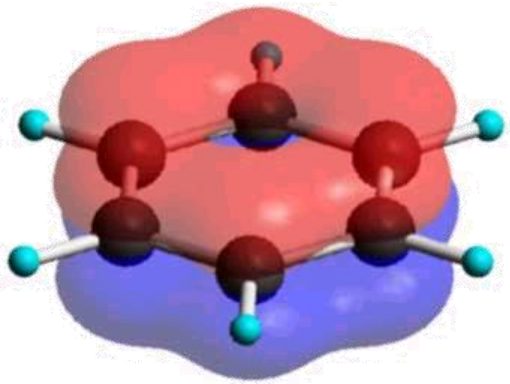
Organic Chemistry
1st Semester 2013 – 2014
Chem 104

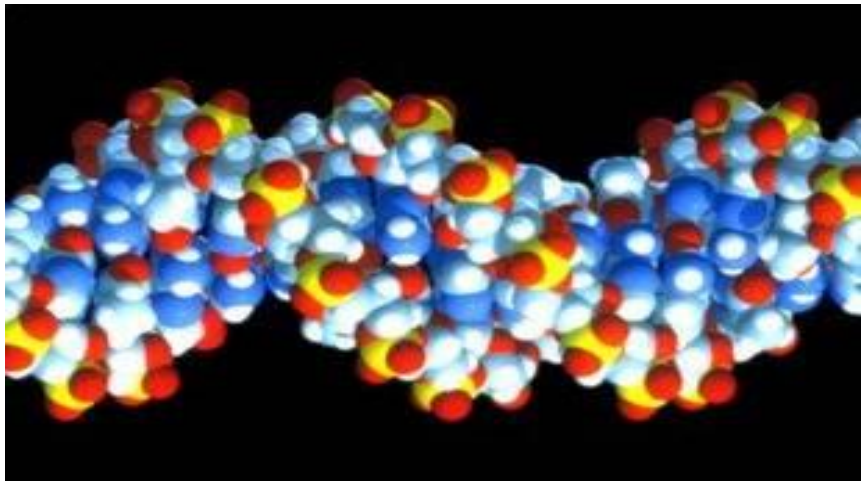
Chapter 1
Structure & Bonding



What is Organic Chemistry?

- "Organic" – until mid 1800's referred to compounds from living sources
- Today, **organic compounds** are those based on carbon structures and **organic chemistry** studies their structures and reactions
  - Includes biological molecules, drugs, solvents, dyes
  - Does not include metal salts and materials (inorganic)

Some Organic Compounds



DNA

Medicines
- Active Pharmaceutical Ingredients
- Excipients

Materials

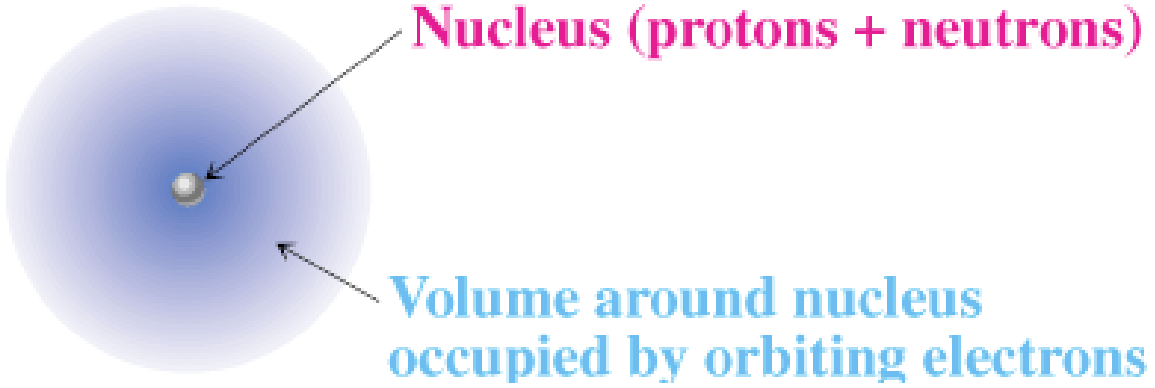
Essential oils

Fuels

Pigments

Atomic Structure

- Structure of an atom
  - Positively charged *nucleus* (very dense, protons and neutrons) and small (10^{-15} m) in diameter
  - Negatively charged electrons are in a cloud (10^{-10} m) around nucleus



Atomic Number and Atomic Mass

- The *atomic number* (*Z*) is the number of protons in the atom's nucleus
- The *mass number* (*A*) is the number of protons plus neutrons
- All the atoms of a given element have the same atomic number
- **Isotopes** are atoms of the same element that have different numbers of neutrons and therefore different mass numbers
- The **atomic mass** (*atomic weight*) of an element is the weighted average mass in atomic mass units (amu) of an element's naturally occurring isotopes

Atomic Structure: Orbitals

- Four different kinds of orbitals for electrons based on those derived for a hydrogen atom
- Denoted *s*, *p*, *d*, and *f*
- *s* and *p* orbitals most important in organic chemistry
- *s* orbitals: spherical, nucleus at center
- *p* orbitals: dumbbell-shaped, nucleus at middle

An s orbital

A p orbital

A d orbital

Numbers of Orbitals and electrons in the First Three Shells

TABLE 1.1 NUMBERS OF ORBITALS AND ELECTRONS IN THE FIRST THREE SHELLS

Shell number	Number of orbitals of each type			Total number of electrons when shell is filled
	s	*p*	*d*	
1	1	0	0	2
2	1	3	0	8
3	1	3	5	18

Atomic Structure: Electron Configurations

- **Ground-state electron configuration** of an atom lists orbitals occupied by its electrons. Rules:
- 1. Lowest-energy orbitals fill first: $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d$
- 2. Electron spin can have only two orientations, up $\uparrow$ and down $\downarrow$. Only two electrons can occupy an orbital, and they must be of opposite spin

Electron Arrangements of the First 18 elements

TABLE 1.2 ELECTRON ARRANGEMENTS OF THE FIRST 18 ELEMENTS

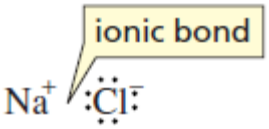
Atomic number	Element	Number of electrons in each orbital				
		1s	*2s*	*2p*	*3s*	*3p*
1	H	1				
2	He	2				
3	Li	2	1			
4	Be	2	2			
5	B	2	2	1		
6	C	2	2	2		
7	N	2	2	3		
8	O	2	2	4		
9	F	2	2	5		
10	Ne	2	2	6		
11	Na	2	2	6	1	
12	Mg	2	2	6	2	
13	Al	2	2	6	2	1
14	Si	2	2	6	2	2
15	P	2	2	6	2	3
16	S	2	2	6	2	4
17	Cl	2	2	6	2	5
18	Ar	2	2	6	2	6

CHEMICAL BONDS: THE OCTET RULE

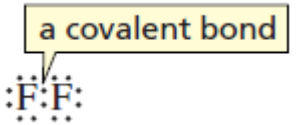
Why do atoms bond together? **more stable (has less energy)**

G. N. Lewis proposed that *an atom is most stable if its outer shell is either filled or contains eight electrons and it has no electrons of higher energy (Octet rule).*

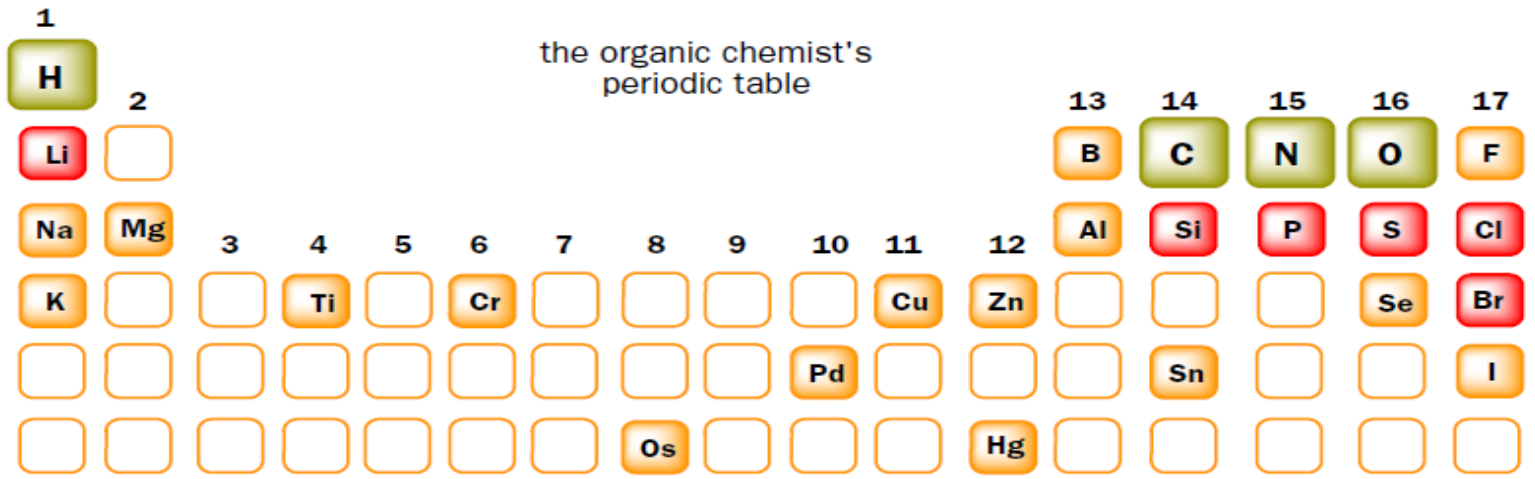
How to describe bonding?

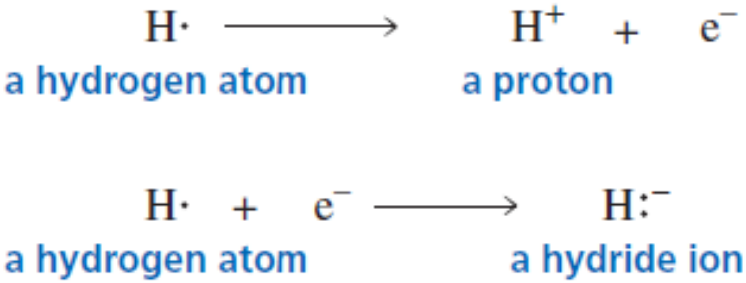


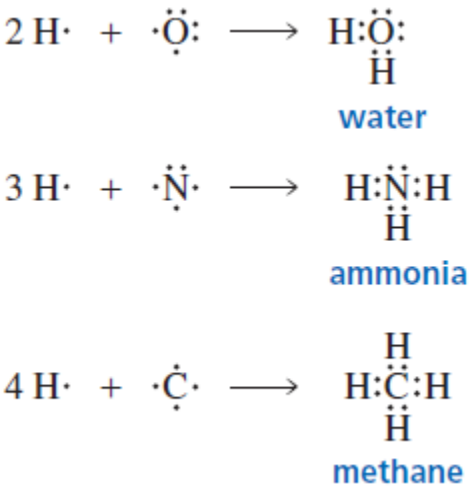
1) The **ionic (or electrovalent) bond:** formed by the transfer of one or more electrons from one atom to another to create ions.



2) The **covalent bond:** results when atoms share electrons.





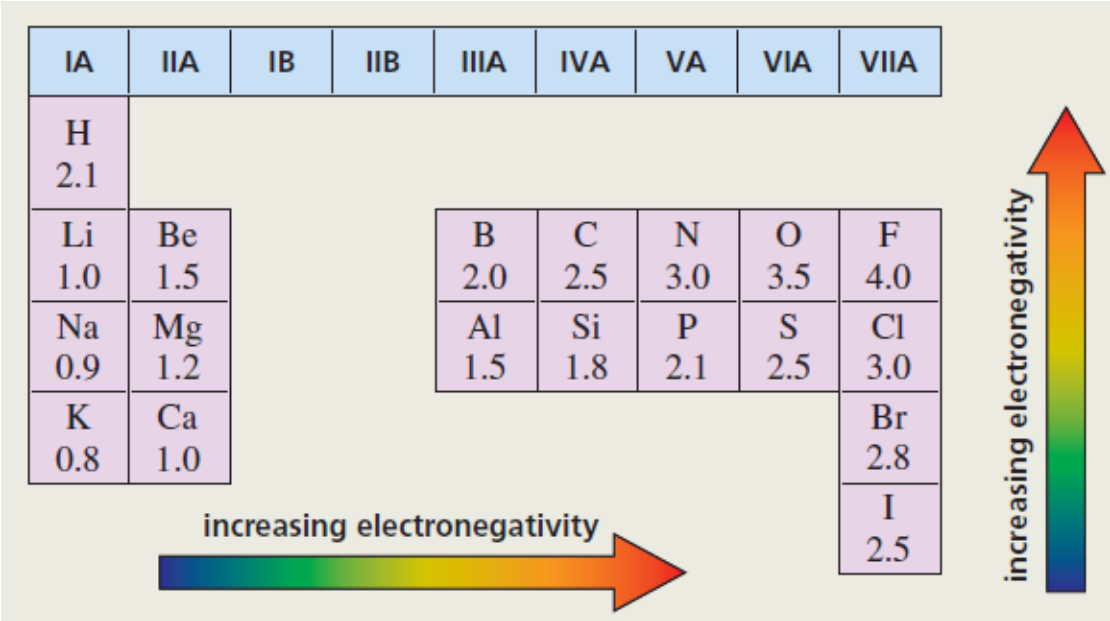


Know also these terminologies:

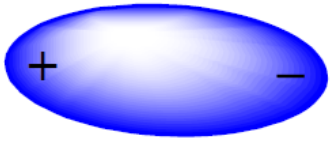
core electrons, valence electrons, valence shell, electropositive atom and electronegative atom.

Hint: remember always Octet rule

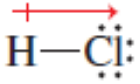
Electronegativity: is the tendency of an atom to pull bonding electrons toward itself.



Polar and non-polar Covalent Bonds:



A dipole

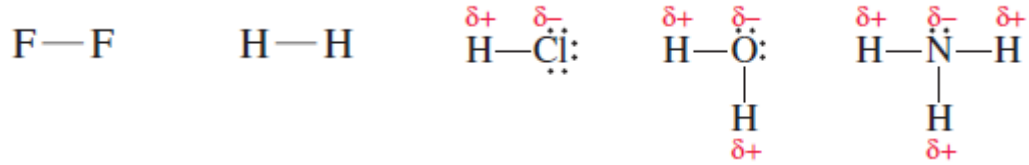


Bond polarity

1) When two atoms of different **EN forms a covalent bond, the electrons are not** shared equally between them.

2) The chlorine atom pulls the bonding electrons closer to it and becomes somewhat electron rich ⇒ bears a ***partial negative charge (δ–).***

3) The hydrogen atom becomes somewhat electron deficient ⇒ bears a ***partial positive charge (δ+).***



continuum of bond types

ionic bond	polar covalent bond	nonpolar covalent bond
K^+F^- Na^+Cl^-	O—H N—H	C—H, C—C

Ask yourself: What is the difference in Electronegativity between two atoms for each bond??

PROBLEM Which of the following has

a. the most polar bond? b. the least polar bond?

NaI LiBr Cl_2 KCl

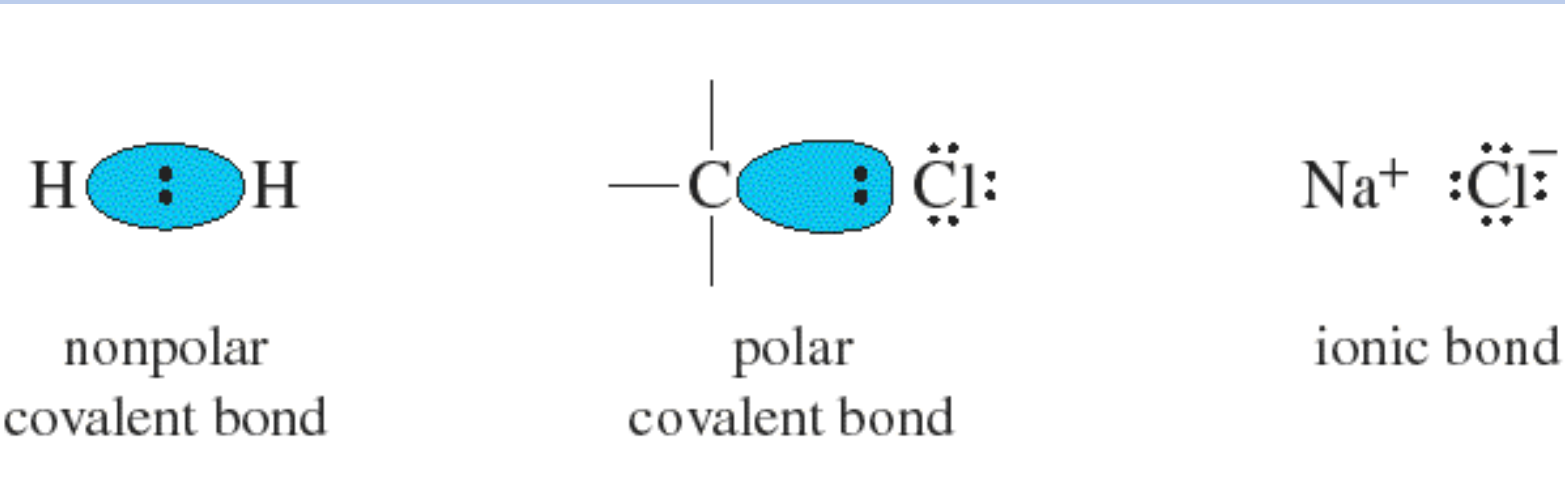
Understanding Organic Reactions

1-Bonding (Bond Formation Bond Making)

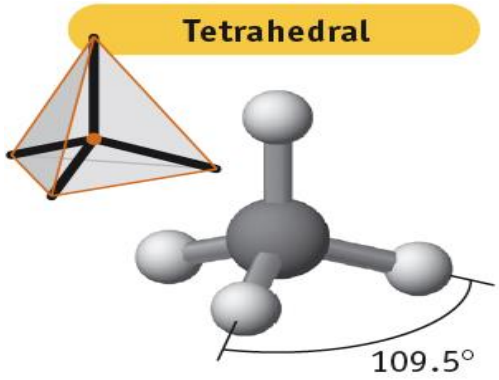
- **Covalent bond**: electron pair is shared.

  (Nonpolar and polar Covalent bond)

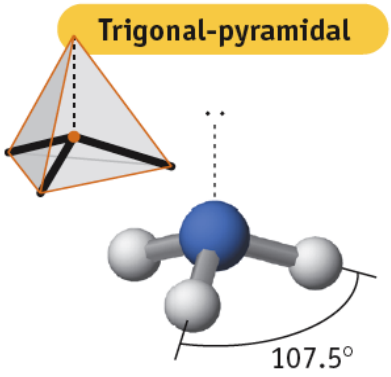
- **Ionic bond**: electrons are transferred.



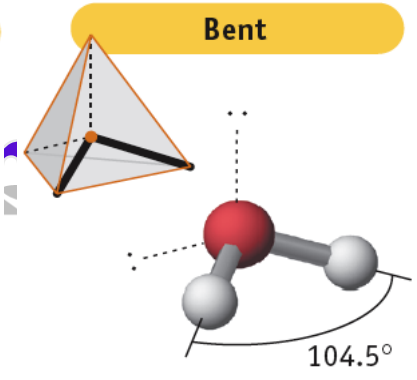
Bonding



Methane, CH_4
4 bond pairs
no lone pairs



Ammonia, NH_3
3 bond pairs
1 lone pair

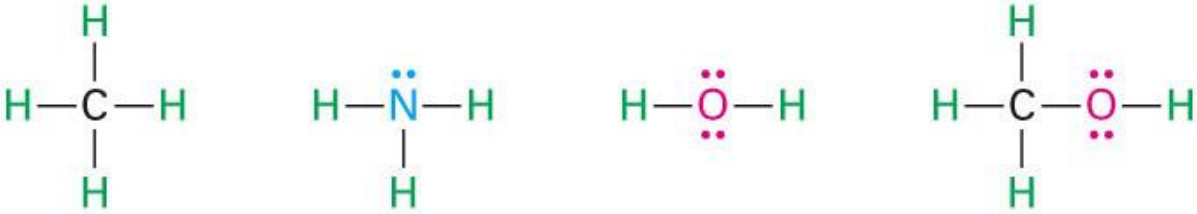


Water, H_2O
2 bond pairs
2 lone pairs

	Valence electrons	# Bonds	# Lone Pair Electrons
C	**4**	**4**	**0**
N	**5**	**3**	**1**
O	**6**	**2**	**2**
Halides (F, Cl, Br, I)	**7**	**1**	**3**

Electron-dot structures (Lewis structures)

Line-bond structures (Kekulé structures)



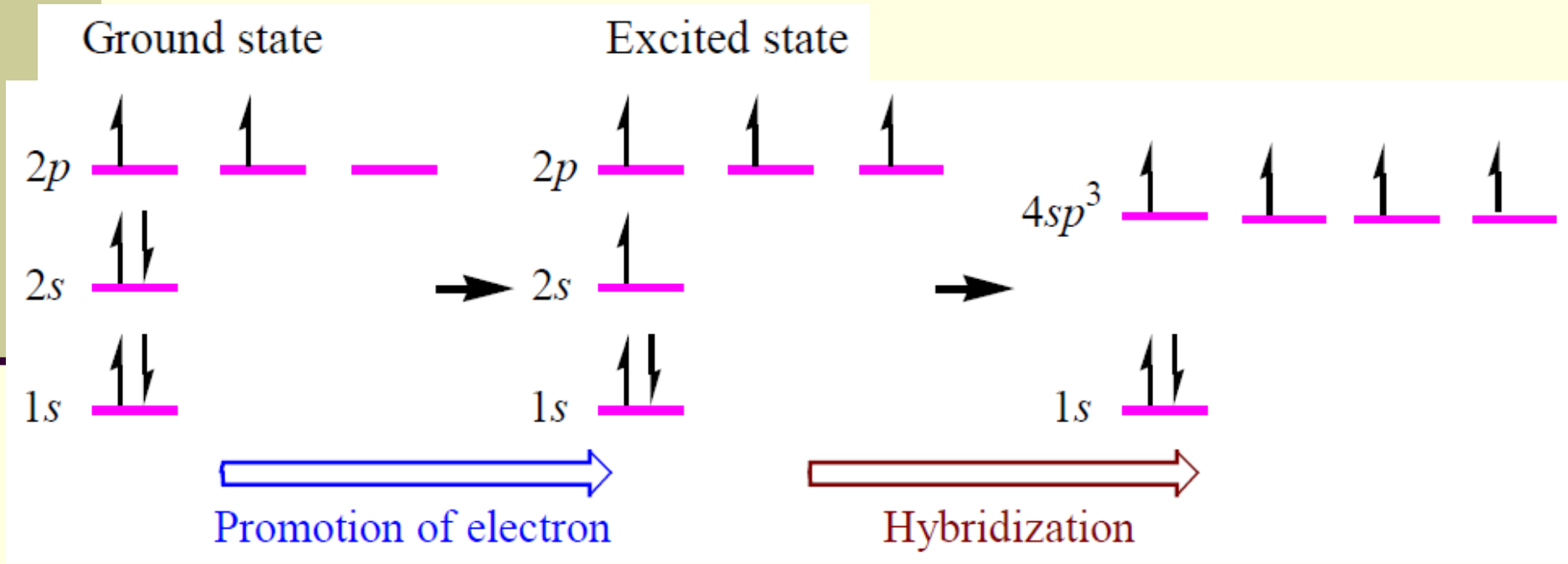
Methane (CH_4) **Ammonia (NH_3)** **Water (H_2O)** **Methanol (CH_3OH)**

One bond **Four bonds** **Three bonds** **Two bonds** **One bond**

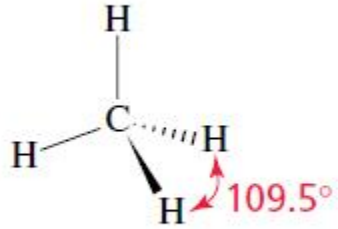
HYBRIDIZATION

The Structure of Methane and Ethane: sp^3 Hybridzation

Orbital hybridization: A mathematical approach that involves the combining of individual wave functions for s and p orbitals to obtain wave functions for new orbitals ⇒ **hybrid atomic orbitals**

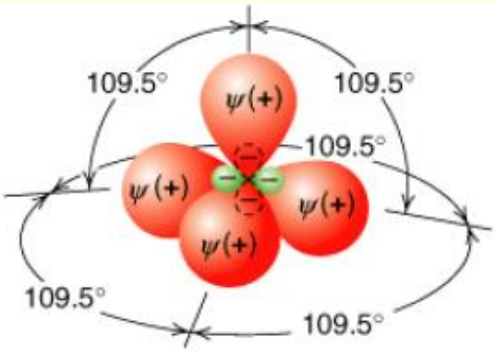


Bonding in Methane



perspective formula of methane


ball-and-stick model of methane



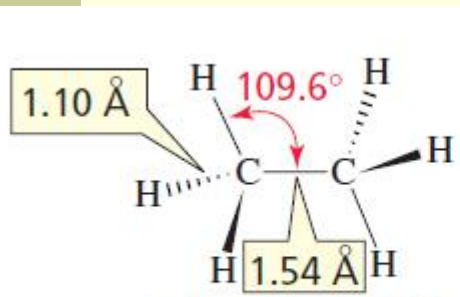
The four sp^3 orbitals should be oriented at angles of 109.5° with respect to each other ⇒ an sp^3-hybridized carbon gives a tetrahedral structure for methane.

The greater the overlap achieved (the larger integral), the stronger the bond formed.

Sigma (σ) bond:

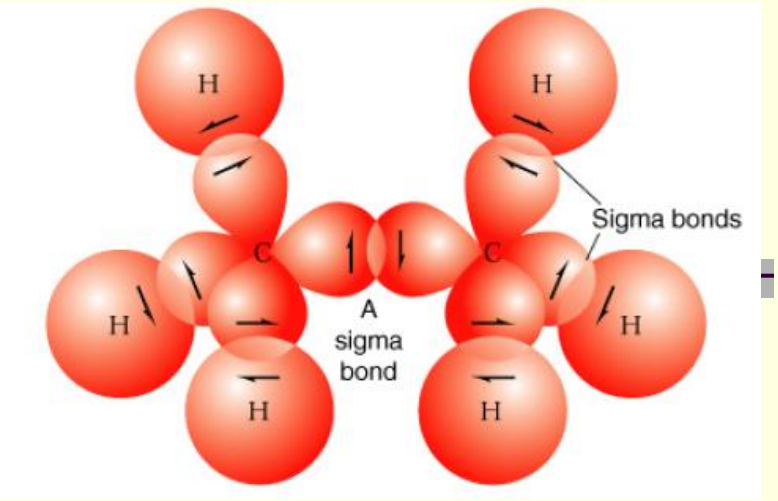
1) A bond that is ***circularly symmetrical in cross section when viewed along the bond axis.***
2) ***All purely single bonds are sigma bonds.***

Bonding in Ethane



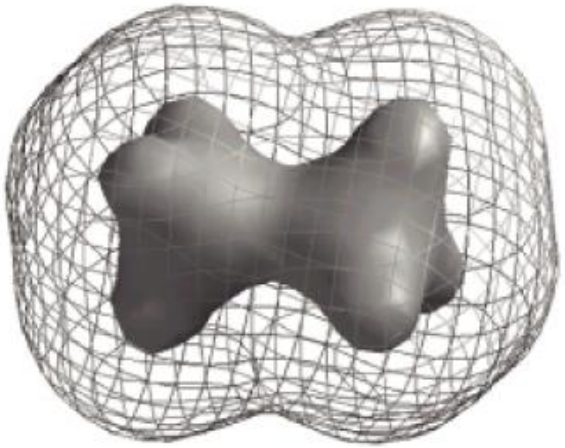
perspective formula of ethane

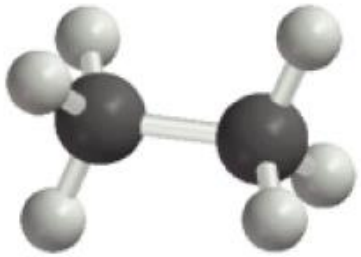

ball-and-stick model of ethane



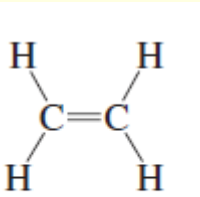
Free rotation about C–C:

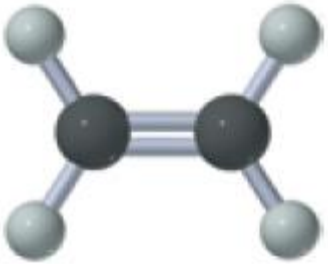
A sigma bond has cylindrical symmetry along the bond axis ⇒ **rotation of groups joined by a single bond does not usually require a large amount of energy ⇒ free rotation**.

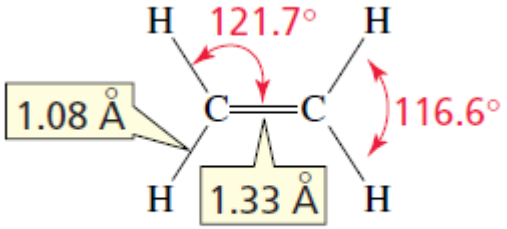




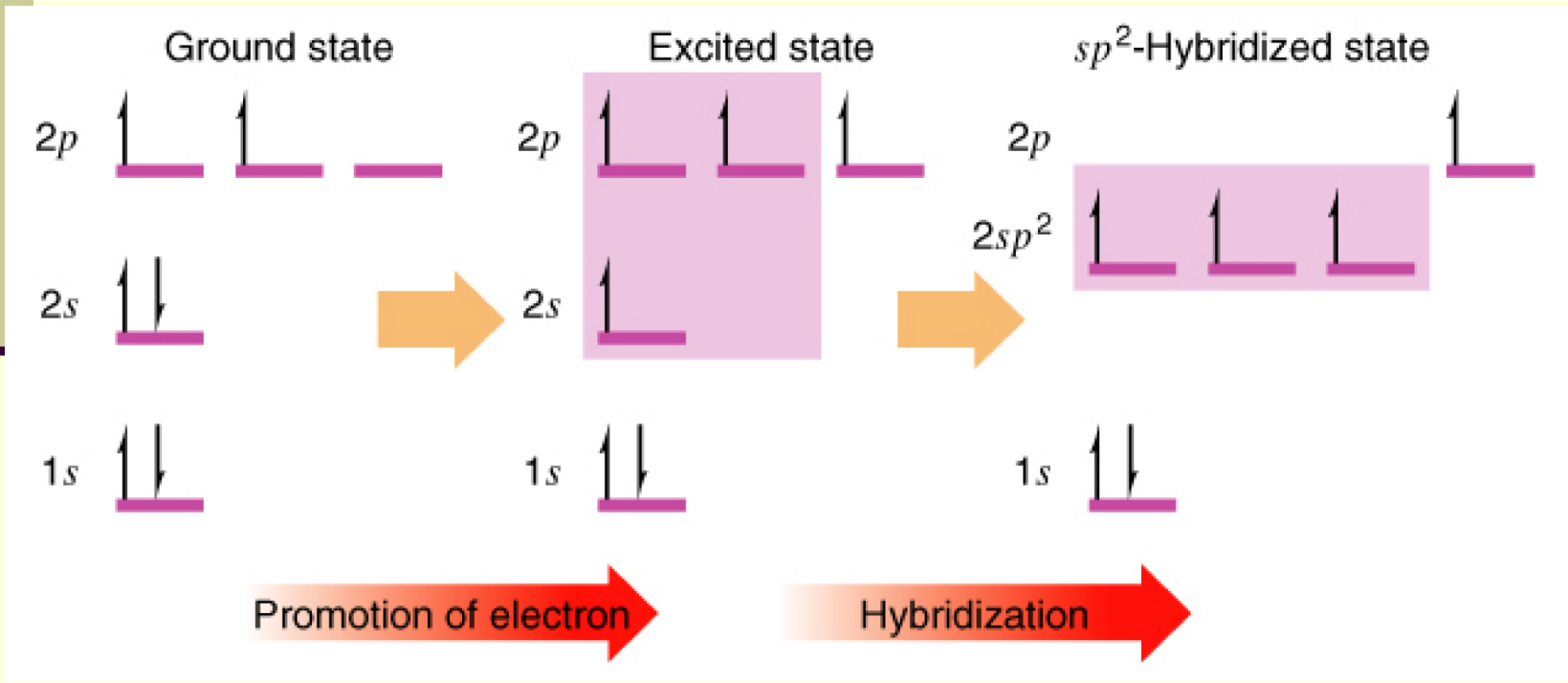
The Structure of Ethene (Ethylene): sp^2 Hybridzation

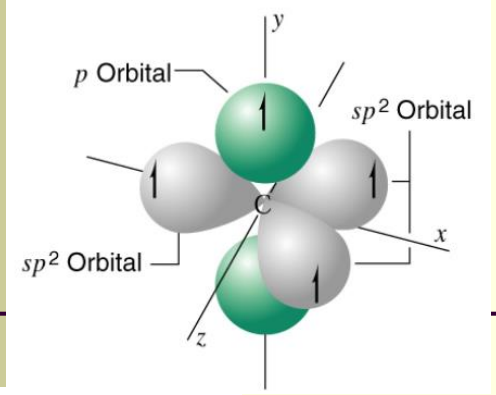


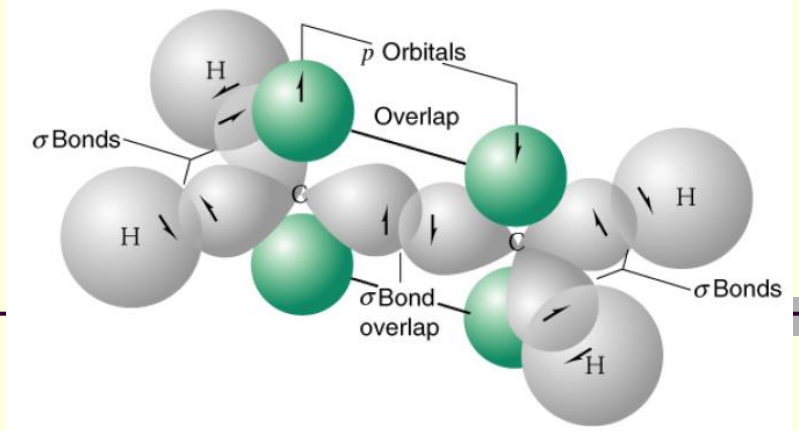

ball-and-stick model of ethene



a double bond consists of one σ bond and one π bond







Pi (π) bond:

The parallel *p* orbitals ***overlap above and below the plane of the σ framework***.

The sideway overlap of *p* orbitals results in the formation of a ***π bond***.

A π bond has a nodal plane passing through the two bonded nuclei and between the π molecular orbital lobes.

Restricted rotation in double bond

There is a large energy barrier to rotation associated with groups joined by a double bond.

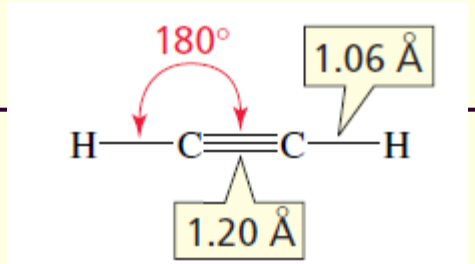
The strength of the π bond is 264 KJ mol^{-1} (63.1 Kcal mol^{-1})⇒ the rotation barrier of double bond.

The rotation barrier of a C–C single bond is 13-26 KJ mol^{-1} (3.1-6.2 Kcal mol^{-1}).

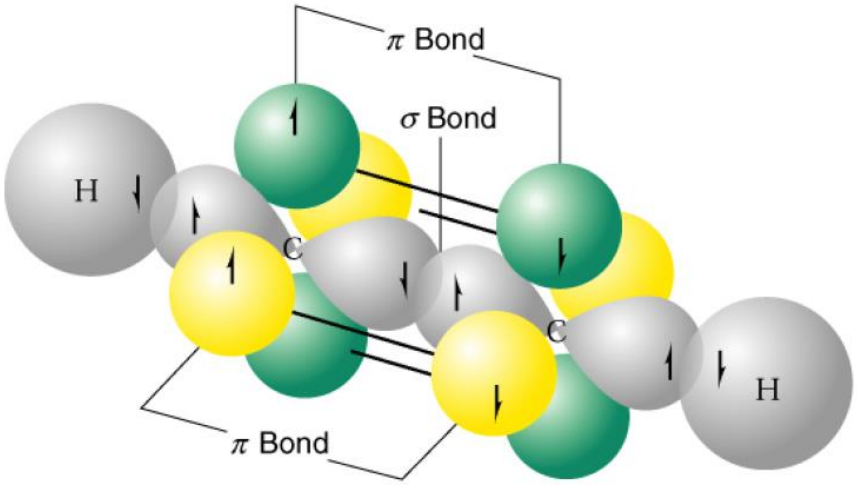
The Structure of Ethyne (Acetylene): *sp* Hybridzation

H—C≡C—H

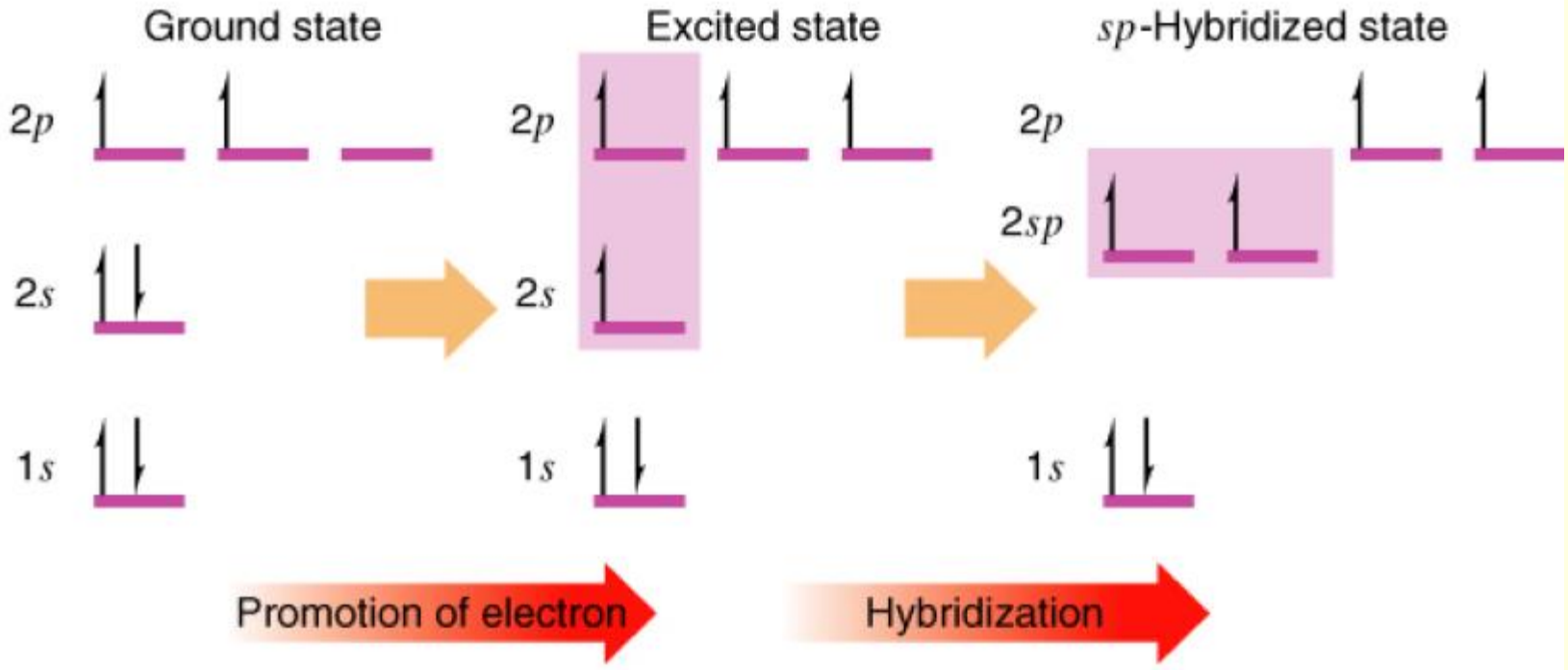
ethyne
(acetylene)



a triple bond consists of one σ bond and two π bonds



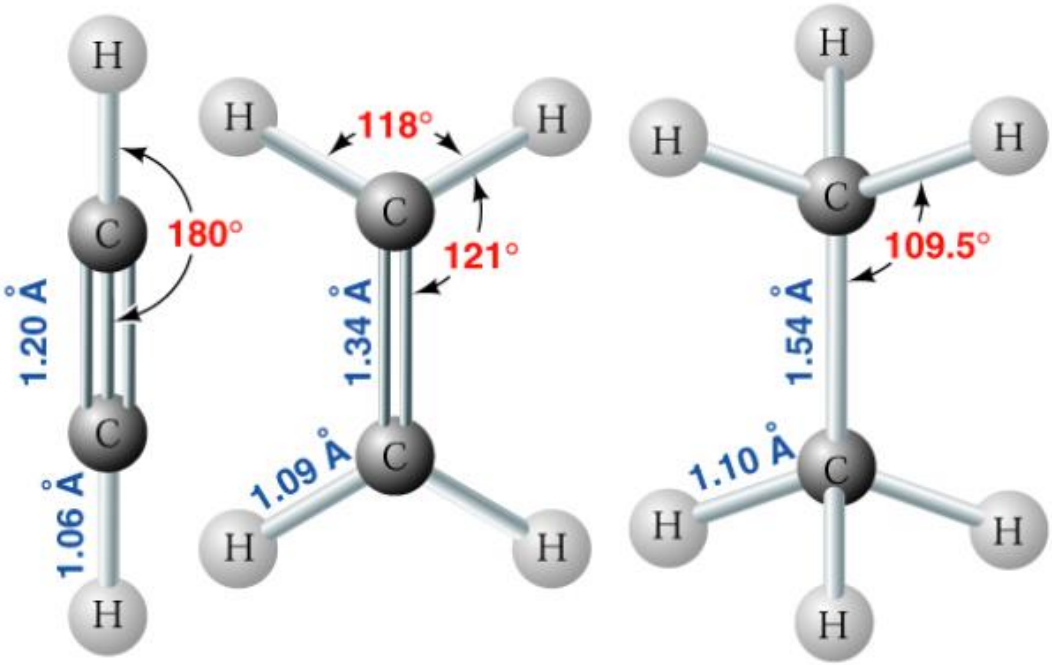
sp Hybridization:



Summary

Bond lengths of Ethyne, Ethene, and Ethane

The shortest C–H bonds are associated with those carbon orbitals with the greatest *s* character.



sp^3 orbitals ⇒ tetrahedral

sp^2 orbitals ⇒ trigonal planar

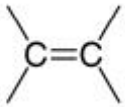
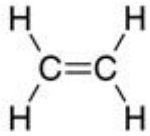
sp orbitals ⇒ linear

Organic Molecules and Functional Groups

Functional Groups: Hydrocarbons

Hydrocarbons are compounds made up of only the elements carbon and hydrogen. They may be aliphatic or aromatic.

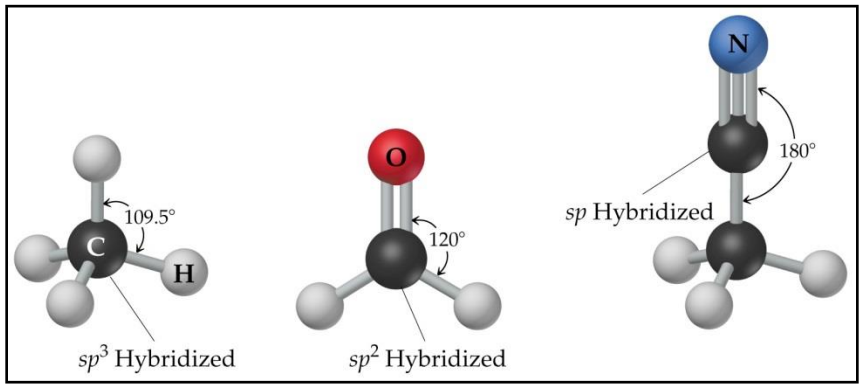
Table 3.1 Hydrocarbons

Type of compound	General structure	Example	Functional group
Alkane	R—H	CH_3CH_3	– –
Alkene			double bond
Alkyne	—C≡C—	H—C≡C—H	triple bond
Aromatic compound			phenyl group

Carbon's Hybridization

Carbon can exhibit three different types of hybridization…

- ***sp*³** hybridized carbons for **tetrahedral** geometries (**Alkanes**).
- ***sp*²** hybridized carbons for **trigonal planar** geometries (**Alkenes**).
- ***sp*** hybridized carbons for **linear** geometries (**Alkynes**).



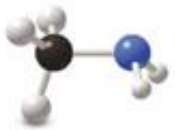
Remember: Carbon's hybridization relates to the # of atoms that it is bonded to…

4 atoms= sp^3 3 atoms= sp^2 2 atoms= sp

Organic Molecules and Functional Groups

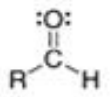
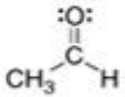
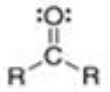
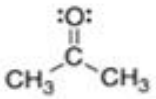
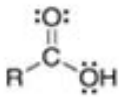
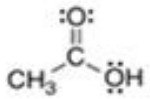
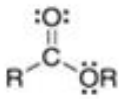
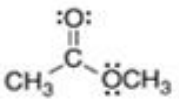
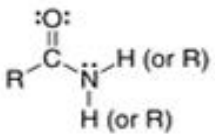
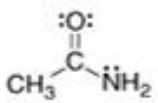
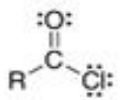
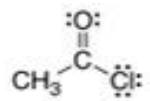
Functional Groups: Heteroatoms

Table 3.2 Compounds Containing C–Z σ Bonds

Type of compound	General structure	Example	3-D structure	Functional group
Alkyl halide	R—X: (X = F, Cl, Br, I)	CH_3—Br:		–X halo group
Alcohol	R—OH	CH_3—OH		–OH hydroxy group
Ether	R—O—R	CH_3—O—CH_3		–OR alkoxy group
Amine	R—NH_2 or R_2NH or R_3N	CH_3—NH_2		–NH_2 amino group
Thiol	R—SH	CH_3—SH		–SH mercapto group
Sulfide	R—S—R	CH_3—S—CH_3		–SR alkylthio group

Functional Groups: Carbonyl groups

Table 3.3 Compounds Containing a C=O Group

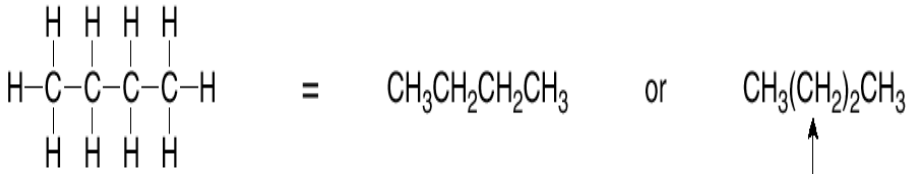
Type of compound	General structure	Example	3-D structure	Functional group
Aldehyde				C=O carbonyl group
Ketone				C=O carbonyl group
Carboxylic acid				−COOH carboxy group
Ester				−COOR
Amide				$-CONH_2$, −CONHR, or $-CONR_2$
Acid chloride				−COCl

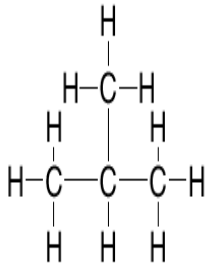
Structure and Bonding

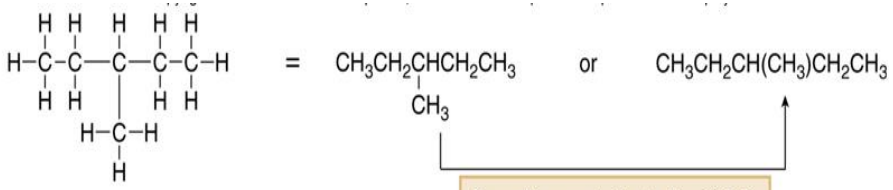
Drawing Organic Molecules:

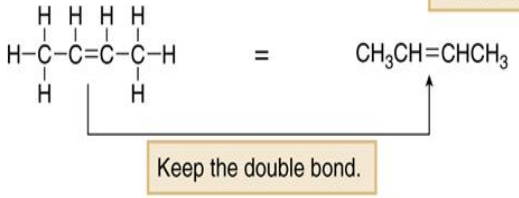
Condensed Structures

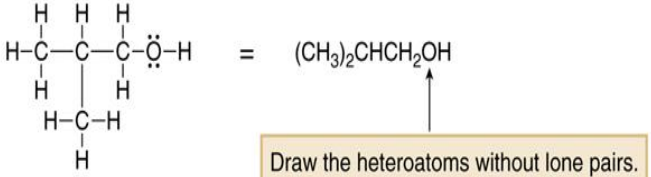
- All atoms are drawn, but the two-electron bond lines are generally omitted.
- Atoms are usually drawn next to the atoms to which they are bonded.
- Parentheses are used around similar groups bonded to the same atom.
- Lone pairs are omitted.

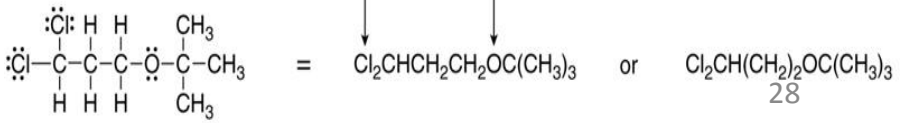








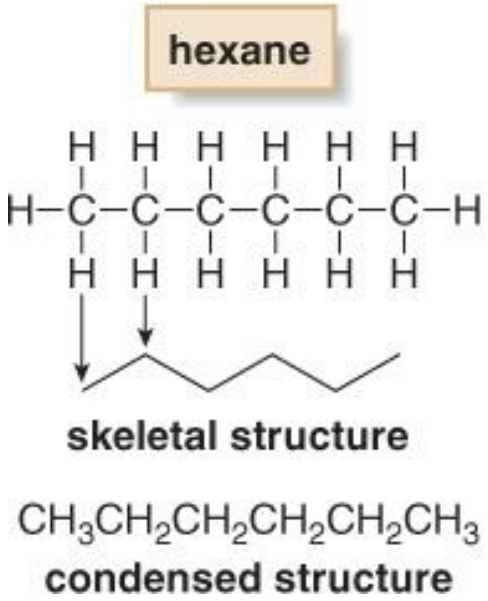


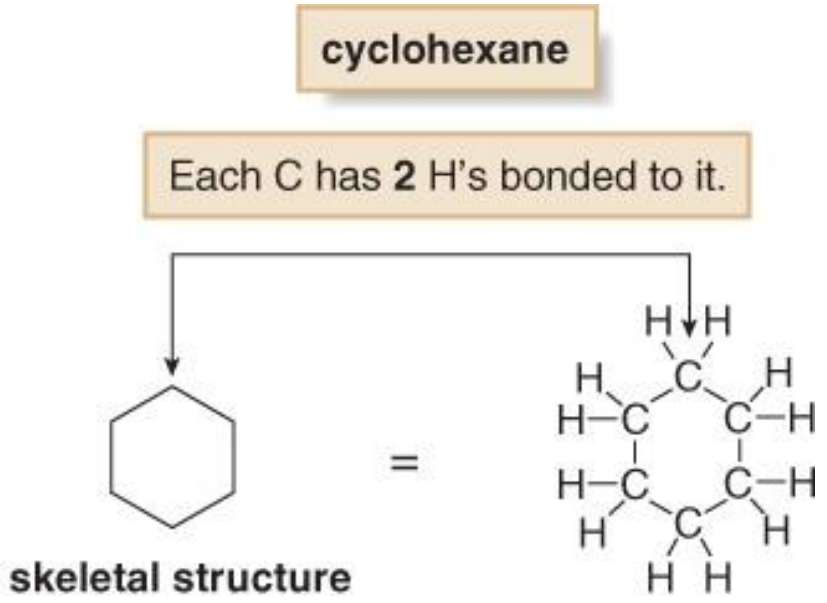


Structure and Bonding

Skeletal (Line) Structures:

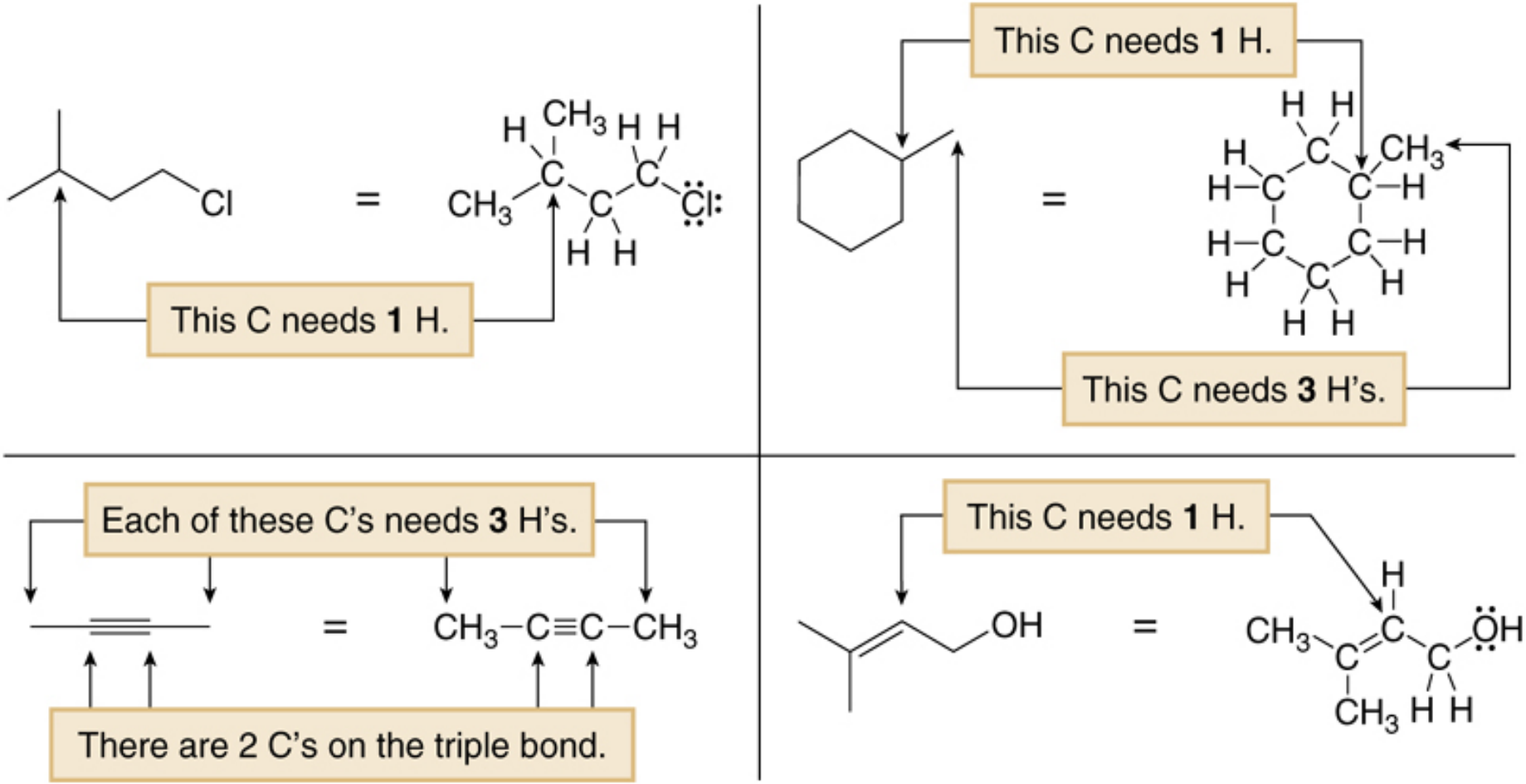
- Assume there is a carbon atom at the junction of any two lines or at the end of any line.
- Assume there are enough hydrogens around each carbon to make it tetravalent.
- Draw in all heteroatoms and hydrogens directly bonded to them.





Structure and Bonding

Examples of Skeletal (LINE) Structures:



THE END OF CHAPTER 1 BONDING AND ISOMERISM

BEST WISHES

AND

GOOD LUCK