

Our textbook: P.Y. Bruice, Organic Chemistry, 5<sup>th</sup> Ed.

Also helpful: D. Klein, Organic Chemistry as a 2<sup>nd</sup> language

## ASSIGNED READINGS:

TODAY'S CLASS: Bruice Ch1: 1.1-1.15

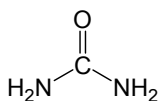
NEXT CLASS: rest of Ch.1, part of Ch.7  
& start Ch.2

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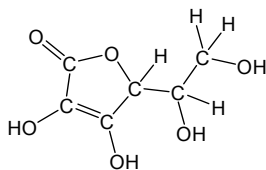
## What is organic chemistry?

### History:

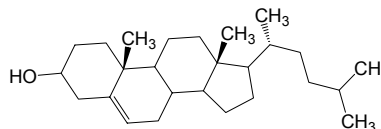
- Jöns Jakob Berzelius (1807): "Organic compounds" come from living organisms; "inorganic compounds" = minerals
- Friedrich Wöhler (1828): made urea in the laboratory, starting from inorganic compounds



Urea  
*found in urine*



Ascorbic acid  
*Vitamin C*



Cholesterol  
*a component of membranes*

### Current definition:

Organic chemistry = chemistry of the compounds of carbon

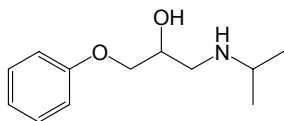
Key elements: C, H, N, O

Also important: F, Cl, Br, I, S, P (non-metals most common!)

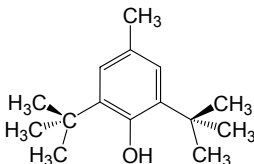
& some metals: Si, Li, Na, K, B, Al, Cr, Cu, Zn, Pd, Hg...

## What do organic chemists do?

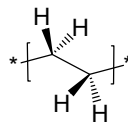
- Study relationship between structures of molecules & their properties and reactions
- Synthesize molecules with desired characteristics: pharmaceuticals, flavourings, pigments, plastics, fabrics...



Tenormin, a drug  
for treating  
heart disease



BHT, a preservative



Polyethylene,  
a plastic

## Why do you need to study organic chemistry?

- To learn how organic matter reacts, and WHY
- To provide a basis for understanding biological processes
- To gain spatial and temporal organizational skills
- To practice thinking logically & solving complex problems
- To learn to recognize trends & extrapolate knowledge to unknowns...

## The big picture: what we're doing & why...

### LEARNING ORGANIC REACTIONS WILL HELP US UNDERSTAND:

- how biological molecules perform their functions
  - intermolecular interactions, enzyme-catalyzed reactions
  - biochemical pathways: respiration, photosynthesis, etc...
- how biomolecules are synthesized in nature
- how synthetic molecules can be made to mimic natural molecules
- how synthetic molecules can be made to perform novel functions
  - plastics, dyes, paints, cosmetics, medicines...

*There are strong relationships between structure & function  
...but it will take more courses to learn all this!*

### Here: we will learn BASIC TYPES OF ORGANIC REACTIONS

- acid-base reactions:
  - pH affects how molecules look: cationic, neutral, anionic
  - deprotonating lets us prepare "building blocks" (nucleophiles!)
- & more complex reaction types: substitution, elimination, addition...
  - will allow us to "build" molecules of interest
  - the more rxns we understand, the more routes we can take!

## How to study organic chemistry

- Like a language: *PRACTICE, & DON'T GET BEHIND.*

Verbal communication	Pictorial communication
<b>TRAIN YOUR MIND:</b> Read the textbook Learn proper vocabulary Practice writing explanations Practice solving problems <b>TRAIN YOUR MOUTH:</b> Discuss material with peers Solve problems together Practice explaining verbally	<b>TRAIN YOUR EYE:</b> Interpret chemical drawings See 3D shapes in flat drawings <b>TRAIN YOUR HAND:</b> Practice drawing in 3D Practice writing structures Write problems out every time

- Learning the general trends and rules will help you **minimize memorization & maximize comprehension.**
  - Too much to try to memorize all!
  - Most successful approach = practice.
- Study Guide: use as a tool, not as a crutch.

(5)

## Chapter 1: Introduction to Organic Chemistry

### Chapter Goals

- Review general chemistry principles: structure, bonding
- Expand knowledge & apply to organic compounds
- Review acid/base chemistry
- Expand to understand organic compounds as acids/bases

### Chapter Outline: *This week (not necessarily in this order)*

- 1.1-1.2 Atomic structure, e<sup>-</sup> distribution
- 1.3-1.4 Types of bonds & representing structures
- 1.5-1.6 Atomic orbitals & molecular orbital theory
- 1.7-1.9 Bonding: single, double, triple bonds
- 1.10 Bonding in cations, anions, radicals
- 1.11-1.13 Bonding in simple compounds
- 1.14 Summary: Bond lengths, strengths & angles
- 1.15 Dipole moments of molecules

(6)

**Organic Chemistry: the chemistry of carbon**

H

2.1

Li

1.0

Be

1.5

Na

0.9

Mg

1.2

K

0.8

Ca

1.0

Sc

1.3

Ti

1.5

V

1.6

Cr

1.6

Mn

1.5

Fe

1.8

Co

1.8

Ni

1.8

Cu

1.9

Zn

1.6

Ga

1.6

Ge

1.8

As

2.0

Se

2.4

Br

2.8

Rb

0.8

Sr

1.0

Y

1.2

Zr

1.4

Nb

1.6

Mo

1.8

Tc

1.9

Ru

2.2

Rh

2.2

Pd

2.2

Ag

1.9

Cd

1.7

In

1.7

Sn

1.8

Sb

1.9

Te

2.1

I

2.5

B

2.0

C

2.5

N

3.0

O

3.5

F

4.0

Al

1.5

Si

1.8

P

2.1

S

2.5

Cl

3.0

Electronegativity

Kotz & Treichel's Figure 9.9

## Characteristics of Carbon:

1. Does not readily give up or accept e-s (*e-s = electrons*)

## WHY?

- Intermediate electronegativity
  - effective nuclear charge too low to steal e<sup>-</sup>s
  - effective nuclear charge too high to give away e<sup>-</sup>s

2. Does readily share e-s (i.e., forms covalent bonds) with other C atoms & other non-metal atoms

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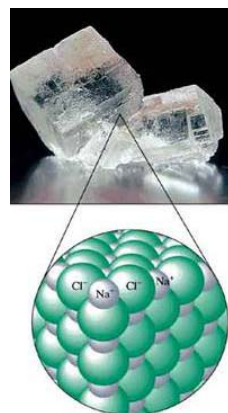
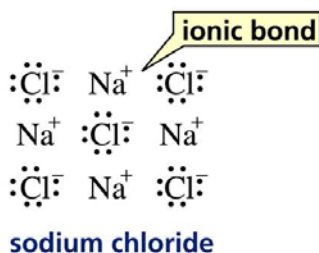
### 1.3: REVIEW: Ionic, Covalent & Polar Bonds

### **Ionic compounds:**

- form when an electropositive element (low electronegativity) transfers electron(s) to an electronegative element
- usually involve metals & nonmetals
- ionic bonds = electrostatic attractions between ions of opposite charge

### Stable ions:

- noble gas e<sup>-</sup> configurations



(8)

## Covalent bonding: atoms' valence shells overlap

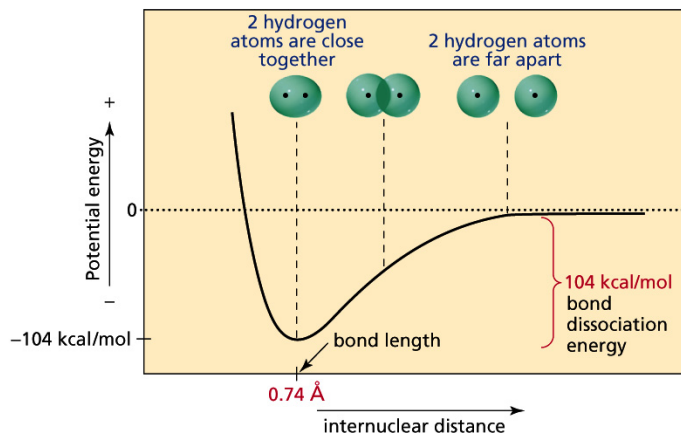
Covalent bonding: valence e<sup>-</sup>s attracted to 2 nuclei at once  
e<sup>-</sup>s occupy valence shells of both atoms

Bond strength described by **bond dissociation energy**

= **energy required to break a bond** (always endothermic!)

= **energy released when a bond forms** (always exothermic!)

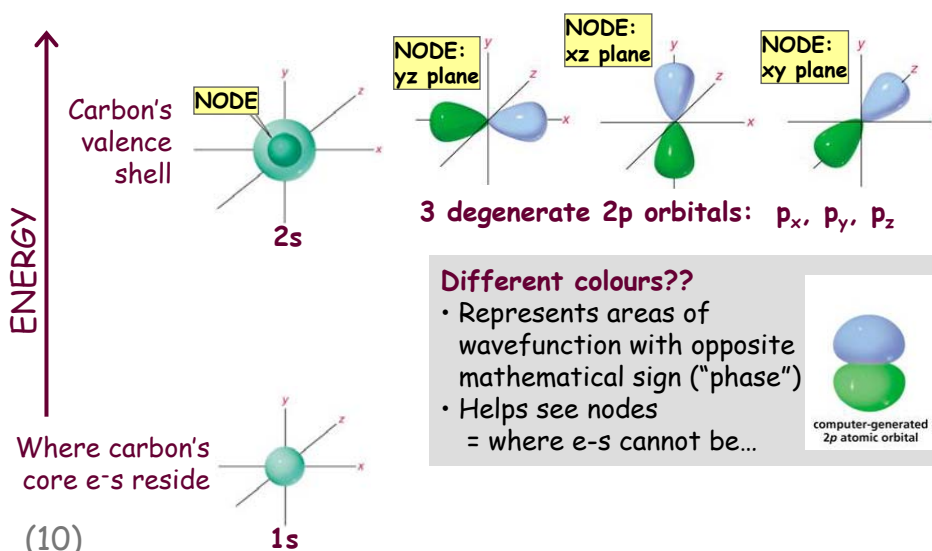
Bruice  
Figure 1.2



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## 1.2: The distribution of e<sup>-</sup>s in free atoms

- Orbital = volume of space around the nucleus where an electron of a given energy is most likely to be found

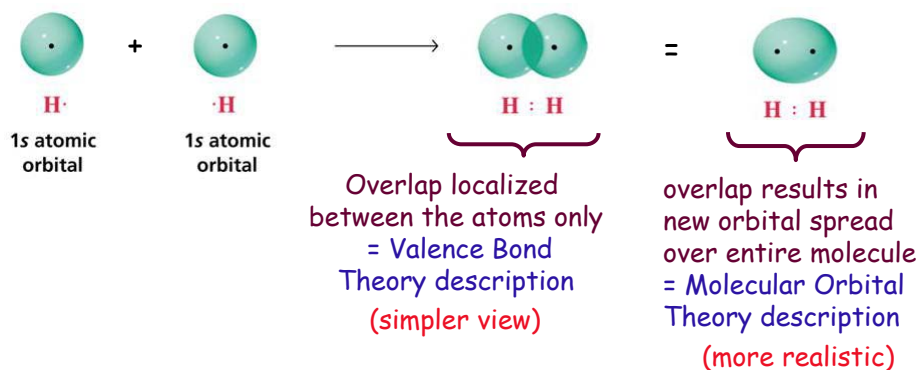


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## 1.6 Molecular Orbital ("M.O.") Theory

### A model to explain covalent bonding

- a  $\sigma$ -bond: can be formed by the overlap of two  $s$  orbitals:



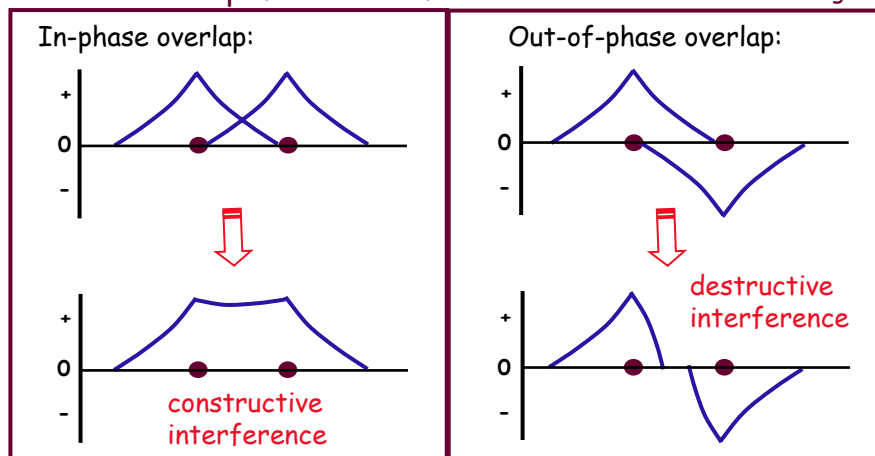
(11) [Note: Gen. Chem. texts also helpful - Kotz & Treichel 10.3; Zumdahl 9.2-5]

## Remember that orbitals are WAVES...

Like waves: orbitals have *phase* & *interfere* if overlapped

Consider a simplified view of 2  $s$ -orbitals:

See Fig.1.3

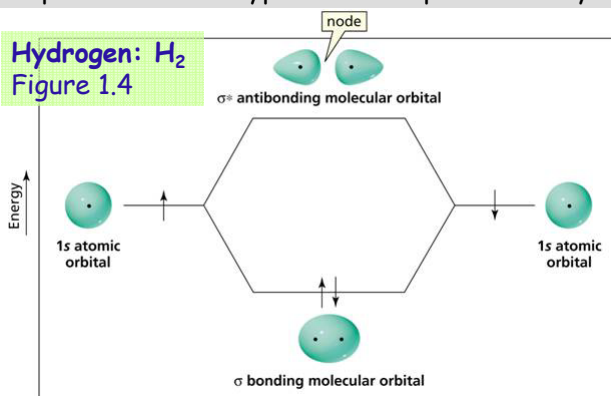


(12)

**In-phase overlap forms a bonding MO**  
**Out-of-phase overlap forms an antibonding MO**

Important: BOTH types of overlap occur every time 2 orbitals overlap!

Hydrogen:  $H_2$   
 Figure 1.4



← An "MO diagram"

ON OUTSIDES:  
 relative energies,  
 names & occupancies  
 of the orbitals of  
 the 2 atoms coming  
 together

& ON INSIDE:  
 the resulting MO's

**IMPORTANT: Bonding occurs if it is energetically favourable.**

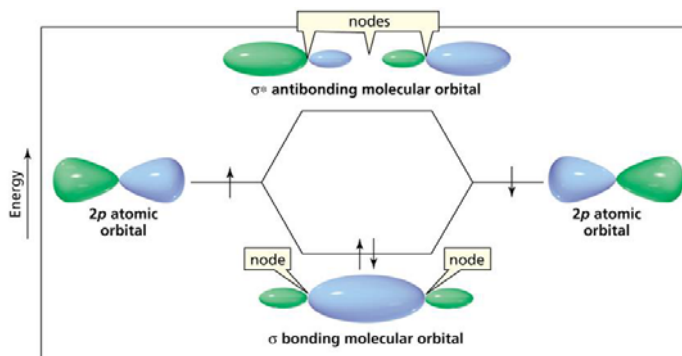
If a bond's  $\sigma$  AND  $\sigma^*$  orbital are simultaneously filled:  
 the bond will not exist.

(13)

So, why not  $He_2$ ?

**A sigma bond can also be formed by end-on overlap of two  $p$  orbitals: (or any other 2 orbitals, same or not...)**

Figure 1.5



**So, what makes a bond a sigma-bond?**

- the lobes of the orbitals that are overlapping are pointing at each other along the "bond axis" (i.e., the space between the nuclei)
- ⇒ the bond can rotate without diminishing the overlap

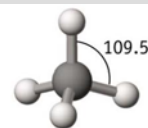
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## 1.7 Bonding in Methane & Ethane: Single Bonds

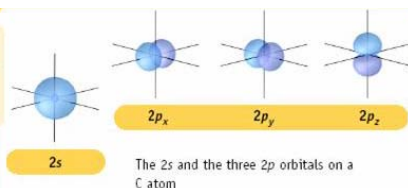
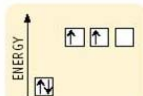
Recall VSEPR model, which predicts geometries

- Lewis structure  $\Rightarrow$  find # of  $\sigma$ -bonds & lone pairs  
 $\Rightarrow$  = number of ORBITALS required...
- will aim as far apart as possible (minimizes repulsion)

Methane,  $\text{CH}_4$



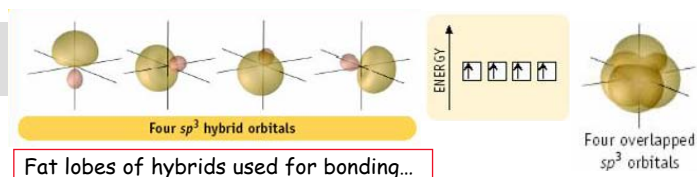
Valence shell of carbon



$\leftarrow$  not Td!  
 $\leftarrow$  & different Es

Atomic orbitals must **HYBRIDIZE** to achieve necessary geometry:

To make a Td C:  
 One *s* & three *p*'s



(15)

Kotz & Treichel Figure 10.6

(Compare to Bruice Fig.1.10-1.12)

### Orbital description of the bonding in Methane, $\text{CH}_4$

$\text{CH}_4$ : requires 4 bonds to C  $\Rightarrow$  tetrahedral geometry

$sp^3$  hybrid set:

- Tetrahedral
- bond angle  $109.5^\circ$

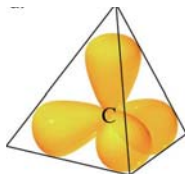
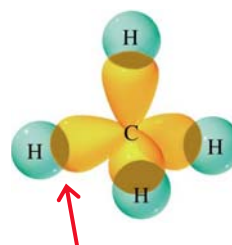


Figure 10.6

Each  $\sigma$ -bond formed by  
 one C  $sp^3$  hybrid  
 overlapping with  
 one H  $1s$  orbital

**Summary:**

4  $\sigma$ -bonds produced by  
 C  $2sp^3$  - H  $1s$  overlap

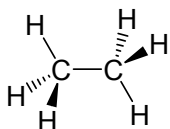


Valence Bond view  
 (easier to see)  
 of the BONDING  
 $\sigma$ -orbitals  
 ...but reality is MO

(16)



## Orbital description of the bonding in Ethane, $\text{CH}_3\text{CH}_3$

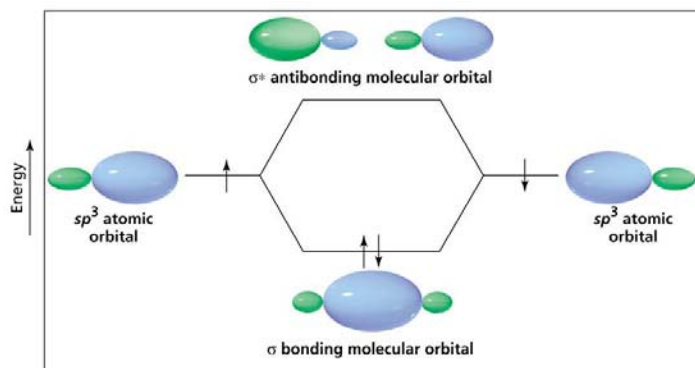


Requires 4 bonds to each C  $\Rightarrow$  each C has Td geometry

6 C-H  $\sigma$ -bonds: C  $2sp^3$  - H  $1s$  overlap

& 1 C-C  $\sigma$ -bond: C  $2sp^3$  - C  $2sp^3$  overlap

**Bruice Fig.1.14**  
MO diagram for  
a C-C  $\sigma$ -bond



Similar diagrams result for: C-E bonds (E = O, N, halogen)

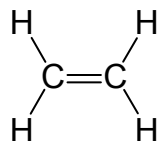
**A simple organic reaction:  $\text{CH}_3\text{I} + \text{F}^- \rightarrow \text{CH}_3\text{F} + \text{I}^-$**

Draw the orbitals involved in the C-H & C-I bonds of methyl iodide  
(both bonding & antibonding):

What would happen if a lone pair on  $\text{F}^-$  entered the C-I  $\sigma^*$  orbital?

IF MIX THESE ATOMIC ORBITALS	GET BACK THESE HYBRID ORBITALS	ANGLE b/w HYBRIDS	GEOMETRY
One <i>s</i> & one <i>p</i>	2 " <i>sp</i> " hybrids	180°	Linear
One <i>s</i> & two <i>p</i> 's	3 " <i>sp</i> <sup>2</sup> " hybrids	120°	Trig. planar
One <i>s</i> & three <i>p</i> 's	4 " <i>sp</i> <sup>3</sup> " hybrids	109.5°	Tetrahedral

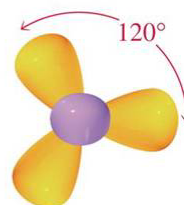
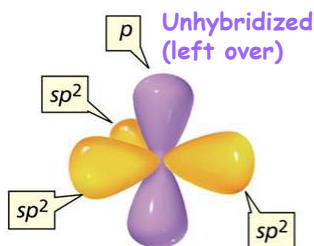
## 1.8 Bonding in Ethene: A Double Bond (=1σ+1π)



Requires 3 bonds to each C  
 ⇒ each C is ∴ trigonal  
 ⇒ *sp*<sup>2</sup> hybridized

Bruice Fig.1.15

*sp*<sup>2</sup>-hybridized  
carbon atom:



(19)

side view

top view

**A pi bond (π) is formed by side-on overlap of 2 *p* orbitals:**

**So, what defines a π-bond?**

→ the overlapping lobes are *parallel* to each other  
 ⇒ the bond *cannot rotate* without diminishing the overlap

**Note:** A σ bond is stronger than a π bond.

**WHY?**

→ Larger parts of the orbitals actually overlap when end-on vs. when oriented side-on.  
 → *i.e.*, higher e<sup>-</sup> density in region of overlap

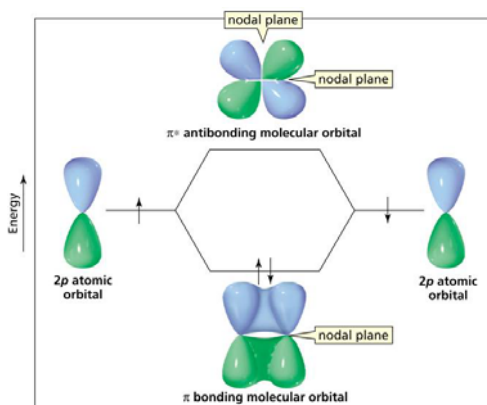
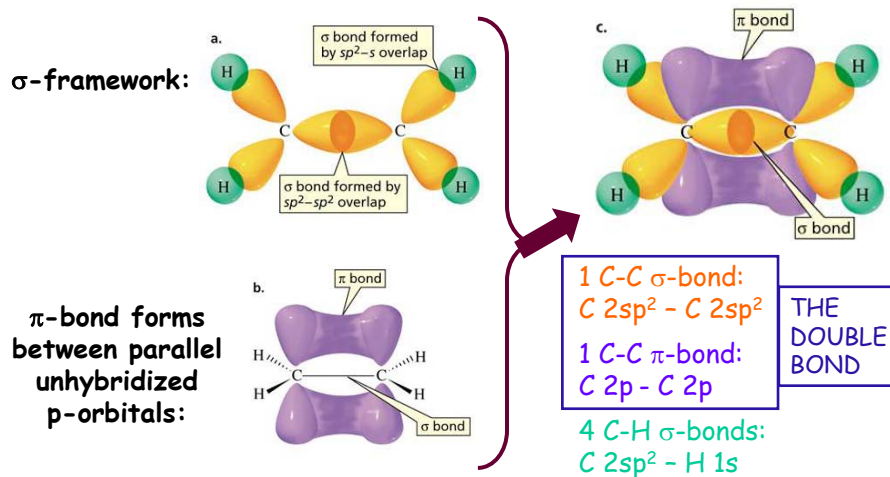


Figure 1.6

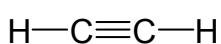
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## 1.8 Bonding in Ethene: A Double Bond ( $=1\sigma+1\pi$ )



(21)

## 1.9 Bonding in Ethyne: A Triple Bond ( $=1\sigma+2\pi$ )

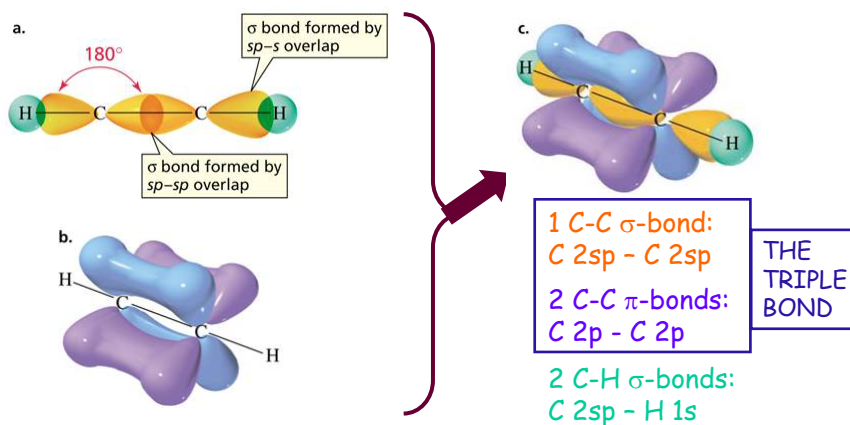


Requires 2 bonds to each C  $\Rightarrow$  linear

$\therefore$  sp hybridized

$\therefore$  2 unhybridized p-orbitals

see Bruice Fig.1.17



(22)

## 1.14 Summary of important bonding principles

Table 1.7 Comparison of the Bond Angles and the Lengths and Strengths of the Carbon–Carbon and Carbon–Hydrogen Bonds in Ethane, Ethene, and Ethyne

Molecule	Hybridization of carbon	Bond angles	Length of C–C bond (Å)	Strength of C–C bond (kcal/mol) (kJ/mol)	Length of C–H bond (Å)	Strength of C–H bond (kcal/mol) (kJ/mol)
$\begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$ ethane	$sp^3$	$109.5^\circ$	1.54	$sp^3-sp^3$ 377	1.10	$sp^3-s$ 423
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$ ethene	$sp^2$	$120^\circ$	1.33	$sp^2-sp^2$ & p-p 720	1.08	$sp^2-s$ 466
$\text{H}-\text{C}\equiv\text{C}-\text{H}$ ethyne	$sp$	$180^\circ$	1.20	$sp-sp$ & 2x p-p 967	1.06	$sp-s$ 548

- 1.) Higher bond order  $\rightarrow$  stronger bond (for same atom types)
- 2.) The greater the "s-character", the stronger the bond.

WHY?

- $\rightarrow$  s-orbitals are closer to nucleus than p's (or hybrids)
- $\rightarrow$  thus: stronger nucleus-to-electron attraction

(23)

### Summary: important bonding principles

- When a bonding / antibonding orbital pair are filled, the bond will break (or never form)
- A  $\pi$  bond is weaker than a  $\sigma$  bond
  - double bond =  $1\sigma + 1\pi$
  - triple bond =  $1\sigma + 2\pi$
- The greater the electron density in the region of orbital overlap, the stronger is the bond
- The more s character:
  - the shorter and stronger is the bond

(24)

## 1.10 Bonding in methyl cation, radical & anion

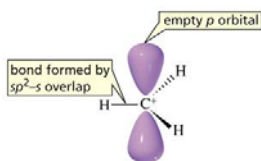
Highly reactive (unstable) ion:

- open valence shell

### Methyl cation

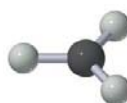


(3 pairs of valence e<sup>-</sup>s)



angled side view

top view

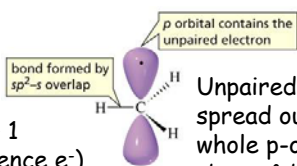


1. Carbocations are planar at their open-shell (e<sup>-</sup>-deficient) centre.
2. Carbon radicals are planar at the radical centre: an unpaired e<sup>-</sup> does NOT exert enough repulsion to make C atom rehybridize

### Methyl radical



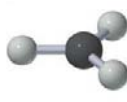
(3 pairs + 1 extra valence e<sup>-</sup>)



Unpaired e<sup>-</sup> spread out over whole p-orbital, above & below plane

angled side view

top view

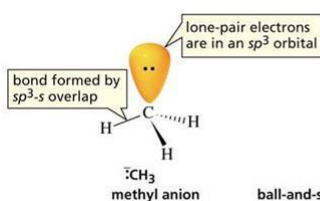


(25)

### Methyl Anion



4 pairs of valence e<sup>-</sup>s



ball-and-stick model of the methyl anion



3. Carbanions are tetrahedral at the anionic centre:

→ another pair of electrons DOES exert enough repulsion to make the C atom rehybridize  
→ just like we see for  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , etc... based on VSEPR model

(26)

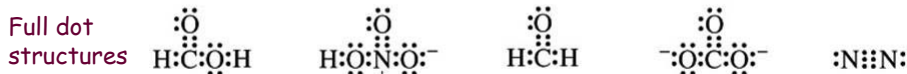
## 1.4 REVIEW & BEYOND: Representation of structure

- Lewis structures: include all valence electrons

bonding e<sup>-</sup>s: as pair of dots *OR* as a line

nonbonding e<sup>-</sup>s: as a pair of dots (*lone pairs*)

### Lewis structures

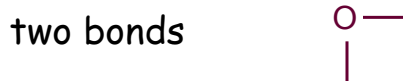


Simplified structures

### Important points to remember:

- add up all valence e<sup>-</sup>s & make bonds to satisfy valences
- left-over e<sup>-</sup>s left as lone pairs on atoms with higher electronegativity
- make multiple bonds to try to minimize formal charges on atoms
- 1<sup>st</sup> row elements: **MUST** obey duet rule
- 2<sup>nd</sup> row elements: **MUST** obey octet rule
- 3<sup>rd</sup> row & below: can exceed octet
- Formal charge = # valence e<sup>-</sup>s - [# lone pair e<sup>-</sup>s +  $\frac{1}{2}$ (# bonding e<sup>-</sup>s)]

### Common Bond Numbers: atoms with zero formal charge



How many lone pairs should each of these atoms have?

## Typical ways to draw organic structures

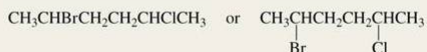
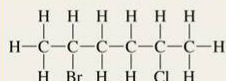
- **Kekulé structures:** show all bonds but not lone pairs
- **Condensed structures:** formulas that show connectivity

Table 1.5 Kekulé and Condensed Structures

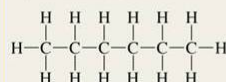
### Kekulé structure

### Condensed structures

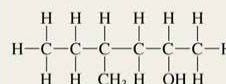
Atoms bonded to a carbon are shown to the right of the carbon. Atoms other than H can be shown hanging from the carbon.



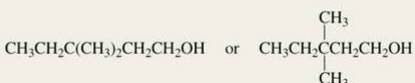
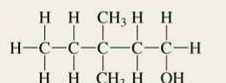
Repeating  $\text{CH}_2$  groups can be shown in parentheses.



Groups bonded to a carbon can be shown (in parentheses) to the right of the carbon, or hanging from the carbon.



Groups bonded to the far-right carbon are not put in parentheses.



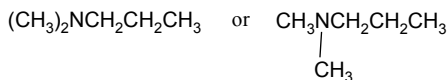
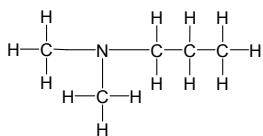
(29)

Table 1.5 Kekulé and Condensed Structures

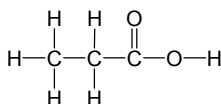
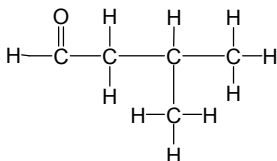
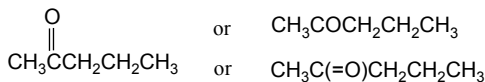
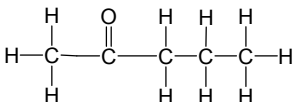
### Kekulé structure

### Condensed structures

Two or more identical groups considered bonded to the first atom on the left can be shown (in parentheses) to the left of that atom, or hanging from the atom.



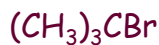
An oxygen doubly bonded to a carbon can be shown hanging off the carbon or to the right of the carbon.



(30)

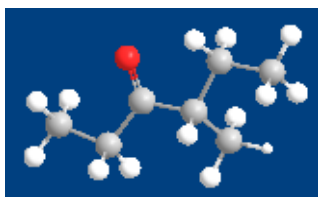
Redraw these to show all bonds & lone pairs

In-chapter  
Problem 18a,c



Write a condensed structure (structural formula) for this:

Problem 16c



(31) Red = O  
Grey = C  
White = H

## REVIEW: Covalent bonding - equal vs. unequal sharing...

- Nonpolar covalent bonds: equal sharing of valence electrons by atoms of *equal electronegativity*  
*e.g.*,  $\text{H}_2$

- Polar covalent bonds: unequal sharing of valence e<sup>-</sup>s between atoms with different electronegativities  
*e.g.*, HF

Larger difference?  
→ more polar

TABLE 1.3 The Electronegativities of Selected Elements<sup>a</sup>

IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5				B 2.0	C 2.5	N 3.0	O 3.5
Na 0.9	Mg 1.2				Al 1.5	Si 1.8	P 2.1	S 2.5
K 0.8	Ca 1.0							Cl 3.0
								Br 2.8
								I 2.5

<sup>a</sup>Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.

Important: know relative electronegativities of nonmetals

COMMON ONES:  $\text{F} > \text{O} > \text{N}, \text{Cl} > \text{Br} > \text{I}, \text{S}, \text{C} > \text{H}$



## Polar bonds have a "Dipole moment"

- A polar bond has a negative end and a positive end  
→ due to unequal distribution of electrons

Table 1.4

The Dipole Moments of Some  
Commonly Encountered Bonds

Bond	Dipole moment (D)
H—C	0.4
H—N	1.3
H—O	1.5
H—F	1.7
H—Cl	1.1
H—Br	0.8
H—I	0.4
C—C	0
C—N	0.2
C—O	0.7
C—F	1.6
C—Cl	1.5
C—Br	1.4
C—I	1.2

$$\text{dipole moment} = \mu = e \times d$$

*In units called Debyes, "D"*

$e$ : magnitude of the charge on the atom

$d$ : distance between the two charges

Note:

- These dipole moments are averages of experimental measured dipoles
- Using electronegativity differences to predict polarity works fairly well, but is **not perfect**

- Suggestion: become familiar with the relative polarities shown here...

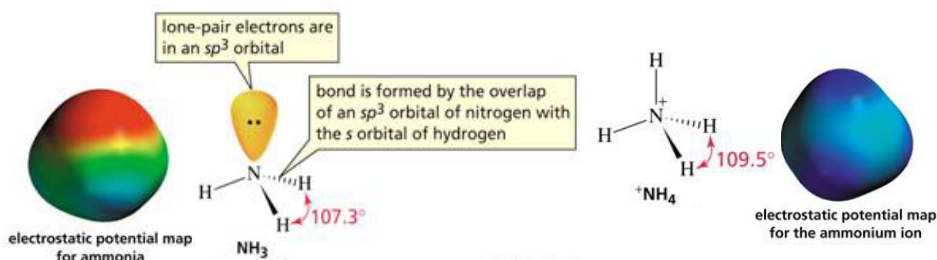
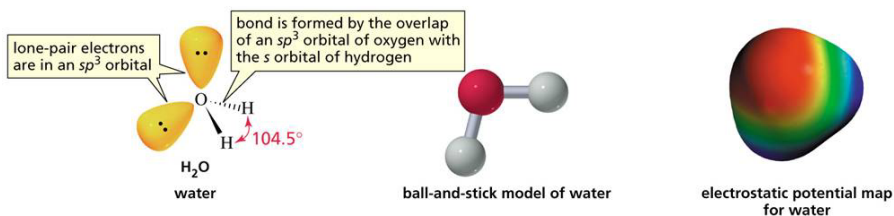
## Visualizing electron distribution in molecules: Electrostatic Potential Maps



### Why is it useful to picture polarity?

- Electron-rich atoms or molecules are attracted to electron-deficient atoms or molecules  
⇒ can predict physical & chemical properties!

## 1.11-12 Bonding in water, ammonia & $\text{NH}_4^+$



(35)

## 1.13 Bonding in the hydrogen halides

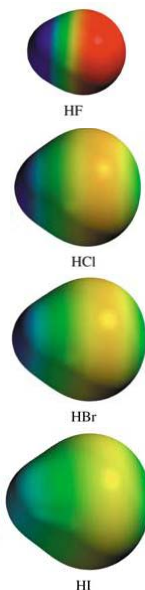


Table 1.6 Hydrogen-Halogen Bond Lengths and Bond Strengths

Hydrogen halide	Bond length (Å)	Bond strength kcal/mol	Bond strength kJ/mol
H—F	0.917	136	571
H—Cl	1.2746	103	432
H—Br	1.4145	87	366
H—I	1.6090	71	298

- H-X bonds involve H  $1s$  - X  $np$  overlap
- larger value of "n" → larger orbital (higher energy)

SO WHAT?

- mismatch in orbital sizes results in less efficient overlap
  - weaker bond
  - reflected in bond energy & bond length

- bond strength: measured via BOND DISSOCIATION ENERGY  
= E required to homolytically cleave bond to yield 2 radicals  
(more stable radicals are easier to form → lower BDE)
- bond length: shorter bonds are not necessarily stronger...

(36)

## ASSIGNED READINGS

### BEFORE NEXT LECTURE:

**Read:** Bruice Ch.1 up to section 1.15

**Work on:** Ch.1 #68-72,75-78,80,83,85-86,90,93,97

**Review:** Chem205: Lewis structures & resonance  
molecular geometry & polarity  
Chem206: acids & bases (concepts, not math...)  
- conjugate pairs  
- pH,  $pK_a$ ,  $pK_b$  (concepts!)  
- reactions of acids & bases  
- effect of structure on acidity

(37)

Note: supplementary orbital figures were taken from  
Kotz & Treichel's *Chemistry & Chemical Reactivity* 5th Ed.  
On reserve at Vanier library for Chem 205/206