Organic Chemistry I, CHM 3140, Dr. Laurie S. Starkey, Cal Poly Pomona

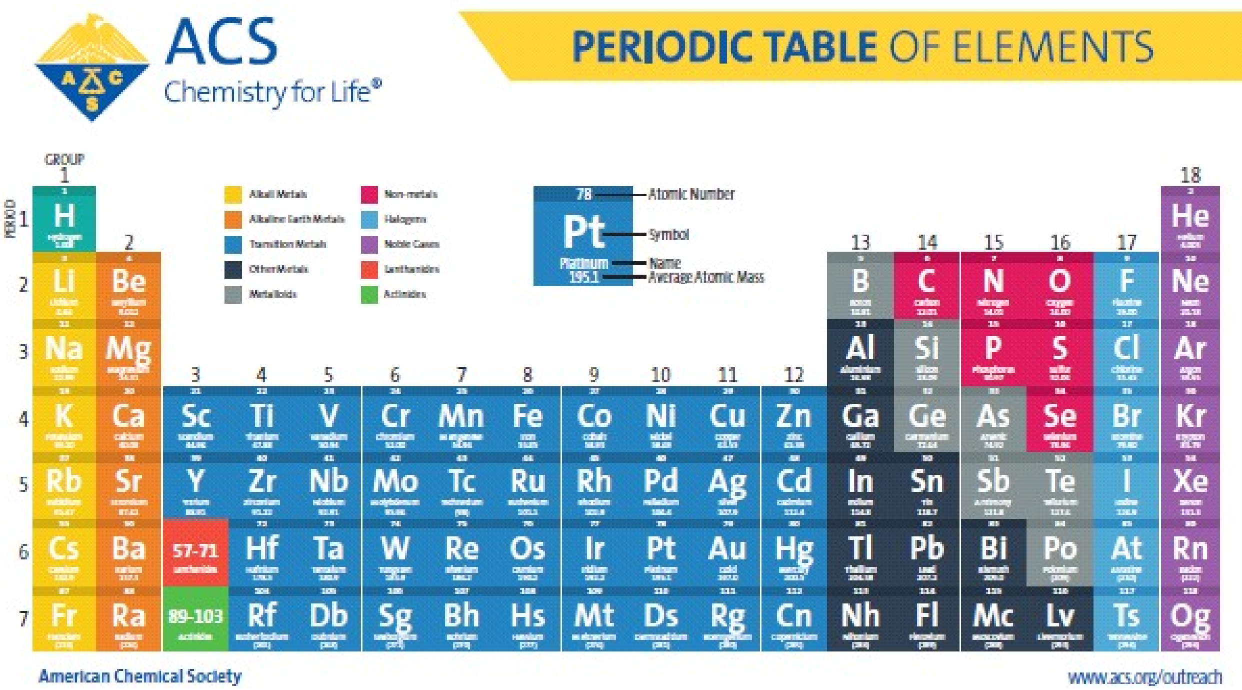
Chapter 1 (Klein) - Chemistry Review & Introduction to Organic Molecules

Organic (living things, chemistry of carbon)

Inorganic (rocks, minerals, metals, glass)

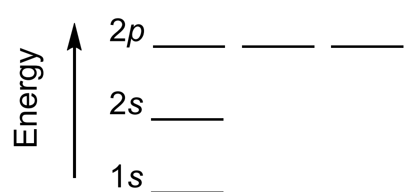
Examples of Organic Compounds:

Products	Materials	in Nature
medicine	paper	hormones/steroids
pesticides	cotton	DNA
dye/paint/ink	tires/rubber	protein/fats/sugars
gasoline/fuels	nylon/polyester	flavors/fragrances
cosmetics	plastic/vinyl	molecular bio. = organic rxns



Review Some Chemistry Basics (Klein 1-1 to 1-8)

electronic configurations and the Periodic Table



- electrons (e^-) are held in atomic orbitals around the nucleus (s, p, d, f), and s orbitals are more stable (lower Energy) than p orbitals
- fluorine is the <u>most</u> <u>electronegative</u> element (pulls electron density toward itself)

  Which is more electronegative: C or N ?

Periodic trends for electronegativity:

F

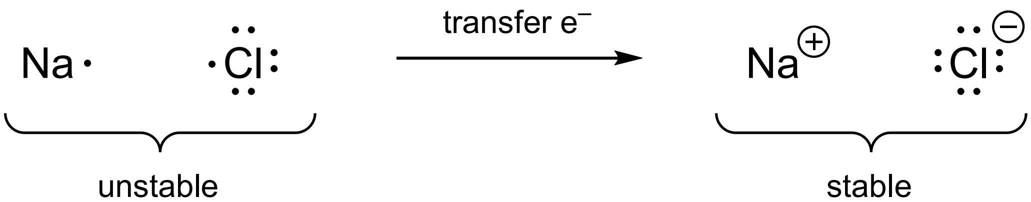
- oxygen is the <u>second-most</u> <u>electronegative</u> element and C ≅ H (no significant difference)

- all elements want to "look like" the Noble gases (have same electronic configuration) atom is <u>stable</u> if it has a filled valence shell

Examples: Na^+ Ca^{2+} Br^-

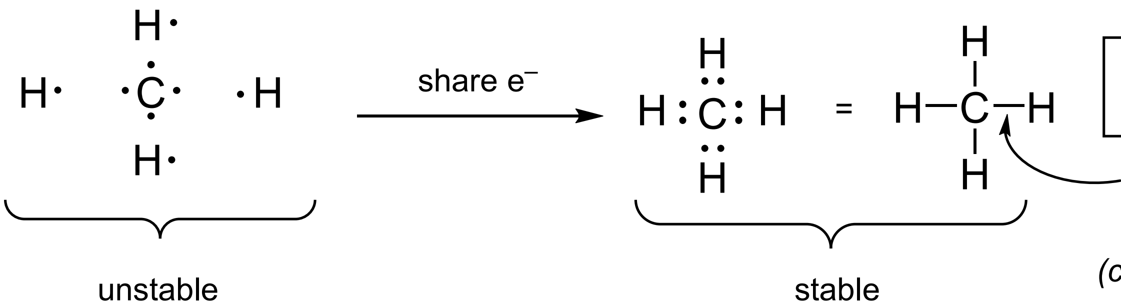
8 e^- = s^2p^6 (or $1s^2$ for He)

ionic bonds are formed between atoms if they have a large difference in electronegativities



a **salt** (network structure)

covalent bonds are formed between atoms if they have similar electronegativities

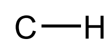


methane **molecule**

Note: carbon needs FOUR electrons to fill its octet, so it typically forms FOUR bonds!

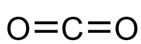
POLAR covalent bonds arise if there is a difference in electronegativities between atoms **(Klein 1.5)**

polar bond
(O is more electronegative than C)



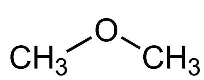
nonpolar bond
(there is no significant difference in electronegativities)

polarity of molecule depends on geometry (**Klein 1.12**, and more on geometry later...)



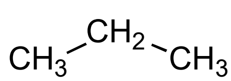
nonpolar

linear molecule: equal and opposite polar bonds, so no net dipole moment



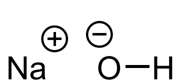
polar

bent molecule: has a net dipole moment



nonpolar

no polar bonds: no net dipole possible (regardless of geometry)



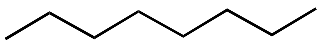
(NaOH)
ionic

ionic: full charges are the ultimate in polarity
hydroxide (OH^-) is called a covalent ion
NaOH has both ionic and covalent bonds

Try SkillBuilder 1.4

line drawings (Klein 1.6) are a short-hand way to draw carbon structures

- end points and intersections represent C atoms
- omit H's attached to C's

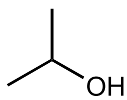
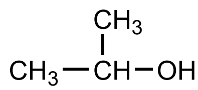
 ≡ $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

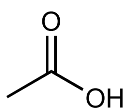
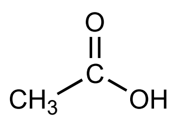
which is which?

one cleans your face

one is for fish & chips

one is a fuel

 ≡ 

 ≡ 

CH_3CO_2H

Try SkillBuilder 1.5

Isomerism (Klein 1.2) Isomers are different compounds that have the same molecular formula.

Constitutional (Structural) Isomers: same formula, different connectivity

Stereoisomers: same formula AND same connectivity, but different spatial arrangement (3D)

Try SkillBuilder 1.1

Drawing Lewis Structures (Klein 1.3, 1.4)

example $ClCH_2CN$

Drawing Lewis Structures (DK 1.3)

1) draw skeleton - connectivity

2) count total # of valence electrons (valence e^- = group no.)

3) subtract charge (if any)

4) fill in missing electrons (fill octets)

5) determine formal charges (if any)

example $CH_3OH_2^+$

Formal Charges (DK 1.4)

- calculate for each atom
- determine "electron count"
  = all nonbonded + 1/2 bonded/shared
- compare "electron count" with valence

missing an electron —> + charge
extra electron —> – charge

Typical, stable bonding (know by inspection)

Atom	example	# bonds*	# lone pairs	"e^- count"	
H					*monovalent*
C					*tetravalent*
N					*trivalent*
O					*divalent*
X					*monovalent*

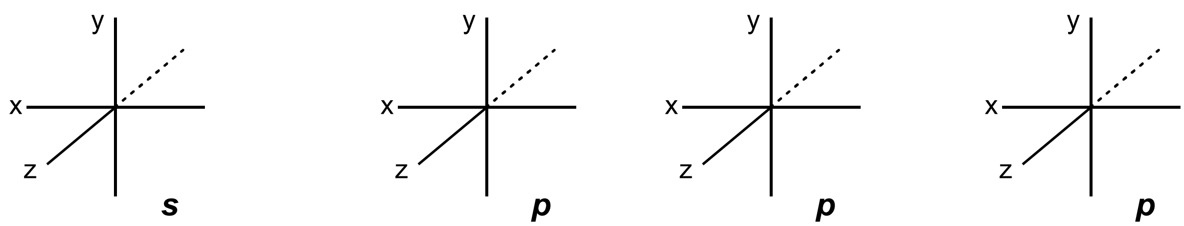
X = halogen
(F, Cl, Br, I)

Try SkillBuilders 1.2, 1.3

Orbitals & Bonding (Klein 1.7-1.9)

Atomic Orbitals (AO)

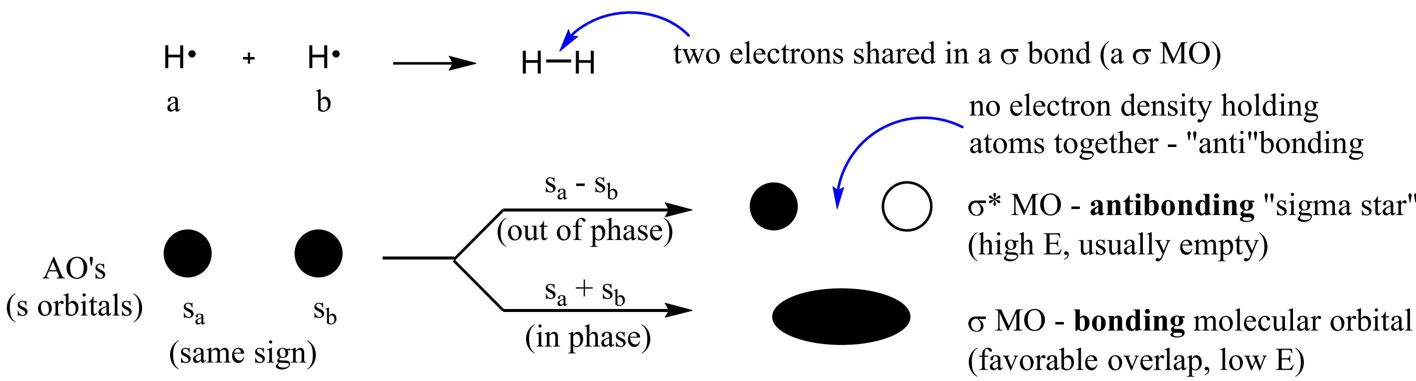
- a region with a high probability of finding electron (e^-) density
- defined by mathematical equations called wave functions
- mathematical sign of the wave function changes at a "node"
- electron density = 0 at any node

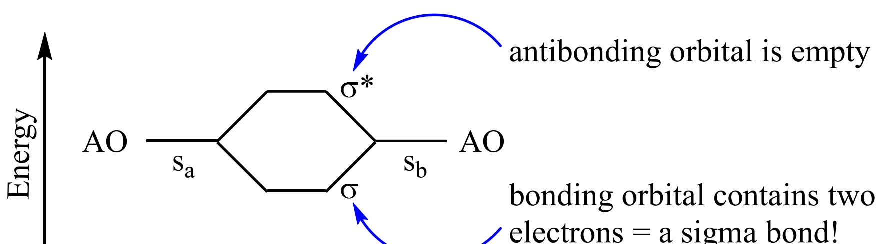


Molecular Orbitals (MO)

- formed by overlap of Atomic Orbitals (AO) to make covalent bonds
- **TWO** AO's combine to give **TWO** MO's (there are **TWO** possible combinations)

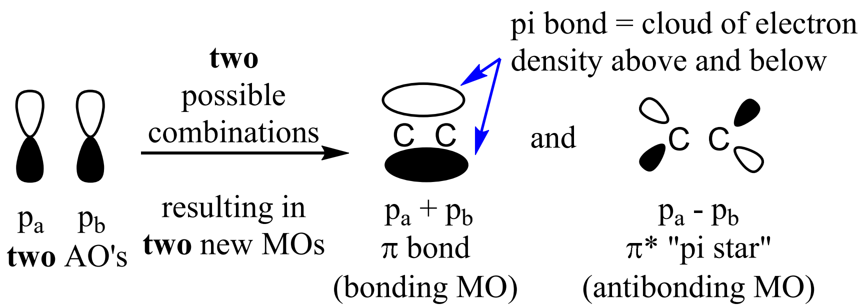
Example 1 Consider the formation of the sigma bond in H_2 by combining two H atoms:

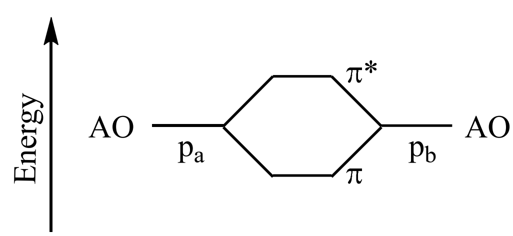




PLEASE NOTE
an **increase** ↑ in # of nodes results in an **increase** ↑ in Energy
(the orbital with MORE nodes is LESS stable)

Example 2 Consider the formation of a pi bond, by overlapping two p orbitals



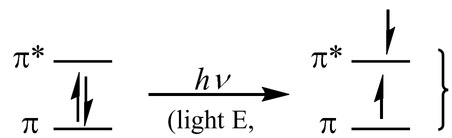


Overall E levels of MO's
(n = nonbonding "lone pairs")

Energy ↑

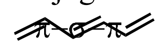
σ* } antibonding orbitals
π* } high E = less stable (usually empty)
n } electrons in these MO's are
π } less stable than σ electrons and are more reactive
σ ← most stable, strongest bond, least reactive

FYI: Electronic Transitions
(Klein 16.11, 16.12, UV-Vis Spectroscopy & Color)

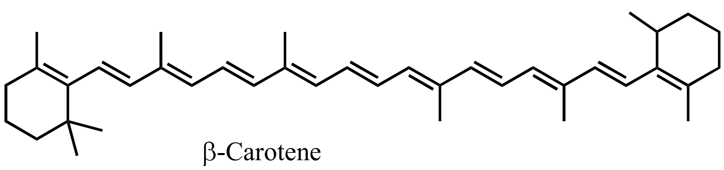


ground state pi bond (low E) — (light E, usually UV light) → excited state pi bond (high E)

this E gap gets smaller if conjugated

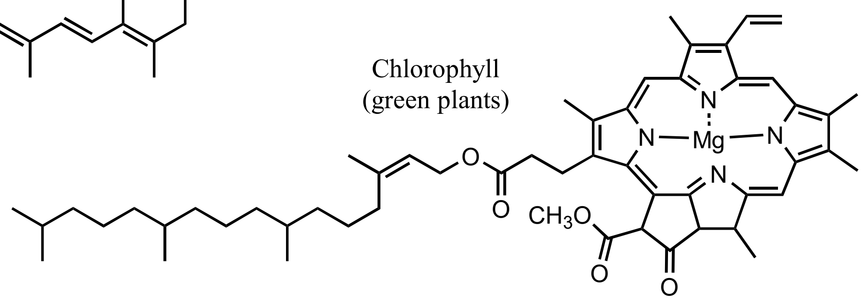


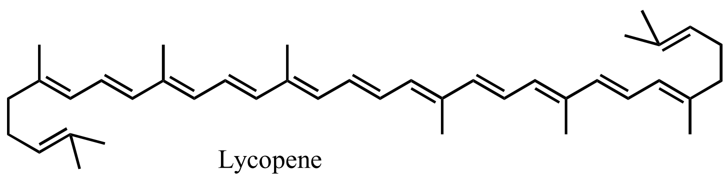
if...**increase** ↑ # of conjugated pi bonds
then...**increase** ↑ resonance stabilization
and...**decrease** ↓ E needed for π → π*
} lower Energy **visible light** is absorbed ***i.e.*, COLOR!**



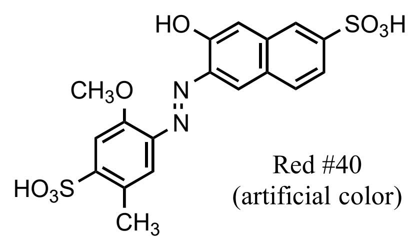
β-Carotene
(orange plants - carrots)
π → π* 454 nm (blue light absorbed)

Chlorophyll
(green plants)





Lycopene
(red plants - tomatoes)



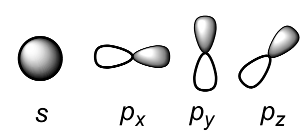
Red #40
(artificial color)

Hybridization (Klein 1.10)

How are the bonds in methane, CH_4, formed?

carbon's atomic orbitals (AOs) contain _________ valence electrons

carbon's AOs

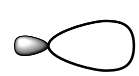


2*p* ____ ____ ____ —add Energy / promote electron→ 2*p* ____ ____ ____

2*s* ____ 2*s* ____

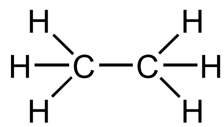
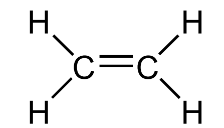
But CH_4 has four identical bonds. *How can that be?*

→ mixing of AOs to give new hybrid orbitals



→ type of hybridization (*sp*, *sp*^{2}, *sp*^{3}) depends on the number of groups around the carbon "regions of electron density"

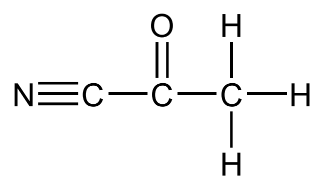
Determining Hybridization

Example molecule	Regions of e^- density	Hybrid-ization	*s* *p* *p* *p*	Result	Geometry (VSEPR)
					
					
H—C≡C—H					

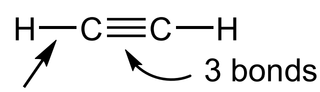
practice: assign hybridizations on given molecule

1) complete Lewis structure
2) hybridization is for each atom
3) count "regions" on each atom

a "region of electron density" is a lone pair or single bond or double bond or triple bond



For the indicated bonds, describe the type of bond and determine which orbitals overlap to form them.



3-D Sketches of Molecules (see Klein 2.6)

CH_3—CH_3

note: can rotate about σ bond (many drawings are possible)

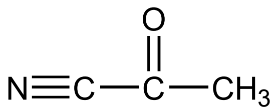
CH_2=CH_2

note: CANNOT rotate about π bond (aligned p orbitals)

HC≡CH

Try SkillBuilders 1.7, 1.8

practice: provide
3D sketch of
given molecule



1) complete Lewis structure

2) assign atom hybridizations

3) sketch with maximum number of atoms in the plane of the page

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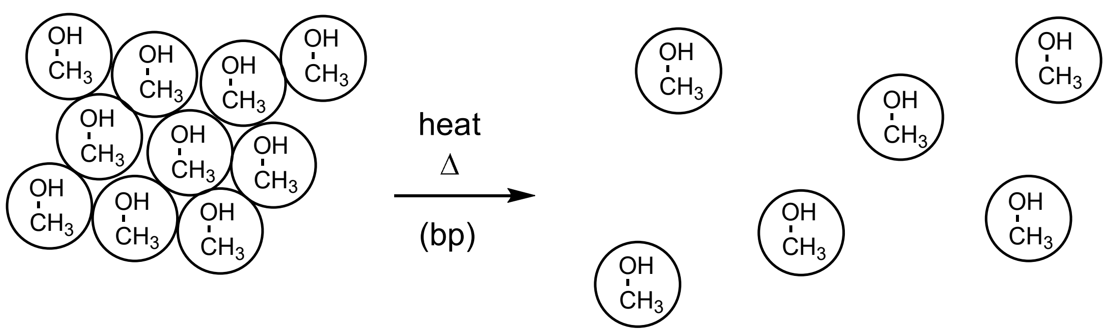
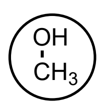
Physical Properties (Klein 1.12, 1.13)

Physical properties, such as water solubility and boiling point (bp) are based on intermolecular forces/attractions.



methanol _______________   methanol ____________

if  **molecules are strongly attracted to one another, then:**

- requires a lot of energy to separate them from each other
- will have a high / low boiling point

Types of "nonbonding" interactions

Molecular Workbench Interactives
http://mw.concord.org/nextgen/

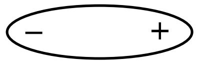
A Dipole-Dipole

B Hydrogen Bonding

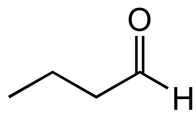
C van der Waals/London Dispersion

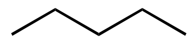
A Dipole-Dipole - attraction between polar molecules (consider geometry! Is CCl_4 polar?)

a polar molecule:



NaCl





bp ºC 1413 76 36

Overall trend:

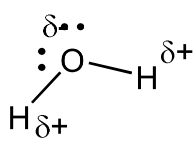
polarity

bp

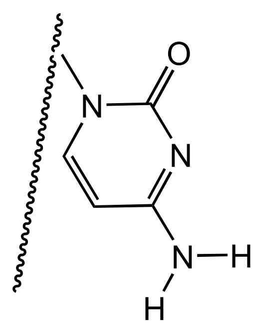
B Hydrogen Bonding - strongest possible dipole-dipole attraction due to H on N or O

H—N H—O both are <u>extremely</u> polar bonds, can cause H-bond formation

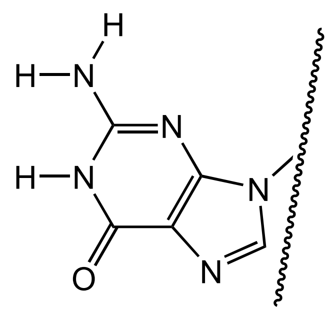
hydrogen-bonding in water:



Demonstrate hydrogen-bonding in DNA base pairs:



cytosine (C)



guanine (G)

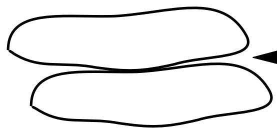
	H_2O	CH_3CH_2OH	CH_3OCH_3	$CH_3CH_2CH_3$
bp ºC	100	78	-24	-42

clicker question: arrange the following compounds by INCREASING boiling point
(from lowest to highest)

CH_3CH_2OH	$CH_2{=}CH{-}CH_3$	$H{-}C({=}O){-}CH_3$
I	II	III

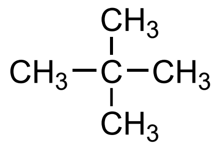
C Van der Waals/London Dispersion Forces - induced (temporary) dipoles

- present between all molecules, but for nonpolar molecules, this is the *only* attractive force



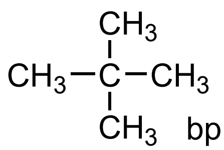
temporary attraction because of uneven distribution of electrons

- the greater the surface area, the greater the VDW/London forces (think "Velcro")
- the higher the MW, the higher the bp (if all polarity is equal)

	$CH_3CH_2CH_2CH_3$		$CH_3CH_2CH_2CH_2CH_3$	$C_{31}H_{64}$
bp ºC	-1	10	36	> 300

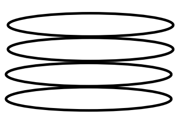
$CH_3CH_2CH_2CH_2CH_3$

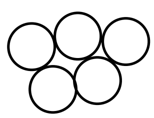
bp 36ºC



bp 10ºC

straight-chain vs. branched





to predict boiling points

1) H-bonding (OH or NH)
2) polar vs. nonpolar

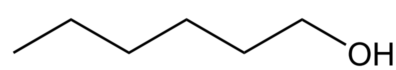
3) ↑ MW, ↑ bp
4) branching (least important!)

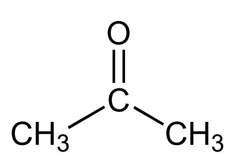
Try SkillBuilders 1.9, 1.10

Water Solubility (Klein 1.14)

- "like dissolves like"
- water is polar and can form hydrogen bonds (H-bonds)

CH_3CH_2OH $CH_3CH_2CH_2OH$





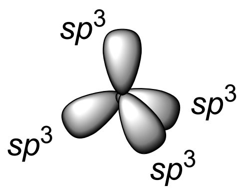
acetone

- miscible with water
- polar
- H-bond acceptor

California State Polytechnic University, Pomona
Organic Chemistry I, CHM 3140, Dr. Laurie S. Starkey

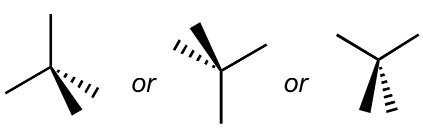
Hybridization of Carbon Atoms

sp^3-hybridized

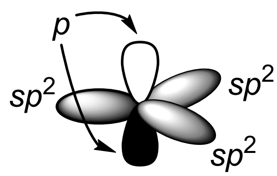


4 regions of electron density

- sp^3 hybrid orbitals
- tetrahedral geometry
- 109.5° bond angles

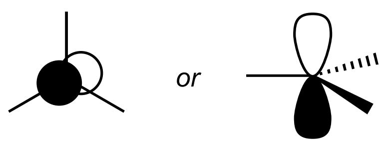


sp^2-hybridized

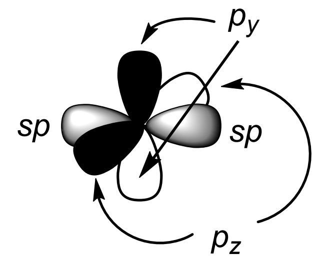


3 regions of electron density

- sp^2 hybrid orbitals
- one *p* orbital remains
- trigonal planar geometry
- 120° bond angles

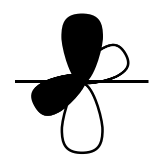


sp-hybridized

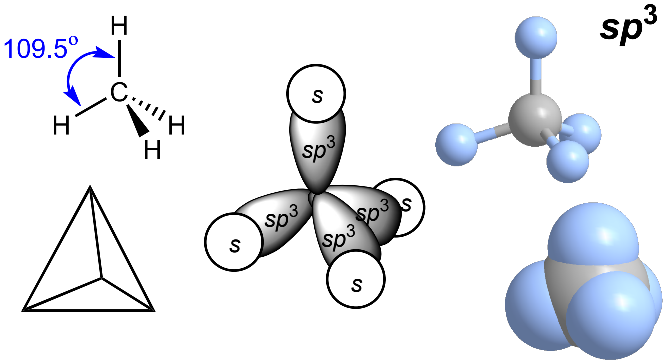


2 regions of electron density

- *sp* hybrid orbitals
- two *p* orbitals remain
- linear geometry
- 180° bond angle

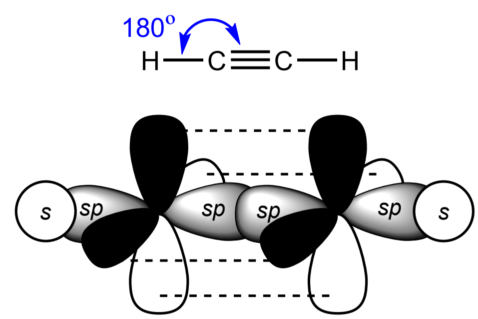


3D Orientation of Sigma (σ) and Pi (π) Bonds

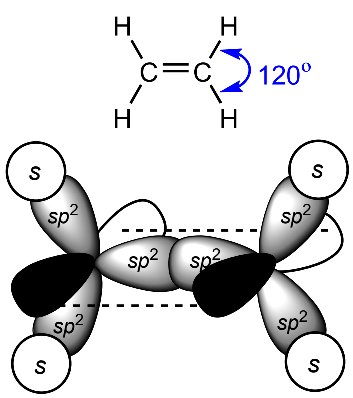


Tetrahedral orientation of sigma bonds in methane (***sp^3* hybridization**).

sp

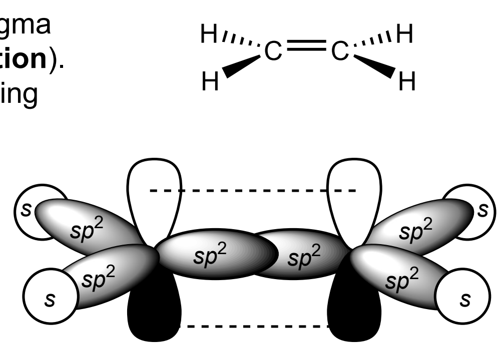


Linear orientation of sigma bonds in acetylene (***sp* hybridization**). Overlapping *p* orbitals form two pi bonds.



Trigonal planar orientation of sigma bonds in ethylene (***sp^2* hybridization**). A pi bond is formed by overlapping *p* orbitals that are orthogonal to sp^2 plane.

sp^2



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Organic Chemistry I, CHM 3140, Dr. Laurie S. Starkey

Ch. 1 Summary (Klein 4th edition) Chemistry Review & Intro to Organic Molecules

I. Review of General Chemistry concepts (1.1 – 1.8)
- A) atomic structure; energy of atomic orbitals (*s, p*)
- B) electronegativity - ability of an atom to attract electron density
  - i) fluorine is most electronegative element (oxygen is second-most!), periodic trends
  - ii) C ≈ H electronegativity, N = Cl electronegativity
- C) a filled valence shell (full octet) imparts stability
- D) covalent vs. ionic bonds
- E) bond polarity (δ+ and δ–) ***SkillBuilder 1.4***

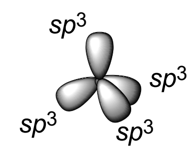
II. Reading Line Drawings (1.6) ***SkillBuilder 1.5***

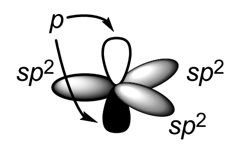
III. Lewis Structures (1.3, 1.4) ***SkillBuilder 1.2***
- A) structures show σ, π and nonbonded electrons
- B) formal charges (1.4) ***SkillBuilder 1.3***
- C) recognize "typical" configurations for common atoms (H, C, N, O, X)

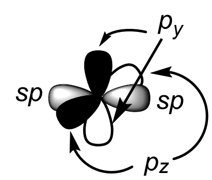
IV. Atomic Orbitals (AO's) combine to give Molecular Orbitals (MO's) (1.7 – 1.9)
- A) Bonding MO's (σ, π) contain electrons in covalent bonds
- B) Antibonding MO's (σ*, π*) are usually empty, can contain excited electrons
- C) Relative energies, stabilities of MO's

V. Hybrid Orbitals (1.10) and Shape/Geometry (1.11) ***SkillBuilders 1.7, 1.8***
- A) sp^3 hybridization: 4 regions of electron density, tetrahedral geometry
- B) sp^2 hybridization: 3 regions of electron density, trigonal planar geometry, contains an unhybridized *p* orbital
- C) *sp* hybridization: 2 regions of electron density, linear geometry, contains two unhybridized *p* orbitals

Hybridization





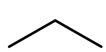
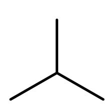
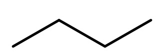
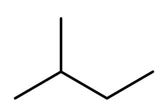


VI. 3-D sketches (2.6)
- A) determine hybridization to learn geometry about each atom
- B) draw aligned p orbitals to show π bonds

VII. Molecular Polarity (1.12) & Physical Properties (1.13, 1.14) ***SkillBuilders 1.9, 1.10***
- A) Nonbonding (intermolecular) Interactions affect bp, mp
  - i) dipole-dipole for polar molecules (δ+, δ-)
  - ii) hydrogen bonding for molecules containing NH, OH or HF (STRONG dipole)
  - iii) van der Waals (London dispersion) temporary dipole moments
    - a) explains why bp varies by MW (higher MW, higher bp)
    - b) straight vs. branched molecules (greater surface area, higher bp)
- B) mp increases for molecules that can pack tighter (more spherical, higher mp)
- C) water solubility increases with polarity, hydrogen-bonding ability

VIII. Isomerism (1.2) ***SkillBuilder 1.1***
- A) structural (constitutional): same molecular formula, different connectivity
- B) cis-trans (stereoisomers): structures vary only by orientation in space

Predicting Boiling Points

				
Formula	C_3H_8	C_4H_{10}	C_4H_{10}	C_5H_{12}
BP (ºC)	- 42.1	- 11.7	- 0.6	27.9

↑ Molecular Weight, ↑ BP. *If MW is the same,* THEN ↑ branching, ↓ BP