Introduction to Organic Chemistry
CHEM 109

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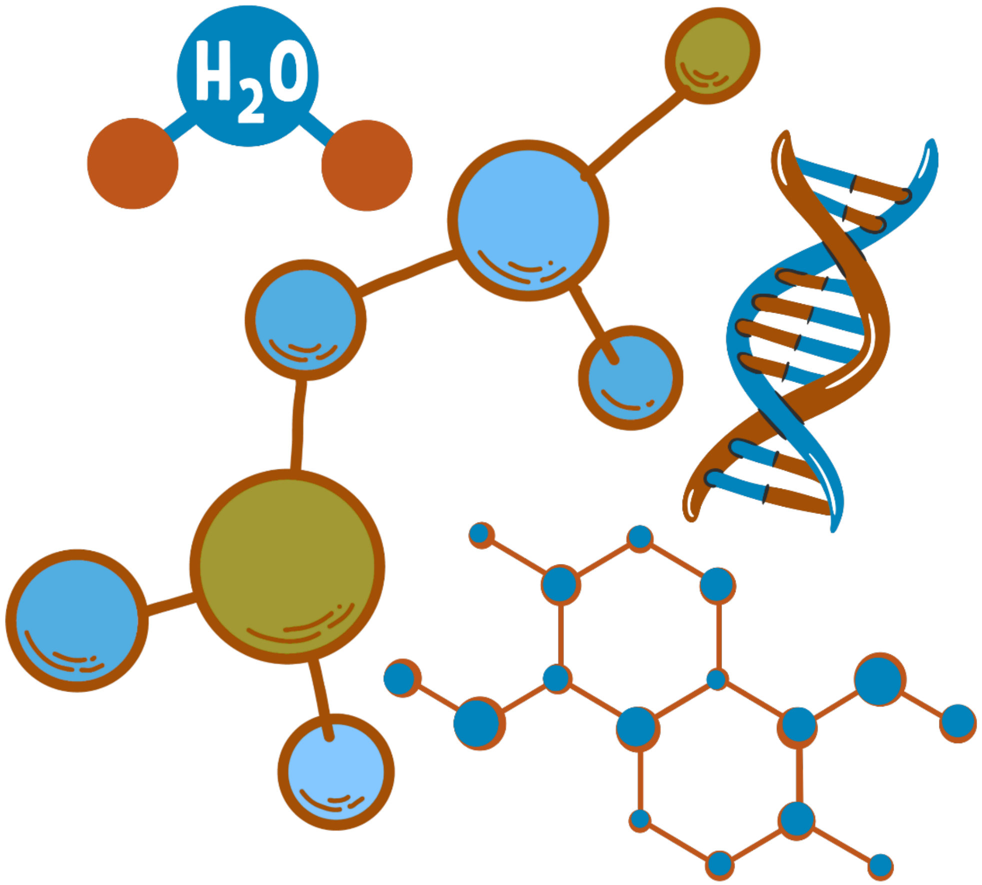
CHEMISTRY DEPARTMENT

Chapter 2: Structure and Classification of Organic Compounds



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1. Aliphatic Hydrocarbons: *Alkanes, Alkenes, Alkynes*

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

Hydrocarbons
- *Aliphatic*
  - *Unsaturated*
    - *Alkynes (Acetylenes)* C_nH_{2n-2}
    - *Alkenes (Olefins)* C_nH_{2n}
  - *Saturated*
    - *Alkanes (Paraffin's)* C_nH_{2n+2}
- *Aromatic*

- **Aliphatic hydrocarbons** are subdivided into:
  - ***Saturated hydrocarbons***
    - Alkanes; C_nH_{2n+2} *(contain carbon-carbon single bond)*
    - Cycloalkanes: C_nH_{2n} *(contain carbon-carbon single bond in a single ring)*

    Alkanes and cycloalkanes are so similar that many of their properties can be considered side by side.

  - ***Unsaturated hydrocarbons***
    - Alkenes; C_nH_{2n} *(contain carbon-carbon double bond)*
    - Alkynes; $C_n H_{2n-2}$ *(contain carbon-carbon triple bond)*

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1. Aliphatic Hydrocarbons

1.1. 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.
- Cycloalkanes 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.

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

1. Aliphatic Hydrocarbons

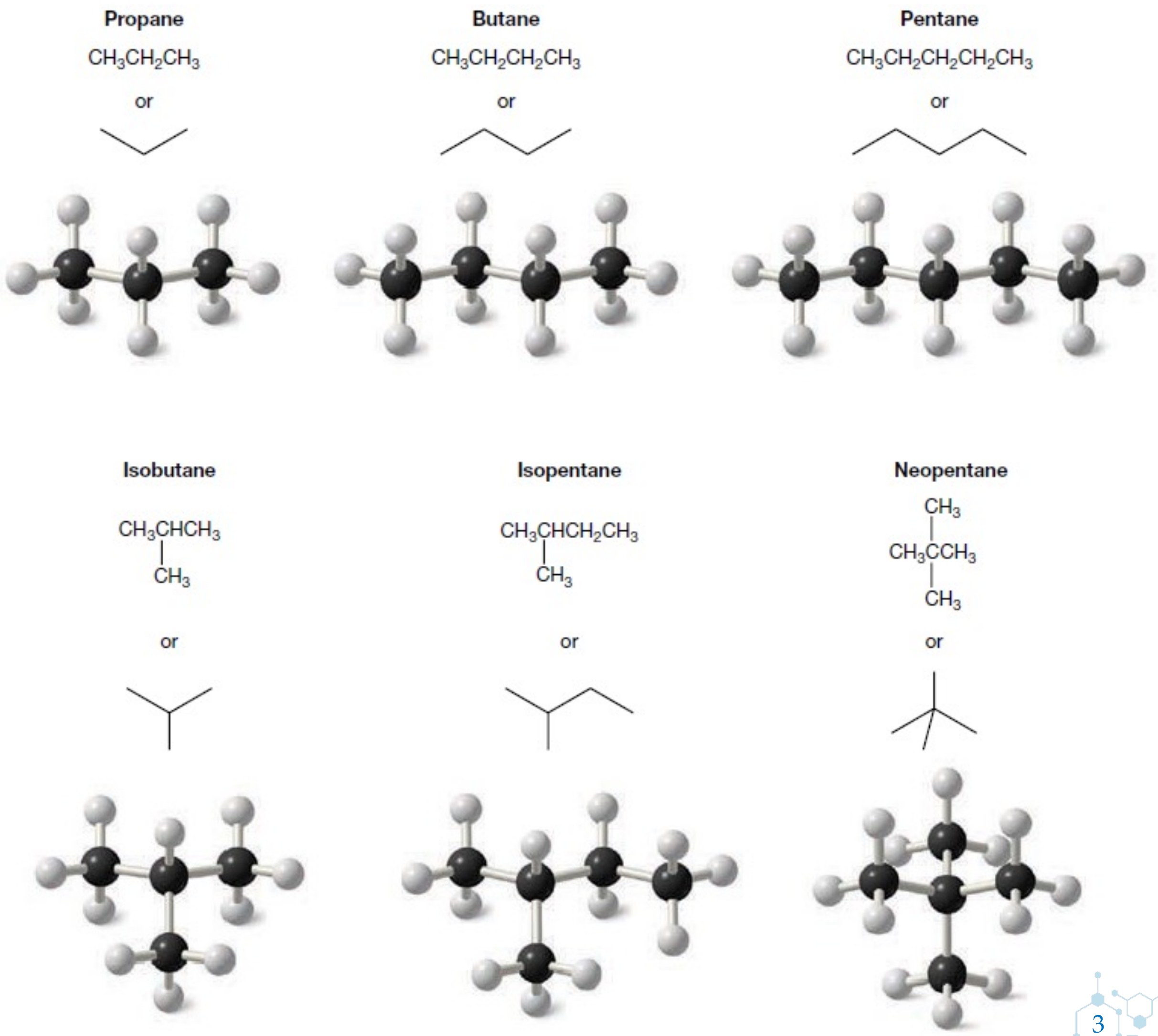
1.1. Alkanes

1.1.1. 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.

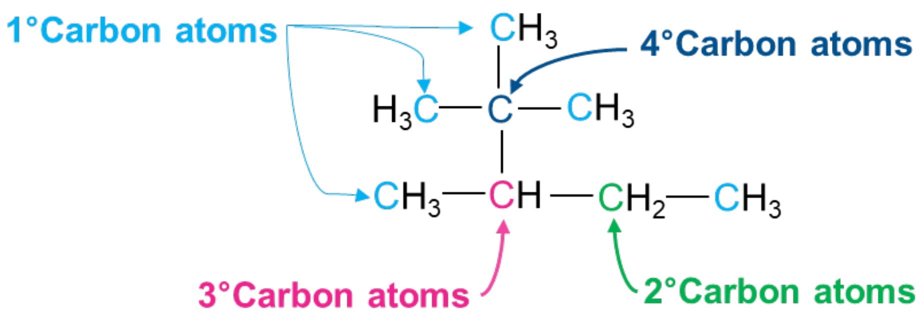


1. Aliphatic Hydrocarbons

1.1. Alkanes

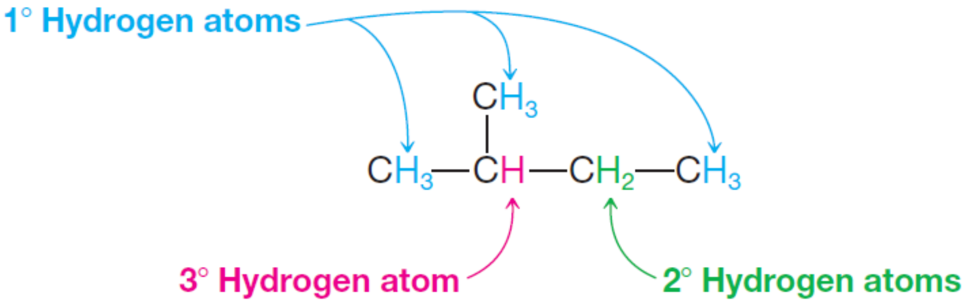
1.1.2. How to classify carbon and hydrogen atoms

- A primary (1°) carbon is one that is bonded to only one other carbon.
- A secondary (2°) carbon is one that is bonded to two other carbons.
- A tertiary (3°) carbon is one that is bonded to three other carbons.



- 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.



- Example:

  2-methylbutane, has primary (1°) , secondary (2°), and tertiary (3°) carbon and hydrogen atoms.

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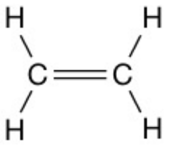
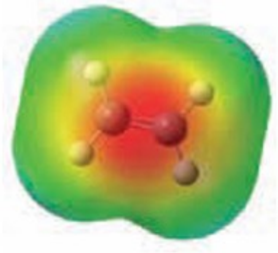
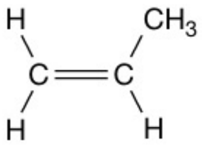
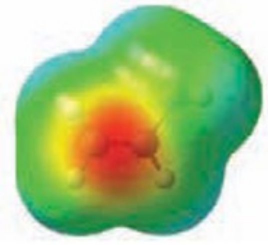
1. Aliphatic Hydrocarbons

1.2. Alkenes

- **Alkenes are hydrocarbons containing a carbon-carbon double bond, historically called olefins.**
- **General formula is C_nH_{2n}.**
- **The simplest alkene, ethene (ethylene) (C_2H_4),**

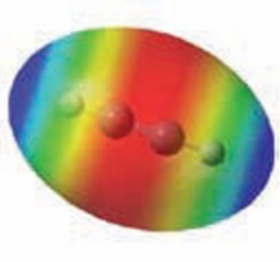
Ethene

Propene

1.3. Alkynes

- **Hydrocarbons whose molecules contain the carbon–carbon triple bond and called acetylenes.**
- **The simplest member, acetylene HC≡CH.**

Ethyne

1. Aliphatic Hydrocarbons

1.4. Isomerism

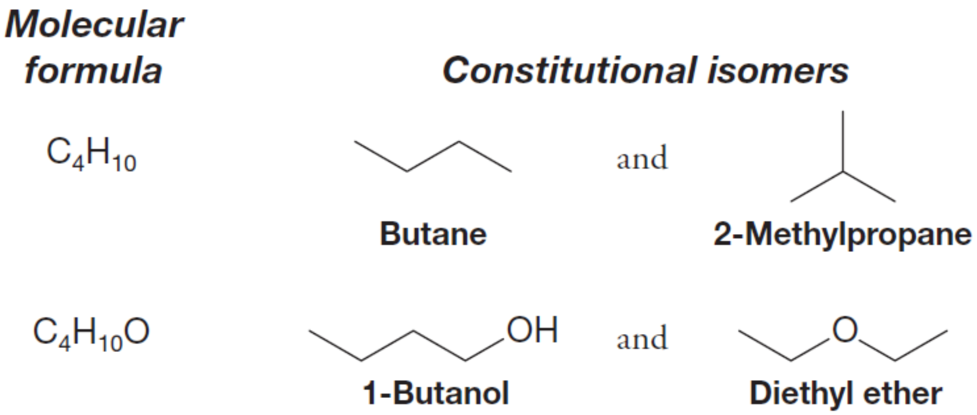
- **Isomers are different compounds with identical molecular formulas.**

Types of Isomerism

- **Structural Isomerism**
- **Geometrical Isomerism**

1.4.1. Structural or constitutional isomers

- **Structural isomers have the same molecular formula but different in the sequence of atoms bonded to each other.**
- Examples:



1. Aliphatic Hydrocarbons

1.4. Isomerism

1.4.2. Geometric Isomerism in Alkenes

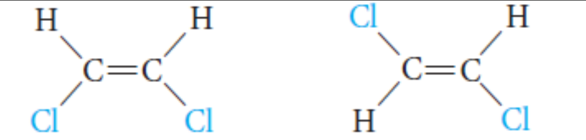
A) The (*cis*)–(*trans*) System for Alkene when W differs from X and Y from Z, Alkenes exist as geometric isomers

Geometric isomers

- In alkenes, geometric isomerism is due to restricted rotation about the carbon - carbon double bond.

  - ***cis* isomer;** **when two similar groups are on the same side or same side of the double bond.**

  - ***trans* isomer;** **when two similar groups are on the opposite direction or opposite sides of the double bond.**

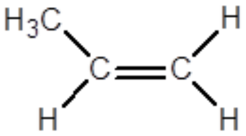


cis-1,2-dichloroethene
bp 60°C, mp −80°C

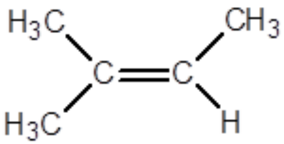
trans-1,2-dichloroethene
bp 47°C, mp −50°C

- *They have different physical properties and can be separated by fractional crystallization or distillation.*

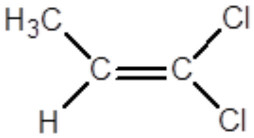
B) If (W = X or Y = Z), geometric isomerism is not possible.



Propene



2-Methyl-2-butene



1,1-Dichloropropene

1. Aliphatic Hydrocarbons

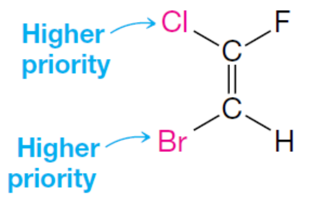
1.4. Isomerism

1.4.2. Geometric Isomerism in Alkenes

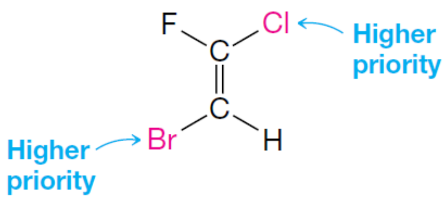
C) The (E)–(Z) System for Alkene

- How To Use the (*E*)–(*Z*) System

1. Examine the two groups attached to one carbon atom of the double bond.
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.
4. (*Z*) from the German word zusammen, meaning together; if the two groups of higher priority are on the same side of the double bond.
5. (*E*) from the German word entgegen, meaning opposite; If the two groups of higher priority are on opposite sides of the double bond.



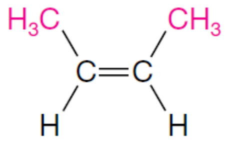
(*Z*)-2-Bromo-1-chloro-1-fluoroethene



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

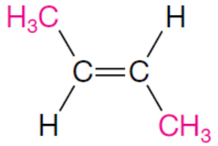
Cl > F

Br > H



(*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)

1. Aliphatic Hydrocarbons

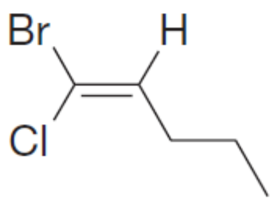
1.4. Isomerism

1.4.2. Geometric Isomerism in Alkenes

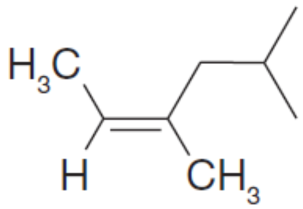
C) The (E)–(Z) System for Alkene

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

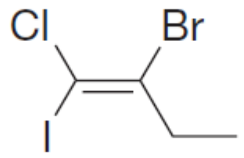
(a)



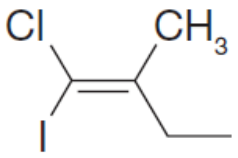
(c)



(b)



(d)



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1. Aliphatic Hydrocarbons

1.4. Isomerism

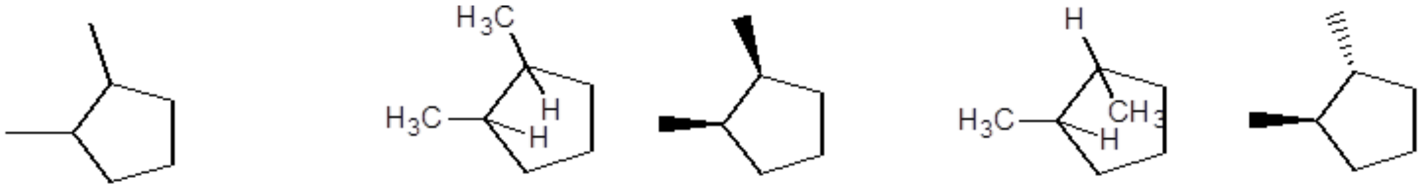
1.4.3. Geometric Isomerism in Cycloalkenes

- For very small rings (5 carbons or fewer), only the *cis* cycloalkene isomer is possible and a *trans* double bond cannot fit into these small rings.
- While *trans* double bonds are too strained to exist in small cycloalkenes, they become possible in larger rings.

Cyclopropene Cyclobutene Cyclopentene Cyclohexene *trans*-Cyclohexene *cis*-Cyclooctene *trans*-Cyclooctene

- ***cis-trans*** **Isomerism in Cycloalkanes**

cis–trans isomerism (sometimes called geometric isomerism) is one kind of stereoisomerism.



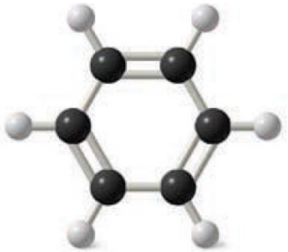
1,2-Dimethylcyclopentane *cis*-1,2-Dimethylcyclopentane *trans*-1,2-Dimethylcyclopentane

2. Aromatic Hydrocarbons

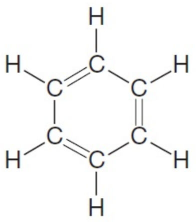
- **The term "aromatic" referred to pleasant-smelling compounds from plants, many of which contained a benzene ring.**
- **Today, *aromaticity* is defined by electronic structure not odor.**
- **Aromatic compounds, are classified based on special stability from a *delocalized ring of π-electrons*, even if they have no scent**
- **Aromatic compounds are a major class of unsaturated cyclic hydrocarbons, with *benzene* being the fundamental example.**

2.1 Benzene: A Representative Aromatic Hydrocarbon

- **Its structure is a six-membered ring with *delocalized electrons*, often depicted by the Kekulé structure with alternating single and double bonds.**
- **The molecule of benzene is Planar and that all of its carbon–carbon bonds are of equal length.**
- **Each carbon is *sp*² hybridized and the bond angles is 120°.**
- **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).**



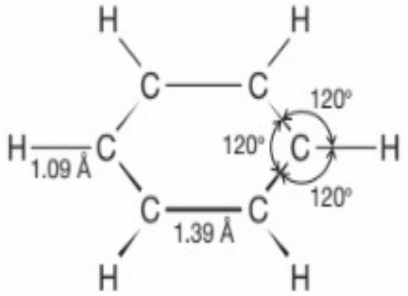
Benzene



Kekulé structure for benzene

or

Bond-line representation of Kekulé structure

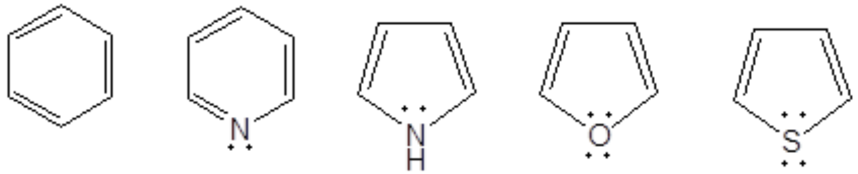


2. Aromatic Hydrocarbons

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).



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

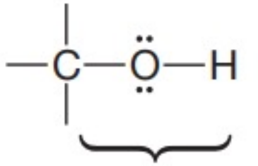
4n+2 =	8	10	2	2	4
n=	1.5	2	0	0	0.5

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

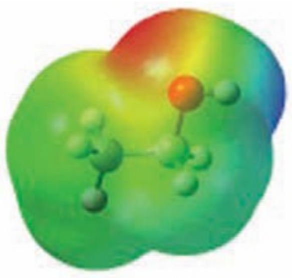
3. Functional Groups

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 *sp*^{3}-hybridized carbon atom.

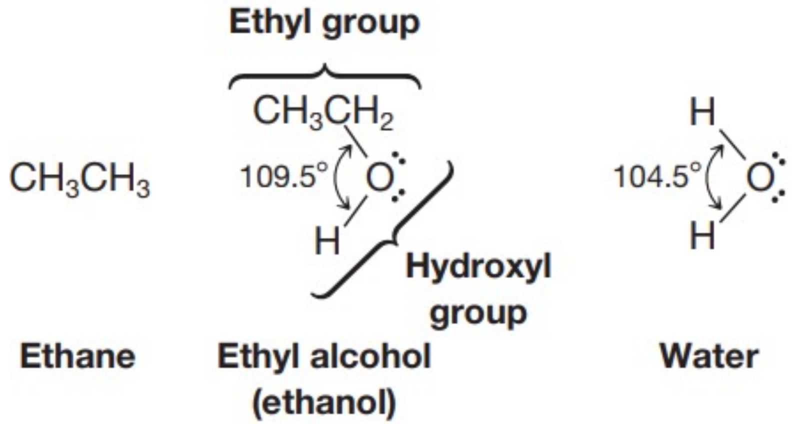


This is the functional group of an alcohol.



Ethanol

- Alcohols may be viewed structurally in two ways:
  - (1) As alkyl derivatives of water.
  - (2) As hydroxyl derivatives of alkanes.
- 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.



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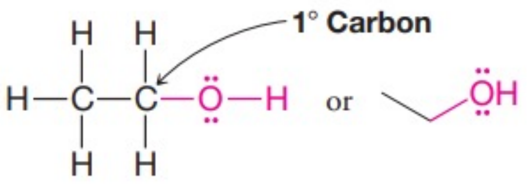
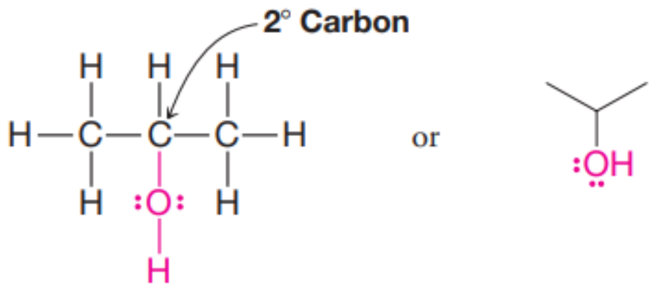
3. Functional Groups

3.1. Alcohols and Phenols

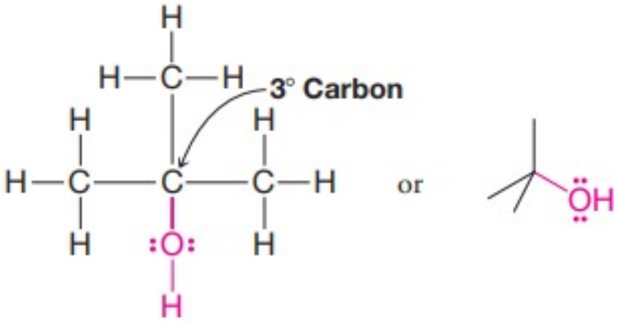
- Alcohols are classified into three groups: primary (1°), secondary (2°), and tertiary (3°) alcohols.
- This classification is based on the degree of substitution of the carbon to which the hydroxyl group is directly attached.
  - Primary alcohol; If the carbon has only one other carbon attached to it.
  - Secondary alcohol; If the carbon atom that bears the hydroxyl group also has two other carbon atoms.
  - Tertiary alcohol; If the carbon atom that bears the hydroxyl group has three other carbons attached to it.



Ethyl alcohol
(a 1° alcohol)



Isopropyl alcohol
(a 2° alcohol)

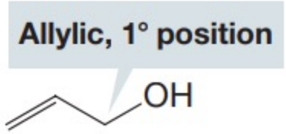


tert-Butyl alcohol
(a 3° alcohol)

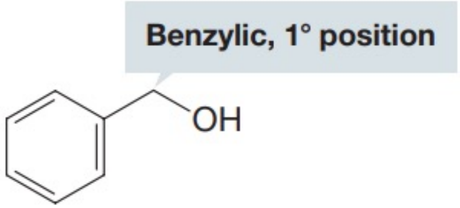
3. Functional Groups

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.

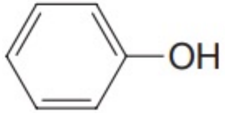


2-Propenol (or prop-2-en-1-ol, or allyl alcohol), ***an allylic alcohol***



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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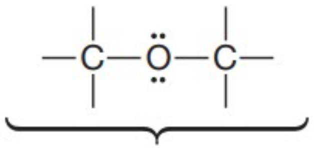
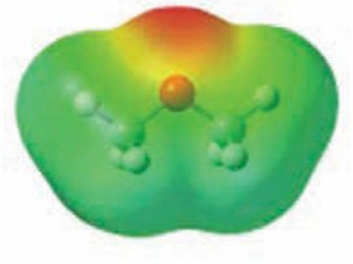
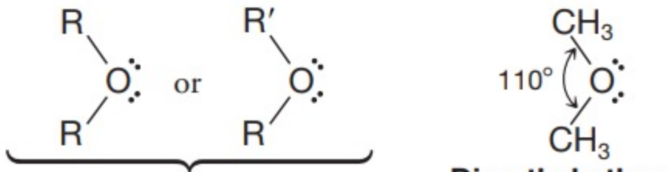
3. Functional Groups

3.2. 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.
- Ethers differ from alcohols in that the oxygen atom of an ether is bonded to two carbon atoms.

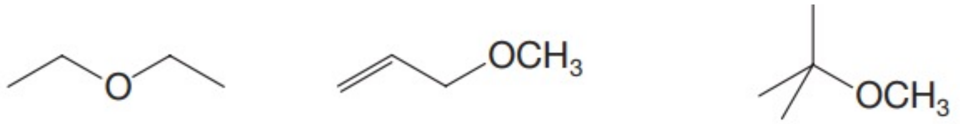

The functional group of an ether


Dimethyl ether



General formula for an ether
Dimethyl ether (a typical ether)

- Examples;



Diethyl ether Allyl methyl ether *tert*-Butyl methyl ethe

- Ethers are classified as
  - Symmetrical ethers;
    When the organic groups attached to the oxygen are identical.
  - Unsymmetrical ethers (*mixed ethers*);
    When the organic groups attached to the oxygen are different.

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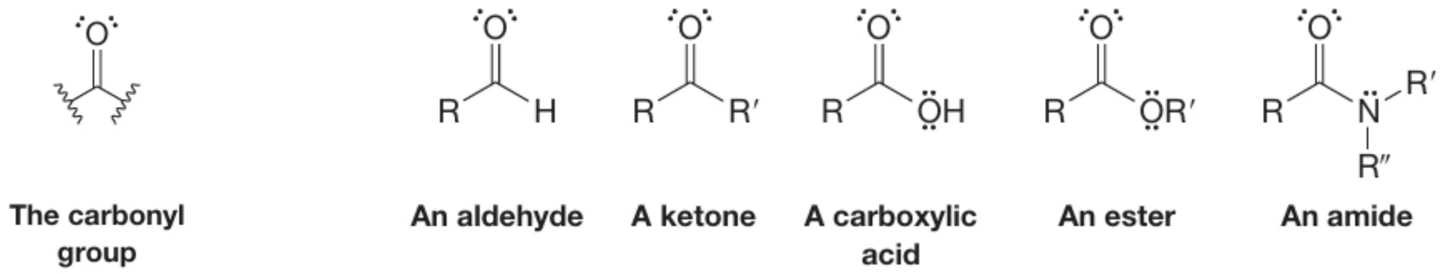
3. Functional Groups

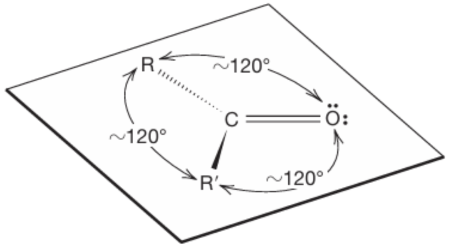
3.3. Containing Carbonyl Group:

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 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.

polarization of the carbonyl group

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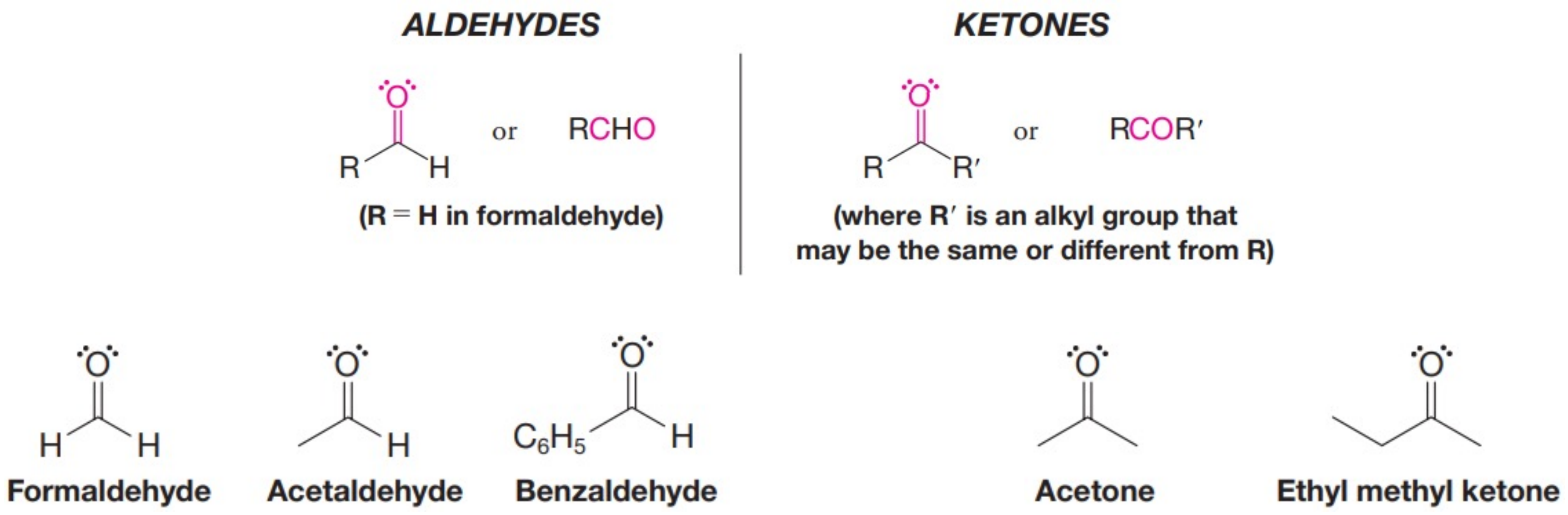
3. Functional Groups

3.3. Containing Carbonyl Group:

3.3.1. Aldehydes and Ketones

- 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.



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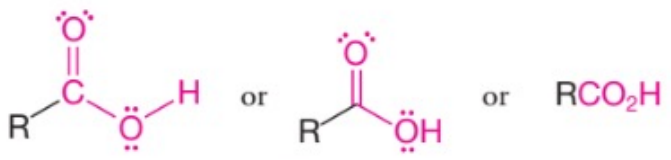
3. Functional Groups

3.3. Containing Carbonyl Group:

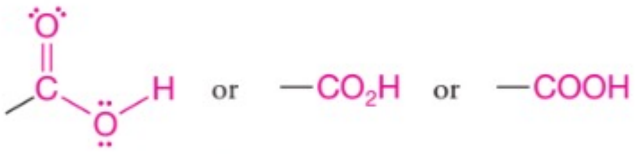
3.3.2. Carboxylic Acids and their derivatives

A) Carboxylic Acids

- Carboxylic acids have a carbonyl group bonded to a hydroxyl group, and they have the general formula, RCOOH.
- The functional group (abbreviated $-CO_2H$ or $-COOH$) is called the carboxyl group (carbonyl + hydroxyl)

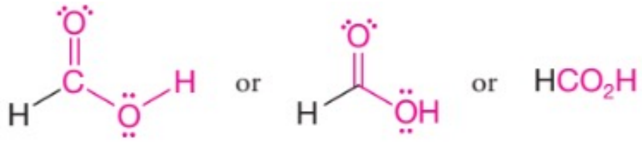


A carboxylic acid

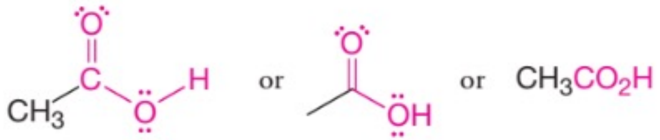


The carboxyl group

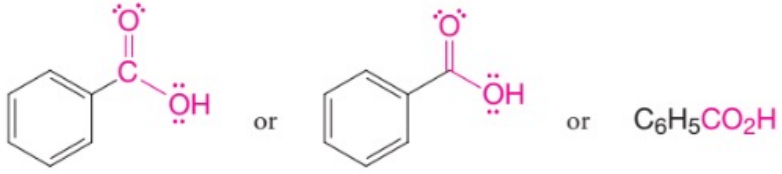
- Examples: formic acid, acetic acid, and benzoic acid.
  - Formic acid is an irritating liquid produced by ants.
  - Acetic acid, the substance responsible for the sour taste of vinegar.



Formic acid



Acetic acid



Benzoic acid

3. Functional Groups

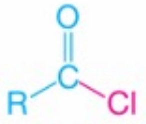
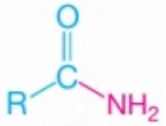
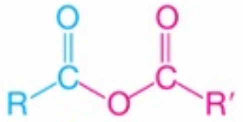
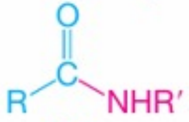
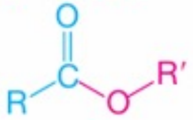
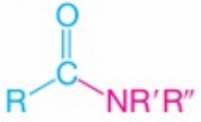
3.3. Containing Carbonyl Group:

3.3.2. Carboxylic Acids and their derivatives

Carboxylic Acids derivatives

- **Esters, Acid Anhydrides, Acyl chlorides and amides all contain a carbonyl group that is bonded to an oxygen or nitrogen atom.**

Carboxylic acid derivatives

Structure	Name	Structure	Name
	Acyl (or acid) chloride		Amide
	Acid anhydride		
	Ester		

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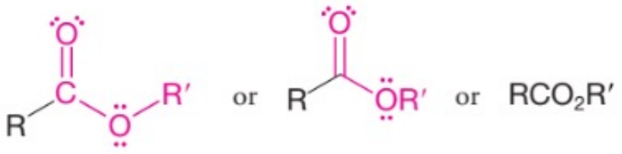
3. Functional Groups

3.3. Containing Carbonyl Group:

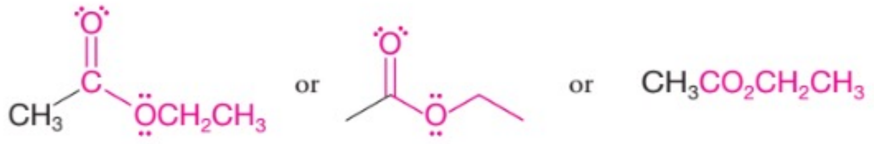
3.3.2. Carboxylic Acids and their derivatives

B) Esters

- **Esters have the general formula RCO_2R' (or $RCOOR'$), where a carbonyl group is bonded to an alkoxyl (–OR) group.**

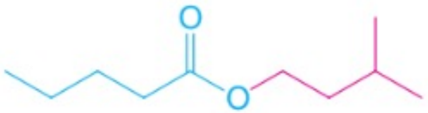


General formula for an ester



Ethyl acetate is an important solvent.

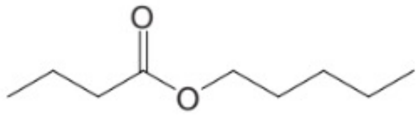
- **Esters usually have pleasant odors, some resembling those of fruits, and are used in the manufacture of synthetic flavors.**



Isopentyl pentanoate
(used in synthetic apple flavor)

Isopentyl acetate
(used in synthetic banana flavor)

- **Your body makes esters from long-chain carboxylic acids called "fatty acids" by combining them with glycerol.**



Pentyl butanoate smells like apricots and pears.

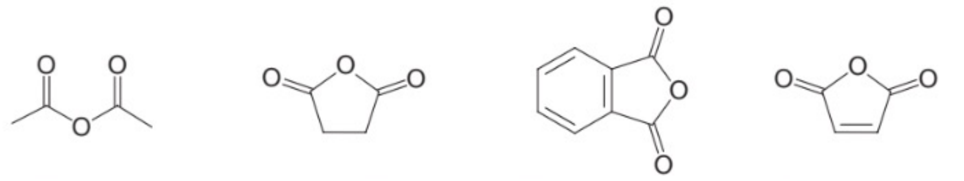
3. Functional Groups

3.3. Containing Carbonyl Group:

3.3.2. Carboxylic Acids and their derivatives

C) Acid Anhydrides

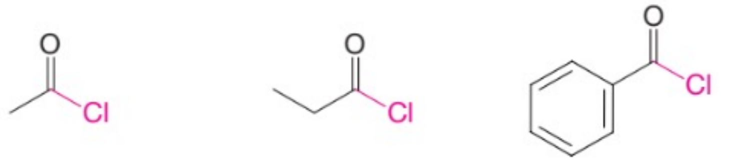
- Acid Anhydrides are named by dropping the word acid from the name of the carboxylic acid and then adding the word anhydride.



Acetic anhydride (ethanoic anhydride) mp −73 °C | Succinic anhydride mp 121 °C | Phthalic anhydride mp 131 °C | Maleic anhydride mp 53 °C

D) Acyl chlorides

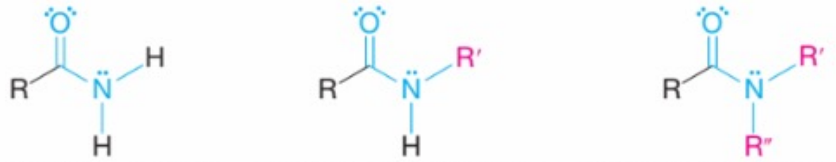
- Acyl chlorides are also called acid chlorides.
- Acyl chlorides and carboxylic anhydrides have boiling points in the same range as esters of comparable molecular weight.



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

E) 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.



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

General formulas for amides

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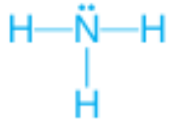
3. Functional Groups

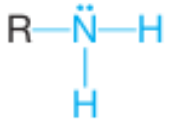
3.4. Containing Nitrogen:

3.4.1. Amines

- **Amines may be considered as organic derivatives of ammonia.**

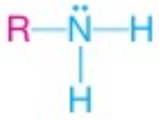


Ammonia

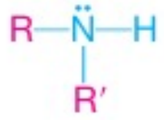


An amine

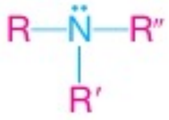
- **Amines are classified as primary, secondary, or tertiary amines. This classification is based on the number of organic groups that are attached to the nitrogen atom.**



A primary (1°) amine

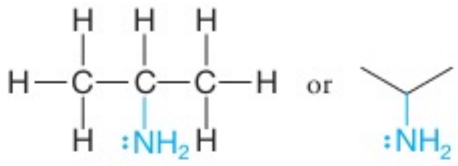


A secondary (2°) amine

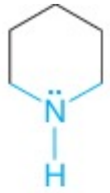


A tertiary (3°) amine

- **Example; Isopropyl amine is a primary amine because only one organic group is attached to the nitrogen atom.**



Isopropylamine
(a 1° amine)



Piperidine
(a cyclic 2° amine)

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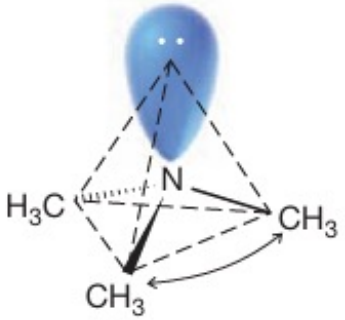
3. Functional Groups

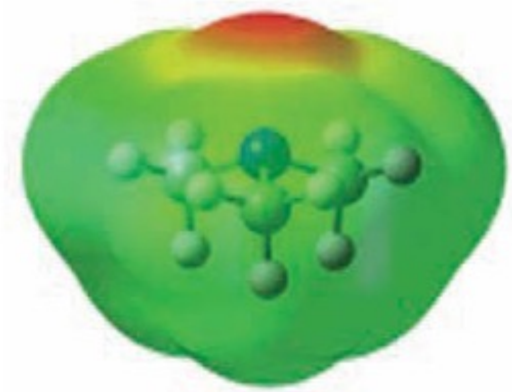
3.4. Containing Nitrogen:

3.4.1. 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.



Bond angle = 108.7°



Trimethylamine

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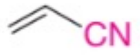
3. Functional Groups

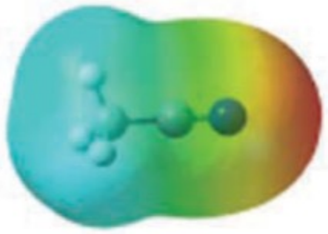
3.4. Containing Nitrogen:

3.4.2. 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.



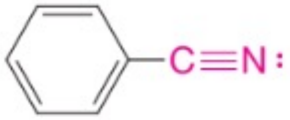
Propenenitrile
(acrylonitrile)



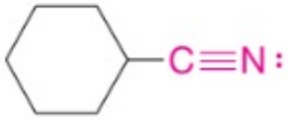
Acetonitrile

$CH_3—C≡N:$
Ethanenitrile
(acetonitrile)

$CH_3CH_2CH_2—C≡N:$
Butanenitrile



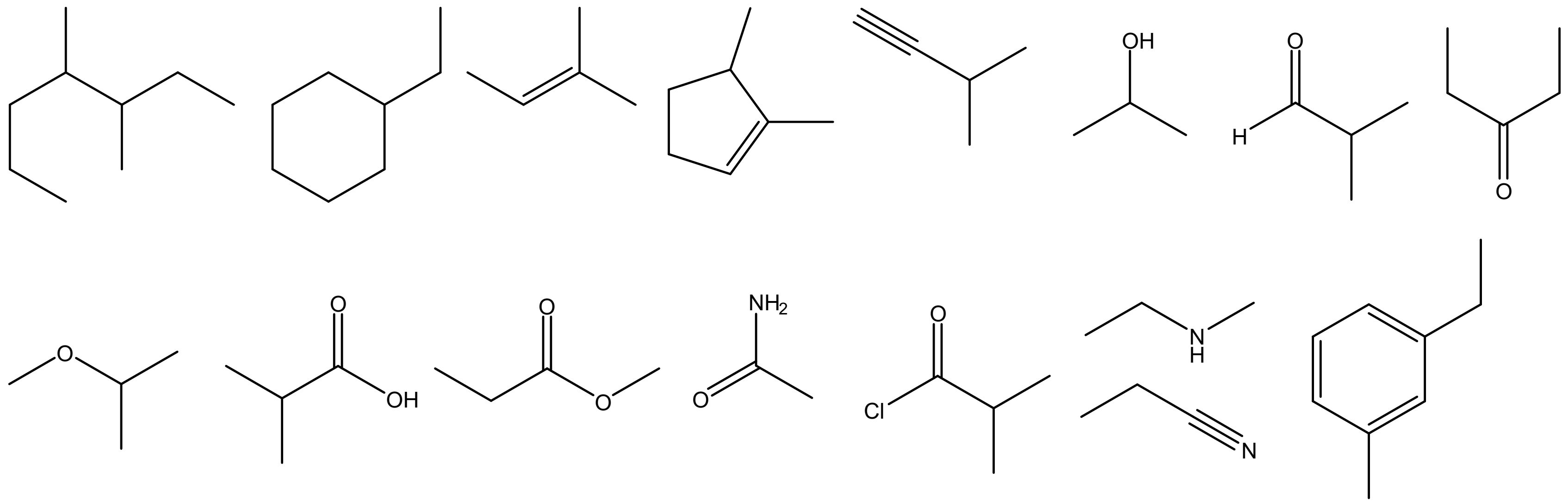
Benzenecarbonitrile
(benzonitrile)



Cyclohexanecarbonitrile

4. Practice Problems

1) Classify the following compounds based on their functional groups:



2) Classify the following alcohol, amine, and amide as primary (1°), secondary (2°), or tertiary (3°):