

Announcements

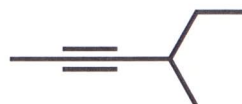
PSI Due Friday

From last time

Our first “functional groups:” alkenes and alkynes

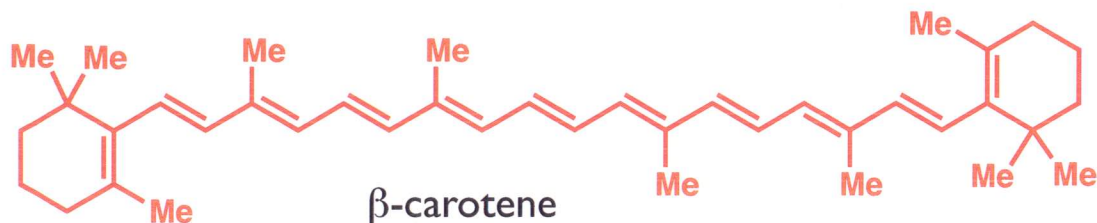


(E)-pent-2-ene

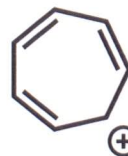
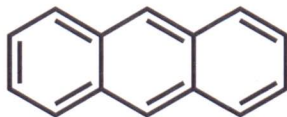


4-methylhex-2-yne

“Conjugated” polyalkenes: two alkenes are separated by only one single bond



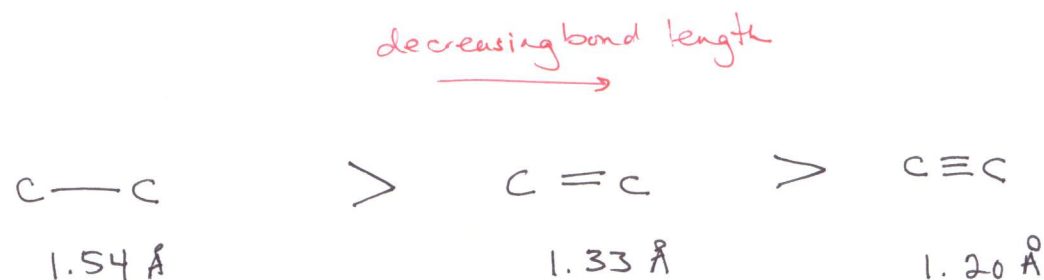
Aromatic compounds: cyclic, fully conjugated molecules that follow Hückel's Rule ($4n + 2$)



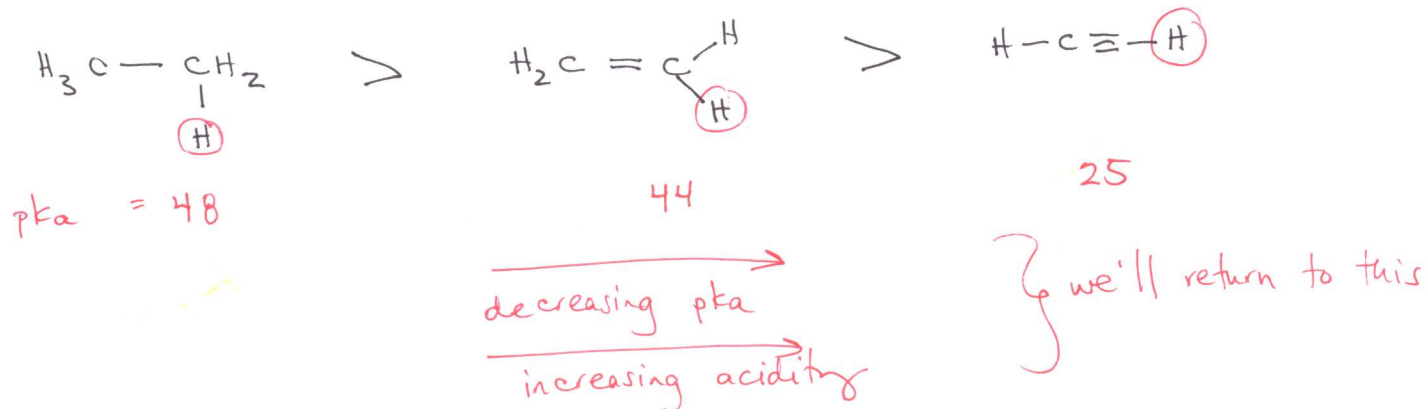
Alkanes, Alkenes, and Alkynes have Different Properties

Key trends:

- bond length:



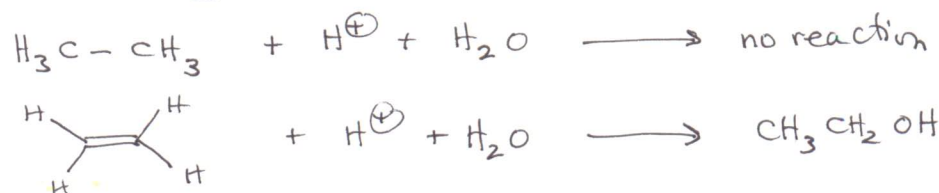
- C-H acidity:



- reactivity:

π bonds are higher in energy than σ bonds; they "react" first.

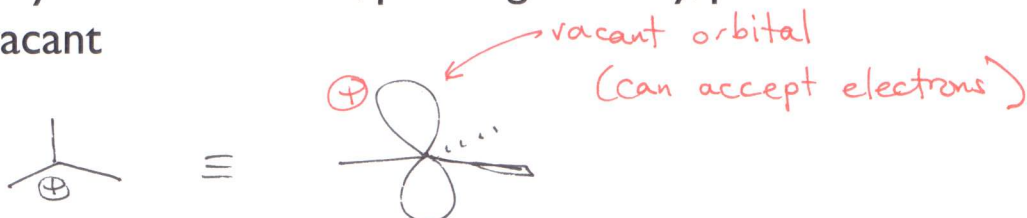
Alkenes + Alkynes are more "reactive" than alkanes



Carbanions, Carbocations, and Radicals: Reactive Species

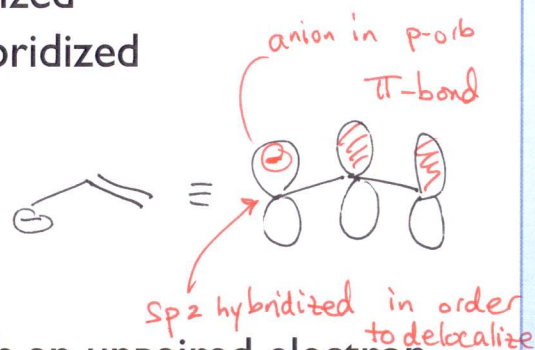
Carbocation: a trivalent carbon

- sp^2 hybridized carbon, planar geometry, p-orbital is vacant



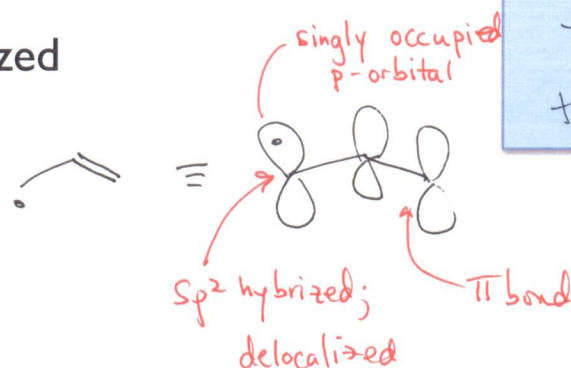
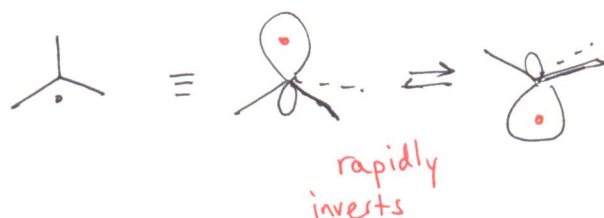
Carbanion: a carbon with a lone pair

- isolated carbanions are sp^3 hybridized
- conjugated carbanions are sp^2 hybridized

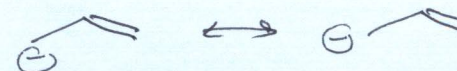
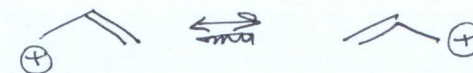


Carbon-based radical: a carbon with an unpaired electron

- isolated radicals are sp^3 hybridized w/low barrier to inversion
- conjugated radicals are sp^2 hybridized



Delocalization of charge is stabilizing!
(resonance stabilization)



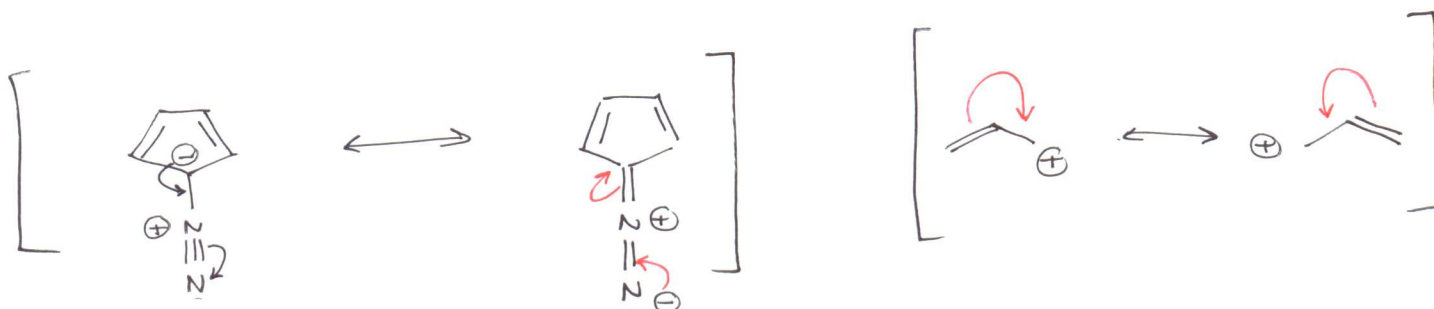
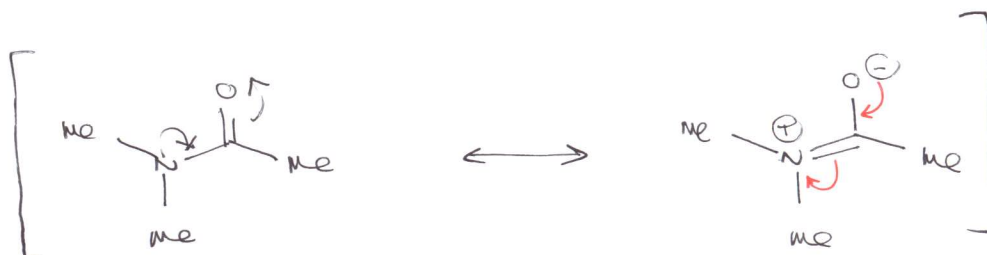
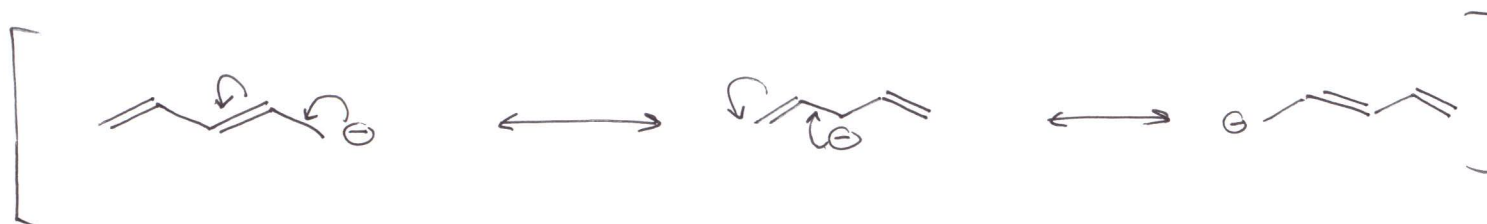
the more resonance structures,
the better! (more delocalized)

Drawing Resonance Structures

Resonance structures show the delocalization of electrons

- bonds, unshared electron pairs, carbocations, or single electrons can be moved using the curved arrow notation without moving any atoms
- arrows should originate at a source of electron density (i.e. a bond or a lone pair)

examples: • resonance contributors that minimize charge are more dominant contributors



all resonance intermediates must still obey the octet rule...

NO TEXAS carbons

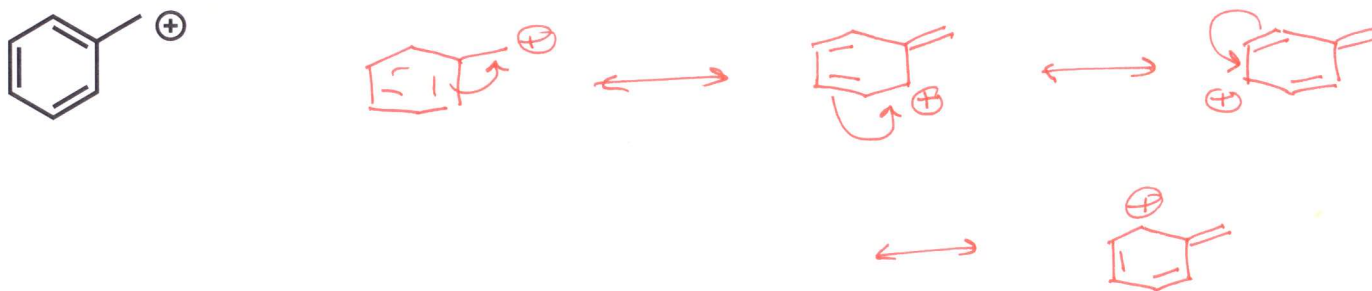
for a discussion of resonance, see RC Ch 6 sec. 5

Drawing Resonance Structures

Resonance structures show the delocalization of electrons

- curved arrows are used to demonstrate that π -electrons, unshared electron pairs (lone pairs), carbocations, or single electrons (radicals) can be delocalized over multiple atoms
- arrows should originate at a source of electron density (i.e. a bond or a lone pair)
- you must be able to push the electrons without moving any atoms

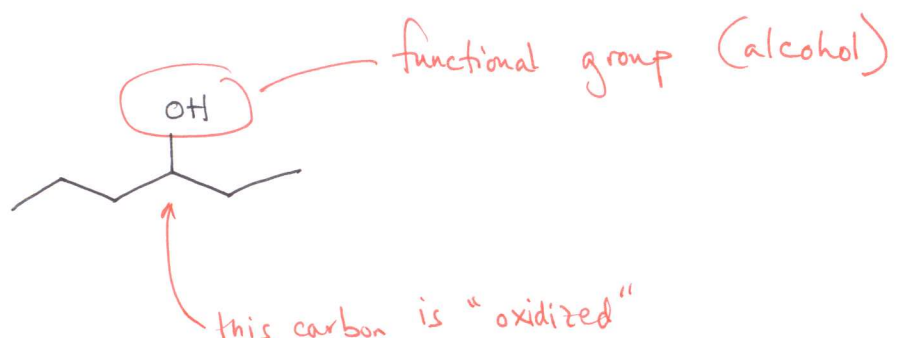
Which carbons share the positive charge?



Functional Groups

Functional groups: the substitution of carbon chains with atoms other than C and H

- A carbon bearing a more electronegative substituent is formally oxidized
- Different functional groups result in different oxidation levels at carbon



Electronegativity

electronegativity (EN): the measure of the ability of a bonded atom (~~or functional group~~) to attract electrons toward itself.

- EN increases as you move up and to the right in the periodic table
- as you move up a column, shielding of outer electrons decreases
- as you move to the right in a column, the nuclear charge increases

(increases effective nuclear charge)

(increased nuclear charge makes it more difficult to remove an e^- , and makes it more favorable to accommodate an e^-)

The Ch I b Electronegativity Chart:

H							an ee)	Pauling scale is most commonly used
2.2								
Li	Be	B	C	N	O	F		
1.0	1.6	2.0	2.6	3.0	3.4	4.0	Pauling value	
1.0	1.5	2.0	2.5	3.0	3.5	4.0	Ch Ib scale	
Na								
0.9	1.25	1.6	1.9	2.2	2.6	3.2	Pauling value	
0.9	1.25	1.6	1.95	2.3	2.65	3.1	Ch Ib scale	
K							Br	
0.8							3.0	
							I	
							2.7	

start at 1,
add 0.5

start at 0.9,
add 0.35

Pauling scale is most commonly used

start at 1,
add 0.5








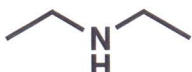

start at 0.9,
add 0.35

a useful tool for estimating electronegativities.

Functional Groups

Functional groups: the substitution of carbon chains with atoms other than C and H



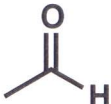

Functional groups with one bond to more EN substituent:

generic name:	alcohol	amine	thiol	alkyl halide	ether
					
	ethanol (ethyl alcohol)	ethyl amine	ethane thiol	ethyl chloride	diethylether
					
		N,N-diethyl amine		ethyl bromide	
					
		N,N,N-triethyl amine		ethyl iodide	

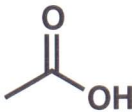
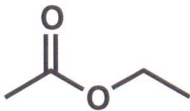
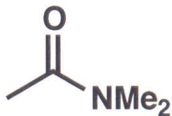

Functional Groups

Functional groups: the substitution of carbon chains with atoms other than C and H

Functional groups with two bonds to more EN substituents:

generic name:	ketone	imine	aldehyde	acetal
				
	acetone (2-propanone)	propan-2-imine	acetaldehyde (ethanal)	2,2-dimethoxy- propane

Functional groups with three bonds to more EN substituents:

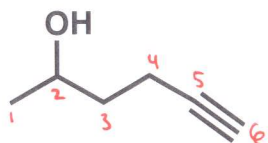
generic name:	carboxylic acid	ester	amide	nitrile (cyano-)
				
	acetic acid	ethyl acetate	N,N-dimethyl- acetamide	acetonitrile (ethanonitrile)

Naming Compounds with Functional Groups

identify the parent hydrocarbon (the longest straight chain)

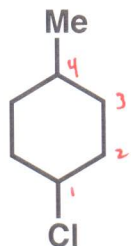
- number the carbons of the parent hydrocarbon, minimizing the sum of the substituent #'s, and assigning the highest priority functional group the lowest number
- the highest priority substituent is listed as a suffix
- the fragments are listed in alphabetical order
- for detailed IUPAC rules, see: <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/nomenI.htm>

name me!



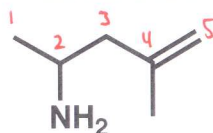
hex-5-yne-2-ol
= alcohol suffix

name me!



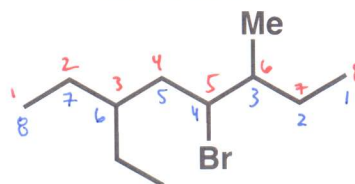
1-chloro-4-methylcyclohexane

name me!



4-methylpent-4-en-2-amine

name me!



4-bromo-6-ethyl-3-methyloctane

highest priority

carboxylic acid
ester
amide
nitrile

aldehyde
ketone
alcohol
thiol
amine

alkene
alkyne
ether
halogen

lowest priority

decreasing
priority

changed
in slide

for nomenclature guidelines, see RC Ch.7

Revisiting Electronegativity

electronegativity (EN): the measure of the ability of a bonded atom (~~or functional group~~) to attract electrons toward itself.

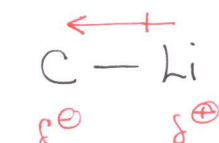
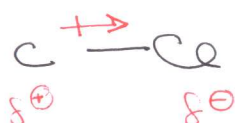
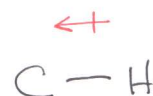
Bonds between atoms of different electronegativities have dipole moments.

- these are 'polar covalent bonds'

atom	EN
C	2.6
F	4.0
O	3.4
Cl	3.2
B	2.0
Li	1.0
H	2.2

Rule of Thumb:

a bond between two atoms with an EN difference between 0.4 and 2.7 is generally considered "covalent" (e^- s are shared)



indicates partial charge on the atom

you should be able to do this qualitatively.

we'll return to this when we discuss organic reactions

dipole moment (μ): describes the distribution of two charges (q) of equal magnitude and opposite sign separated by distance R (bond length), reported in Debyes (D)

larger the μ , the more polarized the bond

$$\mu = qR \quad \rightarrow \text{can be used to determine \% ionic character}$$

1 Debye = 3.34×10^{-30} coulomb · meter

1 Debye = μ for +1/-1 charge separated by 0.2082 Å

dipole moment, typically experimentally determined.
If δ charges are known, it can be calculated
OGC, p. 82-85

Polarity: Molecules with Dipole Moments

molecular dipole moment: a molecule in which the center of positive charge is not coincident with the center of negative charge.

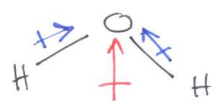
molecular dipoles can be analyzed as the vector sum of the bond dipoles

can calculate using vector mathematics

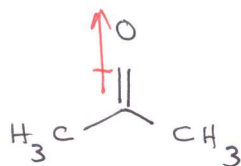
atom	EN
C	2.6
F	4.0
O	3.4
Cl	3.2
B	2.0
Li	1.0
H	2.2

can calculate

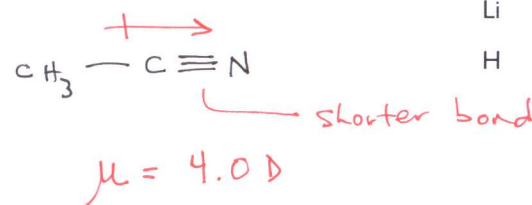
if you know
the δ charge
based on the
bond angle in H_2O
(104.6°) and
the O-H bond length
(1.0 \AA)



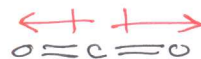
$$\mu = 1.85 \text{ D}$$



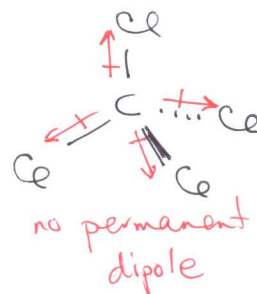
$$\mu = 2.91 \text{ D}$$



$$\mu = 4.0 \text{ D}$$



no permanent
dipole



no permanent
dipole

$$a = 1.0 \cos 52.3 = 0.61 \text{ \AA}$$

Hydrogen Bonding

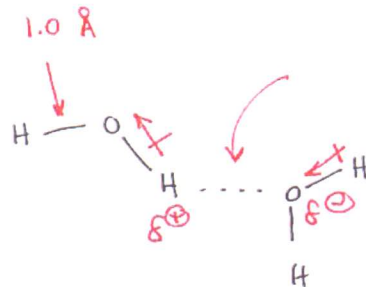
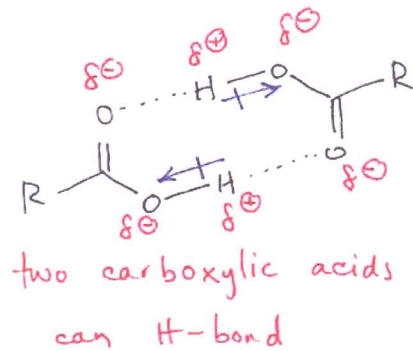
weak : 0-5 kcal/mol
moderate : 5-14 kcal/mol
strong : 15-40 kcal/mol

We have learned about:

- Ionic Bonds
- Covalent Bonds

Hydrogen bonds are a non-covalent interaction between an H and an electronegative atom.

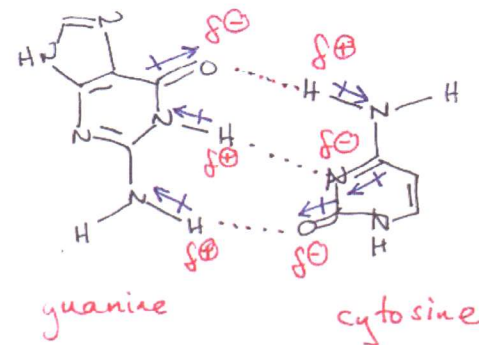
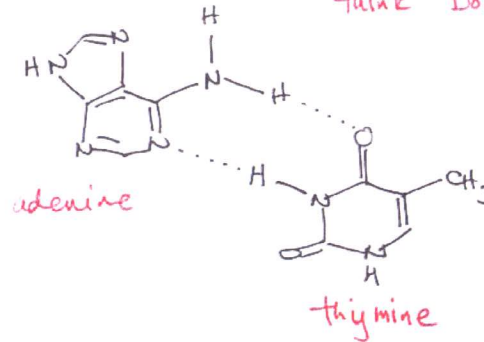
examples of hydrogen bonding:



more on H_2O ...

Watson - Crick Base Pairing:

think Double Helix!!



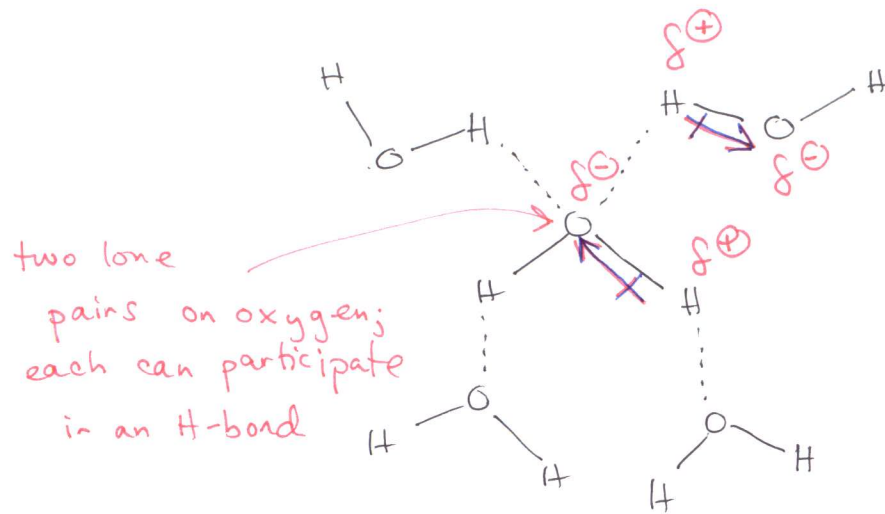
H bond length can be ~1.6 to 2.8 Å

Hydrogen Bonding in Water

Hydrogen bonding is plentiful in water:

- each water can hydrogen bond with 4 other waters

dipole-dipole interaction



bp H_2O 100°

mp H_2O 0°

bp MeOH 65°C

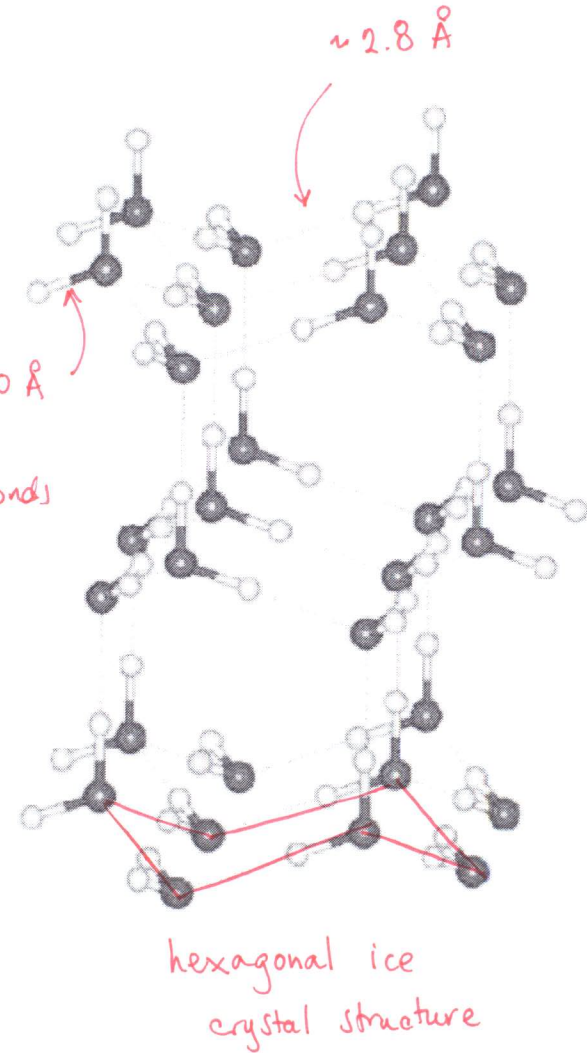
mp MeOH -97°C

(MeOH can only participate in 3 H-bonds per molecule)

each H bond is worth about ~ 5 kcal/mol

an O-H bond is worth ~ 120 kcal/mol

average H bond is about 4 to 5% the strength of a typical covalent bond



the high boiling point and low melting point of water can be attributed to hydrogen bonding

- for an interesting website on ice and snowcrystals: <http://www.its.caltech.edu/~atomic/snowcrystals/ice/ice.htm> (Ken Libbrecht)

(Hydrogen bonds are considerably stronger than vanderwaal forces, which govern mp and bp of alkanes)