

Chapter 7

FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY

INTRODUCTION

Organic chemistry is the chemistry of carbon compounds. Most of the organic compounds also contain hydrogen and many compounds also contain oxygen and other elements. There are few compound which contain carbon but they are not organic compounds. e.g., CO, CO₂ metal carbonates, bicarbonates, cyanide, and carbides.

Early chemists believed that the compounds which are obtained from living things: (animals and plants) are called organic compound and which are obtained from minerals are called inorganic compounds.

SYNTHESIS OF FIRST ORGANIC COMPOUND IN THE LABORATORY

For more than 200 years, chemist divided materials into two categories. Those compounds which were isolated from animal and plants were called organic compounds. At one time, chemists believed that organic compounds require a **vital force** for their synthesis which is only present in animals and plants. This theory was called vital force theory. This theory was rejected by Friedrich Wohler when he obtained urea accidentally. Friedrich Wholer was interested in the chemistry of cyanate compounds which contain OCN⁻. In 1828, he tried to synthesize ammonium cyanate from silver cyanate and ammonium chloride. What he expected can be described by the following equation.



The product had isolated from this reaction was white crystalline solid identical to urea which could be isolated from urine.

Actually ammonium cyanate on heating changed to urea.



Ammonium cyanate Urea (organic)

He synthesized organic compound from inorganic compound in the laboratory and vital force theory was rejected.

MODERN DEFINITION OF ORGANIC CHEMISTRY

“The branch of chemistry which deals with the study of hydrocarbons and their derivatives is called organic chemistry.”

Since the synthesis of urea from ammonium cyanate, millions of organic compounds have been prepared and analyzed. All these compounds contain carbon as an essential element. Apart from carbon, most of the organic compounds also contain hydrogen. Other elements which may also be present include oxygen, nitrogen, sulphur, etc. A few of the carbon compounds such as CO, CO₂, carbonates, bicarbonates, etc. are studied as inorganic compounds. It also has been recognized that the chemical forces in organic compounds are similar to those, which exist, in inorganic compounds. Thus it was felt that organic chemistry should be redefined. According to the modern definition, organic chemistry is the branch of chemistry which deals with the study of hydrocarbons and their derivatives.

SOME FEATURES OF ORGANIC COMPOUNDS

Following are some features of organic compounds:

(1) Peculiar Nature of Carbon:

Carbon forms a large number of compounds. There are millions of organic compounds known at present. The main reason for such a large number of compounds is its unique property of linking with other carbon atoms to form long chains or rings. This self-linking property of carbon is called **catenation**. Carbon also forms stable single and multiple bonds with other atoms like oxygen, nitrogen and sulphur etc. It can thus form numerous compounds of various sizes, shapes and structures.

(2) Non-ionic Character of Organic Compounds:

Organic compounds are generally covalent compounds, therefore, do not give ionic reactions.

(3) Similarity in Behaviour:

Organic compounds are classified according to their functional groups. The compounds which contain same type of functional group have same properties. This property is called **homologous series**. This similarity in behaviour has reduced the study of millions of compounds to only a few homologous series.

(4) Complexity of Organic Compounds:

Organic molecules are usually large and structurally more complex. For example, starch has the formula $(C_6H_{10}O_5)_n$ where n may be several thousands. Proteins are very complex molecules having molecular masses ranging from a few thousands to a millions.

(5) Isomerism:

Isomerism is a very common phenomenon in organic compounds. Very often more than one compounds are represented by the same molecular formula. However, they have different structural formulas.

(6) Rates of Organic Reactions:

The reactions involving organic compounds are slow and in general the yields are low. The slowness of the organic reactions is due to the molecular nature of organic compounds.

(7) Solubility:

Most organic compounds are insoluble in water and dissolve readily in non-polar organic solvents, such as, benzene, petroleum, ether etc.

IMPORTANCE OF ORGANIC CHEMISTRY

Organic chemistry has a variety of applications in our lives and too much important. A few areas are highlighted here.

- (1) All chemical reactions that take place in animals and plants involve life molecules like proteins, carbohydrates, enzymes, lipids, vitamins, fats and oils, nucleic acids.
- (2) We are dependent upon the organic compounds in food, clothing and medicines.
- (3) Chemists synthesize plastic, rubber, detergents, medicines, paints, varnishes, fertilizers, artificial fibers, pesticides, cosmetics, soap, cement, dyes etc.

SOURCES OF ORGANIC COMPOUNDS

Initially organic compounds were obtained only from animals and plants. Now a days petroleum, coal and natural gas are the major sources of organic compounds. Petroleum, coal and natural gas are called **fossil fuels** and are formed, by the decay of animals and plants over a long period of time.

(1) Animals and Plants:

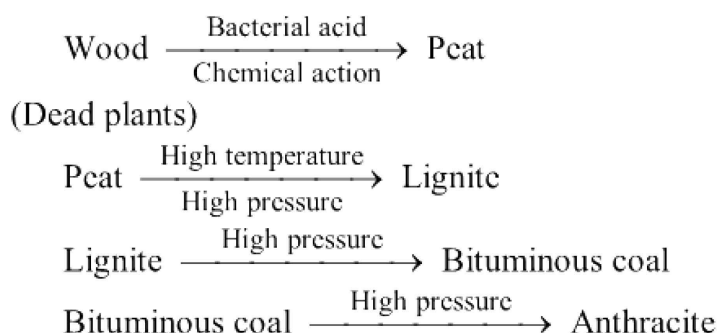
There are so many compounds which are obtained from animals and plants. e.g., proteins, carbohydrates, fats, oils, enzymes, honey, urea, vitamins, dyes, drugs etc.

(2) Coal:

Coal is one of the mankind's primary energy source. Now a days it is a source of many organic compounds as well.

Formation of Coal:

It is believed that coal is formed from vegetable matter (plants) and rocks. About 500 million year ago, under high temperature and pressure and due to some bacterial decomposition, the vegetative material changed to **peat**. Peat is decomposed organic matter. Then, as a result of high temperature and high pressure inside the earth's crust, peat gets transfer into different forms of coal.

**Types of Coal:**

Coal is usually classified on the basis of percentage of carbon contents present in it. Carbon contents in different coals are as follows:

- | | |
|---------------------------|------------------------|
| (1) Peat (59.9%) | (2) Lignite (60 – 70%) |
| (3) Bituminous coal (79%) | (4) Anthracite (91%) |

Destructive Distillation of Coal (Carbonization):

Coal is fuel as well as a source of many organic compounds. Organic compounds from coal are obtained by destructive distillation or carbonization.

"The thermal decomposition of coal in the absence of air at high temperature (500–1000°C) is called carbonization."

In the absence of air, at high temperature coal changes to coke, coal gas and coal tar. Coal tar contains larger number of organic compounds (mostly aromatic) which are separated from each other by fractional distillation.

Composition of Coal Tar:

Coal tar is liquid component of coal. It contains 215 aromatic organic compounds. It is subjected to fractional distillation to get the following products:

- | | |
|---------------------|---------------|
| (i) Light oil | (150 – 200°C) |
| (ii) Middle oil | (200 – 250°C) |
| (iii) Heavy oil | (250 – 300°C) |
| (iv) Anthracite oil | (300 – 350°C) |

Future of Coal in Pakistan:

The total coal resources of Pakistan are estimated by the geological survey of Pakistan to be 184 billion tones. About 80% of this coal is used to bake bricks, in lime kilns, and some quantity is used for domestic purposes.

Sincere efforts are being made by the government to induct coal into industry by setting up coal based power units. The Sindh coal Authority and the directorates of Mineral Development of the Punjab, Baluchistan and NWFP are all keen to expand coal utilization in power generation for which many incentives have been given.

(3) Natural Gas:

Natural gas is a mixture of low boiling hydrocarbons. Major portion of the natural gas is methane (80–85%), 8–10% is ethane and rest of propane and butene, ethene etc.

Natural gas is also formed by the decomposition of organic matter under high pressure.

Natural gas is an important energy source in Pakistan. In Pakistan, natural gas is a cheaper source of energy and used in cement industries, fertilizer industries, thermal power stations and domestic purposes.

(4) Petroleum:

The word “petroleum” means “oil of rocks”. Crude petroleum is black or greenish black in colour. It is a mixture of many hydrocarbons from C_1 to C_{40} . Petroleum is also a **fossil fuel** and called “**rock oil**” or “**crude oil**” or “**mineral oil**”.

Fractional Distillation of Petroleum:

“Fractional distillation is a method used to separate components of a mixture on the basis of difference in their boiling points.”

The fractions of the petroleum, their boiling point ranges and uses are given below in the table:

Table – Principal fractions obtained from petroleum

Boiling point range °C	No. of carbons atoms in the fraction	Name of the fraction and principal uses
Below 20	C_1-C_4	Natural gas: As fuel for heating and cooking. Raw materials for other chemicals.
20–60	C_5-C_6	Petroleum ether: As a non-polar solvent and cleansing fluid.

60–100	C ₆ –C ₇	Ligroin or light naphtha: As a non-polar solvent and cleansing fluid.
40–200	C ₅ –C ₁₀	Gasoline or petrol: Fuel for vehicles.
175–325	C ₁₁ –C ₁₂	Kerosene: Used for domestic purposes, jet fuel.
Nonvolatile liquids	C ₁₈ and up	Lubrication oil: Used for lubrications.
Nonvolatile solids M.P. 50–60°C	C ₂₃ –C ₂₉	Paraffin: Wax products like candles, polishes.
Solids	Residue	Asphalt or petroleum coke: Roofing, paving, fuel, reducing agent.

Oil Refineries in Pakistan:

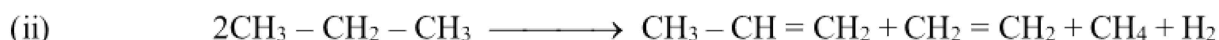
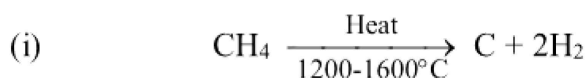
At present, four oil refineries are in operation in our country. One oil refinery known as Attack Oil refinery is located at Morgah near Rawalpindi. It has about 1.25 million tones oil refining capacity. Similarly two oil refineries have been established at Karachi National Oil Refinery and Pakistan Oil Refinery which have about 2.13 million tones of oil refining capacity. Another refinery known as Pak Arab refinery is located at Mahmud Kot near Multan.

CRACKING

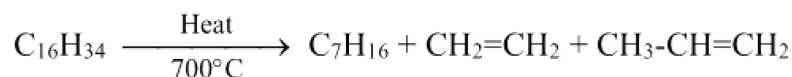
“Thermal decomposition of hydrocarbons in the absence of air is called cracking.”

This is the process in which C-C bonds in long chain alkane molecules are broken, producing smaller molecules of both alkanes and alkenes. The composition of the products depends on the condition under which the cracking takes place.

For example, by cracking of natural gas, hydrogen gas is produced.



A higher hydrocarbon C₁₆H₃₄ splits up as:



Hexadecane

Heptane

Ethene

Propene

(Such reactions cannot be balanced because products are not fixed)

Significance of Cracking:

- (1) With the help of cracking process, industrially, **hydrogen gas** is produced in our country to manufacture vegetable ghee.
- (2) Fractional distillation of petroleum yields only 20% gasoline. Due to its greater demand, deficiency of gasoline is recovered by converting higher hydrocarbon such as kerosene to gasoline by cracking process. In other words, **yield of gasoline** is increased by cracking.
- (3) With the help of cracking process large amount of useful **by-products** such as ethane, propene, butene, benzene etc., are obtained. These by products are used for the manufacture of drugs, plastics, detergents, synthetic fiber, fertilizers, pesticides, weed killers and important industrial and laboratory chemicals like ethanol, acetone and phenol.
- (4) Through cracking process, octane number of gasoline is increased and it is called re-forming process.

TYPES OF CRACKING

(1) Thermal Cracking:

Breaking down of large molecules by heating at high temperature and pressure is called **thermal cracking**. It is particularly useful in the production of unsaturated hydrocarbons such as ethene and propene.

(2) Catalytic Cracking:

Higher hydrocarbons can be cracked at lower temperature (500°C) and lower pressure (2 atm), in the presence of a suitable catalyst. A typical catalyst used for this purpose is a mixture of silica (SiO_2) and alumina (Al_2O_3). Catalytic cracking produces gasoline of higher octane number and, therefore, this method is used for obtaining better quality gasoline.

(3) Steam Cracking:

In this process, higher hydrocarbons in the vapours phase are mixed with steam, heated for a short duration to about 900°C and cooled rapidly. The process is suitable for obtaining lower unsaturated hydrocarbons.

REFORMING OF PETROLEUM

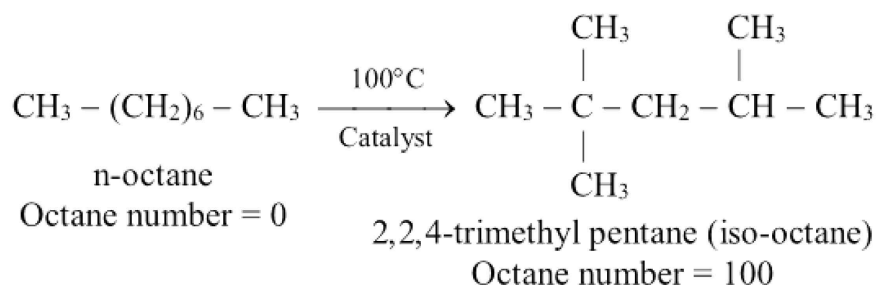
“The process to increase the octane number by conversion of straight-chain alkanes into branched chain alkenes is called reforming of petroleum.”

The octane number of any fuel is the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane.

The octane number of n-heptane is zero, it is a bad fuel while that of iso-octane is 100. The mixture that contains the ratio of iso-octane and n-heptane as 8 : 2 have octane number 80. Gasoline having low octane number have greater knocking and vice versa.

“Knocking is a sharp metallic sound produced in the internal combustion engine.”

In reforming process, gasoline is heated to a temperature of about 100°C for a very short time, in the presence of aluminium chloride, AlCl_3 or platinum catalyst. The high pressure is maintained in such a way that molecules do not crack but are reformed by isomerization. The purpose of reforming is to increase the octane numbers. For example, n-octane can be converted into iso-octane as follows:



The octane number of a poor fuel can also be improved by blending it with a small amount of additive like tetraethyl lead (TEL). **Tetraethyl lead** $(\text{C}_2\text{H}_5)_4\text{Pb}$, is an efficient antiknock agent but has one serious disadvantage; its combustion product, lead oxide, is reduced to metallic lead which is discharged into the air through the exhaust pipe and causes air pollution.

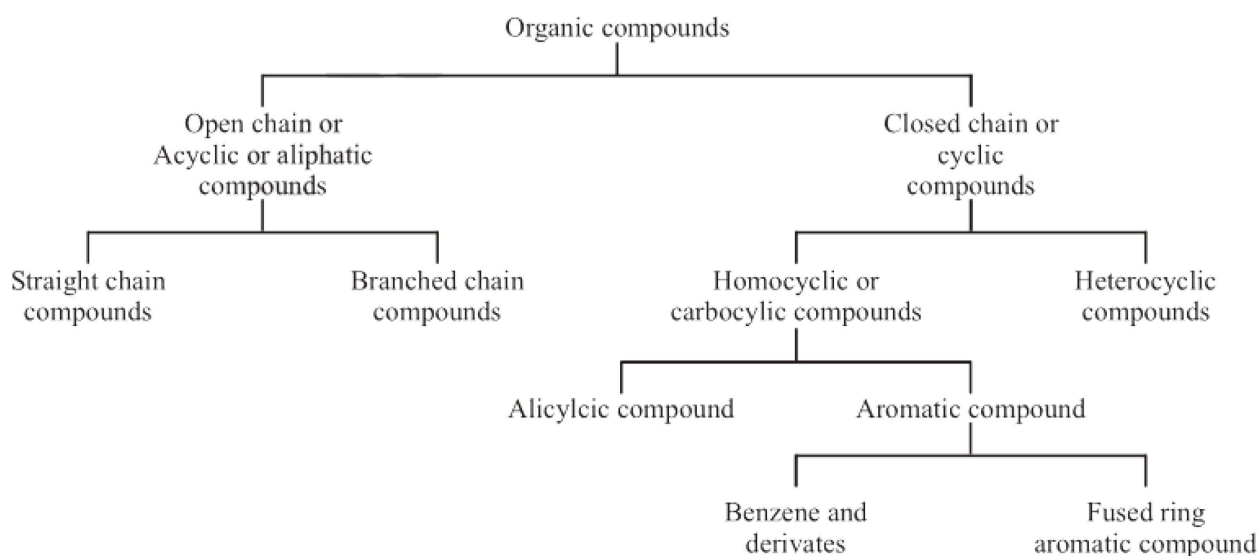
How to Improve Octane Number?

- | | |
|-----------------------------------|-------------------|
| (1) By adding anti-knocking agent | (2) Reforming |
| (3) Hydroforming | (4) Isomerization |

Regular gasoline has octane number 74. It is used in cars and buses. Octane number of 2, 2, 3 trimethyl butane is 124. It is superior to iso-octane.

CLASSIFICATION OF ORGANIC COMPOUNDS

There are millions of organic compounds. It is not possible to study each individual compound to facilitate their study. Organic compounds are classified into various groups and sub-groups. Organic compounds are classified into following groups.

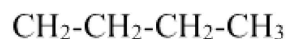


(1) Open Chain or Acyclic or Aliphatic Compounds:

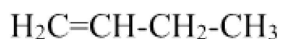
“Organic compounds with open chain of carbon atoms are called open chain or acyclic or aliphatic compounds.”

There are two types of organic compounds:

Open chain and closed chain compounds. Open chain compounds are of two types: straight chain and branched chain compounds.

(i) Straight Chain Compounds:

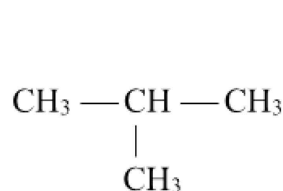
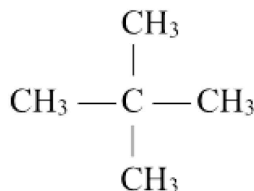
Butane



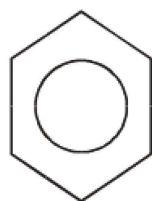
1-Butene



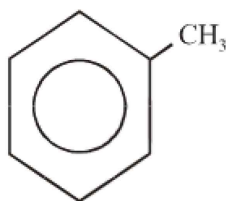
1-Butanol

(ii) Branched Chain Compounds:2-Methylpropane
(iso-Butane)2, 2 Dimethylpropane
(neo-pentane)**(2) Closed Chain or Cyclic Compounds:**

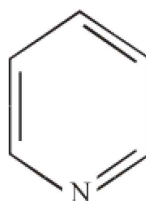
The compounds which contain one or more closed ring of carbon atoms or atoms of carbon and one or more other element (N, S or O) are called cyclic compounds.



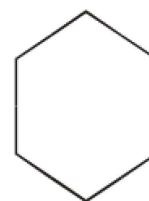
Benzene



Toluene



Pyridine



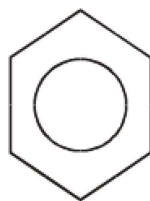
Cyclohexane

Cyclic compounds are of two types:

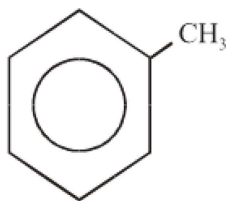
- (a) Homocyclic or carbocyclic compounds
- (b) Heterocyclic compounds

(a) Homocyclic or Carbocyclic Compounds:

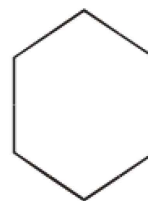
“Organic compounds with closed ring of carbon atoms are called homocyclic or carbocyclic compounds.”



Benzene



Toluene

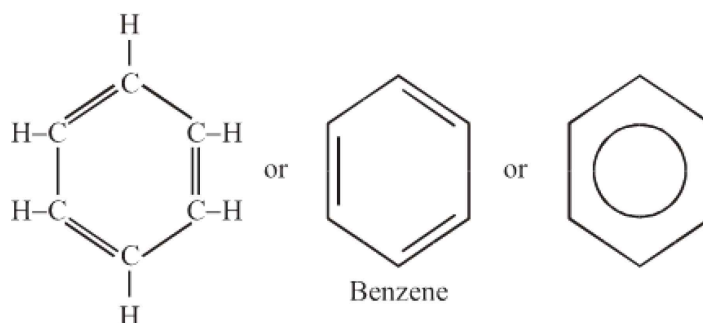


Cyclohexane

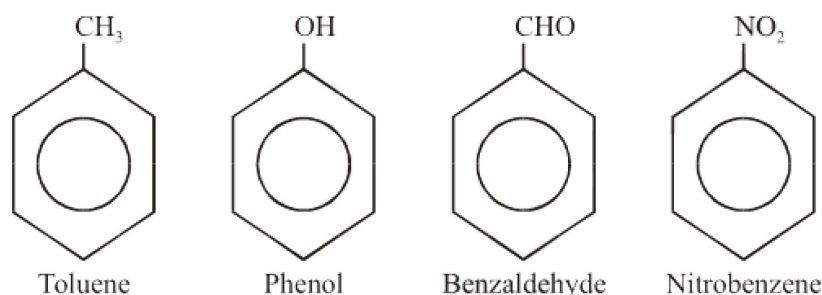
Homocyclic compounds are of two types:

(i) **Aromatic Compounds:**

The carbocyclic compounds which contain at least one benzene ring (six carbon atoms with alternate double and single bonds) are called aromatic compounds. e.g.,

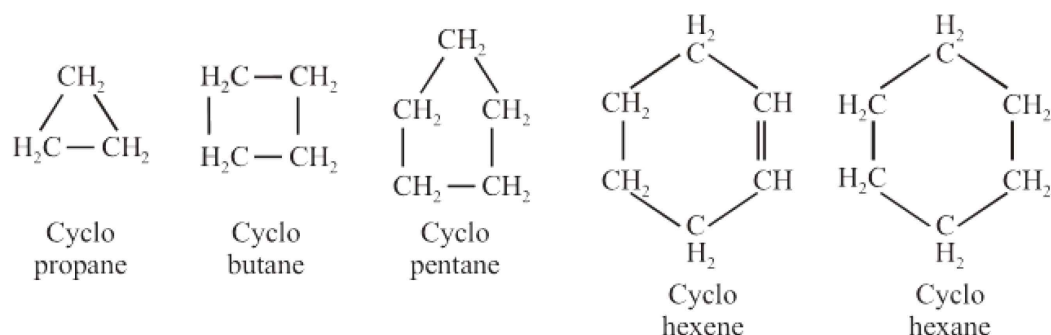


The aromatic compounds may have a side-chain or a functional group attached to the ring. For example:



(ii) **Alicyclic Compounds:**

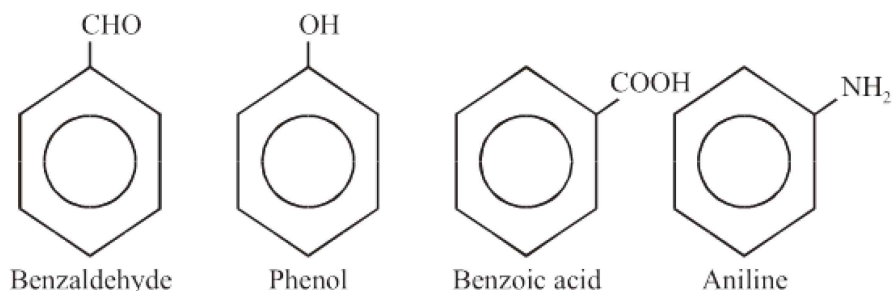
“The homocyclic compounds which contain a ring of three or more carbon atoms and resembling aliphatic compounds are called alicyclic compounds.” The saturated alicyclic hydrocarbons have the general formula C_nH_{2n} . Typical alicyclic compounds are given below.



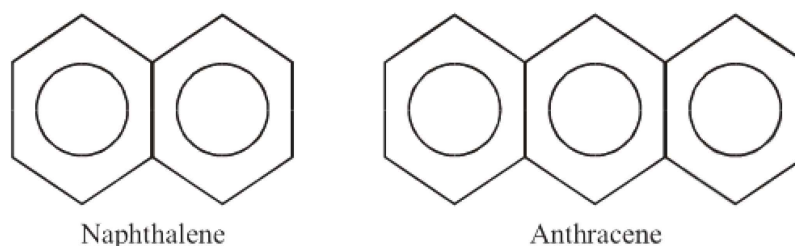
Aromatic compounds are further classified as

- ◆ Single ring compounds or benzene derivatives
- ◆ Fused ring aromatic compounds

- ◆ **Benzene and its derivatives:** The compounds which contain benzene ring with some functional group are called derivative of benzene. e.g.,

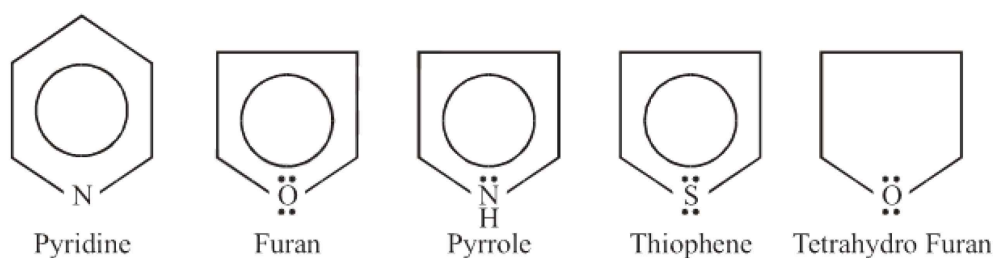


- ◆ **Fused ring compounds:** The compounds which contain more than one benzene rings fused together are called fused ring compounds.



(b) Heterocyclic Compounds:

“The compounds in which the ring consists of atoms of more than one kind are called **heterocyclic** compounds or **heterocycles**.” In heterocyclic compounds, generally one or more atoms of elements such as nitrogen (N), oxygen (O) or sulphur (S) are present. The atom other than carbon present in the ring is called a **hetero atom**.



HYDROCARBONS

“The compounds which contain carbon and hydrogen are called hydrocarbons.” Hydrocarbons may be aliphatic, alicyclic or aromatic.

Alkanes (aliphatic hydrocarbons):

The aliphatic hydrocarbons in which carbon atoms are joined by single covalent bonds only. The compounds in which carbon atoms are joined by single covalent bonds are called saturated hydrocarbons.

All alkanes are saturated hydrocarbons e.g., methane, ethane, propane etc. The general formula of saturated hydrocarbons is C_nH_{2n+2} . Where n is the number of carbon atoms in alkanes.

The term alkane can be split up into two parts.

Alk-This is the general term for meth, eth, prop, but, pent. This indicates the number of carbon atoms in the alkane or alkyl group.

-ane indicates that hydrocarbon is saturated.

Alkane	Formula	Alkane	Formula
Methane	CH_4	Hexane	C_6H_{14}
Ethane	C_2H_6	Heptane	C_7H_{16}
Propane	C_3H_8	Octane	C_8H_{18}
Butane	C_4H_{10}	Nonane	C_9H_{20}
Pentane	C_5H_{12}	Decane	$C_{10}H_{22}$
Eicosane	$C_{20}H_{42}$	Hectane	$C_{100}H_{202}$

Alkyl Radicals:

“A group of atoms formed when a hydrogen atom is removed from an alkane is called alkyl radical.”

It is represented by a symbol “R” and the general formula C_nH_{2n+1} . It is a portion of molecule and has no independent existence. The group is named by replacing the “ane” of alkane by “yl”.

Table – Alkane and Alkyl group

Alkane	Formula	Alkyl group	Formula
Methane	CH_4	Methyl	CH_3^-
Ethane	C_2H_6	Ethyl	$C_2H_5^-$
Propane	C_3H_8	Propyl	$C_3H_7^-$
Butane	C_4H_{10}	Butyl	$C_4H_9^-$

Structure of some alkyl radicals

Alkane	Alkyl	
CH ₄ methane	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}- \\ \\ \text{H} \end{array} \quad \text{or} \quad \text{CH}_3-$ Methyl	
CH ₃ -CH ₃ Ethane	CH ₃ -CH ₂ - Ethyl	
CH ₃ -CH ₂ -CH ₃ Propane	CH ₃ -CH ₂ -CH ₂ - n-Propyl	$\begin{array}{c} \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$ Iso-propyl
CH ₃ -CH ₂ -CH ₂ -CH ₃ n-butane	CH ₃ -CH ₂ -CH ₂ -CH ₂ - n-butyl	$\begin{array}{c} \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$ Sec-butyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$ Iso-butane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2- \end{array}$ Iso-butyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}- \\ \\ \text{CH}_3 \end{array}$ Ter-butyl
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ Neopentane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$ Neopentyl	

FUNCTIONAL GROUP

“An atom or a group of atoms or a double bond or a triple bond which confers characteristic properties to an organic compounds is called a functional group, because they are chemically functional parts of molecules.”

The compounds which have same functional group in them, have same chemical properties. There are about six millions of organic compounds but there are very few

functional groups. e.g., -OH alcohol, $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{OH} \end{array}$ carboxylic acid, -NH₂ amine, $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{H} \end{array}$ aldehyde, etc.

A list of functional groups and their associated types of compounds are given below. This list is not comprehensive, functional groups are usually written as suffix after the name of root or as prefix (before the name).

Type of compound	Structure of functional group	Suffix or prefix	Examples (common name is in bracket)
Alkane	$\begin{array}{c} \quad \\ -C-C- \\ \quad \end{array}$	-ane	CH ₃ -CH ₃ Ethane
Alkene	$\begin{array}{c} \quad \\ -C=C- \end{array}$	-ene	CH ₂ =CH ₂ Ethene
Alkyne	-C≡C-	-yne	HC≡CH Ethyne
Alkyl halide	-X	Halo (chloro, bromo, iodo)	CH ₃ -Cl Chloromethane
Alcohol	-OH	-ol	CH ₃ -OH Methanol
Amine	-NH ₂	amine	CH ₃ -CH ₂ -NH ₂ (Ethyl amine)
Imine	=NH	imine	$\begin{array}{c} H \\ \diagup \\ C=NH \\ \diagdown \\ H \end{array}$ (Methyl imine)
Ether	C-O-C	ether	CH ₃ -O-CH ₃ (Dimethyl ether)
Aldehyde	$\begin{array}{c} O \\ \\ -C-H \end{array}$	-al	$\begin{array}{c} O \\ \\ CH_3-C-H \end{array}$ Ethanal
Ketone	$\begin{array}{c} O \\ \\ R-C-R \end{array}$	-one	$\begin{array}{c} O \\ \\ CH_3-C-CH_3 \end{array}$ (Dimethyl ketone) 2-Propanone

Carboxylic acid	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OH} \end{array}$	–oic acid	CH_3COOH Ethanoic acid (Acetic acid)
Acid halide	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{X} \end{array}$	–oyl halide	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{Cl} \end{array}$ Ethanoyl chloride (Acetyl chloride)
Acidamide	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{NH}_2 \end{array}$	–amide	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{NH}_2 \end{array}$ Ethanamide (Acetamide)
Ester	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OR} \end{array}$	–oate	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{OC}_2\text{H}_5 \end{array}$ Ethyl ethanoate (Ethyl acetate)
Acid anhydride	$\begin{array}{cc} \text{O} & \text{O} \\ & \\ -\text{C}-\text{O}-\text{C}- \end{array}$	–oic anhydride	$\begin{array}{cc} \text{O} & \text{O} \\ & \\ \text{CH}_3-\text{C}-\text{O}-\text{C}-\text{CH}_3 \end{array}$ Ethanoic anhydride (Acetic anhydride)
Thio alcohol or thiol	–SH	–thiol	CH_3-SH Methanethiol (Methane thio alcohol) (Methyl mercaptan)
Alkyl cyanide or alkyl nitrile	–C≡N	cyano	$\text{CH}_3-\text{C}\equiv\text{N}$ Cyanomethane (Methyl cyanide) (Ethane nitrile) IUPAC name
Nitroalkane	$\begin{array}{c} \text{O} \\ \\ -\text{N}\rightarrow\text{O} \end{array}$	nitro	$\text{CH}_3-\text{CH}_2-\text{NO}_2$ Nitroethane

SOME DERIVATIVES OF HYDROCARBONS

“The study of hydrocarbons and their derivatives is called organic chemistry.”

Definition and examples of some derivatives are given below:

(1) Alkenes ($> \text{C} = \text{C} <$):

The hydrocarbon in which double bond is present between two carbon atoms. It is called alkene. Alkenes have general formula C_nH_{2n} . e.g.,

Formula	Common name	IUPAC name	Radical
$\text{CH}_2 = \text{CH}_2$	Ethylene	Ethene	$\text{CH}_2 = \text{CH} -$ Vinyl
$\text{CH}_2 = \text{CH} - \text{CH}_3$	Propylene	Propene	$\text{CH}_2 = \text{CH} - \text{CH}_2 -$ Allyl
$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$	Butylene	1-butene	$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 -$ Butenyl
$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$	Butylene	2-butene	$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 -$ Crotyl

(2) Alkynes ($-\text{C} \equiv \text{C}-$):

“The hydrocarbon in which triple bond is present between two carbon atoms are called alkynes.” The general formula of alkyne is $\text{C}_n\text{H}_{2n-2}$. e.g.,

Formula	Common name	IUPAC name
$\text{HC} \equiv \text{CH}$	Acetylene	Ethyne
$\text{HC} \equiv \text{C} - \text{CH}_3$	Methyl acetylene	Propyne
$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	Dimethyl acetylene	2-butyne

(3) Alkyl Halides ($\text{R} - \text{X}$):

“If hydrogen atom of hydrocarbon is replaced by halogen atom, it is called alkyl halides.” The general formula of alkyl halides is $\text{C}_n\text{H}_{2n+1}\text{X}$. e.g.,

Formula	Common name	IUPAC name
$\text{CH}_3 - \text{Cl}$	Methyl chloride	Chloromethane
$\text{C}_2\text{H}_5 - \text{Cl}$	Ethyl chloride	Chloroethane
$\begin{array}{c} \text{Br} \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_3 \end{array}$	Iso-propyl bromide	2-bromopropane

(4) Alcohol ($\text{R} - \text{OH}$):

“If hydrogen atom of hydrocarbon is replaced by hydroxyl group ($-\text{OH}$), it is called an alcohol.” The general formula of monohydric alcohol (having one $-\text{OH}$ group) is $\text{C}_n\text{H}_{2n+1}\text{OH}$.

Formula	Common name	IUPAC name
CH ₃ OH	Methyl alcohol	Methanol
C ₂ H ₅ OH	Ethyl alcohol	Ethanol
CH ₃ – CH ₂ – CH ₂ – OH	n-propyl alcohol	1-propanol

(5) Amines (R – NH₂):

If hydrogen atom of hydrocarbon is replaced by amino group, it is called amine. The general formula of primary amine is C_nH_{2n+1}NH₂.

Formula	Common name	IUPAC name
CH ₃ – NH ₂	Methyl amine	Aminomethane
C ₂ H ₅ – NH ₂	Ethyl amine	Aminoethane
CH ₃ – CH ₂ – CH ₂ – NH ₂	n-propyl amine	1-aminopropane

(6) Ether (R – O – R):

“If oxygen atom is attached with two similar or dissimilar alkyl or aryl group, it is called ether.” e.g.,

Formula	Common name	IUPAC name
CH ₃ – O – CH ₃	Dimethyl ether	Methoxy methane
C ₂ H ₅ – O – C ₂ H ₅	Diethyl ether	Ethoxyethane
CH ₃ – O – C ₂ H ₅	Ethyl-methyl ether	Methoxyethane
C ₂ H ₅ – O – CH ₂ – CH ₂ – CH ₃	Ethyl n-propyl ether	Ethoxy-propane

**(7) Aldehyde (R – C – H):**

If hydrogen atom of hydrocarbon is replaced by aldehydic group (–CHO), it is called aldehyde. Systematic names are obtained by replacing suffix “e” of the alkane by “al”. e.g.,

Formula	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH ₃ – CHO	Acetaldehyde	Ethanal
CH ₃ – CH ₂ – CHO	Propionaldehyde	Propanal

$$\begin{array}{c} \text{O} \\ || \\ \text{R} - \text{C} - \text{R} \end{array}$$

(8) Ketone (R – C – R):

“The carbonyl compound, $> \text{C} = \text{O}$, in which two valencies of carbon are satisfied by the two alkyl group are called ketones.” Systematic names are obtained by replacing suffix “e” of the alkane by “one”. e.g., General formula of ketone is $\text{R} - \text{CO} - \text{R}$.

Formula	Common name	IUPAC name
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \end{array}$	Dimethyl ketone	2-propanone
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 \text{CH}_3 \end{array}$	Ethyl-methyl ketone	2-butanone
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 \text{CH}_3 \end{array}$	Diethyl ketone	3-pentanone

$$\begin{array}{c} \text{O} \\ || \\ \text{R} - \text{C} - \text{OH} \end{array}$$

(9) Carboxylic Acids (R – C – OH):

“The carbonyl compound $> \text{C} = \text{O}$ in which one valency of carbon is satisfied by $-\text{OH}$ and other valency is satisfied by alkyl or hydrogen atom is called carboxylic acid.” Systematic names are obtained by replacing “e” of the alkane by suffix “-oic acid”. e.g.,

Formula	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid

(10) Thiols or Thioalcohol or Mercaptans:

“If hydrogen atom of alkane is replaced by SH group, it is called thiols or mercaptans.” Systematic names are obtained by adding suffix “thio” with the name of alkane.

Formula	Common name	IUPAC name
$\text{CH}_3 - \text{SH}$	Methyl mercaptan or Methyl thioalcohol	Methane thiol
$\text{CH}_3 - \text{CH}_2 - \text{SH}$	Ethyl mercaptan or Ethyl thioalcohol	Ethane thiol

HYBRIDIZATION OF ORBITALS AND THE SHAPES OF MOLECULES

Although the most stable electronic configuration of a carbon atom (having two partially filled 2p-orbitals) requires it to be divalent, carbon is tetravalent in the majority of its compounds. In order to explain this apparent anomaly, it is assumed that an electron from the 2s-orbital is promoted to an empty 2p_z orbital, giving the electronic configuration.

Ground state electronic configuration of carbon	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$
Excited state electronic configuration of carbon	$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

The excited state configuration can explain the tetravalency of carbon but these four valencies will not be equivalent. Orbital hybridization theory has been developed to explain the equivalent tetravalency of carbon.

According to this theory, four atomic orbitals of carbon belonging to valence shell may be mixed in different ways to explain the bonding and shapes of molecules formed by carbon atoms.

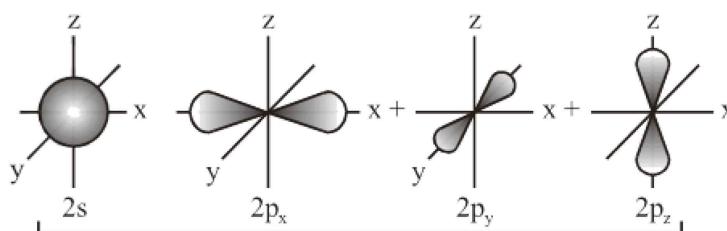
sp³-hybridization:

“The process of mixing of one s-orbital and three p-orbitals of same shell to form four new equivalent orbital with same energy and shape is called sp³-hybridization.”

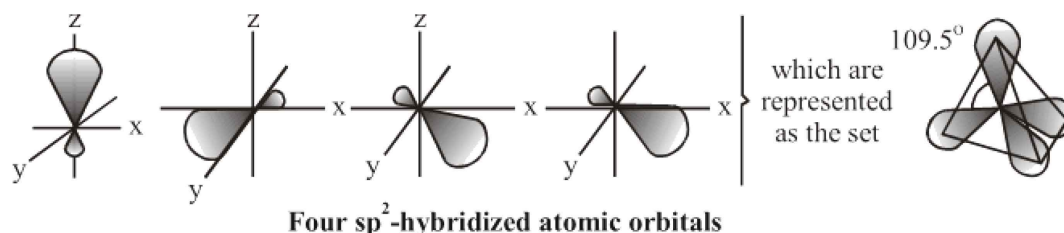
All the carbon atoms which are attached with four atoms are sp³-hybridized. The electronic configuration of carbon in ground state and excited is given below:

Ground state electronic configuration of carbon	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$
Excited state electronic configuration of carbon	$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

One s-orbitals and three p-orbital intermix to four new orbitals.



Unhybridized atomic orbitals of carbon



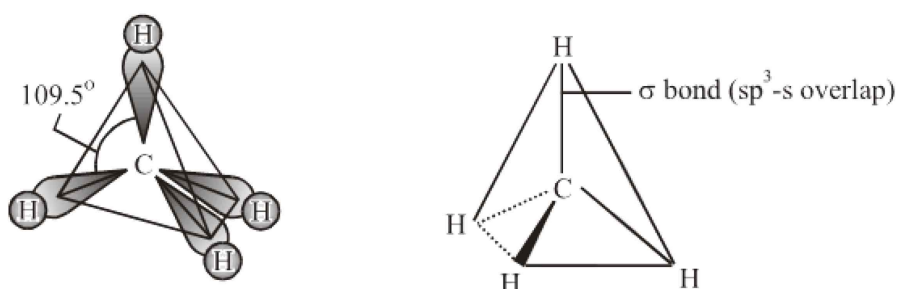
Four sp³-hybridized atomic orbitals

All these sp^3 -hybrid orbitals are degenerate (having equal energy) and are directed at an angle of 109.5° in space to give a tetrahedral geometry.

When a carbon atom forms single bonds with other atoms, these hybrid overlap with the orbitals of other atoms to form four sigma bonds. This type of hybridization explains the bonding and shapes of all those compounds in which carbon atom is saturated.

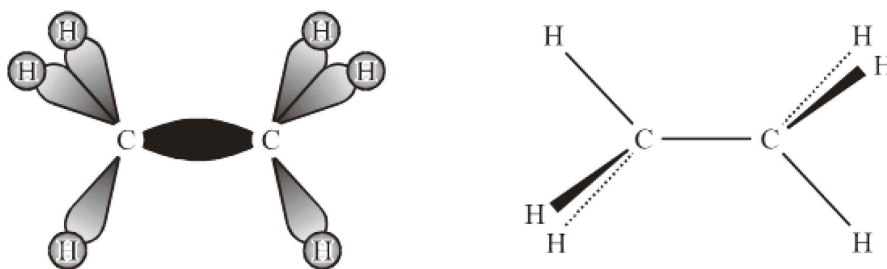
STRUCTURE OF METHANE CH_4

In the formation of methane, the four hybrid atomic orbitals of carbon overlap separately with four $1s$ atomic orbitals of hydrogen to form four equivalent C-H bonds. The shape of methane thus formed is tetrahedral. All the four hydrogen atoms do not lie in the same plane. Electron density is between two nuclei in case of sigma bonds.



STRUCTURE OF ETHANE (CH_3-CH_3)

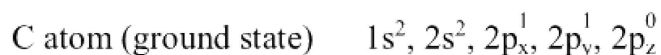
In case of ethane, each carbon is sp^3 -hybridized. Structure on each carbon is tetrahedral and two tetrahedrons join together. In ethane one sigma bond is formed by the overlapping of sp^3 -hybrid orbital one carbon and sp^3 -hybrid orbital of other carbon atom. Six sigma bonds are present between carbon and hydrogen atoms. In these bonds sp^3 -hybrid orbital of carbon overlap with partially filled s -orbital of hydrogen atoms.



Carbon atoms of all saturated hydrocarbons have sp^3 -hybridization. All the bond angles between H-C-H are 109.5° .

Tetravalent carbon atom is more stable than divalent carbon atom, why?

In case of carbon when an electron is promoted from 2s orbital to 2p orbital, same amount of energy is needed. For this purpose 406 kJ/mol^{-1} energy is needed.



After mixing of one 2s-orbital and three p-orbitals, four new orbitals of equivalent energy and shape are formed. In CH_4 , when four partially filled hybrid orbitals overlap with s-orbital of hydrogen, some amount of energy is released and it becomes stable. When CH_4 molecules is formed, it is an exothermic reaction and $-2068 \text{ kJ/mol}^{-1}$ energy is released. The amount of energy released is greater than the amount of energy absorbed. So a tetravalent carbon atom is expected to be more stable than divalent carbon.

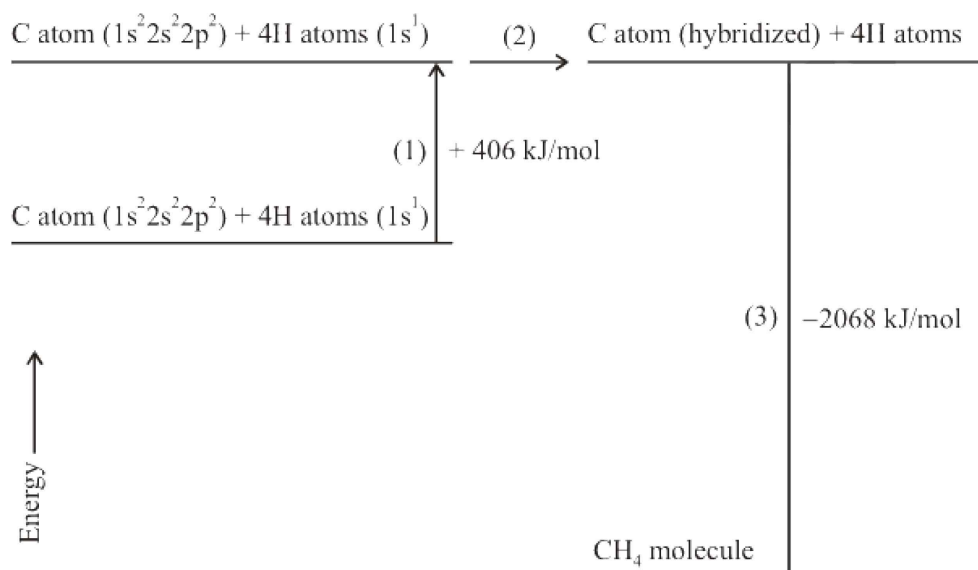


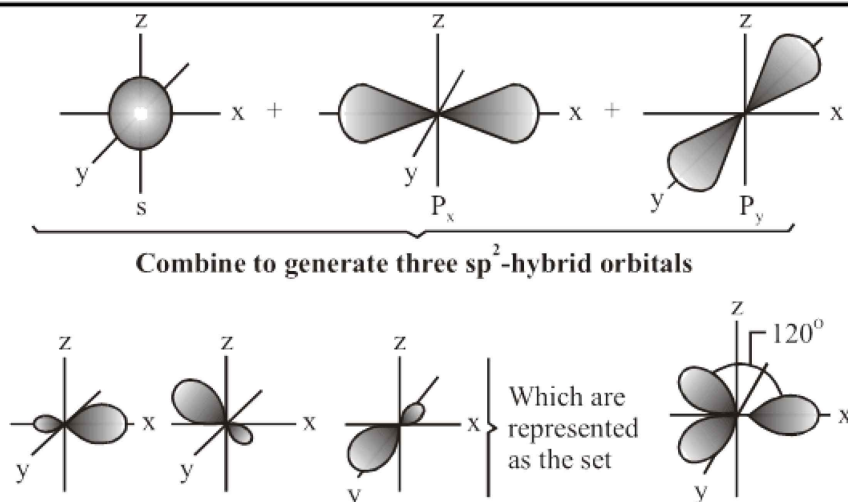
Figure 1 after promotion of electron, orbitals are hybridized 2-formation of CH_4 releases 2068 kJ/mol of energy. These three steps occur simultaneously as bond is formed.

 sp^2 -HYBRIDIZATION

“The process of mixing one s-orbital and two p-orbitals to get three new equivalent sp-hybrid orbitals is called sp^3 -hybridization.”

The sp^2 -hybridization occurs when a carbon atom in a molecule is attached to three other atoms.

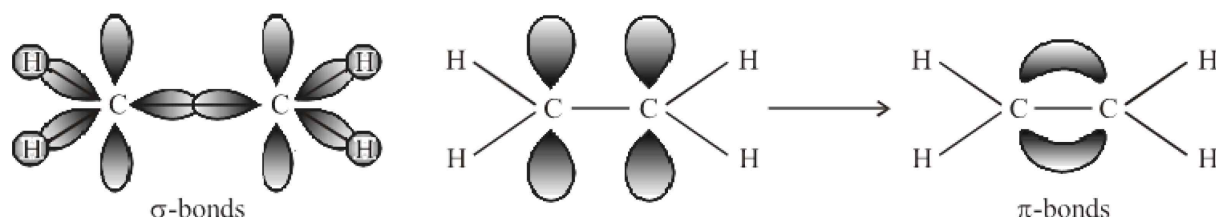
The structure of alkenes can be explained by sp^2 mode of hybridization. In this type, one 2s and two 2p-orbitals are mixed together to give three equivalent and coplanar sp^2 -hybrdized orbitals.



Each sp^2 -hybrid orbital is directed from the centre of an equilateral triangle to its three corners. The bond angle between any two sp^2 -hybrid orbitals is 120° . The unhybridized $2p_z$ orbital will remain perpendicular to the triangle which is formed.

STRUCTURE OF ETHENE ($\text{CH}_2 = \text{CH}_2$)

In ethene, each carbon atom is attached to two hydrogen atoms by single bonds and to another carbon atom by a double bond. Since each carbon is attached to three other atoms, it uses sp^2 -orbitals and an unhybridized p-orbital to form its bonds. There are four C – H single bonds. Each C – H bond is a σ bond and is formed by the overlap of sp^2 -orbital from carbon and $1s$ orbital from hydrogen. One of the two bonds in the double bond is also a σ bond and forms by the linear overlap of sp^2 -orbitals, one from each carbon atom.

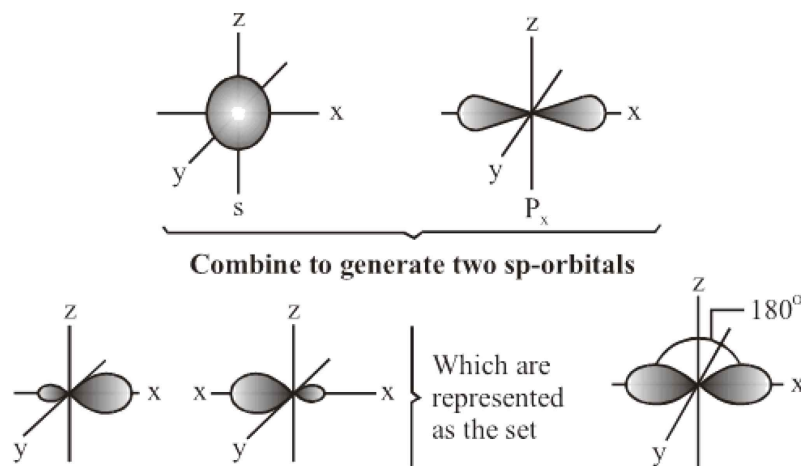


The second bond in the double bond is a π -bond which forms by the parallel overlap of two unhybridized p-orbitals. Ethene is a planar molecule. All bond angles are of 120° . Electron density in case of π -bond is above and below the bond axis. π -bonds is weaker bond than the sigma. Due to this exposed π -bond, alkenes are more reactive than σ -bond. Alkenes are restricted bond and cannot be rotated and gave the idea of geometrical isomers.

sp-HYBRIDIZATION

“The process of mixing of one s-orbital and one p-orbital to form two new hybrid orbitals of equivalent shape and energy is called sp-hybridization.”

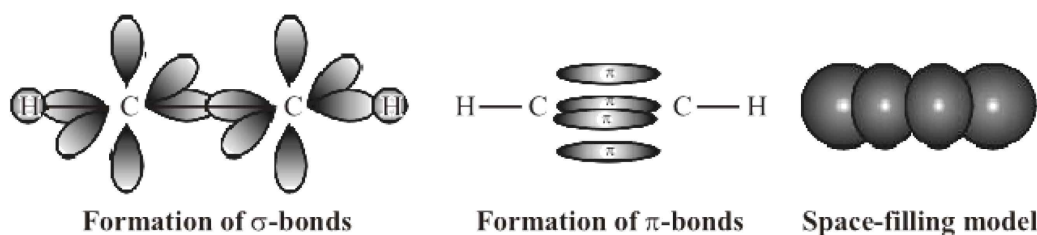
Structure of alkynes can be explained with the help of sp -hybridization. The hybridized orbitals have same energy (degenerate). The orbitals have linear shape with a bond angle of 180° . The two unhybrid p -orbitals, $2p_y$ and $2p_x$ are perpendicular to these sp -hybridized orbitals.



STRUCTURE OF ETHYNE ($\text{HC} \equiv \text{CH}$)

In ethyne, each carbon atom is attached to one hydrogen atom by a single covalent bond and to another carbon atom by a triple bond. Since each carbon is attached to two other atoms, it uses two sp -hybrid orbitals and two unhybridized $2p$ -orbitals. There are two $\text{C} - \text{H}$ single bonds and one carbon-carbon triple bond. Each $\text{C} - \text{H}$ bond is a σ -bond and is formed by the overlap of sp -orbital from carbon and $1s$ orbital from hydrogen. One of the three bonds is a σ -bond and is formed by the linear overlap of the two sp -orbitals, one from each carbon. The other two bonds in the triple bond are π -bonds and are formed due to the parallel overlap of the unhybridized p -orbitals on each carbon. Ethyne is a linear molecule. The bond angle is of 180° .

The presence of a σ and two π -bonds between two carbon atoms is responsible for shortening the bond distance.



Molecular Formula:

“The formula which gives the actual number of different atoms of elements in a molecule is called molecular formula.” e.g., CH_3OH methanol, $\text{C}_2\text{H}_5\text{OH}$ ethanol, CH_3COOH acetic acid, C_4H_{10} butane etc.

Structural Formula:

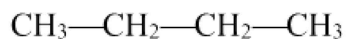
The formula which describe the arrangement of atoms of different elements in a molecule is called structural formula. e.g.,

Name of compound	Molecular formula	Structural formula
Ethanol	C_2H_5OH	$ \begin{array}{c} H \quad H \\ \quad \\ H-C-C-OH \\ \quad \\ H \quad H \end{array} $
Propane	C_3H_8	$ \begin{array}{c} H \quad H \quad H \\ \quad \quad \\ H-C-C-C-H \\ \quad \quad \\ H \quad H \quad H \end{array} $

ISOMERISM

“The compounds which have same molecular formula but different arrangement of atoms are called isomers and phenomenon is called isomerism.”

Methane, ethane and propane have only one arrangement of atoms and have no phenomenon of isomerism. Butane has two isomers or two possible arrangements of atoms.

Isomers of Butane (C_4H_{10}):

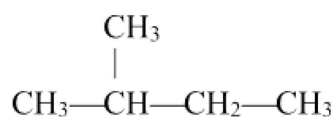
n-Butane



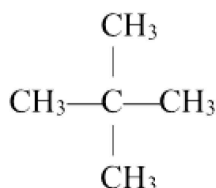
iso-Butane

Isomers of Pentane (C_5H_{12}):

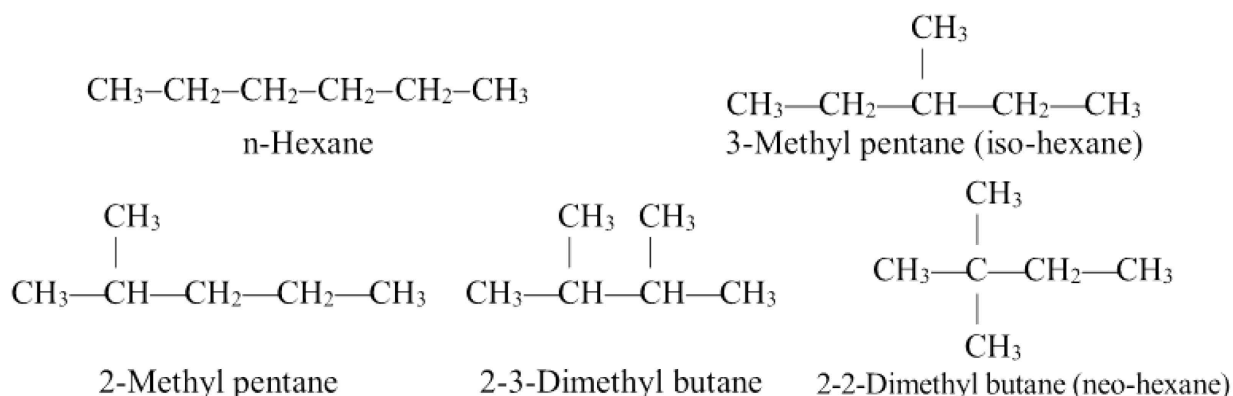
n-Pentane



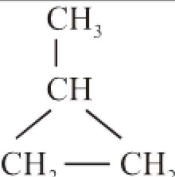
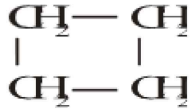


2-Methyl butane



2,2 Dimethyl propane (neo-pentane)

Isomers of Hexane (C₆H₁₄):**Isomers of C₄H₈:**

$\text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{CH}_3$ 1-butene	 Cis-2-butene	 Trans-2-butene
 Methyl cyclopropane		 Cyclobutane

As the number of carbon atoms, in a hydrocarbon increases, the number of possible isomers increases very rapidly. Butane has two, pentane has three and hexane has five structural isomers. Decane has 75 isomers and Eicosane has 366319 isomers. When the number of carbon atoms increases to 30, the number of possible isomers (geometrical and structural) should be over four billions.

TYPES OF ISOMERISM
(1) Structural Isomerism:

“The compounds which have same molecular formula but different structural formula are called structural isomers.”

The structural isomers are not confined only to hydrocarbons. This isomerism is present in every functional group. The structural isomerism arises due to the difference of arrangement of carbon atoms in a molecule. The structural isomers have following four types:

(i) Chain Isomerism (Skeletal Isomerism):

“The compounds which have same molecular formula but different length of chain of carbon atoms, are called chain isomers.” And this phenomenon is called chain isomerism. For example, pentane (C₅H₁₂) has three chain isomers.

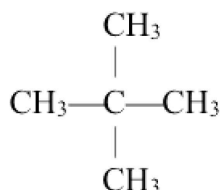
It is also called “Skeletal Isomerism”.



(n-Pentane)



2-Methyl butane (iso-pentane)

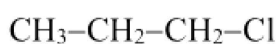


2,2-Dimethyl propane (neo-pentane)

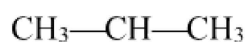
(ii) Positional Isomerism:

“This type of isomerism arises due to the difference in the position of the same functional group on the carbon chain.” The arrangement of carbon atoms remains the same. For example:

- (a) Chloropropane can have two positional isomers given below:

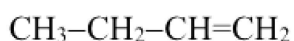


1-Chloropropane

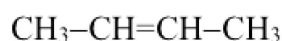


2-Chloropropane

- (b) Butene (C₄H₈) can have two positional isomers.



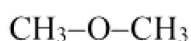
1-Butene



2-Butene

(iii) Functional Group Isomerism:

“The compounds having the same molecular formula but different functional groups are called functional group isomerism.” For example, there are two compounds having the same molecular formula C₂H₆O, but different arrangement of atoms.



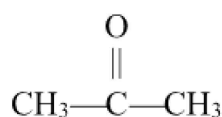
Dimethyl ether



Ethyl alcohol

Isomers of C₃H₆O:

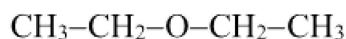
Propanal (Propionaldehyde)



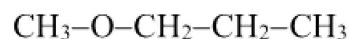
Propanone (dimethyl ketone)

(iv) Metamerism:

“This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group.” Such compounds belong to the same homologous series. For example, diethyl ether and methylpropyl ether are metamers.

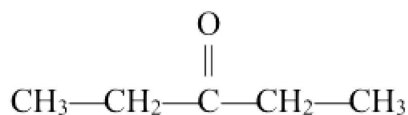
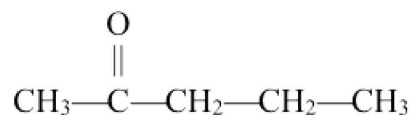


Diethyl ether

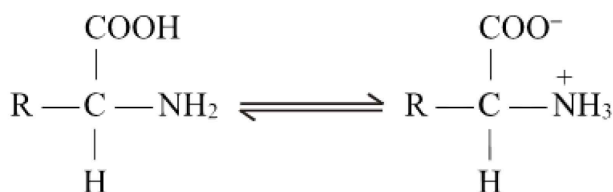


Methyl n-propyl ether

For a ketonic compound having the molecular formula $\text{C}_5\text{H}_{10}\text{O}$, the following two metamers are possible.

(Diethyl ketone)
3-pentanone(Methyl n-propyl ketone)
2-pentanone**(v) Tautomerism:**

This type of isomerism is due to shifting of proton from one atom to the other in the same molecule.



(Zwitter ion)

(2) Stereo Isomerism:

“The compounds which have same molecular formula but different spatial arrangement of atoms or groups are called stereo isomerism.”

There are two kinds of stereo isomerism:

- (i) Geometrical isomerism
- (ii) Optical isomerism

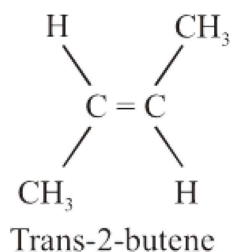
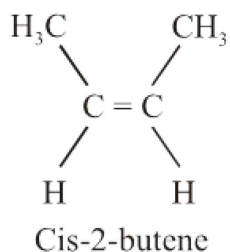
(i) Geometrical Isomerism:

The two carbon atoms joined by a single bond are capable of free rotation. However, when two carbon atoms are joined by a **double bond**, they **cannot rotate** freely. Rotation about carbon-carbon double bond cannot occur without breaking of pi-bonds. This lack of rotation about the double bond give rise to the isomers in certain alkenes. The relative position of various groups attached to double bonded atoms get fixed and give rise to cis-trans isomerism.

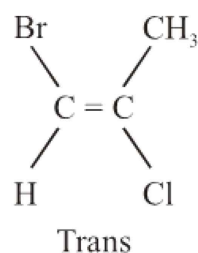
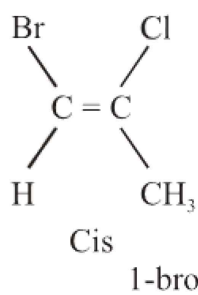
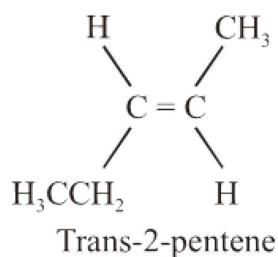
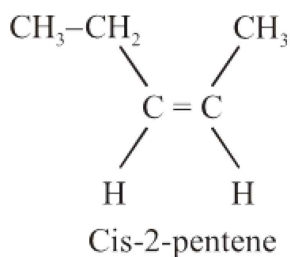
“Such compounds which possess the same structural formula but differ with respect to the positions of the identical groups in space are called cis-trans isomers and the phenomenon is known as the cis-trans or geometric isomerism.”

The necessary and sufficient condition for a compound to exhibit geometric isomerism is that two groups attached to the same carbon must be different.

2-butene can exist in the form of cis and trans isomers



Similarly 2-pentene and 1-bromo-2-chloropropene also show cis-trans isomerism.



In the **cis-form**, the similar groups lie on the same side of the double bond whereas in the **trans-form**, the similar groups lie on the opposite sides of the double bond.

The rotation of two carbon atoms joined by a double bond could happen only if the pi-bond breaks. This ordinarily costs too much energy, making geometric isomers possible.