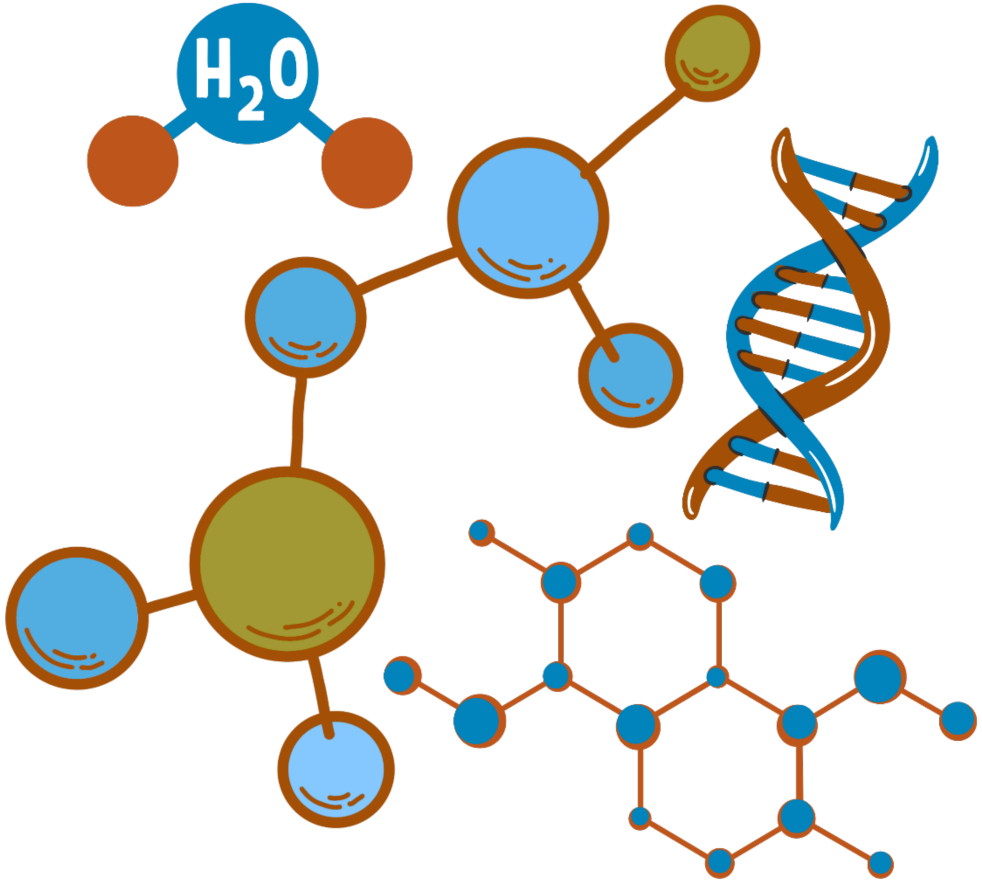
Introduction to Organic Chemistry
CHEM 109

جامعة الملك سعود
King Saud University

COLLEGE OF SCIENCES
CHEMISTRY DEPARTMENT

Chapter 2: Structure and Classification of Organic Compounds



1. Hydrocarbons

- **Hydrocarbons are compounds that contain only carbon and hydrogen atoms.**

1.1 Aliphatic Hydrocarbons: Representative Alkanes, Alkenes, Alkynes

- **Alkanes: are hydrocarbons that do not have multiple bonds between carbon atoms, and we can indicate this in the family name and in names for specific compounds by the -ane ending.**
- **Alkenes contain at least one carbon–carbon double bond, and this is indicated in the family name and in names for specific compounds by an -ene ending.**
- **Alkynes contain at least one carbon–carbon triple bond, and this is indicated in the family name and in names for specific compounds by an -yne ending.**

1. Hydrocarbons

1.2 Alkanes

- Alkanes, whose molecules contain only single bonds, are referred to as saturated compounds because these compounds contain the maximum number of hydrogen atoms that the carbon compound can possess. Alkanes have the general formula C_nH_{2n+2}
- Cycloalkanes: are alkanes in which all or some of the carbon atoms are arranged in a ring. cycloalkanes containing a single ring have two fewer hydrogen atoms and thus have the general formula C_nH_{2n}

- Sources of Alkanes: Natural gas and petroleum are the primary sources of alkanes. Methane, the simplest alkane, is a key component of natural gas and is produced by primitive organisms called methanogens in anaerobic environments.

Methane

Cyclohexane

1. Hydrocarbons

1.3 Shapes Alkanes

- A general tetrahedral orientation of groups and thus *sp*^{3} hybridization is the rule for the carbon atoms of all alkanes and cycloalkanes.

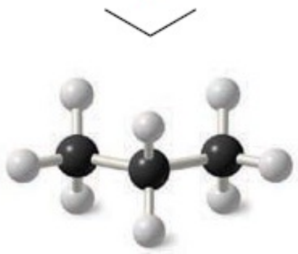
- **Straight-chain**: Alkanes like butane, as an example, have a zigzag structure due to their tetrahedral carbon atoms. A more accurate term is "unbranched," meaning no carbon is bonded to more than two others.

- **Branched-chain alkanes**: Isobutane, isopentane, and neopentane are examples of branched-chain alkanes. In neopentane the central carbon atom is bonded to four carbon atoms.

Propane

$CH_3CH_2CH_3$

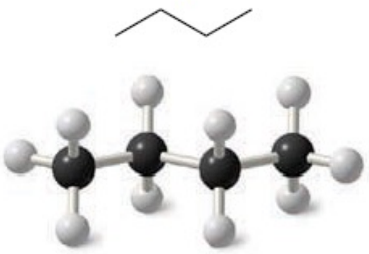
or



Butane

$CH_3CH_2CH_2CH_3$

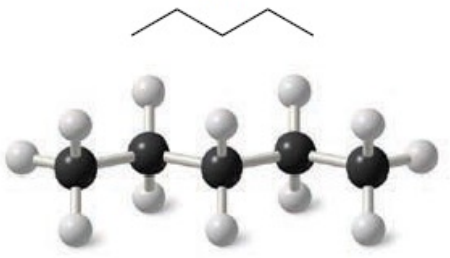
or



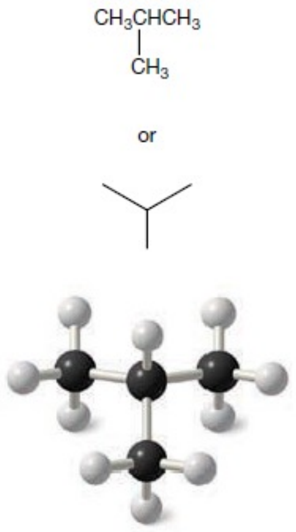
Pentane

$CH_3CH_2CH_2CH_2CH_3$

or



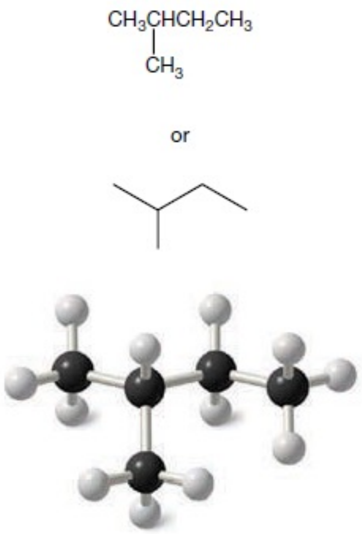
Isobutane



$$\begin{array}{c} CH_3CHCH_3 \\ | \\ CH_3 \end{array}$$

or

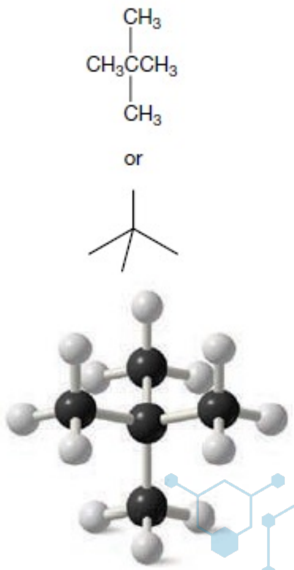
Isopentane



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

or

Neopentane



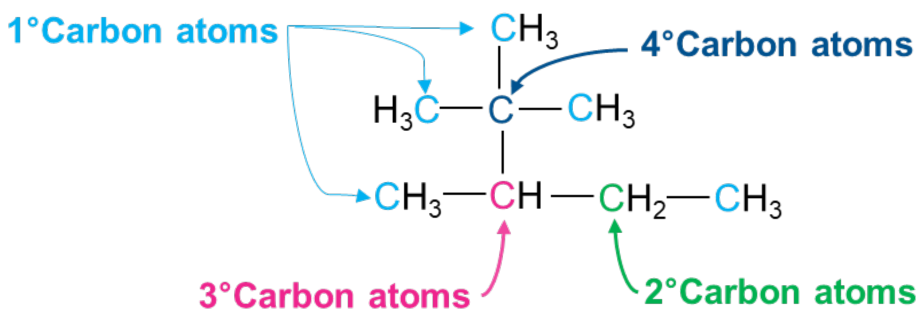
$$\begin{array}{c} CH_3 \\ | \\ CH_3CCH_3 \\ | \\ CH_3 \end{array}$$

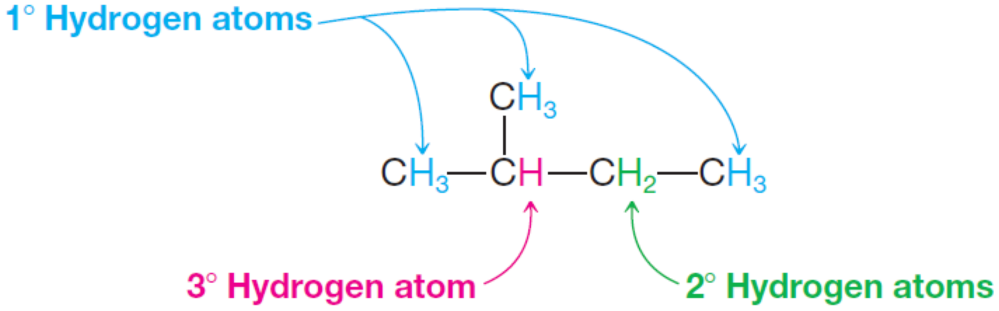
or

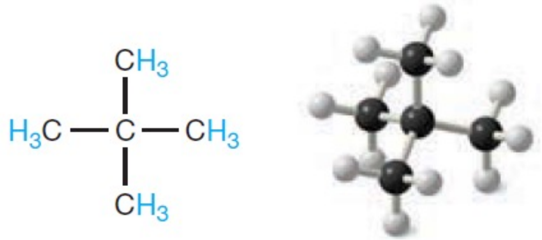
1. Hydrocarbons

1.4 How to classify carbon and hydrogen atoms

- Carbon atoms in alkanes are classified as primary (1°), secondary (2°), tertiary (3°), or quaternary (4°) based on the number of other carbon atoms they are bonded to: A primary carbon is attached to one other carbon, a secondary to two, a tertiary to three, and a quaternary to four. This classification helps describe the molecule's branching and can influence its chemical properties.
- The hydrogen atoms of an alkane are classified based on the carbon atom to which they are attached. A hydrogen atom attached to a primary carbon atom is a primary (1°) hydrogen atom, and so forth.
- The following compound, 2-methylbutane, has primary, secondary (2°), and tertiary (3°) carbon and hydrogen atoms.
- On the other hand, 2,2-dimethylpropane, a compound that is often called neopentane, has only primary hydrogen atoms.





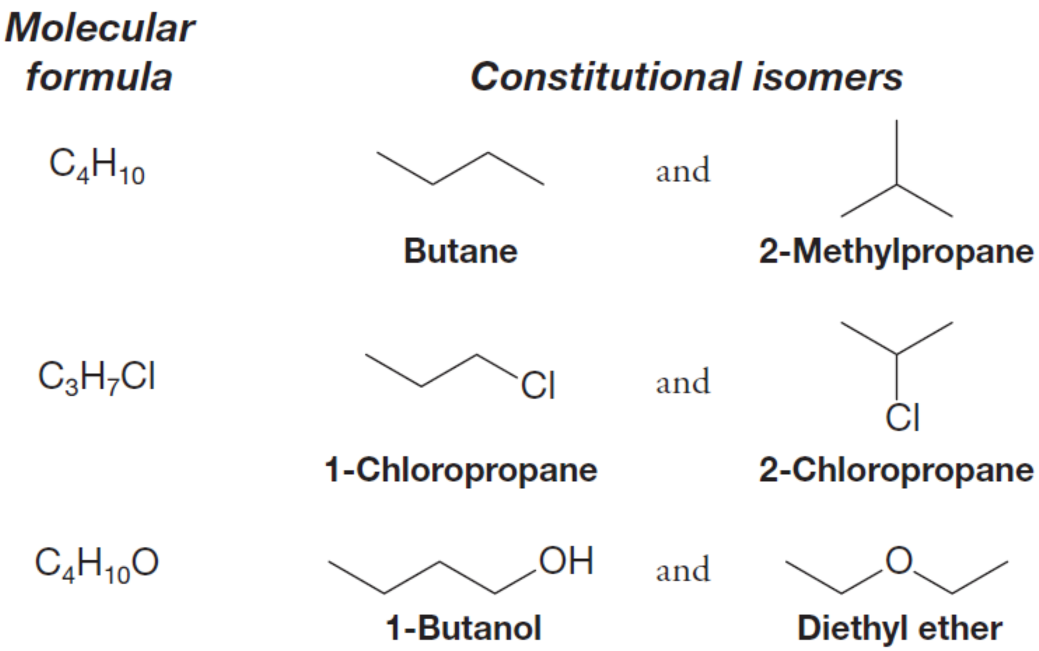


2,2-Dimethylpropane
(neopentane)

1. Hydrocarbons

1.5 ISOMERISM: Constitutional Isomers and Stereoisomers

- **Isomers** are different compounds that have the same molecular formula.
- **Constitutional Isomers** have the same molecular formula but different connectivity, meaning that their atoms are connected in a different order. Examples of constitutional isomers are the following:
- **Stereoisomers** have the same atoms connected in the same order, but their atoms are arranged differently in space. They are divided into two types: **enantiomers** and **diastereomers**.



Chapter 2: Structure and Classification of Organic Compounds

1. Hydrocarbons

1.5 ISOMERISM: Constitutional Isomers and Stereoisomers

Enantiomers are stereoisomers whose molecules are nonsuperposable mirror images of each other.

Enantiomers occur only with compounds whose molecules are chiral.

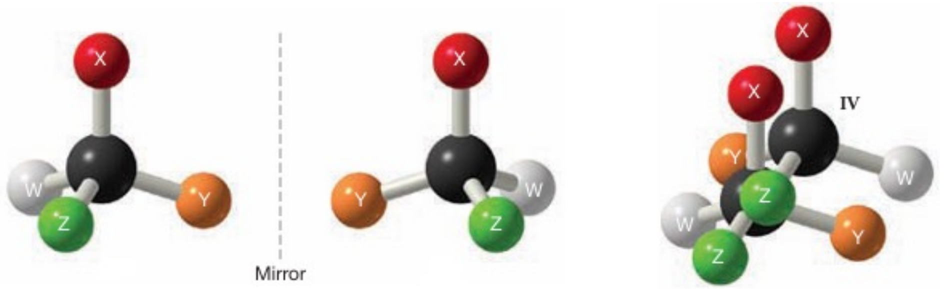
A chiral molecule is not superposable on its mirror image.

A chirality center is a tetrahedral carbon atom that is bonded to four different groups.

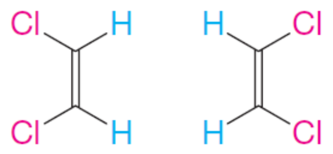
The trans isomer of 1,2-dimethylcyclopentane is chiral because it is not superposable on its mirror image.

An achiral molecule is superposable on its mirror image.

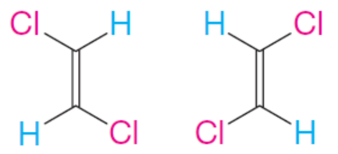
The cis and trans isomers of 1,2-dichloroethene are both achiral because each isomer is superposable on its mirror image.



Mirror images of *trans*-1,2-dimethylcyclopentane are not superposable and therefore are enantiomers.



***cis*-1,2-Dichloroethene mirror images**



***trans*-1,2-Dichloroethene mirror images**

Mirror images of the *cis* and *trans* isomers are superposable

1. Hydrocarbons

1.5 ISOMERISM: Constitutional Isomers and Stereoisomers

- **Diastereomers:** are stereoisomers whose molecules are not mirror images of each other.
- The alkene isomers *cis*- and *trans*-1,2-dichloroethene are stereoisomers that are diastereomers.
- The structural formulas for *cis*- and *trans*-1,2-dichloroethene, they have the same molecular formula ($C_2H_2Cl_2$) and the same connectivity. However, their atoms have a different arrangement in space that is not interconvertible from one to another, making them stereoisomers; therefore, they are diastereomers.
- Cis and trans isomers of cycloalkanes are another example of stereoisomers that are diastereomers.
- These two stereoisomers of C_7H_{14} have identical connectivity but differ spatially: one has both methyl groups on the same face of the ring (cis), while the other has them on opposite faces (trans).

cis-1,2-Dichloroethene ($C_2H_2Cl_2$)   *trans*-1,2-Dichloroethene ($C_2H_2Cl_2$)

Cis and *trans* alkene isomers are diastereomers

cis-1,2-Dimethylcyclopentane (C_7H_{14})   *trans*-1,2-Dimethylcyclopentane (C_7H_{14})

Cis and trans cycloalkane isomers are diastereomers

Chapter 2: Structure and Classification of Organic Compounds

1. Hydrocarbons

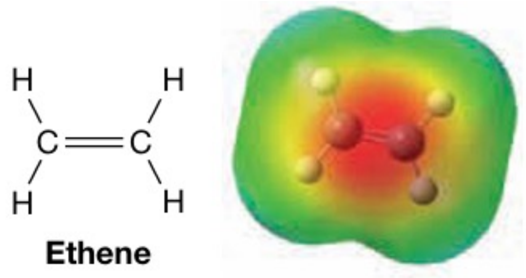
1.6 Alkenes

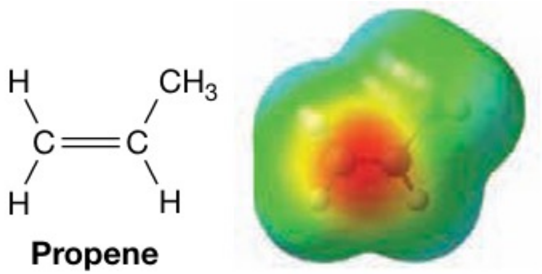
- Alkenes are hydrocarbons containing a carbon-carbon double bond, historically called olefins. The simplest alkene, ethene (ethylene) (C_2H_4), was named "olefiant gas" for its reaction with chlorine to form $C_2H_4Cl_2$; an oily liquid.

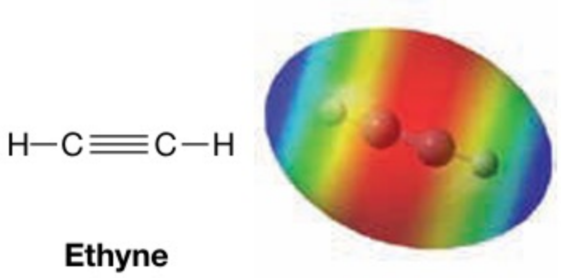
- Ethene and propene are two of the most important industrial chemicals. They are key starting materials for polymers like polyethylene and polypropylene, and ethene also acts as a natural ripening hormone for fruits

1.7 Alkynes

- Hydrocarbons whose molecules contain the carbon–carbon triple bond are called alkynes. The common name for this family is acetylenes, after the simplest member, HC≡CH, which is sold commercially as acetylene.


Ethene


Propene

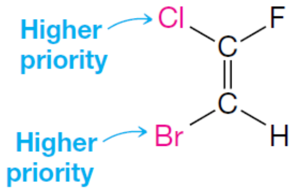

Ethyne

1. Hydrocarbons

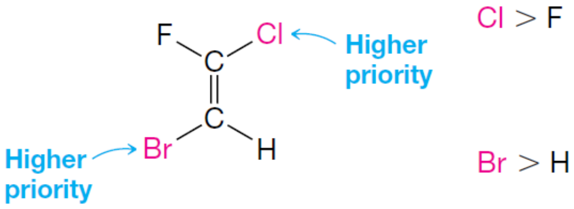
1.8 The (E)–(Z) System for Designating Alkene Diastereomers

- **The terms cis and trans are ambiguous and not applicable for tri- and tetrasubstituted alkenes. The universal solution is the (*E*)-(*Z*) system, which uses the Cahn-Ingold-Prelog priority rules to designate alkene stereochemistry.**

- **How To Use the (*E*)–(*Z*) System**
  1. **Examine the two groups attached to one carbon atom of the double bond and decide which has higher Cahn–Ingold–Prelog priority.**
  2. **Repeat that operation at the other carbon atom.**
  3. **Compare the group of higher priority on one carbon atom with the group of higher priority on the other carbon atom.**



(*Z*)-2-Bromo-1-chloro-1-fluoroethene



(*E*)-2-Bromo-1-chloro-1-fluoroethene

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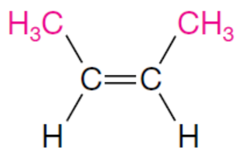
1. Hydrocarbons

1.8 The (*E*)–(*Z*) System for Designating Alkene Diastereomers

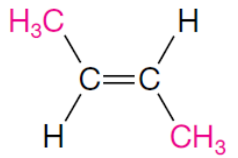
- How To Use the (*E*)–(*Z*) System

4. If the two groups of higher priority are on the same side of the double bond, the alkene is designated (*Z*) from the German word zusammen, meaning together.
5. If the two groups of higher priority are on opposite sides of the double bond, the alkene is designated (*E*) from the German word entgegen, meaning opposite. The following isomers provide another example.



(*Z*)-2-Butene or (*Z*)-but-2-ene
(*cis*-2-butene)

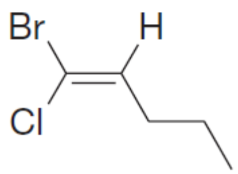
$CH_3 > H$



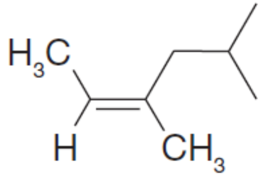
(*E*)-2-Butene or (*E*)-but-2-ene
(*trans*-2-butene)

- Practice Problem: Using the (*E*)–(*Z*) designation for the following:

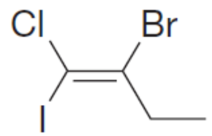
(a)



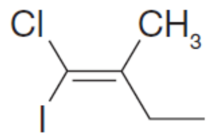
(c)



(b)



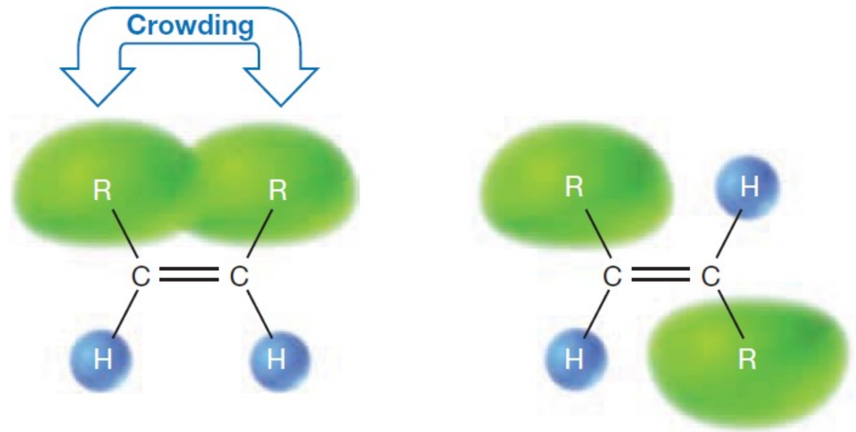
(d)



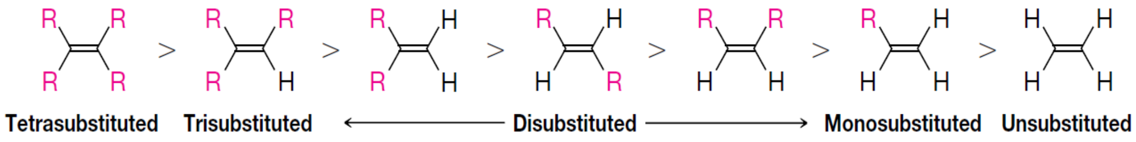
1. Hydrocarbons

1.9 Relative Stabilities of Alkenes

- Cis and trans isomers of alkenes do not have the same stability.
- Strain caused by the crowding of two alkyl groups on the same side of a double bond makes cis isomers generally less stable than trans isomers.
- Studies of numerous alkenes reveal a pattern of stabilities that is related to the number of alkyl groups attached to the carbon atoms of the double bond.
- The greater the number of attached alkyl groups (i.e., the more highly substituted the carbon atoms of the double bond), the greater is the alkene's stability. This order of stabilities can be given in general terms as follows:



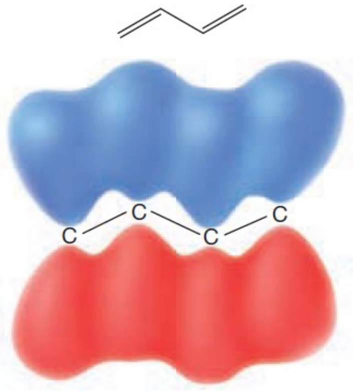
Relative Stabilities of Alkenes



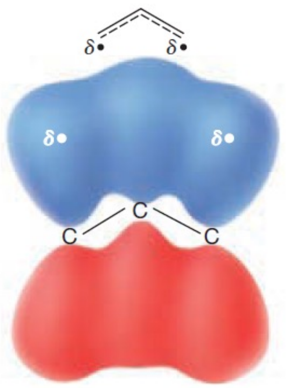
1. Hydrocarbons

1.10 Conjugated system

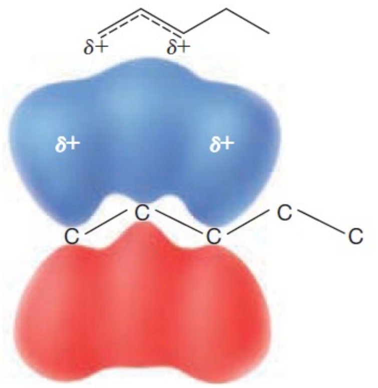
- A conjugated system involves at least one atom with a *p* orbital adjacent to at least one π bond. The adjacent atom with the *p* orbital can be part of another π bond, as in 1,3-butadiene, or a radical, cationic, or anionic reaction intermediate.
- If an example derives specifically from an allyl (propenyl group), the adjacent position is called allylic.
- The system is exemplified by molecules like 1,3-butadiene and allylic radicals or carbocations, which are stabilized by resonance.



1,3-butadiene
(a conjugated diene)



The allyl radical



An allylic carbocation

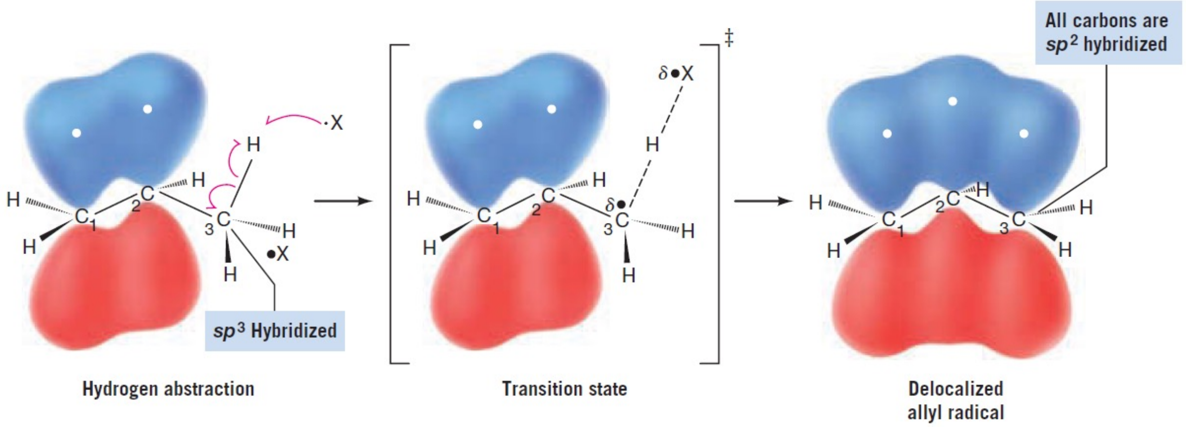
1. Hydrocarbons

1.11 The Stability of the Allyl Radical

- **The allyl radical is unusually stable because its unpaired electron is *delocalized* across three carbon atoms instead of being confined to one. This can be explained in two ways:**

1. **Resonance Theory: The structure is a hybrid of two equivalent forms, spreading the electron density and increasing stability.**
2. **Molecular Orbital Theory: When formed, a new *p* orbital overlaps with the existing double bond, creating a system of three connected *p* orbitals. The unpaired electron occupies a *delocalized molecular orbital* that spans the entire system.**

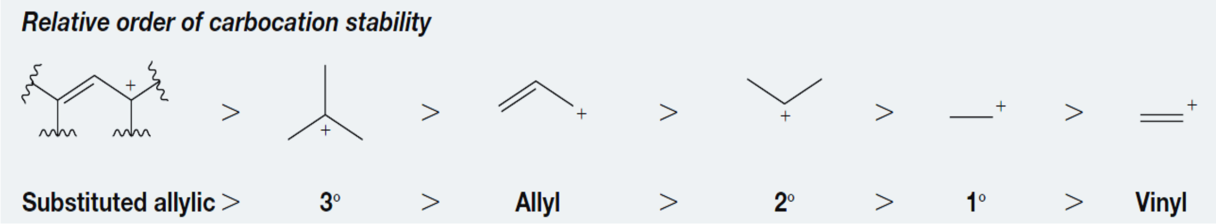
- **In short, this *conjugation* and *electron delocalization* are what makes the allyl radical more stable than a typical alkyl radical.**



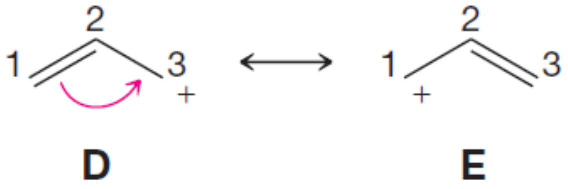
1. Hydrocarbons

1.12 The Allyl Cation

- Carbocations can be allylic as well.
- The allyl (propenyl) cation (+) is even more stable than a secondary carbocation and is almost as stable as a tertiary carbocation.
- In general terms, the relative order of stabilities of carbocations is that given here:



- Resonance theory depicts the allyl cation as a hybrid of structures D and E represented here:



1. Hydrocarbons

1.13 Cycloalkenes

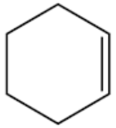
- For very small rings (5 carbons or fewer), only the cis cycloalkene isomer is possible. A trans double bond cannot fit into these small rings without introducing severe and unsustainable angle strain, which would break the bonds.

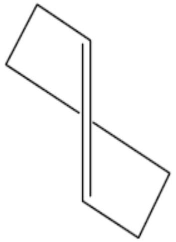
- While trans double bonds are too strained to exist in small cycloalkenes, they become possible in larger rings.
- Trans-Cyclooctene is the smallest isolable trans-cycloalkene and is stable at room temperature. It is also chiral, meaning it has non-superimposable mirror images.

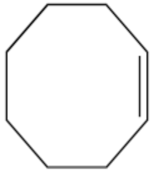

Cyclopropene

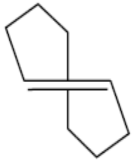

Cyclobutene


Cyclopentene


Cyclohexene


trans-Cyclohexene


cis-Cyclooctene

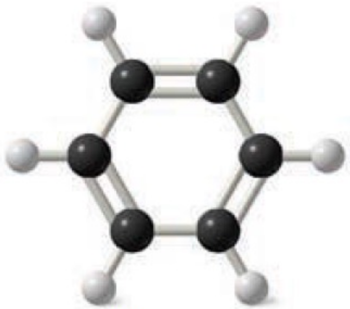

trans-Cyclooctene

2. Aromatic Hydrocarbon

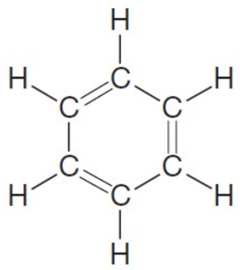
- The term "aromatic" originally referred to pleasant-smelling compounds from plants, many of which contained a benzene ring. Today, *aromaticity* is defined by electronic structure not odor. Aromatic compounds, like aspirin, are classified based on special stability from a *delocalized ring of π-electrons*, even if they have no scent.

2.1 Benzene: A Representative Aromatic Hydrocarbon

- Aromatic compounds are a major class of unsaturated cyclic hydrocarbons, with *benzene* being the fundamental example.
- Its structure is best represented as a six-membered ring with *delocalized electrons*, often depicted by the **Kekulé structure** with alternating single and double bonds.

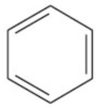


Benzene



Kekulé structure for benzene

or



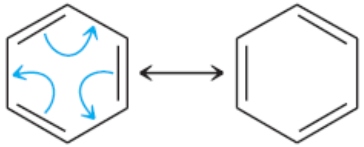
Bond-line representation of Kekulé structure

2. Aromatic Hydrocarbon

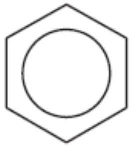
2.1 Benzene: A Representative Aromatic Hydrocarbon

- The **Kekulé structure** is an incomplete model for benzene because it inaccurately suggests alternating long and short bonds. In reality, all carbon-carbon bonds in benzene are identical in length (1.39 Å), a value between a single and double bond. This is explained by two key theories:

1. **Resonance Theory:** Benzene is a hybrid of two identical Kekulé structures, meaning its true structure is an average of both, with the *electrons delocalized* around the ring.
2. **Molecular Orbital Theory:** The *p* orbitals on each carbon atom overlap to form a *continuous ring of electron density* above and below the plane of the atoms, making all bonds equivalent.



Two contributing Kekulé structures for benzene

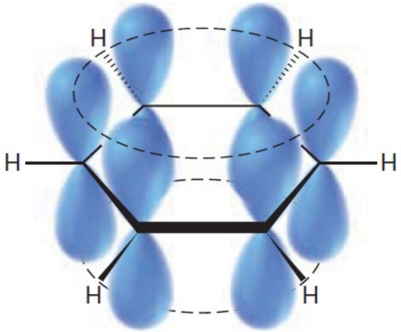


A representation of the resonance hybrid

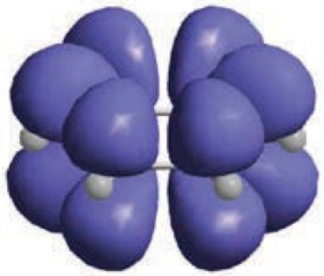
2. Aromatic Hydrocarbon

2.1 Benzene: A Representative Aromatic Hydrocarbon

- In benzene, each carbon atom is *sp^2* hybridized, leaving one *p* orbital perpendicular to the ring. These *p* orbitals overlap continuously, forming a delocalized π system—a single molecular orbital that encompasses all six carbon atoms.
- This delocalization means the six π electrons are shared equally by the entire ring, which explains why all carbon-carbon bonds are identical in length and strength.



Schematic representation of benzene *p* orbitals



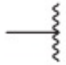
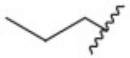
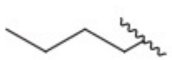
Calculated *p* orbital shapes in benzene

Calculated benzene molecular orbital resulting from favorable overlap of *p* orbitals above and below plane of benzene ring

3. Functional Groups

3.1 Alkyl Groups and the Symbol R

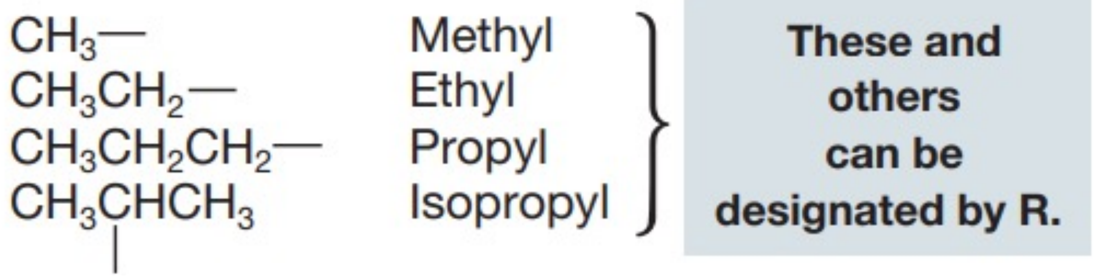
- **Alkyl groups are the groups that we identify for purposes of naming compounds. They are groups that would be obtained by removing a hydrogen atom from an alkane.**

Alkane	*Alkyl Group*	*Abbreviation*	*Bond-line*	*Model*
CH_3-H **Methane**	H_3C- **Methyl**	Me-		
CH_3CH_2-H **Ethane**	CH_3CH_2- **Ethyl**	Et-		
$CH_3CH_2CH_2-H$ **Propane**	$CH_3CH_2CH_2-$ **Propyl**	Pr-		
$CH_3CH_2CH_2CH_2-H$ **Butane**	$CH_3CH_2CH_2CH_2-$ **Butyl**	Bu-		

3. Functional Groups

3.1 Alkyl Groups and the Symbol R

- While only one alkyl group can be derived from methane or ethane (the methyl and ethyl groups, respectively), two groups can be derived from propane.
- Removal of a hydrogen from one of the end carbon atoms gives a group that is called the propyl group; removal of a hydrogen from the middle carbon atom gives a group that is called the isopropyl group.
- The names and structures of these groups are used so frequently in organic chemistry: The symbol R.
- R is used as a general symbol to represent any alkyl group. For example, R might be a methyl group, an ethyl group, a propyl group, or an isopropyl group.
- Thus, the general formula for an alkane is R–H.



CH_3-	Methyl
CH_3CH_2-	Ethyl
$CH_3CH_2CH_2-$	Propyl
$CH_3\underset{|}{C}HCH_3$	Isopropyl

These and others can be designated by R.

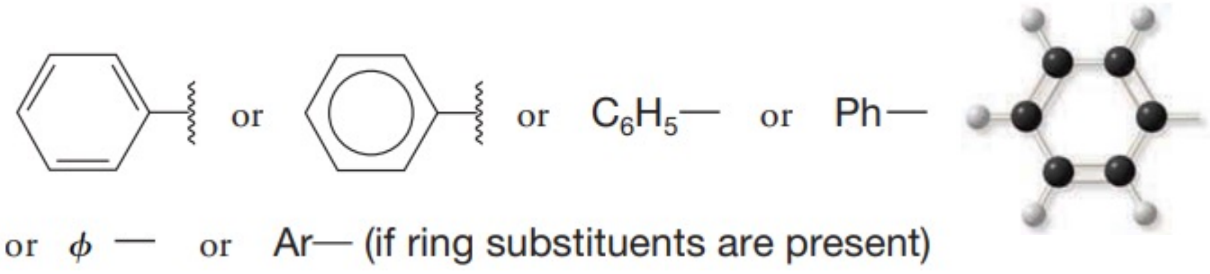
3. Functional Groups

3.2 Phenyl and Benzyl Groups

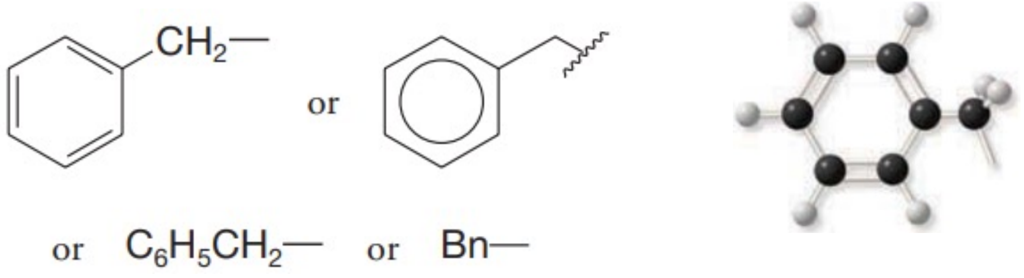
- **When a benzene ring is attached to some other group of atoms in a molecule, it is called a phenyl group, and it is represented in several ways.**

- **The combination of a phenyl group and a methylene group (–CH_2–) is called a benzyl group.**

Ways of representing a phenyl group



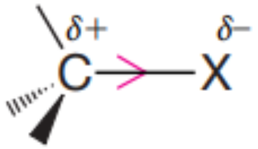
Ways of representing a benzyl group



3. Functional Groups

3.3 Alkyl Halides or Haloalkanes

- Alkyl halides are compounds in which a halogen atom (fluorine, chlorine, bromine, or iodine) replaces a hydrogen atom of an alkane.
- An alkyl halide has a halogen atom bonded to an *sp^3*-hybridized (tetrahedral) carbon atom. For example, CH_3Cl and CH_3CH_2Br are alkyl halides.
- Alkyl halides are also called haloalkanes.
- The generic formula for an alkyl halide is $R-\ddot{\underset{..}{X}}:$ where X = fluorine, chlorine, bromine, or iodine.
- The carbon–halogen bond in an alkyl halide is polarized because the halogen is more electronegative than carbon. Therefore, the carbon atom has a partial positive charge (δ+) and the halogen has a partial negative charge (δ−).

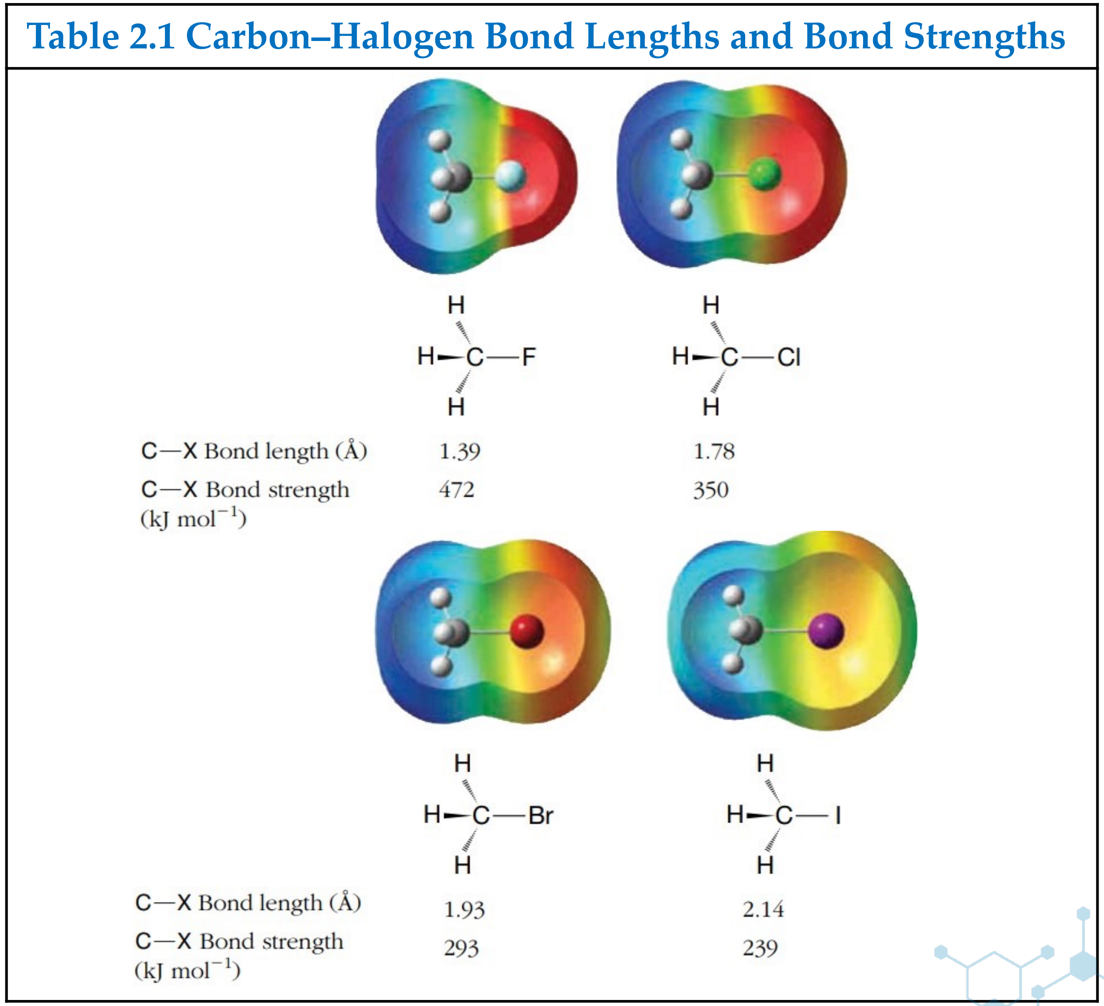


3. Functional Groups

3.3 Alkyl Halides or Haloalkanes

- **Halogen atom size increases as we go down the periodic table: fluorine atoms are the smallest and iodine atoms the largest. Consequently, the carbon–halogen bond length increases and carbon–halogen bond strength decreases as we go down the periodic table (Table 2.1).**
- **Fluoromethane is highly polar and has the shortest C–X bond length and the strongest C–X bond. Iodomethane is much less polar and has the longest C–X bond length and the weakest C–X bond.**

Table 2.1 Carbon–Halogen Bond Lengths and Bond Strengths

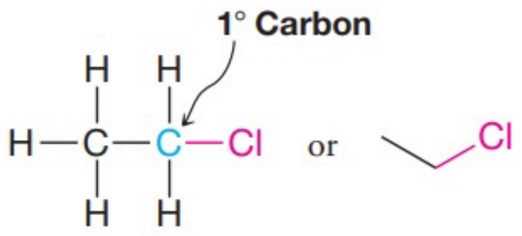


	H H—C—F H	H H—C—Cl H	H H—C—Br H	H H—C—I H
C—X Bond length (Å)	1.39	1.78	1.93	2.14
C—X Bond strength (kJ mol^{-1})	472	350	293	239

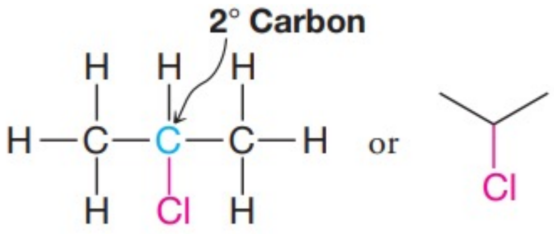
3. Functional Groups

3.3 Alkyl Halides or Haloalkanes

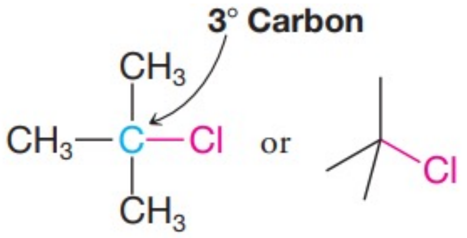
- Alkyl halides are classified as being primary (1°), secondary (2°), or tertiary (3°). This classification is based on the carbon atom to which the halogen is directly attached.
- If the carbon atom that bears the halogen is directly attached to only one other carbon, the carbon atom is said to be a primary carbon atom and the alkyl halide is classified as a primary alkyl halide. If the carbon that bears the halogen is itself directly attached to two other carbon atoms, then the carbon is a secondary carbon and the alkyl halide is a secondary alkyl halide. If the carbon that bears the halogen is directly attached to three other carbon atoms, then the carbon is a tertiary carbon and the alkyl halide is a tertiary alkyl halide.
- Examples of primary, secondary, and tertiary alkyl halides are the following:



A 1° alkyl chloride



A 2° alkyl chloride



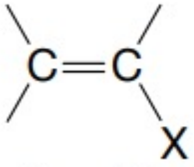
A 3° alkyl chloride

3. Functional Groups

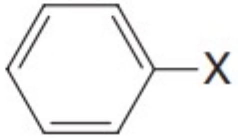
3.4 Alkenyl Halides and Aryl Halide

- **An alkenyl halide is a compound with a halogen atom bonded to an alkene carbon.**
- **In older nomenclature such compounds were sometimes referred to as vinyl halides.**

- **An aryl halide is a compound with a halogen atom bonded to an aromatic ring.**
- **When the aromatic ring is specifically a benzene ring these compounds are called phenyl halides.**



An alkenyl halide

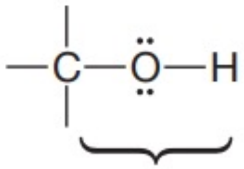


A phenyl halide or aryl halide

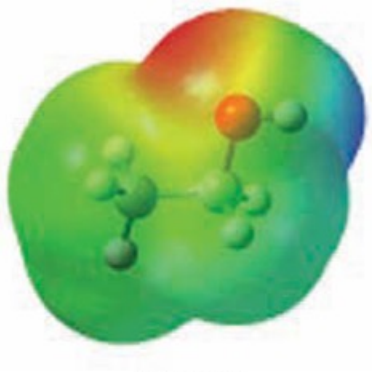
3. Functional Groups

3.5 Containing Oxygen: Alcohols And phenols

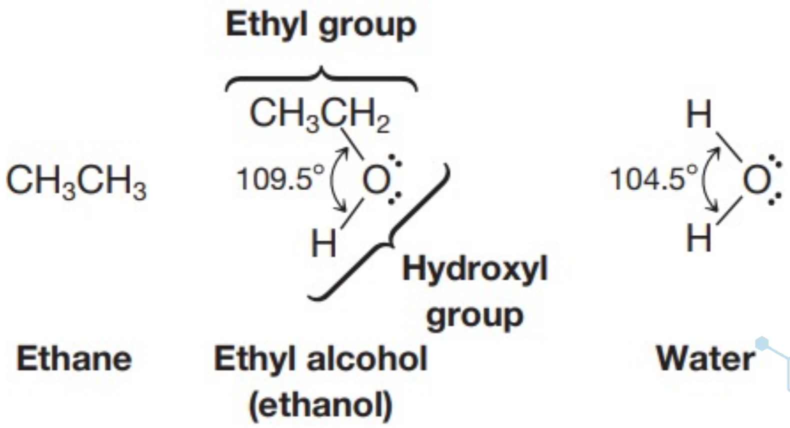
- Methyl alcohol (also called methanol) has the structural formula CH_3OH and is the simplest member of a family of organic compounds known as alcohols. The characteristic functional group of this family is the hydroxyl (–OH) group attached to an *sp3*-hybridized carbon atom. Another example of an alcohol is ethyl alcohol, CH_3CH_2OH also called (ethanol).
- Alcohols may be viewed structurally in two ways:
  - (1) As hydroxyl derivatives of alkanes.
  - (2) As alkyl derivatives of water.
- Ethyl alcohol, for example, can be seen as an ethane molecule in which one hydrogen has been replaced by a hydroxyl group or as a water molecule in which one hydrogen has been replaced by an ethyl group.



This is the functional group of an alcohol.



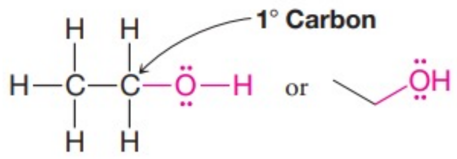
Ethanol



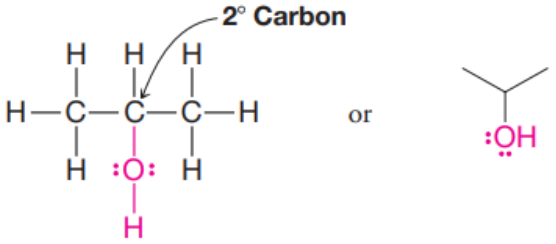
3. Functional Groups

3.5 Containing Oxygen: Alcohols And phenols

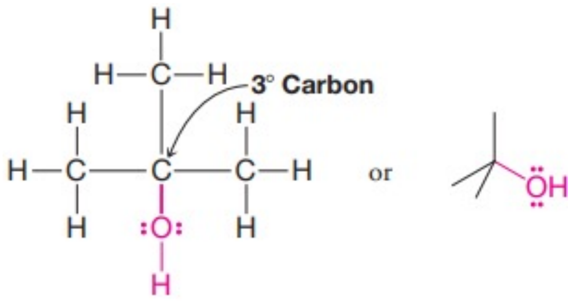
- As with alkyl halides, alcohols are classified into three groups: primary (1°), secondary (2°), and tertiary (3°) alcohols.
- This classification is based on the degree of substitution of the carbon to which the hydroxyl group is directly attached.
- If the carbon has only one other carbon attached to it, the carbon is said to be a primary carbon and the alcohol is a primary alcohol.
- If the carbon atom that bears the hydroxyl group also has two other carbon atoms attached to it, this carbon is called a secondary carbon, and the alcohol is a secondary alcohol.
- If the carbon atom that bears the hydroxyl group has three other carbons attached to it, this carbon is called a tertiary carbon, and the alcohol is a tertiary alcohol.



Ethyl alcohol
(a 1° alcohol)



Isopropyl alcohol
(a 2° alcohol)



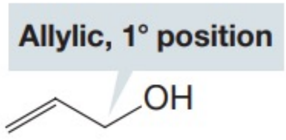
***tert*-Butyl alcohol**
(a 3° alcohol)

3. Functional Groups

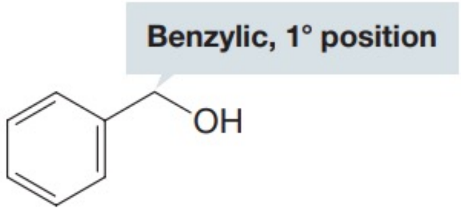
3.5 Containing Oxygen: Alcohols And phenols

- The alcohol carbon atom may also be a saturated carbon atom adjacent to an alkenyl group, in which case it is called allylic, or the carbon atom may be a saturated carbon atom that is attached to a benzene ring in which case it is called benzylic.

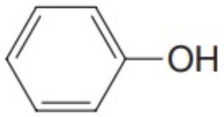
- When a hydroxyl group is bonded to a benzene ring the combination of the ring and the hydroxyl is called a phenol.
- Compounds that have a hydroxyl group attached directly to a benzene ring are called phenols.



**2-Propenol
(or prop-2-en-1-ol,
or allyl alcohol),
*an allylic alcohol***



**Benzyl alcohol,
*a benzylic alcohol***



Phenol

***p*-Methylphenol,
*a substituted phenol***

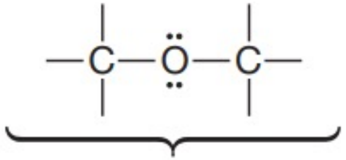
$Ar-OH$

**General formula
for a phenol**

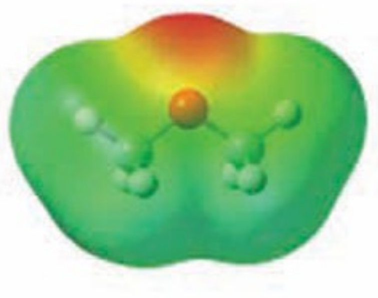
3. Functional Groups

3.6 Containing Oxygen: Ethers

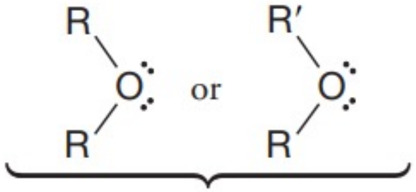
- Ethers have the general formula R–O–R or R–O–R′, where R′ may be an alkyl (or phenyl) group different from R.
- Ethers can be thought of as derivatives of water in which both hydrogen atoms have been replaced by alkyl groups. The bond angle at the oxygen atom of an ether is only slightly larger than that of water:
- Ethers differ from alcohols in that the oxygen atom of an ether is bonded to two carbon atoms. The hydrocarbon groups may be alkyl, alkenyl, vinyl, alkynyl, or aryl.
- Several examples are shown here:



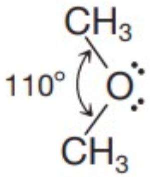
The functional group of an ether



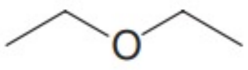
Dimethyl ether



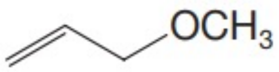
General formula for an ether



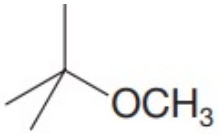
Dimethyl ether (a typical ether)



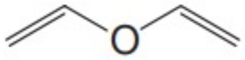
Diethyl ether



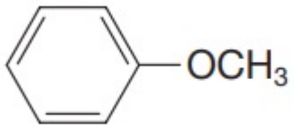
Allyl methyl ether



***tert*-Butyl methyl ethe**



Divinyl ether



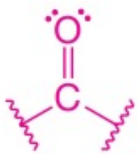
Methyl phenyl ether

3. Functional Groups

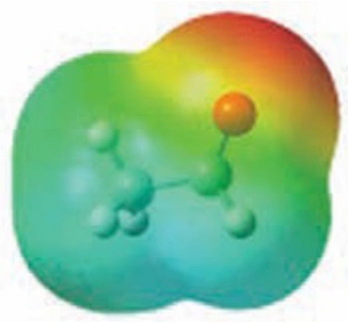
3.7 Containing Oxygen: Aldehydes and Ketones

- Aldehydes and ketones both contain the carbonyl group a group in which a carbon atom has a double bond to oxygen.

- The carbonyl group of an aldehyde is bonded to one hydrogen atom and one carbon atom (except for formaldehyde, which is the only aldehyde bearing two hydrogen atoms).
- The carbonyl group of a ketone is bonded to two carbon atoms.
- Using R, we can designate the general formulas for aldehydes and ketones as follow:

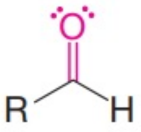


The carbonyl group



Acetaldehyde

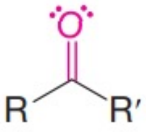
ALDEHYDES



or RCHO

(R = H in formaldehyde)

KETONES



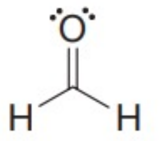
or RCOR′

(where R′ is an alkyl group that may be the same or different from R)

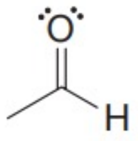
3. Functional Groups

3.7 Containing Oxygen: Aldehydes and Ketones

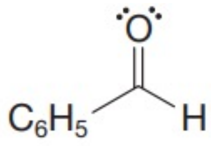
- **Some specific examples of aldehydes and ketones are the following:**



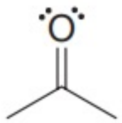
Formaldehyde



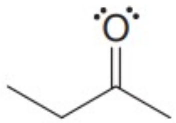
Acetaldehyde



Benzaldehyde



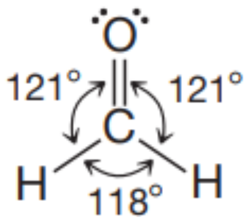
Acetone



Ethyl methyl ketone

- **Aldehydes and ketones have a trigonal planar arrangement of groups around the carbonyl carbon atom. The carbon atom is *sp*^{2} hybridized.**

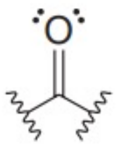
In formaldehyde, for example, the bond angles are as follows:



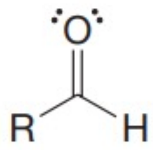
3. Functional Groups

3.8 Structure of the Carbonyl Group

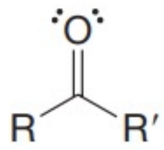
- Carbonyl compounds are a broad group of compounds that includes aldehydes, ketones, carboxylic acids, esters, and amides.
- The carbonyl carbon atom is *sp*^{2} hybridized; thus, it and the three atoms attached to it lie in the same plane. The bond angles between the three attached atoms are what we would expect of a trigonal planar structure; they are approximately 120°.
- The carbon–oxygen double bond consists of two electrons in a σ bond and two electrons in a π bond. The π bond is formed by overlap of the carbon *p* orbital with a *p* orbital from the oxygen atom. The electron pair in the π bond occupies both lobes (above and below the plane of the σ bonds).



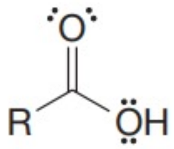
The carbonyl group



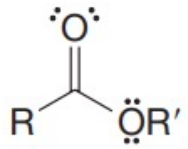
An aldehyde



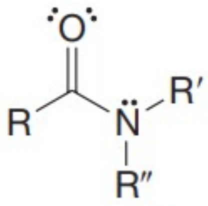
A ketone



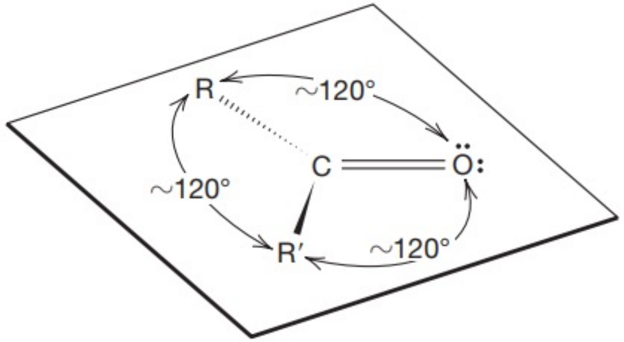
A carboxylic acid



An ester



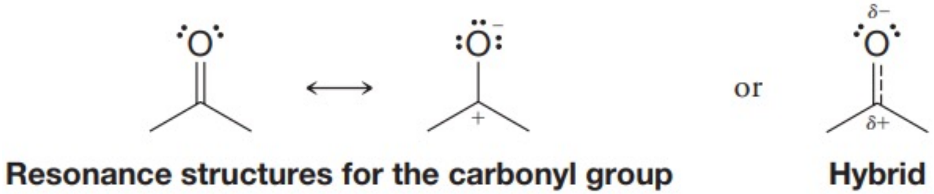
An amide



3. Functional Groups

3.8 Structure of the Carbonyl Group

- **The more electronegative oxygen atom strongly attracts the electrons of both the σ bond and the π bond, causing the carbonyl group to be highly polarized; the carbon atom bears a substantial positive charge and the oxygen atom bears a substantial negative charge.**
- **Polarization of the π bond can be represented by the following resonance structures for the carbonyl group.**



Resonance structures for the carbonyl group **Hybrid**

3. Functional Groups

3.9 Containing Oxygen: Carboxylic Acids, Esters, and Amides

- Carboxylic acids, esters, and amides all contain a carbonyl group that is bonded to an oxygen or nitrogen atom.

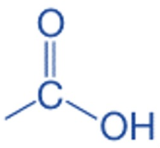
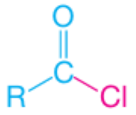
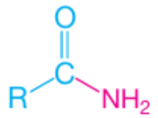
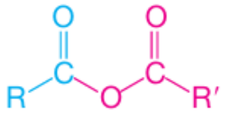
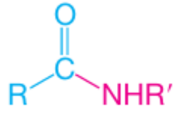
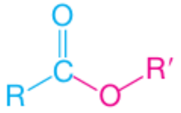
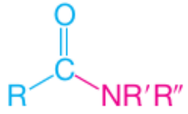
- The carboxyl group,  (abbreviated $-CO_2H$ or $-COOH$), is one of the most widely occurring functional groups in chemistry and biochemistry. Not only are carboxylic acids themselves important, but the carboxyl group is the parent group of a large family of related compounds called acyl compounds or carboxylic acid derivatives, shown in Table 2.2.

Table 2.2 carboxylic acid derivatives

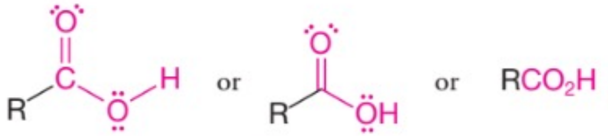
Structure	Name	Structure	Name
	Acyl (or acid) chloride		Amide
	Acid anhydride		
	Ester		
$R{-}C{\equiv}N$	Nitrile		

3. Functional Groups

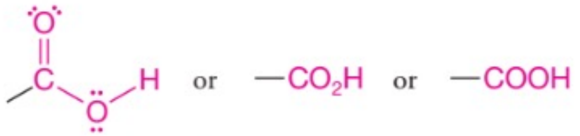
3.9 Containing Oxygen: Carboxylic Acids, Esters, and Amides

- Carboxylic acids
  - Carboxylic acids have a carbonyl group bonded to a hydroxyl group, and they have the general formula, RCOOH.
  - The functional group, -COOH is called the carboxyl group (carbonyl + hydroxyl)

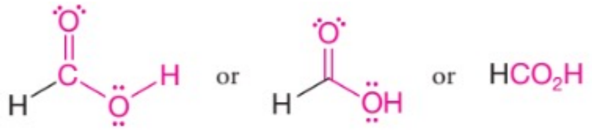
  - Examples of carboxylic acids are formic acid, acetic acid, and benzoic acid.
  - Formic acid is an irritating liquid produced by ants. (The sting of the ant is caused, in part, by formic acid being injected under the skin. Formic is the Latin word for ant).
  - Acetic acid, the substance responsible for the sour taste of vinegar.



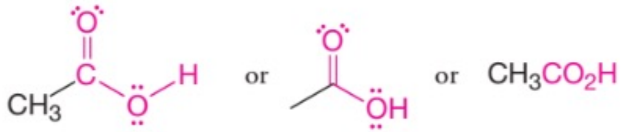
A carboxylic acid



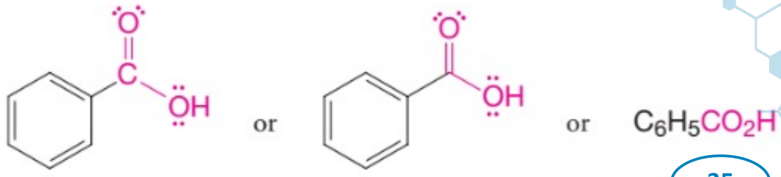
The carboxyl group



Formic acid



Acetic acid

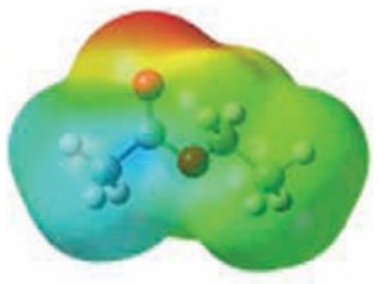


Benzoic acid

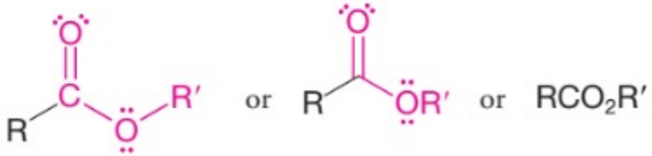
3. Functional Groups

3.9 Containing Oxygen: Carboxylic Acids, Esters, and Amides

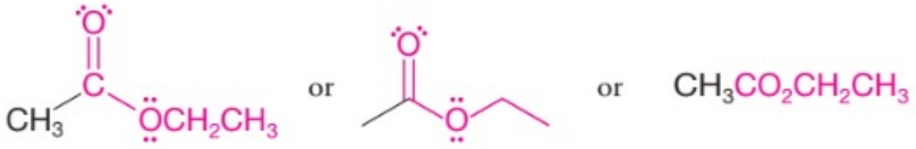
- **Esters**
  - Esters have the general formula RCO_2R' (or $RCOOR'$), where a carbonyl group is bonded to an alkoxyl (–OR) group.
  - Esters can be made from a carboxylic acid and an alcohol through the acid-catalyzed loss of a molecule of water.
  - Your body makes esters from long-chain carboxylic acids called “fatty acids” by combining them with glycerol.



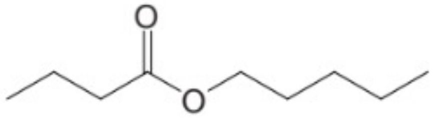
Ethyl acetate



General formula for an ester



Ethyl acetate is an important solvent.



Pentyl butanoate smells like apricots and pears.

3. Functional Groups

3.9 Containing Oxygen: Carboxylic Acids, Esters, and Amides

- **Esters** are polar compounds, but, lacking a hydrogen attached to oxygen, their molecules cannot form strong hydrogen bonds to each other. As a result, esters have boiling points that are lower than those of acids and alcohols of comparable molecular weight.

- The boiling points of esters are about the same as those of comparable aldehydes and ketones.

- Unlike the low-molecular-weight acids, esters usually have pleasant odors, some resembling those of fruits, and these are used in the manufacture of synthetic flavors.

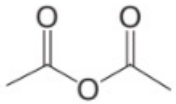
Isopentyl acetate
(used in synthetic banana flavor)

Isopentyl pentanoate
(used in synthetic apple flavor)

3. Functional Groups

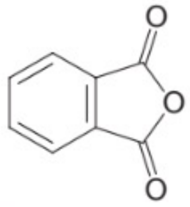
3.9 Containing Oxygen: Carboxylic Acids, Esters, and Amides

- Carboxylic Anhydrides
  - Most anhydrides are named by dropping the word acid from the name of the carboxylic acid and then adding the word anhydride.



Acetic anhydride
(ethanoic anhydride)
mp −73 °C

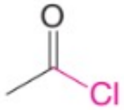
Succinic anhydride
mp 121 °C



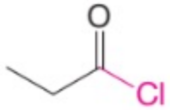
Phthalic anhydride
mp 131 °C

Maleic anhydride
mp 53 °C

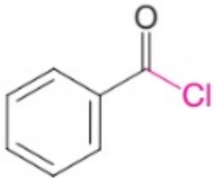
- Acyl Chlorides
  - Acyl chlorides are also called acid chlorides.
  - Acyl chlorides and carboxylic anhydrides have boiling points in the same range as esters of comparable molecular weight.



Acetyl chloride
(ethanoyl chloride)
mp −112 °C; bp 51 °C



Propanoyl chloride
mp −94 °C; bp 80 °C

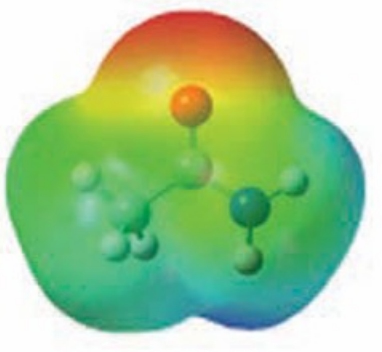


Benzoyl chloride
mp −1 °C; bp 197 °C

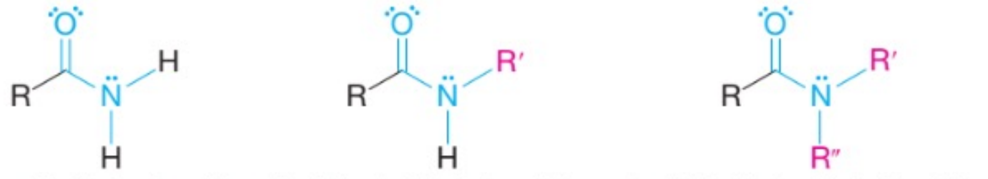
3. Functional Groups

3.9 Containing Oxygen: Carboxylic Acids, Esters, and Amides

- **Amides**
  - Amides have the formulas $RCONH_2$, $RCONHR'$, or $RCONR'R''$ where a carbonyl group is bonded to a nitrogen atom bearing hydrogen and/or alkyl groups.
  - General formulas and some specific examples are shown:

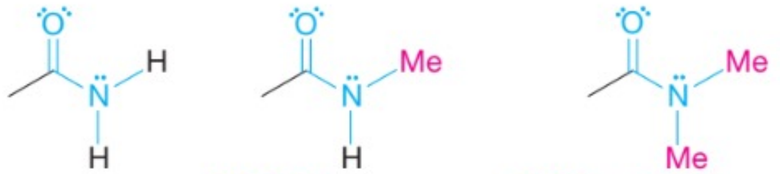


Acetamide



An unsubstituted amide An *N*-substituted amide An *N*,*N*-disubstituted amide

General formulas for amides



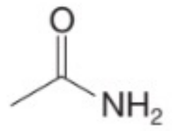
Acetamide *N*-Methylacetamide *N*,*N*-Dimethylacetamide

Specific examples of amides

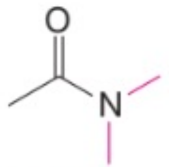
3. Functional Groups

3.9 Containing Oxygen: Carboxylic Acids, Esters, and Amides

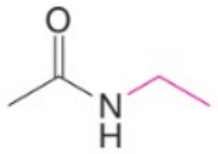
- Amides
  - Amides with nitrogen atoms bearing one or two hydrogen atoms are able to form strong hydrogen bonds to each other. Such amides have high melting points and boiling points.
  - On the other hand, molecules of *N*,*N*-disubstituted amides cannot form strong hydrogen bonds to each other, and they have lower melting points and boiling points.
  - Hydrogen bonding between amide groups plays a key role in the way proteins and peptides fold to achieve their overall shape.
  - Proteins and peptides (short proteins) are polymers of amino acids joined by amide groups. One feature common to the structure of many proteins is the β sheet, shown:



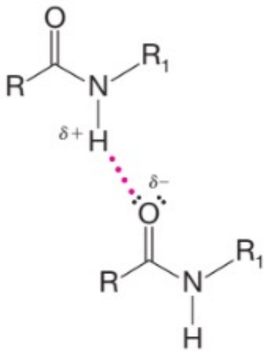
Acetamide
(ethanamide)
mp 82 °C; bp 221 °C



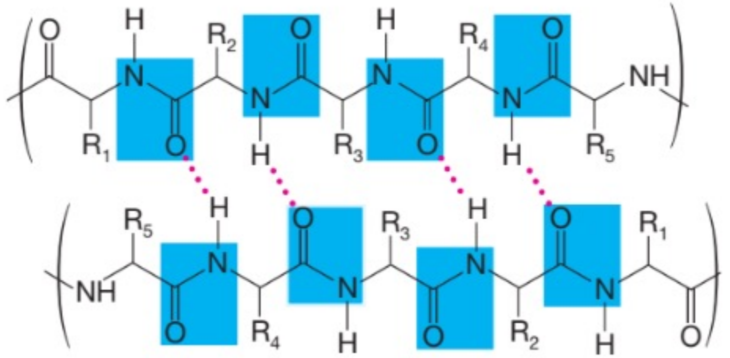
***N*,*N*-Dimethylacetamide**
mp −20 °C; bp 166 °C



***N*-Ethylacetamide**
bp 205 °C



Hydrogen bonding (red dots) between amide molecules



Hydrogen bonding between amide groups of peptide chains. This interaction between chains (called a β sheet) is important to the structure of many proteins.

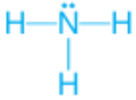
3. Functional Groups

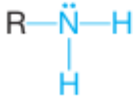
3.10 Containing Nitrogen: Amines

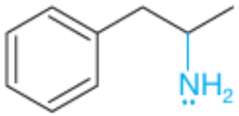
- Amines
  - Just as alcohols and ethers may be considered as organic derivatives of water, amines may be considered as organic derivatives of ammonia.
- Classification of amines

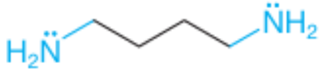
AMINES ARE CLASSIFIED AS PRIMARY, SECONDARY, OR TERTIARY AMINES. THIS CLASSIFICATION IS BASED ON THE NUMBER OF ORGANIC GROUPS THAT ARE ATTACHED TO THE NITROGEN ATOM.

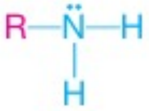
NOTICE THAT THIS IS QUITE DIFFERENT FROM THE WAY ALCOHOLS AND ALKYL HALIDES ARE CLASSIFIED. FOR EXAMPLE, IS A PRIMARY AMINE EVEN THOUGH ITS $-NH_2$ GROUP IS ATTACHED TO A SECONDARY CARBON ATOM. IT IS A PRIMARY AMINE BECAUSE ONLY ONE ORGANIC GROUP IS ATTACHED TO THE NITROGEN ATOM.

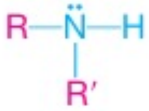

Ammonia


An amine

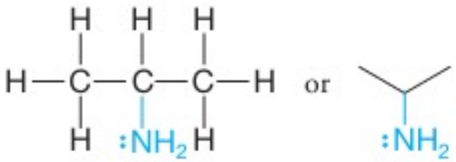

Amphetamine
(a dangerous stimulant)

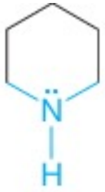

Putrescine
(found in decaying meat)


A primary (1°) amine


A secondary (2°) amine


A tertiary (3°) amine

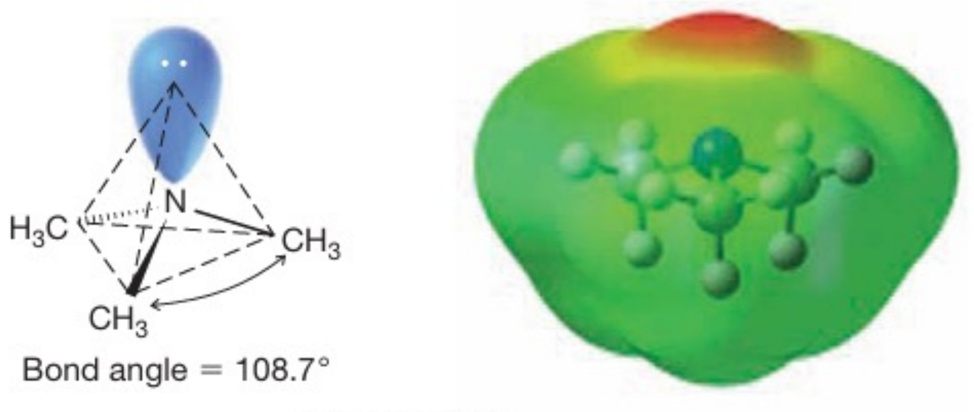

Isopropylamine
(a 1° amine)


Piperidine
(a cyclic 2° amine)

3. Functional Groups

3.10 Containing Nitrogen: Amines

- Structure of Amines
  - Amines are like ammonia in having a trigonal pyramidal shape.
  - The C–N–C bond angles of trimethylamine are 108.7°, a value very close to the H–C–H bond angles of methane.
  - The nitrogen atom of an amine can be considered to be *sp*^{3} hybridized with the unshared electron pair occupying one orbital. This means that the unshared pair is relatively exposed, and as we shall see this is important because it is involved in almost all of the reactions of amines.

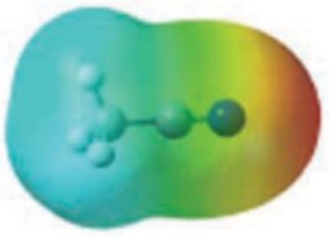


Trimethylamine

3. Functional Groups

3.11 Containing Nitrogen: Nitriles

- **Nitriles**
  - A nitrile has the formula $R-C\equiv N:$ (or $R-CN$).
  - The carbon and the nitrogen of a nitrile are *sp* hybridized.
  - Carboxylic acids can be converted to nitriles and vice versa.



Acetonitrile

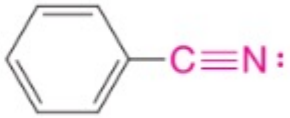
$CH_3-C\equiv N:$

Ethanenitrile (acetonitrile)

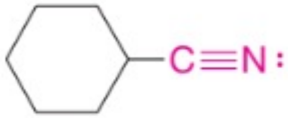
$CH_3CH_2CH_2-C\equiv N:$

Butanenitrile

Propenenitrile (acrylonitrile)



Benzenecarbonitrile (benzonitrile)



Cyclohexanecarbonitrile