Improper, Blue-Shifting Hydrogen Bonds 1998-2005

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X-H…Y H-bond

- X-H stretches
- Small ammount of el. density (~0.01e) transferred from Y to proton donor
- The band corresponding to X-H stretch shifts to lower frequency (red shift), increases in intensity and broadens
- Red shift – fingerprint of H-bonding

„no red shift – no stabilization” rule

X-H…Y H-bond

Electrostatic and charge-transfer models

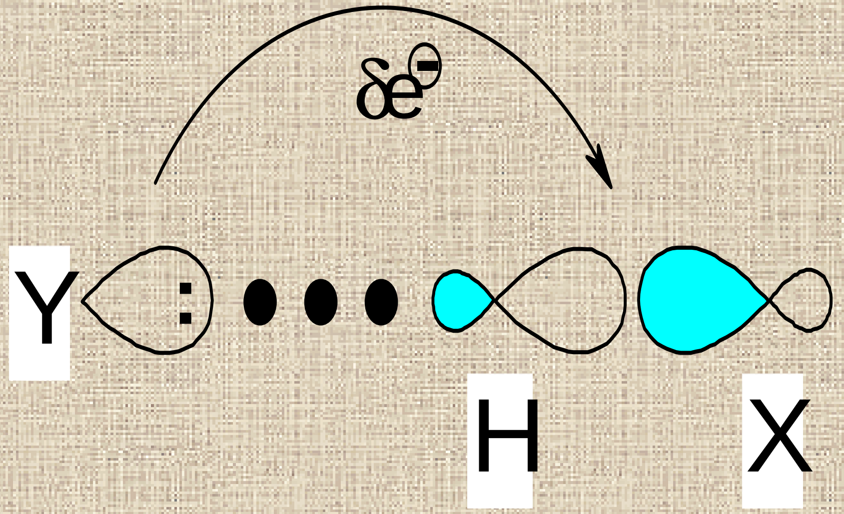
El.m. - elongation of X-H increase the μ of proton donor → larger attraction between donor and accptor

CT m. – hyperconjugation

Increase in intensity of the X-H stretching vibration cannot be explained without allowing el. transfer

(Coulson 1957)

Concept of CT proven by NBO analysis



Charge-transfer from Y (lone el. pairs or π-electrons) to σ* orbitals of XH *(hyperconjugation)* ⇒weakening of XH bond accompanied by its elongation and a concomitant decrease of the X-H strech vibration frequency – red shift

G.A.Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press:New York, 1997.

S.Scheiner, Hydrogen Bonding, Oxford University Press:New York, 1997.

G.R.Desiraju, T.Steiner, An Introduction to Hydrogenn Bonding, Oxford University Press: Oxford, 1999.

More than 3000 references covering the area of H-bonding -

no evidence about violation of red-shift rule

Violation of the red shift rule – experimental evidence

G.T.Trudeau,J.M.Dumas,P.Dupuis, M.Guerin, C.Sandorfy: Top. Curr. Chem. 93, 91 (1980)

fluoroparafins with $-CHF_2$ with various proton acceptors → blue shift of υ(C-H)

M.Buděšinský, P.Fiedler, Z.Arnold: Synthesis 858 (1989)

complexation of chloroform with triformylmethane

→ blue shift of υ(C-H)

I.E.Boldeskul et al, THEOCHEM 167, 436 (1997)

chloroform, bromoform with various proton acceptors

→ blue shift of υ(C-H)

First systematic theoretical study of blue shifts of the X-H stretch frequencies in X-H…Y complexes

- *P.Hobza, V.Špirko, H.L.Selzle, E.W.Schlag: JPC A 102, 2501 (1998)*

  benzene…H-X (X=CH_3, CCl_3, C_6H_5)

  anti-hydrogen bond
- *P.Hobza, Z.Havlas: Chem. Rev. 100, 4253 (2000)*

  improper, blue-shifting hydrogen bond
- *More than 1000 references in ICI*

X-H…Y H-bond

	standard	improper
r	increase	decrease
υ	red shift	blue shift
$-\Delta E$	1 - 15	1 - 10
X	O,N,F,C,…	O,N,F,C,…
Y	lone pairs, π el.	lone pairs, π el.
CT	~0.01	~0.01
SAPT	el., ind.	el., disp.

Nature of IBS H-bonding

Electrostatic

Halogenated hydrocarbons $d\mu/dr_{XH} < 0$

PH,ZH: CPL303, 447, 1999; Dannenberg, Masunov, Hermansson

WZ, PJ, PH: ChemPhysChem 6, 609, 2005

11 H-bonded and 11 IBS H-bonded complexes

Optimization of the structure of proton donor in the inhomogenous el. field generated by point charges of the proton acceptor

In 10 H-bonded complexes the electrostatic term is dominant

In 5 IBS H-bonded complexes the nonelectrostatic terms are dominant

El. field of proton acceptor cannot explain different behaviour of H-bonded and IBS H-bonded complexes

Nature of IBS H-bonding

Charge transfer

In all 11 H-bonded complexes the ED in δ* X-H orbital increased (this is valid without exception for all H-bonded complexes)

- CT and electrostatics are acting in the same direction

Nature of IBS H-bonding

In 7 IBS H-bonded complexes the ED in δ* X-H orbital decreased

How to explain this decrease?

Electron density redistribution in proton donor upon formation of complex plays a key role

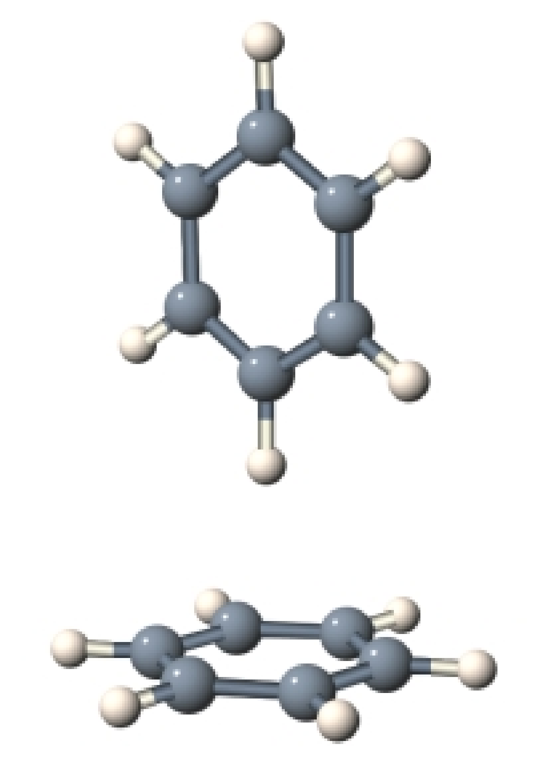
Nature of IBS H-bonding

- Neither El nor CT explain unambiguously the nature of IBS H-bonding (contrary to H-bonding) →

  another factor plays a role

Nature of IBS H-bonding

Dispersion energy

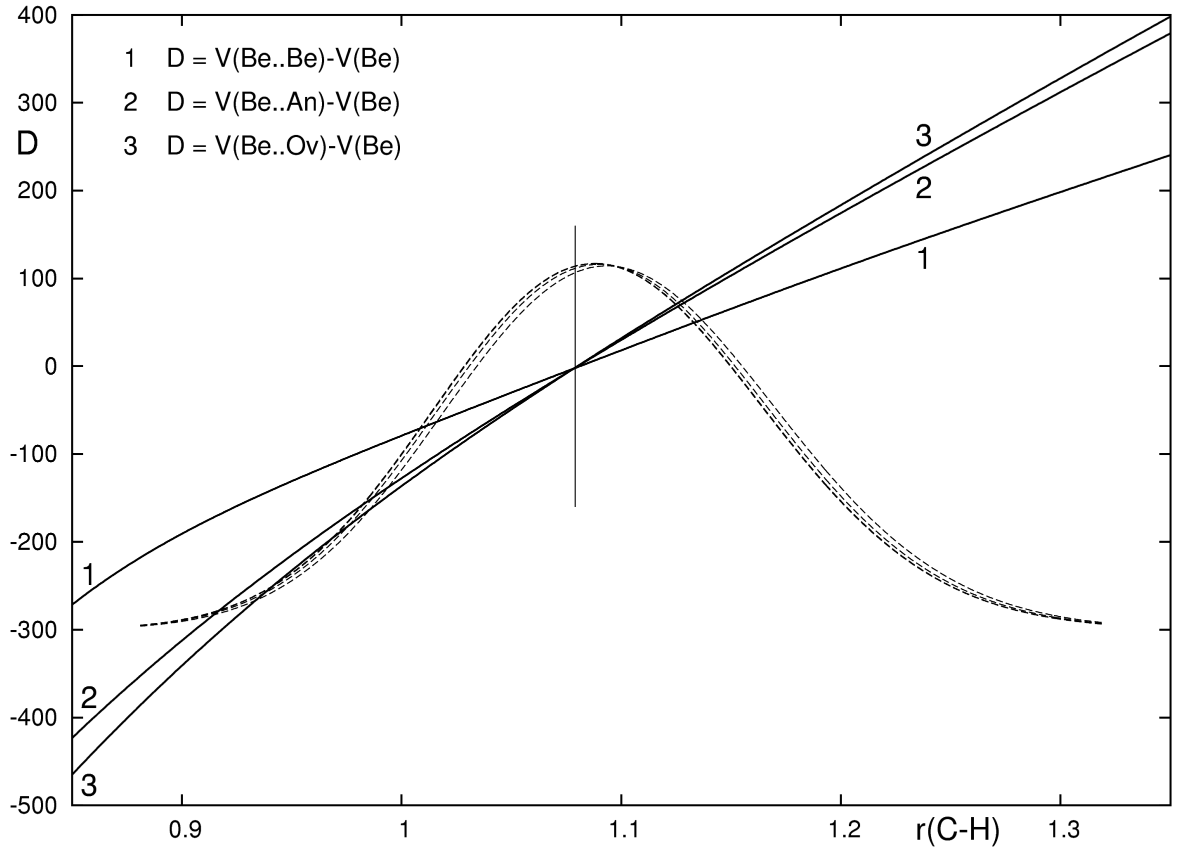


	$-\Delta E$	$-\Delta r$	$\Delta\upsilon$
Benzene	1.18	0.0035	27.7 (29.1)
Antracene	2.25	0.0052	41.6 (40.6)
Ovalene	2.87	0.0055	42.9 (40.8)

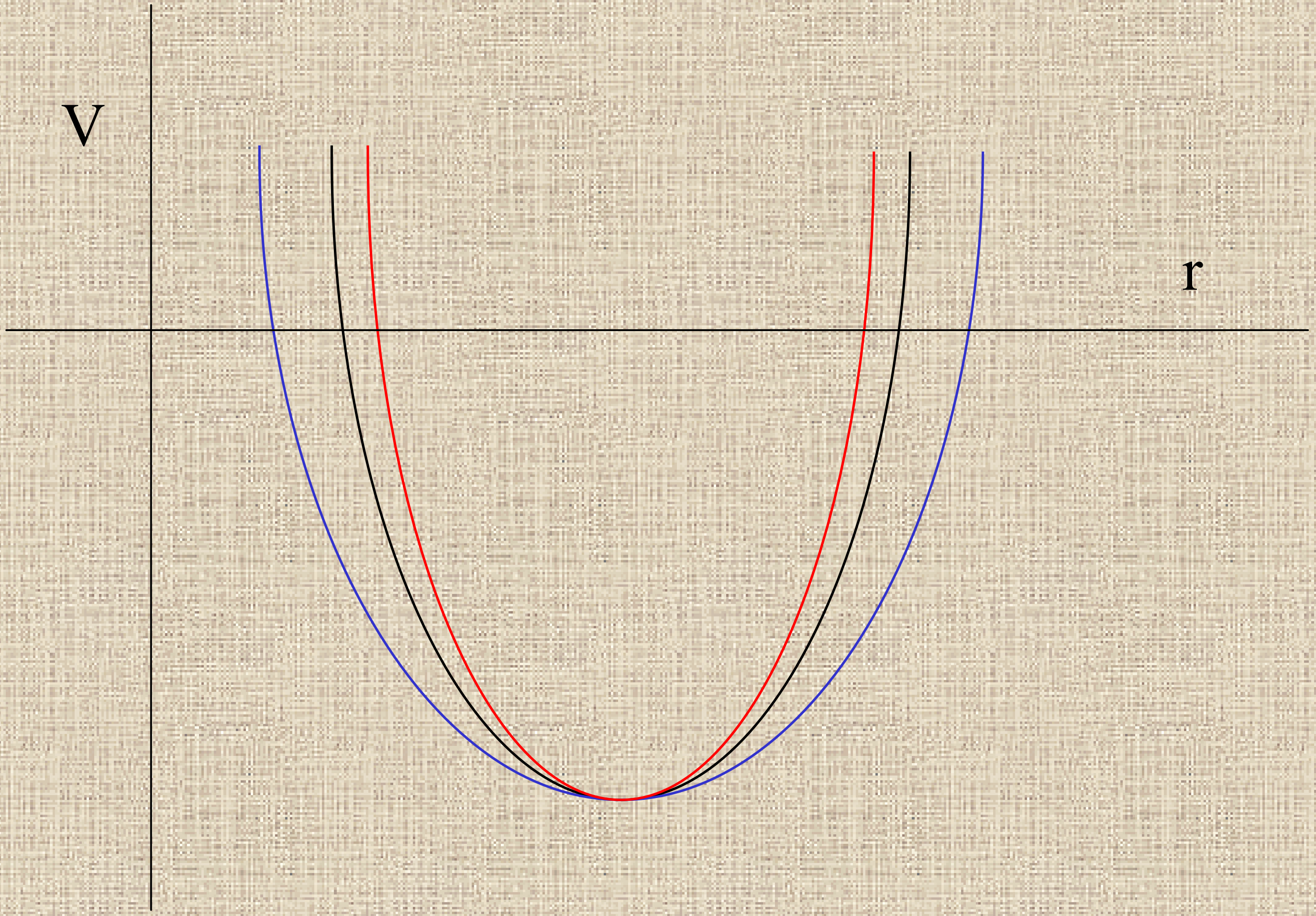
kcal/mol; Ǻ; cm-1

$\Delta\delta^* \sim 0$; $E^{el} \sim 0$; CT to B, A, O proton donors identical → only $\mathbf{E^{Disp}}$

Differences in dimer and monomer potentials (in cm^{-1}) and anharmonic vibrational wave function



Harmonic potential energy curve



Conclusions

El. field (electrostatic model) explains in many cases the nature of IBS H-bonding by negative derivatives of dipole moment; electrostatic itself cannot explain differences between both H-bondings

Hyperconjugation fully explained H-bonding but says nothing about IBS H-bonding; ED redistribution explain the nature of IBS H-bonding

IBS H-bonding in systems where neither electrostatic nor ED redistribution play a role is explained by dispersion energy (repulsion wall)

Nature of H-bonding and IBS H-bonding is different

- Under present definition H-bonding and IBS H-bonding represent different phenomena
- H-bond : hydrogen between two electronegative atoms and with one of them it is covelently bound

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