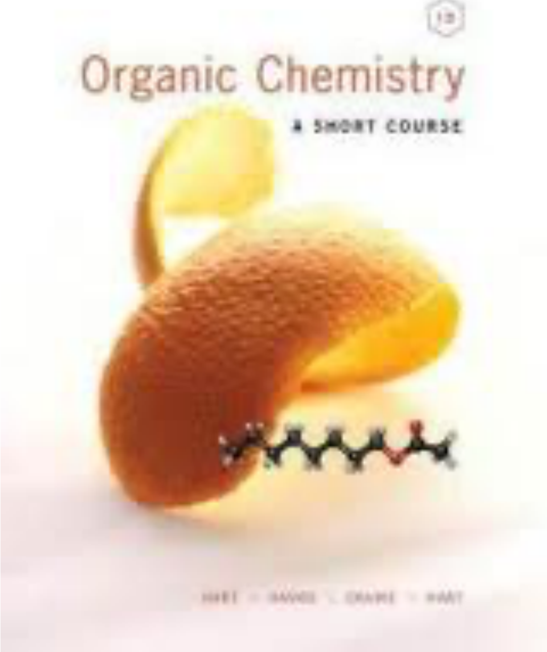
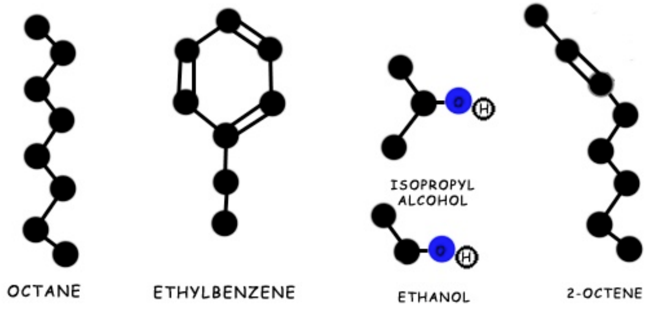
CHEM 226
Organic Chemistry



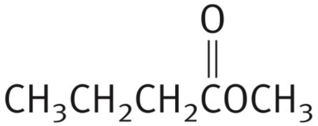
- Text Book
- Course Website: http://employees.oneonta.edu/odagomo/
- OWL Homework Access and Registration
- Lab Materials

What is organic chemistry?

Study of carbon, the compounds it makes, and the reactions it undergoes over 16 million carbon-containing compounds are known because the C-C single bond (348 kJ mol-1) and the C-H bond (412 kJ mol-1) are strong, carbon compounds are stable carbon can form chains and rings

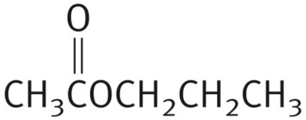


Chapter 1: Bonding and Isomerism



$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$$

methyl butyrate



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2CH_3$$

propyl acetate

Methyl butyrate and propyl acetate are both organic flavors that are found in apples and pears respectively and are structural isomers.

Structural Isomers are compounds that have the molecular formula (C5H10O2), but have different connectivity hence different structural formulas.

Bonding and Isomerism

Questions ?

Why does sucrose melt at 1850C while table salt melts at 801o C?

Why do both substances dissolve in water and olive oil does not?

Why does methyl butyrate smell like pears while propyl acetate smell like apple yet they have the same number and kind of atoms?

Bonding is the key to the structure, physical properties and chemical behavior of different kinds of matter.

1.1 electrons are arranged in atoms

Atoms contain a small, dense **nucles** surrounded by electrons.

The nucleus is positively charged and contains most of the mass of the atom.
The nucleus consists of **protons** which are positively charged, and **neutrons**, which are neutral.

The **atomic number** of an element is equal to the **number of protons** (and to the number ofelectrons around the nucleus in a neutral atom.

Atomic weight is approximately equal to the **sum** of the number of protons and the number of neutrons in the nucleus. Electrons are very light.

Electrons are concentrated in certains region of space around nucleus called orbitals.
Each orbital can contain a maximum of two electrons.

The orbitals, which differ in shape, are designated by the letters, ***s***, ***p***, ***d***, and ***f***.

Outer electrons, or **valence electrons**, are mainly involved in chemical bonding.

Table 1.1 ▰ Numbers of Orbitals and Electrons in the First Three Shells

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

Table 1.2 ▰ Electron Arrangements of the First 18 Elements

Atomic number	Element	Number of electrons in each orbital				
		1*s*	2*s*	2*p*	3*s*	3*p*
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

Table 1.3 ▰ Valence Electrons of the First 18 Elements

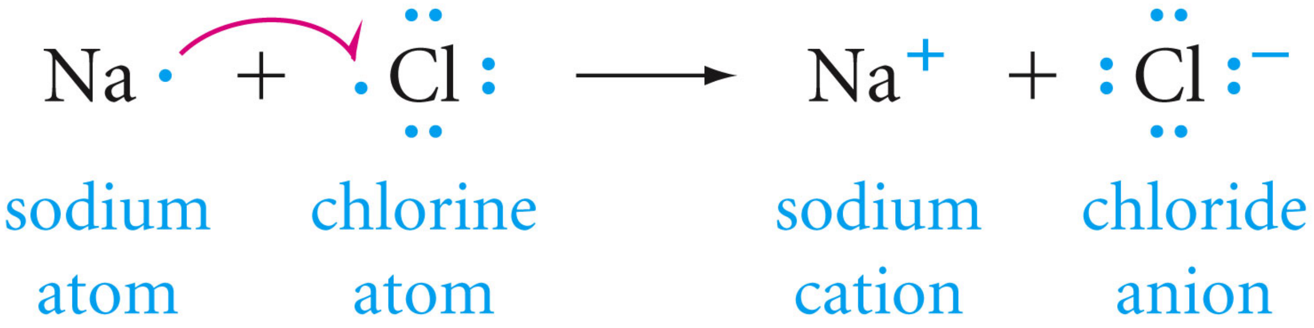
Group	I	II	III	IV	V	VI	VII	VIII
	$\mathrm{H}\cdot$							$\mathrm{He}:$
	$\mathrm{Li}\cdot$	$\overset{\cdot}{\mathrm{Be}}\cdot$	$\cdot\overset{\cdot}{\mathrm{B}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{N}}}:$	$\cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{O}}}:$	$:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{F}}}:$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ne}}}:$
	$\mathrm{Na}\cdot$	$\overset{\cdot}{\mathrm{Mg}}\cdot$	$\cdot\overset{\cdot}{\mathrm{Al}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{Si}}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{P}}}:$	$\cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{S}}}:$	$:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{Cl}}}:$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ar}}}:$

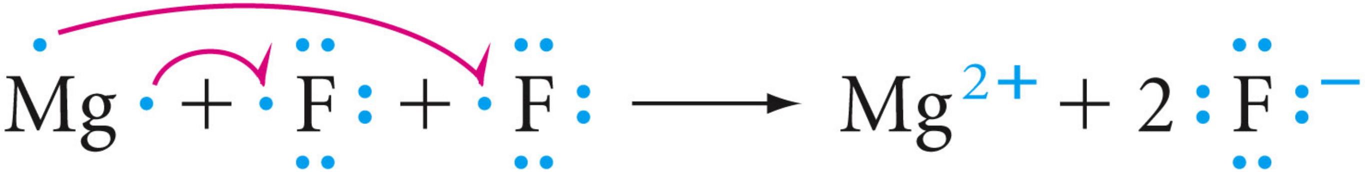
1.2 ionic and covalent bonding

A- Ionic bond (consider the "**Electrogenativity**")

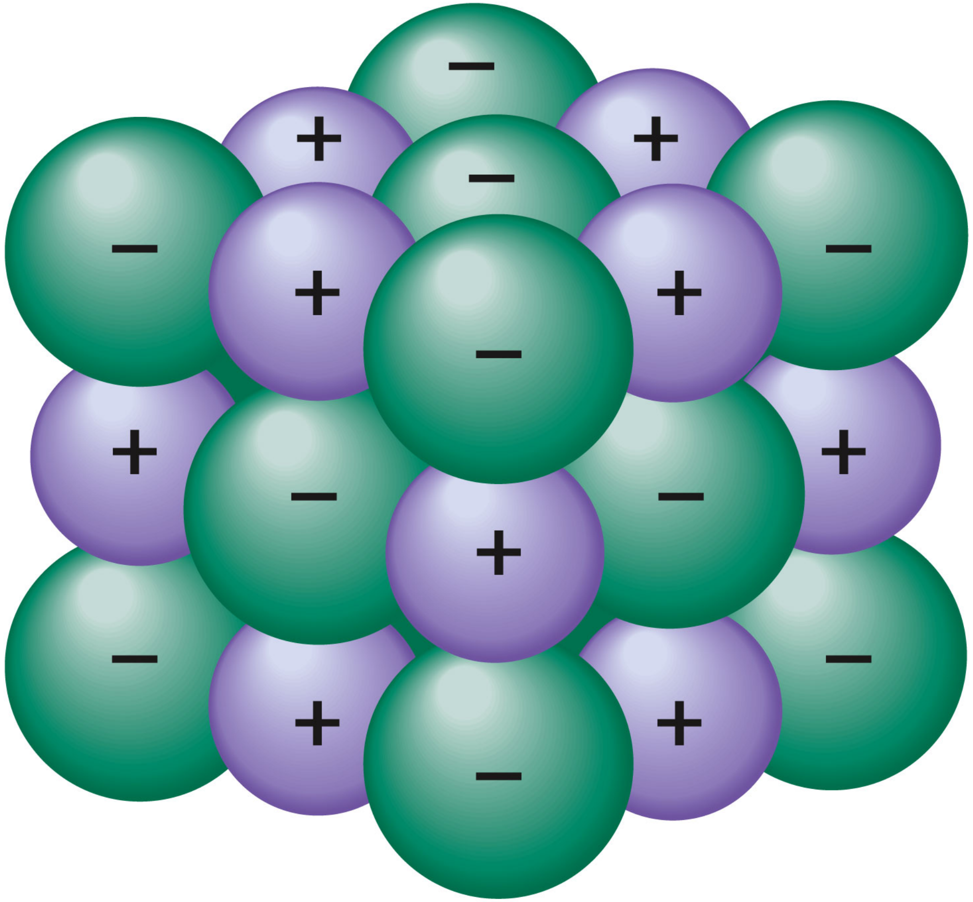
The atom that gives up electrons becomes positively charged, a **cation**.
The atom that receives electrons becomes negatively charged, an **anion**.

Ionic Compounds





$$\dot{\mathrm{Mg}}\cdot + \cdot\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\colon + \cdot\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\colon \longrightarrow \mathrm{Mg}^{2+} + 2\,\colon\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\colon^{-}$$



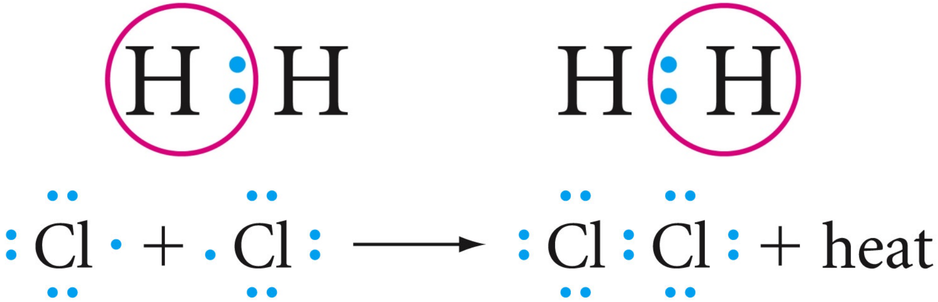
B- The Covalent Bond

Covalent bonding (similar electronegativity)
Elements that are neither strongly electronegative nor strongly electropositive, or that **have similar electronegativity's**, tend to form covalent bonds by **sharing electron pairs** rather than completely transferring electrons.

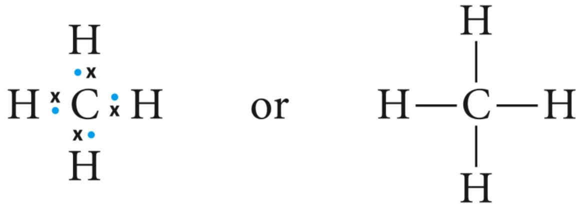
Two (or more) atoms **joined by covalent bonds** constitute a **molecule**.

The energy to break it apart into atoms, we called **bond energy**.

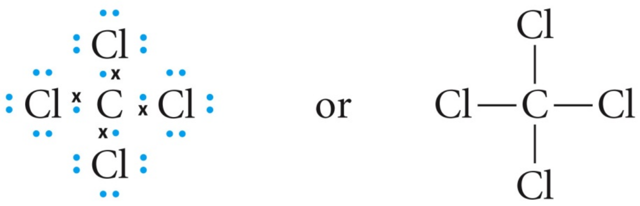
The distance between two nuclei is **bond length**.



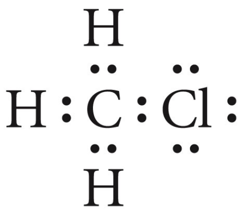
Carbon and the Covalent Bond



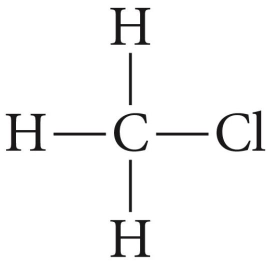
methane



tetrachloromethane
(carbon tetrachloride)

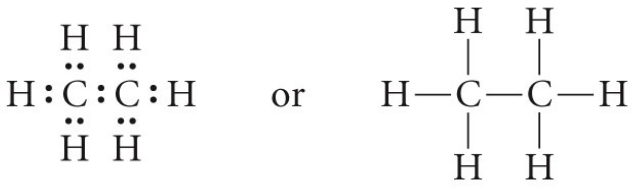


or

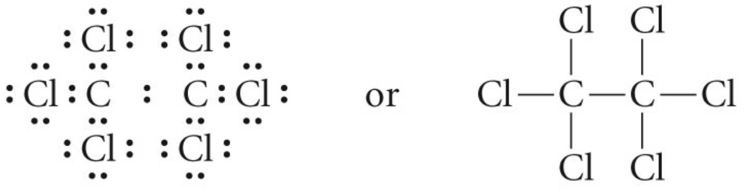


Draw the structures of dichloromethane and trichloromethane (chloroform)

Carbon-Carbon Single Bonds

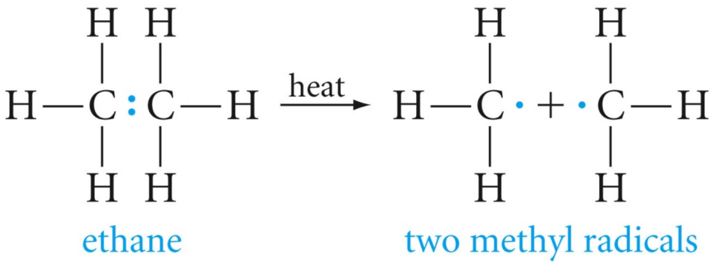


ethane



hexachloroethane

C-C	1.54 Å
H-H	0.74 Å
C-H	1.09 Å
Cl-Cl	1.98 Å



A radical is a molecular fragment with an odd number of electrons

Polar Covalent Bonds

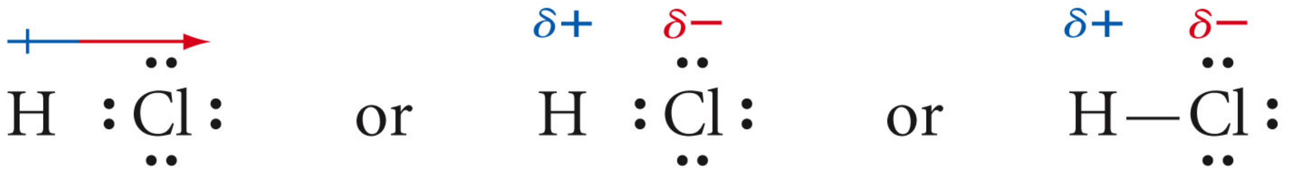
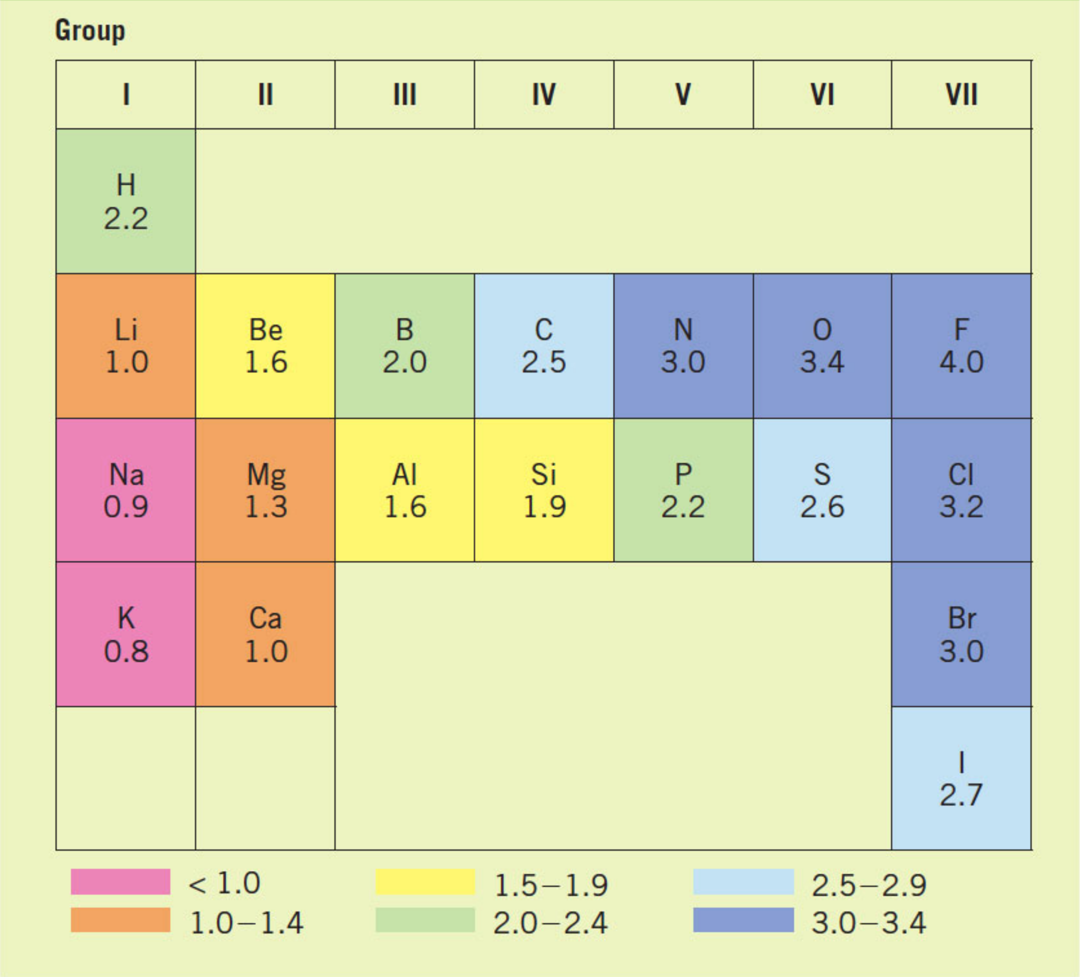


Table 1.4 ▰ Electronegativities of Some Common Elements



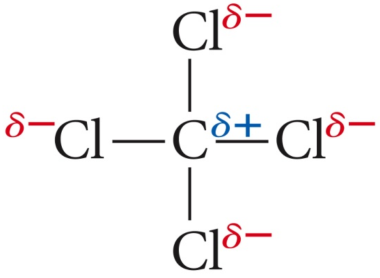
Group

I	II	III	IV	V	VI	VII
H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0					Br 3.0
						I 2.7

🟥 < 1.0
🟧 1.0–1.4
🟨 1.5–1.9
🟩 2.0–2.4
⬜ 2.5–2.9
🟦 3.0–3.4

p. 10, Table 1-4

Bond polarization in tetrachloromethane

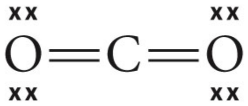


Draw the structure of the refrigerant dichlorodifluoromethane CCl2F2 and indicate the polarity of the bonds. (Prob. 1.11)

Multiple covalent bonds

A

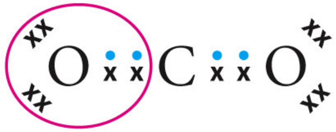
or

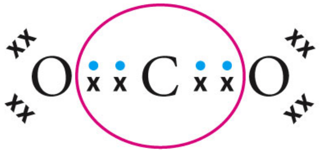


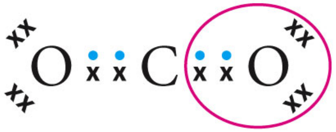
B

or

C







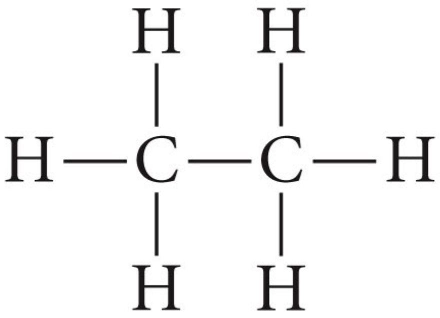
Valence

The **valence** of an element is simply the number of bonds that an atom of the element can form.

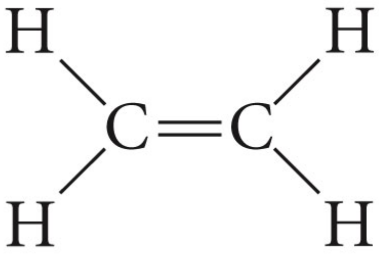
The number is normally equal to ***the number of electron needed to fill the valence shell***.

hydrogen cyanide

Determine What, if anything is wrong with the following electron arrangement for carbon dioxide



ethane



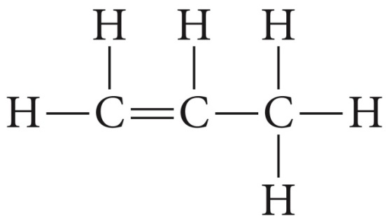
ethene

(ethylene)

$$H-C\equiv C-H$$

ethyne

(acetylene)



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & = & C & - & C & - & H \\ & & & & & & | & & \\ & & & & & & H & & \end{array}$$

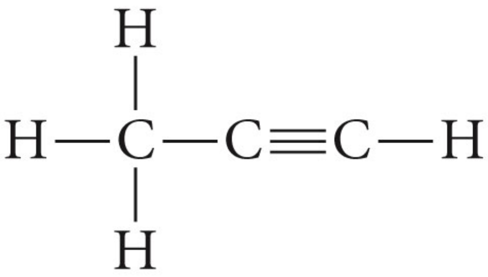
Table 1.5 ▰ Valences of Common Elements

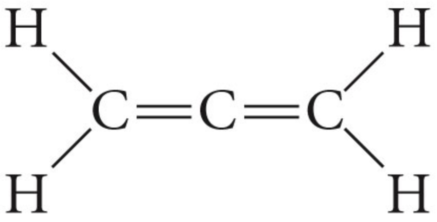
Element	$\mathrm{H}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{N}}}:$	$\cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{O}}}:$	$:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{F}}}:$	$:\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{Cl}}}:$
Valence	1	4	3	2	1	1

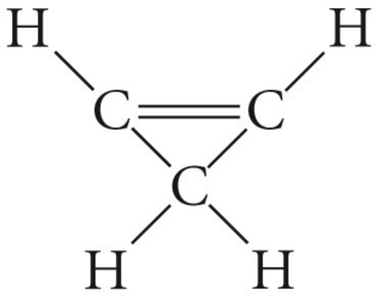
p. 12, Table 1-5

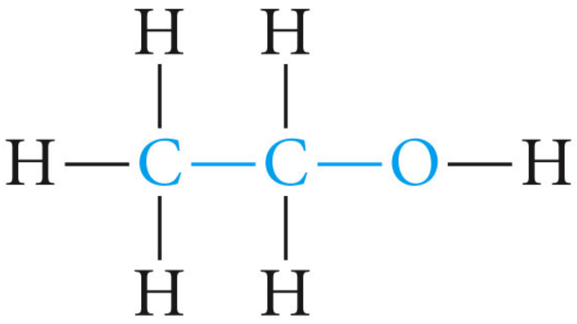
Isomerism and Writing Structural Formulas

Molecules that have the same kinds and numbers of atoms but different arrangements are called **isomers**.
Structural (or **constitutional**) isomers are the compounds that have the same molecular formula but different structural formulas.





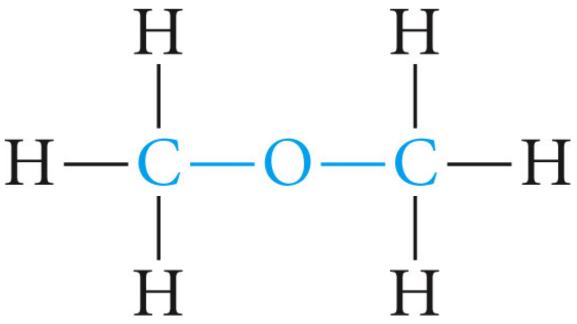




$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

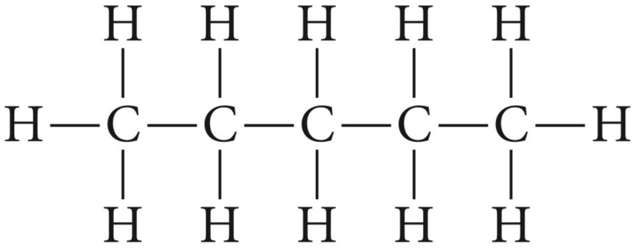
ethanol
(ethyl alcohol)
bp 78.5°C

and



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

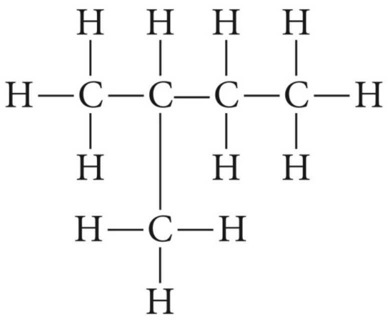
methoxymethane
(dimethyl ether)
bp −23.6°C



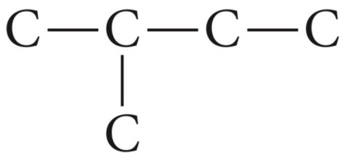
$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$$

pentane, bp 36°C

Abbreviated structural Formulas

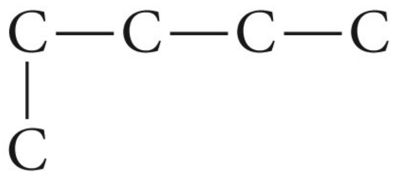


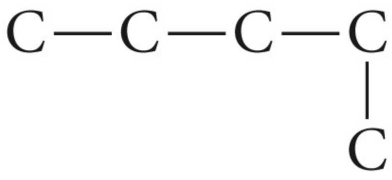
2-methylbutane, bp 28°C
(isopentane)

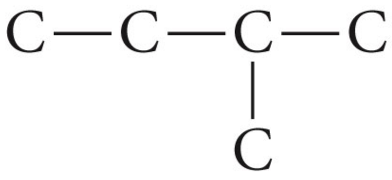


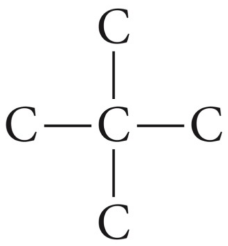
$C-\underset{C}{C}-C-C$

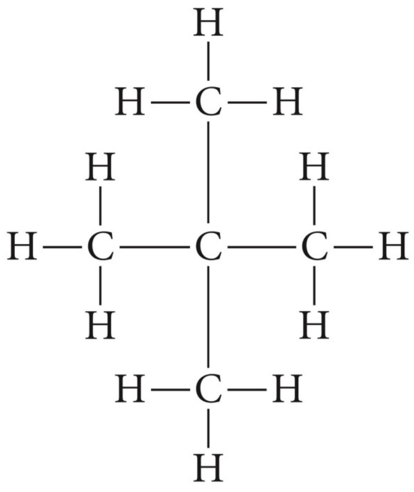
a branched chain



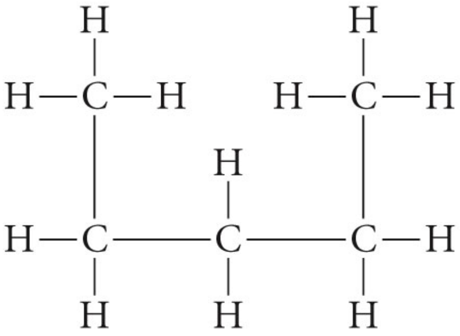


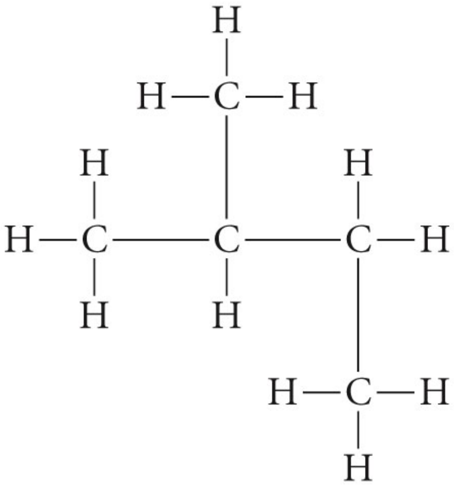


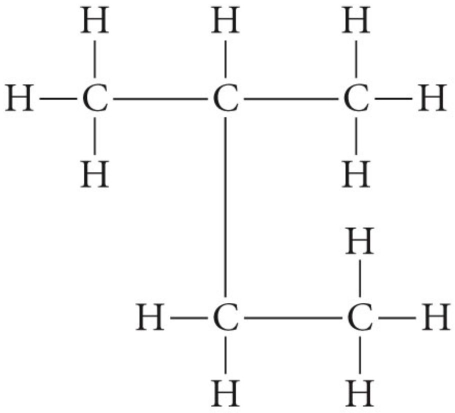


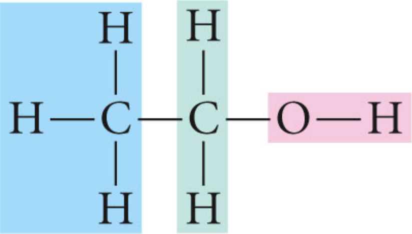


2,2-dimethylpropane, bp 10°C
(neopentane)



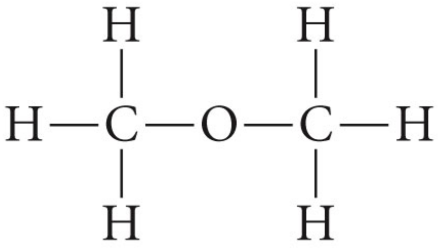






$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

to $CH_3—CH_2—OH$ or CH_3CH_2OH

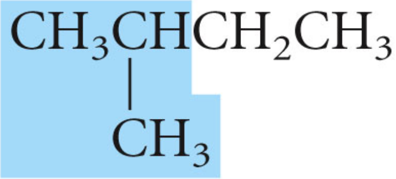


$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & — & C & — & O & — & C & — & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

to $CH_3—O—CH_3$ or CH_3OCH_3

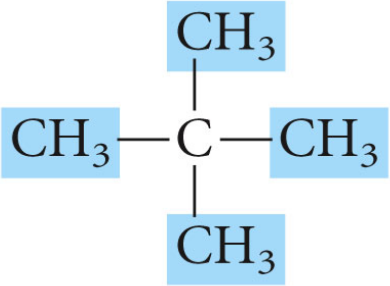
$CH_3CH_2CH_2CH_2CH_3$

n-pentane



$$\begin{array}{l} CH_3CHCH_2CH_3 \\ \quad\quad\;\; | \\ \quad\quad\; CH_3 \end{array}$$

isopentane



$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

neopentane

$CH_3(CH_2)_3CH_3$

n-pentane

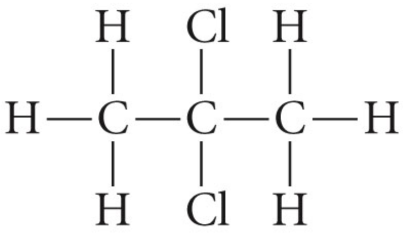
$(CH_3)_2CHCH_2CH_3$

isopentane

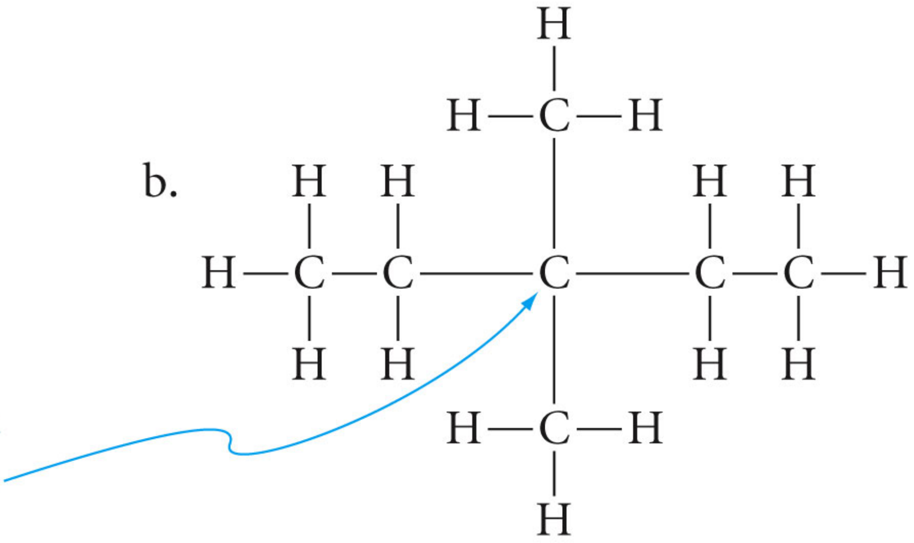
$(CH_3)_4C$

neopentane

a.

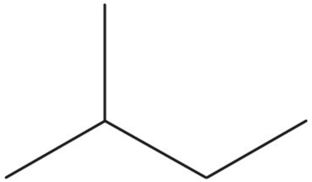


b.

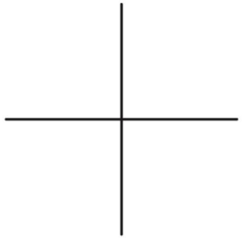


This is the carbon atom to which two —CH_3 and two —CH_2CH_3 groups are attached.

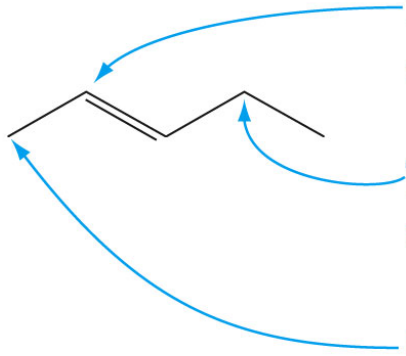
n-pentane



isopentane



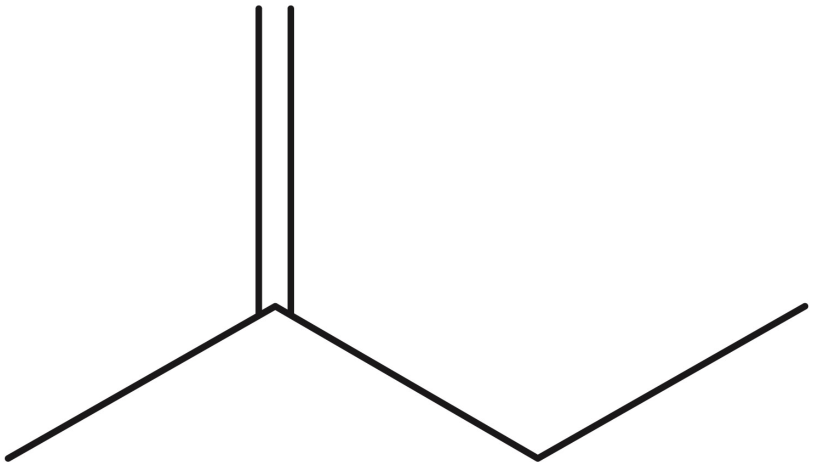
neopentane



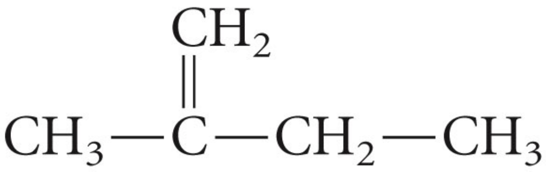
Three line segments emanate from this point; therefore, this carbon has one hydrogen (4 − 3 = 1) attached to it.

Two line segments emanate from this point; therefore, this carbon has two hydrogens (4 − 2 = 2) attached to it.

One line segment emanates from this point; therefore, this carbon has three hydrogens (4 − 1 = 3) attached to it.

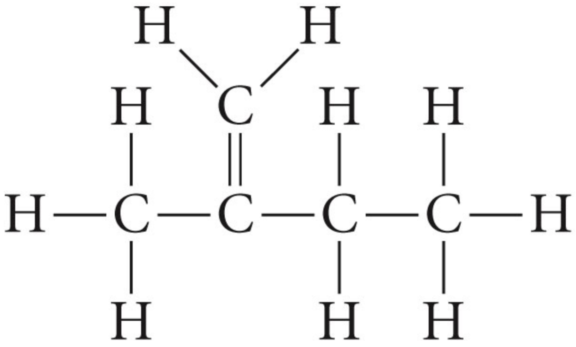


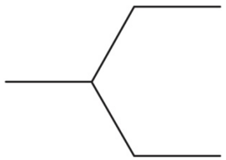
p. 18b

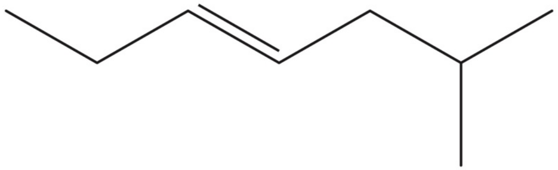


$CH_3-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_2-CH_3$

or





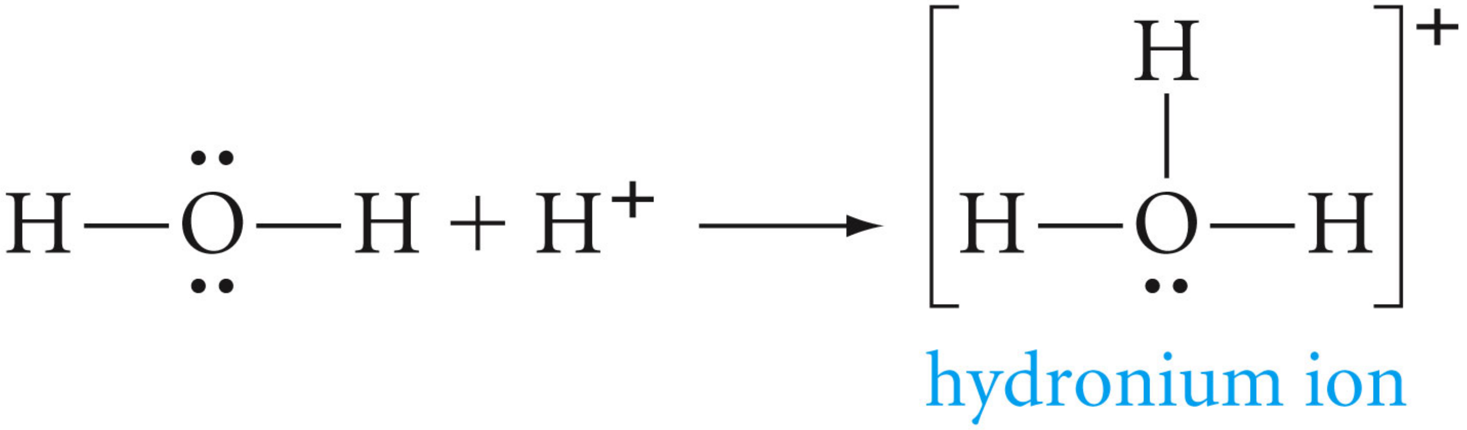


p. 18d

Formal Charge

In some molecules may be charged, either positively or negatively. Because such charges usually affect chemical reactions. Therefore, it is very important to know how to tell the charge is located.

Consider the formula for hydronium ion, H3O+, the product of the reaction of a water molecule with a proton.



To determine formal charge, we consider each atom to “own” all of its unshared electrons plus only half of its shared electrons

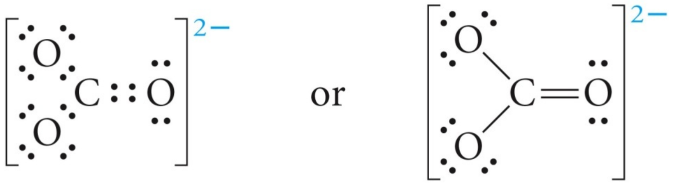
$$\text{Formal charge} = \text{number of valence electrons in the neutral atom} - \left(\text{unshared electrons} + \text{half the shared electrons}\right)$$

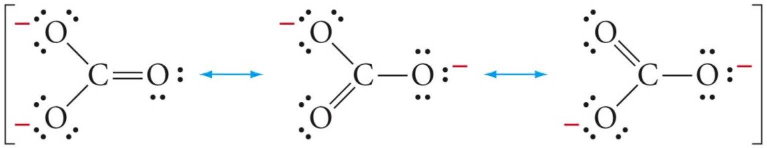
$$\text{Formal charge} = \text{number of valence electrons in the neutral atom} - \left(\text{dots} + \text{bonds}\right)$$

Resonance

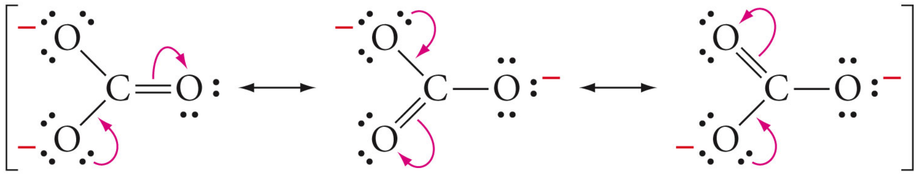
Sometimes, an electron pair is involved with more than two atoms.

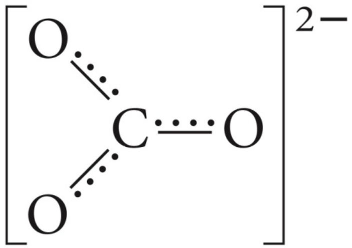
Molecules and ions in which this occurs can not be adequately represented by a single electron-dot structure


carbonate ion, CO_3^{2-}


three equivalent structures for the carbonate ion

Physical measurement tell us that all three C-O bond length are identical: 1.31 Angstrom (Å)
This distance is between the normal C=O (1.20 Å) and C-O (1.41 Å). We usually say the real carbonate ion has s structure that is **resonance hydride** of the three contributing **resonance structures**.





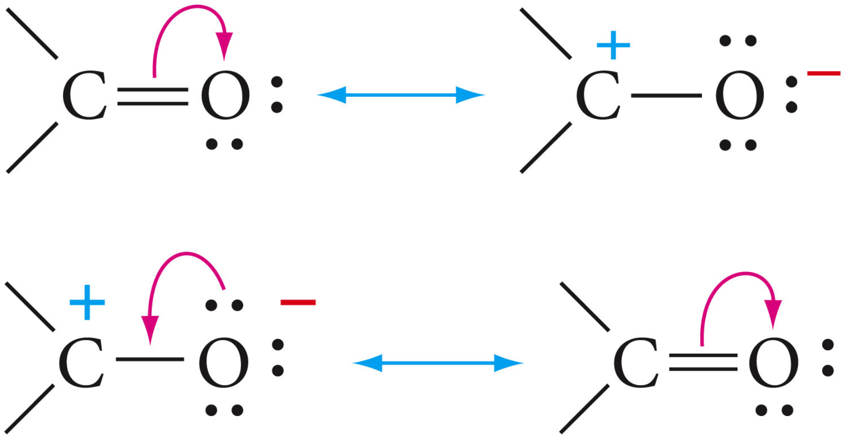
carbonate ion
resonance hybrid

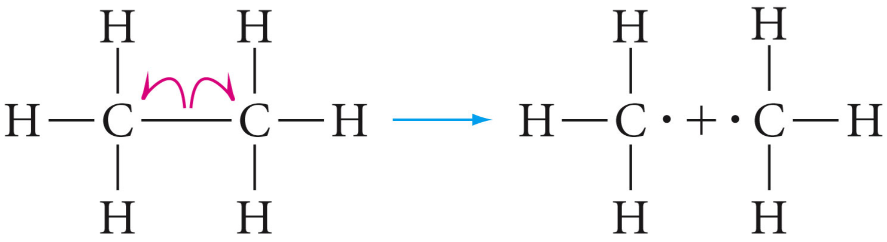
⟷	double-head arrow	between contributing structures
⇌	an equilibrium	between different compounds

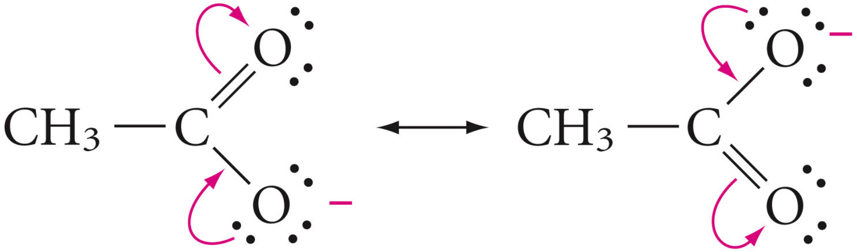
Arrow Formalisn

Arrow system is very important in Chemistry and has specific meaning.

Curved arrows	↷	a pair of electron moving
Fishhook arrows	⌒	single electron moving
Straight arrows	→	point from reactants to products in chemical reaction equactions
Straight arrow with half-heads	⇌	used in pairs to indicate that the reaction is reversible.
double-headed straight arrow	↔	between two structures indicates that they are resonance structure

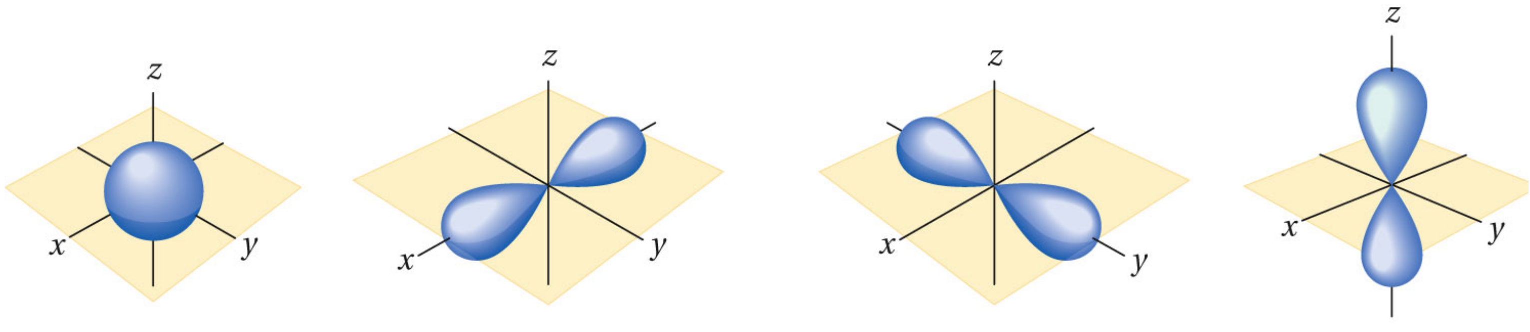




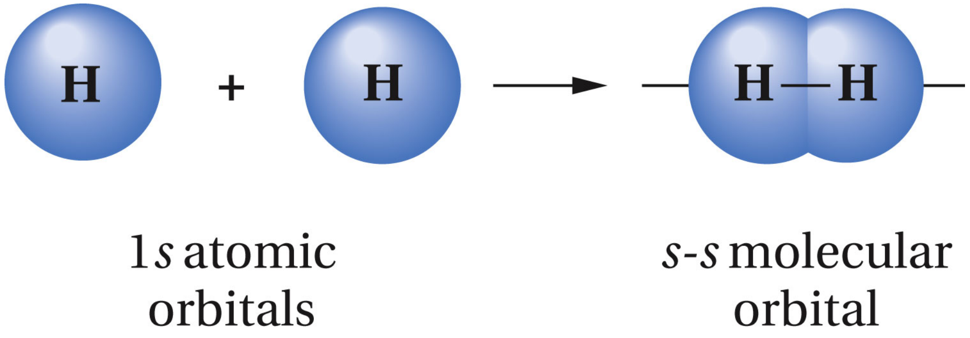


Bonding: the sigma bond

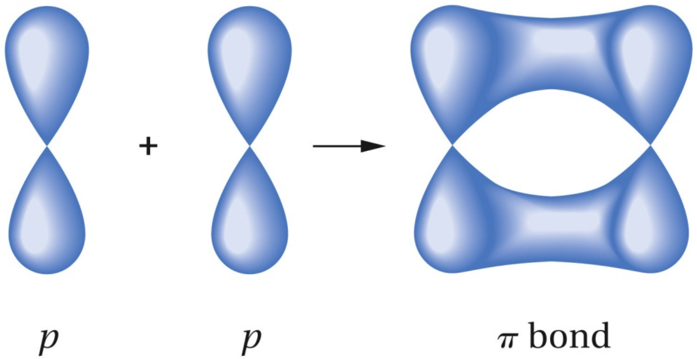
Atomic orbitals. The s orbitals are spherical. The three orbitals are dumbbell shaped and mutually perpendicular, oriented along the three coordinate axes, x, y, and z.

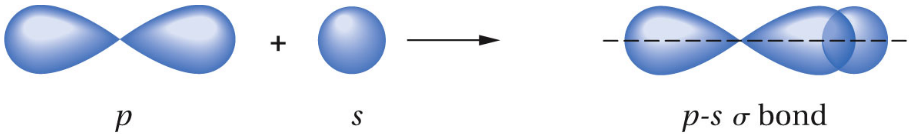


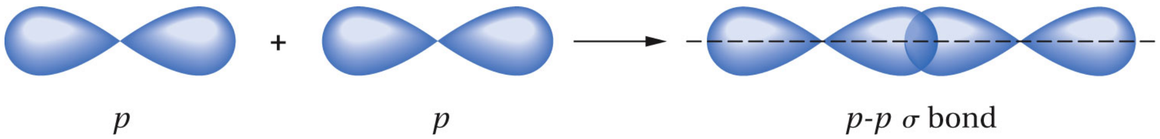
$2s$ $2p_x$ $2p_y$ $2p_z$



p. 23, Fig. 1-2

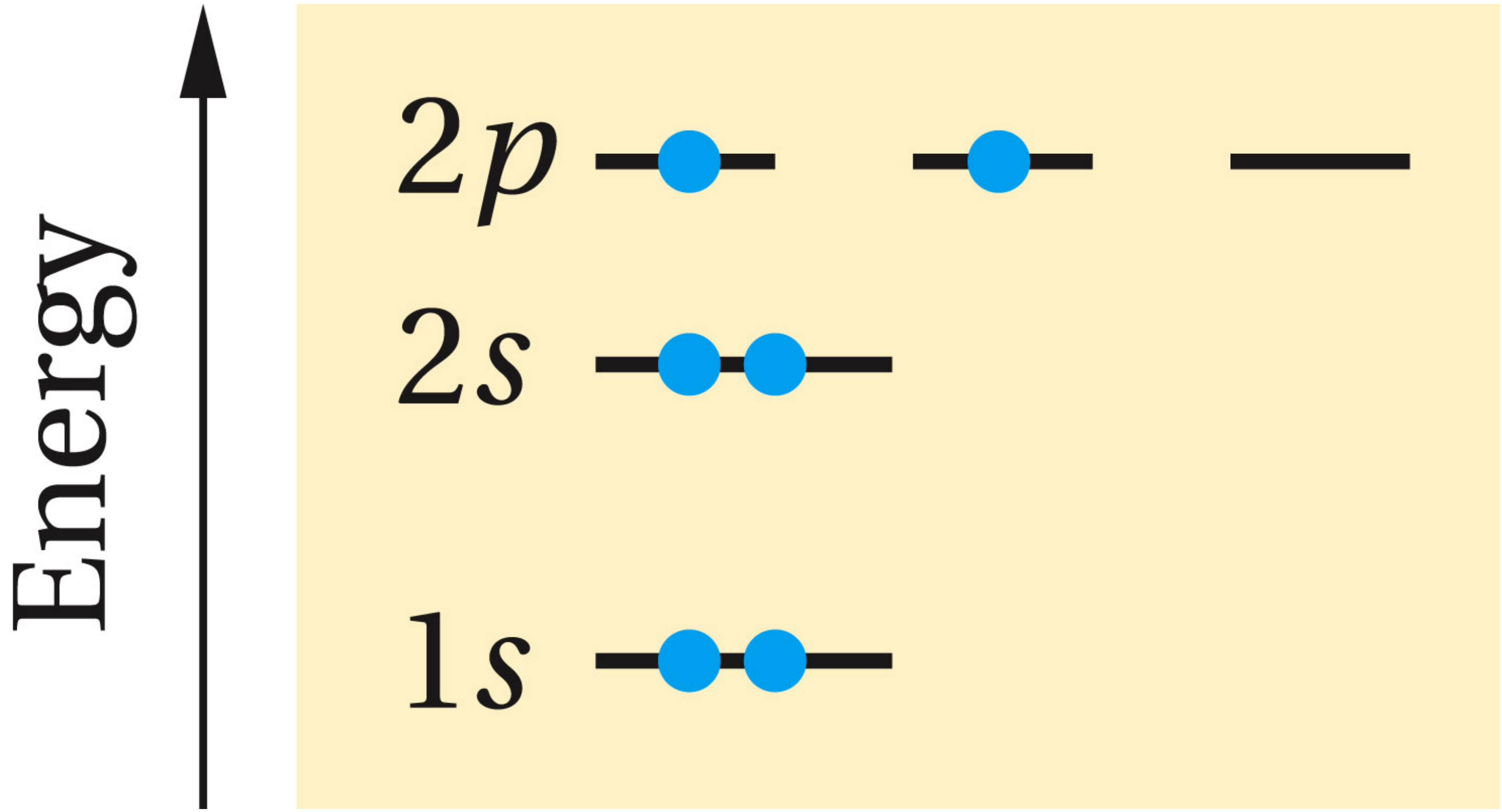

+
p
p
π bond


+
p
s
p-s σ bond

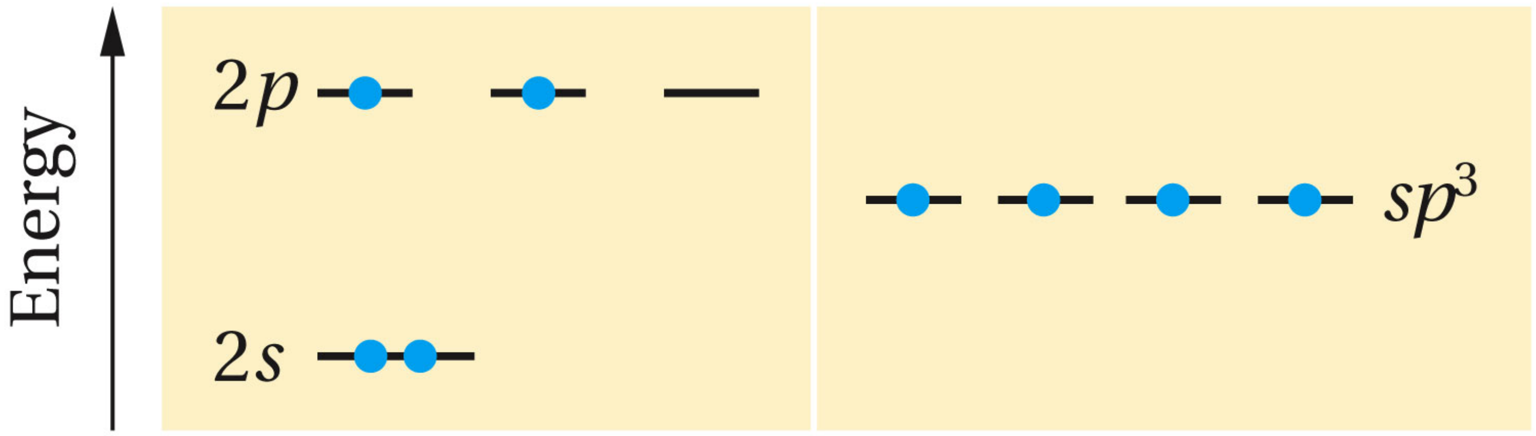

+
p
p
p-p σ bond

Carbon sp3 hybrid orbitals

In a carbon atom, the six electrons are arranged as shown below



p. 24, Fig. 1-5

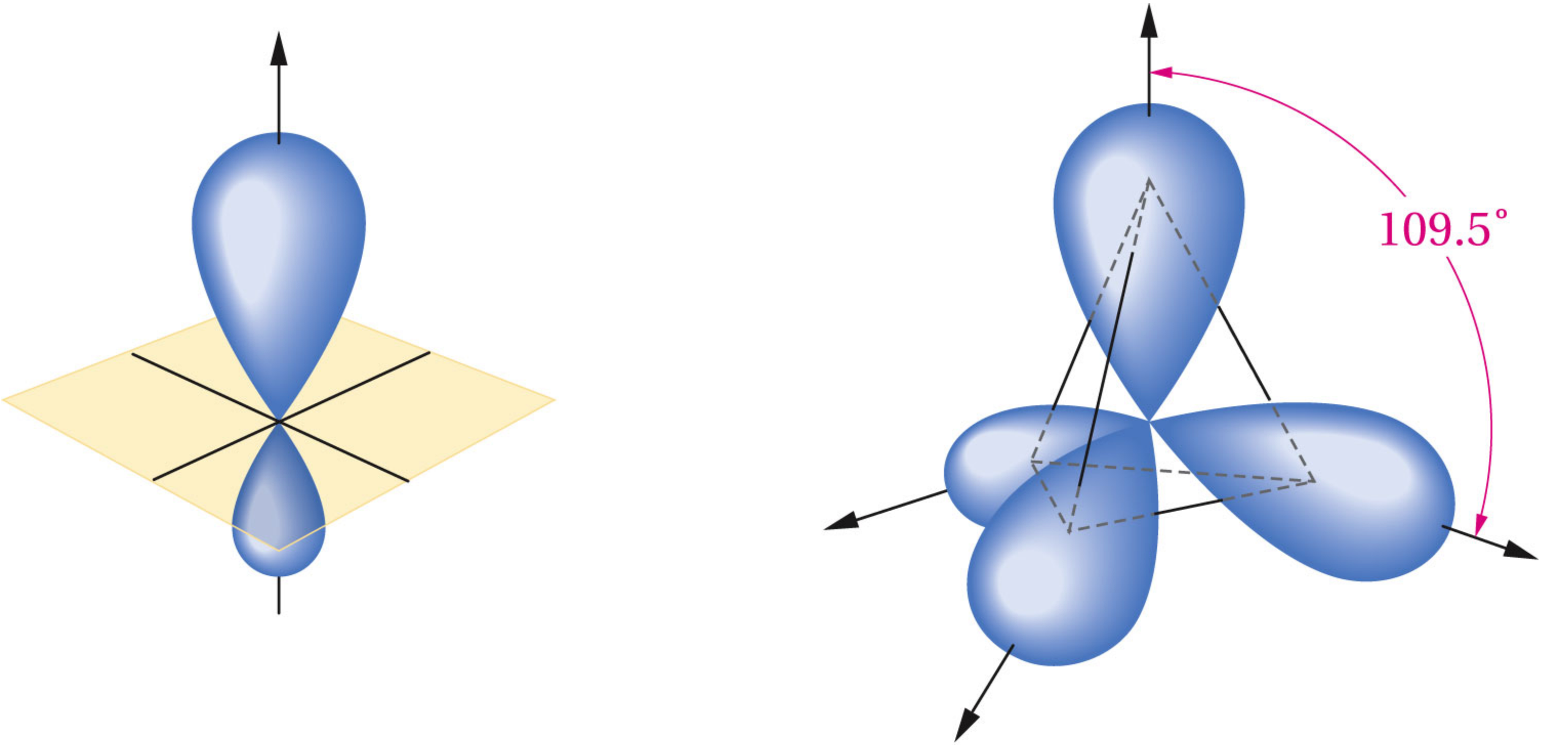


Atomic orbitals of carbon

Four equivalent sp^3 hybrid orbitals

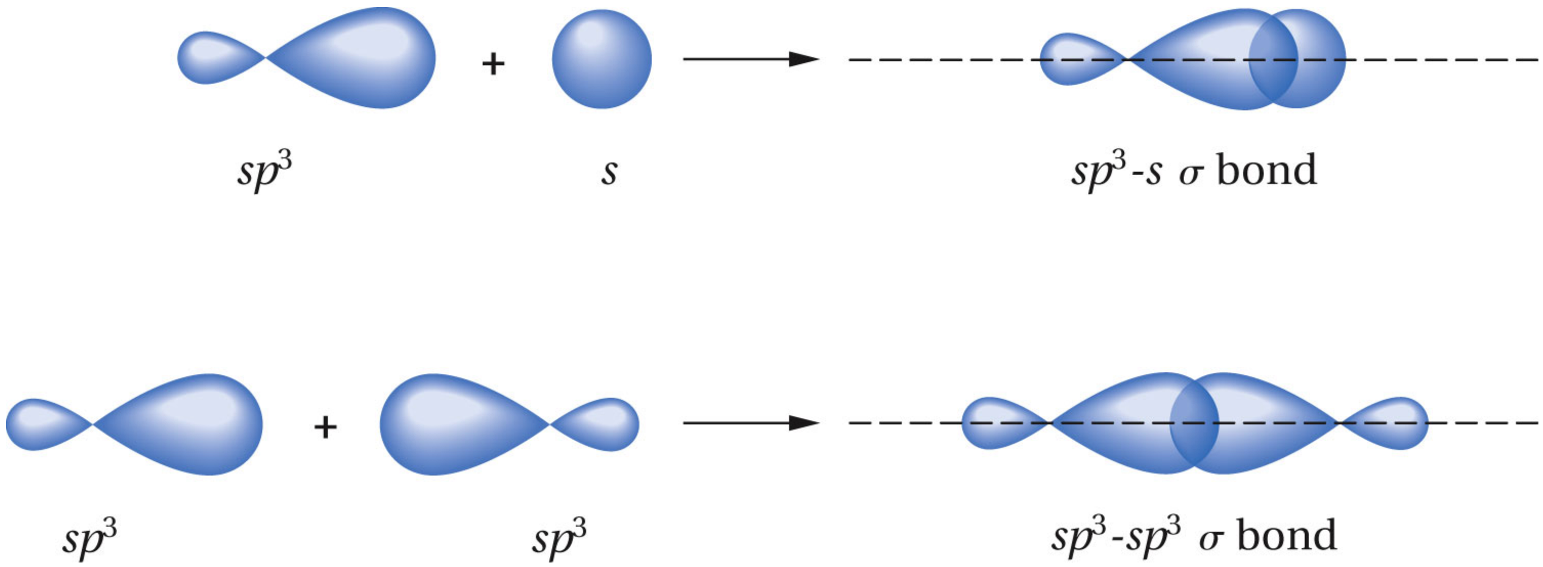
p. 24, Fig. 1-6

Tetrahedral carbon; the bonding in methane

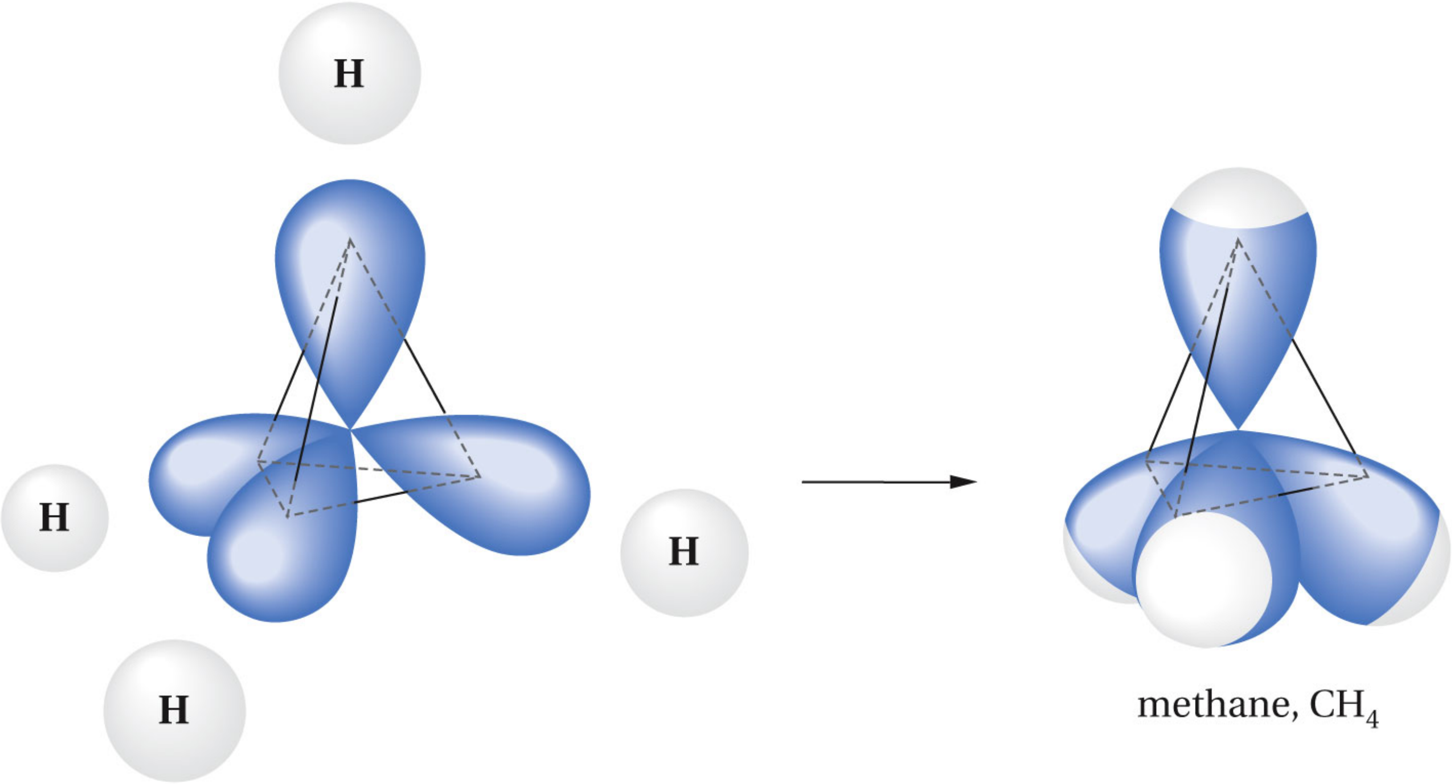


sp^3

p. 25, Fig. 1-7

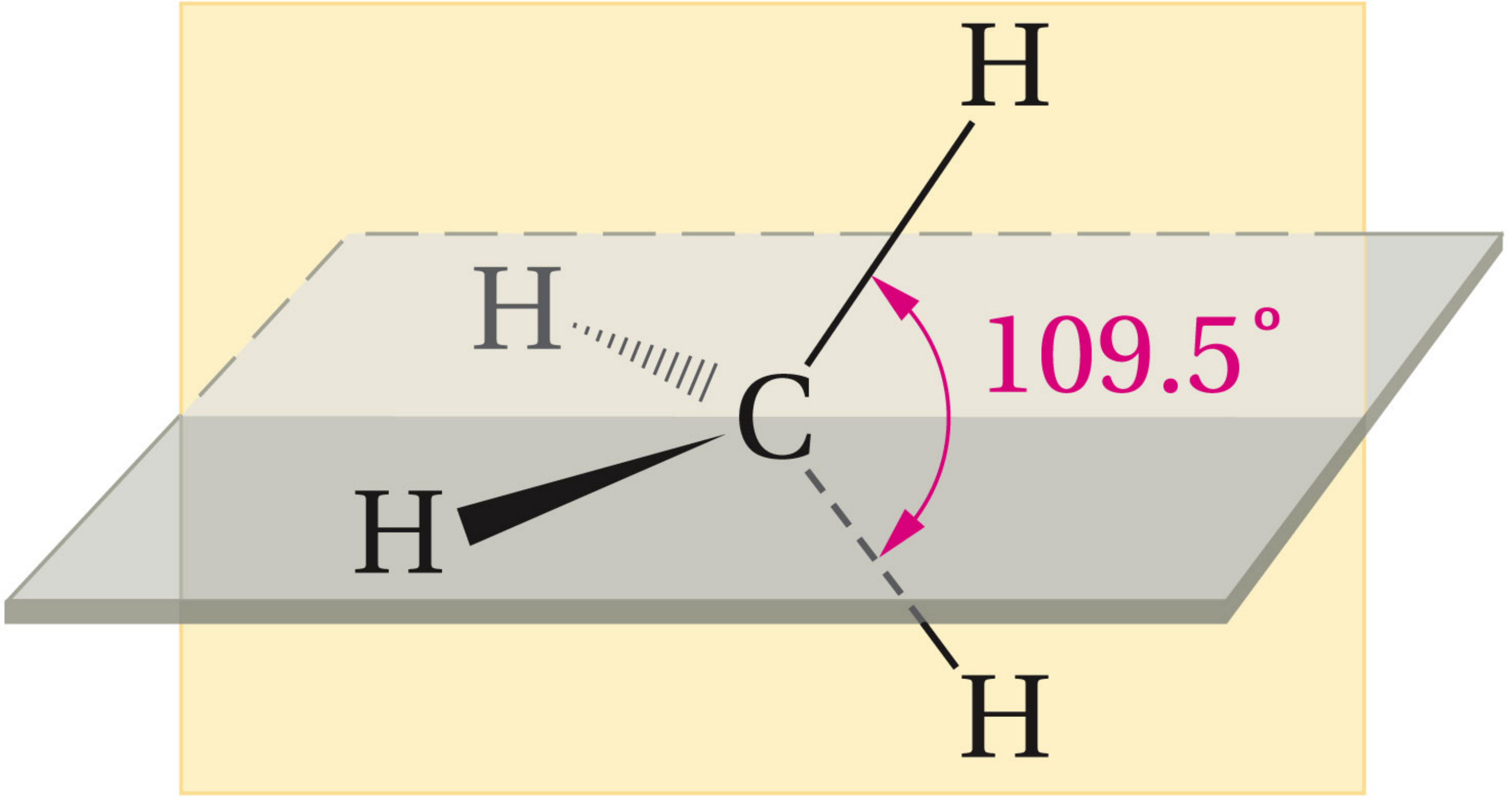


p. 25, Fig. 1-8

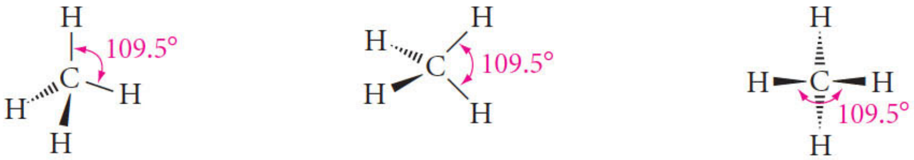


methane, CH$_4$

p. 25, Fig. 1-9

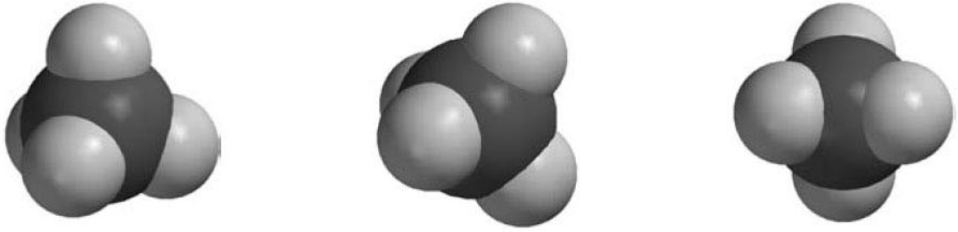


p. 26, Fig. 1-10

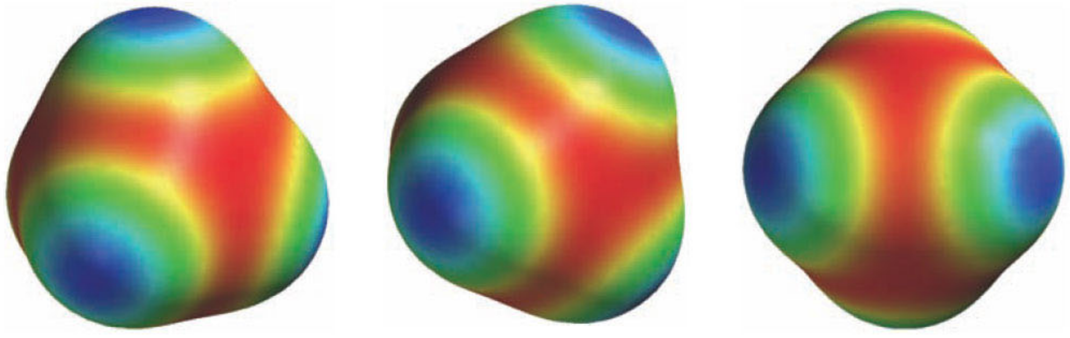


(a) In a **3D structure, solid lines** lie in the plane of the page (C and H in C—H lie in the plane). **Dashed wedges** extend behind the plane (H in C┉H lies behind the plane). **Solid wedges** project out toward you (H in C◄H is in front of the plane).

(b) A **ball-and-stick model** of a molecule emphasizes the bonds that connect atoms.



(c) A **space-filling model** emphasizes the space occupied by the atoms.



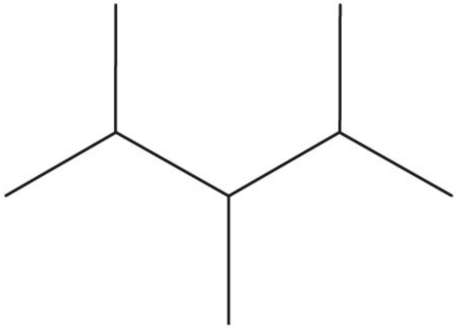
(d) An **electrostatic potential map** shows the distribution of electrons in a molecule. Red indicates partial negative charge, and blue indicates partial positive charge.

p. 26, Fig. 1-11

classification according to molecular framework

Acyclic Cyclic Heterocyclic and Carbocyclic

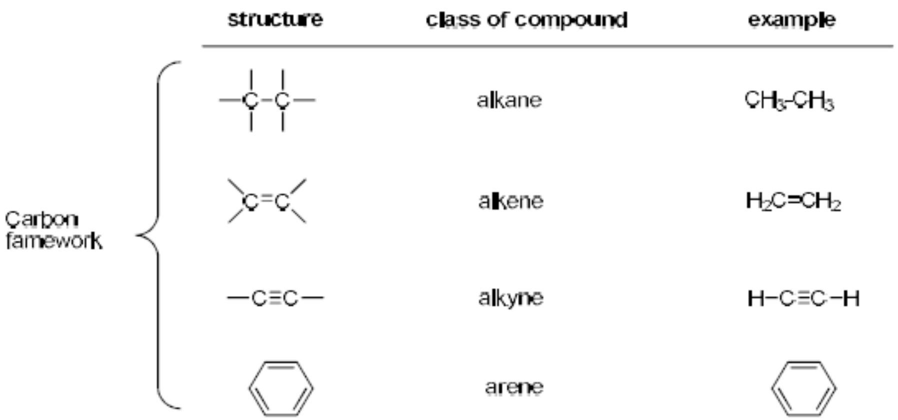
unbranched chain of
eight carbon atoms



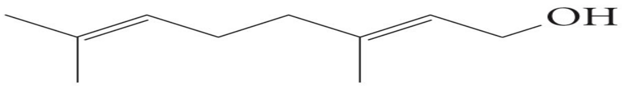
branched chain of
eight carbon atoms

Classification according to functional group

A list of main functional group



	structure	class of compound	example
Carbon famework	$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$	alkane	CH_3-CH_3
	$>C=C<$	alkene	$H_2C=CH_2$
	$-C\equiv C-$	alkyne	$H-C\equiv C-H$
		arene	



geraniol
(oil of roses)
bp 229–230°C

A branched chain compound used in perfumes

$CH_3(CH_2)_5CH_3$

heptane
(petroleum)
bp 98.4°C

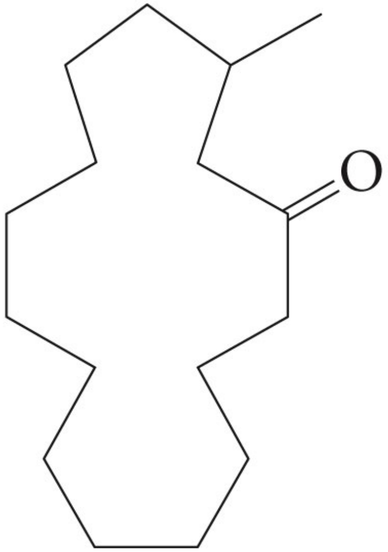
A hydrocarbon present in petroleum, used as a standard in testing the octane rating of gasoline

$$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3$$

2-heptanone
(oil of cloves)
bp 151.5°C

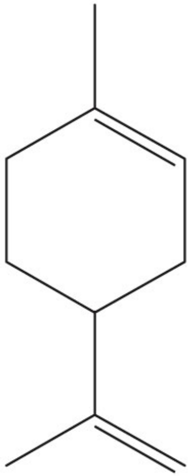
A colorless liquid with a fruity odor, in part responsible for the "peppery" odor of blue cheese

p. 27, Fig. 1-12



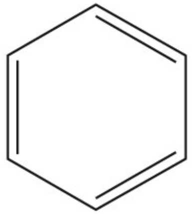
muscone
(musk deer)
bp 327–330°C

A 15-membered ring ketone, used in perfumes



limonene
(citrus fruit oils)
bp 178°C

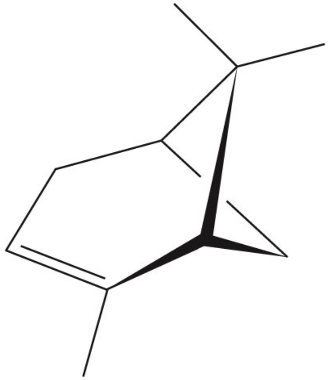
A ring with two side chains, one of which is branched



benzene
(petroleum)
mp 5.5°C, bp 80.1°C

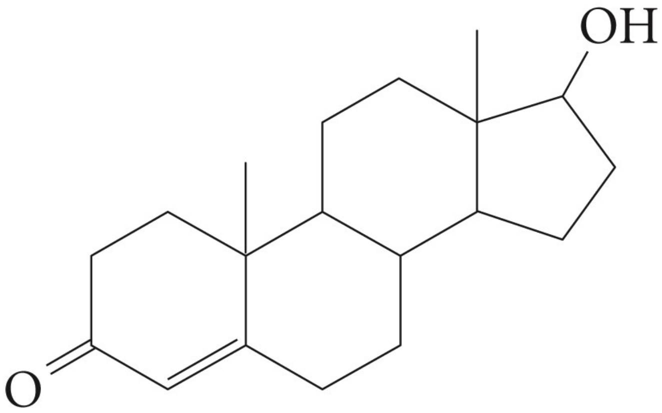
A very common ring

p. 28, Fig. 1-13a



α-pinene
(turpentine)
bp 156.2°C

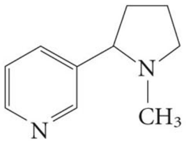
A bicyclic molecule; one would have to break *two* bonds to make it acyclic



testosterone
(testes)
mp 155°C

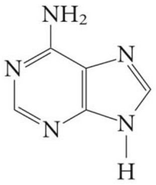
A male sex hormone in which several rings of common sizes are *fused* together; that is, they share two adjacent carbon atoms

p. 28, Fig. 1-13b



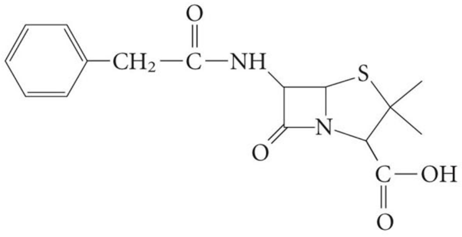
nicotine
bp 246°C

Present in tobacco, nicotine has two heterocyclic rings of different sizes, each containing one nitrogen.



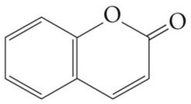
adenine
mp 360–365°C
(decomposes)

One of the four heterocyclic bases of DNA, adenine contains two fused heterocyclic rings, each of which contains two heteroatoms (nitrogen).



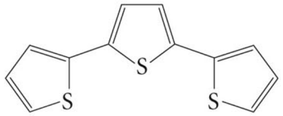
penicillin-G
(amorphous solid)

One of the most widely used antibiotics, penicillin has two heterocyclic rings, the smaller of which is crucial to biological activity.



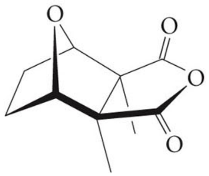
coumarin
mp 71°C

Found in clover and grasses, coumarin produces the pleasant odor of new-mown hay.



α-terthienyl
mp 92–93°C

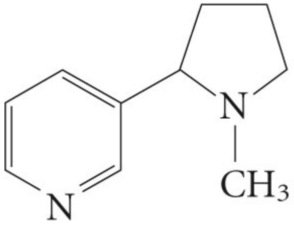
This compound, with three linked sulfur-containing rings, is present in certain marigold species.



cantharidin
mp 218°C

This compound, an oxygen heterocycle, is the active principle in cantharis (also known as Spanish fly), a material isolated from certain dried beetles of the species *Cantharis vesicatoria* and incorrectly thought by some to increase sexual desire.

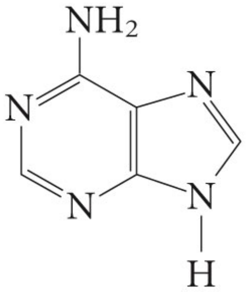
p. 29, Fig. 1-14



nicotine

bp 246°C

Present in tobacco, nicotine has two heterocyclic rings of different sizes, each containing one nitrogen.

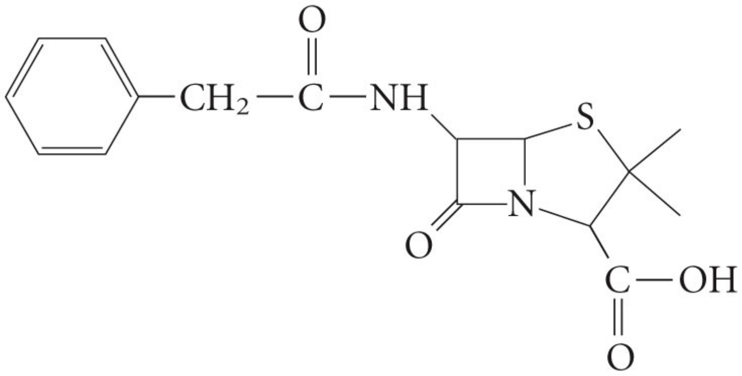


adenine

mp 360–365°C

(decomposes)

One of the four heterocyclic bases of DNA, adenine contains two fused heterocyclic rings, each of which contains two heteroatoms (nitrogen).

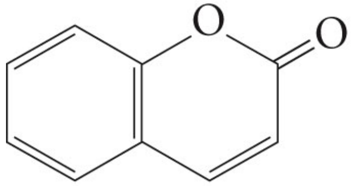


penicillin-G

(amorphous solid)

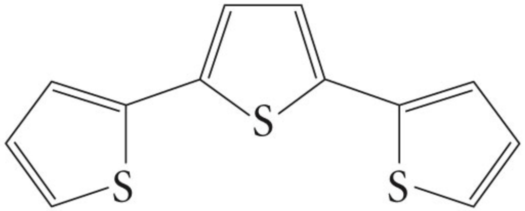
One of the most widely used antibiotics, penicillin has two heterocyclic rings, the smaller of which is crucial to biological activity.

p. 29, Fig. 1-14a



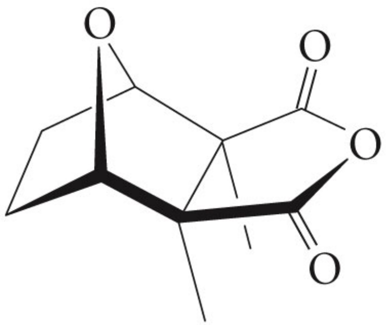
coumarin
mp 71°C

Found in clover and grasses, coumarin produces the pleasant odor of new-mown hay.



α-terthienyl
mp 92–93°C

This compound, with three linked sulfur-containing rings, is present in certain marigold species.

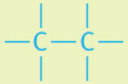
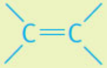
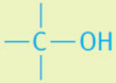
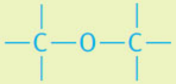


cantharidin
mp 218°C

This compound, an oxygen heterocycle, is the active principle in cantharis (also known as Spanish fly), a material isolated from certain dried beetles of the species *Cantharis vesicatoria* and incorrectly thought by some to increase sexual desire.

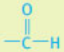
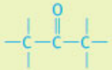
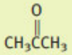
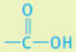
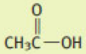
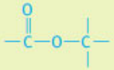
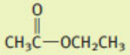
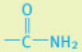
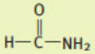
p. 29, Fig. 1-14b

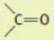
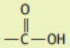
Table 1.6 ▰ The Main Functional Groups

	Structure	Class of compound	Specific example	Common name of the specific example
A. Functional groups that are a part of the molecular framework	 $-\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$	alkane	$CH_3{-}CH_3$	ethane, a component of natural gas
		alkene	$CH_2{=}CH_2$	ethylene, used to make polyethylene
	$-C{\equiv}C-$	alkyne	$HC{\equiv}CH$	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
B. Functional groups containing oxygen				
1. With carbon–oxygen single bonds	 $-\overset{\mid}{\underset{\mid}{C}}-OH$	alcohol	CH_3CH_2OH	ethyl alcohol, found in beer, wines, and liquors
	 $-\overset{\mid}{\underset{\mid}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-$	ether	$CH_3CH_2OCH_2CH_3$	diethyl ether, once a common anesthetic

p. 30, Table 1-6a

Table 1.6 continued

	Structure	Class of compound	Specific example	Common name of the specific example
*2. With carbon–oxygen double bonds**	 $-\overset{\overset{O}{\|}}{C}-H$	aldehyde	$CH_2{=}O$	formaldehyde, used to preserve biological specimens
	 $-\underset{\vert}{\overset{\vert}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\vert}{\overset{\vert}{C}}-$	ketone	 $CH_3\overset{\overset{O}{\|}}{C}CH_3$	acetone, a solvent for varnish and rubber cement
3. With single and double carbon–oxygen bonds	 $-\overset{\overset{O}{\|}}{C}-OH$	carboxylic acid	 $CH_3\overset{\overset{O}{\|}}{C}-OH$	acetic acid, a component of vinegar
	 $-\overset{\overset{O}{\|}}{C}-O-\underset{\vert}{\overset{\vert}{C}}-$	ester	 $CH_3\overset{\overset{O}{\|}}{C}-OCH_2CH_3$	ethyl acetate, a solvent for nail polish and model airplane glue
*C. Functional groups containing nitrogen***	$-\underset{\vert}{\overset{\vert}{C}}-NH_2$	primary amine	$CH_3CH_2NH_2$	ethylamine, smells like ammonia
	$-C{\equiv}N$	nitrile	$CH_2{=}CH-C{\equiv}N$	acrylonitrile, raw material for making Orlon
D. Functional group with oxygen and nitrogen	 $-\overset{\overset{O}{\|}}{C}-NH_2$	primary amide	 $H-\overset{\overset{O}{\|}}{C}-NH_2$	formamide, a softener for paper
E. Functional group with halogen	$-X$	alkyl or aryl halide	CH_3Cl	methyl chloride, refrigerant and local anesthetic
F. Functional groups containing sulfur[†]	$-\underset{\vert}{\overset{\vert}{C}}-SH$	thiol (also called mercaptan)	CH_3SH	methanethiol, has the odor of rotten cabbage
	$-\underset{\vert}{\overset{\vert}{C}}-S-\underset{\vert}{\overset{\vert}{C}}-$	thioether (also called sulfide)	$(CH_2{=}CHCH_2)_2S$	diallyl sulfide, has the odor of garlic

*The  $>C{=}O$ group, present in several functional groups, is called a **carbonyl group**. The  $-\overset{\overset{O}{\|}}{C}-OH$ group of acids is called a **carboxyl group** (a contraction of *carb*onyl and hydr*oxyl*).

The $-NH_2$ group is called an **amino group.

[†] Thiols and thioethers are the sulfur analogs of alcohols and ethers.

p. 31, Table 1-6b