Improper, Blue-Shifting Hydrogen Bonds 1998-2005

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X-H...Y H-bond

- X-H stretches
- Small amount 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 \( \mu \) of proton donor → larger attraction between donor and acceptor

*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 \(\pi\)-electrons) to \(\sigma^*\) orbitals of XH

\(\text{(hyperconjugation)}\) \(\Rightarrow\) weakening of XH bond
accompanied by its elongation and a concomitant decrease of the X-H strech vibration frequency – red shift

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.Sandorfý:
fluoroparafins with –CHF₂ with various proton acceptors
→ blue shift of υ(C-H)

complexation of chloroform with triformylmethane
→ blue shift of υ(C-H)

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

  benzene...H-X (X=CH₃, CCl₃, C₆H₅)
  anti-hydrogen bond
  improper, blue-shifting hydrogen bond
- More than 1000 references in ICI
## X-H...Y H-bond

<table>
<thead>
<tr>
<th></th>
<th>standard</th>
<th>improper</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$</td>
<td>increase</td>
<td>decrease</td>
</tr>
<tr>
<td>$\nu$</td>
<td>red shift</td>
<td>blue shift</td>
</tr>
<tr>
<td>$-\Delta E$</td>
<td>1 - 15</td>
<td>1 - 10</td>
</tr>
<tr>
<td>$X$</td>
<td>O,N,F,C,…</td>
<td>O,N,F,C,…</td>
</tr>
<tr>
<td>$Y$</td>
<td>lone pairs, $\pi$ el.</td>
<td>lone pairs, $\pi$ el.</td>
</tr>
<tr>
<td>CT</td>
<td>~0.01</td>
<td>~0.01</td>
</tr>
<tr>
<td>SAPT</td>
<td>el., ind.</td>
<td>el., disp.</td>
</tr>
</tbody>
</table>
Nature of IBS H-bonding

**Electrostatic**
Halogenated hydrocarbons  \( \frac{d\mu}{dr_{XH}} < 0 \)

*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 $\delta^* X-H$ 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 $\delta^*$ 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

<table>
<thead>
<tr>
<th></th>
<th>$-\Delta E$</th>
<th>$-\Delta r$</th>
<th>$\Delta \nu$</th>
<th>$\text{kcal/mol}$; Å; cm$^{-1}$</th>
<th>$\Delta \delta^*$</th>
<th>$E^{cl}$</th>
<th>CT to B, A, O proton donors identical</th>
<th>$\rightarrow$ only $E^{\text{Disp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.18</td>
<td>0.0035</td>
<td>27.7 (29.1)</td>
<td></td>
<td>~ 0</td>
<td>~ 0</td>
<td></td>
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<tr>
<td>Antracene</td>
<td>2.25</td>
<td>0.0052</td>
<td>41.6 (40.6)</td>
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<td></td>
<td></td>
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<tr>
<td>Ovalene</td>
<td>2.87</td>
<td>0.0055</td>
<td>42.9 (40.8)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
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 covalently bound
Acknowledgements

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