int}
HCCH	-166.0
FCCH	-172.3
FCCF	-194.0
$H_2C{=}CH_2$	-169.6
$HFC{=}CH_2$	-154.4
HFC=CHF (*Z*)	-143.6
HFC=CHF (*E*)	-144.5
$H_2C{=}CF_2$	-146.2
$HFC{=}CF_2$	-129.0
$F_2C{=}CF_2$	-140.6

Values in kJ mol^{-1}

Is bonding so different in both series of compounds?

What is the origin of this bonding?

Nothing really new: Dewar–Chatt–Duncanson model



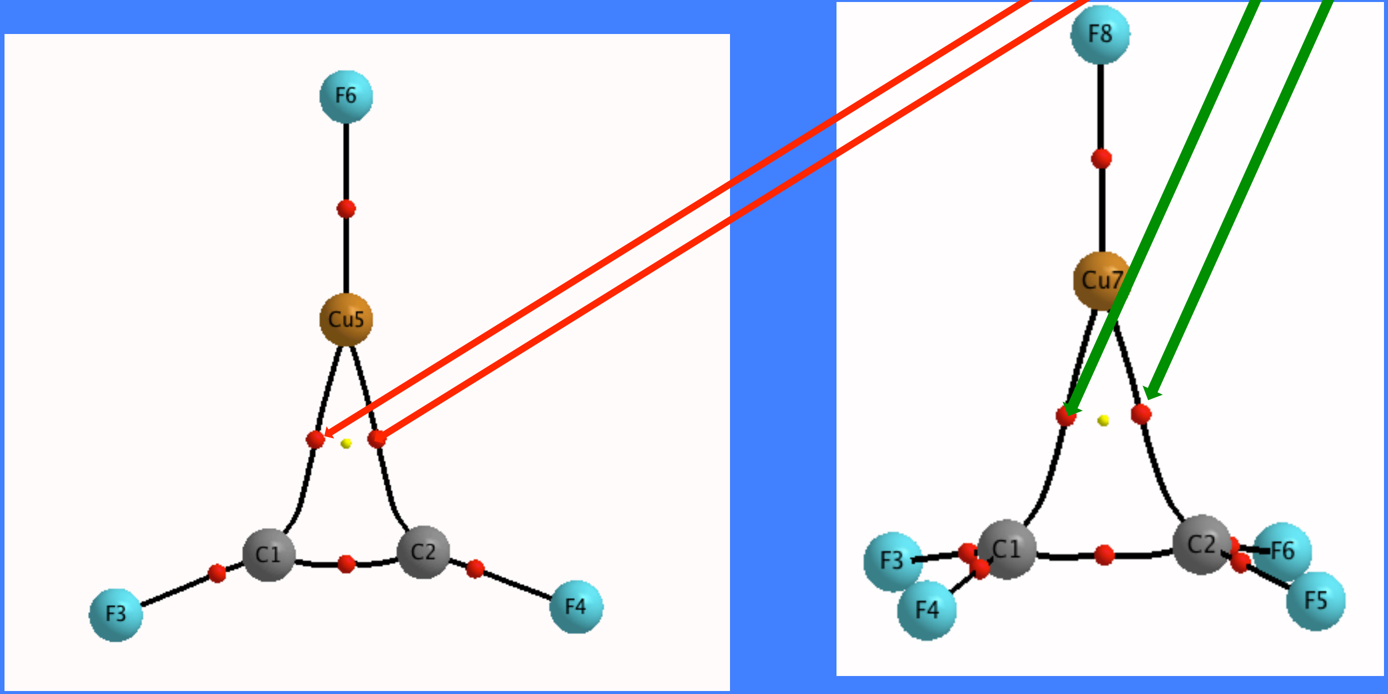
This is indeed ratified by the orbital interaction energies (Second order perturbation NBO)

	$\pi_{CC} \rightarrow$ 4s (Cu)		Cu(LP) $\rightarrow \pi_{CC}^*$
HCCH:CuF	55.4	12.9	26.6
FCCH:CuF	71.3	16.5	30.3
FCCF:CuF	97.5	21.6	36.1
$H_2C{=}CH_2$:CuF	57.7	9.1	31.1
$HFC{=}CH_2$:CuF	60.1	9.7	32.2
HFC=CHF (*Z*):CuF	63.6	10.3	30.9
HFC=CHF (*E*):CuF	65.1	10.9	33.0
$H_2C{=}CF_2$:CuF	61.4	10.9	29.4
$HFC{=}CF_2$:CuF	71.9	12.4	34.1
$F_2C{=}CF_2$:CuF	84.2	15.2	39.8

But the interaction energies go in the same sense for both series of compounds

Values in kJ mol^{-1}

Consistently with the NBO analysis the AIM theory locates a BCP between Cu and each of the C atoms of the unsaturated organic compound.


F6
Cu5
C1
C2
F3
F4
F8
Cu7
C1
C2
F3
F4
F6
F5

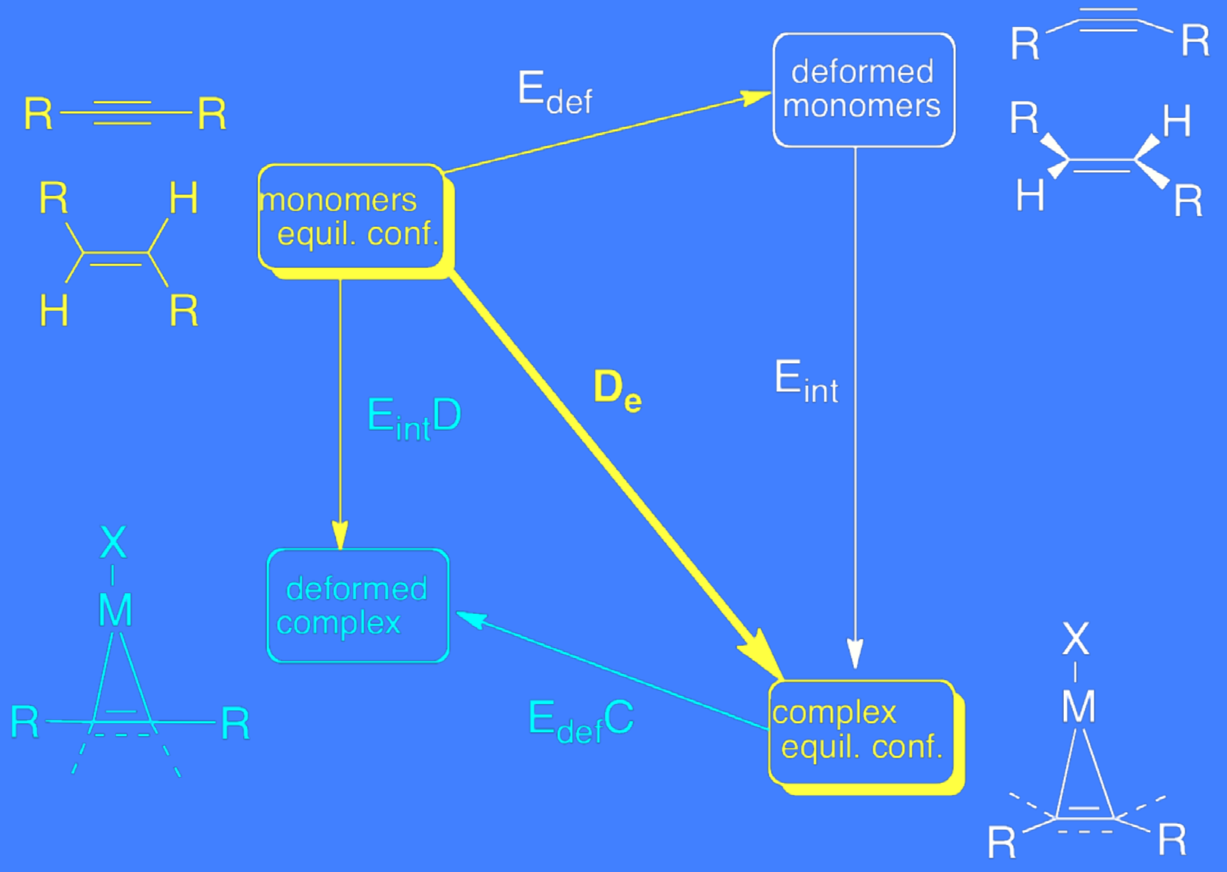
But again in both series the electron density at the Cu-C BCPs INCREASE with the number of fluorine substituents in BOTH series

0	**1**	**2**		**0**	**1**	**2**	**3**	**4**
0.098	**0.106**	**0.111**		**0.090**	**0.091**	**0.093**	**0.096**	**0.098**

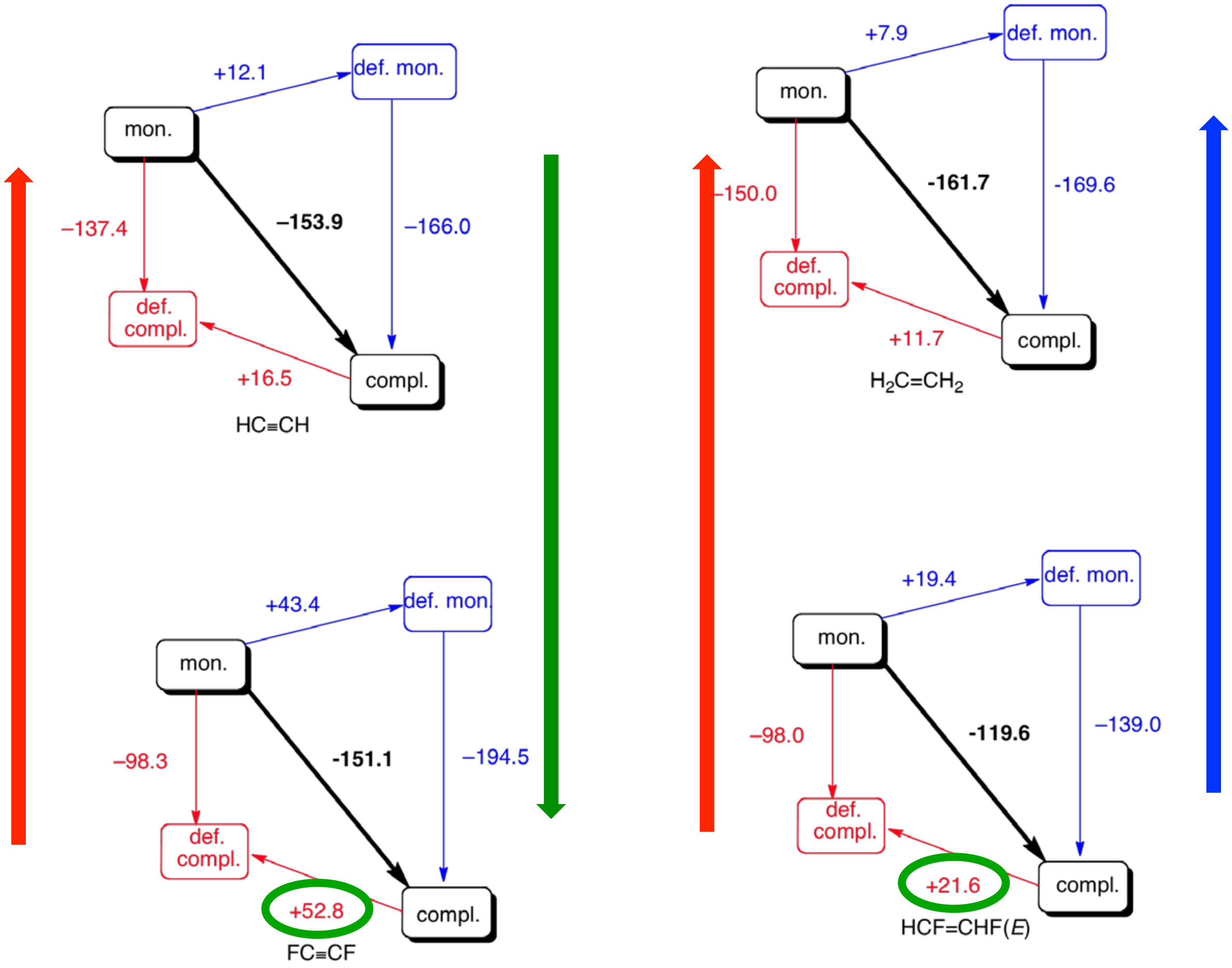
So, no matter which bond descriptor you used the bond seems to reinforced as the number of F subsituents increase in BOTH series…

Why then the interaction energy decreases in the ethylene series?

Once more, these trends can only be explained if the effect of the deformation is taken into account


R
R
R
H
H
R
E_{def}
deformed monomers
R
R
R
H
H
R
monomers equil. conf.
$E_{int}D$
D_e
E_{int}
X
M
R
R
deformed complex
$E_{def}C$
complex equil. conf.
X
M
R
R

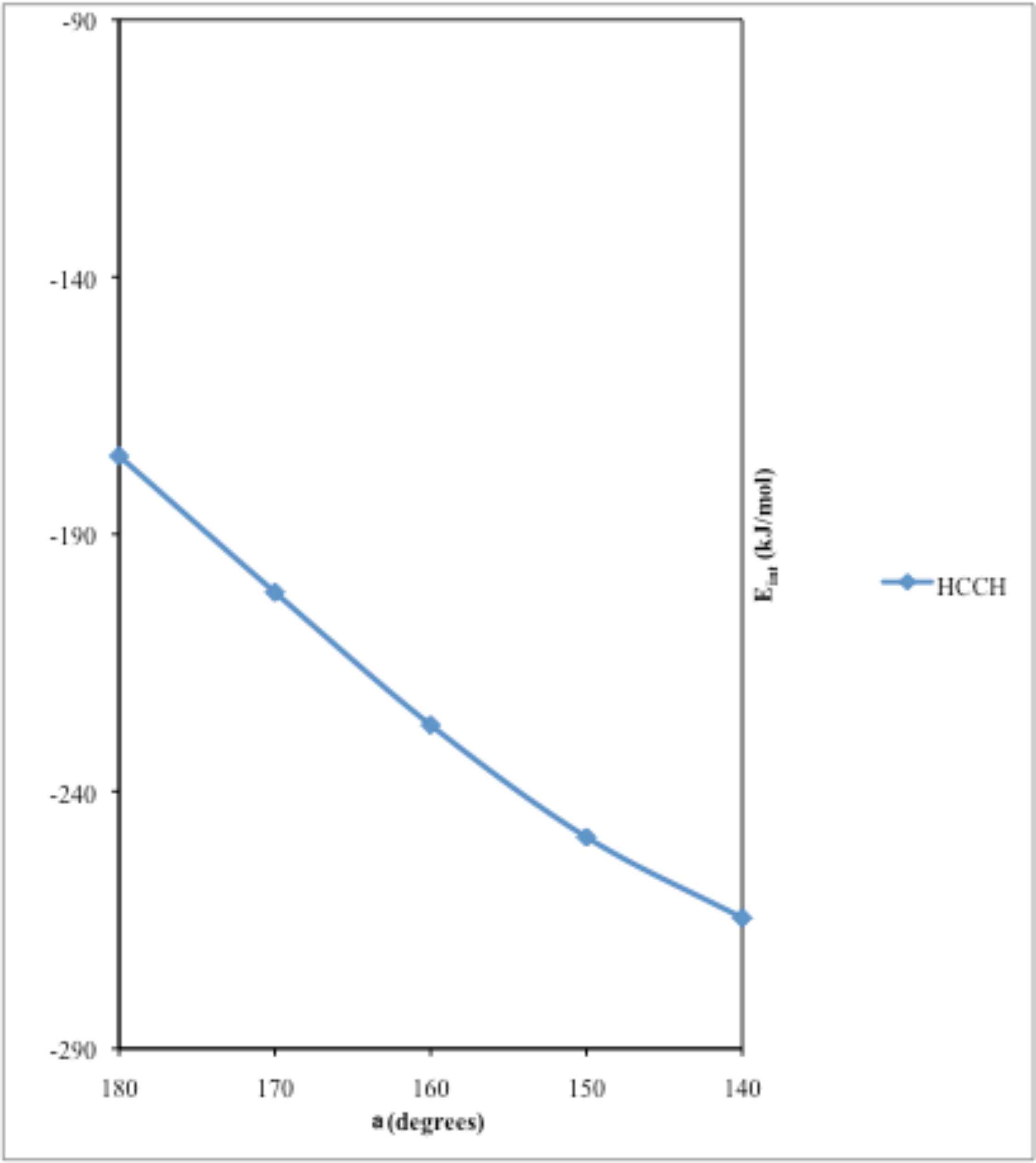
PCCP 14, 11468 (2012)

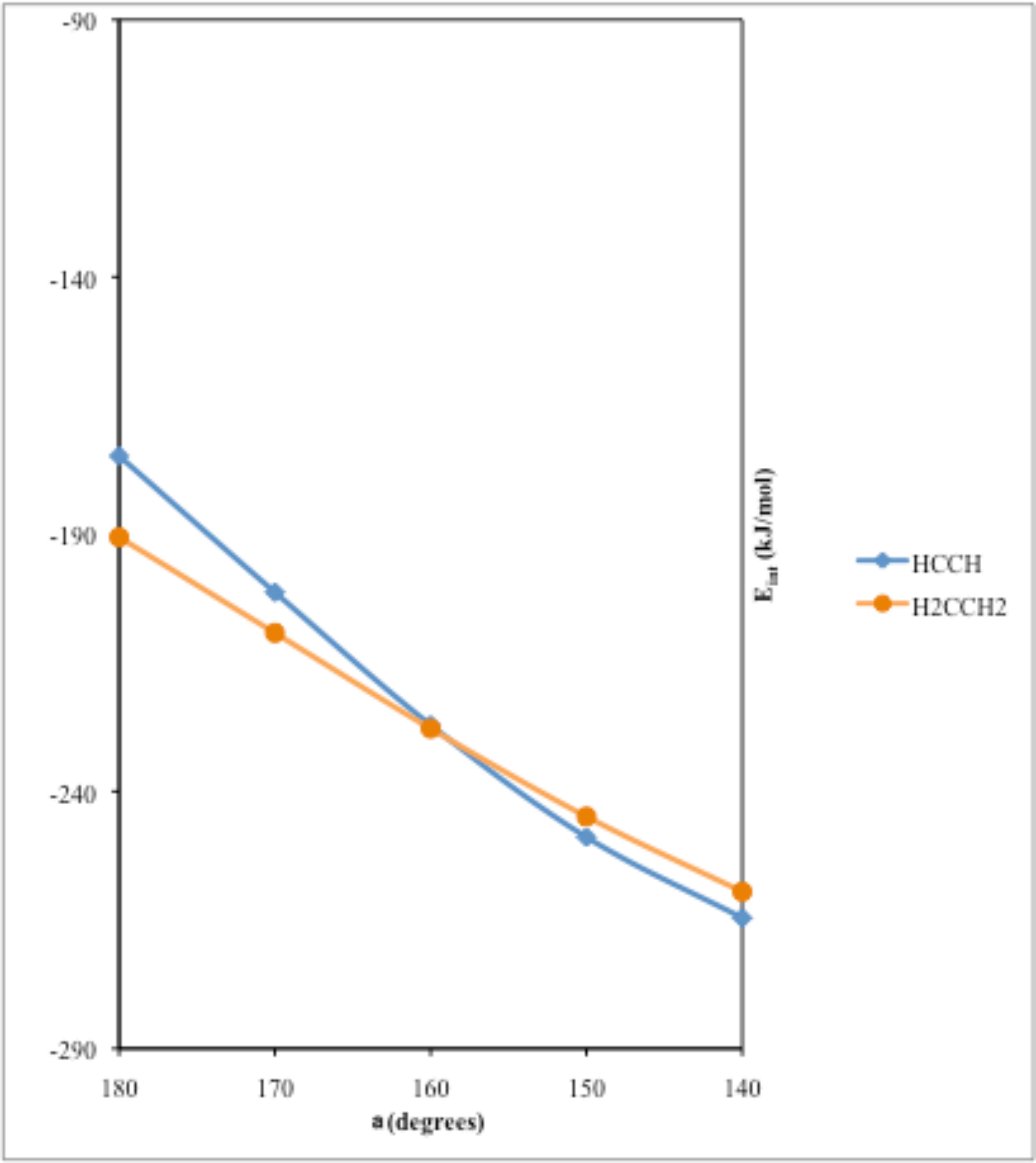


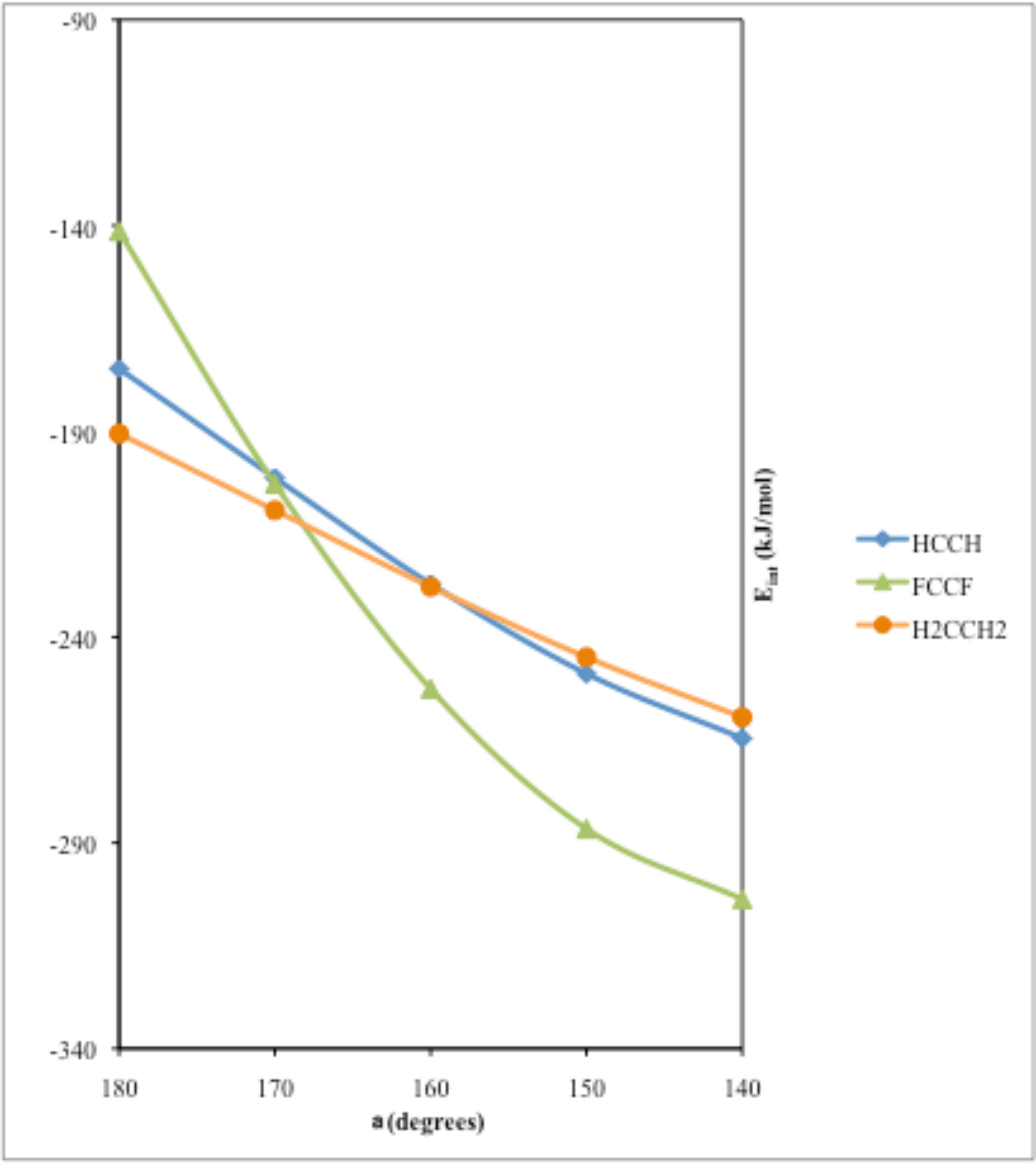
mon.
def. mon.
+12.1
–153.9
–166.0
–137.4
def. compl.
+16.5
compl.
HC≡CH
mon.
def. mon.
+7.9
-161.7
-169.6
-150.0
def. compl.
+11.7
compl.
$H_2C{=}CH_2$
mon.
def. mon
+43.4
-151.1
–194.5
–98.3
def. compl.
+52.8
compl.
FC≡CF
mon.
def. mon.
+19.4
-119.6
–139.0
–98.0
def. compl.
+21.6
compl.
HCF=CHF(*E*)

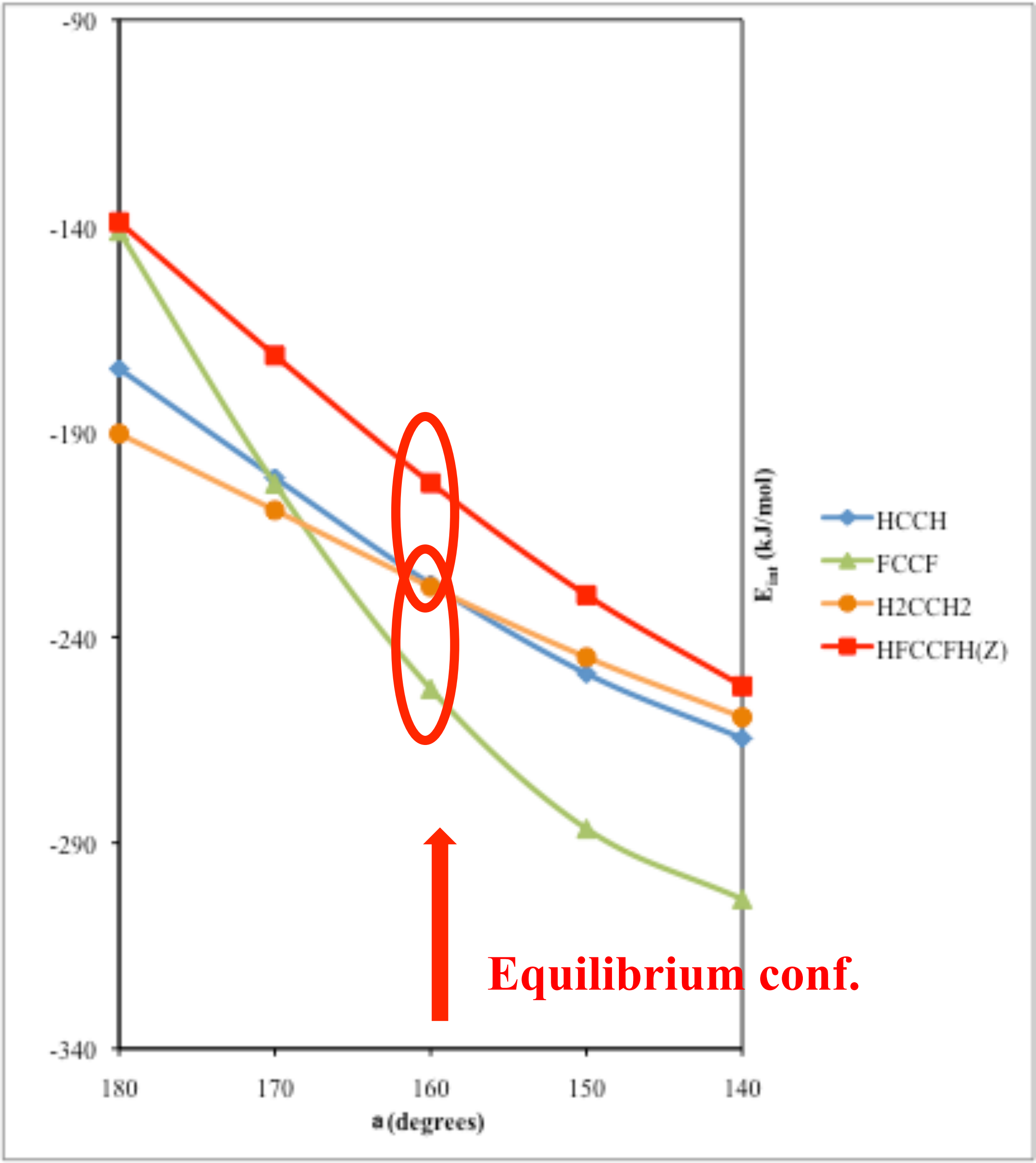
But why this happens?

How does the interaction energy vary with deformation?


-90
-140
-190
-240
-290
180
170
160
150
140
a (degrees)
E_{int} (kJ/mol)
HCCH


-90
-140
-190
-240
-290
180
170
160
150
140
a (degrees)
E_int (kJ/mol)
HCCH
H2CCH2


-90
-140
-190
-240
-290
-340
180
170
160
150
140
a (degrees)
E_{int} (kJ/mol)
HCCH
FCCF
H2CCH2



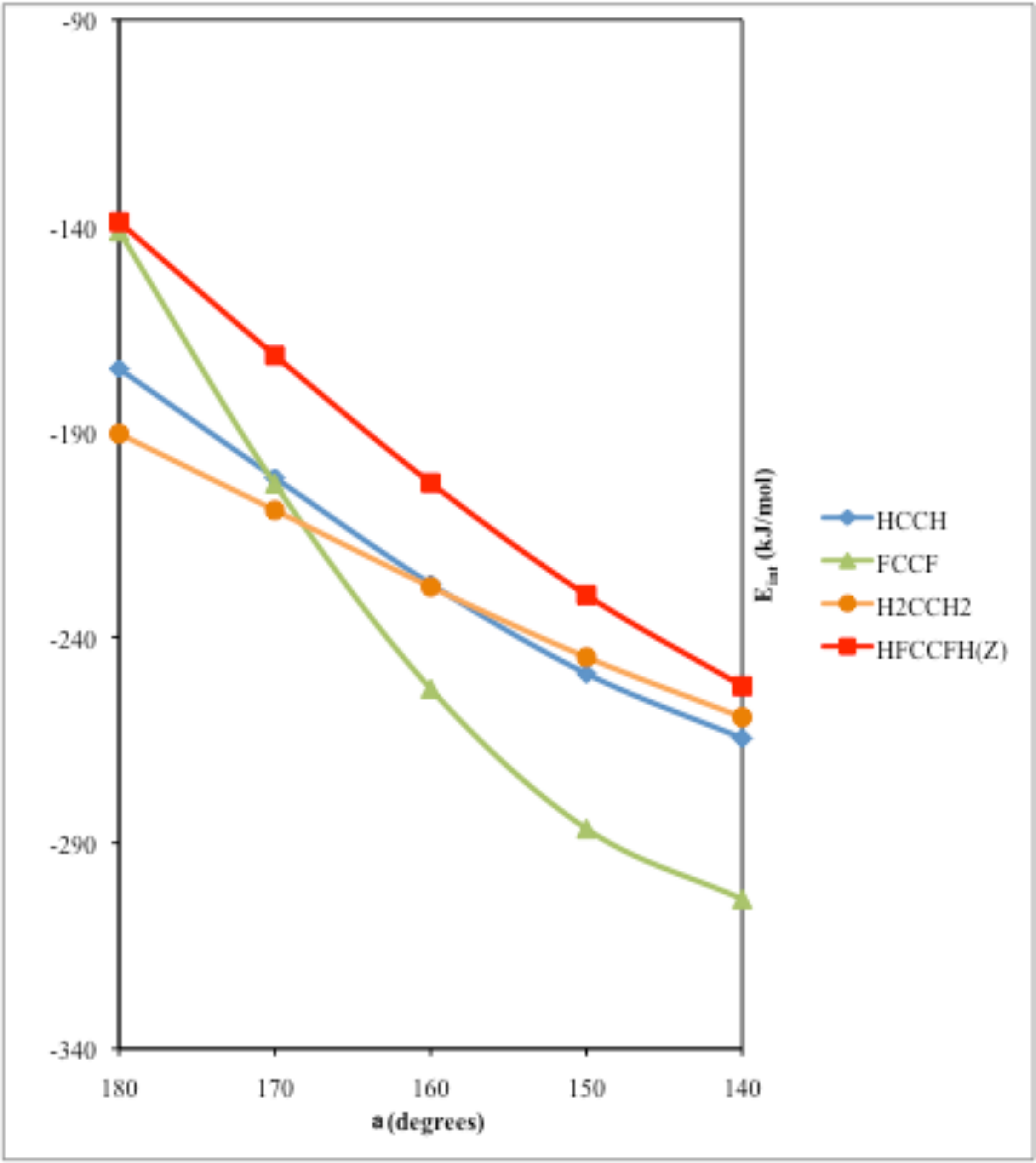
Equilibrium conf.

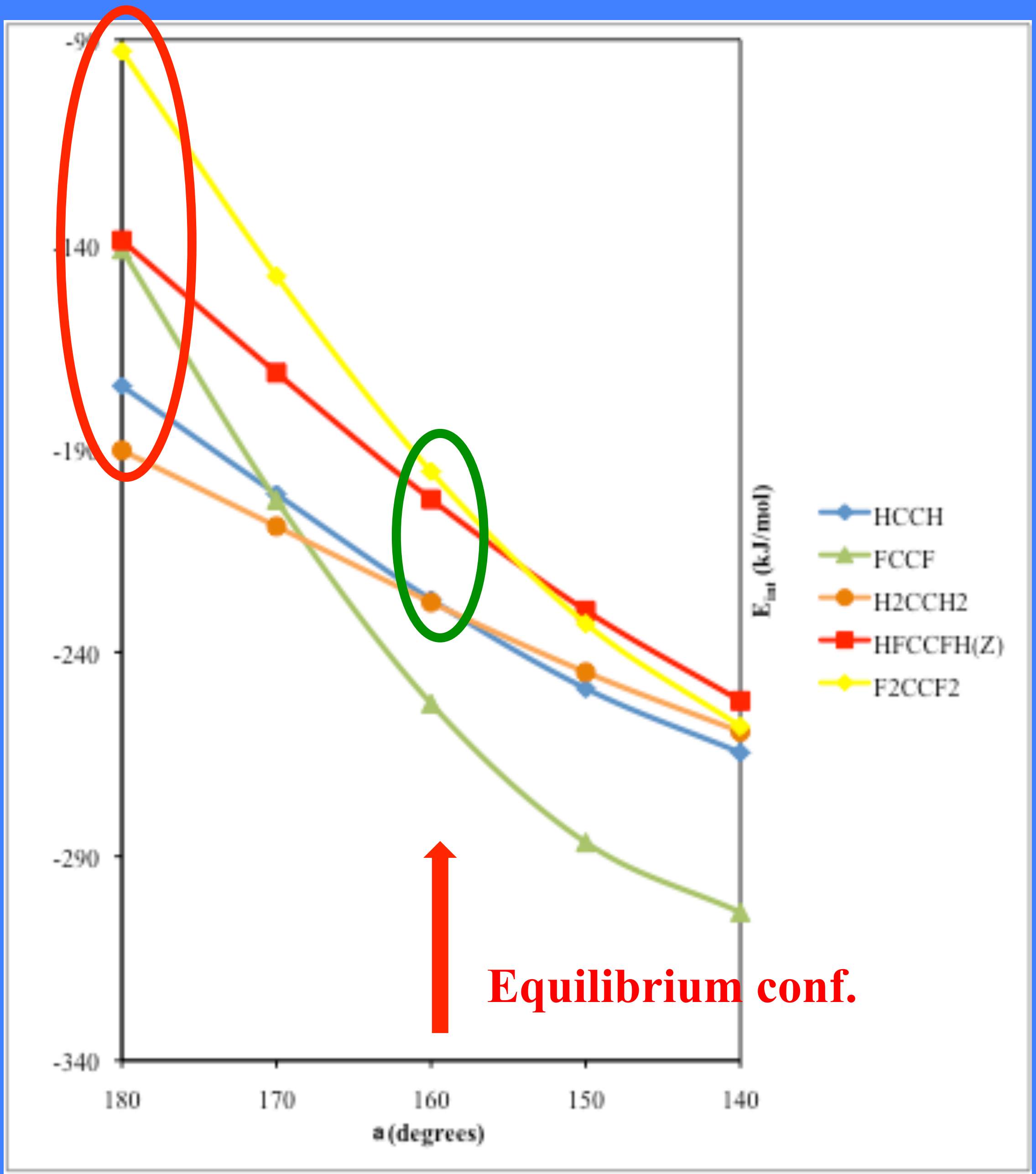
Why the energetic effects are larger for FCCF than for FHCCHF ?

Deformation → change in hybridization → change in the electronegativity of the C atoms

But we have seen, when using the analysis in terms of atomic energy components that the presence of H atoms mitigates the energetic consequences of these density redistributions…..

This would explain the difference between FCCF and FCHCHF; but what about CF_2=CF_2?, why its interaction energy is smaller than that of CH_2=CH_2?


-90
-140
-190
-240
-290
-340
180
170
160
150
140
a (degrees)
E_{int} (kJ/mol)
HCCH
FCCF
H2CCH2
HFCCFH(Z)



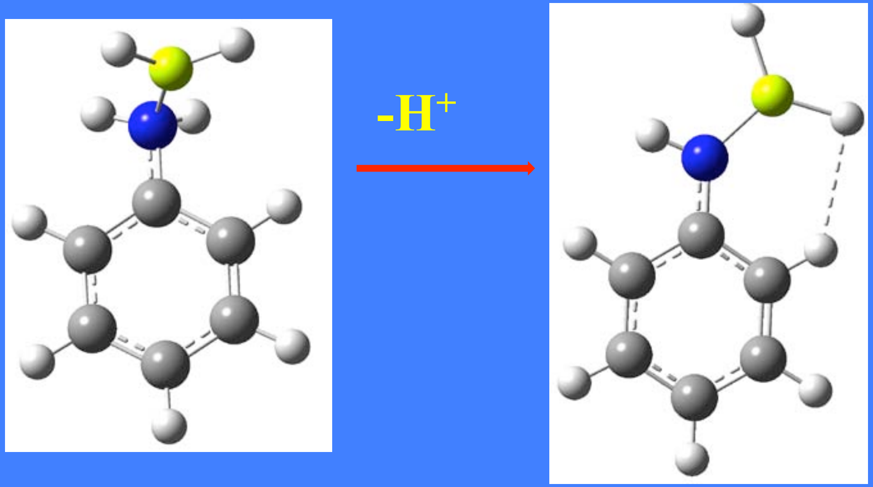
Equilibrium conf.

Dramatic effects on the intrinsic properties

The reinforcement of the HBs in imidazole dimer by Be bonds was related with its acidity enhancement. Can we quantify this acidity enhancement?

Aniline is a good base in the gas phase and a weak acid:
$\Delta_{acid}G$= 1502. ± 8.4 kJ mol^{-1} G4 estimate: 1506.7 kJ mol^{-1}

Our G4 prediction for the corresponding aniline-BeH_2:



$\Delta_{acid}G$= 1355.3 kJ mol^{-1}

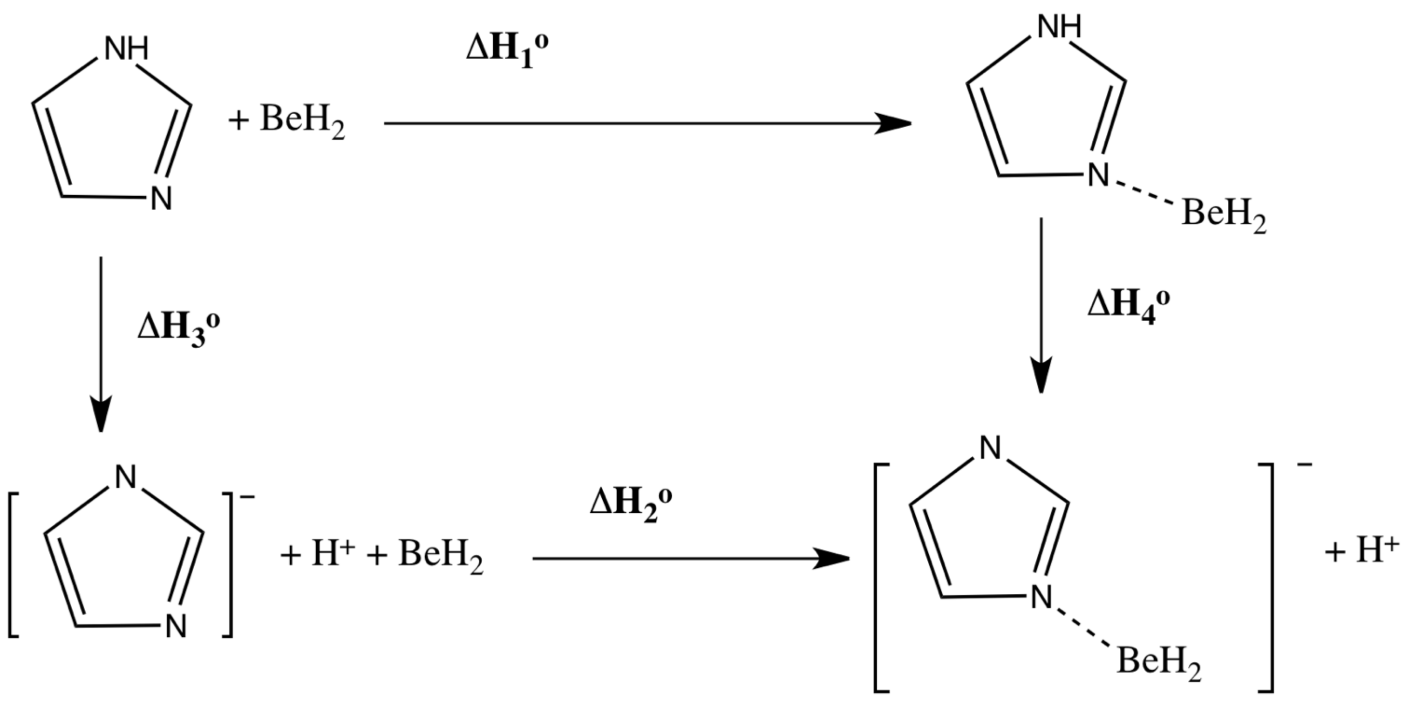
An acidity increase of 150 kJ mol^{-1}!

16 orders of magnitude in terms of the ionization equilibrium constant!!

As strong as Phosphoric acid!!
Much stronger than formic, acetic, oxalic…. acids

Why?

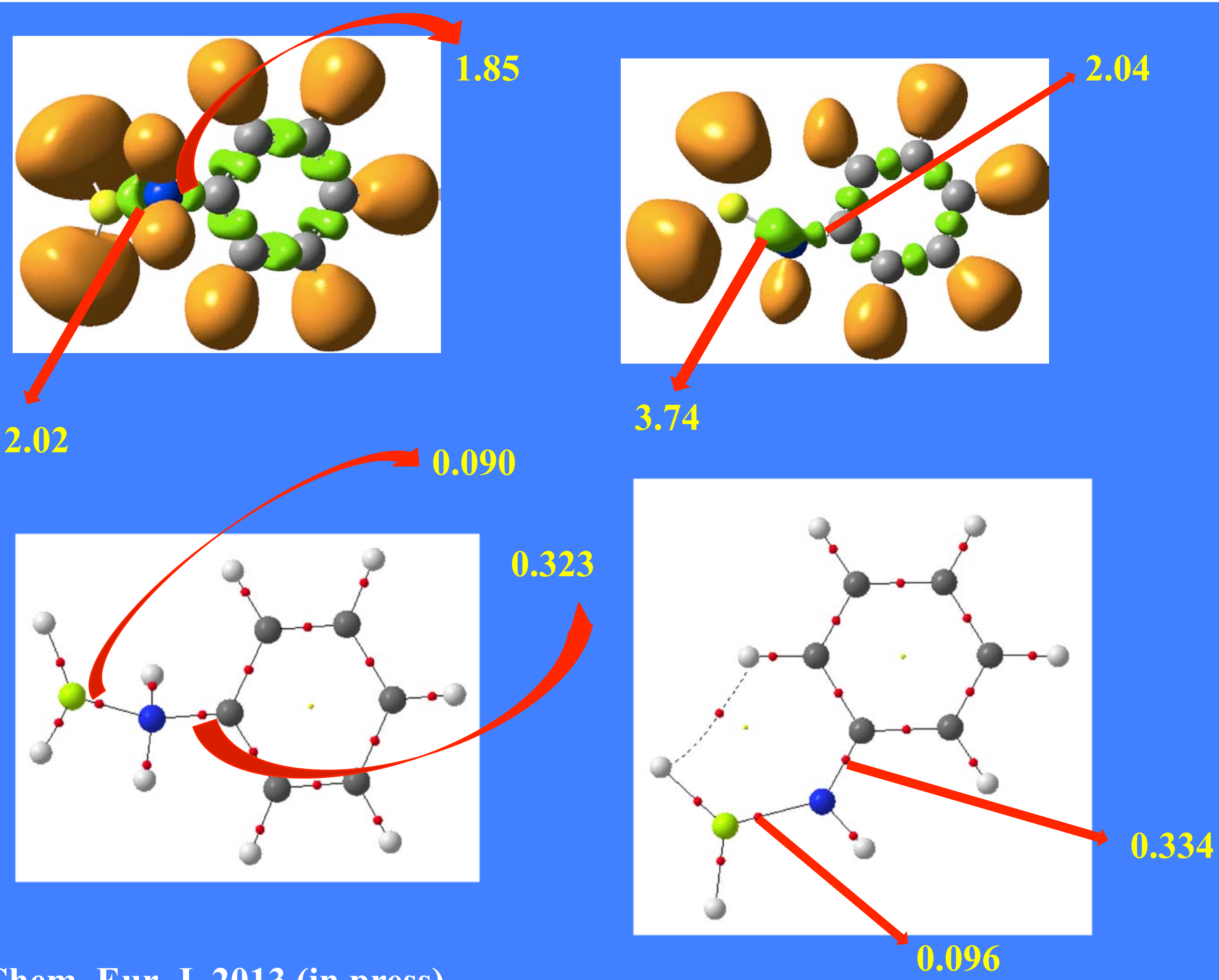
Chem. Eur. J. 2013 (in press)


NH
+ BeH2
ΔH1o
NH
N
N
BeH2
ΔH3o
ΔH4o
N
N
−
+ H+ + BeH2
ΔH2o
N
N
BeH2
−
+ H+

ΔH^0_3 intrinsic acidity of the free amine
ΔH^0_4 intrinsic acidity of the amine-BeH_2 complex
ΔH^0_1 stabilization of the free amine upon BeH_2 attachment
ΔH^0_2 stabilization of the deprotonated free amine upon BeH_2 attachment

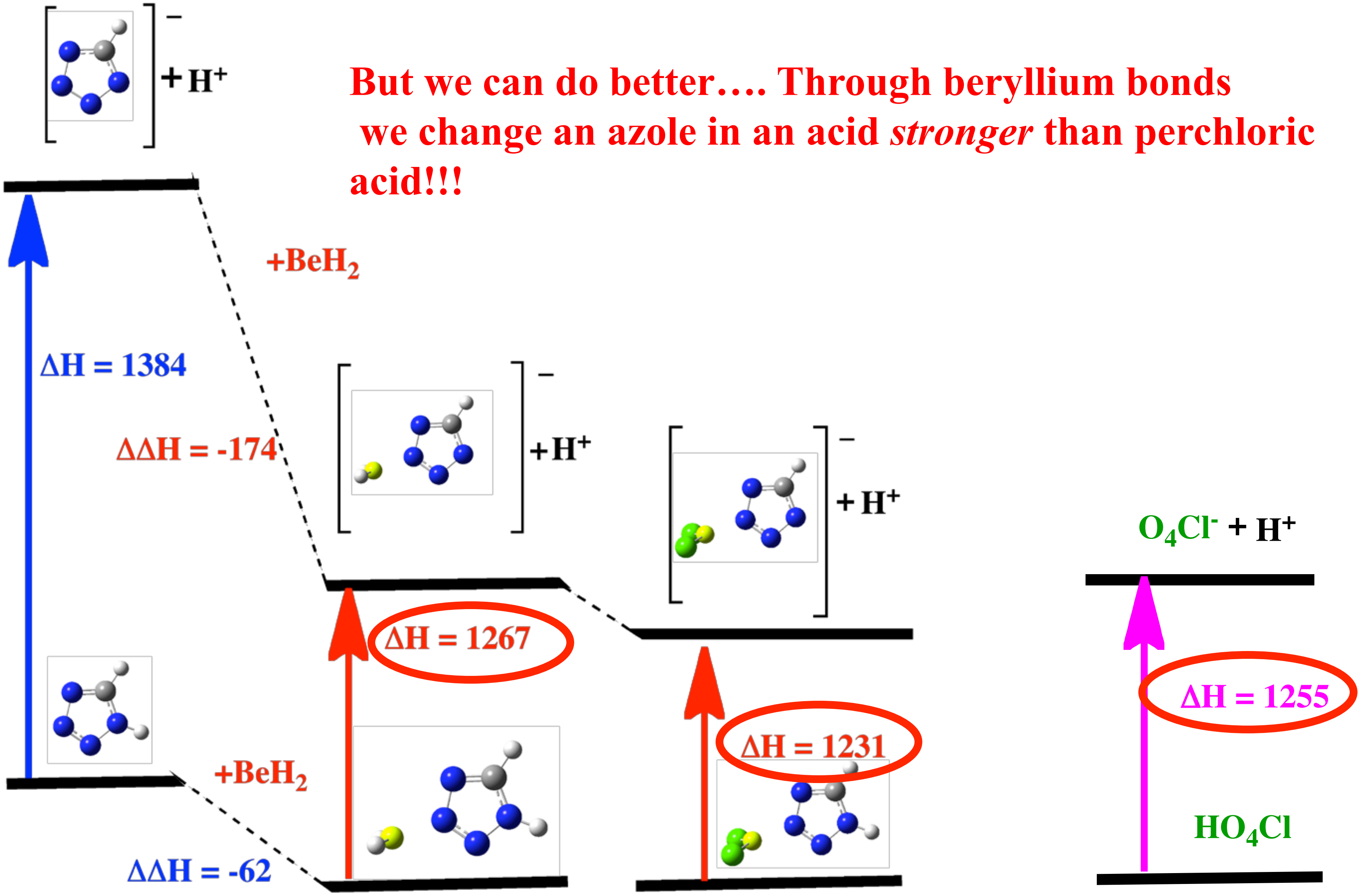
ΔH^0_2 (261 kJ mol^{-1}) >> ΔH^0_1 (88 kJ mol^{-1})

Chem. Eur. J. 2013 (in press)


1.85
2.04
2.02
3.74
0.090
0.323
0.334
0.096

Chem. Eur. J. 2013 (in press)

But we can do better…. Through beryllium bonds we change an azole in an acid *stronger* than perchloric acid!!!



$[\ ]^-$ + H^+

+BeH_2

$\Delta H = 1384$

$\Delta\Delta H = -174$

$[\ ]^-$ + H^+

$[\ ]^-$ + H^+

O_4Cl^- + H^+

$\Delta H = 1267$

$\Delta H = 1255$

$\Delta H = 1231$

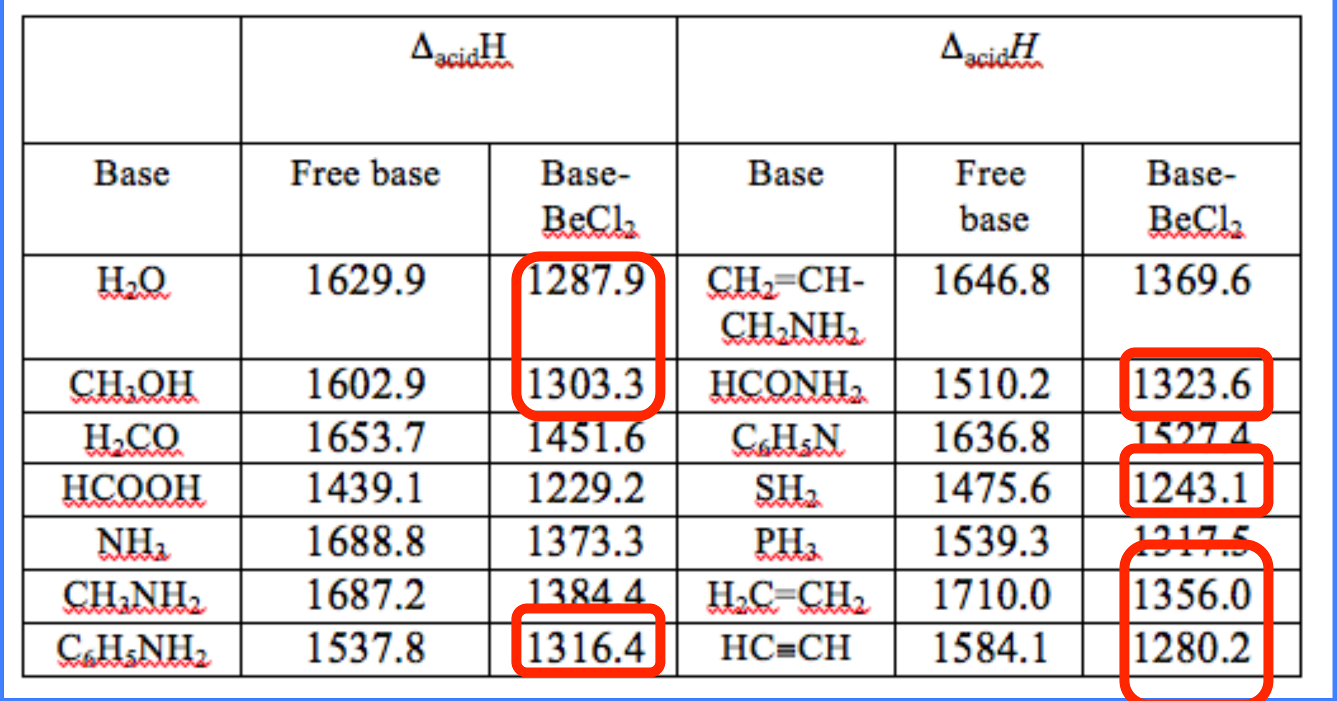
+BeH_2

HO_4Cl

$\Delta\Delta H = -62$

All values in kJ/mol

But this is a general phenomenon !



	$\Delta_{acid}H$		$\Delta_{acid}H$		
Base	Free base	Base-$BeCl_2$	Base	Free base	Base-$BeCl_2$
H_2O	1629.9	1287.9	CH_2=CH-CH_2NH_2	1646.8	1369.6
CH_3OH	1602.9	1303.3	$HCONH_2$	1510.2	1323.6
H_2CO	1653.7	1451.6	C_6H_5N	1636.8	1527.4
HCOOH	1439.1	1229.2	SH_2	1475.6	1243.1
NH_3	1688.8	1373.3	PH_3	1539.3	1317.5
CH_3NH_2	1687.2	1384.4	$H_2C=CH_2$	1710.0	1356.0
$C_6H_5NH_2$	1537.8	1316.4	HC≡CH	1584.1	1280.2

Water, methanol and SH_2 become stronger acids than sulfuric acid ($\Delta_{acid}H = 1295 \pm 23$ kJ mol^{-1})

Aniline or formamide become more acidic than phosphoric acid ($\Delta_{acid}H = 1383. \pm 21.$ kJ mol^{-1})

Unsaturated hydrocarbons such as ethylene and acetylene become almost as acidic as formic and oxalic acids ($\Delta_{acid}H = 1356 \pm 8$ kJ mol^{-1})

Chem. Eur. J. 2013 (in press)

Conclusions

The interactions between closed-shell systems usually involved a certain amount of charge transfer from one subunit (acting as a Lewis base) to the other (acting as a Lewis acid).

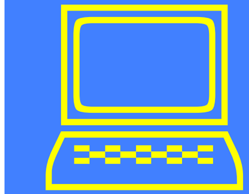
This charge transfer changes the electron distribution of the Lewis acid and leads to its deformation:
Hydrogen bonds ➔ lengthening of the XH bond of the HB donor (spontaneous proton transfer)
Beryllium bonds ➔ bending of the BeX_2 moiety and lengthening of the Be-X bonds.

More importantly:
deformation
i) Is crucial to understand the strength of the bonding
ii) To understand cooperativity
iii) Changes dramatically the chemical properties of the system

Two paradigmatic examples:
When two closed-shell interactions appear in the same system they mutually influence
Beryllium bonds may change a typical N base in a NH acid stronger than the strongest oxyacids.

Acknowledgements

Leticia González (Univ. of Vienna)
Goar Sánchez-Sanz (CSIC, Madrid)
Ibón Alkorta (CSIC, Madrid)
José Elguero (CSIC, Madrid)
Janet E. Del Bene (Youngstown Univ.)
Al Mokhtar Lamsabhi (UAM)
Ana Martín-Sómer (UAM)
Merche Montero-Campillo
Jean-Claude Guillemin (Ecole Sup. De Chimie de Rennes)
Juan Dávalos (Ito. Rocasolano, CSIC; Madrid)
Laura Albrecht (Dalhousie Univ.)
Russell J. Boyd (Dalhousie Univ.)
Otilia Mó (UAM)



Centro de Computación Científica de la UAM and the Ohio Supercomputer Center,

CTQ2006-08558/BQU; COST CM0702, Project MADRISOLAR, Ref.: S-0505/PPQ/0225, Consolider on Molecular Nanoscience , CSD2007-00010

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