SUPRAMOLECULAR CHEMISTRY

CRYSTAL ENGINEERING

"One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition."

Maddox, J. *Nature* **335**, 201 (1988)

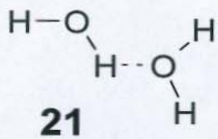
INTERMOLECULAR INTERACTIONS

BOND STRENGTH

1000 — 100 — 10 — [KJ/mol] 1

covalent, metallic, ionic (1000 - 50)

C≡C 840 · C=C 610 · C=O 740 · C≡N 890 · H—F 565 · C—C 415 · O—H 465 · C—F 486 · C—Si 301 · I—I 151 · C—O 360 · AlH_3 160



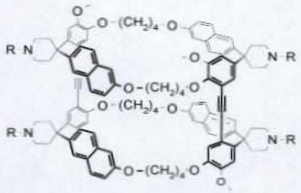
21

hydrogen bonds
8 - 40

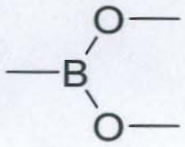
Van-der-Waals
0.5 - 5

dipole-dipole
4 - 25

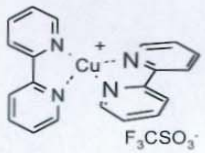
-N···Cl-
3 - 5 (calcd.)



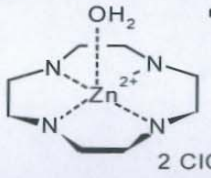
inclusion in hydrophobic cavity 30



reversible bonds

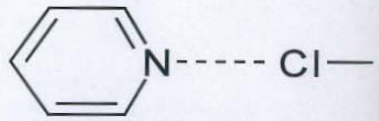


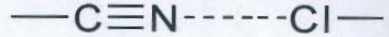
kinetically labile complexes



Lewis acids

CT complexes
5 - 50





Hydrogen bond – Vodíková vazba – Vodíkový můstek

- Jeffrey, G. A. ***An Introduction to Hydrogen Bonding***; Oxford University Press: Oxford, **1997**.

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

- Jeffrey, G. A.; Saenger, W. ***Hydrogen Bonding in Biological Structures***; Springer-Verlag: Berlin, **1991**.

- Nishio, M.; Hirota, M.; Umezawa, Y. ***The CH/p interaction: evidence, nature and consequences***; Wiley-VCH, Inc., **1998**, ISBN 0-471-25290-5.

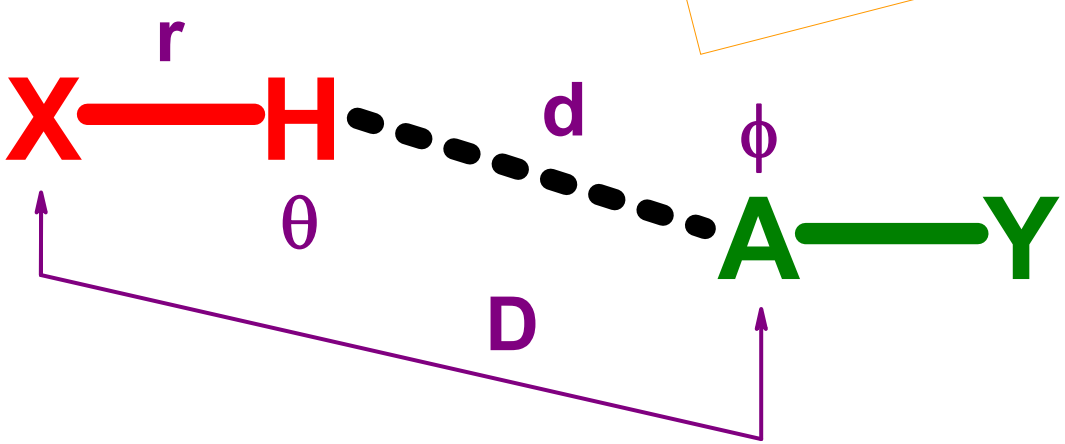
- Desiraju, G. R.; Steiner, T. ***The Weak Hydrogen Bond in structural chemistry and biology****;* Oxford University Press: Oxford, **1999**, ISBN 0-19-850970-7.

- ***Hydrogen Bonding - New Insights****;* Grabowski, S. J., Ed.; Springer: Dordrecht, The Netherlands, **2006**.

Hydrogen bond – Vodíková vazba – Vodíkový můstek

A hydrogen bond is said to exist when (1) there is evidence of a bond, and (2) there is evidence that this bond sterically involves a hydrogen atom already bonded to another atom.

Pimentel and McClellan 1960

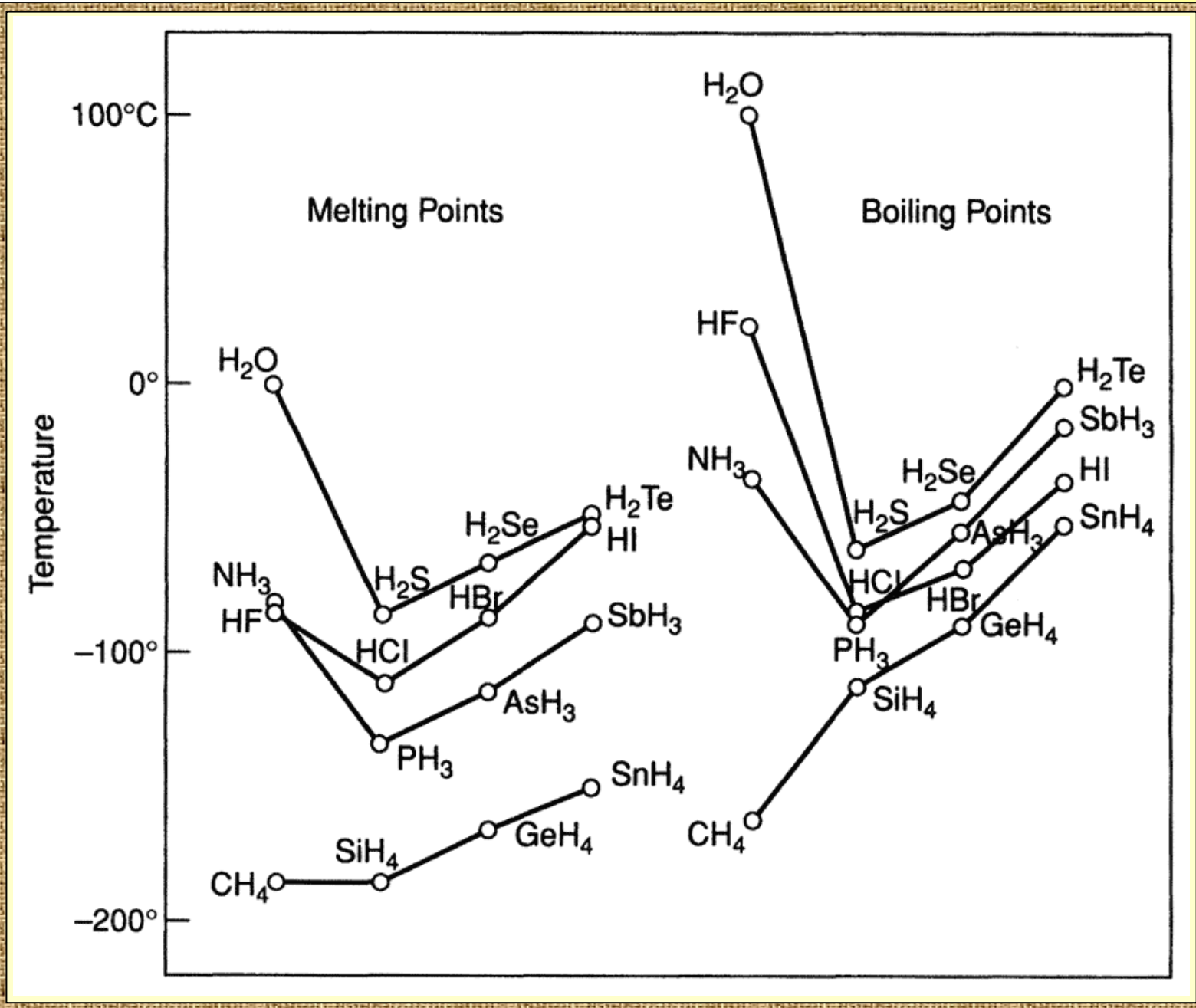


Hydrogen bonding – Affected properties

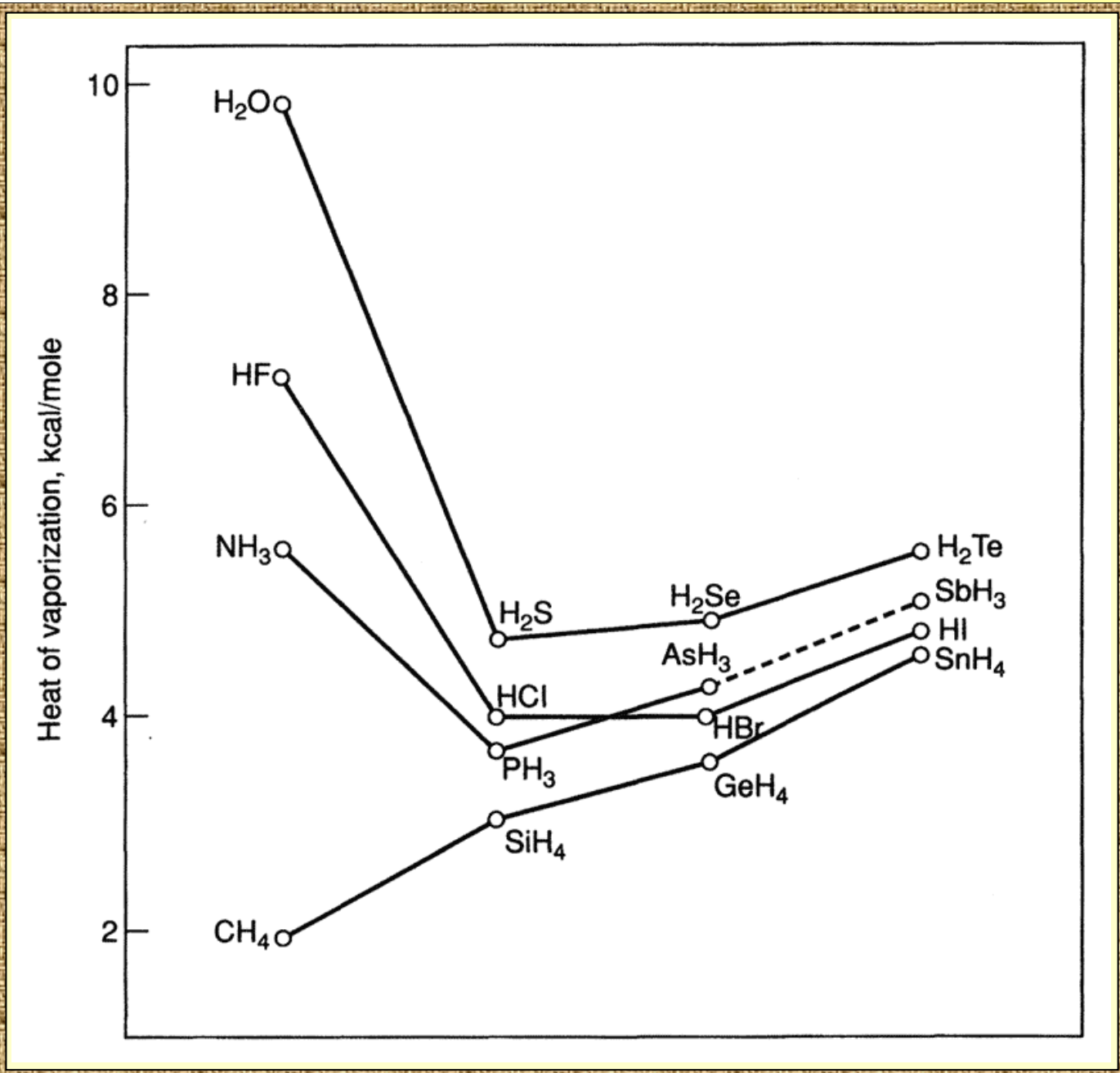
Properties Sensitive to Temperature Which Can Be Used As a Basis for Thermodynamic Measurements of Hydrogen Bond Enthalpies (From Pimental and McClellan, 1960).

Acoustic absorption	Freezing point
Adsorption	Heat conductivity
Absorption of light	Heat of mixing
Boiling point elevation	Heat of solution
Band spectra	Heat of vaporization
Cryoscopy	Infrared spectra
Calorimetry	Nuclear magnetic resonance
Heat capacity	Pressure-volume-temperature
Clausis-Clapeyron equation	Raman spectra
Conduction of electricity	Specific heat
Distribution or partition	Ultrasonic absorption
Dielectric absorption	Ultraviolet spectra
Dielectric constant	Second and higher virial coefficient
Density	Vapor density
Dipole moment	Vapor pressure
Electromotive force	
Fluorescence	

Hydrogen Bonding vs. Melting and Boiling Points

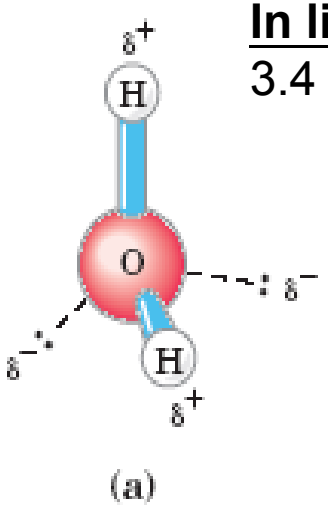


Hydrogen Bonding vs. Evaporation Heat

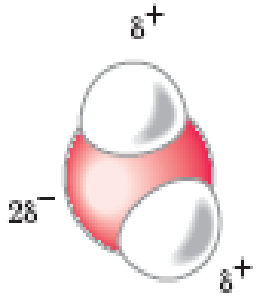


Hydrogen bonding in water

In liquid: each water molecule hydrogen-bonds with an average of 3.4 other water molecules.

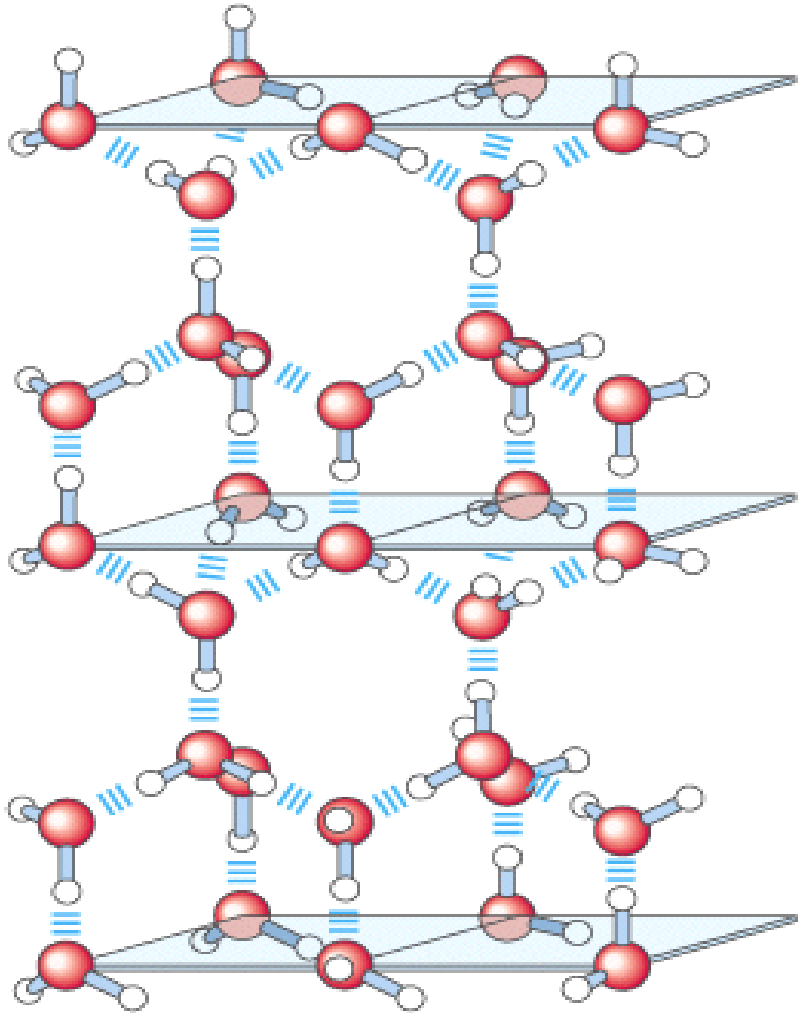


(a)



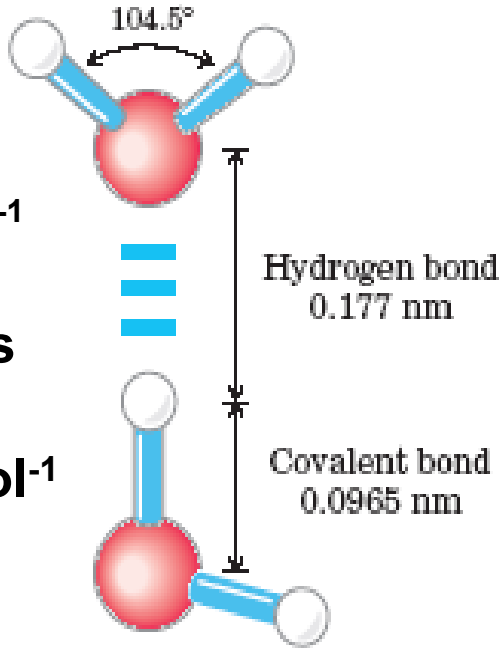
(b)

In ice: each water molecule forms the maximum of four hydrogen bonds



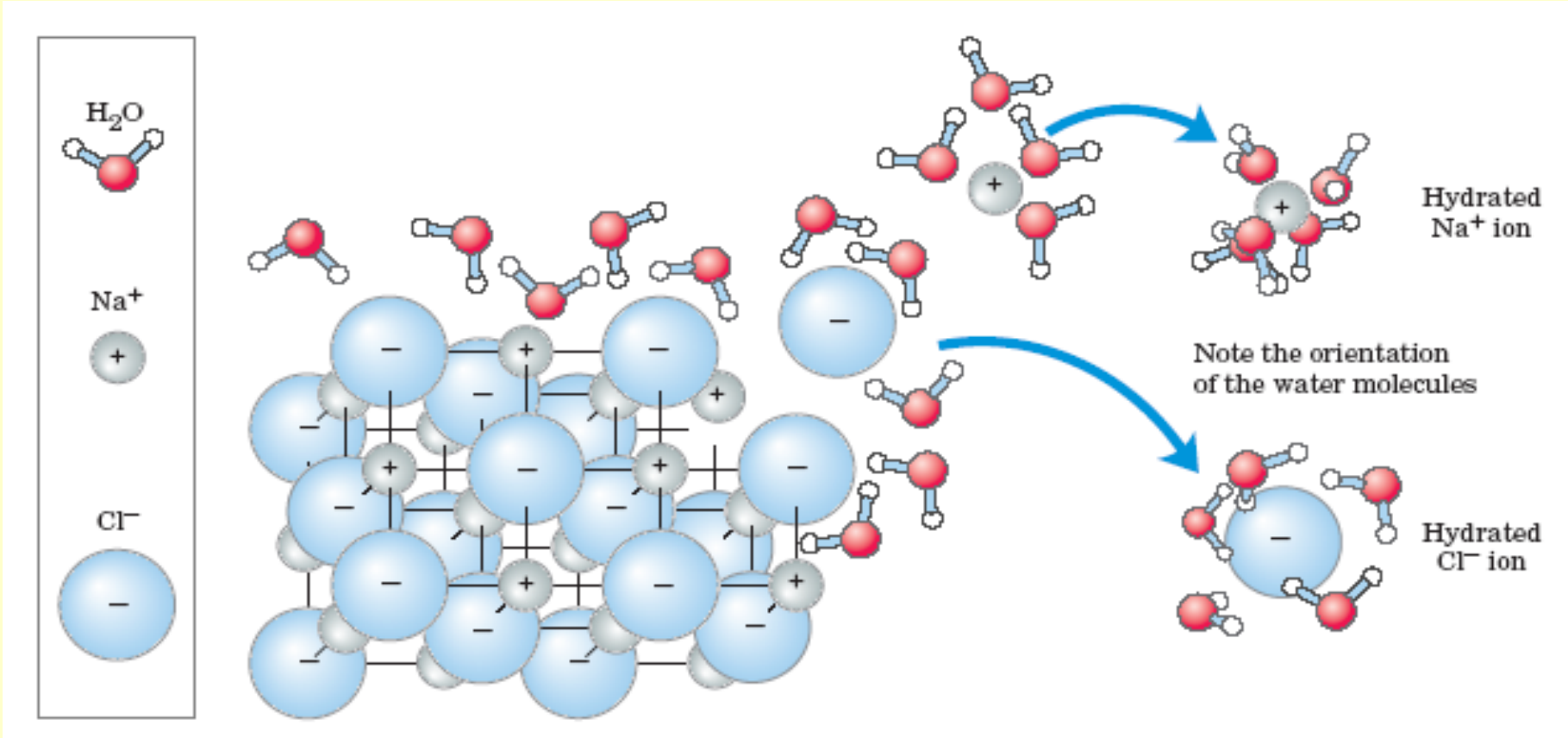
23 kJ. mol^{-1}
lifetime
~ 3.10^{-12} s

470 kJ. mol^{-1}



(c)

Hydrogen bonding

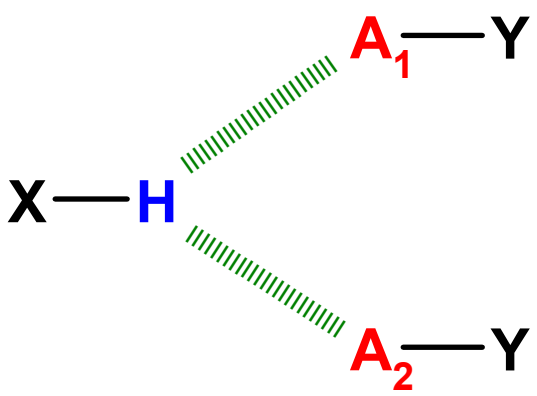


Water as solvent. Water dissolves many crystalline salts by hydrating their component ions. The NaCl crystal lattice is disrupted as water molecules cluster about the Cl and Na ions. The ionic charges are partially neutralized, and the electrostatic attractions necessary for lattice formation are weakened.

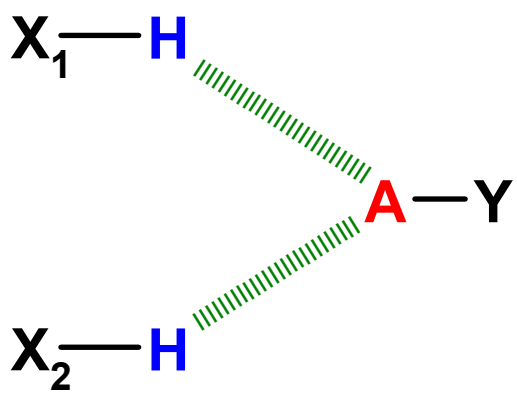
$\Delta G = \Delta H - T\Delta S$, where ΔH has a small positive value and $T\Delta S$ a large positive value; thus ΔG is negative. Entropy driven process.

HYDROGEN BONDS	STRONG	MODERATE	WEAK
A—H····B interaction	mostly covalent (only 2-centered)	mostly electrostatic (2- and more centered)	electrostatic (2- and more centered)
Bond lengths	**A—H ≈ H····B**	**A—H < H····B**	**A—H << H····B**
H····B [nm]	**~ 0.12 – 0.15**	**~ 0.15 – 0.22**	**0.22 – 0.32**
A·····B [nm]	**0.22 – 0.25**	**0.25 – 0.32**	**0.32 – 0.40**
Bond angles A—H····B [°]	**175 – 180**	**130 – 180**	**90 – 150**
Bond energy [kcal.mol^{-1} (kJ.mol^{-1})]	**14 – 40 (59 – 167)**	**4 – 15 (17 – 63)**	**< 4 (< 17)**
Relative IR ν_s vibration shift [cm^{-1}]	**25 %** (< 1600 cm^{-1})	**10 – 25 %** (< 2000-3000 cm^{-1})	**< 10 %** (~ 3000 cm^{-1})
^{1}H NMR chemical shift downfield [ppm]	**14 – 22**	**< 14**	**–**

Hydrogen bond – Furcation, Bifurcation, Trifurcation, …



BIFURCATED DONOR



BIFURCATED ACCEPTOR

THREE-CENTRE HYDROGEN BONDS

Functional Groups That Form Hydrogen Bonds

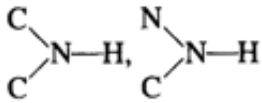
Strong hydrogen bonds

Donors and acceptors

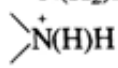
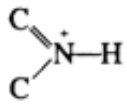
$[F\cdots H\cdots F]^-$	Symmetrical hydrogen bifluoride ion
$[H—F—H]_n^-$	Anions in fluoride HF adducts
$[O—H\cdots\bar{O}]$	Organic hydrogen anions, hydrogen phosphates and sulfates, hydrogen carboxylate ions
$[\overset{+}{O}—H\cdots O]$	Hydroxonium ions, pseudo hydrates
$[\overset{+}{N}—H\cdots N]$	Proton sponges
$[N—H\cdots\bar{N}]$	

Moderate hydrogen bonds

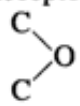
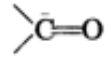
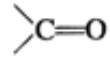
Donors and acceptors

O—H, P—O—H, $H—O_W—H$	Water, hydrates, alcohols, carboxylic acids, phenols, carbohydrates, oligo- and polysaccharides, nucleosides, nucleotides, nucleic acids
	Secondary amines, amides, carbamates, hydrazides, purines, pyrimidines, barbiturates, nucleosides, nucleotides, peptides, proteins (main chain and side chain)

Donors only

$\overset{+}{N}(H_3)H$	Ammonium salts
$—\overset{+}{N}(H_2)H$	Zwitterion amino acids
	
S—H	Cysteine
	Proteins (side chain, nucleic acids (low pH)
C—N(H)H	Primary amines, pyrimidines, purines, barbiturates

Acceptors only

	Ethers, carbohydrates, oligo- and polysaccharides (ring and glycosidic oxygens)
	Carboxylates, zwitterion amino acids
	Carboxylic acids, ketones, esters, N-oxides, pyrimidines, purines, nucleosides, nucleotides, nucleic acids, peptides, proteins (main chain)
$\overline{X}=O$	Oxyanions, nitrates, chlorates, sulfates, phosphates
	Tertiary amines
	Purines, pyrimidines, barbiturates, nucleosides, nucleotides, nucleic acids
N=O	Aromatic nitro compounds
	Methionine

Weak hydrogen bonds

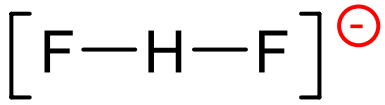
Donors

C—H, Si—H (?)

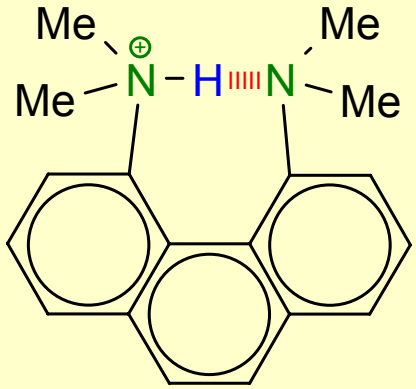
Acceptors

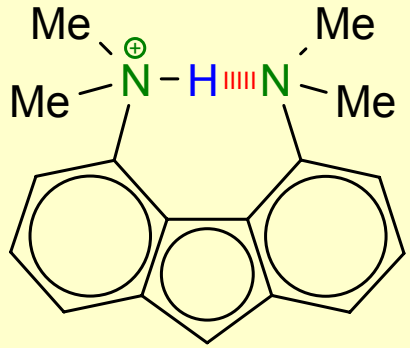
C≡C,  , F—C (?)

Strong Hydrogen Bonds



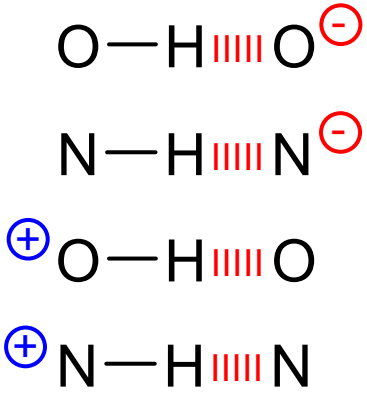
-39 kcal.mol^{-1}
-163 kJ.mol^{-1}

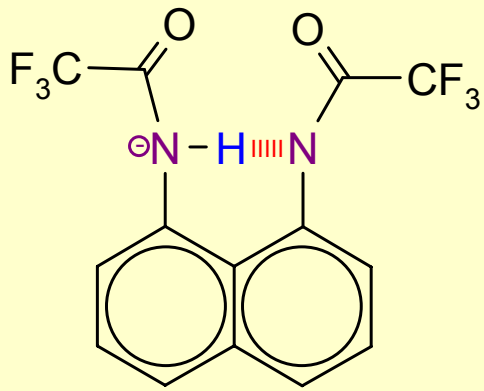


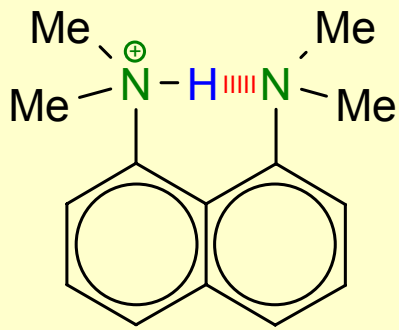


Ionic hydrogen bonds
Positive- or negative-ion hydrogen bonds
Low barrier hydrogen bonds

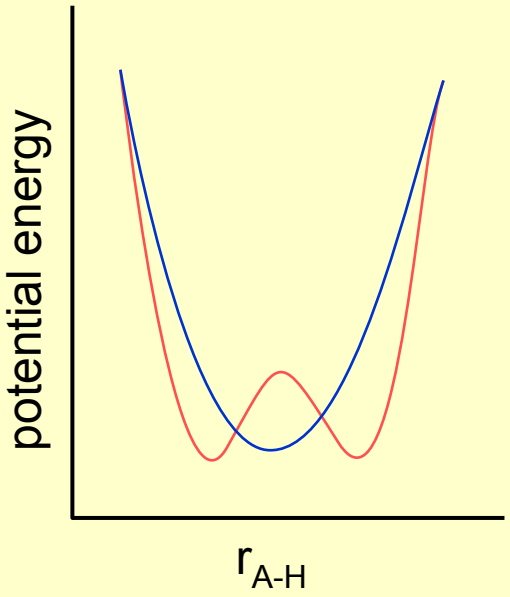
Proton sponges
Protonové houby







Strong Hydrogen Bonds

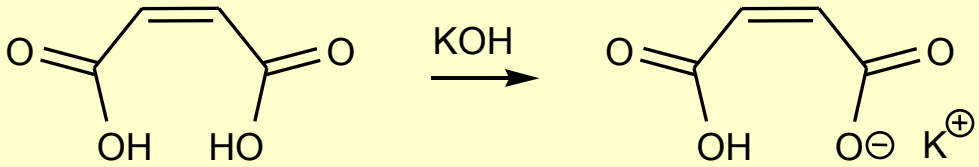


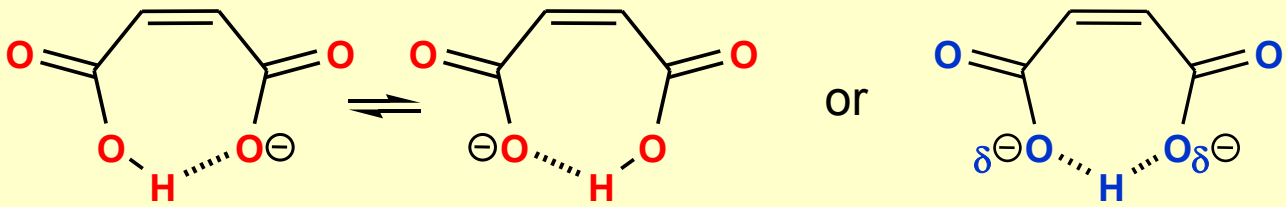
Strong hydrogen bonds exist when the pK_a of the hydrogen bond donor is similar to the pK_a of the conjugate acid of the acceptor.

- Homonuclear bonds
- Heteronuclear bonds

  $O/N—H\cdots F^-$, $F/N—H\cdots O^-$

  $^+N/O—H\cdots O/N$





Situations where $r_{A-H} = r_{H-B}$ are rare.

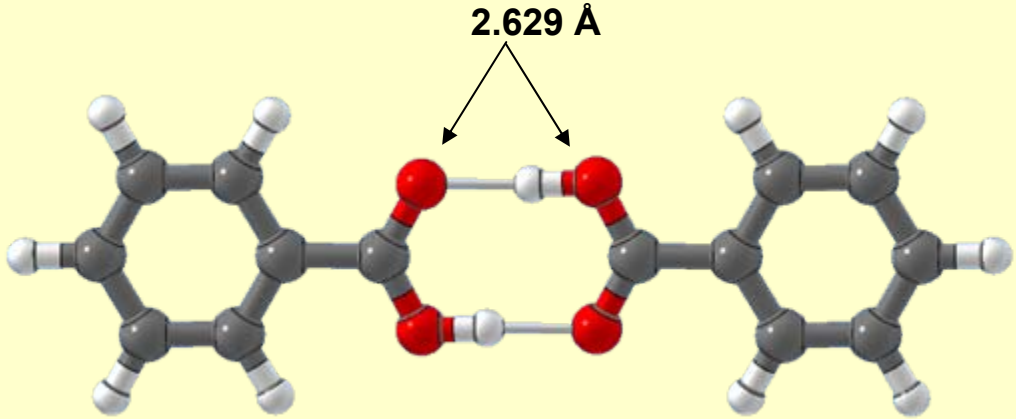
Moderate Hydrogen Bonds

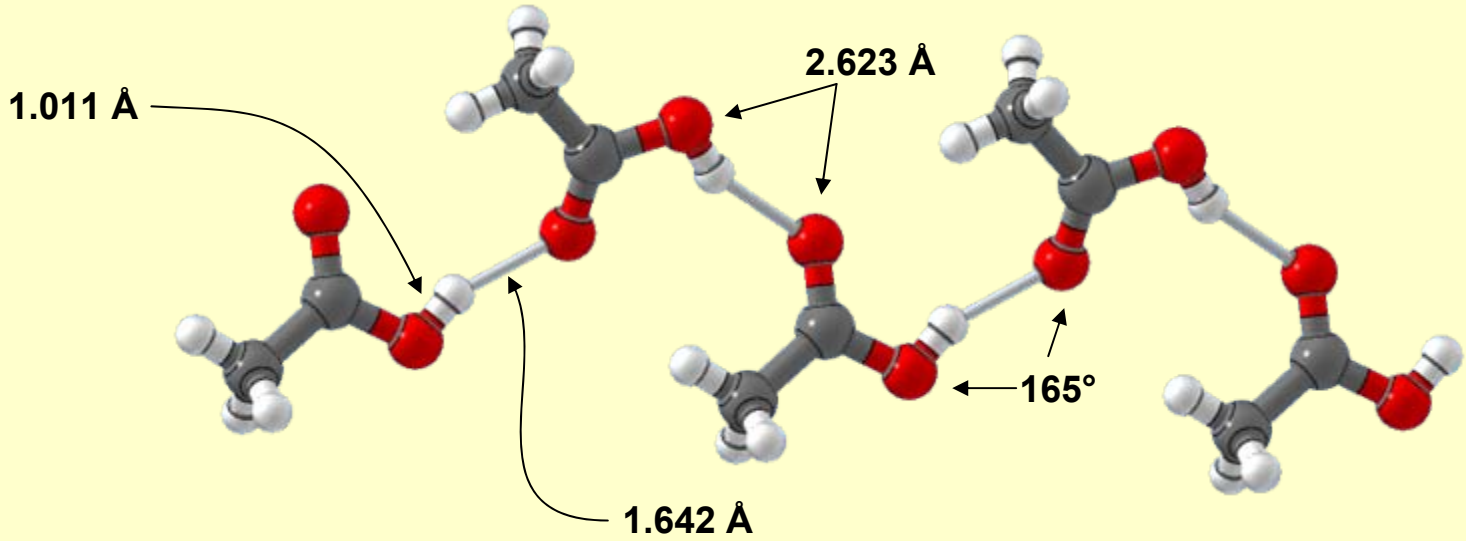
Moderate Hydrogen Bond

$r_{A—H}$ = 1.5 – 2.2 Å

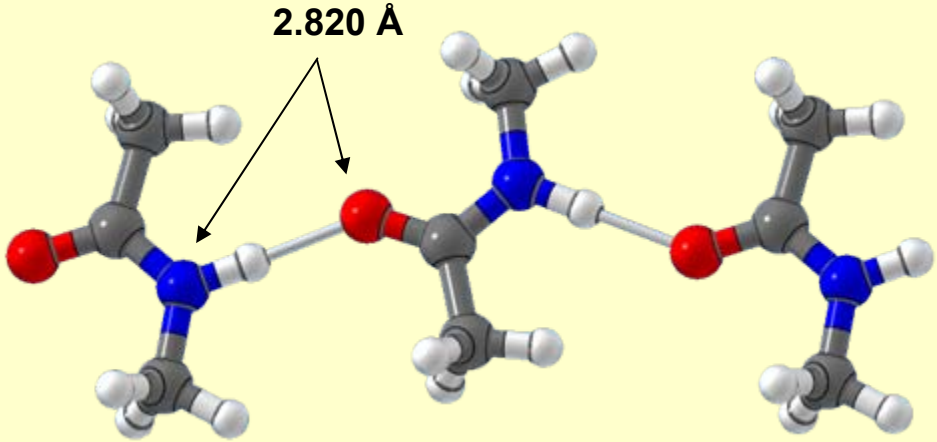
$r_{H\cdots B}$ = 2.5 – 3.2 Å

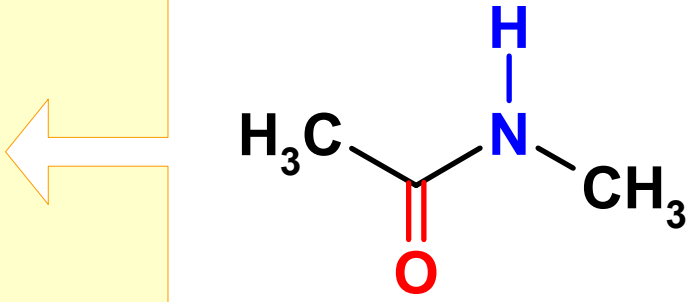
A—H···B = 130 – 180 °

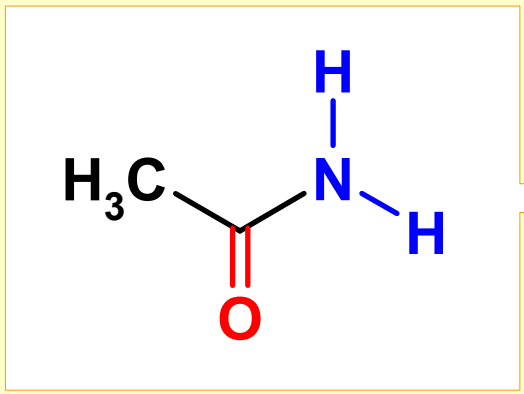


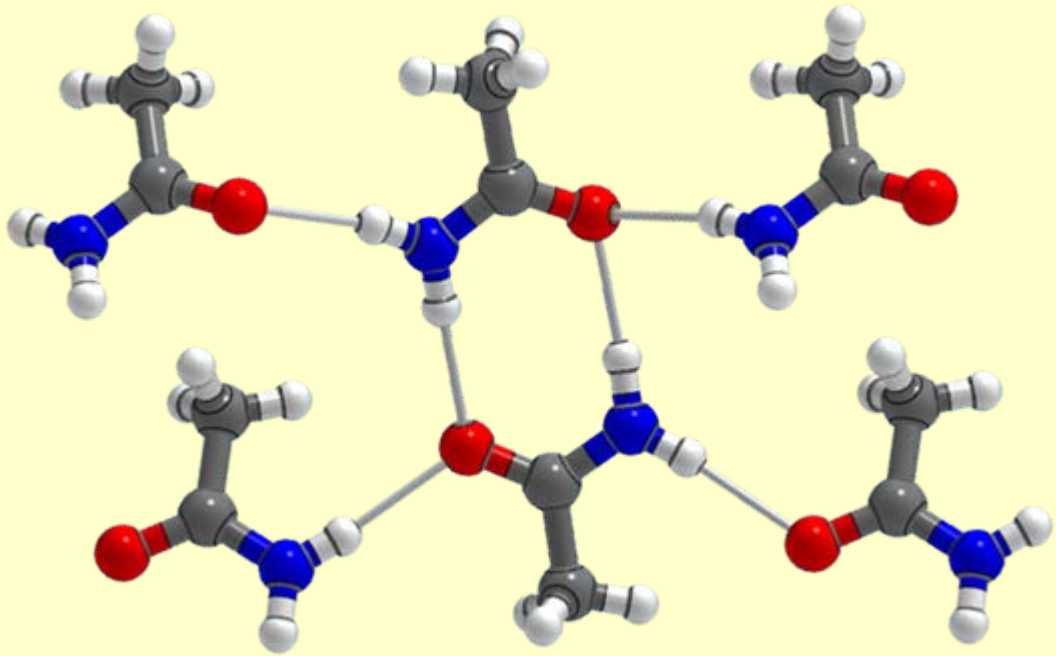


Moderate Hydrogen Bonds







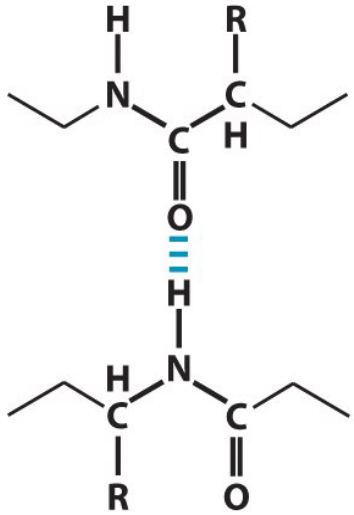


Some biologically important hydrogen bonds

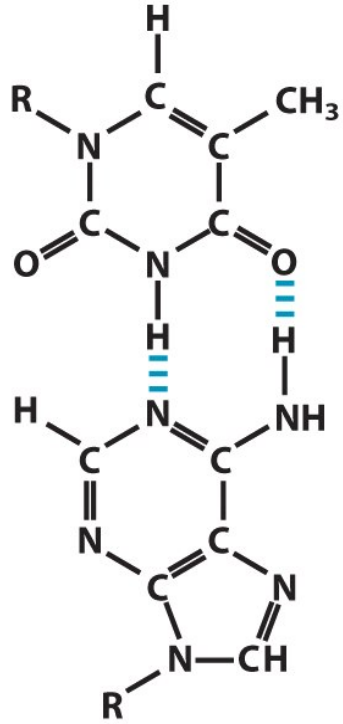
Between the hydroxyl group of an alcohol and water

Between the carbonyl group of a ketone and water

Between peptide groups in polypeptides



Between complementary bases of DNA

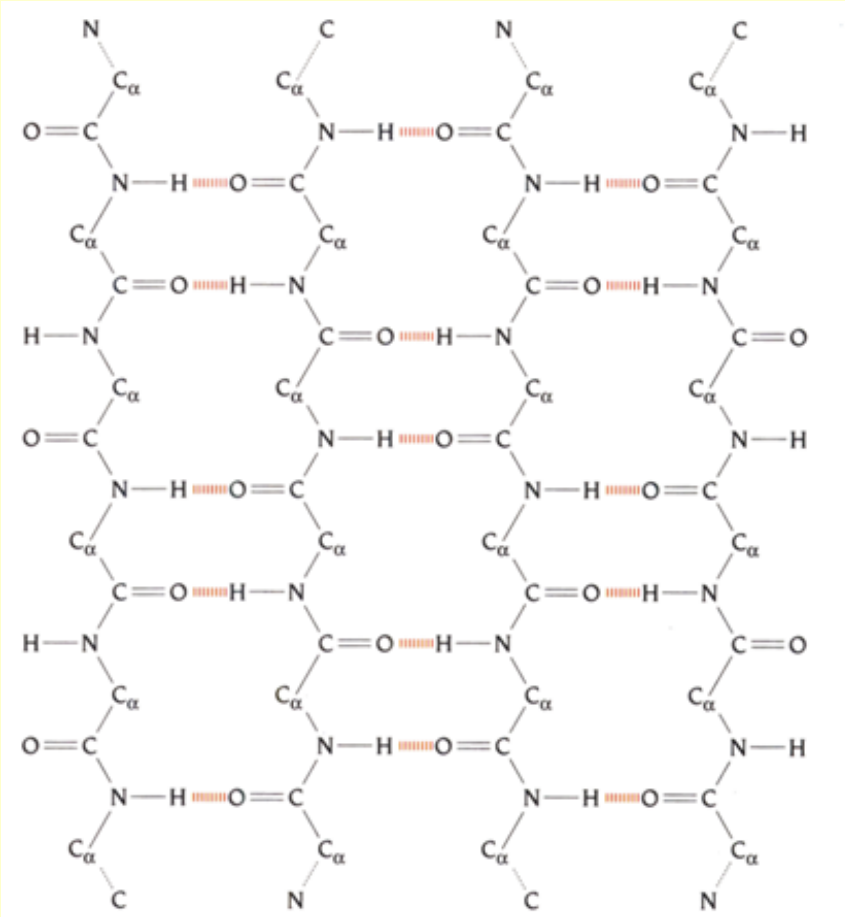


Thymine

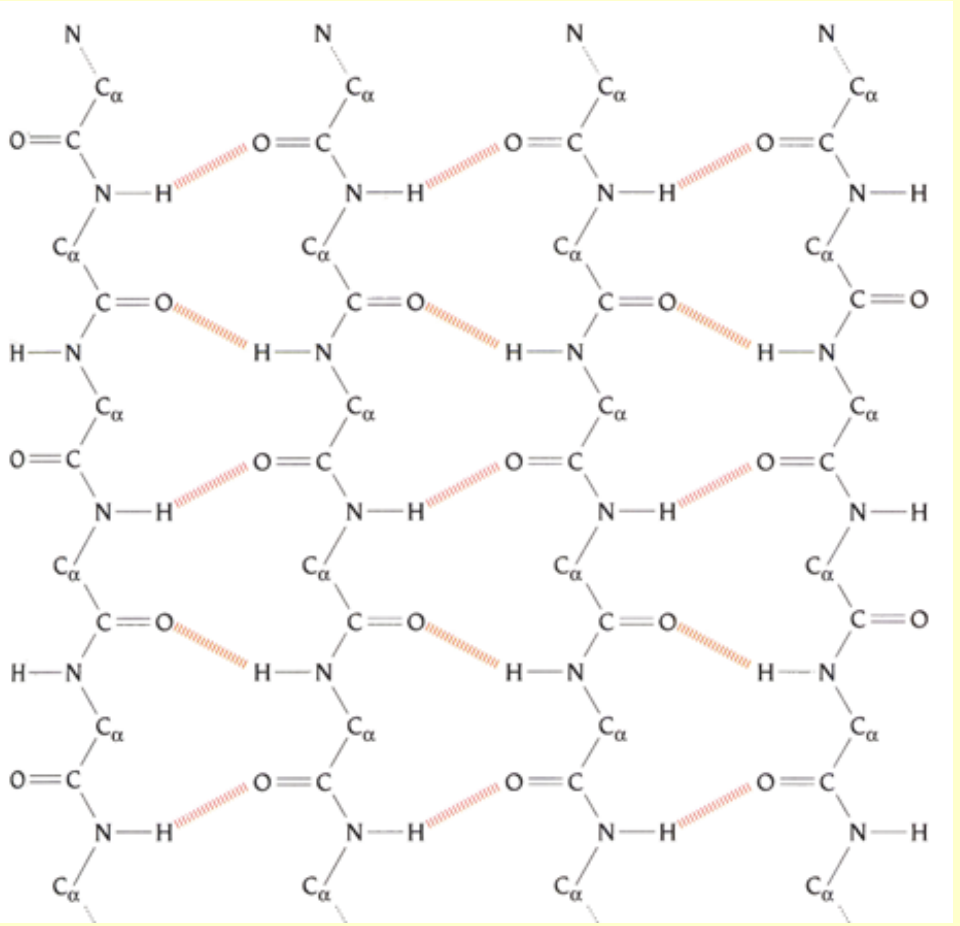
Adenine

Hydrogen bonding in peptides

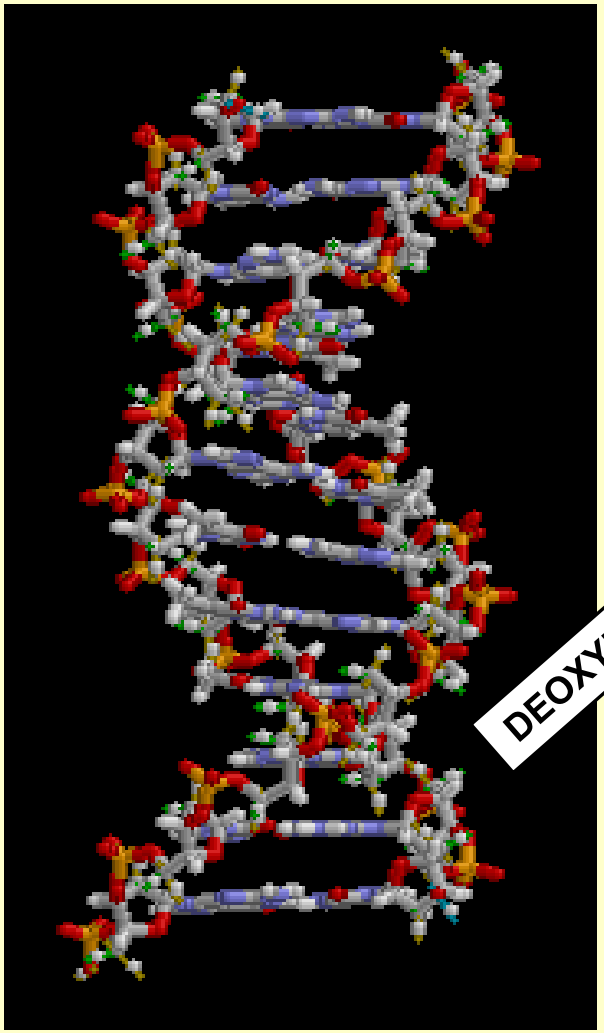
The anti-parallel beta-sheet

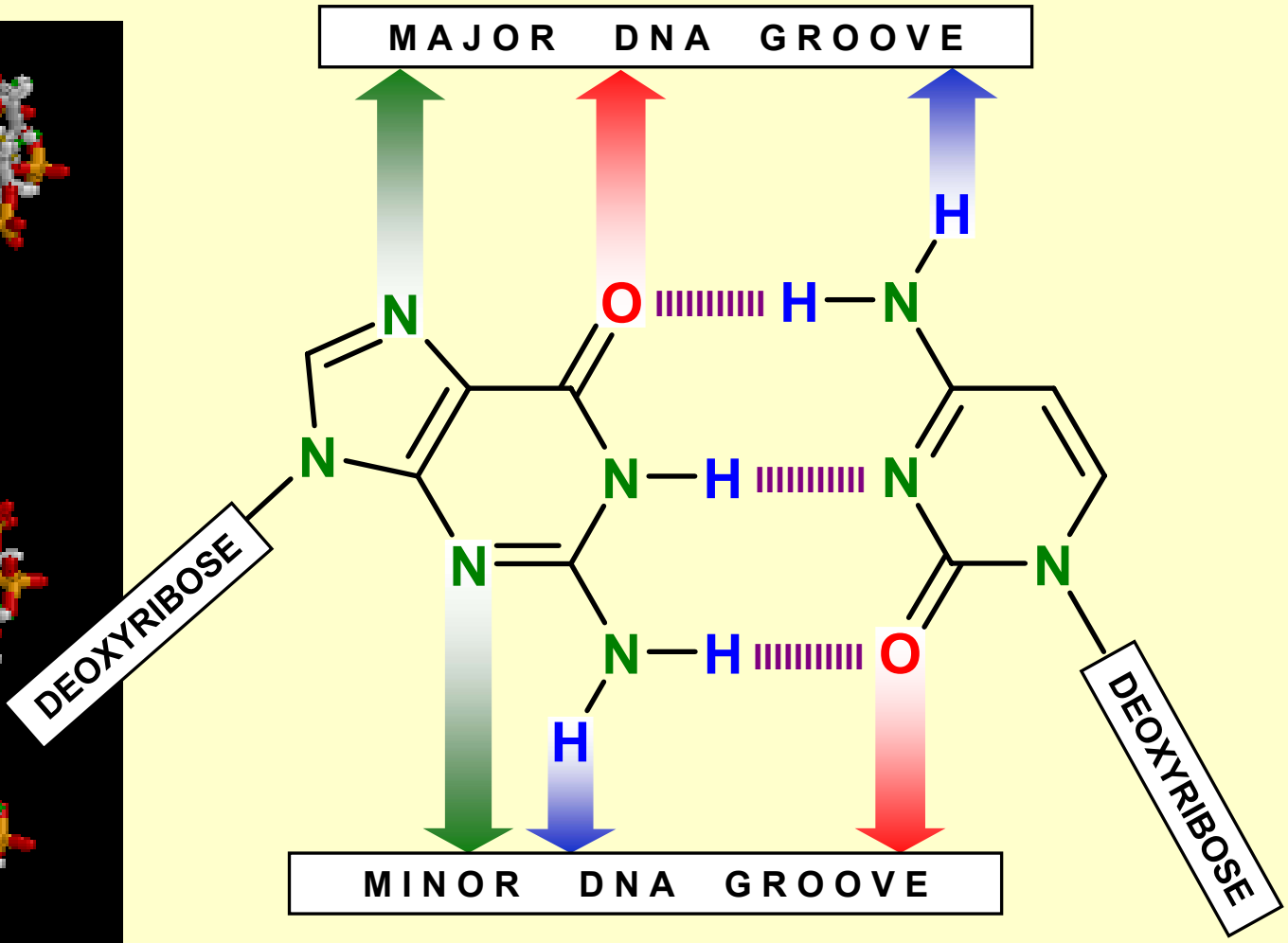


The parallel beta-sheet

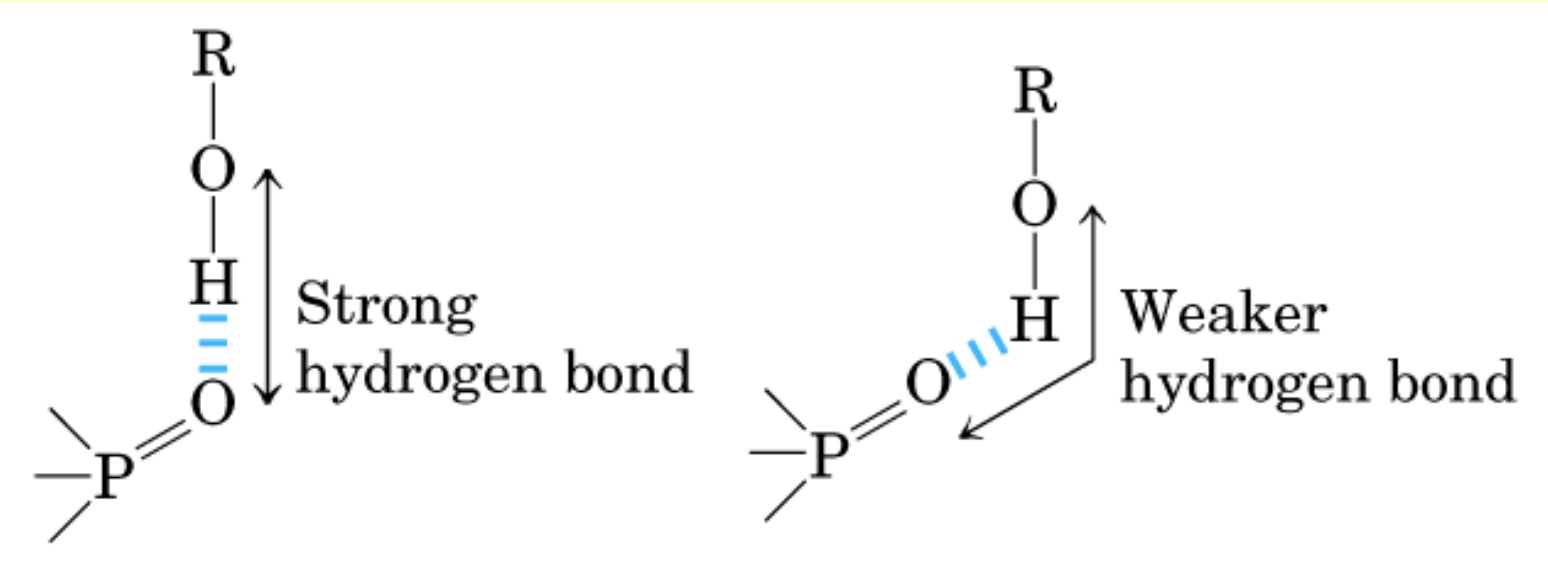


Hydrogen bonding in DNA

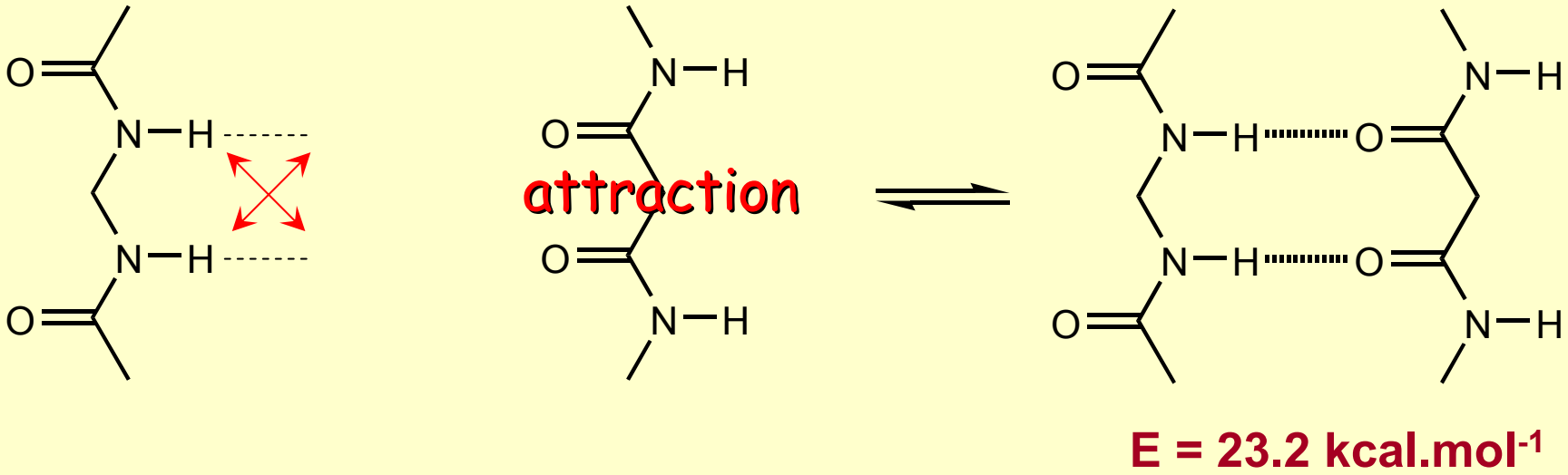


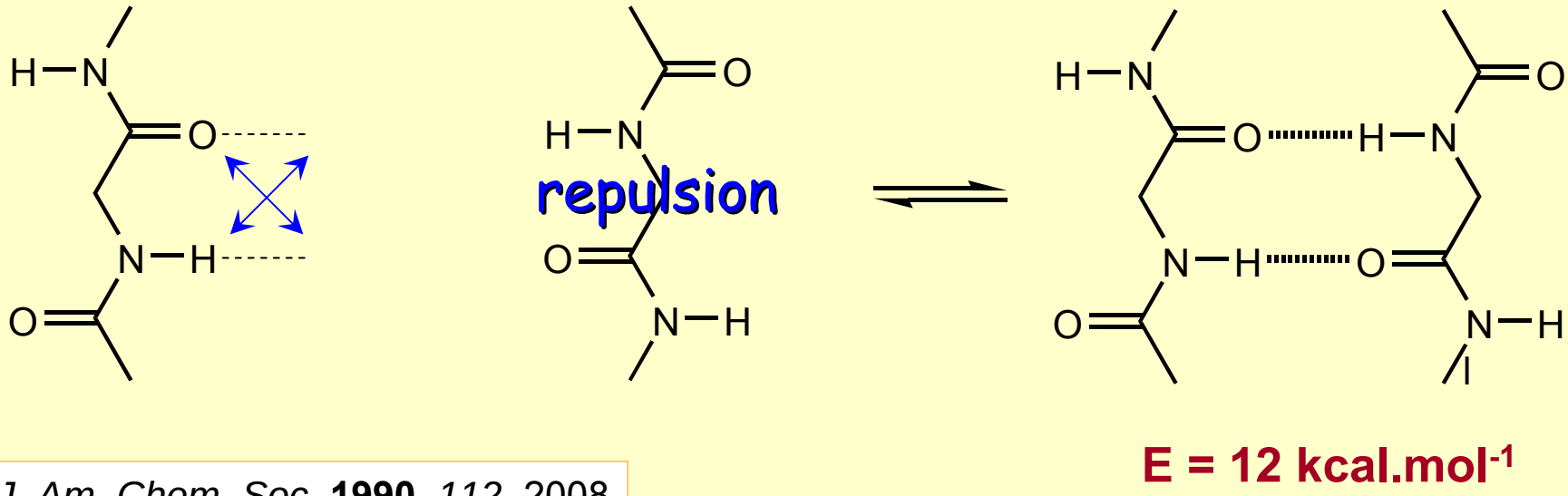


Hydrogen bonding



Hydrogen bonding

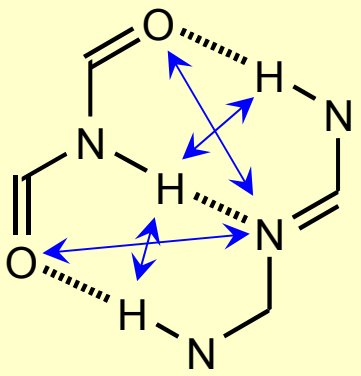


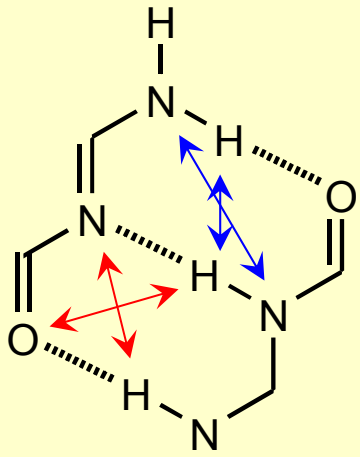


J. Am. Chem. Soc. **1990**, *112*, 2008

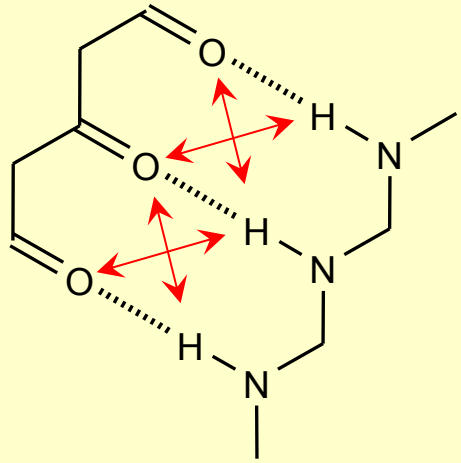
Hydrogen bonding

repulsion

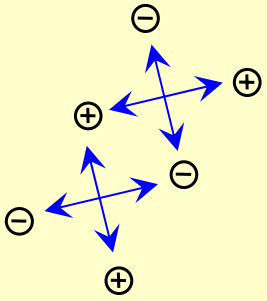




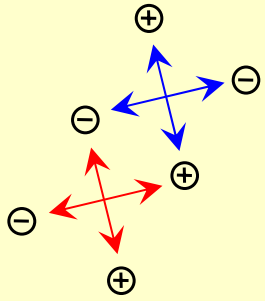
attraction



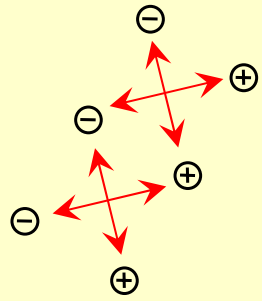
ADA-DAD



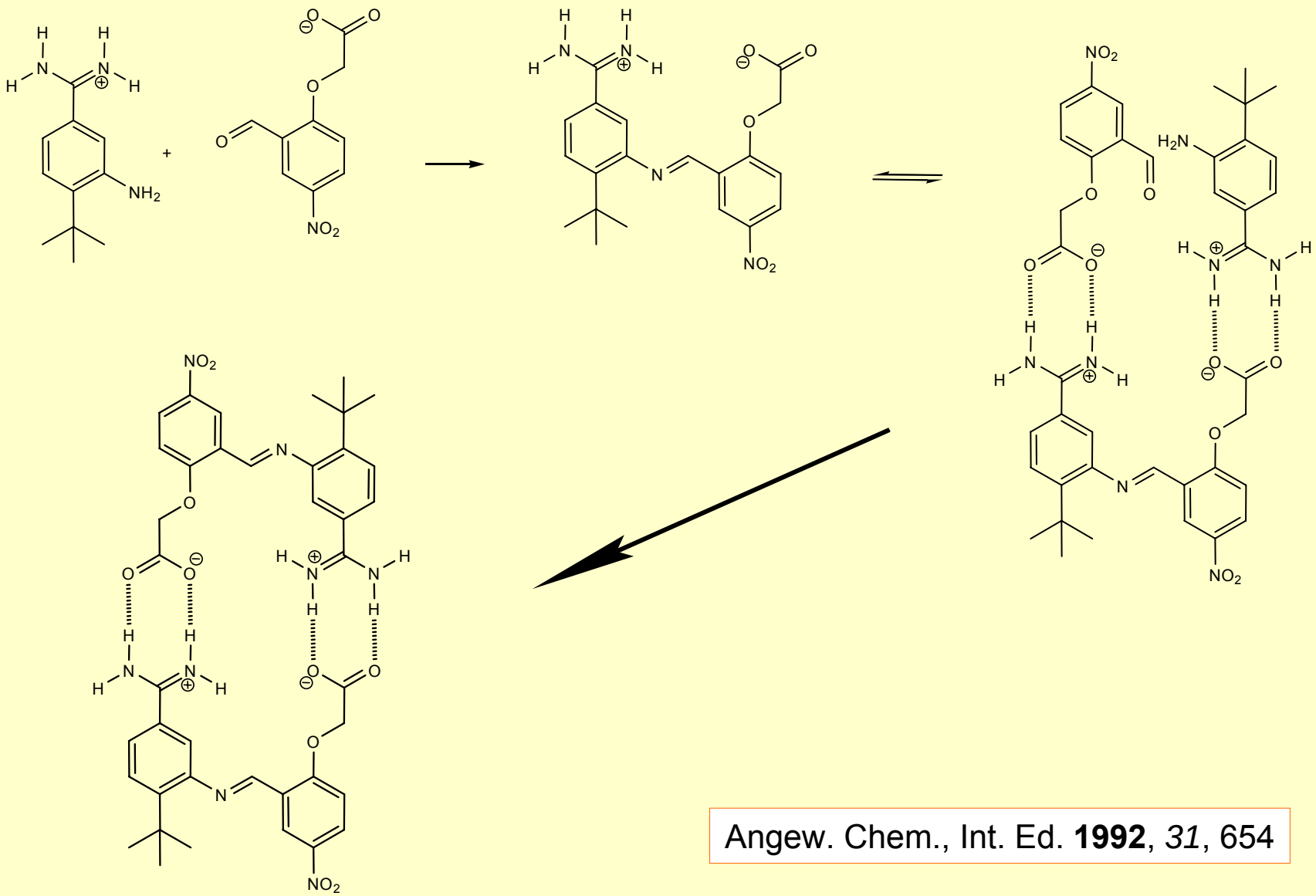
AAD-DDA



AAA-DDD

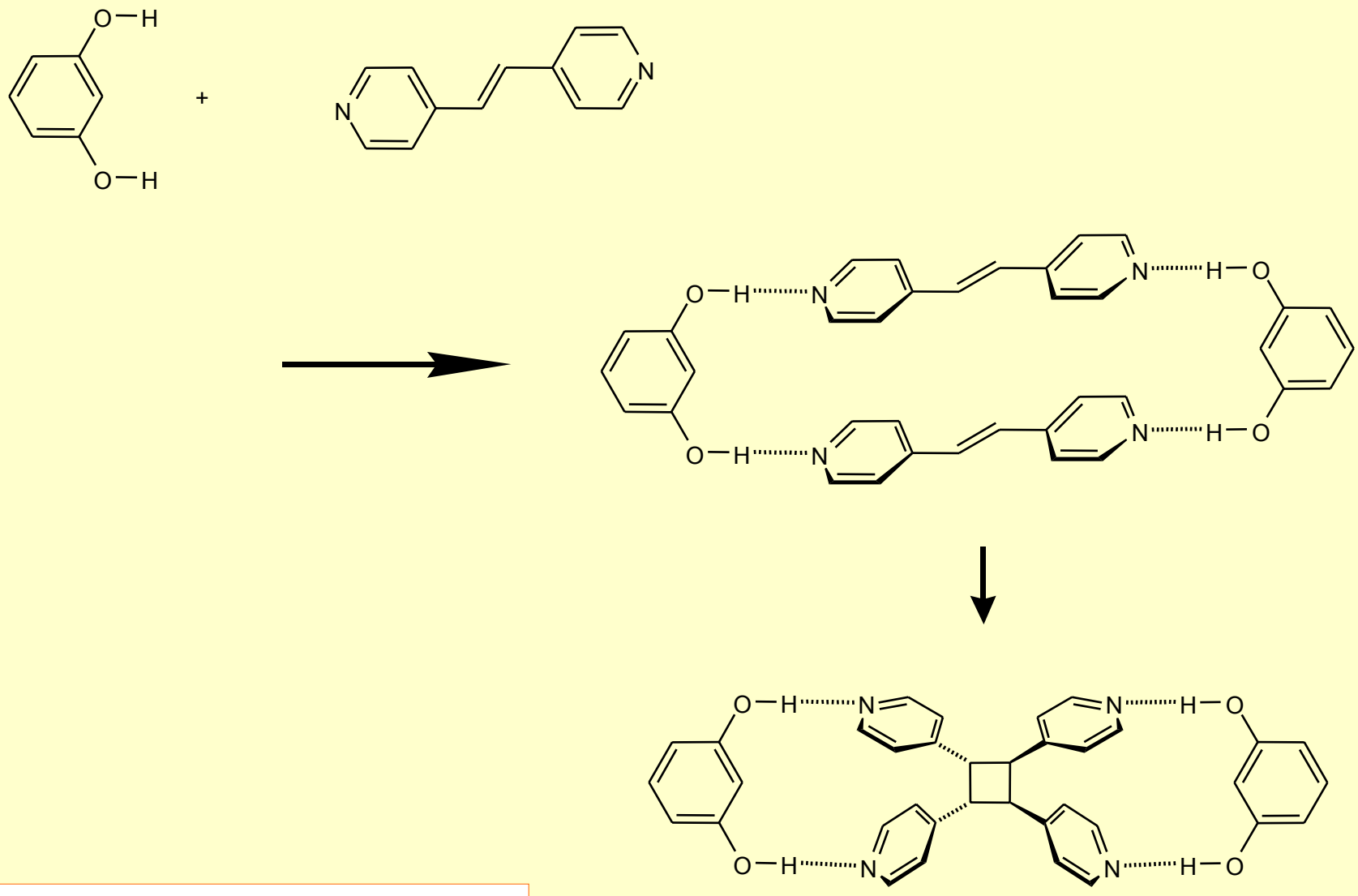


Hydrogen Bonding – Functional Supramolecular Assemblies



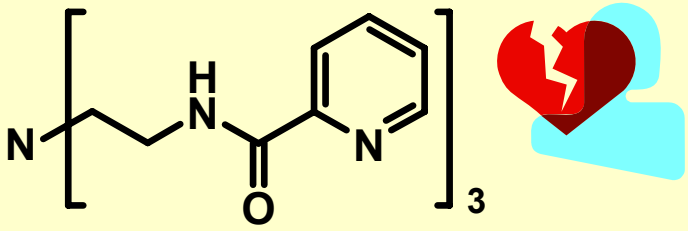
Angew. Chem., Int. Ed. **1992**, *31*, 654

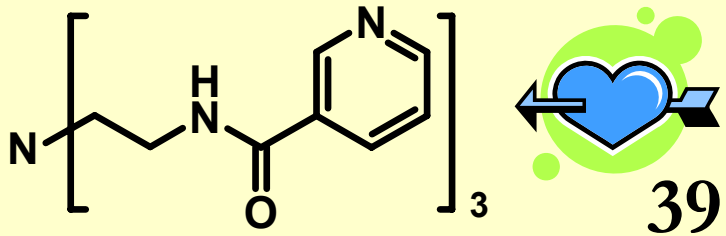
Hydrogen Bonding – Functional Supramolecular Assemblies

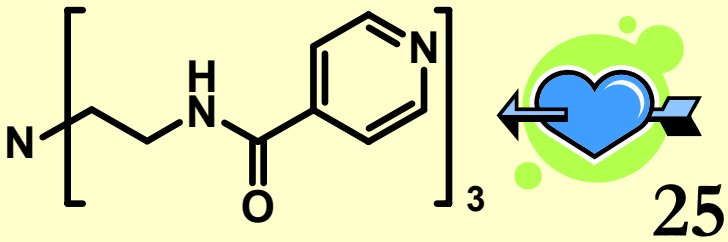


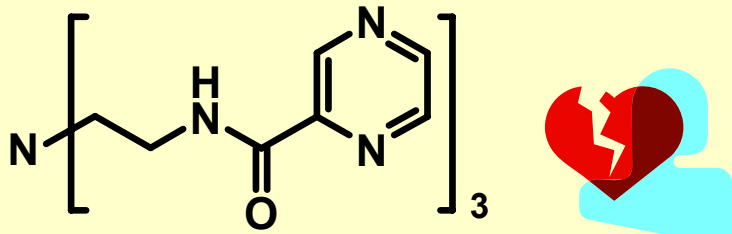
Angew. Chem., Int. Ed. **2004**, *43*, 232

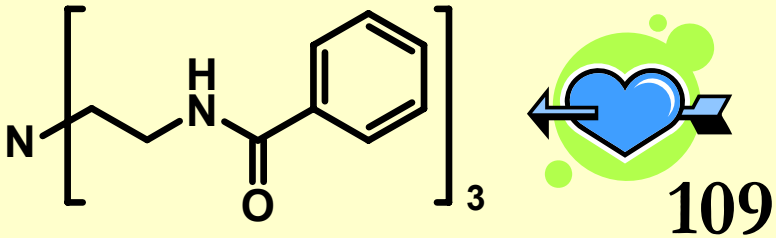
Saccharide Recognition via Hydrogen Bonds

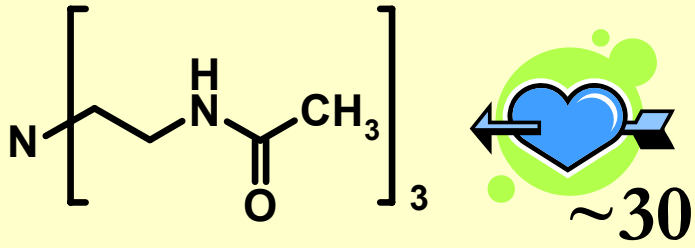




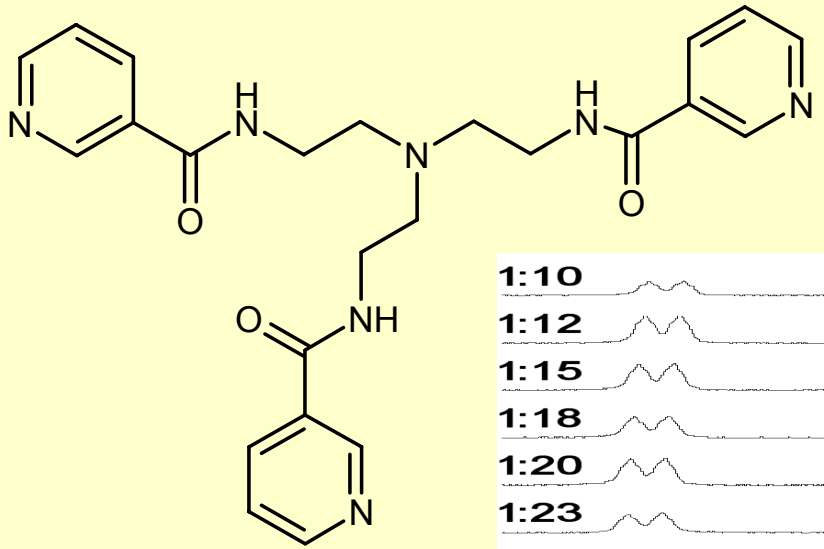








Saccharide Recognition via Hydrogen Bonds



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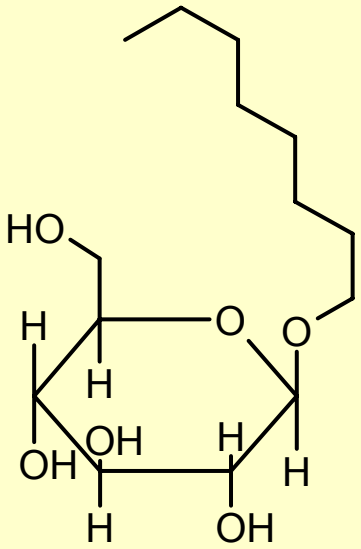
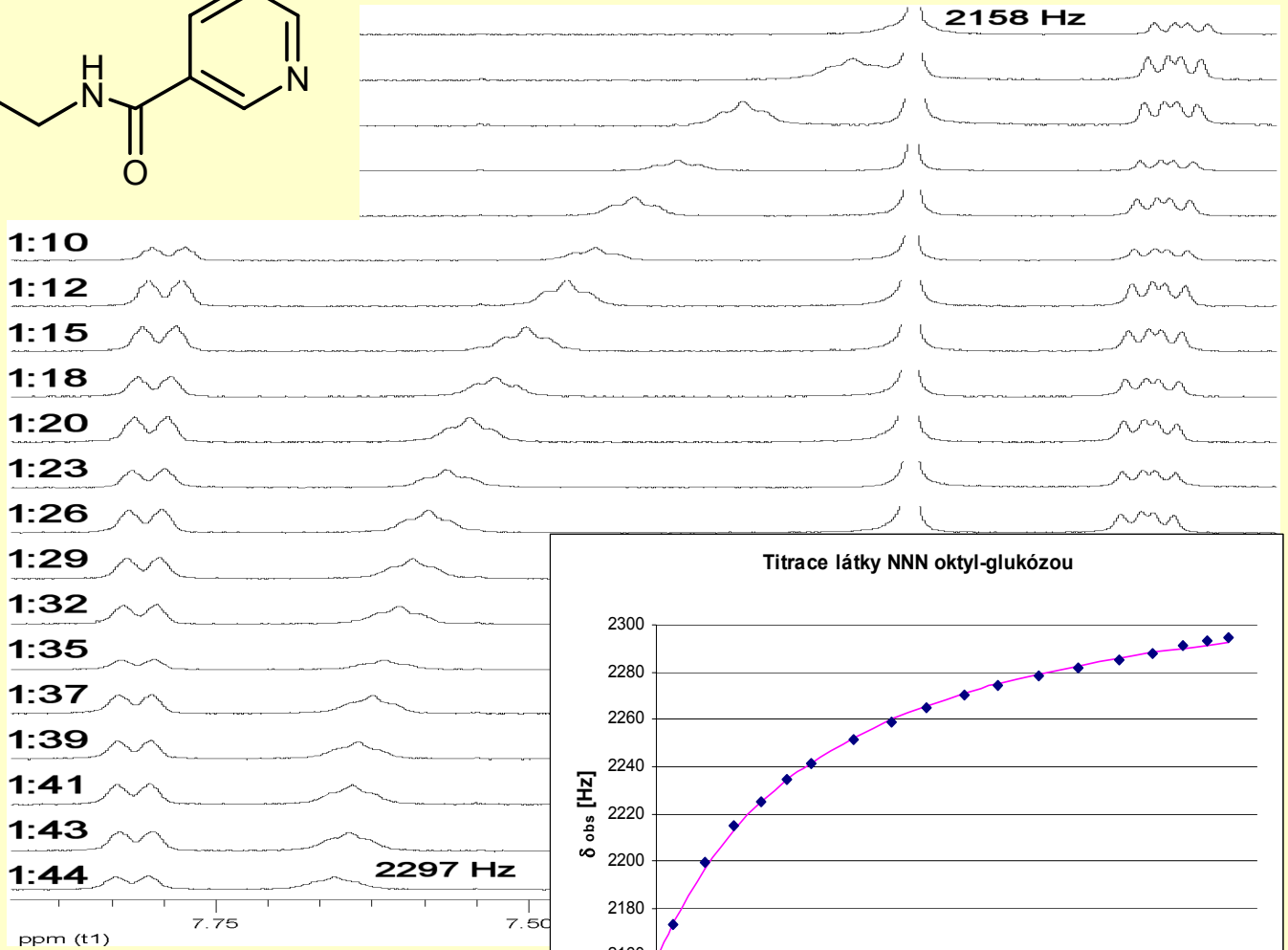


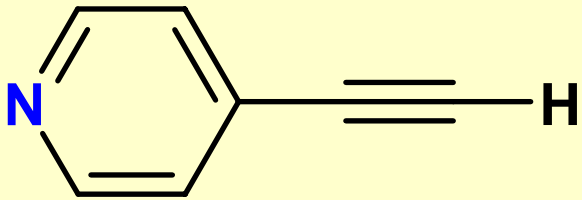


$K_{ass} = 59,7 \pm 2,9\ M^{-1}$

Infrared Spectral Criteria For Hydrogen Bonding

1. A-H stretching frequency, ν_s, moves to lower frequencies
2. This is accompanied by an increase in intensity and band width
3. A-H bending frequencies, ν_b, move to higher frequencies
4. Upon cooling, ns shifts to high frequencies with increase in intensity and decrease in band width; ν_b moves to lover frequencies with decrease in band width
5. Substitution of H by D lowers ν_s frequencies by a factor of ~0.75

Weak Hydrogen Bonds

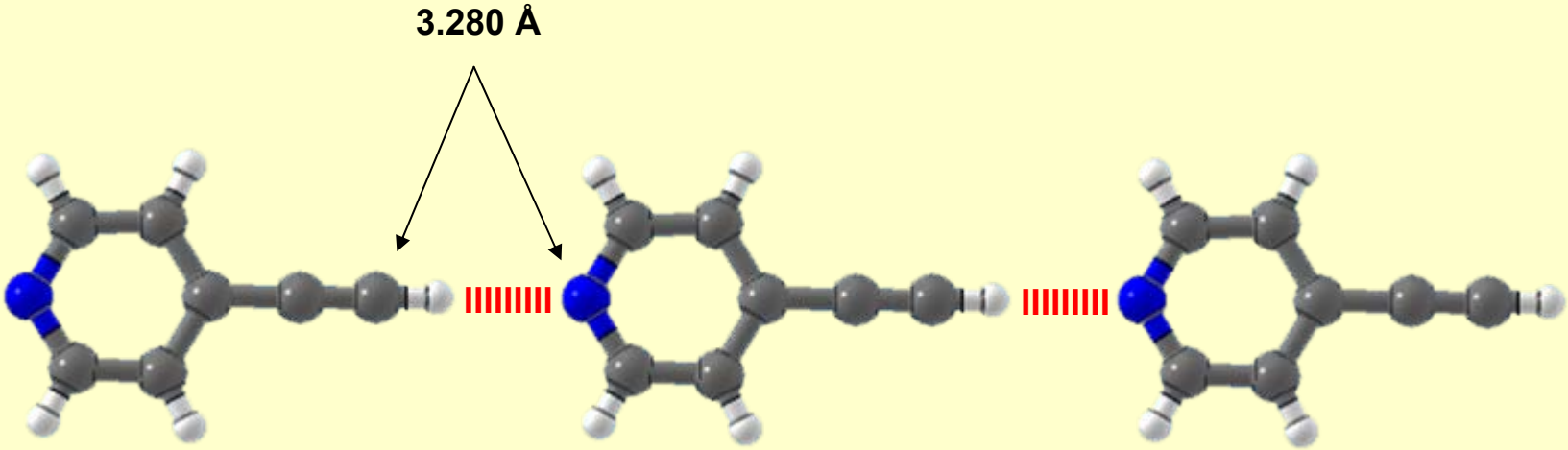


Weak Hydrogen Bond

$r_{A—H}$ = 2.2 – 3.2 Å

$r_{H\cdots B}$ = 3.2 – 4.0 Å

A—H···B = 90 – 150 °



Weak Hydrogen Bonds

Weak donor – Strong acceptor

C—H····O=C	C—H····N	C—H····Cl $^-$
P—H····O	Mo—H····O≡C	Ir—H····Cl—Ir

Strong donor – Weak acceptor

N—H····Ph	Cl—H···· C≡C	O—H····C=C
O—H····F—C	O—H····Se	N—H····Co

Weak donor – Weak acceptor

C≡C—H····C≡C	C≡C—H····Ph	C—H····F—C
C—H····Pt	C—H···· Cl—C	C—H····H—Re

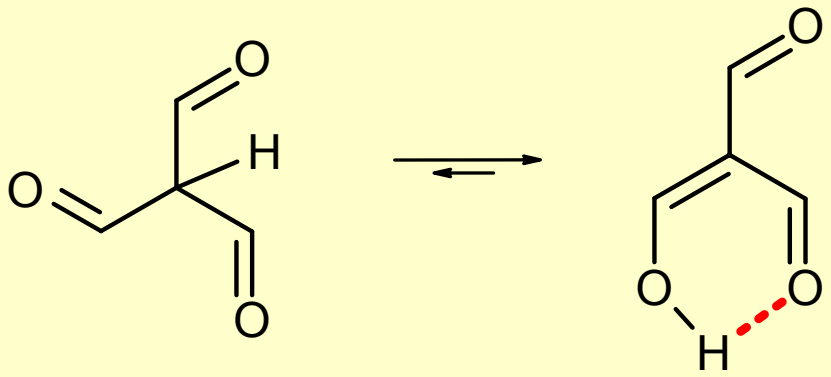
Other varieties

Agostic	N—H····H—B
$^-$O—H····O—H	Formyl hydrogen bond

Hydrogen bonds

	O-H…O hard acid … hard base	C-H…O soft acid … hard base	O-H…π hard acid … soft base	C-H…π soft acid … soft base
Interaction energy [kcal.mol^{-1}]	**10 - 3**	**< 3**	**~ 2**	**< 2.5**
Delocalization (charge-transfer)	**variable**	**unimportant**	**important**	**important**
Electrostatic (Coulombic)	**strong**	**important**	**weak**	**unimportant**
Dispersion (London)	**unimportant**	**unimportant**	**important**	**important**
Repulsive van der Waals	**similar**			

Hydrogen bonding: Blue-shift improper hydrogen bond



in $CHCl_3$ ν = 3021 cm^{-1}

+ new sharp band at 3028 cm^{-1} = **blue shift 7 cm^{-1}**

in $CDCl_3$ ν = 2255 cm^{-1}

+ new sharp band at 2259 cm^{-1} = **blue shift 4 cm^{-1}**

Buděšínský,M.; Fiedler, P.; Arnold, Z. *Synthesis* **1989**, 858-860

Hydrogen bonding: Blue-shift improper hydrogen bond

Benzene complexes

complex	symmetry	q(H)	ΔE (kcal/mol)[a,b]	Δr (Å)[c]
$(C_6H_6)_2$[d]	C_{2v}	0.20 (0.15)	1.1	−0.0033 (−0.0033)
$C_6H_6\cdots CH_4$[e]	C_{3v}	0.17 (0.12)	0.3	−0.0008 (−0.0009)
$C_6H_6\cdots HCCl_3$	C_{3v}	0.30 (0.30)	3.2	−0.0025 (−0.0023)
$C_6H_6\cdots HCN$[f]	C_{6v}	0.32 (0.27)	3.2	+0.0018 (+0.0017)

	ν(C−H);[a] I(C−H)[b]		
proton donor	isolated state	donor$\cdots C_6H_6$	$\Delta\nu$[a,c]
C_6H_6	3250 (3283);[d] 1.5	3299 (3325); 0	+49 (+42)
CH_4[e]	3248 (3279); 6.4	3263 (3294); 21.3	+15 (+15)
$CHCl_3$	3242 (3255); 39	3297 (3307); 0.3	+55 (+52)
HCN[f]	3513 (3533); 216	3497 (3515); 66	−16 (−18)

Hobza, P.; Špirko, V.; Selzle, H. L., Schlag, E. W. *J. Chem. Phys. A* **1998**, *102* (15), 2501-2504

ANTI-HYDROGEN BONDING (anti-H-bond)

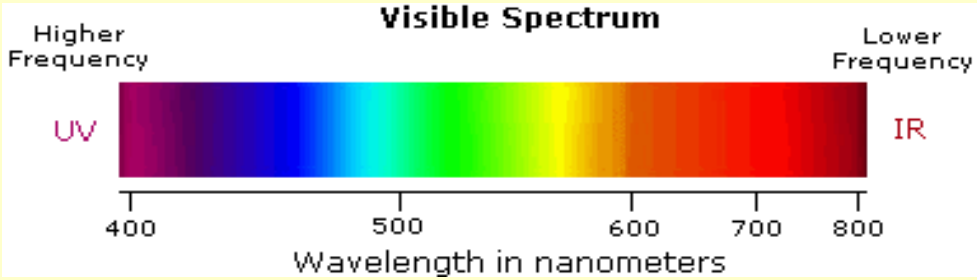
Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253-4264

IMPROPER HYDROGEN BONDING (blue shift hydrogen bond)

Blue-shift *versus* Red-shift Hydrogen Bond

X—H ····· Y—C

Klasická vodíková vazba (standard hydrogen bond)
Red shift (batochromní), delší vazebná délka, zvýšení intenzity
EDT z π nebo *n* do σ^* vazby X-H → přímé oslabení vazby X-H



Neklasická vodíková vazba (improper hydrogen bond)
Blue shift (hypsochromní), kratší vazebná délka, snížení intenzity
Nedochází k EDT do σ^* vazby X-H, ale …

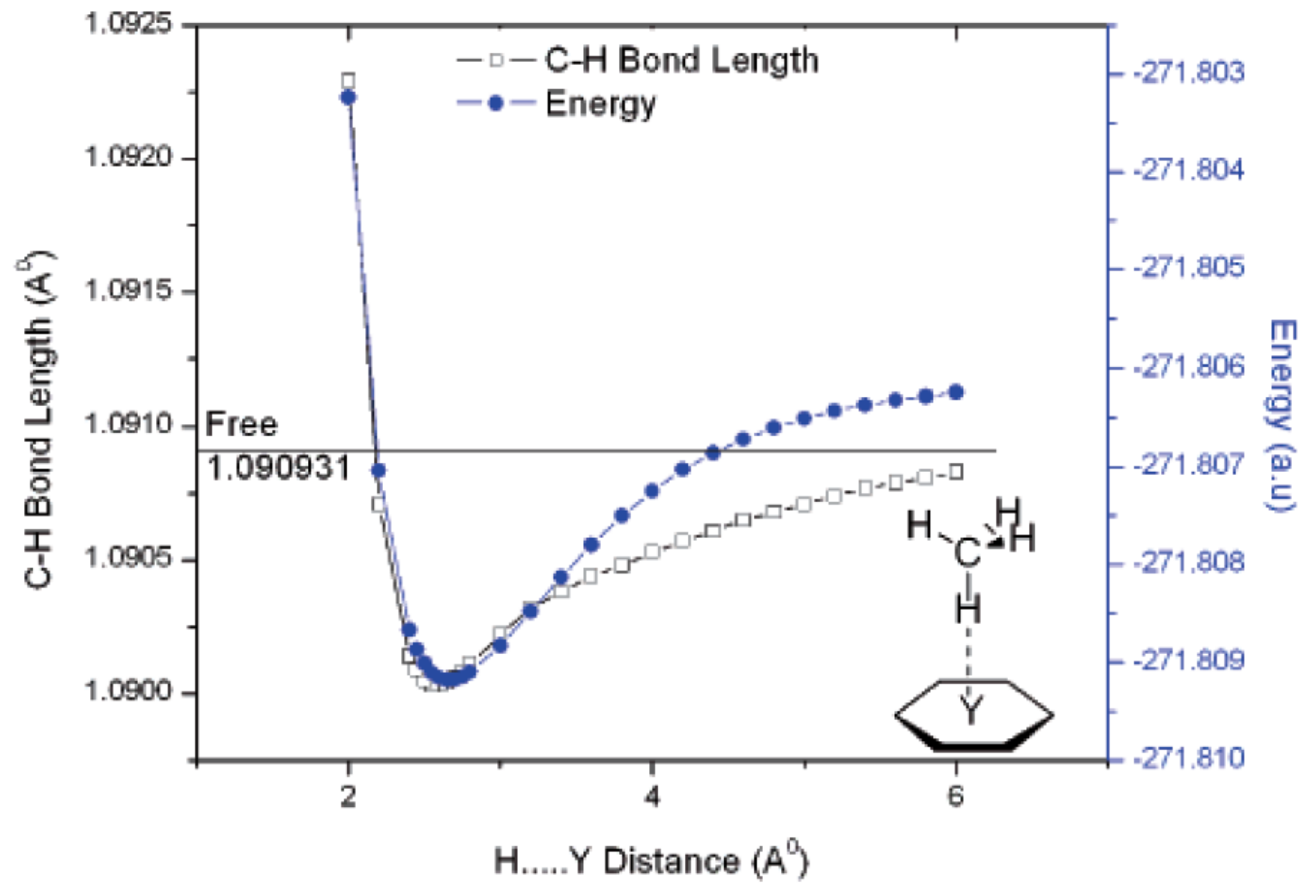
P. Hobza, *Chem. Rev.* **2000**, *100*, 4253-4264
E.D. Jammis, J. Am. Chem. Soc. **2007**, *129*, 4620-4632

Red-, Blue-, or No-Shift in Hydrogen Bonds: A Unified Explanation

Jorly Joseph and Eluvathingal D. Jemmis

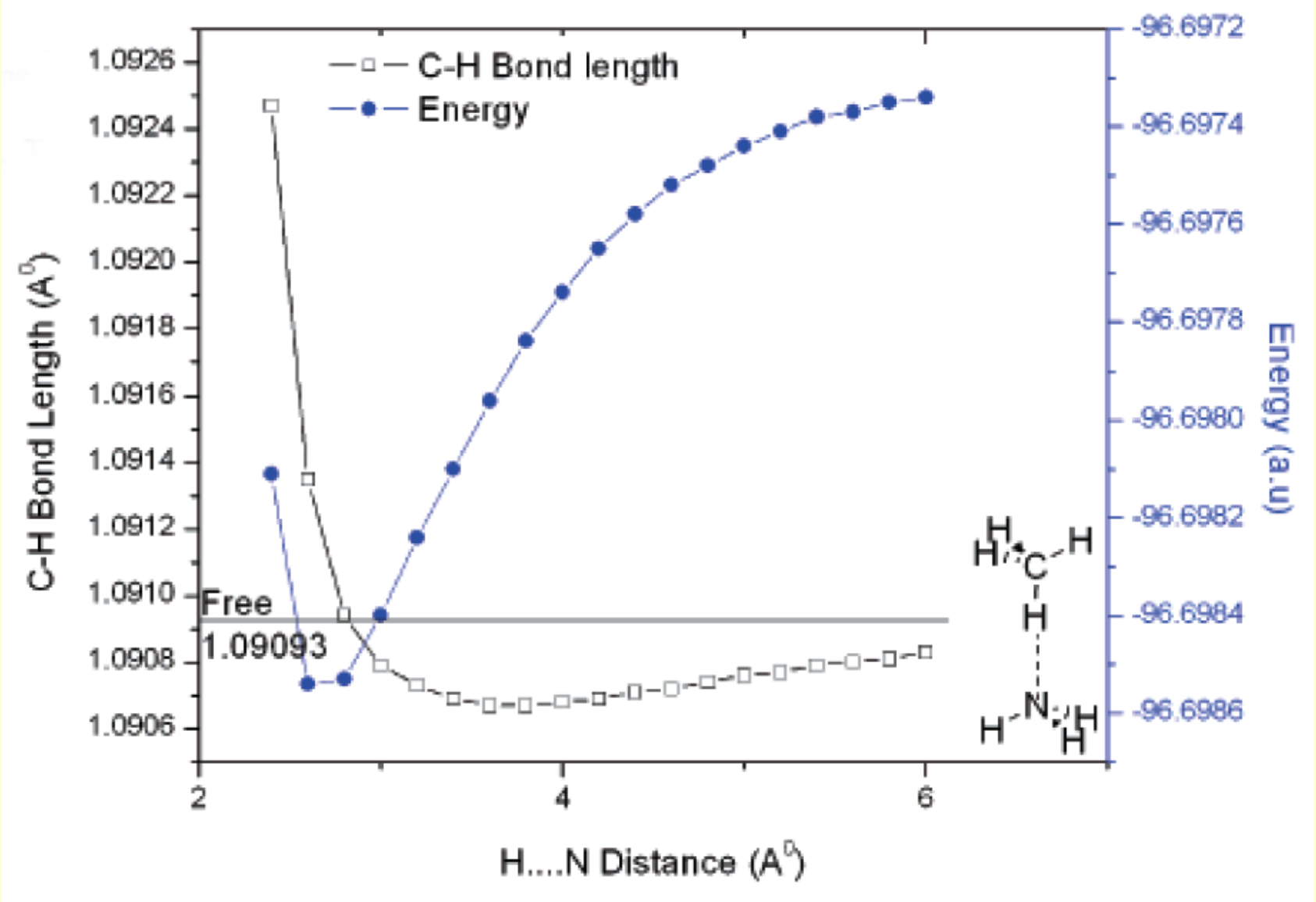
J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Hydrogen bonding: $H_3C\text{-}H\ldots C_6H_6$



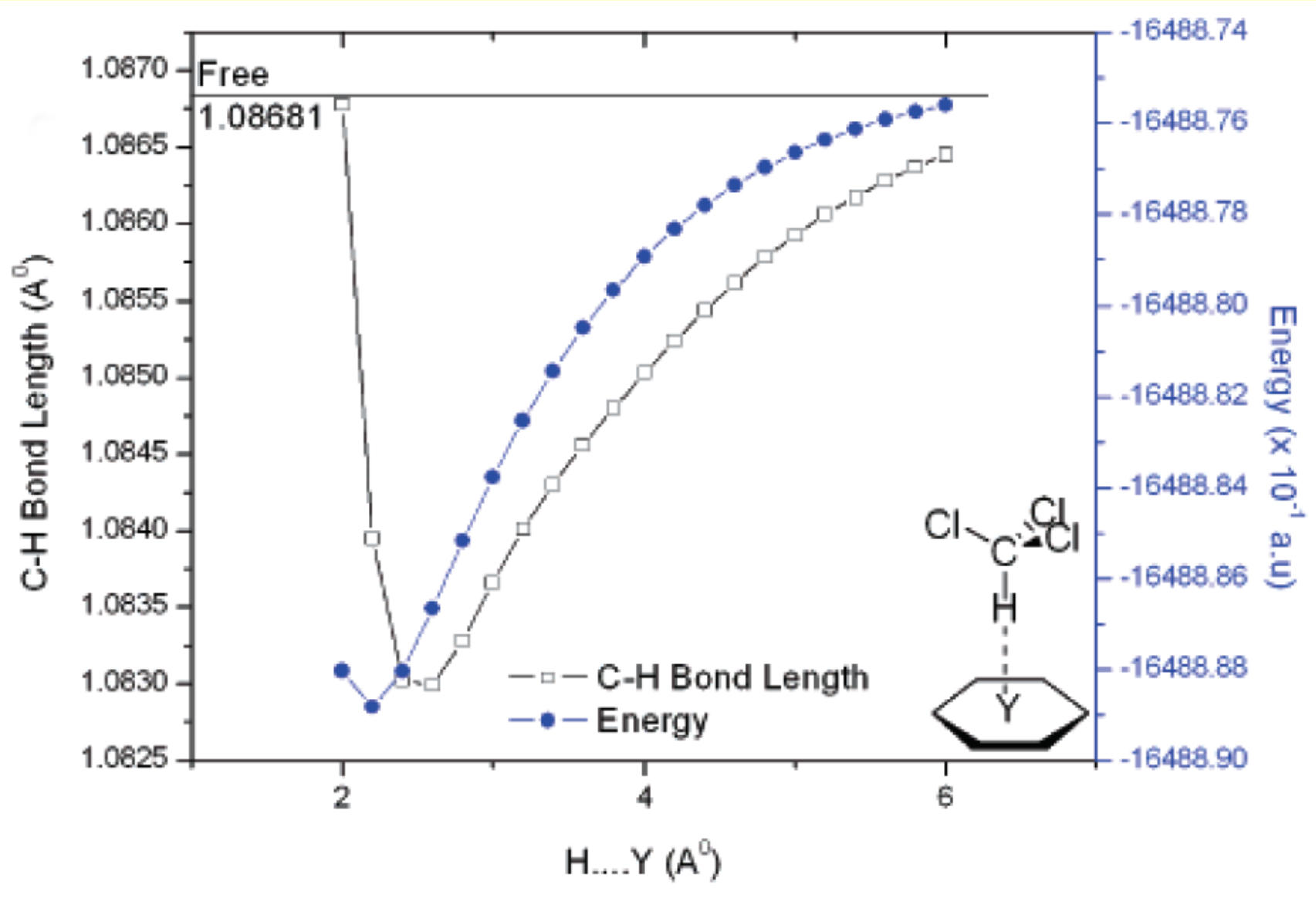
J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Hydrogen bonding: $H_3C\text{-}H\ldots NH_3$



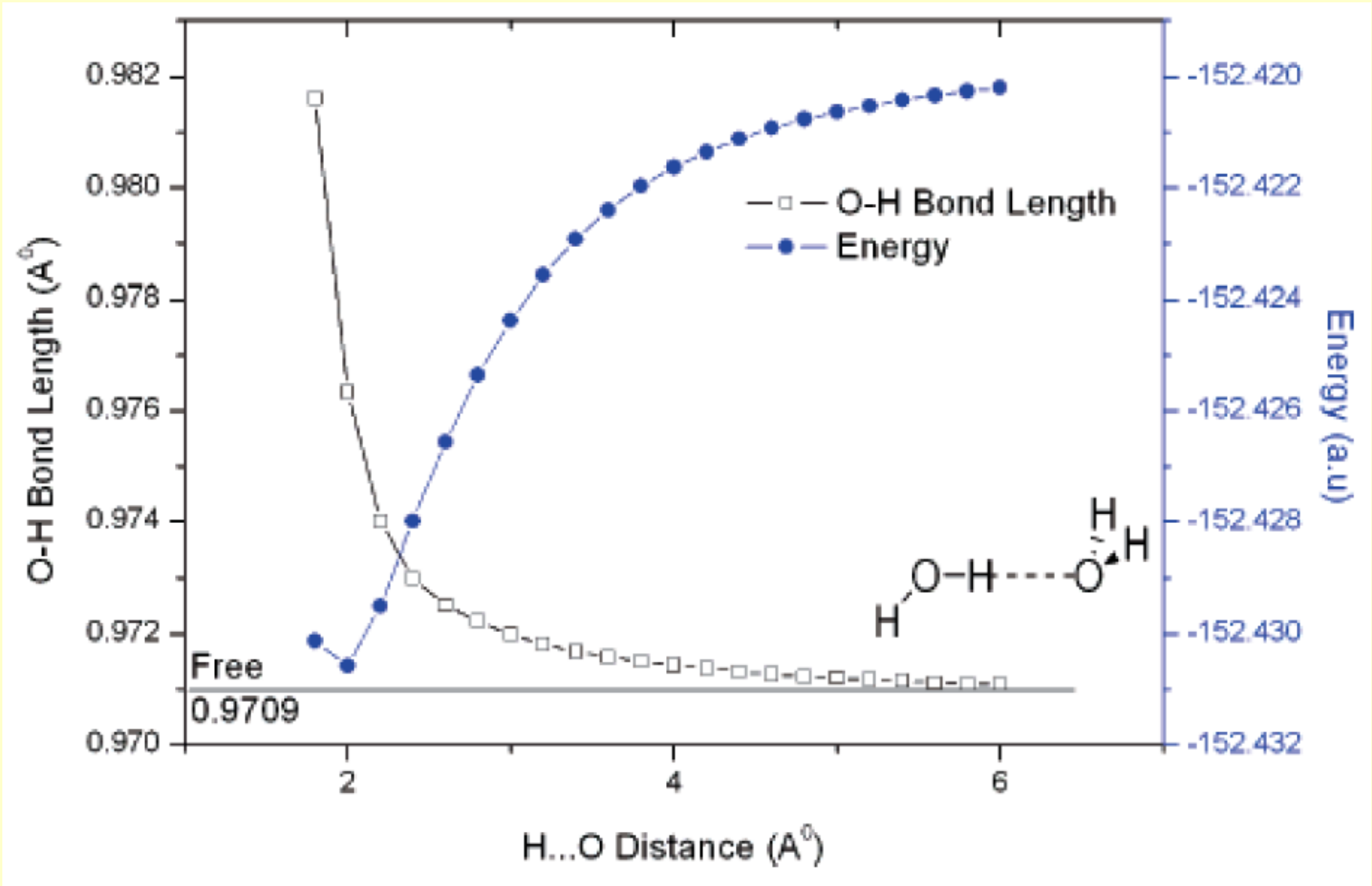
J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Hydrogen bonding: $Cl_3C\text{-}H\ldots C_6H_6$



J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Hydrogen bonding: H-O-H…OH_2



J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

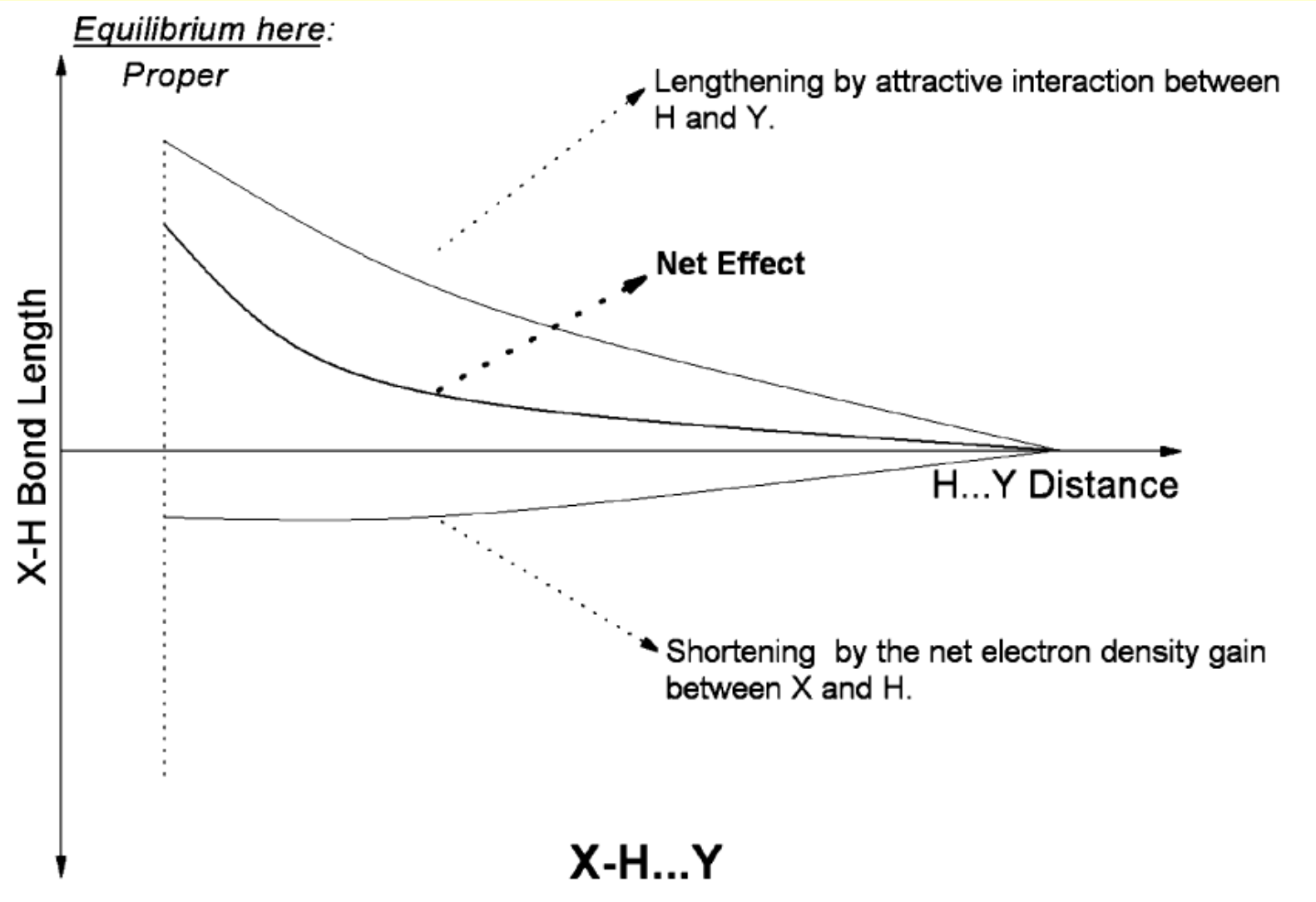
Hydrogen bonding: Proper and pro-improper HB donors

Based on Equilibrium Geometry	
proper (red shift, bond lengthening)	improper (blue shift, bond shortening)
HO−H, H_2N−H, F−H, Cl−H, etc., with all HB acceptors.[22]	F_3C−H with FH, ClH, OH_2, SH_2, and with π electron donors such as enzene, acetylene, etc.[1,33,40]
HCC−H, NC-H with OH_2,[29] π electron donors, etc.[2]	F_2ClC−H, FCl_2C−H with oxygen-based HB acceptors.[10]
F_3C−H with electron donors like Cl^-, F^-, $N(CH_3)_3$, $NH(CH_3)_2$.[33,40]	Cl_3C−H with benzene, fluorobenzene, etc.[14]
Cl_3C−H with $O(CH_3)_2$.[8]	H_3C−H with π electron donors,[2] with OH_2, OHMe, OCH_2.[25]
H_3C−H with Cl^-.[9]	Benzene dimer.[2]
	X−Ng−H with OC, N_2, CO, OH_2, etc. (X = F, Cl, OH; Ng = noble gas).[55−57]
	F_3Si−H with various HB acceptors.[33,47]
	F_2N−H with FH.[33, 51] ON−H with CO.[50]
	F_4P−H dimer.[58]

Based on HB Donor	
proper (red shift, bond lengthening)	pro-improper (blue/red shift, bond shortening/lengthening)
H_2O, FOH, HF, NH_3, HCl, HF, etc.	alkanes, alkenes, aldehydes, CH_xF_{4-x}, CH_xCl_{4-x}, C_6H_6
$F_2C{=}CH_2$	F_3SiH, F_2NH, HNO, F_2PH, F_4PH
HCC−H, NC−H, FCC−H	X−Ng−H, (X = F, Cl, OH; Ng = noble gas)

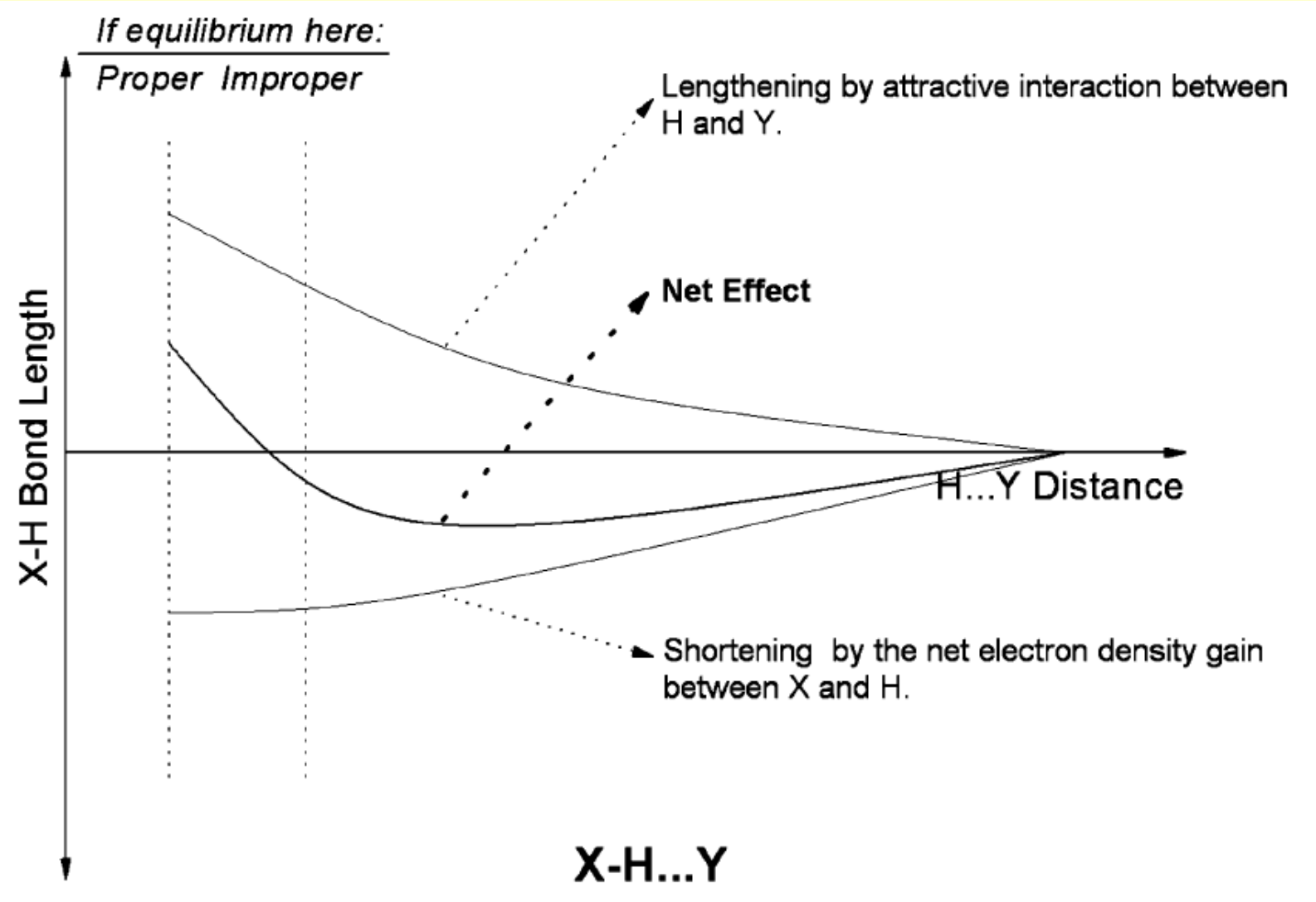
J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Hydrogen bonding: Proper and pro-improper HB donors



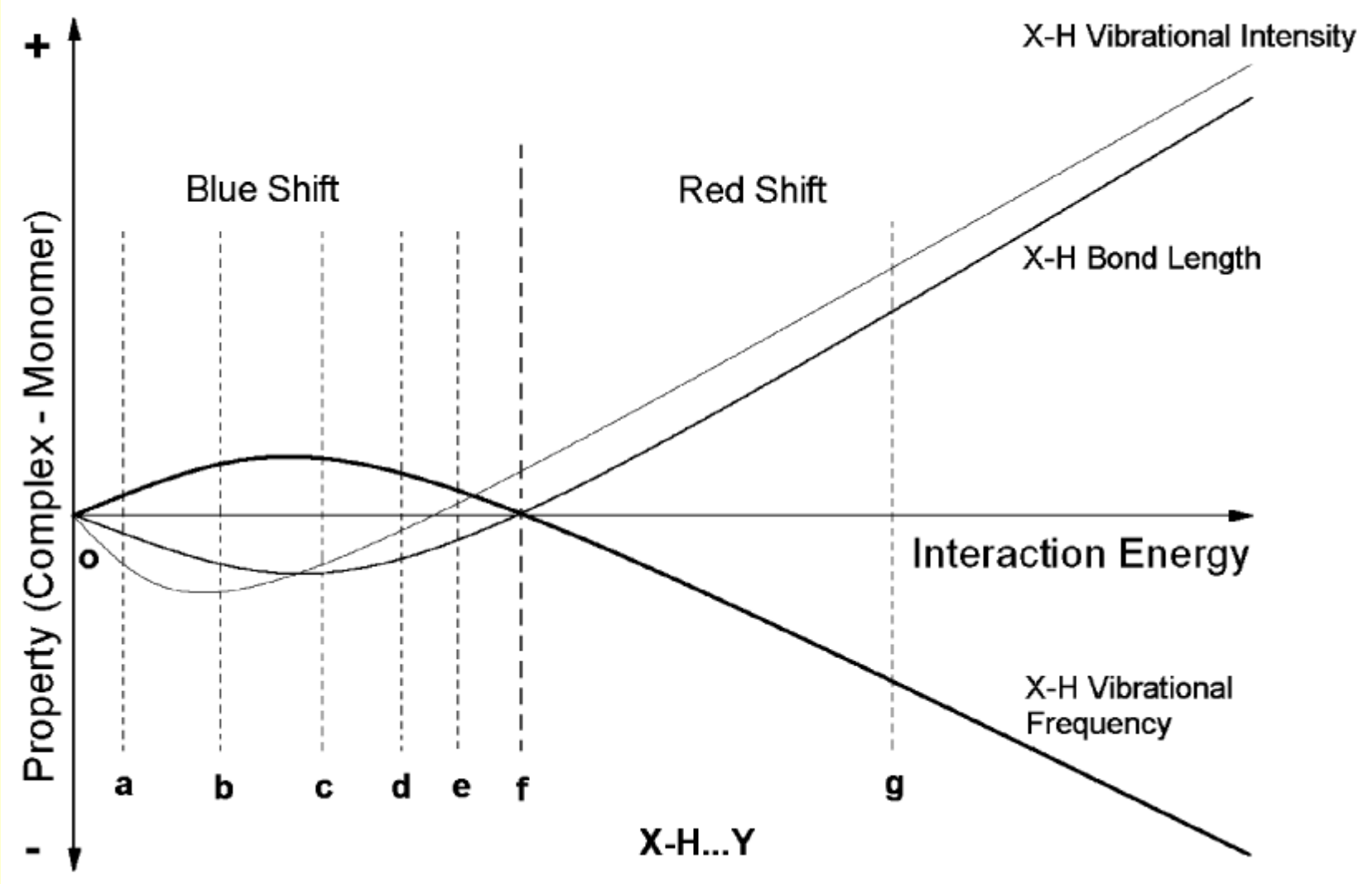
J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Hydrogen bonding: Proper and pro-improper HB donors



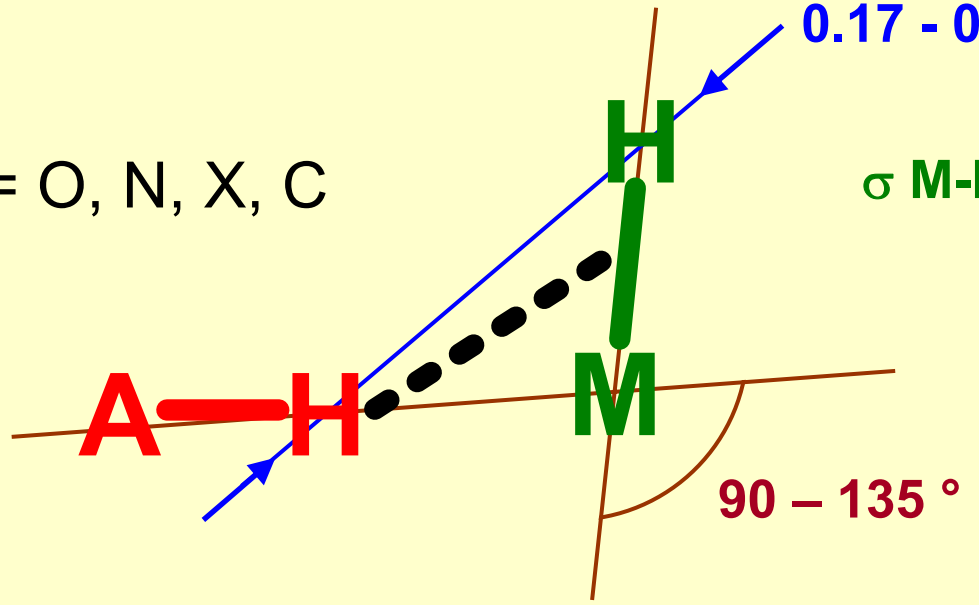
J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Hydrogen bonding: Proper and pro-improper HB donors



J. Am. Chem. Soc. **2007**, *129* (15), 4620-4632

Dihydrogen Bond



Interaction energy

1-7 kcal.mol^{-1}

Moderate Hydrogen Bond

Dihydrogen Bonding: Structures, Energetics, and Dynamics
Chem. Rev. **2001**, *101*, 1963-1980

Dihydrogen bond

- Dihydrogen bond = hydridic-to-protonic interaction
  = proton-hydride bonding
  = H…H hydrogen bonding
  = hydrogen-hydrogen bonding

- Has strength and directionality comparable with those found in conventional hydrogen bonding.

- Consequently, it can influence structure, reactivity, and selectivity in solution and solid state

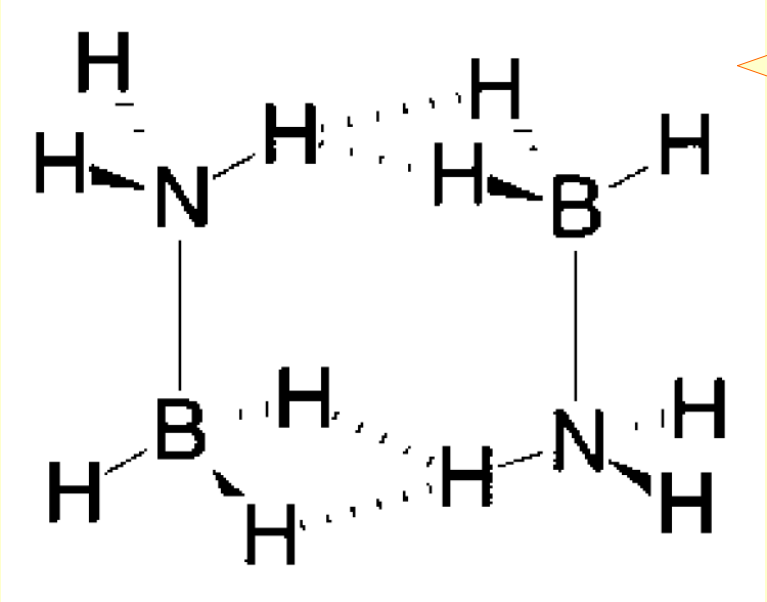
- Finding thus potential utilities in catalysis, crystal engineering, and materials chemistry.

- Their nature is mostly electrostatic, although a weak covalent contribution may be found sometimes

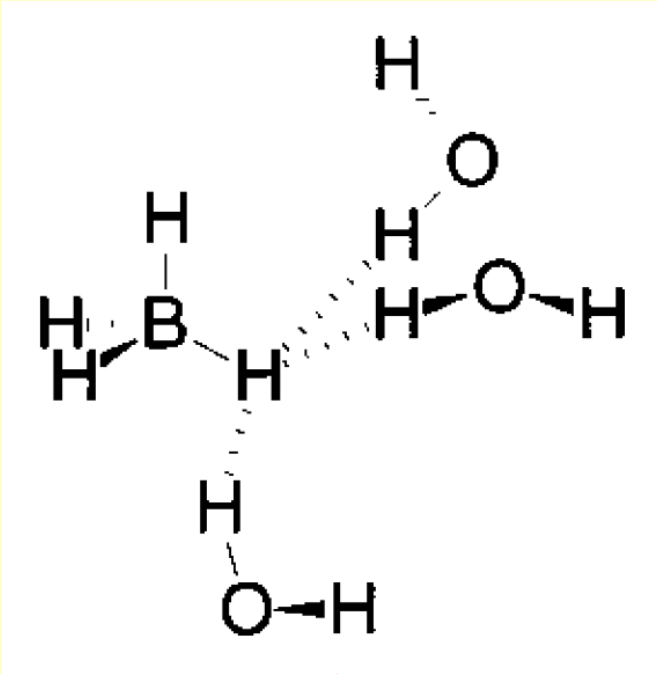
Dihydrogen Bonding: Structures, Energetics, and Dynamics
Chem. Rev. **2001**, *101*, 1963-1980

Interaction of Carboranes with Biomolecules: Formation of Dihydrogen Bonds
J. Fanfrlík, M. Lepšík, D. Horinek, Z. Havlas, P. Hobza,
ChemPhysChem **2006**, *7*, 1100–1105.

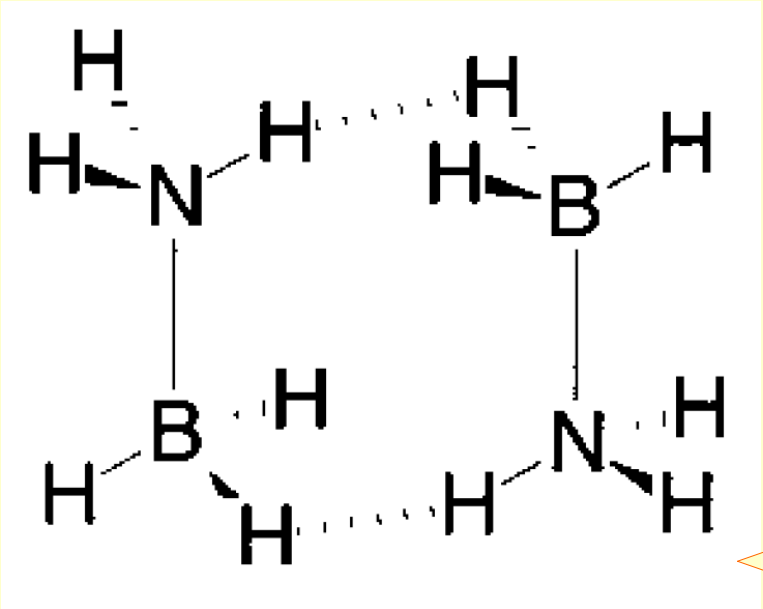
Dihydrogen bond examples



C_{2h} isomer of the NH_3BH_3 dimer



$NaBH_4 \cdot 2H_2O$

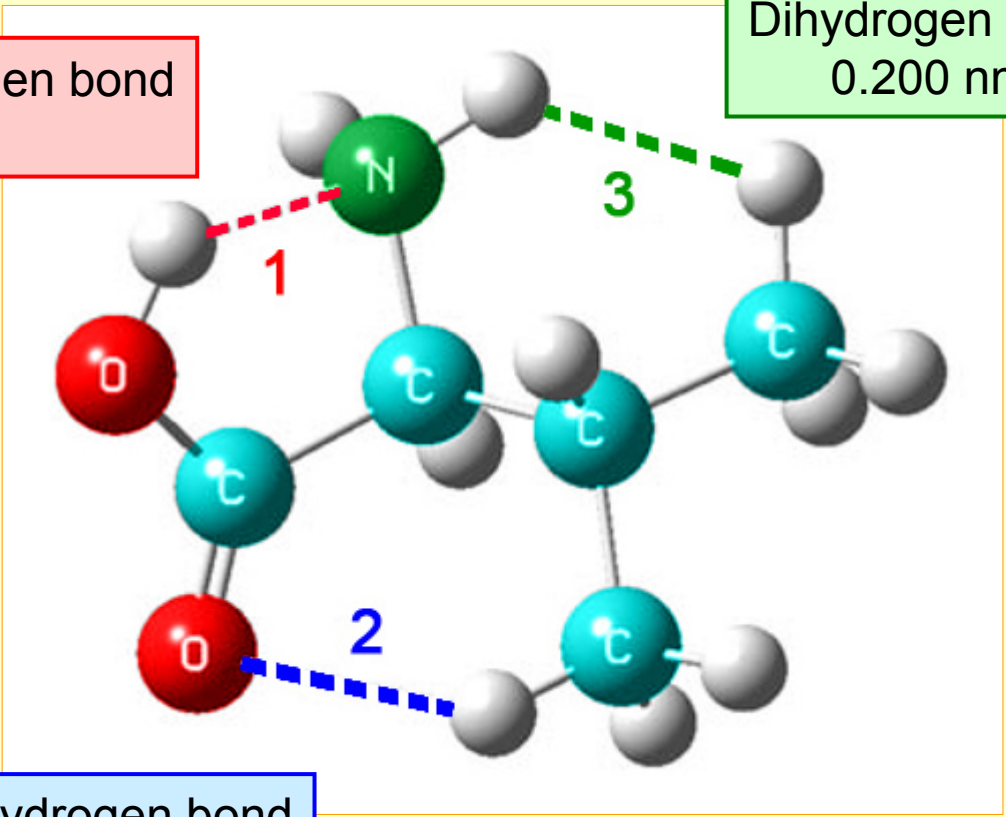


C_2 isomer of the NH_3BH_3 dimer

Hydrogen bonding: Valine conformer

Proper red-shift hydrogen bond
0.194 nm

Dihydrogen bond
0.200 nm



Improper blue-shift hydrogen bond
0.255 nm

ChemPhysChem **2006**, *7*, 828-830

Others Types of Hydrogen Bonding

- Metal atoms as acceptors X-H…M Hydrogen Bonds
- Metal atom groups as donors M-H…A hydrogen bonds
- Agostic interactions M…(C-H) … three centre
- Inverse hydrogen bond (lithium bond) $X^{\delta+}$-$H^{\delta-}$…A^{+}