Fundamental concepts of Organic Chemistry

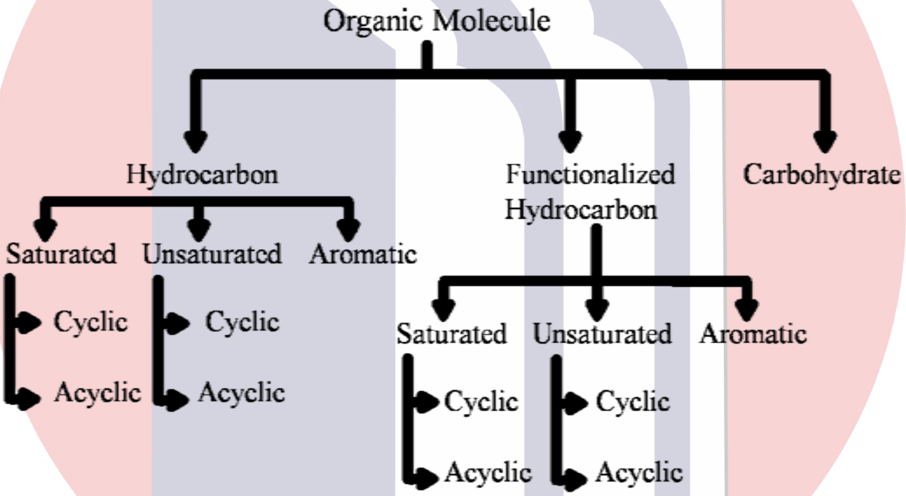
Day – 1

1. Representation and Nomenclature of organic molecules

1.1 What is an organic molecule?

An organic molecule is a carbon-containing compound. Many of them are ‘C’ and ‘H’ containing natural compounds. Most of them contains ‘O’, ’N’, ’S’ and ‘P’ and other elements.

Molecules containing ‘C’ and ‘H’ only are called hydrocarbons. Molecules containing ’C’, ’H’ and a collection of other atoms (functional group) are called functionalized hydrocarbons. Another category of molecules, which are hydrated form of carbon are called carbohydrates.



1.2 How organic molecules are represented?

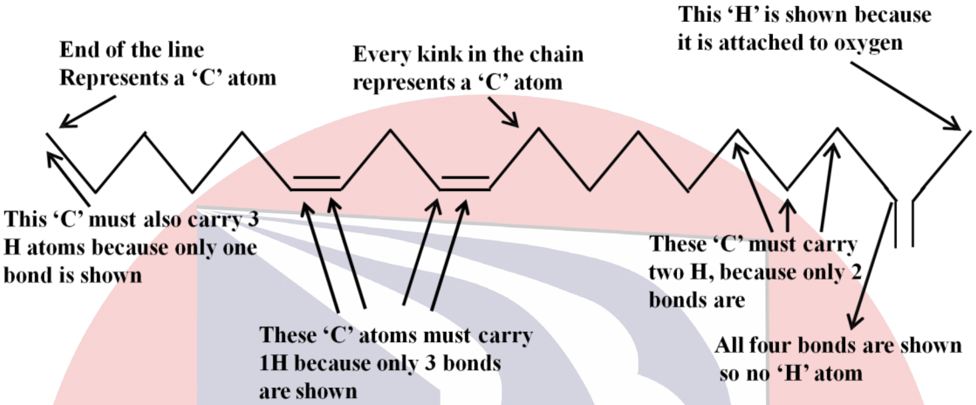
Representation of molecular structure

Most of the organic molecules either contain only a hydrocarbon skeleton or skeleton plus collection of other atoms called functional groups, which determines the way the molecule works. To draw a molecular structure **bond line** the following points are to be considered.

(1) Draw chain of atoms as zig – zag.
(2) Get rid of the H_s attached to carbon atoms along with the C – H bonds.
(3) Miss out capital C_s representing carbon atom.
(4) Every kink in the zig- zag line representing carbon atoms.
(5) The ends of the zig- zag line also representing carbon atoms.
(6) H_s attached to atoms other than C` atoms should be written.
(7) All carbon atoms in the chain must be tetravalent.

Illustration

A long chain carboxylic acid known as linoleic acid.



A combination of bond- line and condensed form of structure is clear and quick to draw. The zig-zag is clear to the carbon chain and the functional group stands out clearly.

1.3. Can structural diagrams on a two dimensional page show there dimensional information

These types of structural drawing are of the following:

(i) Three dimensional

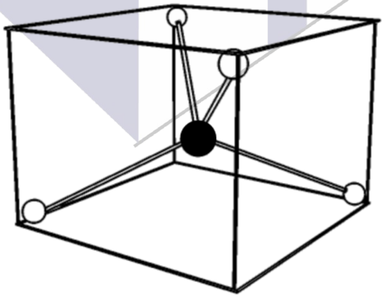
(ii) Fisher projection

(iv) Sawhorse

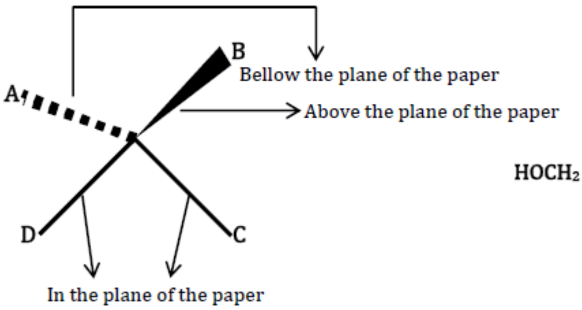
(v) Flying wedge representation

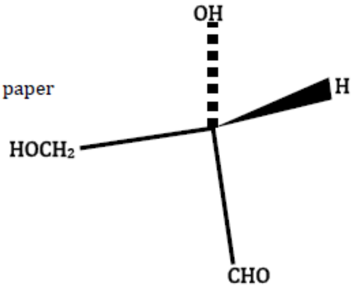
1.3.1. Three dimensional representation

This type of representation helps to study the stereo chemical property of a molecule. Four groups or atoms attached to a tetravalent carbon can be represented as directing towards the four alternate corners of a cube, with carbon at the center of the cube

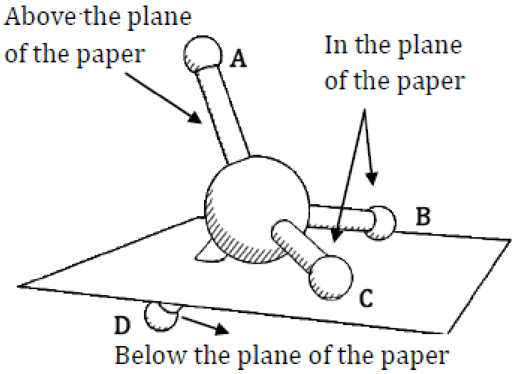


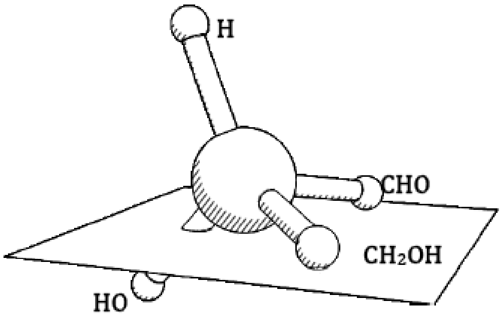
This can be drawn in a two dimensional paper as follows. Bold wedge bond suggests a perspective view of the bond coming towards the observer, while the hashed bond suggests a bond fading away from the observer. The other two normal bonds are in the plane of the paper. It is inconvenient to represent molecules having more tetravalent atoms in their three dimensional reality.





Glyceraldehyde

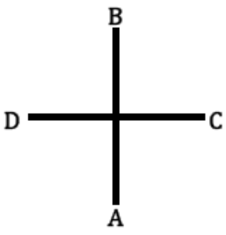


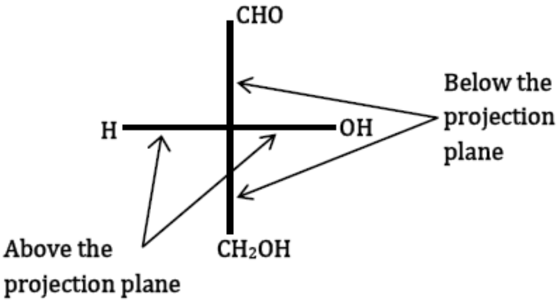


Glyceraldehyde

1.3.2. Fisher projection

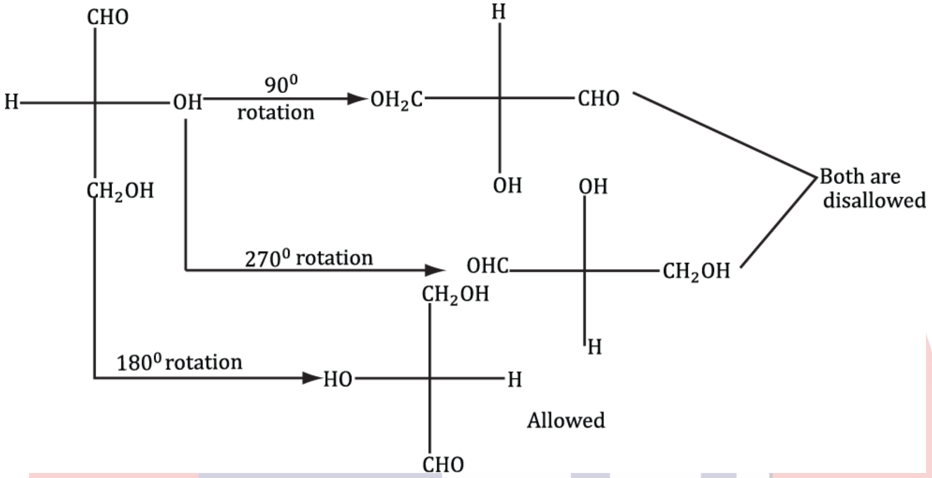
Three-dimensional structure is represented as a two dimensional reality. In this projection, the molecule is so oriented in such a way that the asymmetric carbon is in the plane of projection (plane of the paper). The groups at the top and bottom are inclined equally below the plane of projection and the groups on the left and right are similarly inclined equally above the plane of projection.





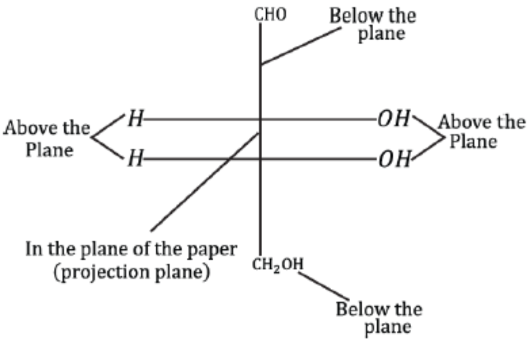
The projection formula, being two dimensional, may never be lifted out of the projection plane and turned over. It is not permissible to rotate the projection formula within the plane of the paper by either 90^0 or 270^0 angle, but it is allowed to rotate by an angle of 180^0

Illustration

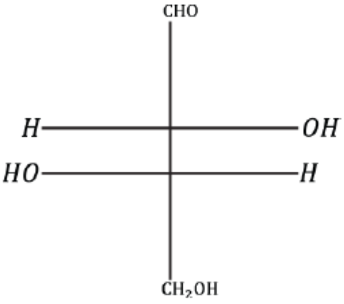


Fisher projection with more than one asymmetric carbon atom

The carbon chain must be in the vertical line, the groups on two sides stick out above the projection plane, and groups on top and bottom stick out below the projection plane.



(A)



(B)

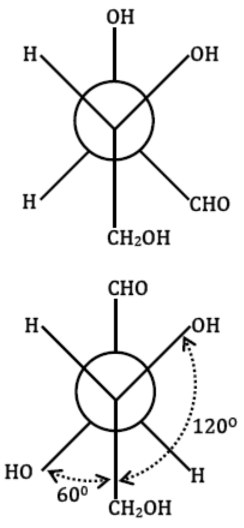
This projection formula helps in the understanding of optical isomers. The two tetroses shown above have different physical and chemical properties even though both of them are identical in structure, except a difference in the spacial orientation of one of the group. Structure' A' is erythrose and 'B' is threose, both are stereo isomers.

1.3.3. Newman projection

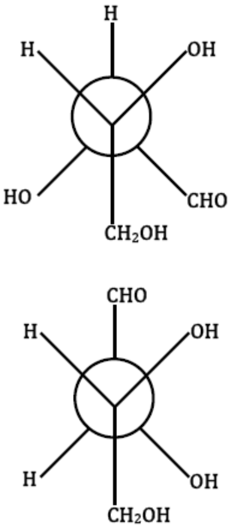
In fisher projection representation of molecules, with more than one asymmetric carbon, the spacial orientation of groups attached to one carbon atom is fixed with respect to another. This fixed orientation is called eclipsed orientation. In reality the molecule, many not be existing in this orientation. This type of spacial orientation (dynamic stereo chemistry) of group in a molecule is depicted in Newman projection

In Newman projection, the molecule is observed from front to back in the direction of bond linking the carbon atoms. The two carbon atoms exactly eclipse each other and are represented by two superimposed circles. In the drawing only one circle appears the other is assumed to be behind. Bonds and groups attached to the carbon are projected into vertical plane. The bonds appear as spokes of a wheel at angles of 120^o for each carbon. The spokes of the rear carbon being displayed by an angle of 60^o with respect to the bond on the front carbon. Set of bonds of the front carbon is drawn center of the circle and that for the rear carbon ends at the periphery.

Illustration



Erythrose



Threose

1.3.4. Sawhorse representation

In this projection, the molecule is observed through the bond linking the carbon atoms in the same way as in Newman projection. The superimposed carbon atoms are shown separately by drawing the bond between the carbons. Other bonds and groups are projected in the same way as in Newman projection

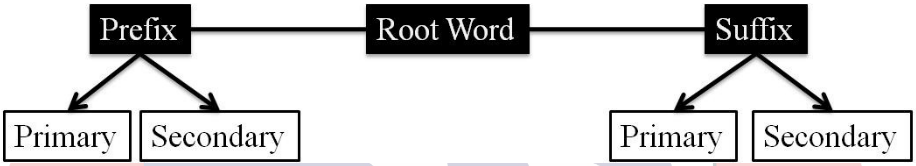
The advantage of this representation over Newman projection is that it is convenient to represent both eclipsed as well as staggered forms, but the Newman projection is awkward for representation of eclipsed formula. The complete geometry is depicted in this representation.

Day- 2

2.1. Nomenclature of organic molecules

How an organic molecule is named?

A systematic method of nomenclature of organic compounds is given by "International Union of Pure and Applied Chemistry" abbreviated as IUPAC. The naming is based on certain rules (guidelines) which are called IUPAC rules of nomenclature. The name of an organic compound consist of mainly three parts



(i) Root – word

This indicates the nature of the carbon skeleton, the longest continuous carbon chain. It is called the parent name. Chains containing one to four atoms are known by special root word and the others are by Greek numerals

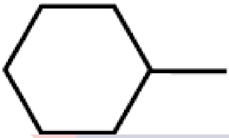
Chain length	Root word
C_1	Meth-
C_2	Eth-
C_3	Prop-
C_4	But-
C_5	Pent-
C_6	hex-
C_7	Hept-
C_8	Oct-
C_9	Non-
C_{10}	Dec-
C_{11}	undec-
C_{12}	Dodec-

C_{13} . . .	Tridec-
C_{20}	Eicos-
C_{21}	Henicos-
C_{22}	Docos-
C_{30}	Tricont-
C_{31}	Hentricont
C_{40}	Tetracont-
C_{50} . . .	Pentacont-
C_{100}	Hect-

(ii) Prefix

Primary prefix denotes the molecule alicyclic or cyclic. Secondary prefix indicates the nature of the substituent present in the carbon chain

Prefix	Secondary Prefix	Root Word
Cyclo	Methyl	Hex



Name:- Methylcyclohexane

(iii) Suffix

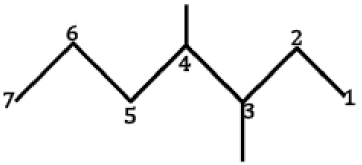
Primary suffix denotes the degree of unsaturation and number of unsaturation. Secondary suffix indicates the nature of functional group.

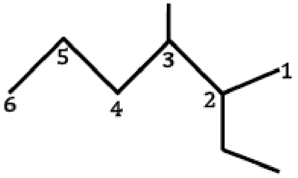
Degree and Number of unsaturation	Primary suffix
$C-C$	-ane
$C=C$	-ene
$C\equiv C$	-yne
$C=C-C=C$	-diene
$C\equiv C-C\equiv C$	-diyne

2.2. IUPAC Rules for Alkenes

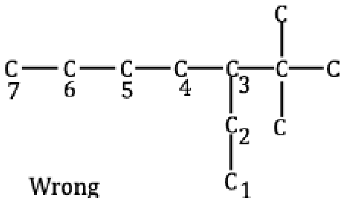
Rule No. 1

The longest continuous sequence of atoms in the molecule is taken for the root – word



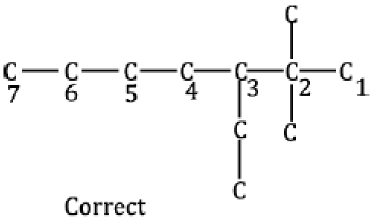


For two equally long carbon chains the one carrying larger number of side chains is selected



Wrong

(Less number of substituent)



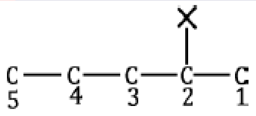
Correct

(More number of substituents)

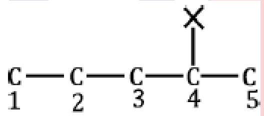
Rule No. 2 – (lowest sum rule)

A secondary prefix is employed to designate the structure of side chain group attached to the parent chain

(a):- The numbering of the parent chain must be in such a way the substituent attachment gets minimum number

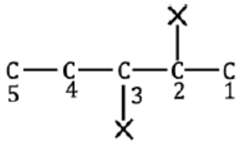


Correct



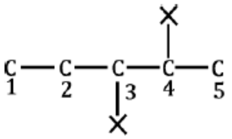
Wrong

(b):- If more that one identical substituent are present the numbering must be in such a way that the sum of the locants on parent chain is the lowest as possible



Sum of locants (2 + 3)5

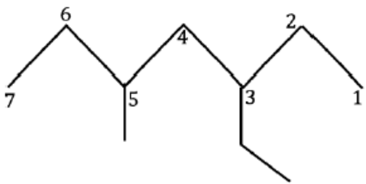
Correct



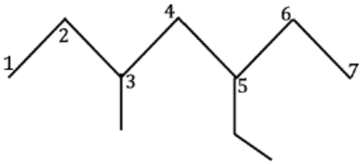
Sum of locants (3 + 4) = 7

Wrong

(c):- If two different alkyl substituents are present on identical positions in relation to the ends of the chain, numbering should be done in such a way that the first cited group receives the minimum number (alphabetical order)

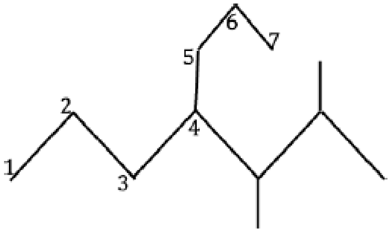


3 – Ethyl – 5 – methylheptane
(Correct)

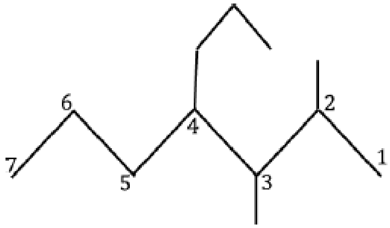


5 – Ethyl – 3 – methylheptane
(Wrong)
[Numbering is not in alphabetical order]

(d):- When two chains of equal length compete, choose the parent chain with greater number of substituents.



Wrong

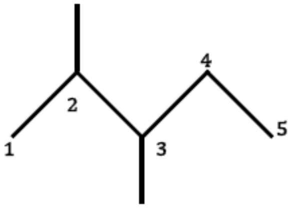


correct

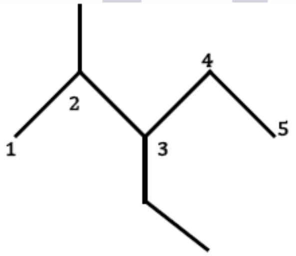
Rule No. 3

Numbers are separated by a hyphen, words are written without a space between their parts, and side chains must be written in alphabetical order.

Illustration



2,3-Dimethylpentane

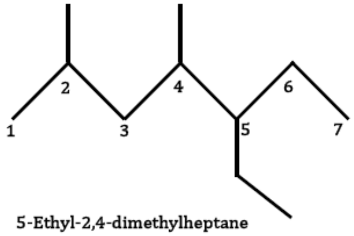


3-Ethyl-2-methylpentane

Rule No. 3

If the number of identical substituents denoted by di, tri, etc, the spelling is not considered for arranging substituent alphabetically.

Illustration

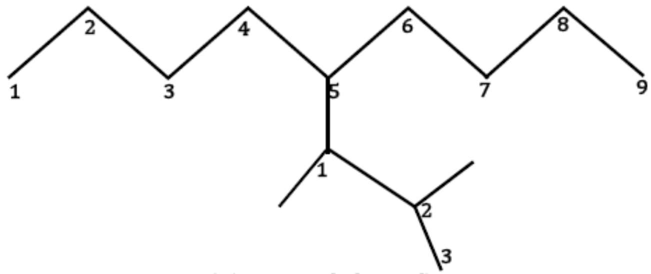


5-Ethyl-2,4-dimethylheptane
(Correct)

2,4-dimethyl-5-ethylheptane
(Wrong)

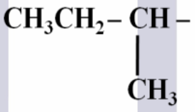
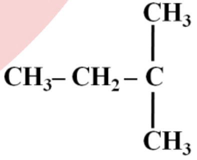
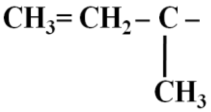
Rule No. 5

In case of side chain also possesses an additional side chain, the numbering of side chain beginning at its point of attachment of the parent chain.



5-(1,2-Dimethylpropyl)nonane

Some of the acceptable branched alkyl groups name used in IUPAC nomenclature are:

Primary (1^o)	Secondary (2^o)	Tertiaary (3^o)
Isobutyl $(CH_3)_2CHCH_2–$ Isopentyl $(CH_3)_2CH_1CH_2CH_2–$ Neopentyl $(CH_3)_3C–CH_2–$ Isohexayl $(CH_3)_2$ CH – CH_2 – CH_2– Alkyl CH_2 = CH – CH_2	Isopropyl $(CH_3)_2CH–$ Secburyl  $CH_3CH_2-\underset{\substack{\vert\\CH_3}}{CH}-$	Ter.butl $(CH_3)_3$–C– Terpentyl  $CH_3-CH_2-\overset{\substack{CH_3\\\vert}}{\underset{\substack{\vert\\CH_3}}{C}}$ Isopropenyl  $CH_3=CH_2-\underset{\substack{\vert\\CH_3}}{C}-$

Day – 3

3. Determination of molecular formula of an organic compound

Molecular formula of a compound is the actual number of constituent atoms present in the molecule. The determination of molecular formula involves;

(i):- Calculation of empirical formula

(ii):- Determination of molecular weight

(iii):- Determination of molecular formula

3.1. Calculation of empirical formula

The empirical formula of a compound is the simplest formula, which shows the relative number of atoms present in the molecule. It can be calculated if the percentage composition of elements present in the molecule is known. The percentage composition can be determined by combustion method (elemental analysis).

3.1.1. Estimation of carbon and hydrogen

(Liebi g's method)

The organic compound is heated strongly with dry copper oxide in presence of oxygen.

$$C(from\ Org.compound) + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu$$

$$2H(from\ Org.compound) + CuO \rightarrow H_2O + Cu$$

The weight of CO_2 and H_2O formed is determined by absorbing them separately in potash

$$\boxed{\begin{aligned} Percentage\ of\ C &= \frac{Wt.of\ CO_2}{Wt.of\ compond} \times \frac{12}{44} \times 100 \\ Percentage\ of\ H &= \frac{Wt.of\ H_2O}{Wt.of\ Compond} \times \frac{2}{18} \times 100 \end{aligned}}$$

Illustration

0.36 g of an organic compound on combustion gave 0.01mol of CO_2 and 0.005 mol of H_2O. Calculate the percentage of carbon and hydrogen in the compound?

Solution

Weight of 0.01 mol of CO_2

$$\Longrightarrow \quad 44 \times 0.01 = 0.44g$$

Weight of 0.005 mol of H_2O

$$\Longrightarrow \quad 18 \times 0.005 = 0.09g$$

% of C

$$\Rightarrow \frac{12}{44} \times \frac{0.44}{0.36} \times 100$$

$$= 33.33\%$$

% of H

$$\Rightarrow \frac{\mathbf{2}}{\mathbf{18}} \times \frac{\mathbf{0.09}}{\mathbf{0.36}} \times \mathbf{100}$$

= 2.77%

3.1.2 Estimation of Nitrogen

(a) Dumas's method

The organic compound is heated with CuO.CO_2, H_2O, SO_2 and N_2 are formed along with little nitrogen oxide, if the compound centaurs C, H, S and 'N' elements. Nitrogen oxides are reduced back to nitrogen by passing it over bright reduced copper gaze. CO_2, H_2O and SO_2 are absorbed by caustic potash solution and free nitrogen is collected. Form the volume of nitrogen collected, the percentage of nitrogen is calculated.

$$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu$$

$$2H + CuO \xrightarrow{\Delta} H_2O + Cu$$

$$2N + CuO \xrightarrow{\Delta} N_2 + \text{Oxides of } 'N'$$

$$\text{Oxides of } \ 'N' + Cu \xrightarrow{\Delta} N_2CuO$$

$$\%\ \text{Nitrogen} = \frac{28 \times \text{vol.of } N_2 \text{colleceed at N.T.P}}{22400 \times \text{Wt.of Org.Com}}$$

$$= \frac{Wt.of\ Nitrogen}{Wt.of\ Org.Com} \times 100$$

Illustration

0.29 g of an organic compound containing nitrogen gave 50 ml of nitrogen at N.T.P. Calculate the % of nitrogen in the compound

Solution

% of Nitrogen

$$\Rightarrow \frac{\mathbf{28}}{\mathbf{22400}} \times \frac{\mathbf{50 \times 100}}{\mathbf{0.29}} = \mathbf{21.5\%}$$

(b) Kjeldahl's method

This method is applicable mainly to amino compounds. Not applicable to nitro, azo, diazo or pyridine type of molecules. The compound is heated with con: H_2SO_4 in presence of K_2SO_4 and $CuCO_4$ The nitrogen of the compound is quantitatively converted to ammonium sulphate. The ammonium sulphate is converted to ammonia and is titrated against standard acid to get the volume of ammonia produced.

$$\text{Nitrogen of the Org. com} + H_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + \underset{\text{(Standard)}}{H_2SO_4} \xrightarrow{\Delta} (NH_4)_2SO_4$$

$$\% \text{ Nitrogen in the given compound } = \frac{14}{1000} \times \frac{\text{Vol. of acid} \times \text{Normality of acid}}{\text{Wt. of compound}}$$

Illustration

If the ammonia obtained from 0.216g of an organic compound by Kjeldahl's method of analysis neutralizes 23.85 ml of 0.115 N acid. What is the percentage of nitrogen in the compound?

Solution

% of Nitrogen

$$= \frac{14}{1000} \times \frac{23.85 \times 0.115 \times 100}{0.216}$$

$$\Rightarrow \frac{1.4 \times 23.85 \times .115}{0.216}$$

$$\Rightarrow 17.77\%$$

3.13. Estimation of halogen

(Carius method)

The organic compound containing halogen is heated in a sealed tube with fuming HNO_3 is presence of $AgNO_3$. Carbon, hydrogen and sulphur are oxidized to their respective oxides, while halogen is converted to silver halide. From the weight of silver halide formed, the percentage of halogen in the organic compound can be calculated.

$$\% \text{ Halogen} = \frac{\text{At At: of Halogen} \times \text{w\Wt. of AgX} \times 100}{\text{Mol: Wt. of AgX Wt. of the Org. Com.}}$$

This method does not give correct value of iodine

3.1.4. Estimation of Sulphur

(Carius method)

The organic compound is heated with con: HNO_3 in a sealed tube. Carbon, hydrogen and sulfur are oxidized to CO_2, H_2O and H_2SO_4 . The H_2SO_4 formed is converted to $BaSO_4$ by treating with $BaCl_2$. From the weight of $BaSO_4$ the percentage of sulphur is calculated.

$$C + 2[O] \xrightarrow{\Delta} CO_2$$

$$2H + [O] \xrightarrow{\Delta} H_2O$$

$$S + H_2O + 3[O] \rightarrow H_2SO_4$$

$$H_2SO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + HCl$$

$$\% \text{ of Sulphur} = \frac{32}{233} \times \frac{\text{Wt.of } BaSO_4 \text{ formed} \times 100}{\text{Wt.of Org.Com.}}$$

Illustration

0.2595 g of an organic compound gave 0.35 g of $BaSO_4$ by Carus method. Find the % of sulphur present in the compound?

Solution

% of Sulphur

$$\Rightarrow \frac{32}{233} \times \frac{0.35}{0.2595} \times 100$$

$$\Rightarrow 18.52\%$$

3.1.5. Estimation of Oxygen

There is no direct method of estimation of oxygen; hence, it is usually calculated by difference.

% oxygen = 100 – Sum of percentages of all other elements

From the percentage of elements, the empirical formula is calculated as follows:

(a) Determination relative number of atoms

% Composition of each element is divided by its atomic weight.

(b):- Determination of simplest ratio.

The lowest one among them divides the relative number of different atoms obtained.

(c) Whole number

If the numbers are not a whole numbers, all the numbers are multiplied by a suitable common factor to get the smallest possible whole number.

Determination of empirical formula

The symbols of each element is written with subscripts to the lower right hand corner, the relative number as a whole number

Illustration

Calculate the empirical formula of the compound from the following elemental analysis

C%	H%	N%	O%
42.6	3.5	20	

Solution

(a) Atomic ratio

42.6/12=3.55	3.5/1=3.5	20/14=1.43	33.9/16=2.12 (By Differnt)

(b) Divide by the lowest value

$$\frac{3.55}{1.43} \Rightarrow 2.48 \qquad \frac{3.5}{1.43} \Rightarrow 2.48 \qquad \frac{1.43}{1.43} \Rightarrow 1 \qquad \frac{2.12}{1.43} \Rightarrow 1.48$$

(c) To get whole number each multiply by 2

4.90 4.96 2 2.96

(d) The empirical formula is

$$\boxed{C_5H_5N_2O_3}$$

3.2. Determination of molecular weight

The molecular weight of a compound is the relative mass of one molecule of it as compared with the mass of carbon atom, which is taken as 12 amu. It is a only number.

Illustration

If the molecular weight of a compound is 60, it means that the molecule is 60/12 – 5 times as heavy as an atom of carbon.

Gram – molecular weight

Molecular weight expressed in grams.

Gram – molecular volume

The volume occupied by the vapor of a gram molecular weight of substance at N. T. P is 22400 ml., which is gram molecular volume. Molecular weight can be determined either by physical methods or by chemical methods.

3.2.1. Victor Meyers method

This is a physical method

A known weight of the organic compound is vaporised and the volume so obtain is recued to volume at N. T. P. The weight of 22.4 of every gas at N. T. P is equal to its molecular weight is grams.

PV X Mol. Wt. = Wt. of the compound X RT PV =n RT

$$\therefore Mol.wt = \frac{weight\ of\ the\ compound}{PV} \times RT$$

$V = Volume\ in\ litres$

$P = Pressure\ in\ atomsphere$

$T = Temperature\ in\ Kelvin$

$R = 0.082\ L\ atm.mol^{-1}K^{-1}$

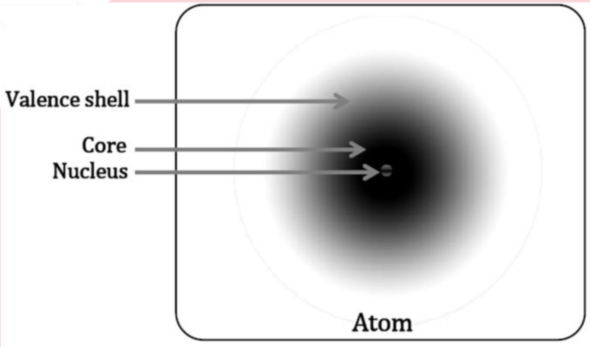
3.2.2. Cryoscopic or depression of freezing point method

This is also a physical method, but for non - volatile compounds. The freezing point of a solvent

Day – 4

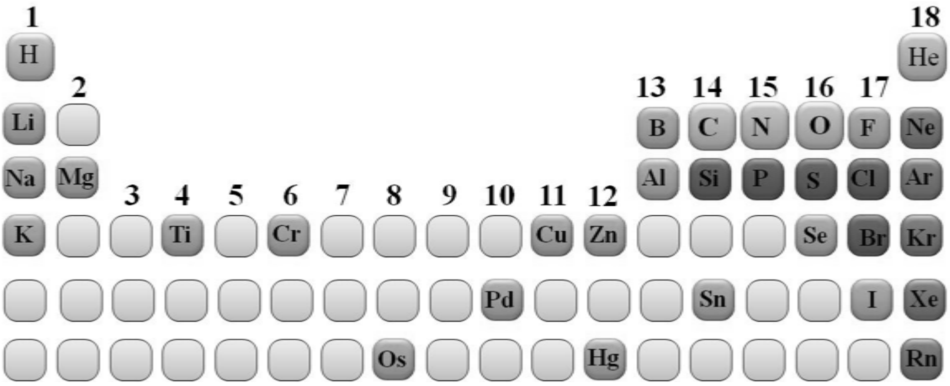
4.1. Concepts of chemical bonding

In 1916 Gilbert Lewis deduced that the nucleus of an atom is centered within a core of inner electrons beyond which there is an outer electrons shell. This outer shell contains electrons involved in linking atoms together. The electrons of this shell is called valence electrons and the shell is called valence shell.



Atoms are arranged according to their electronic arrangement. This classification is called periodic classification of atoms or elements. The properties of these elements can be defined according to their position in the periodic table. Since organic chemistry deals with molecules containing carbon hydrogen and few of heteroatoms, the entire periodic table of classification is not required. The most widely used elements in the construction of organic molecules are shown here as organic chemist's periodic table.

The Organic Chemist's Periodic Table



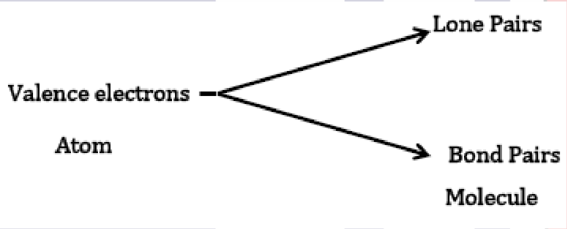
The position of noble gases in the modern periodic table reflects their electronic structure. With the electron of each noble gas atom, producing complete electronic shell about the nucleus. Expect helium all gets '8' electron in the outer most shell.

$_{2}$He – 2
$_{10}$Ne = 2, 8
$_{18}$Ar = 2, 8, 8
$_{36}$Kr = 2, 8, 18, 8
$_{56}$Xe = 2, 8, 18, 18, 8
$_{80}$Rn = 2, 8, 18, 32, 18, 8

Any atom lying in between these noble gasses have incomplete electronic shells. In order to get the noble gas configuration, or to fill the incomplete outer orbits, atoms combine to form molecule. The combining capacity is called valence.

4.1.1. Covalent bond

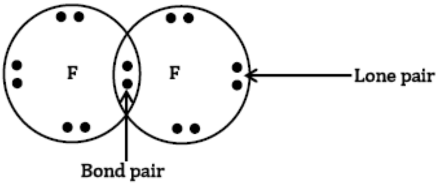
When an atom combines with another atom, they share their valence electrons. The link formed between the atoms is called a chemical bond. A link means single chemical bond between the atoms, which consist of a pair of electrons. The bonding electron pair is localized between the nuclei linked in the molecule. The link formed between the two atoms by mutual sharing of electrons is called a covalent bond. Each atom in the molecule completes its valence shell by eight electrons. An atom shares sufficient valence electrons to fill the valence shell of each atom in the molecule, which is called octet rule. When a chemical bond is formed, the valence electrons of an atom divide themselves in to bond pairs and lone pairs.



Illustration

Formation of F_2

$^{19}_{9}F$ atom has seven electrons in the valence shell, one short of octet. First shell carries two, and the second one, the valence shell carries, seven electrons. Two fluorine atoms combine to form a molecule, and by this each fluorine atom gets the octet in the valence shell. The atomic link in this way is referred as covalent bonding. In the valence shell of each fluorine gets three lone pairs and one bond pair.

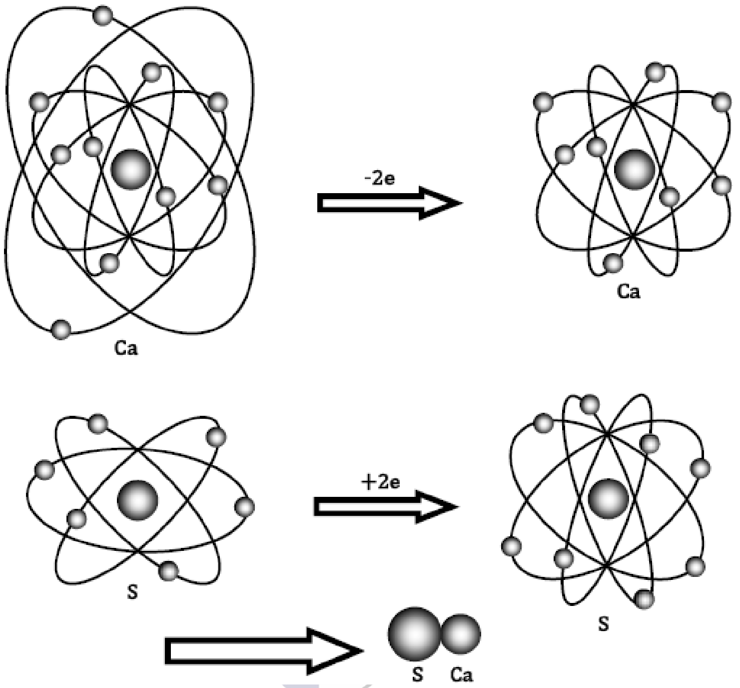


4.1.2. Ionic bond

Electron transfer can achieve the creation of an octet of valence electrons about each atom in a molecule. One or more electrons are transferred from one atom to another to form ions. Formation of ionic species from neutral species is due to a requirement to acquire the electronic structure similar to that of noble gas. Electron removal produce +ive ions (cations) and electron acceptance produce –ive ions (anions). Cations are ions attached to –ively charged electrode (cathode) and anions are attached to +ivly charged electrode (anode). Electrostatic attraction between these ions is the link between atoms and this link is termed as ionic bond. Elements that lie near noble gases in the modern periodic classification of elements tend to electron transfer producing ions. Such ions are more stable than the parent atoms due to noble gas outer electronic structure.

Illustration

Formation of CaS



The electronic structure of $^{40}_{20}Ca$ is 2, 8, 8, 2 = [Ar], 2. The atom is close in electronic configuration to argon noble gas. If it releases the outer two electron the electronic structure becomes same as that the argon.

$$^{40}_{20}Ca \xrightarrow{-2e} {}^{38}_{20}Ca^{2+}$$

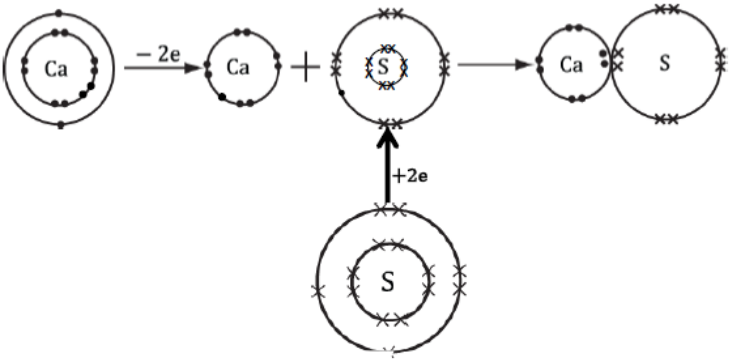
Similarly neutral sulphur atom has the electronic structure $^{32}_{16}S = 2,8,,6 = [Ne], 6.$ close to that of noble gas argon. If it takes two electrons, the structure becomes identical with argon.

$$^{32}_{16}S \xrightarrow[+2e]{} {}^{32}_{16}S^{2-}$$

The two ions of equal and opposite changes with electronic structure identical with argon, forms CaS.

$$Ca^{2+} = 2,8,8$$
$$s^{2-} = 2,8,8$$

Both are octet at their valence shell, and the electrostatic attraction between these ions result in the formation of CaS molecule.

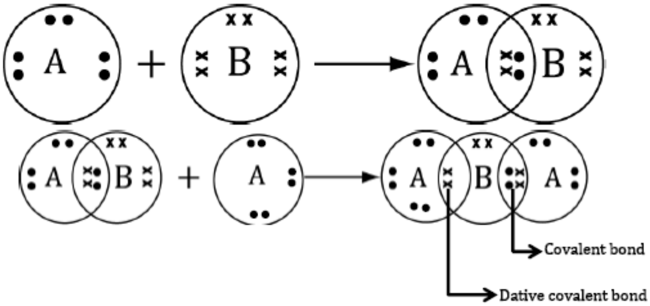


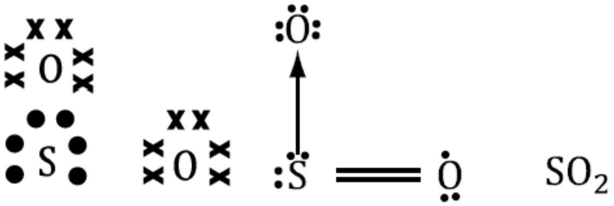
4.1.3. Dative covalent bond

Mutual donation of one electron each result in covalent bonding and transfer of one electron from one atom to another result in ionic bonding. If both electron of a bond are donated by one atom, the bond is called dative covalent bond.

Illustration: Formation of SO_2

Consider a molecule BA. Both atoms of A and B are octet in their valence shell in the molecular form. This molecule combines with another atom A with only six valence electrons to form ABA molecule. By doing this all the atoms in ABA molecule completes the valence shell. All get octet arrangement the valence shell.

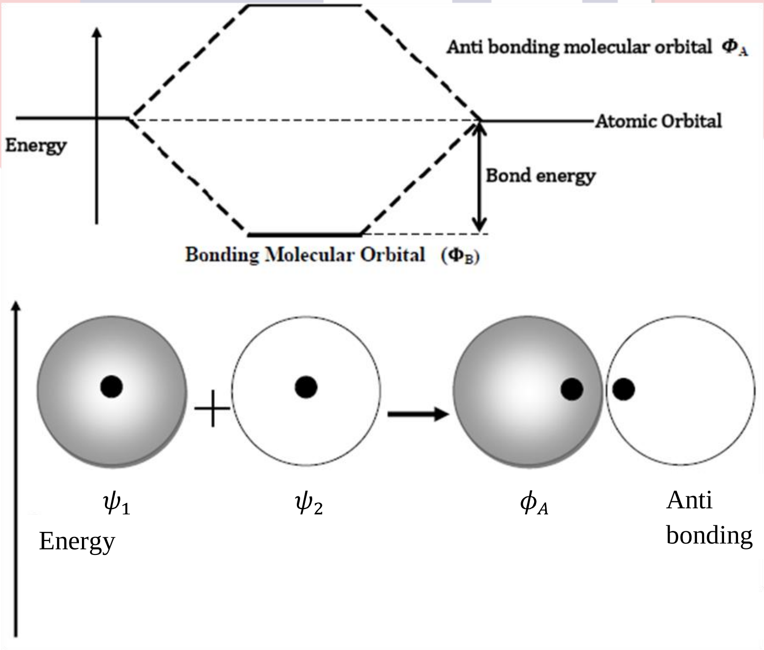




4.2. Chemical bonding in organic molecules

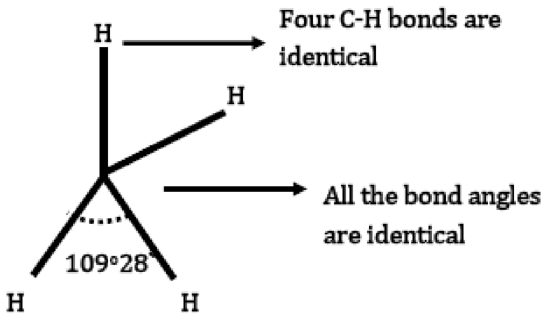
Modern interpretation of chemical bonding is based on the quantum description of atoms and molecules. Fast moving electron has wave characteristics. Thus, the precise classical Bohr orbits are replaced by three-dimensional atomic orbitals of different energy levels. Electrons are structure less point particles and are indivisible, with mass localized and change is not localised at a point if, they are the part of atomic or molecular system. An electronic configuration is an assignment of atoms electrons to a set of orbital energy levels.

This can be extended to interaction between atoms that is, to bonding. Two wave equations describe the electrons of two atoms are combined to give molecular orbitals. The new wave function is a linear combination of atomic orbitals (LCAO). According to this the constructive combination of atomic orbitals increase electron probability between the nuclei and leads to energetically favorable bonding molecule orbitals $(\emptyset_B)$ and destructive interaction leads to zero electron probability (node) between the nuclei, gives antibonding molecular orbitals $(\emptyset_A)$ of higher energy.



Day – 5

5.1 Hybridization



The molecule is tetrahedral

The electronic configuration of carbon is $1S^2\ 2S^2 2P_x^1 2P_y^1 2P_z^0$. Only two unpaired electrons ($2P_x^1\ 2P_y^1$) are available for bond formation. In almost all cases carbon is tetravalent.

(a) How this is possible?

This is possible by uncoupling of the $2S^2$ electrons and promotion of an electron to 2p (higher level). Additional energy requirement for this promotion is compensated by the energy release by bond formation.

The new state is $1S^2\ 2S^1\ 2P^1\ 2P_x^1 2P_y^1 2P_z^1$ which can explain the tetravalent state, but cannot explain the equal bond strength (overlapping power of 's' orbital = 1.00, 'P' orbital = 1.72)

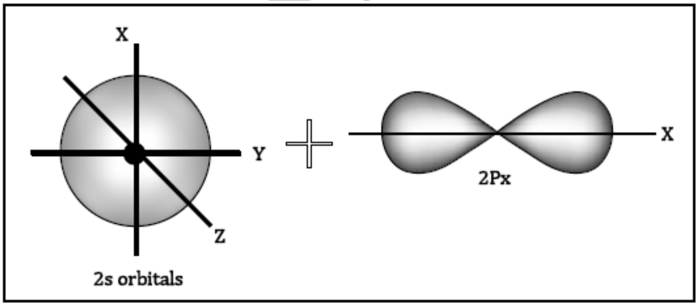
This is solved by formulating a mathematical model of hybrid orbitals.

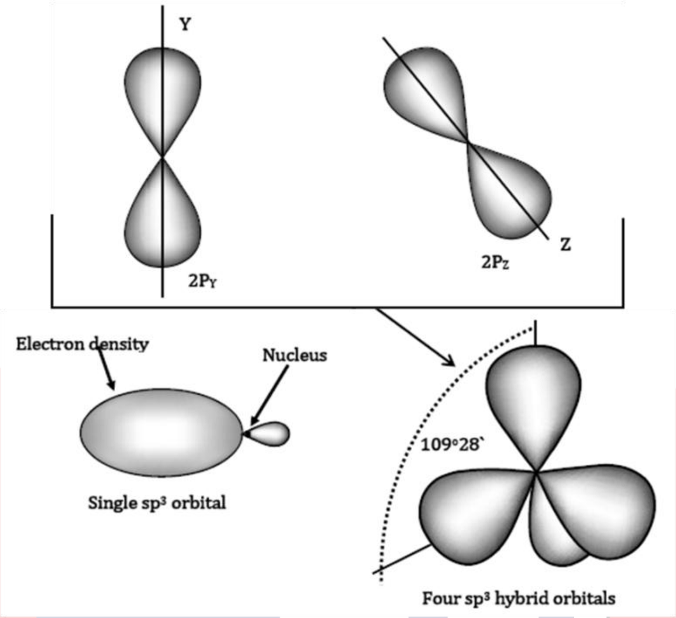
(b) What is Hybridization?

Hybridization is the concept of mixing of orbitals of different energy to form equal number of orbitals of identical energy, and the orbitals thus formed are called hybrid orbitals.

(c) What are the types of hybrid orbitals possible for carbon atom?

5.1.1. Sp^3 Hybrid orbitals





(a) Mixing of one 2s and three 2p atomic orbitals of carbon to form four equivalent hybrid orbitals, that are designated as sp^3.

(b) Since orbitals are of equal energy as per Hund's rule of maximum multiplicity each get one electron each with identical spin.

(c) The hybrid orbitals are of higher energy than 2s and lower than of 2p atomic orbital of carbon.

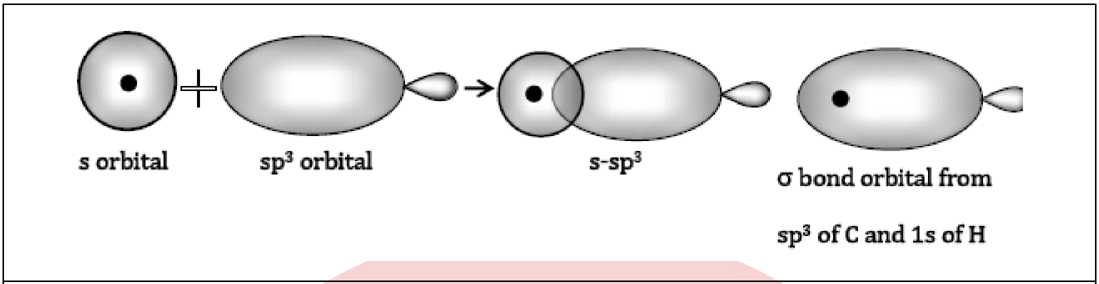
(d) The four identical orbitals will be directed to the four corners of a tetrahedron, which have the minimum energy, accounts for the four equivalent bonds of methane and tetrahedral shape of methane.

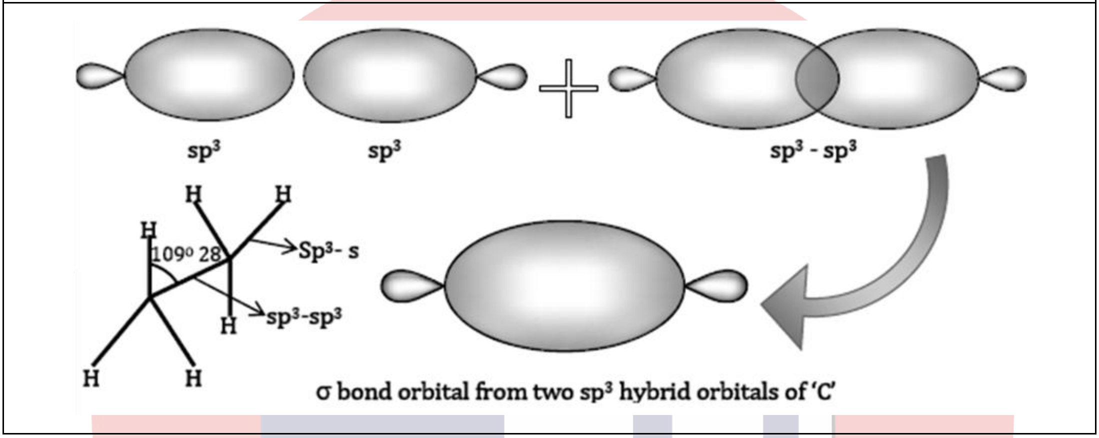
(e) The shape of an sp^3 orbital is neither that of 's' nor 'p' atomic orbitals. The major electron density probability associated with each sp^3 hybrid orbital is located one side of the nucleus rather than symmetrical to the nucleus as in the case of 's' and 'p' atomic orbitals.

(f) Due to the above reason the overlapping power of sp^3 orbital is higher than that the 's' and 'p' atomic orbitals. This fact account for the stronger bond from hybrid orbitals.

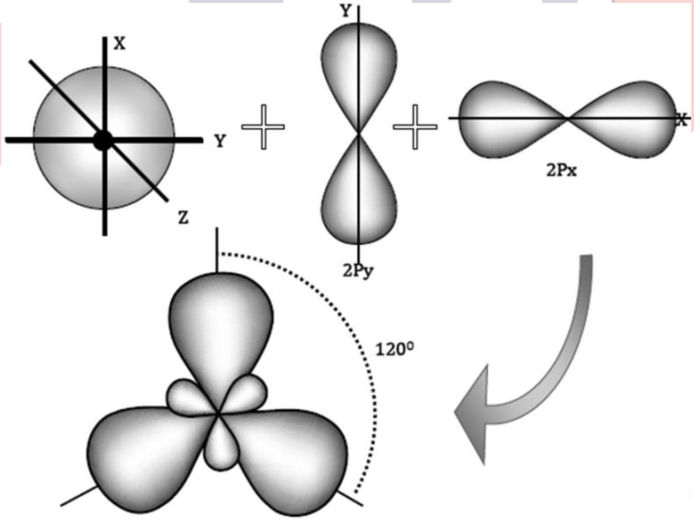
(h) The development of stranger bonds by hybrid orbitals compensates for the energy required to form the hybrid orbitals.

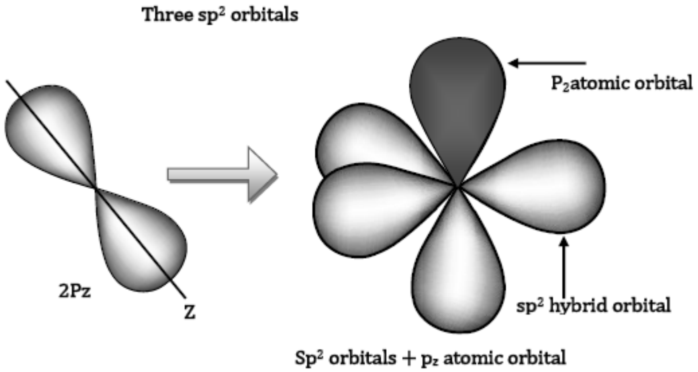
(i) The effect of hybridization is to increase the electron density along the C – H bond axis, thus increasing bond strength.

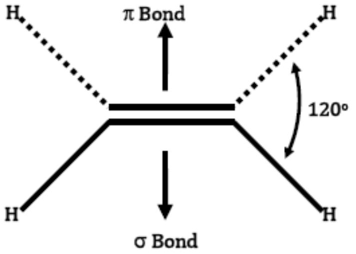




5.1.2. sp^2 Hybrid orbitals







(a):- Mixing of 2s and two 2p atomic orbitals of carbon to form three equivalent orbitals designated as sp^2.

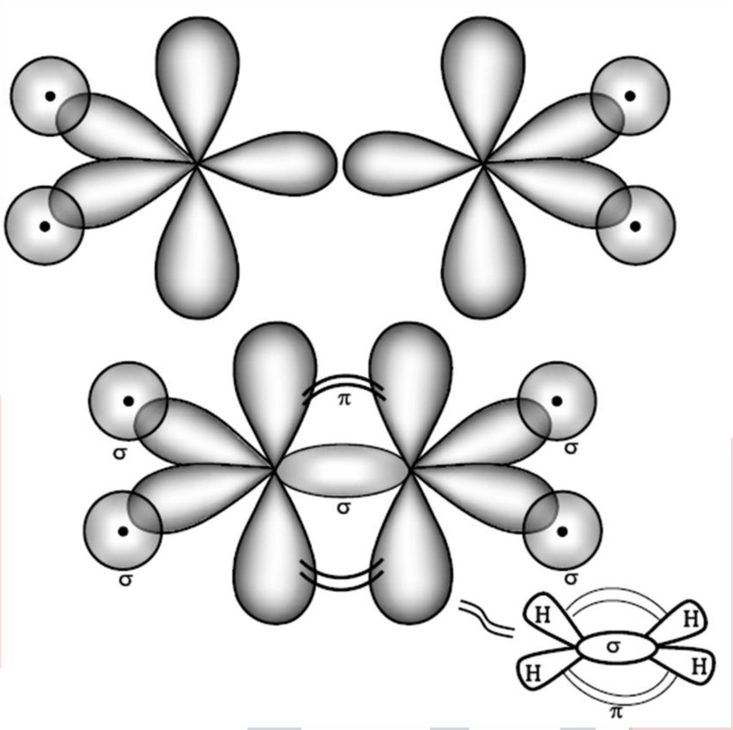
(b):- These hybrid orbitals are of higher energy than‘s’ atomic orbital and lower energy than ‘p’ atomic orbital.

(c):-The major electron density of (orbital lobes) the sp^2 hybrid orbitals lie in a common plane. perpendicular to the unhybridised ‘p’ orbital and 120^0 angle between their axes. (d) The orbital orientation is trigonal; hence, it is called trigonal hybridization.

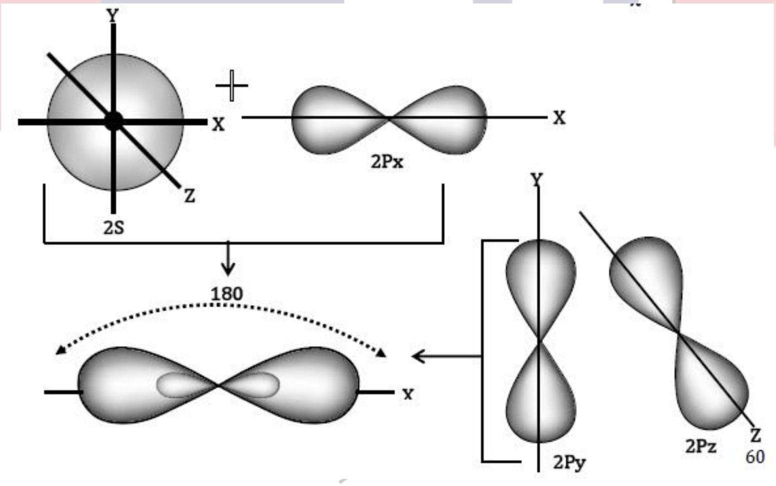
(e):- The overlapping power of sp^2 hybrid orbitals (1.99) is higher than both ‘s’ and ‘p’ atomic orbitals and lower than that of sp^3 hybrid orbital (2.0).

(f):- sp^2 hybrid orbital is more inner compared to sp^3 orbital because of more % of ‘s’ character.

(g):- The molecular orbitals resulting from the overlap of two sp^2 hybrid orbitals, one each from carbon atom, form carbon – carbon sigma bond. Parallel overlap of unhybridised ‘p’ orbital of each carbon atom forms molecular orbital of the Pi bond. The remaining two sp^2 orbitals of each carbon atom combine with each of the hydrogen ‘s’ orbital to form four C – H sigma bonds.



5.1.3. sp Hybrid orbitals



Day – 6

6.1. Bonding weaker than covalent bonding (intermolecular forces)

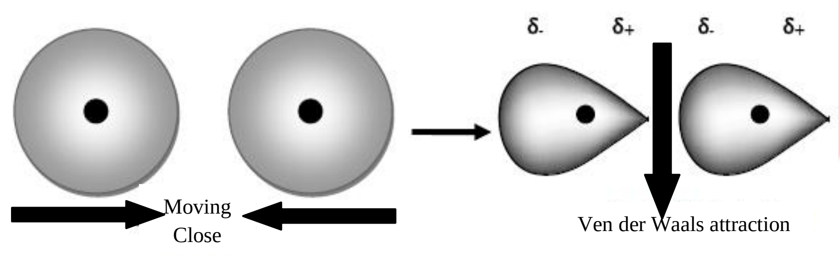
The forces that hold molecules together are called intermolecular forces. They are weaker than covalent bonding. Three types of forces are there, which are:

(1) London forces (Van der Waals forces)
(2) Dipole – dipole interaction forces
(3) Hydrogen bonding,

The relative order of these forces are, hydrogen bonding > dipole – dipole interaction > Van der Waals interaction.

6.1.1. London (Van der Waals) forces

This is the weak intermolecular attraction due to the electrostatic interaction between electrons of one molecule with that of the other. This is possible only if the molecules are very close together.



(a) The interaction is maximum in solid state and minimum in gaseous state.

(b) Interaction between the surface of molecules, hence surface area increases interaction increases.

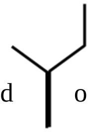
(c) Molecular weight increases, the number of electron increases hence interaction increases.

(d) Pressure increases, inter- molecular distance decreases, hence Van der Waals attraction increases.

6.1.2. Effect of Van der Waals force on physical properties of compounds

(a) The relative order of dipole in methyl halide is $CH_3Cl > CH_3Br > CH_3I$, where as that of boiling point is $CH_3I > CH_3Br > CH_3Cl$ why?

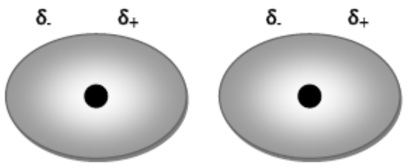
The increase of mass increases the number of electrons in the molecule, hence more Van der Waals force of attraction, which cause more association that is molecular. More association of molecule increases the boding point.

(b) Two hydrocarbons  and  of same molecule weight but differ in boiling point. Why?

Greater the surface area of the molecule greater the Van der Waals interaction and grater will be the boiling point. Greater the branching in a hydrocarbon lesser the surface area, and laser the interaction, hence decrease of boiling point. n-Pentane has higher b.p. than 2-metyl butane.

6.2.1. Dipole – dipole interaction

This is the force of attraction that holds the polar molecules together. This force is stranger than Van der Waals force of attraction. Positive end of one polar molecule is attracted by the negative end of another polar molecule.



Polar Interaction

Polar interaction is the reason of association of molecules. Association due to polar interaction is stronger than association due to Van der Waals interaction.

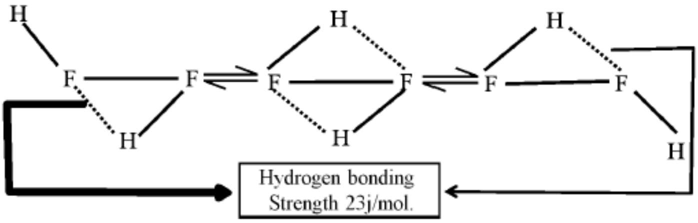
6.2.2. Effect of dipole – dipole interaction in physical properties of compounds

Physical properties like melting and boiling points are higher for molecules having dipole – interaction compared to that of non - polar molecules of comparable molecular mass. Solubility also increases due to more dipole interaction between solvent molecules and solute.

6.3.1. Hydrogen bonding

This is stronger than both Van der Waals and dipole – dipole interaction and weaker than covalent bonding. Condition for hydrogen bonding is that a hydrogen atom of a molecule should come in between two strong electro- negative atoms ,….H – X….H – X….., then hydrogen will be bonded to both electro-negative atoms.

$(HF)_2$



6.3.2. Condition of Hydrogen Bonding

(a) ‘H’ in between two strong electro- negative atoms (F, O, N).

(b) Size of the electronegative atom must be small.

Illustration

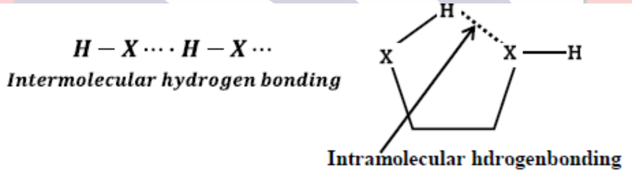
Chlorine and nitrogen have same electro negativity but ‘N’ provides better hydrogen bonding due to smaller size compared to nitrogen.

$$KCl + HCl \xrightarrow{X} KHCl_2$$
$$KF + HF \rightarrow KHF_2$$
$$KHF_2 = K^+F^- - -H^{\delta-} - F^{\delta-}$$

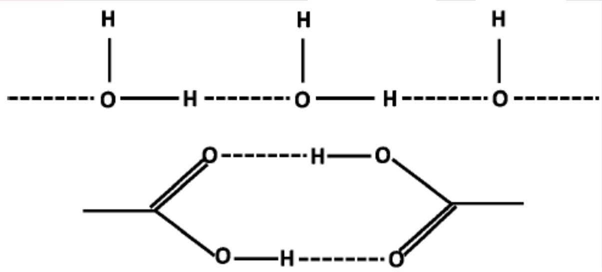
Such equilibrium does not exist between HCl and KCl.

6.3.3. Types of hydrogen bonding

There are two types of hydrogen bonding, one is hydrogen bonding between hydrogen’s of two or more molecules and the other is that of hydrogen of the same molecule. First one is intermolecular and the second one is intramolecular.



(1) Intermolecular hydrogen bonding



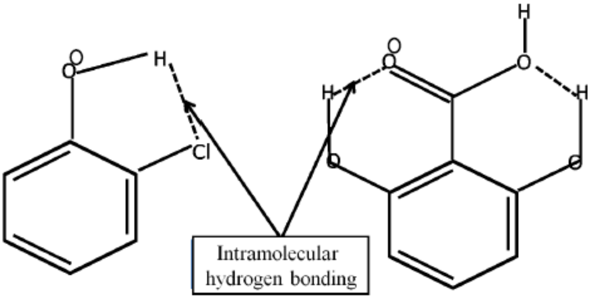
Effect of intermolecular hydrogen bonding is that it increases the melting point, boiling point or solubility of the compound. This is attributed to the extra energy required to break the molecular association due to hydrogen bonding.

Illustration

H_2O is a liquid were as H_2S is a gas even though H_2S is heavier than H_2O. Oxygen is more electro negative and smaller in size compared to ‘S’, hence stronger hydrogen bonding in H_2O compared to than in H_2S. Stronger molecular association in H_2O as compared to H_2S.

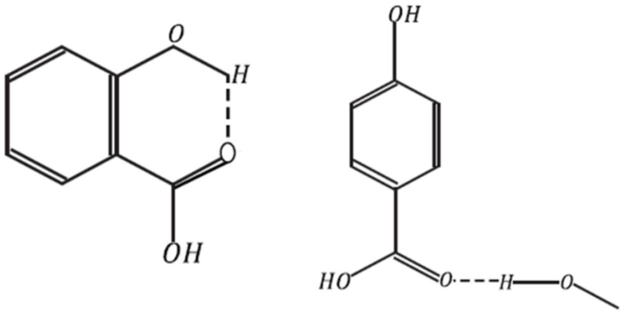
(2) Intramolecular hydrogen bonding

This occurs with two atoms of same molecule. Intramolecular hydrogen bonding is possible, when a six or five membered ring can be formed. Higher or smaller rings are not possible due to angle strain which overcome the hydrogen bonding



The effect of intramolecular hydrogen bonding is that it decreases the boiling point and solubility. The decrease in boiling point and solubility is attributed to the decrease in molecular association which is due to the absence of intermolecular hydrogen bonding.

Illustration



Less soluble in water

More soluble in water

- Less solubility due to less hydrogen bonding with water.
- More hydrogen bonding with water solvent means more soluble.

6.3.4. Effect of Hydrogen bonding on some physical properties of compounds

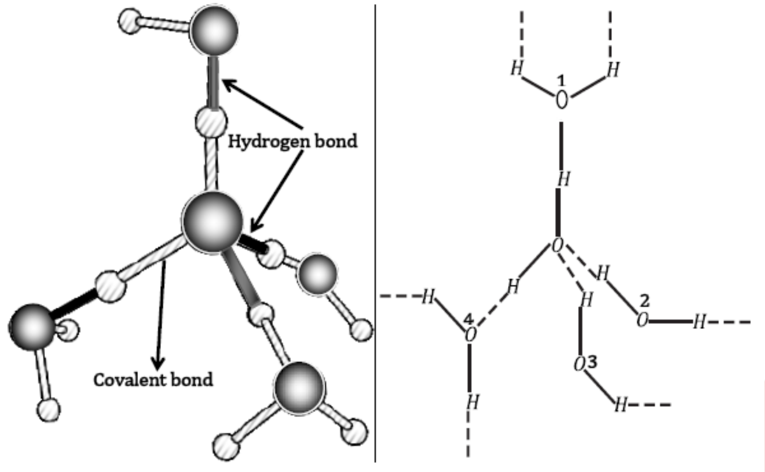
(a) Unusual properties of water

(1):- Low density in solid state as compared to solution state.

(2):- Higher density at 4^0 as compared to that at 0^0C.

(3):- Universal solvent nature.

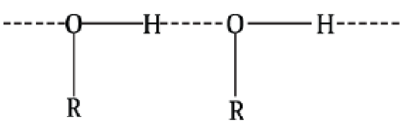
This unusual property of water is due to intermolecular hydrogen bonding



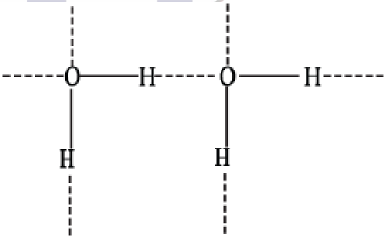
1. There are four molecules of water in each unit cell.
2. The H_2O is oriented tetrahedrally with respect to one another.
3. Four hydrogen atoms surround each oxygen atom tetrahedrally.
4. One water molecule is capable of forming four hydrogen bonding.
5. Hydrogen bonding is weaker hence longer than covalent bonding.
6. The crystal lattice is composed of puckered hexagonal rings of H_2O in a chair conformation.

6.3.5. Effect of hydrogen bonding on the physical properties of alcohols

Due to intermolecular hydrogen bonding, association of alcohol molecule takes place. Hence, boiling point increases. However, the magnitude of hydrogen bonding in alcohol is less than that in water. Hence, alcohols are low boiling compared to water.



Less hydrogen bonding
low boiling point



More hydrogen bonding
High boiling point

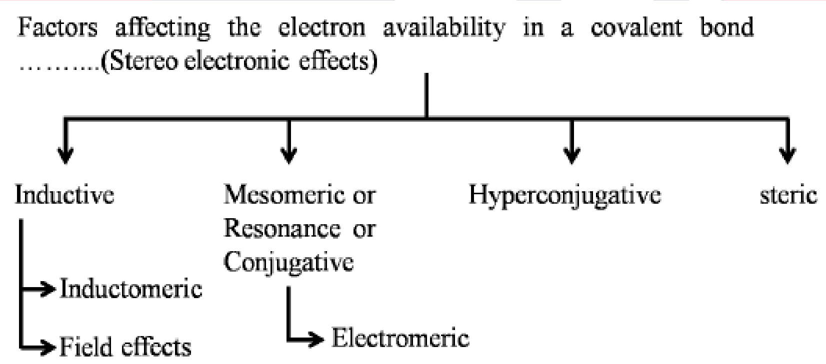
1. Alcohols boiling point increases when branching decreases. Association due to s hydrogen bonding decreases as the branching increases. Order of boiling point is primary alcohol > secondary > tertiary alcohol.
2. Boiling point increases on increasing number of OH group.

Day – 7

7.1. Factors affecting the nature of covalent bond

An ideal covalent bond between two atoms keeps the electron density maximum between the atoms. The bonded electron pair is shared absolutely equally between the atoms. This is possible if both the atoms are of same electro-negativity. For a covalent bond between two unlike atoms, the bonded electrons are not shared equally. This unequal sharing is due to the following reasons;

1. **Inductive effect**
2. **Field effect**
3. **Inductomeric effect**
4. **Mesomeric or resonance effect**
5. **Electromeric effect**
6. **Hyper conjugative effect**
7. **Steric effect**



7.1. Inductive effect

Inductive effect is the effect due to partial and permanent displacement of sigma-bonded electrons towards the most electro-negative atom in a molecule of unlike atoms in the ground state.

Salient features of inductive effect

(1) It is operative in the ground state of the molecule.

(2) It is a permanent effect.

(3) Effect due to partial shifting of electron density.

(4) Operative through sigma bonds only.

(5) The effect decreases from $C_1 – C_2 – C_3$ and vanishes at C_4.

(6) Inductive effect is represented by an arrow mark at the centre of the bond.

(7) Direction of arrow is towards the electro negative atom of the molecule.

(8) Classified as electron attracting (– I) and electrodonating (I) groups.

(9) Electron density increase near the electro negative atom by inductive effect.

(10) All inductive effects are permanent polarizations in the ground state of a molecule and are therefore manifested in its physical properties, for example its **dipole moment.**

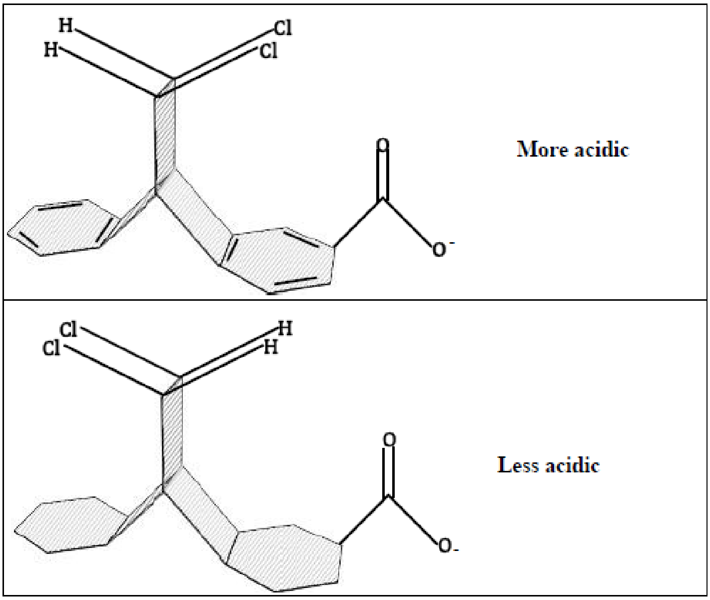
(+I) Group	**(– I) Group**
Any group that repel electrons stronger than ‘H’	**Any group that attracts electron stronger than ‘H’**
> COO– (CH3)C → $(CH_3)_2CHCH_3CH_2CH_2$ > CH_3CH_2 > CH_3 > D > H	**$+N(CH_3)_3$ > NO_2 > CN > CO_2H > F > OR > OH > NH_2 > C_6H_6**

Compared to hydrogen most of the groups are electron with drawing. Deuterium is electron donating with respect to hydrogen. Other things being equal, atoms with SP bonding generally have a greater electron withdrawing power than those with sp^2 bonding which in turn have more electron with drawing power than those with sp^3. This is the reason aryl, vinyl, and ethynyl groups are electron withdrawing and alkyl groups are electron donating.

7.2. Field effects

In addition to any inductive effect operating through sigma bonds in a compound, an essentially analogous effect can operate either through space surrounding the molecule, or via, the molecule of solvent that surround it. This analogous effect is called field effects.

It is often very difficult to separate the two kinds of effect. In many cases, it can be separated by taking the advantage of the fact that field effect depends on the geometry of the molecule, but inductive effect depends on the nature of the bonds only.



In most cases, inductive and field effects are considered together, and the combined effect is observed or measured as dipole moment.

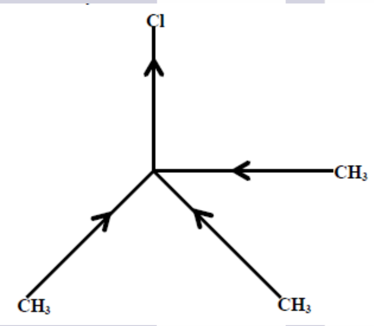
7.3. Inductomeric effect

Changes in electron distribution that may result either on close approach of a reagent or in the transition that is formed from the reagent's initial attack. The effect caused by the reagent approach on the sigma bond is called inductomeric effect. This is a temporary effect. The effect vanishes when the reagent is removed. This will not be reflected in the physical properties of the compound. It is impossible to distinguish experimentally between permanent and time variable effect but it is found that the actual close approach of a reagent have a profound effect in enhancing the reactivity of the reactant molecule.

7.3.1. Inductive / field effect and physical and chemical properties of molecules

(1). Chemical relactivity of alkyl halides

Alkyl halides are more reactive than the corresponding alkanes due to the polarity of the compound. This polarity is due to inductive effect. The electron donating (+ I) effect of the three methyl groups and the electron attracting (– I) effect of the chlorine atom enhances the reactivity of the compound. Thus in ter: butyl chloride, the removal of chlorine is faster than that of methyl chloride.



(2) Strength of carboxylic acids

An acid is a species that has a tendency to lose proton. More tendencies to lose H^+ means more acidic.

$$HA \rightleftharpoons A^- + H^+$$

Factors that may affect the acidity are those which influence the above equilibrium they are;

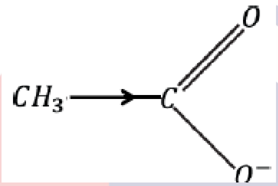
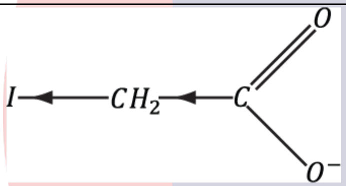
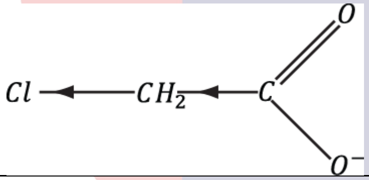
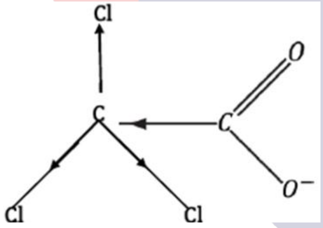
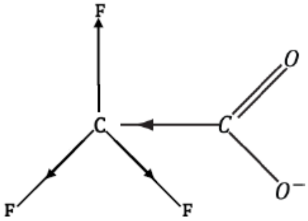
(a):- The strength of H – A bond.
(b):- The electro negatively of A.
(c):- Factors stabilizing A^- compared to AH.
(b):- Nature of the solvent.

The most influencing factor is stabilization of A^- compared to AH. The acid becomes more acidic if A^- is stabilized. Field effects inductive effects explain this stabilization. More acidic means less pKa .

Illustration

Acid	pKa
CH_3CO_2H	**4.76**
$1 – CH_2 – CO_2H$	**3.12**
$Cl – CH_2CO_2H$	**2.85**
Cl_3CCO_2H	**0.7**
F_3CCO_2H	**0.23**

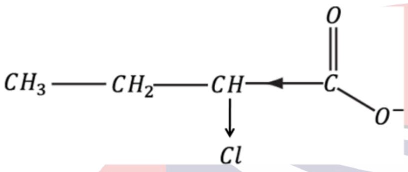
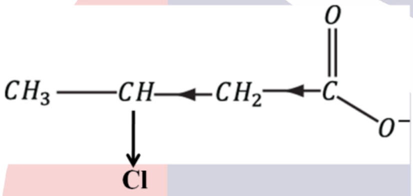
The difference in acidity in the above acids are due to the stabilization of the corboxylate ion by electron pulling inductive effect of halogen atoms (– I).

	Destabilizes the ion(conjugate base)
	Stabilizes the ion
	Stabilizes more due to more electron pulling effect of chlorine
	Stabilizes more due to cumulative inductive effect of three chlorine atoms
	Cumulative inductive effect is more due to the presence of more electronegative fluorine atoms

Illustration

2–Chlorobutanoic acid has pKa = 2.86 and that of 3–chlorobutanoic acid pKa = 4.05. Why?

It is due to the stability of the conjugate base of the acid. The stability is explained based on inductive effect (electron withdrawing) as follows; 2-chlorobutanoic acid is more acidic than 3-chlorobutanoic acid.

	More stable because 'Cl' is close to CO_2^-
	Less stable because 'Cl' is away from CO_2^- inductive effect decreases as distance increases

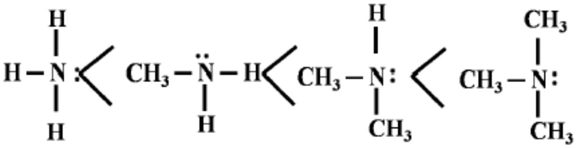
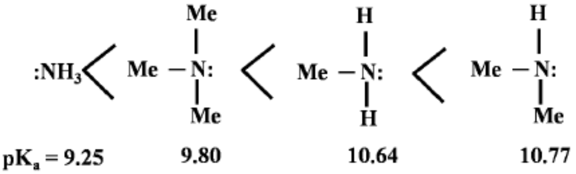
(3) Basic character of amines

The basic character of amines is due to the presence of unshared electron pair on nitrogen, which accepts proton. Any factors that increase the electron availability at nitrogen atom will increase the basicity. Strength of bases are expressed as pKa for BH^+

$$B{:}+H^+ \rightleftharpoons B\,H^+$$

Stronger BH^+ as an acid (low pKa of BH^-) weaker the base (B): and weaker BH^+ as an acid (higher pKa of BH^+) stronger the base. pK_{BH+} Is simply written as pKa. Hence, higher pKa means strong the base, which depends upon the availability of electron at nitrogen.

Basicity order of nitrogenous bases in gas phase

The increase of basicity due to +I effect of alkl group. Basicity order in gaseous sate	
This is due to the decreasing stabilization of BH^+ by solvalion Basicity order in aqueous phase	

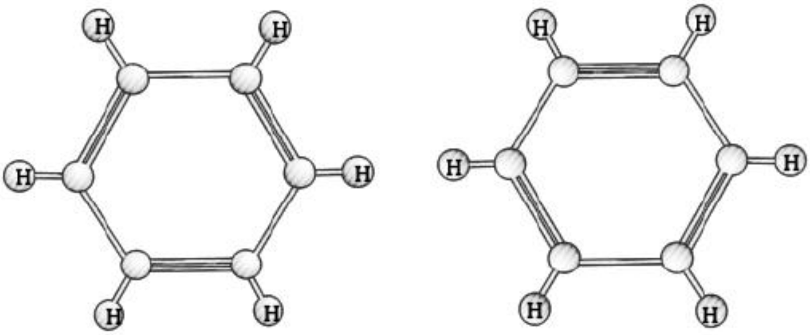
Day – 8

Aromaticity-1

8.1. The concept of aromaticity

Originally, aromaticity was associated with a special chemical reactivity. Aromatic compounds are characterized by a special stability, and they are unsaturated, but undergo substitution rather than addition. One of such compound is benzene.

An aromatic property of benzene ring is related to the presence of a closed loop of six electrons.



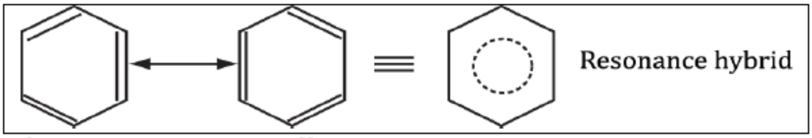
A closed loop six electrons in benzene is responsible for aromaticity. The delocalization ofelectrons is the reason of stability. The above given representation is known as Kekule representation of benzene. T he special properties of benzene are the following;

- The unusual stability
- Ability to undergo substitution rather than addition
- Lower heat of hydrogenation (enthalpy predicted by summation of normal bond energies 28.6× 3 = 85.5 Kcal. $\Delta H_{obs} = 49.8\ Kcal.$
- Only one di substituted product.
- Identical C – C bond length (1.39A^{o}) which is in between C –C (1.54 A^{0}) and C = C (1.34A^{0}).
- Lower heat of combustion (789.1 Kcal.) than calculated (824.1 Kcal.).

The help of valence bond theory and the molecular orbital theory can explain the above points.

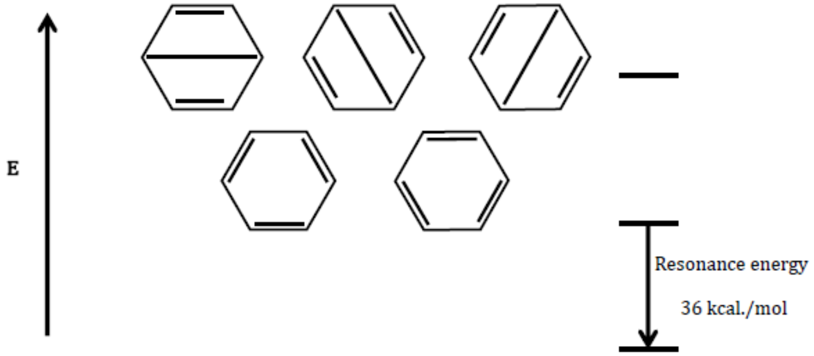
8.1.1. Valence bond theory of aromaticity of benzene

According to this theory benzene is a hybrid form of I and II



1 11

The resonance hybrid is of lower energy by 36 Kcal. than that of the two equivalent canonical forms. This energy is called resonance energy.

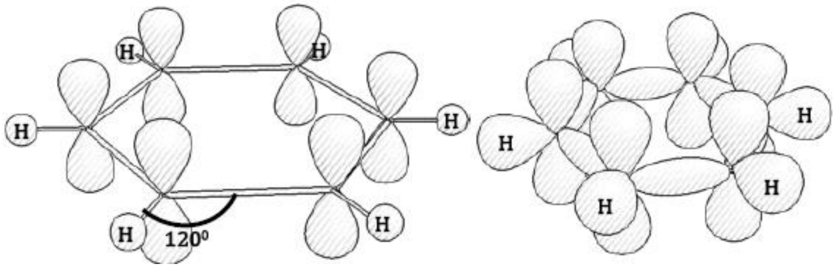


Resonance energy is the energy difference between the actual molecule (resonate hybrid) and the canonical form of lowest energy. Isomer number, low enthalpy, equal bond length and unusual stability are explained by the theory. Substitution reaction in benzene rather than addition reaction is because in the former reactions resonance stabilized benzene system is retained, while the addition reaction leads to the destruction of the benzene system.

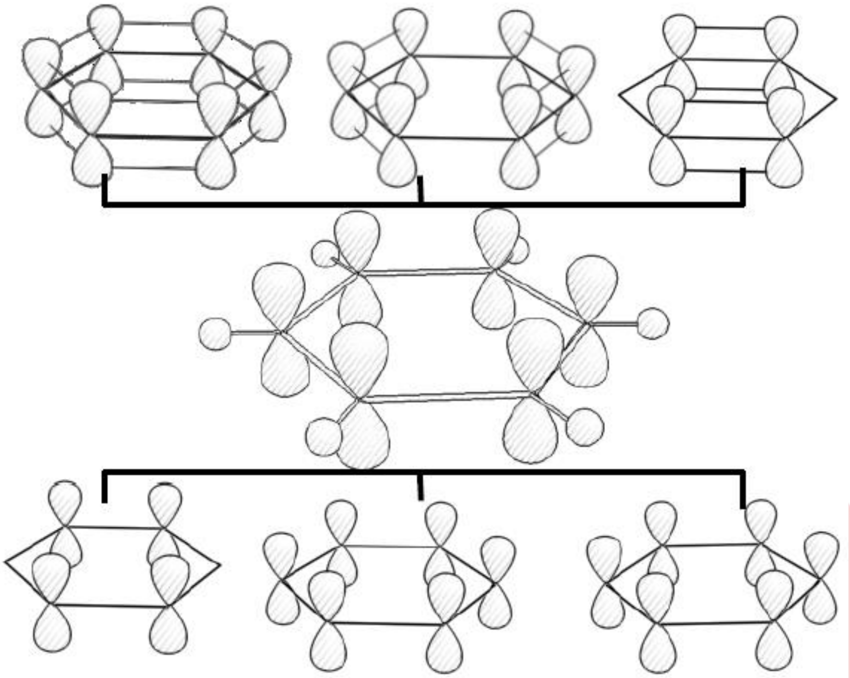
8.1.2. Molecular orbital theory of aromaticity of benzene

Cyclic structures that have a particularly stable arrangement of occupied π molecular orbitals are called aromatic. The simple relationship between an MO description of structure and aromaticity is known as Huckel rule. It states that planar, monocyclic, completely conjugated hydrocarbons will be aromatic when the ring contains $(4n + 2)\pi$ electrons.

Benzene contains six π electrons $= 4 \times 2 + 2$. Hence as per Huckel theory, it is aromatic. The basic carbon skeleton is formed by the combination of sp2 hybrid orbitals of carbon and ‘s’ orbitals of hydrogen leaving behind the unhybridize P_z orbitals.



The six p_z orbitals combine to form six molecular orbitals. Three are bonding orbitals are three are antibonding orbitals. The six electrons are accommodated in three bonding molecular orbitals leaving the antibonding orbitals empty.



Putting the three bonding MOs together, obtained a closed loop of six electrons above and below the hexagonal carbon skeleton.

Aromaticity is a chemical property in which a conjugated ring of unsaturated bonds, lone pairs of electrons or empty orbitals exhibit stabilization stronger than would be expected by stabilization of conjugation alone.

An aromatic compound has the following characteristics (eg. Benzene)

(1) Stable
(2) Planer cyclic conjugated
(3) Presence of diamagnetic ring current
(4) Equal or approximately equal bond lengths
(5) Ability to undergo electrophilic substitution
(6) Presence of vibrational fine bands in the electronic spectrum.

Both valence bond theory and molecular orbital theory can explain the aromaticity of benzene. The most accepted theory is molecular orbitals theory.

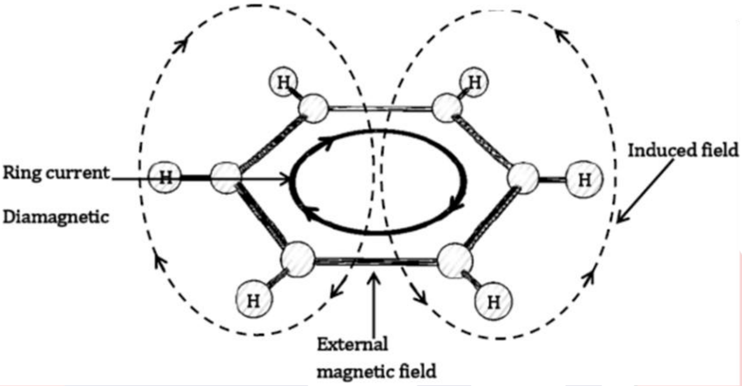
8.2. Aromaticity in molecules other than benzene

The stability of benzene is suggested to arise from the fact that it is a conjugated planar polyene with (4n + 2) electrons, (where n =1). This property described by Huckel is called aromaticity and is known as Huckel theory of aromaticity. However, it is not easy to determine whether rings other than the benzene ring possessed such a loop electrons. The following are the methods of finding this type of cyclic loop of electrons.

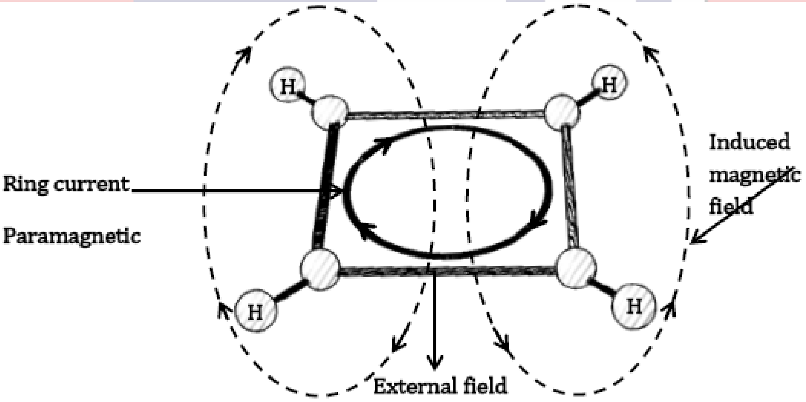
8.2.1. Nuclear magnetic resonance study to determine aromaticity

The molecule is brought under an external magnetic field, and if the molecule is aromatic the electronic ring current induce a magnetic field, which will be diamagnetic.

Thus, aromaticity can be defined as the ability to sustain an induced ring current.



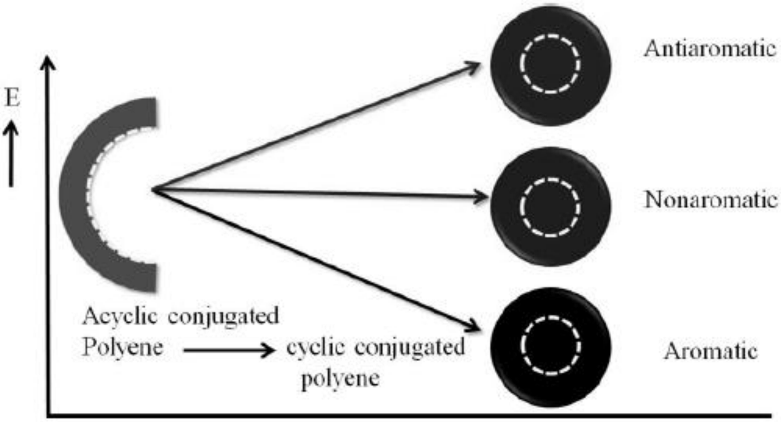
If the ring current induces a paramagnetic field, then the compound will be antiaromatic and as per Huckel theory, it will be planar conjugated polyene of π(4n) electrons.
Eg. Cyclobutadiene.



It there is no ring current the molecule is non- aromatic, which is probably due to the non- planar nature of the molecule.

8.2.2.Predicting aromatic, antiaromatic or nonaromatic in terms of energy or stability

If a cyclic conjugated, planar polyene is more stable (lower in energy) than the corresponding acyclic conjugated polyene, then the cyclic polyene is aromatic. If the cyclic polyene is of higher energy than the corresponding acyclic conjugated polyene, then the cyclic compound is antiaromatic. If the acyclic and cyclic conjugated polyenes are of same energy or same stability, then the cyclic compound is nonaromatic. Non-aromatic compounds are non-planar where as aromatic and anti aromatic compounds are planar.



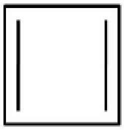
The stability due to aromaticity does not mean that it will be infact stable to air, light or common regents. This stability is determined not by resonance energy but by the difference in free energy between the actual molecule and the transition states for the reactions involved. This may be quite small even if the resonance energy is large.

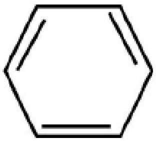
8.2.3. Huckle’s rule (4n +2) of aromaticity

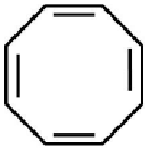
Huckle’s rule, based on the molecular orbital calculation predicts that electron ring will constitute an aromatic system only if they contain a number of the form (4n +2), where ‘n’ is any positive integer, including zero. Systems with 4n electrons are predicted to be nonaromatic or antiaromatic. Molecular orbital calculations predict that the aromaticity of (4n + 2) systems decreases with increasing ‘n’, so that large systems will show alternation of single and double bonds and no aromaticity. Alternation begin at n = 6, so that the largest aromatic ring should have $(4 \times 5 + 2) =$ 22 electrons. Antiaromaticity of (4n) systems increases with the decrease of ‘n’, and large system alters the planarity and remains as nonaromatic (no extra stability compared to acyclic analogue). There are different classes of compounds shows aromaticity or nonaromaticity.

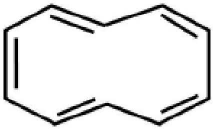
8.3. Annulenes

Annulenes are monocyclic polyenes, with conjugation of π orbitals. The simplest one is [4] annulene, and others [6] annulene, [8] annulene, [10] annulene etc. The number given in square brackets is the number of atoms in conjugation.


[4] Annulene
cyclobutadiene


[6] Annulene
benzene


[8] Annulene
cyclooctatetraene

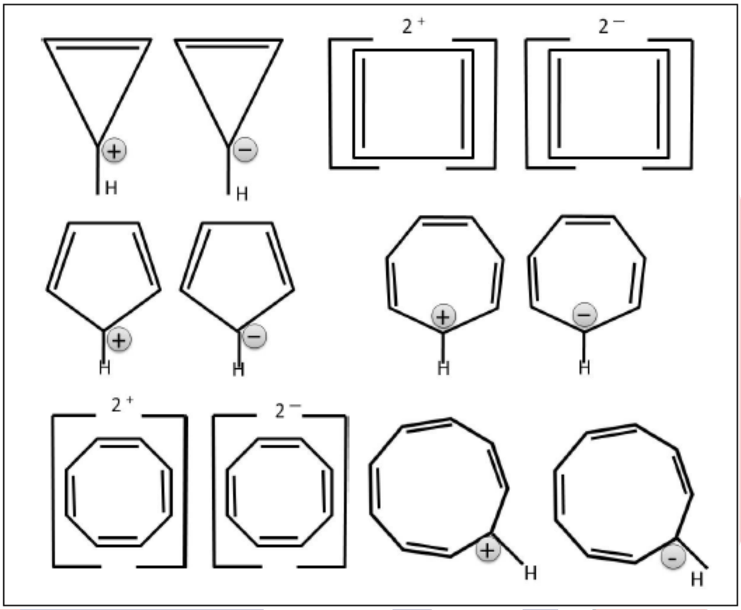

[10] Annulene
cyclodecapentaene

Day- 9

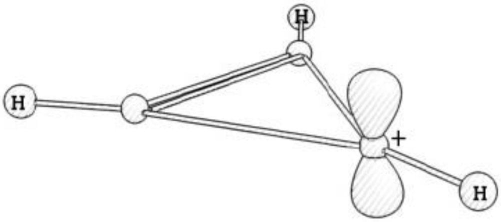
AROMATICITY 2

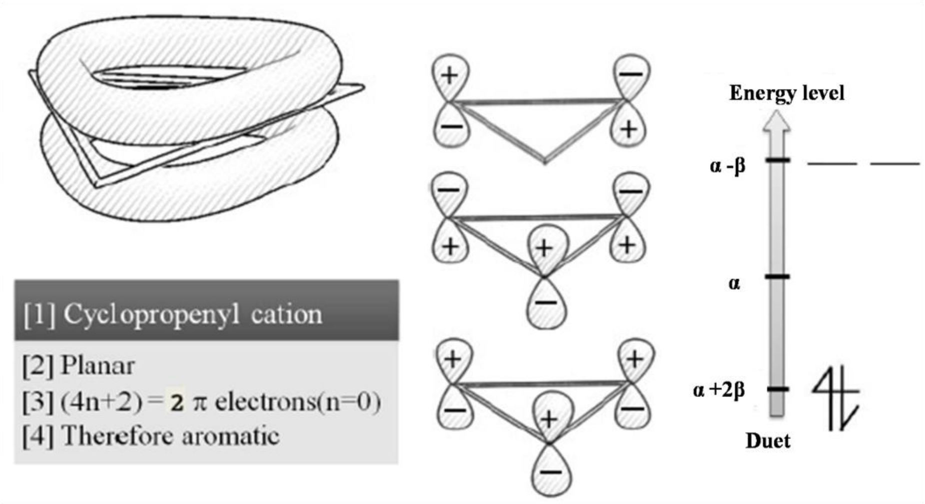
9.1. Charged cyclic polyenes

Huckel’s (4n + 2) rule of aromaticity can be applied to not only neutral conjugated planar polyenes, but also to ionic conjugated planar polyenes. The simplest one in this category is cyclopropenyl carbocation.



9.1.1 Cyclopropenyl cation

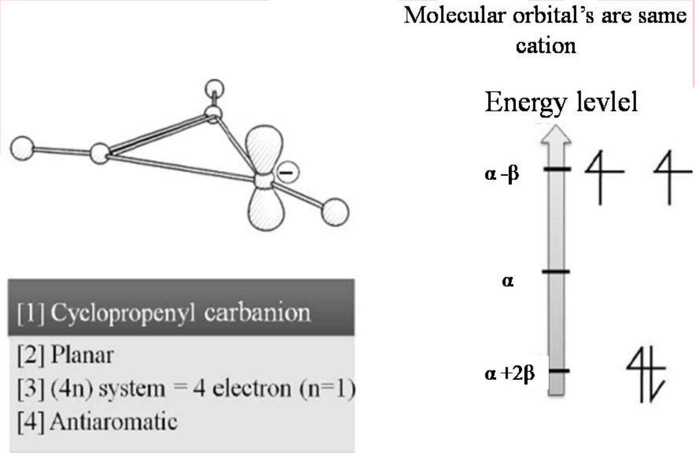




[1] Cyclopropenyl cation
[2] Planar
[3] (4n+2) = 2 π electrons(n=0)
[4] Therefore aromatic

Cyclopropenyl carbocation according to Huckel's theory is aromatic. It contains two π electrons as a cyclic loop $(4 \times 0 + 2 = 2)$. This is responsible for the aromaticity. According to MO theory three 'P' orbitals of carbon combine to form three molecular orbitals. One bonding $(\alpha + 2\beta)$ and two antibonding $(\alpha - \beta)$ The two electrons occupy the bonding orbitals, thus the electronic configuration becomes similar to neutral aromatic compounds (HOMO is completely filled). The carbocation is stable despite the angle is only 600. The aromatic duet is the reason of stability.

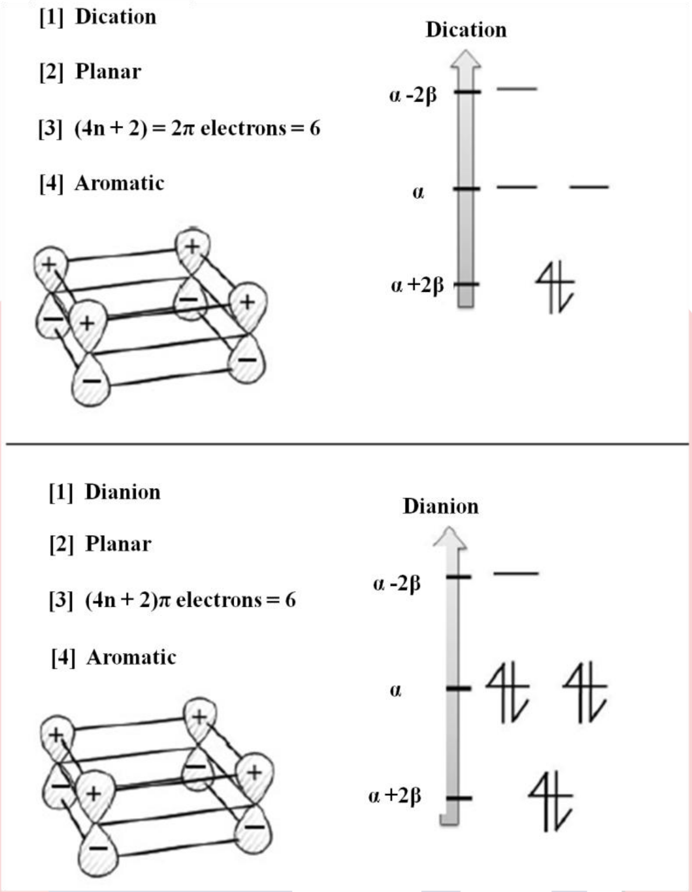
9.1.2. Cyclopropenyl carbanion



[1] Cyclopropenyl carbanion
[2] Planar
[3] (4n) system = 4 electron (n=1)
[4] Antiaromatic

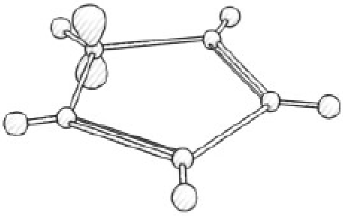
The electronic configuration shows that the highest energy occupied molecular orbital is half filled. It is like a diradical. Due to this, if resonance takes place, the system will be unstable. Distortion of geometry to avoid resonance is also not possible due to large angle strain. Hence, the anion is highly unstable and antiaromatic.

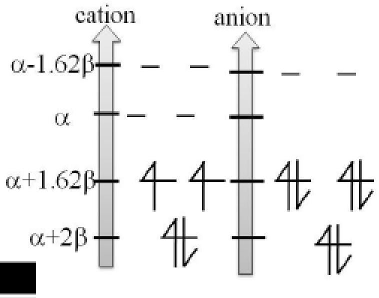
9.1.3. Cyclobutadiene dication and dianion

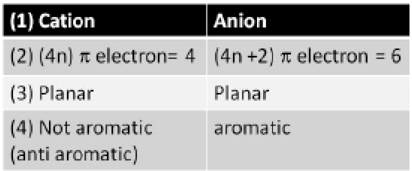


The electronic configuration of both is identical. The highest occupied molecular orbitals are completely filled. Hence, they form a closed loop of two and six electrons respectively for dication and dianion. Both ions are aromatic and stable at room temperature. They are planar and the geometry is square planar. Both dication and dianion have equal bond lengths and undergoes typical electrophilic substitution reaction. The neutral cyclobutadiene is highly unstable and cannot be synthesized. The geometry of neutral antiaromatic cyclobutadiene is found to be rectangular rather than square but the reduced form as well as the oxidized form of cyclobutadiene is found to be stable and square planar in geometry.

9.1.4. Cyclopentadiene carbanion and cation



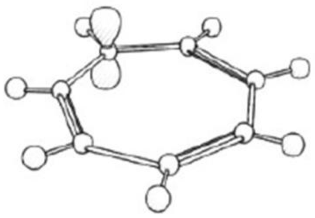


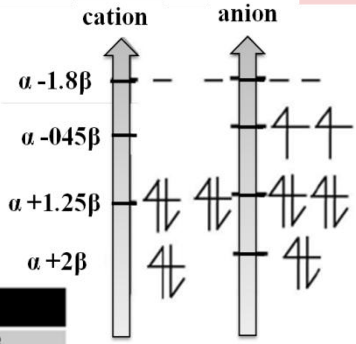


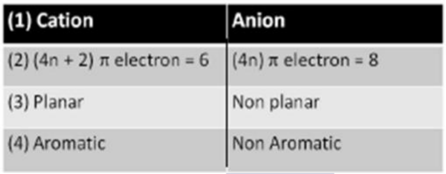
(1) Cation	Anion
(2) (4n) π electron= 4	(4n +2) π electron = 6
(3) Planar	Planar
(4) Not aromatic (anti aromatic)	aromatic

Cyclopentadiene carbocation is antiaromatic and cannot be prepared, where as the anion is stable and aromatic and can be easily prepared. Both cations and anion are planar.

9.1.5. Cycloheptatriene carbocation and anion



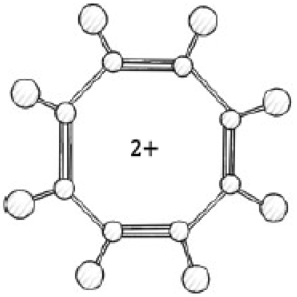


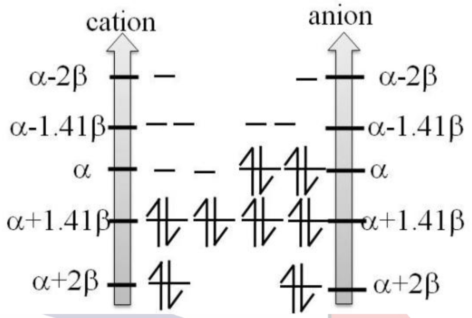


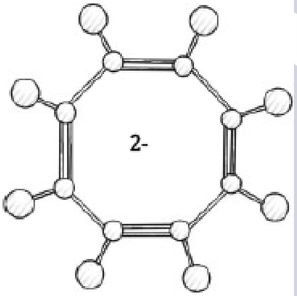
(1) Cation	Anion
(2) (4n + 2) π electron = 6	(4n) π electron = 8
(3) Planar	Non planar
(4) Aromatic	Non Aromatic

Cycloheptatriene carbocation is aromatic and planar; where as the corresponding, anion is nonplanar and nonaromatic.

9.1.6. Cyclooctatetraene dication and dianion





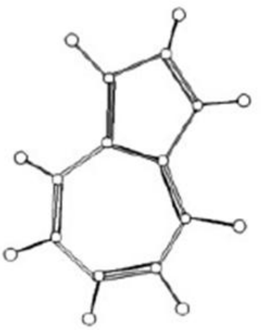


(1) Cyclooctatetraene dication	Cyclooctatetraene dianion
(2) (4n + 2) π electron = 6	(4n +2)π electron = 10
(3) Planar	Planar
(4) Aromatic	Aromatic

Both dication and dianion of cyclooctatetraene are planar and aromatic. The highest energy occupied orbitals are completely filled hence, no point of distortion or deviation from planarity. As the size of the ring increases, stability decreases due to the tendency of the system to attain nonplanar geometry, as well as deviation from ideal bond angle (120^0). It is found that small ring aromatics are more aromatic than the large ring. In the case of antiaromaticity, small ring are more antiaromatic than large rings.

9.2. Polycyclic compounds

Azulenes



Azulenes
(1) Planar
(2) (4n+2)π electron = 10
(3) Aromatic

Day – 10

10.0. Isomerism

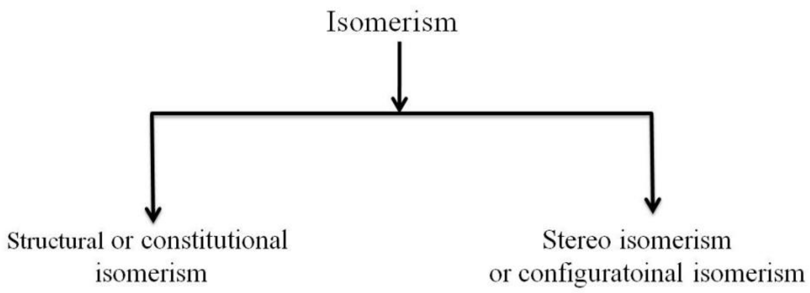
Isomerism is the phenomenon of existence of two or more compounds with the same molecular formula. Molecules with same molecular formula and different physical, or chemical or both properties are called isomers. The difference in properties is due to the difference in arrangement of atoms within the molecule of the isomers. The constitution of atoms in isomers differ, hence they are called constitutional isomers. Depending on the type of difference in arrangements of atoms (constitution), there are two type of isomerism

(a) Structural isomerism
(b) Stereo isomerism

Structural isomers are having same molecular formula but differ in their structural formula. These are also called constitutional isomers.

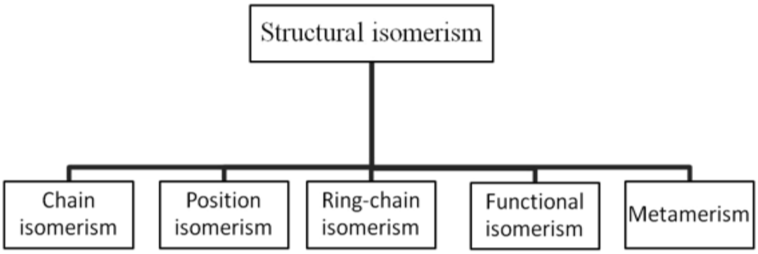
10.1. Constitutional isomers

Stereo isomers are compounds with same molecular and structural formula, but differ in their relative arrangement of atoms or groups in space. The phenomenon is called stereoisomerism. The spacial arrangement of atoms or groups in a molecule is referred as configuration. Hence stereoisomers are also called configurational isomers.



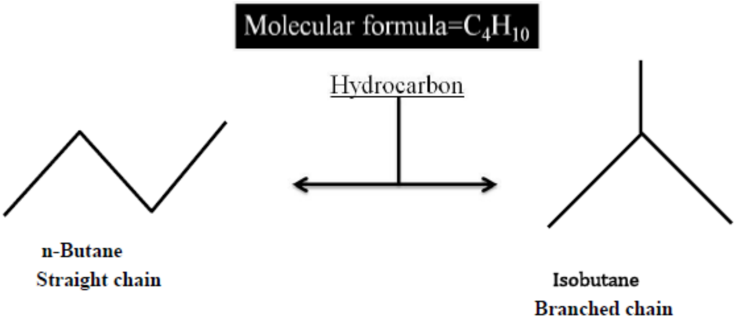
Structural or constitutional isomerism

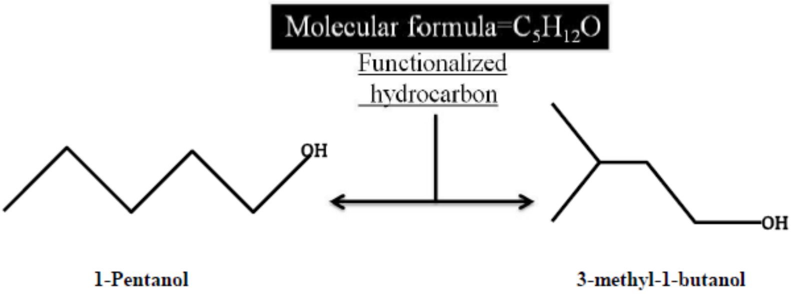
A single molecular formula represents more than one chemically or physically different molecules, where differences are due to the main difference in their structures, or constitutions, such a phenomenon is termed as structural isomerism and the different molecules are called structural isomers. Structural isomerism may are of different types. They are the following;



10.1.1. Skeletal or chain isomerism

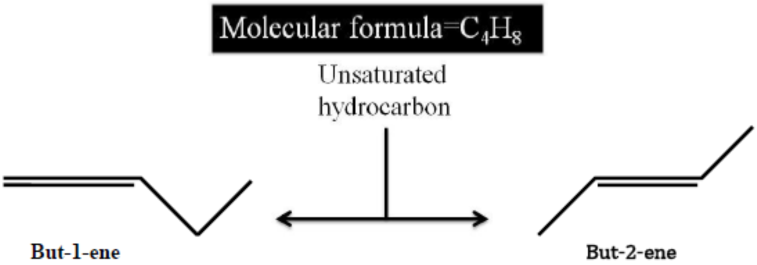
Molecules differ in their structure of carbon chain are known as skeletal or chain isomers and the phenomenon is known as chain or skeletal isomerism. As the number of carbon atom increases the number of chain isomers increases.



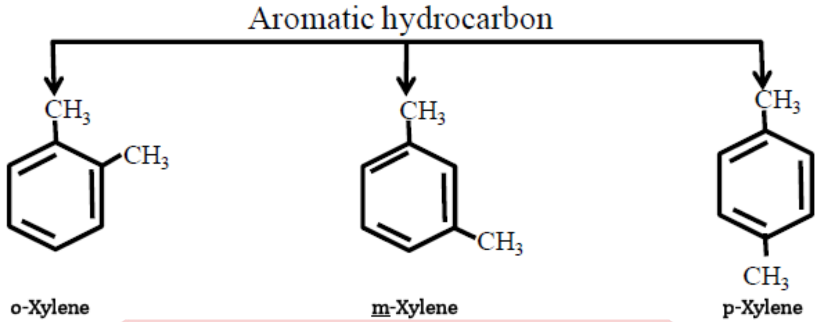


10.1.2. Position isomerism

Compounds with similar carbon chain, but differ in position occupied by a particular atom or group (substituent, unsaturated linkage, functional group etc.) in the carbon chain.

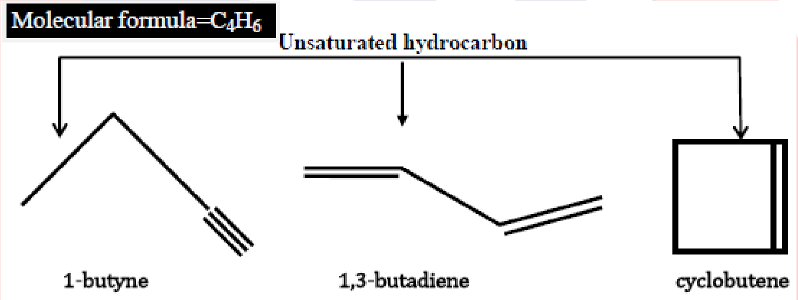


Molecular formula=C_8H_{10}



10.1.3. Ring – chain isomerism

This type of isomerism is due to the difference in carbon linkage to form cyclic or acyclic compound.



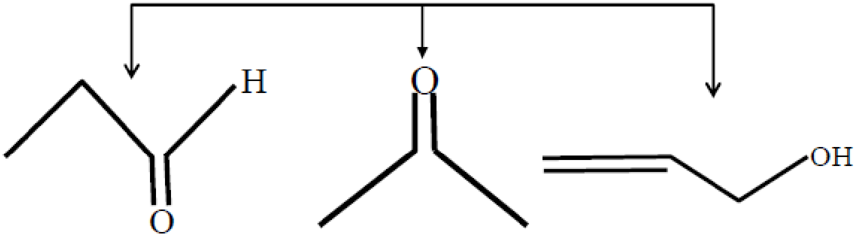
10.1.4.Functional isomerism

Isomerism exhibited by compounds differing in functional group is called functional isomerism. Functional groups are the groups that define the physical and chemical properties of the compound. Therefore, these isomers differ in their physical as well as chemical properties.

Common functional Isomers are

(a) Dienes, allenes, alkynes
(b) Alcohols, ethers
(c) Aldehydes, ketones and unsaturated alcohols
(d) Carboxylic acid and esters
(e) Primary, secondary, tertiary amines
(f) Nitro alkanes and alkyl nitrites
(g) Cyanides and isocyanides
(h) Aromatic alcohols, phenols and ethers

Molecular formula=C_3H_6O

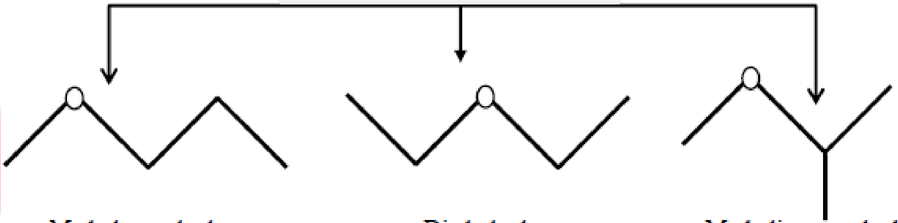


Propanal (aldehyde) 2-Propanone (Ketone) Prop-2-enol (alcohol)

10.1.5. Metamerism

This isomerism is due to unequal distribution of carbon atoms on either side of the functional group in the molecule. Compounds of the same homologous series show this type of isomerism.

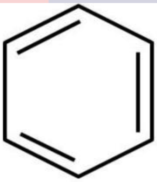
Molecular formula=$C_4H_{10}O$



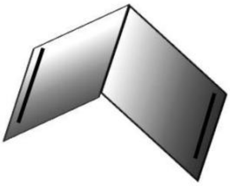
Methylpropyl ether Diethyl ether Methylisopropyl ether

10.1.6. Valence isomers

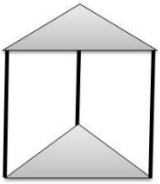
A constitutional isomer interrelated with another by a pericyclic relation. The isomers are different entities and are of different chemical and physical properties and are not inrapid equilibrium **(Molecular formula=C_6H_6)**



Benzene



Dewar benzene



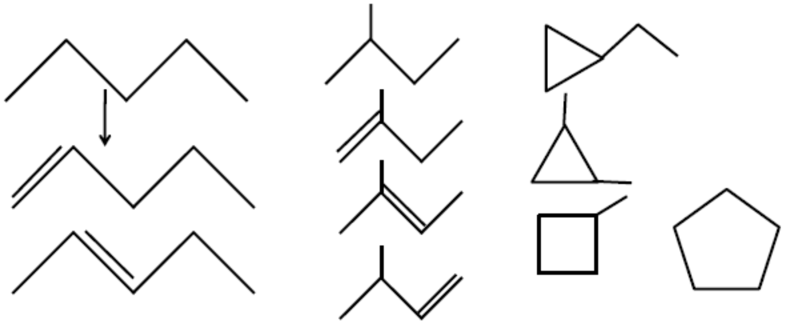
Benzvalene

To find out the possible number of structural isomers of a compound, the following points are to be considered

(1) Find out the possible number of isomeric parent alkanes

(2) Take each alkane and introduce the functional group or unstaurations at different positions

Eg: C_5H_{10}



Unsaturated structural form = 5
Cyclic form = 4
Total = 9 (Structural isomers)

10.2. Tautomerism

It is a special case of functional isomerism, where the isomers are in dynamic equilibrium. Tautomerism is the property exhibited by certain compounds, of behaving in different reactions, as if they possessed two or more structures. The different forms are called tautomers. Substances, which are isomeric under certain conditions, may be tautomers under drastic conditions. Since dynamic equilibrium exists between two isomers, the phenomenon is also known as dynamic isomerism.

$$G-X-Y-Z \rightleftharpoons X-Y-Z-G$$

In tautomerism or dynamic isomerism, if the migrating group 'G' is a cation, the tautomeric transformation is cationotropic where as if 'G' is an anion it is anionotropic. Common cationotropic transformation involves H^+, hence, it is called prototropic transformations.
Tautomerism is of two types based on the igration of atom

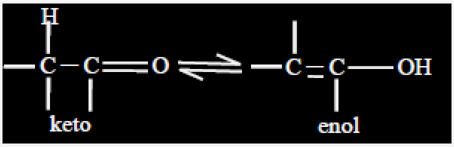
Dyad system

Hydrogen atom migrates from atom number one to atom number two,

$$\underset{\text{Ntrile}}{H-C\equiv N} \rightleftharpoons \underset{\text{isonitrile}}{C\equiv N-H}$$

Triad system

Hydrogen atom migrate from atom number one to atom three in a chain,



$$\underset{\text{keto}}{-\overset{H}{\overset{|}{\underset{|}{C}}}-\underset{|}{C}=O} \rightleftharpoons \underset{\text{enol}}{-\overset{|}{C}=\underset{|}{C}-OH}$$

Different types of triad system tautomerism

(1) (Keto-enol tautomerism
(2) Phenol-keto tautomerism