Introduction to Organic Chemistry
CHEM 109

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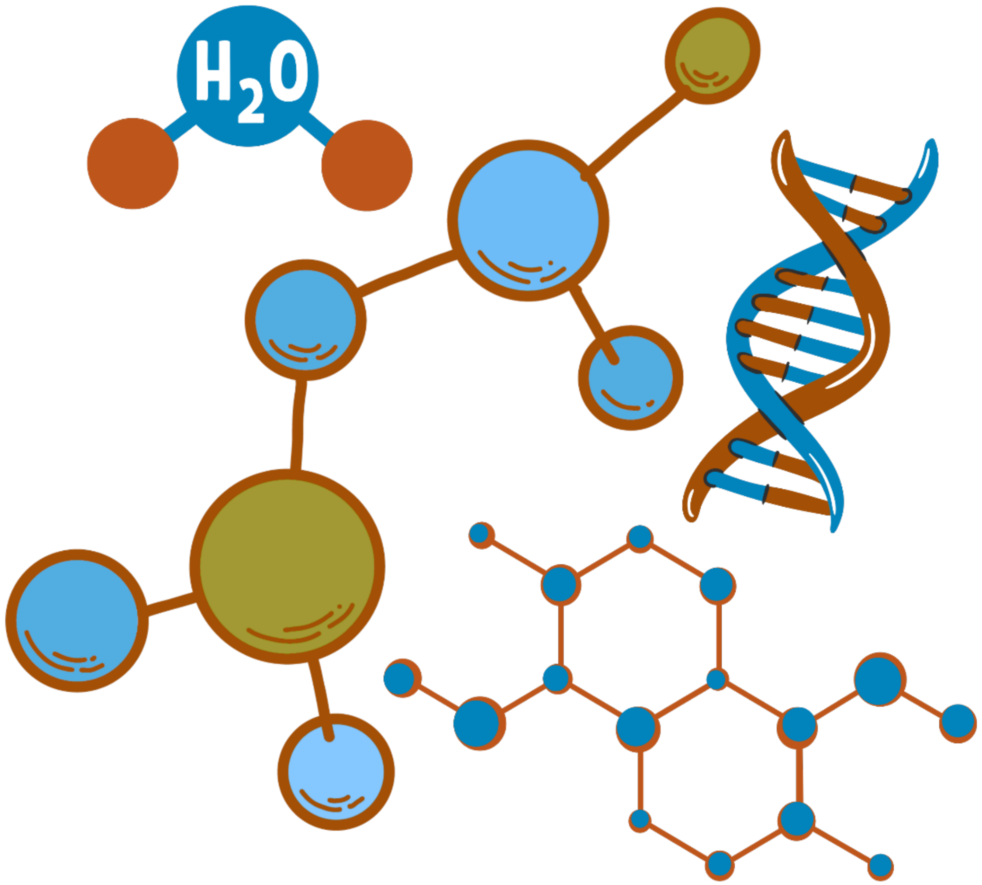
Chapter 2: Structure and Classification of Organic Compounds

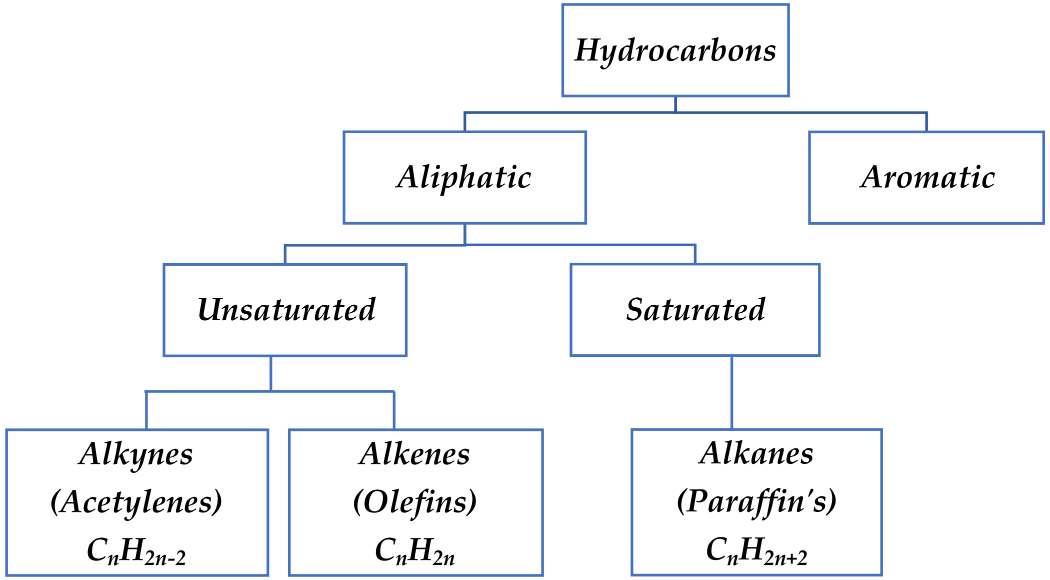


1. Hydrocarbons

- 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.



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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

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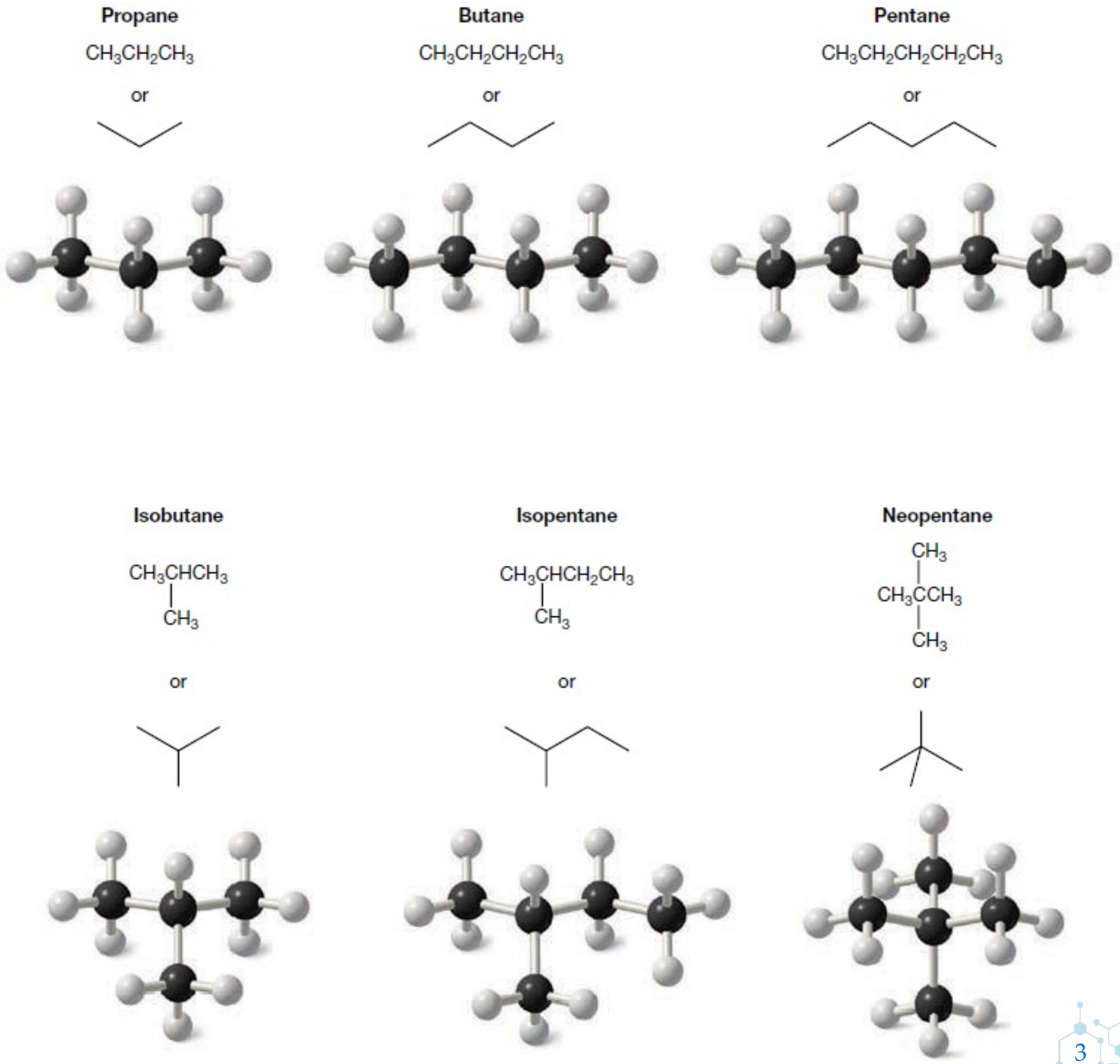
1. Hydrocarbons

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.



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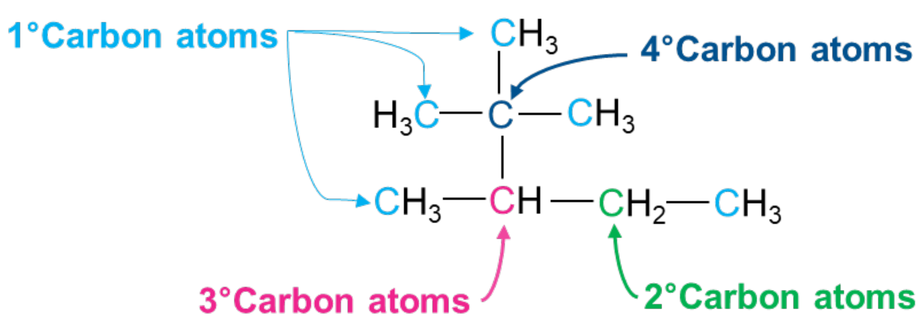
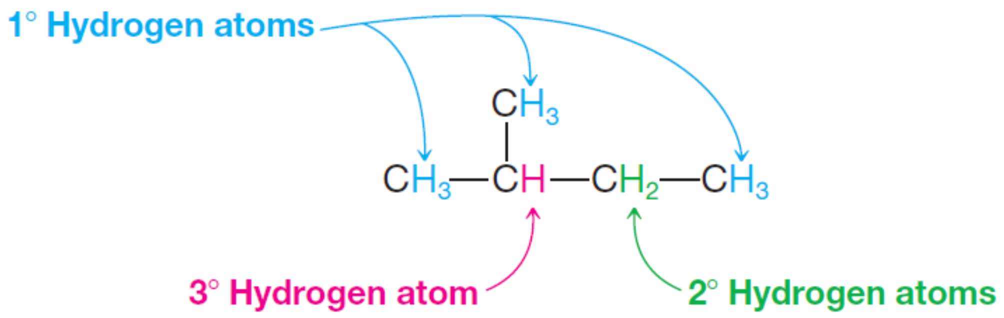
1. Hydrocarbons

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 (1°), secondary (2°), and tertiary (3°) carbon and hydrogen atoms.





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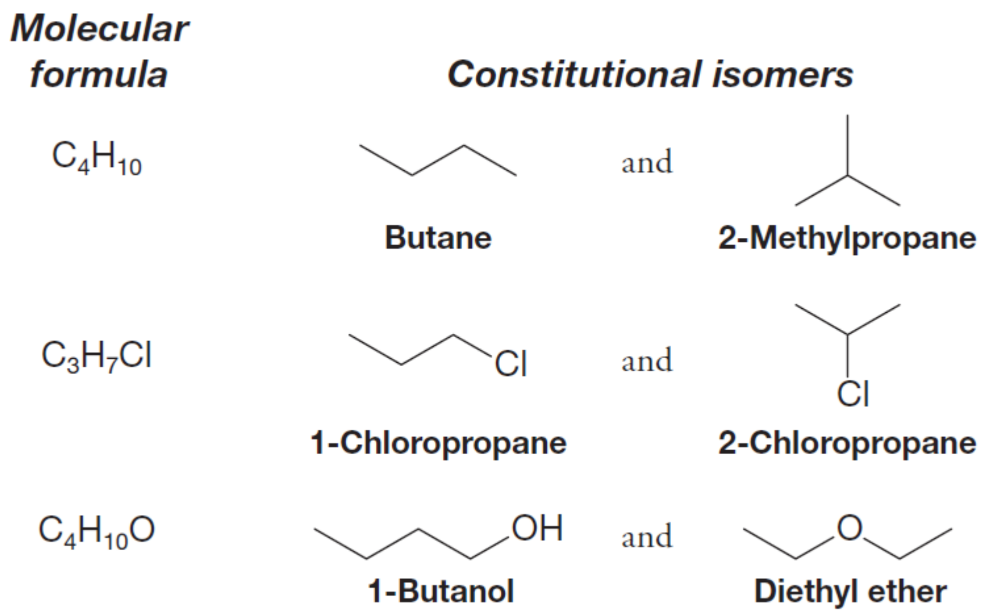
1. Hydrocarbons

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**.



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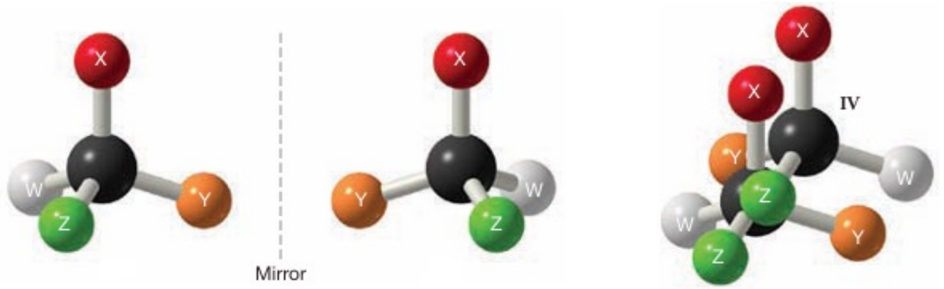
1. Hydrocarbons

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 one that is not superposable on its mirror image. A chiral centre is a carbon atom bonded to the four different substituents.
- 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

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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.

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

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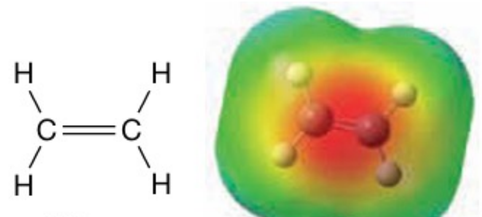
1. Hydrocarbons

1.6 Alkenes

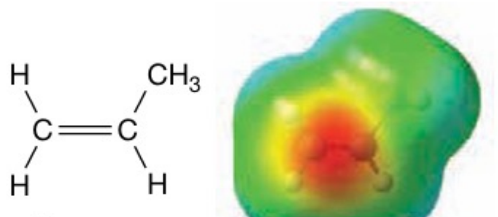
- Alkenes are hydrocarbons containing a carbon-carbon double bond, historically called olefins. The simplest alkene, ethene (ethylene) (C_2H_4), was named "olefiant gas" for its reaction with chlorine to form $C_2H_4Cl_2$; an oily liquid.
- Ethene and propene are two of the most important industrial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

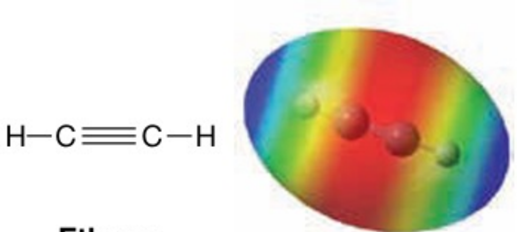
- Hydrocarbons whose molecules contain the carbon–carbon triple bond are called alkynes. The common name for this family is acetylenes, after the simplest member, HC≡CH, which is sold commercially as acetylene.



Ethene



Propene



Ethyne

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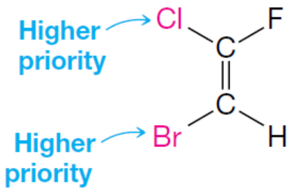
1. Hydrocarbons

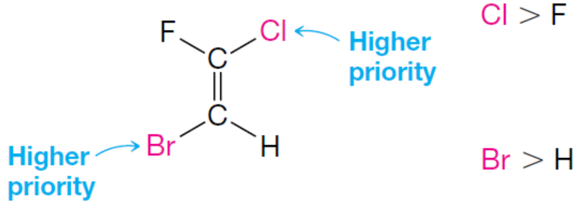
1.8 The (E)–(Z) System for Designating Alkene Diastereomers

- 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



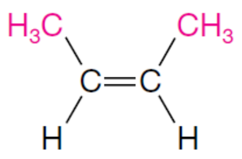
(*E*)-2-Bromo-1-chloro-1-fluoroethene

1. Hydrocarbons

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

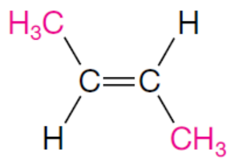
- **How To Use the (*E*)–(*Z*) System**

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)

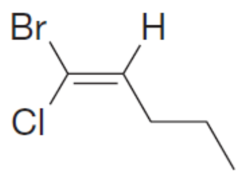
$CH_3 > H$



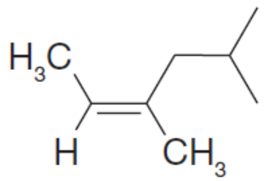
(*E*)-2-Butene or (*E*)-but-2-ene (*trans*-2-butene)

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

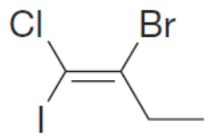
(a)



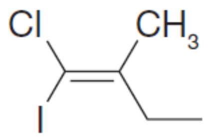
(c)



(b)



(d)



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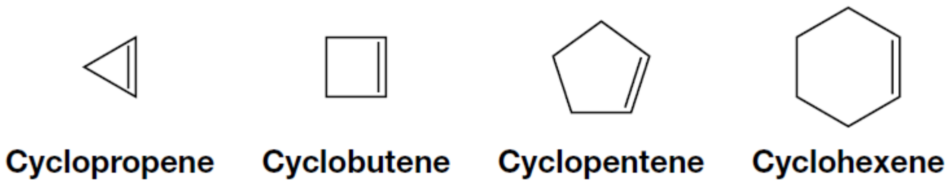
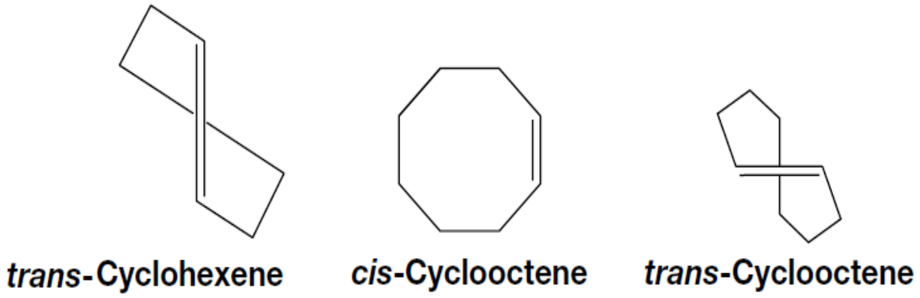
1. Hydrocarbons

1.9 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.





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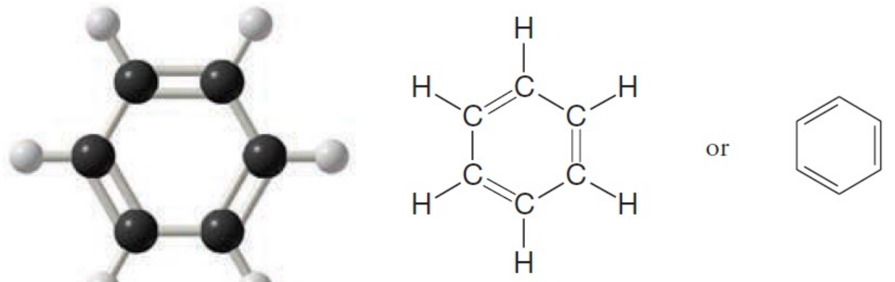
2. Aromatic Hydrocarbon

- 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

Bond-line representation of Kekulé structure

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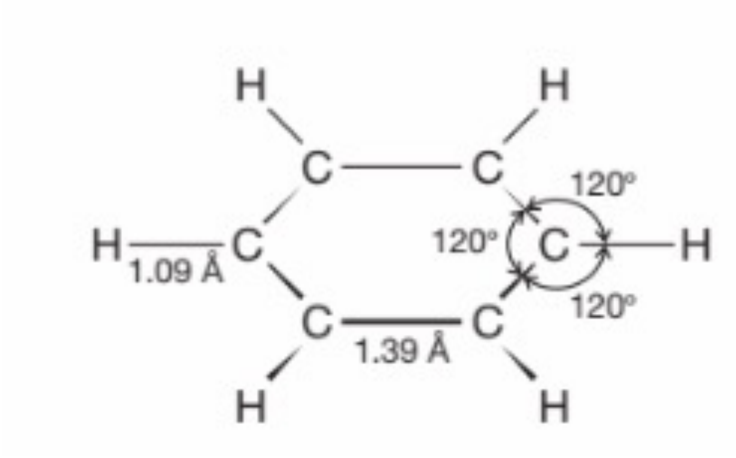
2. Aromatic Hydrocarbon

2.1 Benzene: A Representative Aromatic Hydrocarbon

- The molecule of benzene is planar and that all of its carbon–carbon bonds are of equal length. In benzene each carbon is sp^2 hybridized and the bond angles is 120°.
- Moreover, the carbon–carbon bond lengths in benzene are 1.39 Å, a value in between that for a carbon–carbon single bond between sp^2 hybridized atoms (1.47 Å) and that for a carbon–carbon double bond (1.34 Å).



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2. Aromatic Hydrocarbon

2.2 Aromatic Character (Aromaticity)

- **To be classified as aromatic, a compound must have:**

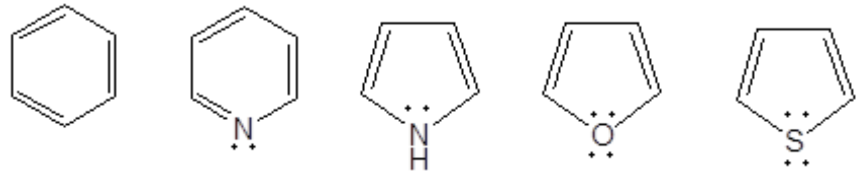
  1. **Cyclic structure.**
  2. **Cyclic structure contains what looks like a continuous system of alternating double and single bonds.**
  3. **Aromatic compounds must be planar.**
  4. **Fulfill Huckel rule:**

The number of π electrons in the compound = (4n + 2)

Where (n = 0,1, 2, 3, and so on).

4n+2 =	8	10	2	2	4
n=	1.5	2	0	0	0.5

4n+2 =	4	4	6	4
n=	0.5	0.5	1	0.5



	Benzene	Pyridine	Pyrrole	Furan	Thiophene
4n+2=	6	6	6	6	6
n=	1	1	1	1	1

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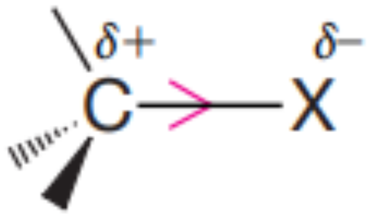
3. Functional Groups

3.1 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−).



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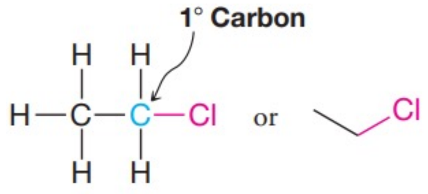
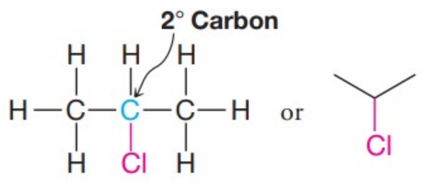
3. Functional Groups

3.1 Alkyl Halides or Haloalkanes

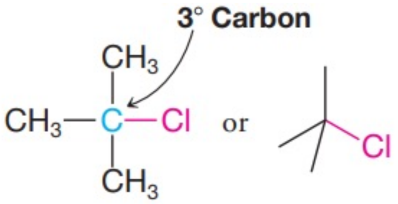
- Alkyl halides are classified as being primary (1°), secondary (2°), or tertiary (3°). This classification is based on the carbon atom to which the halogen is directly attached.
- For example: If the carbon atom that bears the halogen is directly attached to only one other carbon, the carbon atom is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



A 1° alkyl chloride



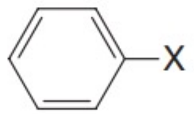
A 2° alkyl chloride



A 3° alkyl chloride

3.2 Alkenyl Halides and Aryl Halide

- 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.



A phenyl halide or aryl halide

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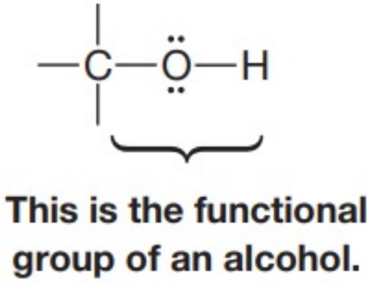
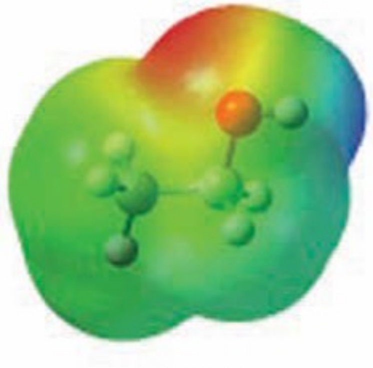
3. Functional Groups

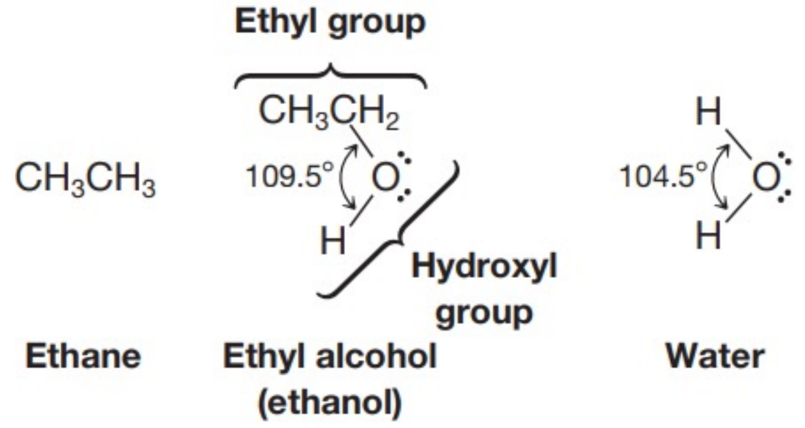
3.3 Containing Oxygen:

3.3.1 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.




Ethanol



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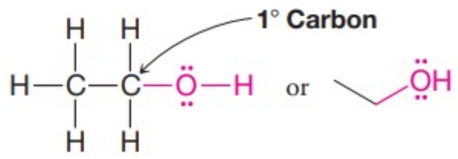
3. Functional Groups

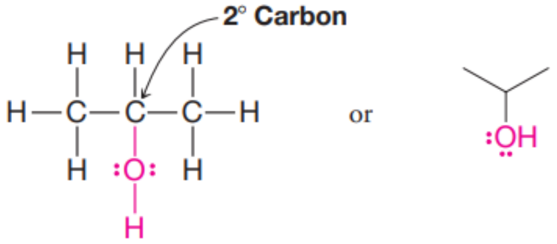
3.3 Containing Oxygen:

3.3.1 Alcohols And phenols

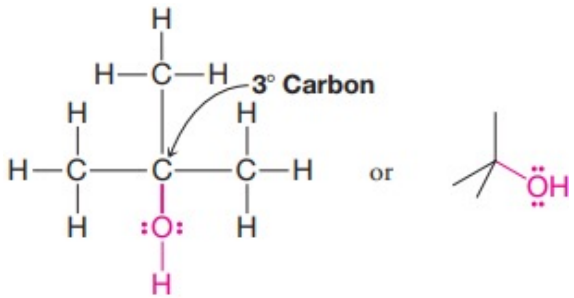
- As with alkyl halides, alcohols are classified into three groups: primary (1°), secondary (2°), and tertiary (3°) alcohols.
- This classification is based on the degree of substitution of the carbon to which the hydroxyl group is directly attached.
- If the carbon has only one other carbon attached 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)

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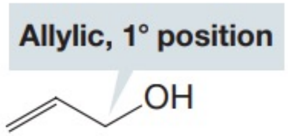
3. Functional Groups

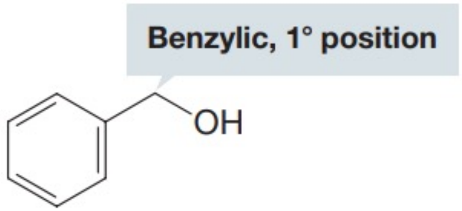
3.3 Containing Oxygen:

3.3.1 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.

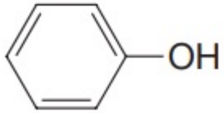


2-Propenol
(or prop-2-en-1-ol,
or allyl alcohol),
an allylic alcohol



Benzyl alcohol,
a benzylic alcohol

- 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.



Phenol

p-Methylphenol,
a substituted phenol

Ar—OH

General formula
for a phenol

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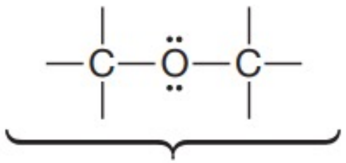
3. Functional Groups

3.3 Containing Oxygen:

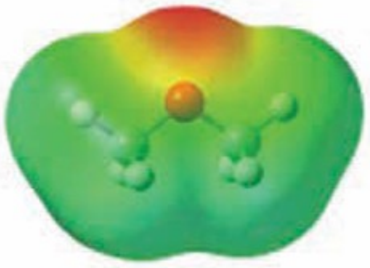
3.3.2 Ethers

- 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.

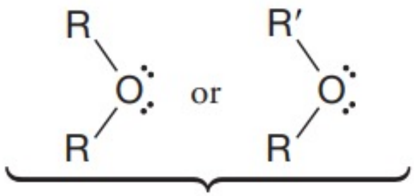
- Several examples are shown here:



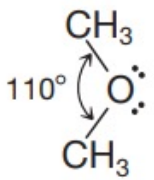
The functional group of an ether



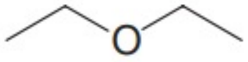
Dimethyl ether



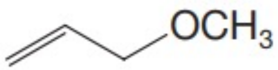
General formula for an ether



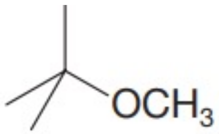
Dimethyl ether (a typical ether)



Diethyl ether



Allyl methyl ether



tert-Butyl methyl ethe

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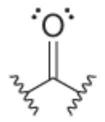
3. Functional Groups

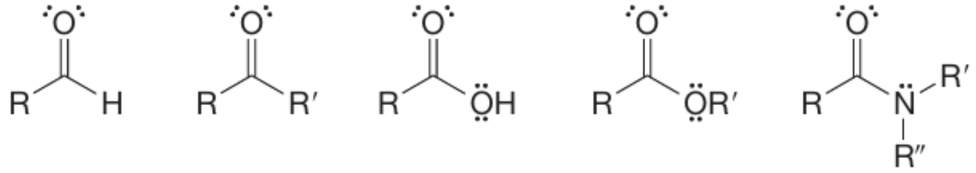
3.4 Containing Carbonyl Group:

3.4.1 Structure of the Carbonyl Group

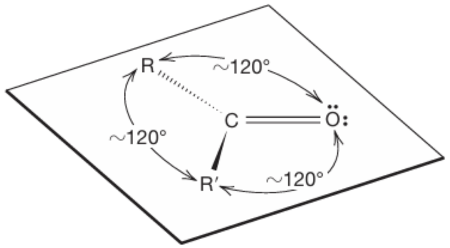
- Carbonyl compounds are a broad group of compounds that includes aldehydes, ketones, carboxylic acids, esters, and amides.
- The carbonyl carbon atom is *sp*^{2} hybridized; thus, it and the three atoms attached to it lie in the same plane. The bond angles between the three attached atoms are what we 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.
- Oxygen is much more electronegative than carbon. Therefore, the electrons in the C=O bond are attracted to the oxygen, producing a highly polarized bond.



The carbonyl group



An aldehyde | A ketone | A carboxylic acid | An ester | An amide



polarization of the carbonyl group

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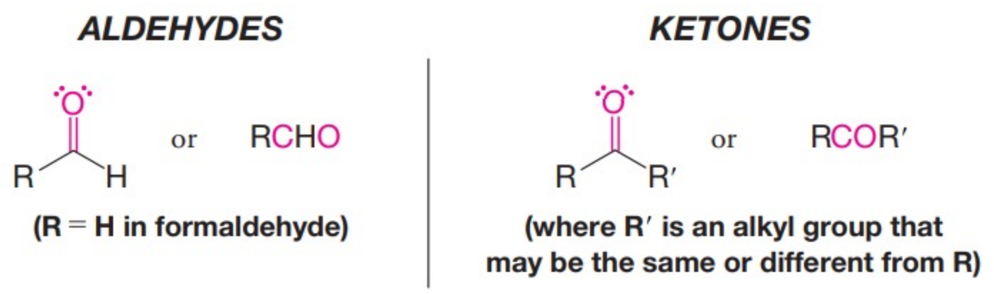
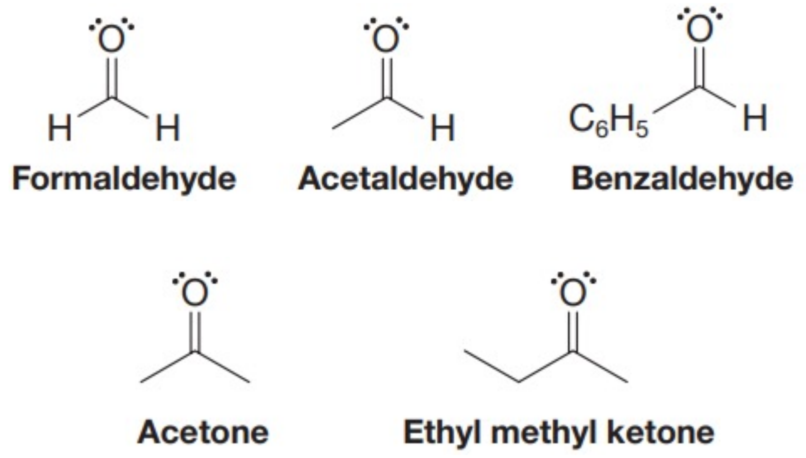
3. Functional Groups

3.4 Containing Carbonyl Group:

3.4.2 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.
- Some specific examples of aldehydes and ketones are the following:



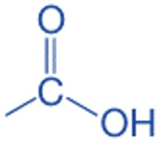


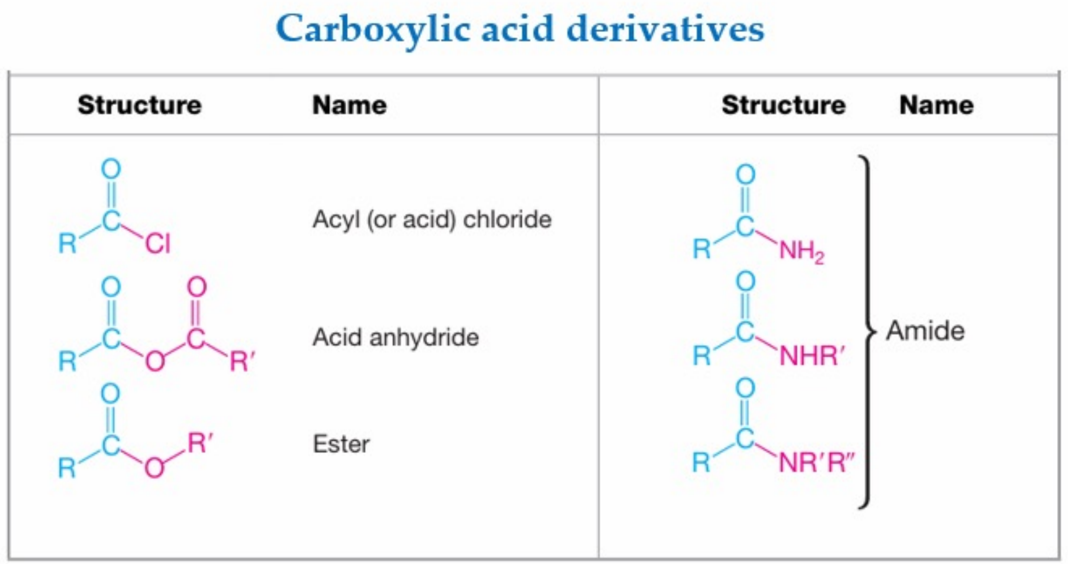
3. Functional Groups

3.4 Containing Carbonyl Group:

3.4.3 Carboxylic Acids and their derivatives

- **Carboxylic acids, esters, Acid Anhydrides, Acyl chlorides 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.**



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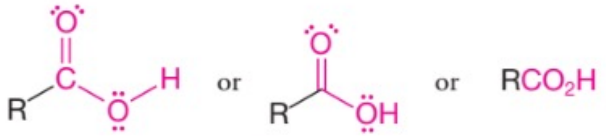
3. Functional Groups

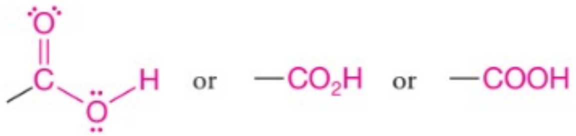
3.4 Containing Carbonyl Group:

3.4.3 Carboxylic Acids and their derivatives

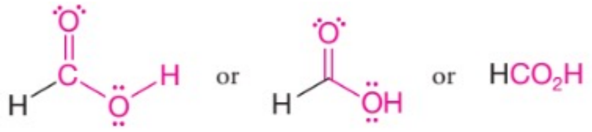
- Carboxylic acids have a carbonyl group bonded to a hydroxyl group, and they have the general formula, RCOOH.
- The functional group, -COOH is called the carboxyl group (carbonyl + hydroxyl)
- Examples of carboxylic acids are formic acid, acetic acid, and benzoic acid.
- Formic acid is an irritating 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.



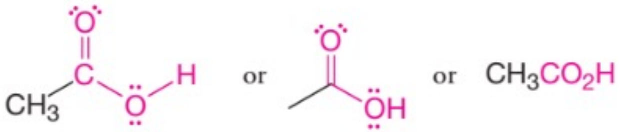
A carboxylic acid



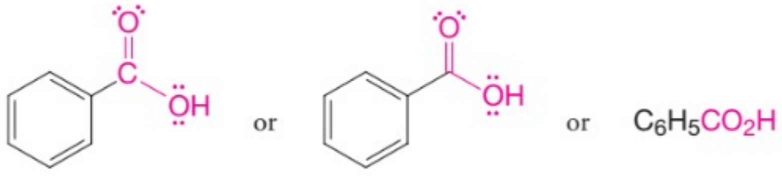
The carboxyl group



Formic acid



Acetic acid



Benzoic acid

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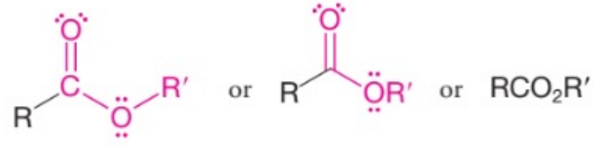
3. Functional Groups

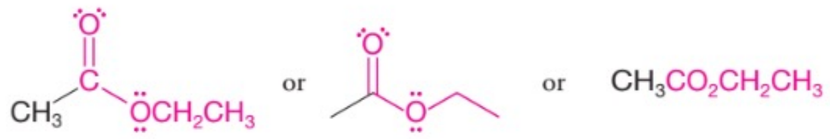
3.4 Containing Carbonyl Group:

3.4.3 Carboxylic Acids and their derivatives

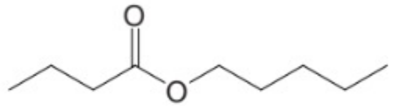
- Esters have the general formula RCO_2R' (or $RCOOR'$), where a carbonyl group is bonded to an alkoxyl (–OR) group.
- Your body makes esters from long-chain carboxylic acids called "fatty acids" by combining them with glycerol.
- Esters usually have pleasant odors, some resembling those of fruits, and these are used in the manufacture of synthetic flavors.



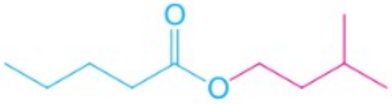
General formula for an ester



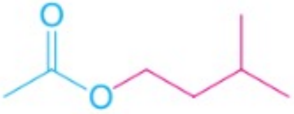
Ethyl acetate is an important solvent.



Pentyl butanoate smells like apricots and pears.



Isopentyl pentanoate
(used in synthetic apple flavor)



Isopentyl acetate
(used in synthetic banana flavor)

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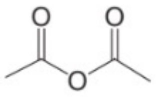
3. Functional Groups

3.4 Containing Carbonyl Group:

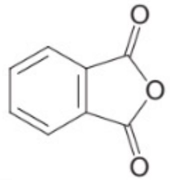
3.4.3 Carboxylic Acids and their derivatives

- **Acid Anhydrides** are named by dropping the word acid from the name of the carboxylic acid and then adding the word anhydride.
- **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.
- **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:

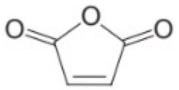


Acetic anhydride (ethanoic anhydride) mp −73 °C

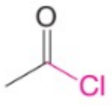
Succinic anhydride mp 121 °C



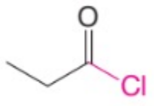
Phthalic anhydride mp 131 °C



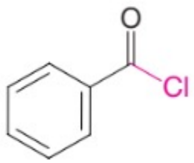
Maleic anhydride mp 53 °C



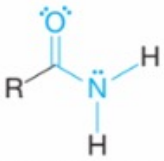
Acetyl chloride (ethanoyl chloride) mp −112 °C; bp 51 °C



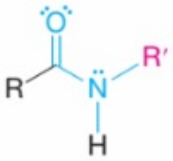
Propanoyl chloride mp −94 °C; bp 80 °C



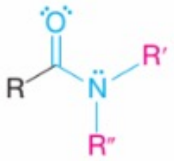
Benzoyl chloride mp −1 °C; bp 197 °C



An unsubstituted amide



An *N*-substituted amide



An *N*,*N*-disubstituted amide

General formulas for amides

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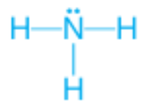
3. Functional Groups

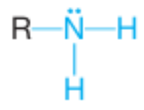
3.5 Containing Nitrogen:

3.5.1 Amines

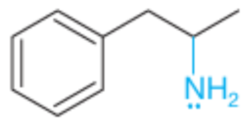
- Just as alcohols and ethers may be considered as organic derivatives of water, amines may be considered as organic derivatives of ammonia.
- Amines are classified as primary, secondary, or tertiary amines. This classification is based on the number of organic groups that are attached to the nitrogen atom.
- Notice that this is quite different from the way alcohols and alkyl halides are classified.
- For example, Isopropyl amine is a primary amine because only one organic group is attached to the nitrogen atom.



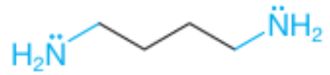
Ammonia



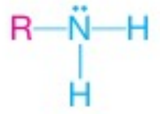
An amine



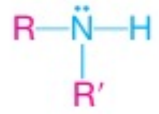
Amphetamine
(a dangerous stimulant)



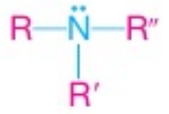
Putrescine
(found in decaying meat)



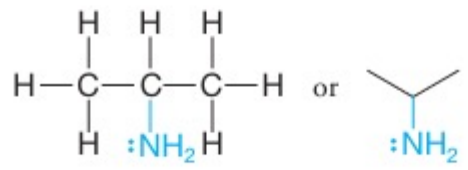
A primary (1°) amine



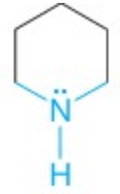
A secondary (2°) amine



A tertiary (3°) amine



Isopropylamine
(a 1° amine)



Piperidine
(a cyclic 2° amine)

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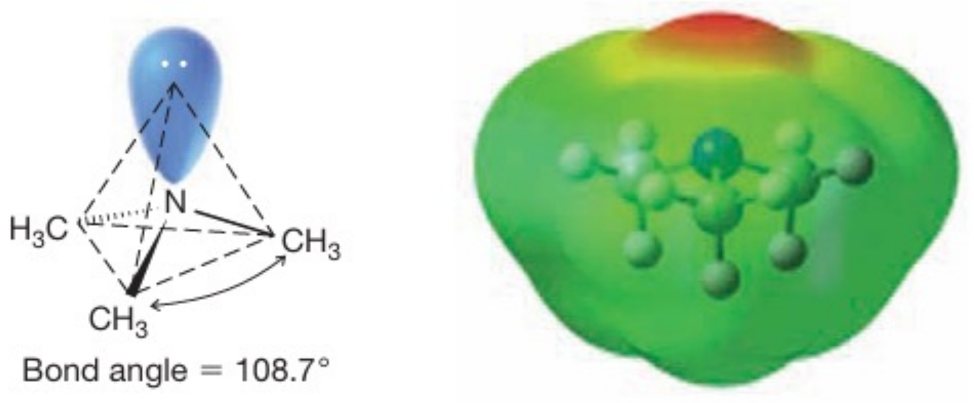
3. Functional Groups

3.5 Containing Nitrogen:

3.5.1 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

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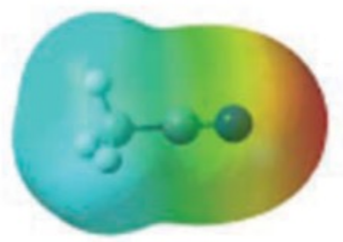
3. Functional Groups

3.5 Containing Nitrogen:

3.5.2 Nitriles

- A nitrile has the formula R–C≡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.



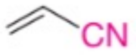
Acetonitrile

$CH_3-C\equiv N:$

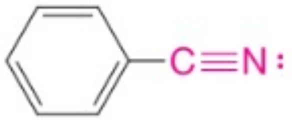
Ethanenitrile (acetonitrile)

$CH_3CH_2CH_2-C\equiv N:$

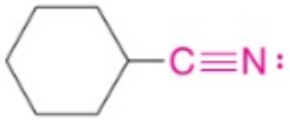
Butanenitrile



Propenenitrile (acrylonitrile)



Benzenecarbonitrile (benzonitrile)



Cyclohexanecarbonitrile