

Unit- III

COVALENT BOND

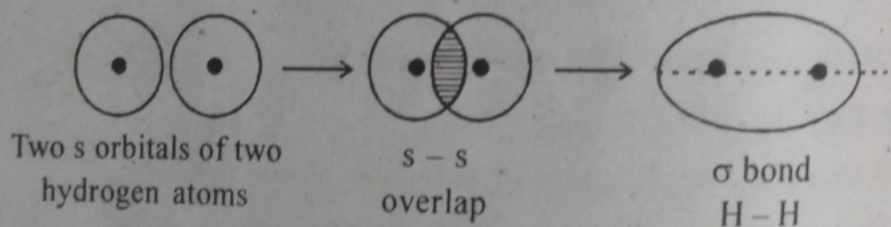
Orbital Overlap :

Organic compounds contain covalent bonds. A covalent bond is formed by the sharing of a pair of electrons between two atoms. For the purpose the two atoms must be so located that an orbital of one of the combining atoms overlaps with the orbital of the other atom; the overlapping orbital containing one electron. The strength of the chemical bond is proportional to the extent of overlapping of the orbitals.

Types of orbital overlapping : *v.v. Important*

i. **s - s Overlapping :** If one s - orbital of an atom overlaps with the s - orbital of another atom to form a covalent bond, it is called s-s overlapping.

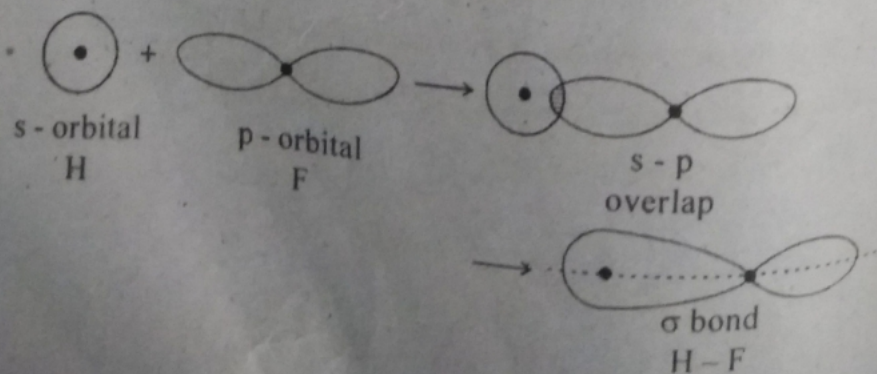
Eg., A molecule of hydrogen is formed by the overlapping of one 1s orbital of a hydrogen atom with one 1s orbital of another hydrogen atom.



ii. **s - p Overlapping :**

If one s - orbital of an atom overlaps with one p - orbital of another atom to form a covalent bond, it is called s - p overlapping.

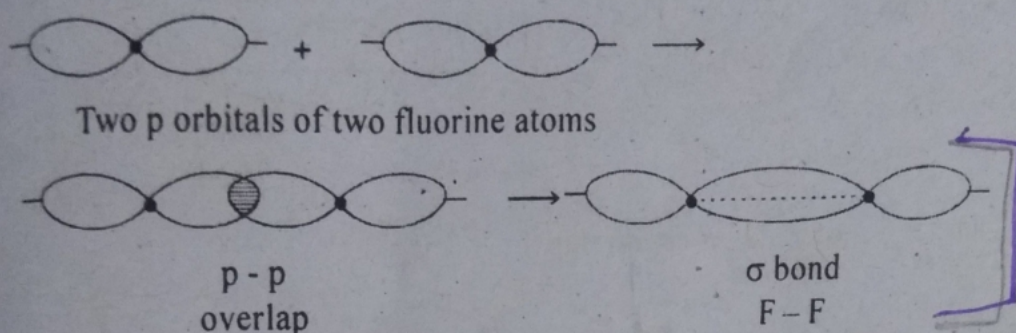
Eg., A molecule of hydrogen fluoride is formed by the overlapping of one s - orbital of a hydrogen atom with one p - orbital of a fluorine atom.



iii. p - p Overlapping :

If one p - orbital of an atom overlaps with one p - orbital of another atom to form a covalent bond then it is called p - p overlapping

Eg., A molecule of fluorine is formed by the overlapping of one 2p orbital of a fluorine atom with one 2p orbital of another fluorine atom.



σ - bond and π - bonds

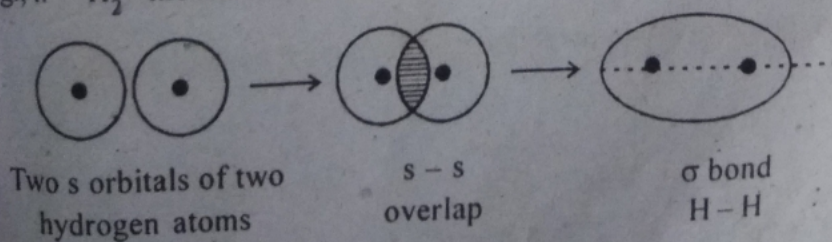
σ - bond :

When two bonding orbitals overlap to form a molecular orbital (MO), which is symmetrically distributed about the nuclear axis (the line joining the nuclei of the two atoms) then the bond so formed is called a sigma bond.

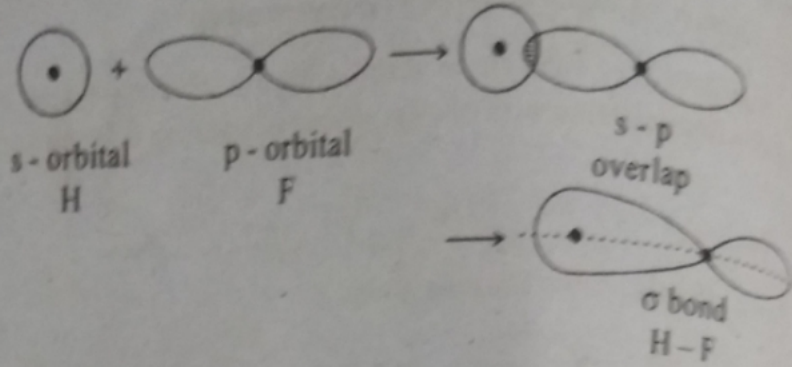
Sigma bonds are formed as the result of the orbital overlaps of

- i. s - orbital of one atom and s - orbital of the other ;
- ii. s - orbital of one atom and p - orbital of the other ;
- iii. p - orbital of one atom and p - orbital of the other (in a linear fashion).

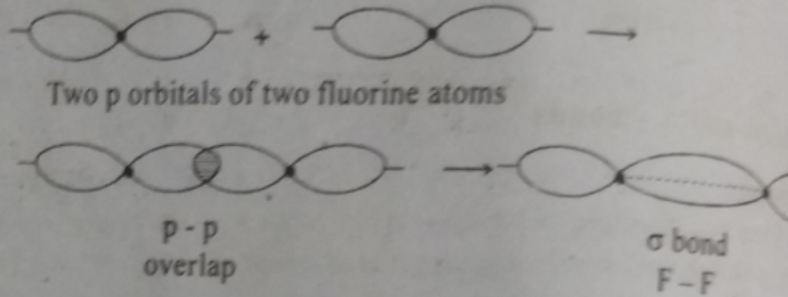
Eg., i. H_2 - molecule ; s - s overlap



ii. HF - molecule ; s - p overlap



iii. F₂ - molecule ; p - p overlap



In practice a single horizontal line is used to indicate a sigma bond

Eg.

H-H
Hydrogen

H-F
Hydrogen fluoride

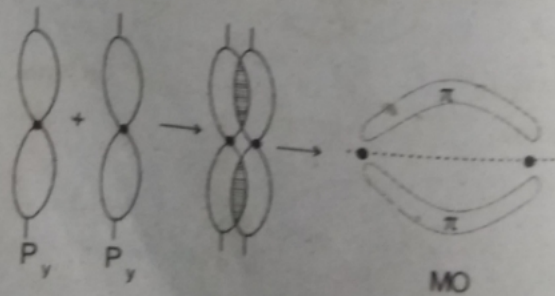
F-F
Fluorine

π - bond :

When two p - orbitals overlap in a sidewise fashion or laterally form a molecular orbital (MO), then, the bond so formed is called π - bond.

For a lateral overlap, the two p - orbitals must be held parallel.

2M



P_z - P_z - σ

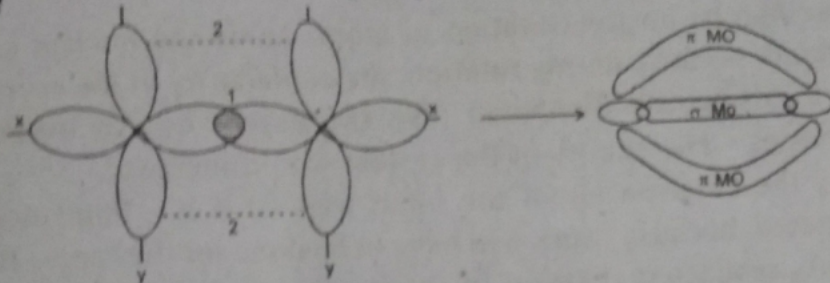
P_x - P_x - π

P_y - P_y - π

The MO thus formed lies above and below the nuclear axis.

Examples of molecules involving one or more π bonds :

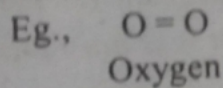
i. O_2 - Molecule



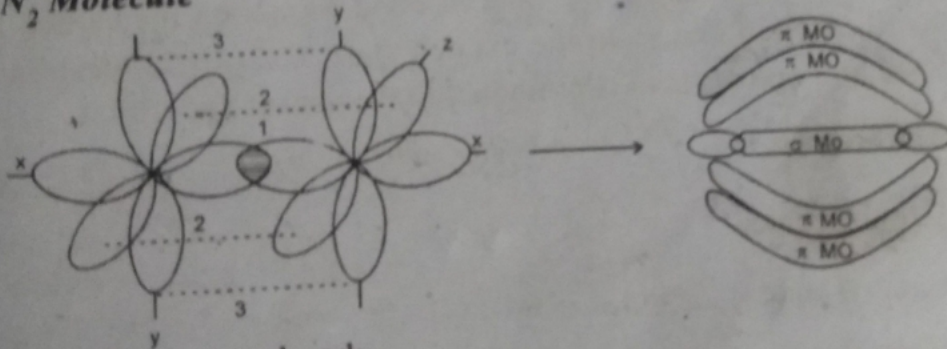
1. Head on overlap - σ bond;
2. Sidewise (lateral) overlap - π bond; A = Axis of the molecule.

Thus in oxygen molecule there are two bonds: one σ - bond and one π - bond. Both of these together are called a double bond.

In practice two horizontal lines are used to indicate a double bond.



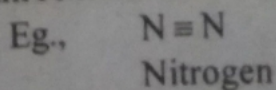
ii. N_2 Molecule



- 1 Head on overlap - σ bond;
- 2 and 3 Lateral overlaps - two π bonds.

Thus in nitrogen molecule there are three bonds : one σ - bond and two π - bonds. All the three bonds put together are called a triple bond.

In practice three horizontal lines are used to indicate a triple bond.



Differences between σ - bond and π - bonds :

- i. The π - bond has an increased electron density in the inter-nuclear region than in σ - bond. But in σ - bond the electron density is

concentrated along the bond axis. In π bond it is concentrated above and below the bond axis.

- ii. π - bond is weaker than σ - bond; because the extent of overlap in π - bond is less than that in σ - bond and hence the decrease in the internal energy of the system is less.
- iii. There can be no free rotation of atoms about the nuclear axis in a π - bond; because during rotation, the coplanarity of the overlapping p -orbitals would disappear. So the extent of p - p overlapping decreases. The energy of the system would increase.

Thus the rotation about the bond axis of a π - bond would be restricted, because, work will have to be done for the same. Because of this restricted rotation, many π - bonded compounds exhibit *cis-trans* isomerism.

Hybridisation

We have also seen the shapes of orbitals and formation of various types of bonds, but these concepts are not enough to explain the observed shapes of various molecules. So, to account for the shapes of various molecules the concept of *hybridisation* was introduced.

The tetra valency of carbon is explained as follows :

It is assumed that, at the time of bond formation the carbon atom attains an excited state. In the excited state, the two $2s$ electrons are unpaired and one of them is promoted to the vacant $2p$, orbital.

Carbon	$2s$	$2p_x$	$2p_y$	$2p_z$
Ground state	$\uparrow\downarrow$	\uparrow	\uparrow	
Excited state	\uparrow	\uparrow	\uparrow	\uparrow

Now the tetra-valency of carbon has been accounted for, by proposing an excited state structure for carbon atom with four unpaired electrons. The four unpaired electrons are not identical. There is one s - electron and three p - electrons. To explain the equivalent nature of the four bonds of carbon in its saturated compounds a new concept called hybridisation has been proposed.

According to this concept, the atomic orbitals of an atom which lie close to one another in energy, tend to merge or mix and then re-distribute their energy and shape to produce an equivalent number of new orbitals which are identical in all respects called hybridised orbitals.

V.V. Important cont
Definition : 2m

Hybridisation⁴³ is the concept of mixing or merger of orbitals of an atom having nearly equal energies, to produce entirely new orbitals, which are equal in number to the mixing orbitals. The hybridised new orbitals will have equal energies; identical shapes and are symmetrically placed in space. X

Conditions for hybridisation of atomic orbitals :

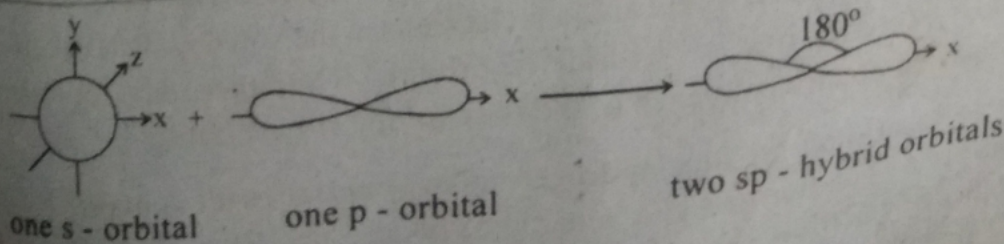
1. The orbitals of an isolated, single atom only could undergo hybridisation.
2. The hybridising orbitals must differ only slightly in their energy content. } 2m

Characteristics of hybrid orbitals : X

1. The number of hybridised orbitals is equal to the number of pure atomic orbitals which mix up.
2. A hybrid orbital can have only two electrons as the pure atomic orbitals. The two electrons must have opposite spins.
3. The electron waves in hybrid orbitals repel each other. So they tend to be as far away as possible.
4. The hybrid orbitals distribute themselves in such a way that they assume the direction of the dominating orbitals. } 2m

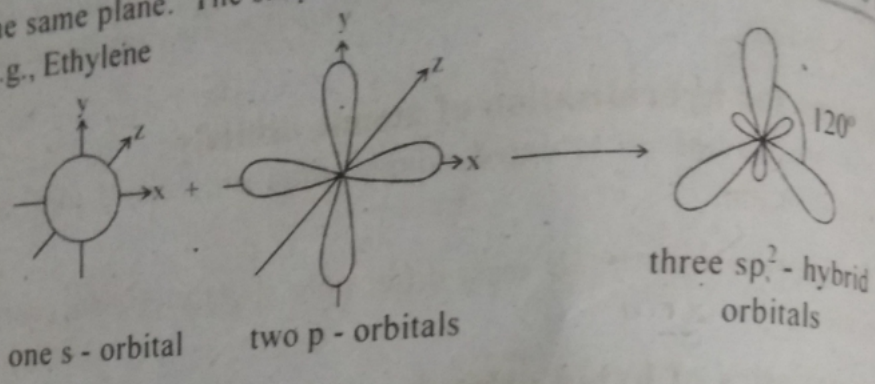
Modes of hybridisation and shapes of hybrid orbitals :

1. sp - hybridisation : 5m X X V.V. I.M.
One s and one p orbitals mix and give two identical hybrid orbitals. This is known as sp hybridisation. These hybrid orbitals are co-linear. The bond angle is 180° . E.g., BeCl_2 .

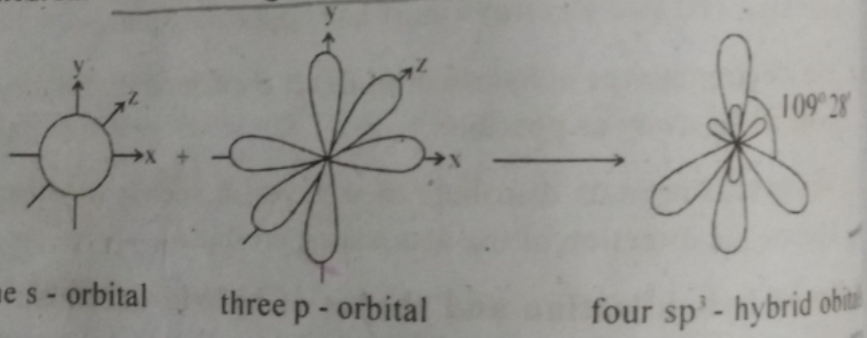


2. sp^2 - hybridisation :

One s orbital and two p orbitals mix and give **three** identical hybrid orbitals. This is known as sp^2 hybridisation. These hybrid orbitals lie in the same plane. The shape is plane triangular. The bond angle is 120° .
E.g., Ethylene



3. sp^3 - hybridisation : One s orbital and three p orbitals mix and give **four** identical orbitals. This is known as sp^3 hybridisation. The four hybrid orbitals are oriented towards the four corners of a regular tetrahedron. The bond angle is $109^\circ 28'$. E.g., : Methane



Geometry of molecules *v.v. Important*

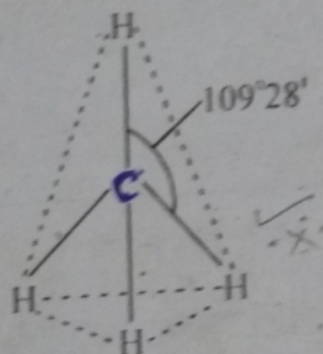
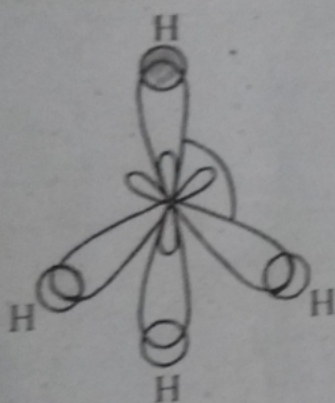
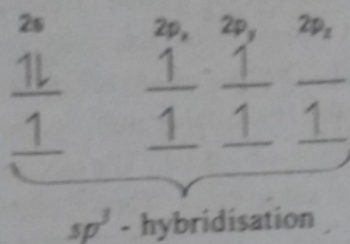
1. Methane *STO X*

In methane the carbon atom is in a state of sp^3 hybridisation. One s orbital and three $2p$ orbitals of carbon hybridise and give four sp^3 hybridised orbitals. There are four electrons in the valency shell of carbon. Each occupies one sp^3 hybridised orbital. Thus there are four single unpaired electrons in each of the four sp^3 hybrid orbitals.

1s orbitals of four hydrogen atoms overlap with four sp^3 hybrid orbitals of carbon and give four sigma bonds. i.e., there are four bonded pairs of electrons around carbon in methane. As per **VSEPR** theory, only if they are arranged tetrahedrally the bonded pairs will be as far apart as possible. That is why the methane molecules assumes a **tetrahedral** shape H-C bond angle is $109^\circ 28'$.

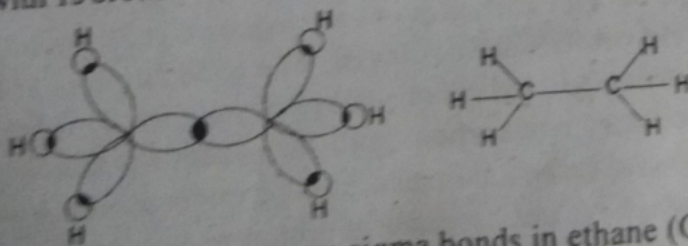
Carbon in ground state

Carbon in excited state



2. Ethane

In ethane, both the carbon atoms are in a state of sp^3 hybridisation. One sp^3 hybrid orbital of one carbon atom overlaps with one sp^3 hybrid orbital of the second carbon atom and forms a sigma bond. Each of the two carbon atoms now has three sp^3 hybrid orbitals left. Each of these overlaps with $1s$ orbitals of three hydrogen atoms and form three $s-sp^3$ sigma bonds.



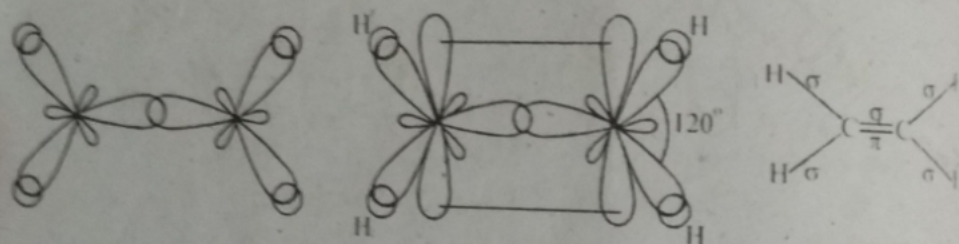
Thus there are totally seven sigma bonds in ethane (One C-C sigma bond and six C-H sigma bonds.)

3. Ethylene

In ethylene both the carbon atoms are in a state of sp^2 -hybridisation. These sp^2 -hybrid orbitals lie in the same plane. The bond angles are 120° . Each carbon atom has three sp^2 -hybrid orbitals and one pure p -orbital. One sp^2 -hybrid orbital of one carbon atom overlaps with one

sp^2 - hybrid orbital of the second carbon and forms a sigma bond. Each of the two carbon atoms now has two sp^2 -hybrid orbitals and one pure p -orbital left. The two sp^2 - hybrid orbitals on each of the two carbon atoms overlap with the $1s$ orbital orbitals on each carbon atom overlap in a side wise fashion and form a π - bond. The electron cloud of the π - bond lies above and below the C-C sigma bond. Thus in ethylene the following bonds are present.

Type of bond	Name of bond	Number of bond
C - C	σ	1
C - H	σ	4
C - C	π	1



Ethylene has a double bond in it. The double bond in ethylene contains one σ -bond one π -bond. The shape of the molecule is **trigonal planar**.

4. Acetylene

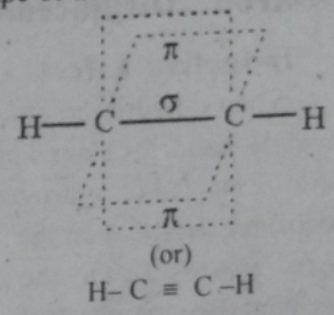
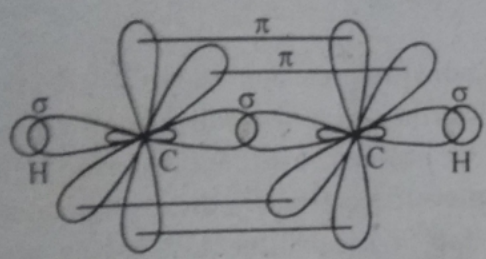
In acetylene both the carbon atoms are in a state of sp - hybridisation. These sp - hybrid orbitals are co-linear. The bond angle is 180° . Each carbon atom has two sp - hybrid orbitals and two pure p - orbitals. One sp - hybrid orbital of one carbon atom overlaps with one sp - hybrid orbital of the second carbon atom and forms a σ - bond. Each of the two carbon atoms now have one sp - hybrid orbital and two pure p - orbitals left. The hybrid sp - orbital on each of the two carbon atoms overlaps with $1s$ orbital of the hydrogen atom and forms s - sp sigma bond. The two pure p - orbitals on each carbon atom overlap in a sidewise fashion and form two π - bonds. The electron clouds of the π - bonds lie above and below the C - C sigma bond. These two π - bonds are in two planes which are perpendicular, to each other. Each of the π - bonds is perpendicular the following bonds are as well.

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Thus in acetylene the following bonds are present :

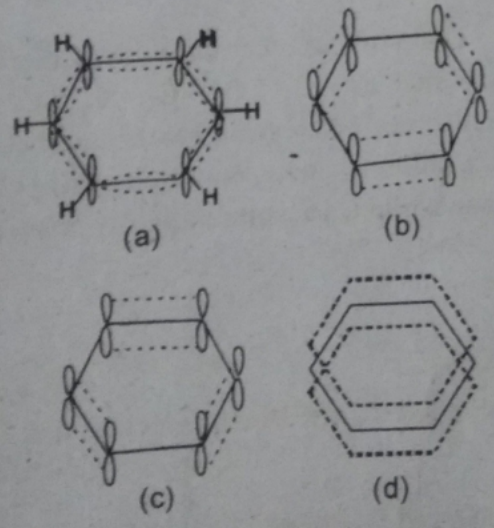
Type of bond	Name of bond	Number of bond
C-C	σ	1
C-H	σ	2
C-C	π	2

We say acetylene has a triple bond in it. The triple bond in acetylene contains one σ - bond and 2π - bonds. The shape of the molecule is **linear**.



5. Benzene

In benzene molecule the carbon atoms are in a state of sp^2 - hybridisation.



The three hybridised orbitals of each carbon are involved in the formation of three σ - bonds. (Two bonds are formed with adjacent carbon atoms and one with hydrogen).

Thus all the six carbon and the six hydrogen atoms lie in the same plane. The unhybridised p - orbitals are perpendicular to the plane of the

steering
= effective

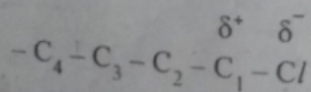
carbon hexagon (fig.a). Side overlap of these orbitals takes place. They can give three localised π -bonds (fig. b or c). But there is no reason why the overlap should be limited in this way. Thus the mutual overlapping of all the unhybridised p -orbitals give a delocalised molecular orbital. The net result is that there are two continuous ring-like electron clouds, one lying above and the other below the plane of atoms as shown in fig. d.

Electron Displacement Effects

1. Inductive Effect

When a hydrogen atom is attached to a carbon atom ($C-H$) by a covalent bond, the shared pair of electron is symmetrically placed between them. If instead of hydrogen atom we have a substituent X having higher electronegativity, then the shared pair of electrons in the $C-X$ bond will move towards X . On the other hand, if a substituent Y having lower electronegativity is attached to carbon as $C-Y$ then the shared pair of electrons in the $C-Y$ bond will move towards C . Thus if the electronegativity values of the atoms forming a bond are different, the bond is said to be polarised.

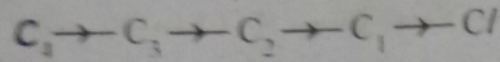
Let us consider a chain of carbon atoms with a chlorine atom linked to the end carbon atom such as $-C_4-C_3-C_2-C_1-Cl$. Due to greater electronegativity of chlorine, the electron pair shared between C_1 and Cl is displaced towards the chlorine atom. As a result of this, chlorine acquires a small negative charge while C_1 becomes slightly positively charged as shown below :



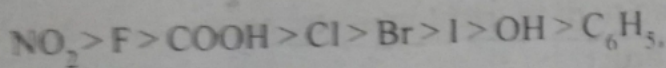
The positively charged C_1 attracts the electron pair shared between C_1 and C_2 .

The positively charged C_1 attracts the electron pair shared between C_1 and C_2 . The shared pair of electron moves slightly towards C_2 . Thus C_2 gets a slight positive charge. But the charge on C_2 is smaller than that on C_1 . The positive charge on C_2 in turn attracts the electron pair between C_2 and C_3 . This effect falls rapidly as we move away from C_1 .

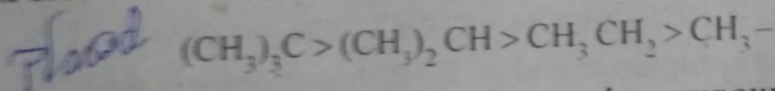
This process of electron shift along a chain of atoms due to the presence of a polar bond in the molecule is called **inductive effect**. It is represented as



The inductive effect is a permanent effect. When the substituent X attached to the carbon atom is electron attracting it develops a negative charge on X and the effect is called negative inductive effect or **-I effect**. The following groups cause -I effect. They are given in the order of their decreasing effect.

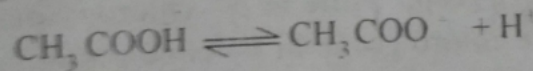


If the substituent Y attached to the carbon atom is electron repelling, it develops a positive charge on Y and the effect is called positive inductive effect or **+I effect**. The following groups cause +I effect. They are given in the order of their decreasing effect.

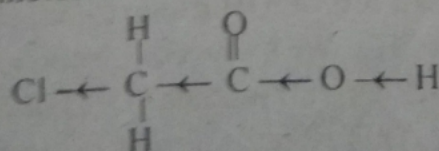


Inductive effect and properties of organic compounds :

1. Why monochloro acetic acid is more acidic than acetic acid? We know that acetic acid is a weak mono basic acid. It ionises as follows :



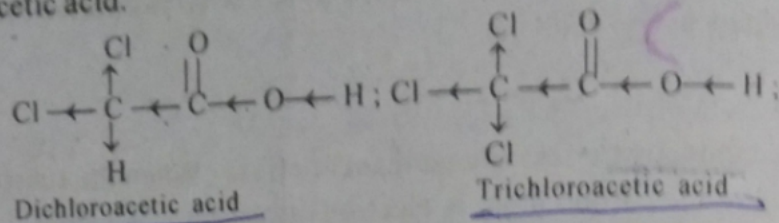
The strength of the acid is a measure of the ease with which H^+ ion leaves from COOH. If one of the hydrogen atoms of methyl group is replaced by a chlorine atom, the following situation arises. The chlorine atom is electron withdrawing. The electron pair between carbon and chlorine moves towards chlorine. In turn the electron pair between C and CO moves towards carbon and so on. Thus the **-I effect** prevails in the chloroacetic acid molecule as shown below:



This makes the separation of hydrogen atom as ion easier. Thus chloroacetic acid is stronger than acetic acid.

In a similar manner we can show that dichloroacetic acid is stronger

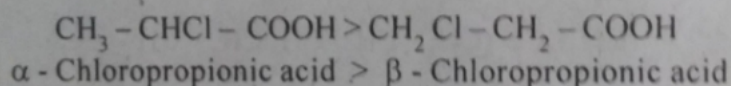
than chloroacetic acid and trichloroacetic acid is stronger than dichloroacetic acid.



In dichloroacetic acid there are two chloro group with -I effect and in trichloroacetic acid there are three chloro groups with -I effect. Thus the separation of hydrogen atom as ion becomes progressively easier as we move from mono to di to trichloroacetic acids. Thus their acid strengths increase in the order.

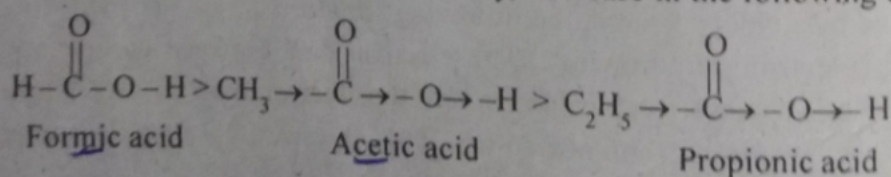
Monochloroacetic acid < dichloroacetic acid < trichloroacetic acid.

2. Why α -Chloropropionic acid is stronger than β -chloropropionic acid?



This is because inductive effect decreases with distance. In β -chloropropionic acid the chloro group with -I effect is two carbons away from the COOH group while in α -chloropropionic acid it is one carbon away. So the chloro group in β -chloropropionic acid has only less electron withdrawing effect. So it is weaker.

3. Strengths of aliphatic acids : They, decrease in the following order.



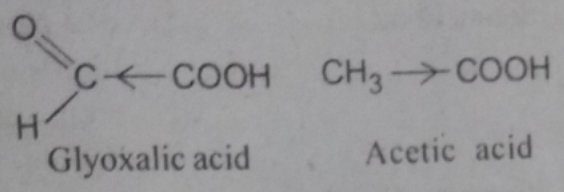
Reason : In formic acid the COOH group is attached to H while in acetic acid it is attached to CH₃. We know CH₃ group has +I effect. This pushes electrons towards H. This strengthens OH bond. i.e., removal of H as H⁺ becomes difficult. This effect is absent in formic acid.

Between acetic acid and propionic acid the stronger is acetic acid. It is because in acetic acid a CH₃ group is attached to COOH. In propionic acid a C₂H₅ group is attached to COOH. C₂H₅ is bulkier than CH₃. So it has more +I effect than CH₃. Thus it pushes electrons towards the OH

05x

bond more forcibly than CH₃. So it becomes more difficult for H to leave as H⁺ from propionic acid than from acetic acid.

4. Glyoxalic acid is stronger than acetic acid :

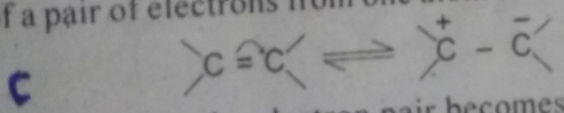


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This is because CHO groups is a strong - I group. This facilitates H to leave as H⁺. But in acetic acid the CH₃ group is a +I group. This pushes electrons towards the OH bond making it difficult to part with H⁺.

2. Electromeric Effect

In a molecule in which two atoms are linked together by a double bond, one of the pairs of electrons forming a bond may move to one of the atoms. The other pair continues to form a covalent bond between the two atoms. When the compound containing the double bond (or triple bond) is exposed to electrophilic reagent, this change occurs. There is a complete transfer of a pair of electrons from one atom to the other as shown bellow:



The atom that takes the electron pair becomes negatively charged and the other positively charged. This is purely a temporary effect and remains in the presence of electrophilic reagent. As soon as the attacking reagent is removed, the polarised molecule comes back to the original state.

The electromeric effect is a temporary effect which involves the complete transfer of a shared pair of electrons of multiple bond, to one of the bonded atoms, under the influence of an electrophilic reagent.

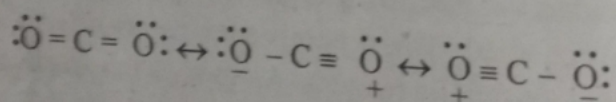
The electromeric effect is usually denoted as E effect. If both inductive and electromeric effects occur together, these may assist or oppose each other. In case they are opposed to each other, the electromeric effect generally predominates the inductive effect.

Differences between inductive and electromeric effects

	Inductive effect	Electromeric effect
1. Nature of electron displacement	Partial-along a Sigma bond	Complete Movement of a pair π electrons to one of the two atoms bond by a double bond.
2. Charge	Respective atoms attain partial negative and positive charges.	Respective atoms attain a full positive and negative charges.
3. Nature of effect	Permanent	Temporary
4. When occurs	Even in the absence of an electrophile	Only in the presence of electrophile
5. Prodominancy	Less	More

3. Mesomeric Effect or Resonance Effect

A molecule containing multiple bond may be represented by several electronic formula. For example, carbondioxide has the following electronic arrangements.



But the actual condition of the molecule is in between these three structures. This type of effect is known as mesomeric effect or resonance effect. It is represented by the symbol M or R respectively.

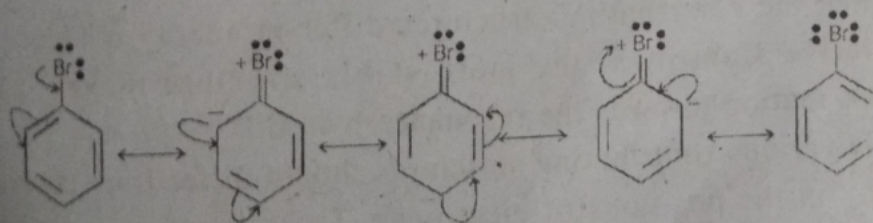
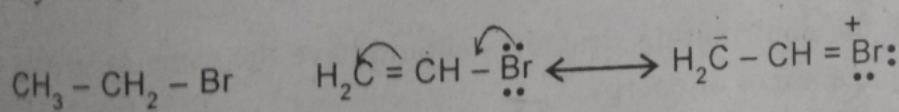
If a molecule can be assigned two or more structural formulae, each of which can explain most but not all the properties of the compound, the actual structure lies in between the various possible structures. This phenomenon is called mesomerism or resonance. [Ingold called this phenomenon mesomerism based on chemical grounds. Heisenberg called it resonance based on theoretical background. (Resonance is the name that is widely used).

The effects arising out of the presence of mesomerism or resonance is called mesomeric or resonance effect respectively.

The various possible structures are called **canonical structures**. The actual structure is called resonance hybrid. The canonical structures are represented by putting double headed arrow (\longleftrightarrow) in between them. The resonance hybrid is not a mixture of the various structures. It is an entirely new and individual structure which is in between the several canonical structures.

The mesomeric effect, like the inductive effect, may be + or - and is denoted by + M or - M. A group of atoms is said to have + M effect, when the direction of electron displacement is away from it. Such groups have lone pairs of electrons. - OH, - OR, - NH₂ and - SR groups have + M effect. A group of atoms is said to have - M effect, when the direction of electron displacement is towards it. > C = O, -NO₂, -CN and -SO₃H groups have - M effect.

The +M effect of halogen atom brings a double bond character between the halogen and the carbon atom attached to the halogen. Because of the double bond character, the halogen is held firmly. Thus the halogen atom in vinyl halides and aryl halides are less reactive than alkyl halides.



(The halogen in alkyl halide cannot have resonance and hence it cannot have double bond character. So It can be easily hydrolysed).

Differences between inductive and mesomeric effects

	Inductive effect	Mesomeric effect
1. Nature of electron displacement	σ -electrons-along a single bond-transmitted though the chain-decreases as the the distance.	π -electrons-negative charge flows towards on side of the molecule-effect is uniform.
2. Charge	Respective atoms attain partial negative and positive charges.	Charge separation is complete.
3. Relation with stability of the molecule.	None	Stabilises the molecule
4. Effect on bond length	None	Affected.
5. Effect on colour	Nil	Causes perceptible Colour.

Conditions for mesomerism or resonance :

1. The contributing structures must be reasonably stable.
2. The number of electrons in each contributing structure must be the same.
3. All the contributing structures should have the same or nearly the same amount of energy.
4. When the contributing structures differ in energy contents, i.e., relative stabilities, the more stable structure makes greater contribution towards the resonance hybrid.
5. The various contributing structures should differ from each other only in the positions of electrons. The relative arrangement of atoms must be the same.

Resonance energy :

The energy of a resonance hybrid is always less than any one of the contributing structures. The difference between the energy of the most stable contributing structure and that of the resonance hybrid is known as the resonance energy or delocalisation energy.

A resonance hybrid i.e., the actual molecule is always more stable than any one of the contributing structures. Because of this fact we say that the compound is stabilised by resonance.

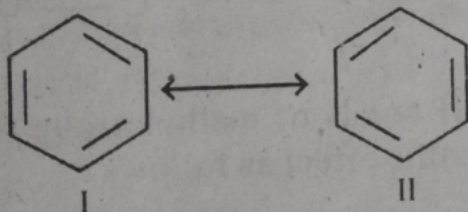
Example :

The enthalpy of formation of benzene calculated from bond energy values is $-5384.1 \text{ kJ mole}^{-1}$. The experimental value of enthalpy of formation of benzene is $-5535.1 \text{ kJ mole}^{-1}$. This is called the *resonance energy of benzene*. We say benzene is stabilised by resonance to an extent of 151 kJ/mole .

Effects of resonance :

1. Stability :

The compounds which exhibit resonance are more stable than their contributing structures. E.g., Though there are three double bonds in the contributing structures of benzene I and II, it behaves as a saturated compound. It does not undergo addition reactions instead undergoes only substitution reactions. The resonance energy is a measure of the stability caused by resonance.



2. Bond lengths :

The bond lengths in a resonance hybrid are different from those in the contributing structures. E.g., The contributing structures of benzene suggest that there are three $\text{C}-\text{C}$ and three $\text{C}=\text{C}$ bonds. Actually in benzene all the six carbon-carbon bond lengths are the same. Their lengths are in between those of $\text{C}-\text{C}$ and $\text{C}=\text{C}$ bonds.

3. Dipole moments :

The observed dipole moments are different from the values expected from the contributing structures.

4. Colour:

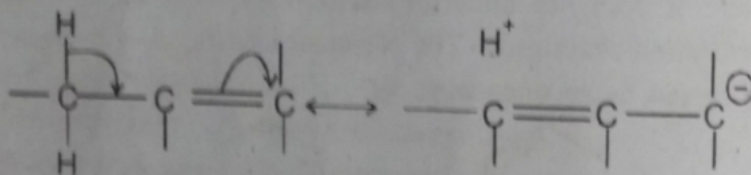
The colour of organic compounds is a consequence of resonance. E.g., Dyes. When the number of contributing structures increase, the intensity of the colour also increases.)

4. Hyperconjugation

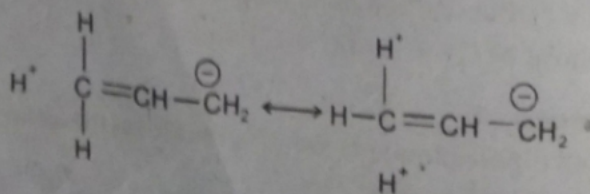
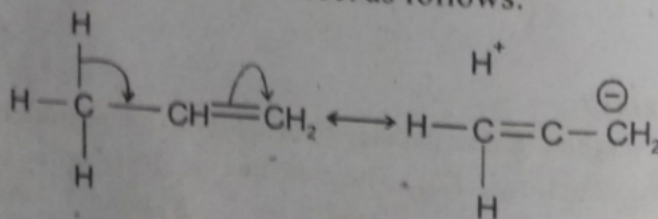
The resonance involving the delocalisation of σ -electrons conjugation with the π -electrons of an adjacent double bond is called hyperconjugation.

Explanation:

The hyperconjugative effect operates in a system containing C-H bond directly attached to a double bond. In other words, the hyperconjugative effect takes place through the interaction of σ -electrons of the carbon-hydrogen bond with π -electrons of the double bond. In hyperconjugation the electron displacement takes place towards the double bond as shown below.



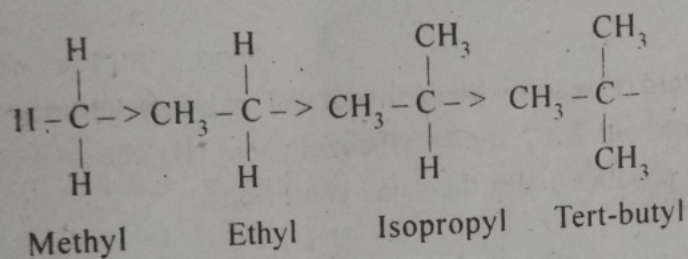
The three C-H bonds of methyl group in the propylene molecule contribute to this effect as follows.



While discussing inductive effect, it was pointed out that the inductive effect of the alkyl group is in the order.

tertiary > secondary > primary

This order is reversed when an unsaturated system (C=C) is attached with the alkyl group. As we have seen just now, the σ -electron from the C-H bonds at the α -carbon the unsaturated system gives the no bond resonance. As the number of C-H bonds are greater, greater would be the hyperconjugative effect. Thus methyl group (3C-H bonds) has the maximum hyperconjugative effect. Ethyl group (2C-H bonds) has lesser effect. Isopropyl group (1C-H bond) has the least effect. Tertiary butyl group (0C-H bond) has no hyperconjugative effect at all.



Hyperconjugation is a temporary effect. In the canonical forms, there is no bond between carbon and hydrogen. The proton in such hyperconjugative form does not move any distance away than its normal bonding distance to carbon. This type of resonance is different from tautomerism where the proton moves from one position to another. Hyperconjugation can also be regarded as an overlap of σ -orbital of the C-H bond with the π -orbital of the carbon-carbon double bond. This is analogous to the π - π orbital overlap in resonance. Hyperconjugation can also be regarded as a second order resonance.

Hyperconjugation is also called **Baker-Nathan effect** or **No bond Resonance**.

5. Steric Effect :

The presence of a bulky group or groups near a reaction site in a compound makes it behave in a peculiar way.

The effects of size of substituents and their spatial arrangement in compound are called steric effects.

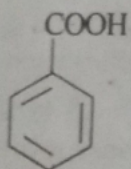
2m - X, X
v. v. Impact

Steric effects may affect the speed and mechanism of a reaction. When the steric effect slows down a reaction, it is called **steric hindrance**; when it speeds up a reaction, it is called **steric acceleration**.

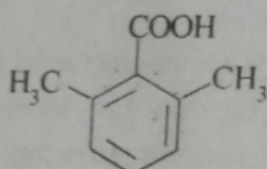
In aromatic compounds the properties of *ortho* substituted compounds differ considerably from those of the *meta* or *para* isomers. In *ortho* substituted compounds the attack of the reagent at the reactive centre is hindered by the bulky groups present in the *ortho* positions. These effects are also known as *ortho effects* or *proximity effects*.

Examples :

- i. Benzoic acid (I) reacts with methanol and hydrogen chloride to form methyl benzoate; but 2, 6 - dimethylbenzoic acid (II) does not form the corresponding product under the same conditions.

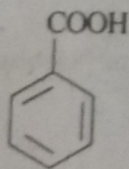


I

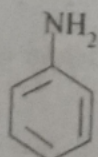


II

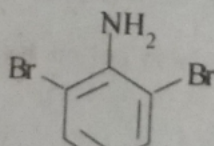
- ii. Benzaldehyde (III) reacts with aniline (IV) to form anil but not with *s*-tribromoaniline (V).



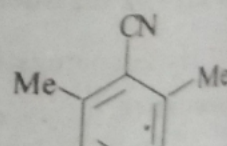
III



IV



V



VI

Rea

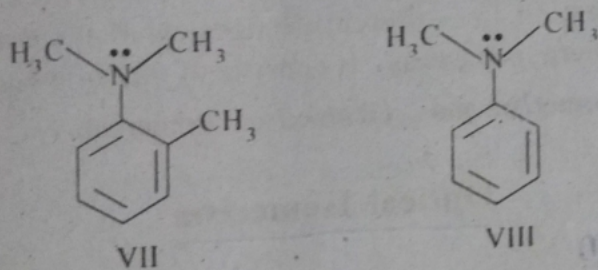
bec

mor

iii. Phenyl cyanide undergoes hydrolysis whereas 2,6-dimethyl phenyl cyanide (VI) does not.

In all these cases, the *ortho* groups mechanically interfere with the reactions of the functional groups, viz., carboxyl, amino and cyano groups. The *ortho* groups tend to shield the reacting groups from the attacking reagent.

iv. N,N-dimethyl o-toluidine (VII) is more basic than N,N-dimethylaniline VIII.

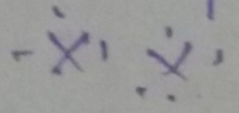


Reason :

The extra stabilisation due to resonance is less in VII than in VIII, because of steric hindrance the lone pair of electrons over the nitrogen is more readily available in VII. So it is more basic.

[60 - 73] . X v.v. Impart

v.v. Impart. STEREOISOMERISM



Stereo Isomerism

Optical Isomerism
E.g., Lactic acid and
Tartaric acid

Clock
wise

Geometrical Isomerism
E.g., Maleic and
Fumaric acid

2- SIM
ANTI
CLOCK

What is stereoisomerism? The phenomenon in which different compounds have the same molecular and structural formula but have different configuration, i.e., different arrangement of atoms and groups in space, is called stereoisomerism. It consists of the following two types

1. Optical Isomerism and 2. Geometrical isomerism

D
form

Optical
activity

Optical Isomerism

Definition: 2M

Optical isomerism is the phenomenon in which different compounds have same molecular formula, same structural formula but have different configurations, i.e., the arrangement of atoms and group in them are different. They rotate the plane of the plane polarised light in different directions.]

Optical isomers :

The two compounds which have the same molecular and structural formulae and have different configurations and which rotate the plane of plane polarised light in different directions are called optical isomers. E.g., d - and l - lactic acids.

Optical activity :

Solutions of some organic compounds have an unique property of rotating the plane of the plane polarised light. This property is called **optical activity**. Such substances are called **optically active substances**. If they rotate the plane of the plane polarised light towards the right (clock wise) they are called dextro-rotatory. If they rotate the plane polarised light towards the left (anti-clock-wise) they are called laevo-rotatory.

optical active

symmetric operation

The amount of rotation depends, for a given substance, on a number of factors like

- i. the thickness of layer traversed
- ii. the nature of solvent
- iii. the temperature and
- iv. the wave length of the light used.

covalent
meth
ester

H₂

If $[\alpha]$ represents the specific rotation, l the thickness of the layer in decimeters, c , the number of grams of substance (per 100 ml of solution) and the determination is carried out at temperature $t^\circ\text{C}$ using light with wave length λ , then if θ is the observed rotation (+ or -).

$$[\alpha]_{\lambda} = \frac{100 \theta}{l \cdot c}$$

optical

$T = \lambda \cdot \text{Time}$

If we use sodium light (the D line)

$$[\alpha]_D = \frac{100 \theta}{l \cdot c}$$

dia carbon
Asymmetric

Since the value of rotation depends on the solvent, this should also be given.

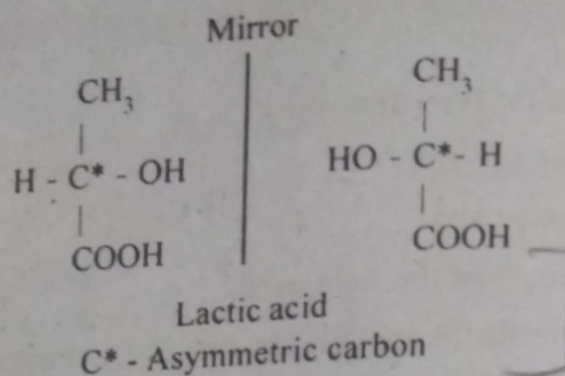
Conditions for optical activity (or) cause of optical activity

2/10 * The molecule must be chiral i.e., it must have two structures which are mirror images and which cannot be superimposed on one another.

1. **Chiral molecule (asymmetric carbon)**

Chiral molecule

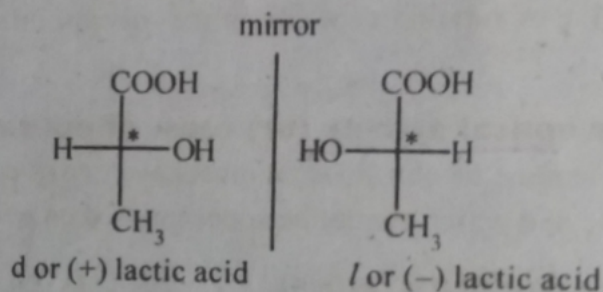
According to Vant Hoff and Le Bel theory in a molecule like methane the carbon atom is at the centre of a regular tetrahedron and the four atoms or groups are present at the four corners. If the four groups attached to a central carbon atom of a molecule are different, then the molecule is not superimposable on its mirror image. Such a molecule is called chiral molecule and that carbon is called **chiral carbon** or **chiral centre** or **asymmetric carbon** or asymmetric centre. The phenomenon is called chirality. Chirality is the necessary condition for the existence of enantiomers. Eg. Lactic acid.



Meaning of (+) and (-) signs

Lactic acid $\text{CH}_3\text{CHOHCOOH}$, contains an asymmetric carbon atom. So it exists in two forms. One of the isomers rotates plane polarised light towards the right. It is called **dextro rotatory** lactic acid (or) (+) lactic acid. It means when the plane polarised light is rotated towards right is denoted by + sign

The other isomer rotates the plane polarised light towards the left. It is called **laevo rotatory** lactic acid (or) (-) lactic acid. It means the plane polarised light is rotated left side and it is denoted by (-) sign.



So, from the signs when can say whether it rotates the plane polarised light towards left or right.

Elements of Symmetry

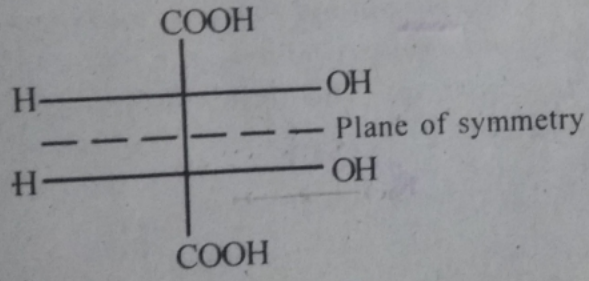
Presence of asymmetric carbon atom is not sufficient to decide whether the molecule is optically active or not. The molecule as a whole must be asymmetric. A simple device to decide whether a molecule is symmetrical or not is to ascertain whether it contains the elements of symmetry. The following are the elements of symmetry.

- 1. Plane of symmetry ✓
- 2. Centre of symmetry ✓
- 3. Alternating axis of symmetry. ✓

If any one of the elements of symmetry is present in the molecule, then the molecule is symmetrical. That is, the molecule becomes superimposable on its mirror image. So it will not be optically active.

1. Plane of Symmetry சீர்மைத் தளம் :

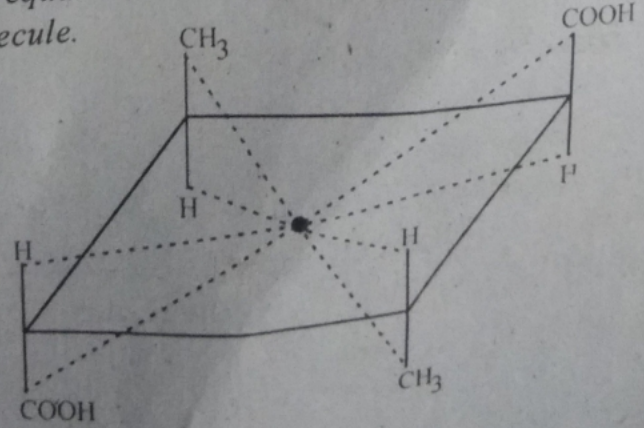
A plane which divides an object into two identical halves is called plane of symmetry. A ball can be divided by a plane into two identical halves. It is a non chiral object i.e., it possesses a plane of symmetry. A plane of symmetry divides a molecule in such a way that points (atoms or groups of atoms) on the one side of the plane form mirror images of those on the other side. The following molecule possesses a plane of symmetry. E.g., Meso tartaric acid



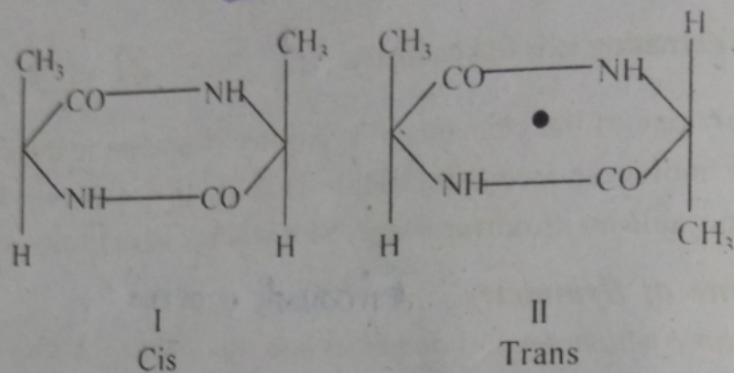
2. Centre of symmetry : சீர்மை மையம் :

A centre of symmetry is a point from which lines, when drawn on one side and produced an equal distance on the other side, will meet identical points in the molecule.

This test is possible only to three dimensional formula, particularly those of ring systems. The following molecule possesses a centre of symmetry.

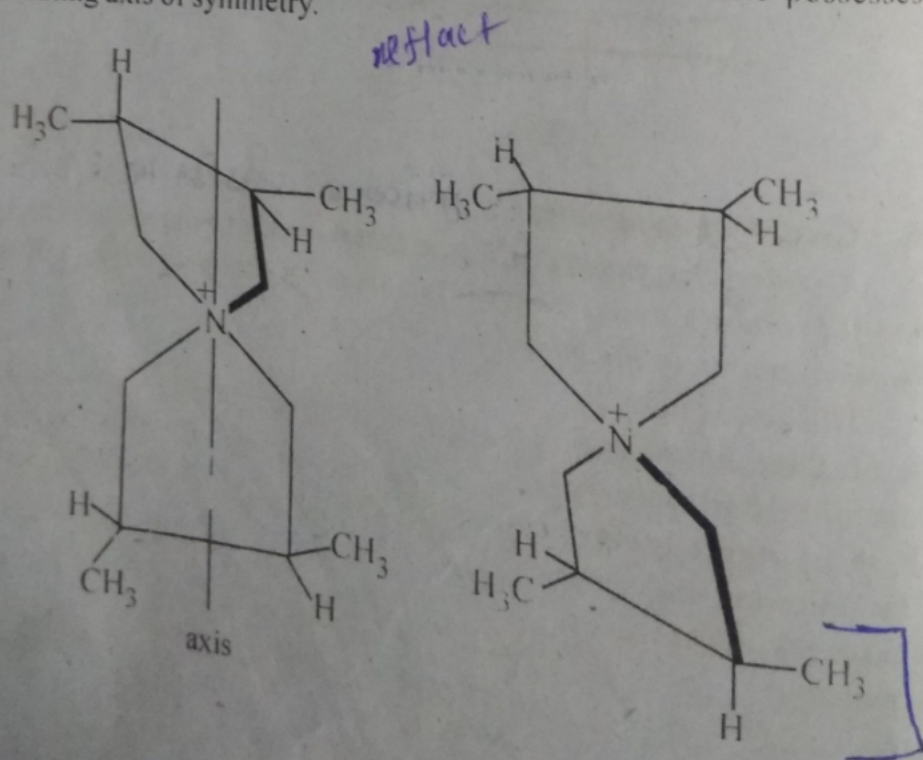


In the following example dimethyldiketopiperazine exists in two geometrical forms namely cis and trans forms.



Structure I has neither a plane nor a centre of symmetry. So it is optically active. Structure II has a centre of symmetry. So it is not optically active.

3. **Alternating axis of symmetry** అంతర అక్షాన్ని కలిగినది
 A molecule possesses an n fold alternating axis of symmetry if, when rotated through an angle of $360/n$ about this axis and then followed by reflection in a plane perpendicular to the axis, the molecule is the same as it was in the starting position. The following molecule possesses an alternating axis of symmetry.



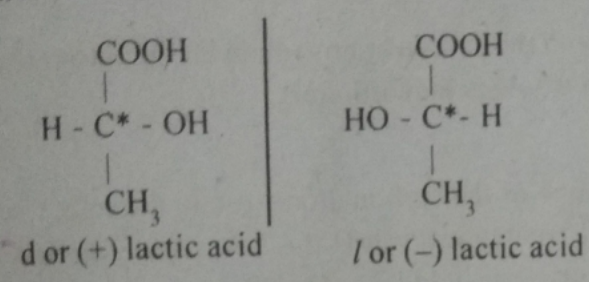
* 5m 10m 2m 65 v.v. Important.

1. Optical Isomerism of Lactic acid

Lactic acid $\text{CH}_3^*\text{CHOHCOOH}$, contains an asymmetric carbon atom. So it exists in two forms.

d - Lactic acid : One of the isomers rotates plane polarised light towards the right. It is called dextro rotatory lactic acid or (+) lactic acid. 50%

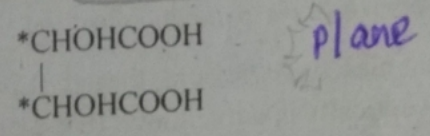
l - Lactic acid : The other isomer rotates the plane polarised light towards the left. It is called laevo-rotatory lactic acid or (-) lactic acid. 50%



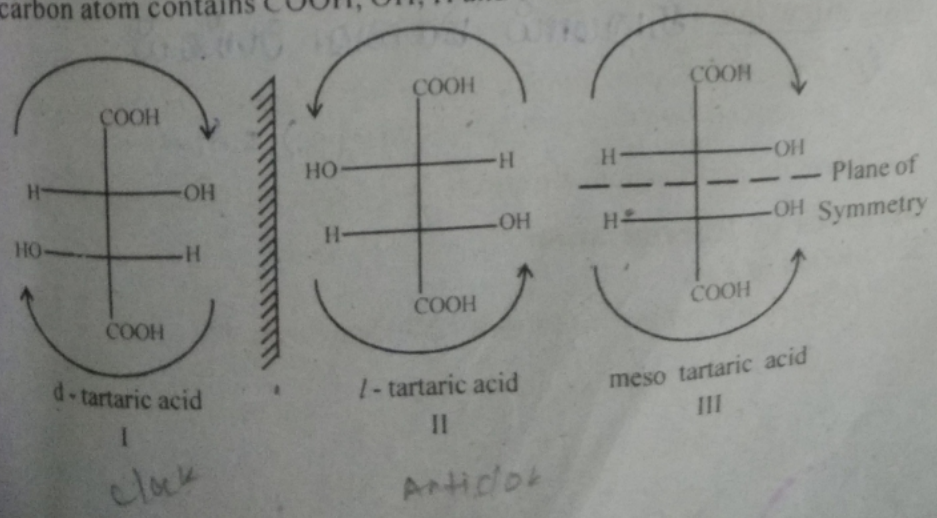
The (+) and (-) lactic acids have identical physical properties except in the sign of rotation.

The lactic acid prepared by synthesis is always optically inactive. It is because it contains a mixture of equimolecular amounts of d-and l-lactic acids. Such a mixture is called **racemic mixture**.

2. Optical Isomerism of Tartaric Acid



Tartaric acid contains two similar asymmetric carbon atoms. Each carbon atom contains COOH, OH, H and CHOH COOH groups.



According to **Vant Hoff-La-Bel theory** it should exist in 2^2 isomeric forms. Since the two asymmetric carbon atoms are similar it exists in $4 - 1 = 3$ isomeric forms. They are (1) dextrorotatory or (+) tartaric acid (2) laevorotatory or (—) tartaric acid II and (3) mesotartaric acid III.

d - tartaric acid

In structure I both the carbon atoms rotate the light towards right. So the molecule as a whole is dextrorotatory.

l - tartaric acid

In structure II both the carbon atoms rotate the light towards the left. So the molecule as a whole is laevorotatory.

Meso tartaric acid

In structure III one of the carbon atoms rotate the light towards right while the other rotates it towards the left. Hence **the net effect is zero**. Therefore mesotartaric acid is **internally** compensated. Further the molecule has a plane of symmetry. Because of these, it is optically inactive.

Racemic Mixture சுழிமையீகமடைவு :

When d-tartaric acid l-tartaric acid are mixed in equal proportions again we get a form which does not rotate light. But this form is externally compensated and it is called **racemic mixture**. Thus tartaric acid exists in d-, l-, meso- and dl (racemic) forms. *The racemic form can be resolved into d- and l-forms while meso-form cannot be resolved.*

The fact that meso tartaric acid, though it is having two asymmetric carbon atoms, is optically inactive shows that a substance may be optically inactive though it may contain asymmetric carbons.]

Racemization V.V. Important சுழிமையீகமடைவு சமீகம்

(Definition : Racemisation is the process of converting an optically active compound into the racemic modification.) 2m

Racemic modifications are also called racemic mixtures or racemates.

Methods of Racemisation

I. Action of heat

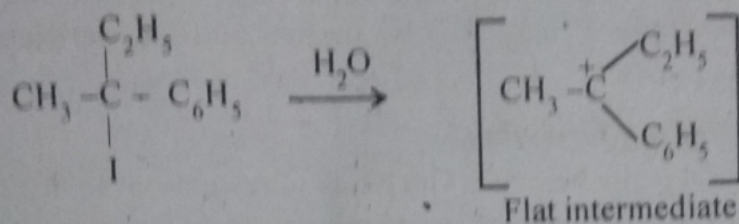
When d or l isomer is heated we get the d/l mixture.

ii. Treatment with chemical reagents

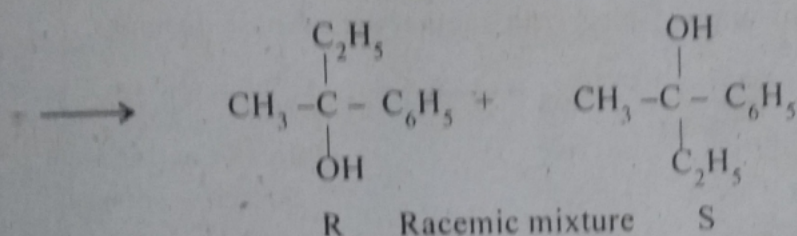
Many substances undergo racemisation when treated with chemical reagents. E.g., mandelic acid ($C_6H_5CHOHCOOH$) forms (+) bromo-acid when treated with hydrobromic acid.

iii. Substitutions and rearrangements

Substitutions and rearrangement reactions which take place via S_N1 type stepwise mechanism end up in racemised products. E.g.



4-Plane
different



iv. Auto - racemisation

In some cases racemisation occurs spontaneously at room temperature, e.g., dimethyl bromo succinate undergoes racemisation on standing at room temperature. This type of racemisation is termed as **auto racemisation**.

Resolution : (பரிசீலனை) 2m

Definition : "The separation of a racemic mixture into its enantiomers (dextro-and laevo-components) is termed as resolution".

Explanation : Any attempt to prepare an optically active form of a compound ends up in a racemic mixture only. So they have to be separated into d and l forms. The process of such separation is called **resolution**.

Methods used for resolving racemic compounds

1. Mechanical separation :

When the enantiomers [(+) and (-) forms] of the optically active compound or their salts form well-defined crystals, showing hemihedral faces, they can be separated by simple hand-picking.

Pasteur separated in this manner crystals of sodium ammonium racemate, $NaNH_4C_4H_4O_6 \cdot 2H_2O$.

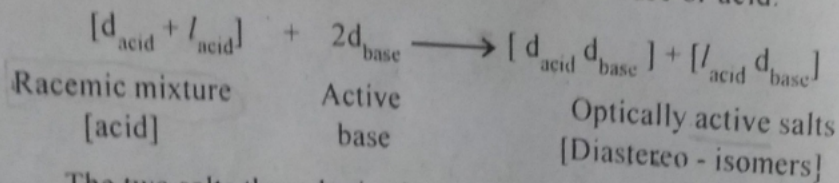
v.v Important

ii. **Bio - chemical separation :**

Certain bacteria or fungi when allowed to grow in a solution of the racemic compounds destroy one of the optical isomers at much quicker rate than the other due to selective assimilation. For example when penicillium glaucum is allowed to grow in a solution of ammonium racemate, it destroys the d-tartrate by assimilation leaving behind the l-tartrate practically unaffected. However, the separation is not always complete and one component is always lost. Some other side-products may also be formed and the sample may be difficult to purify.

iii. **By means of salt formation :**

This method is the best of all methods of resolution. In this method the active constituents of a racemic mixture are converted into diastereoisomers [salts] with another active base or acid.

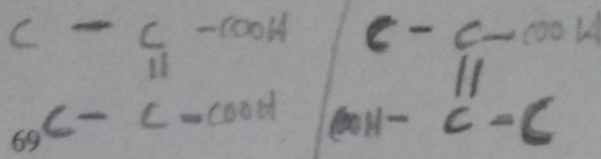


The two salts thus obtained often differ in their solubilities and can be separated by fractional crystallization. The salts can be hydrolysed with inorganic acids or alkalis to get the original active compounds. For example, racemic tartaric acid is separated by this method. The optically active bases used for this purpose are mainly alkaloids like quinine, brucine, cinchonine, and morphine. Similarly racemic bases can be separated by using optically active acids like tartaric acids, camphor sulphonic acid, etc.

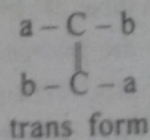
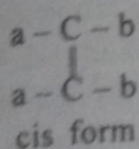
Geometrical Isomerism [എറുവ തന്നിടങ്ങൾ] = bond

When two carbons are connected by a single bond, free rotation about the bond joining the two carbon atoms are possible. But when the two carbon atoms are connected by a double bond, the free rotation about the double bond is restricted. If the group attached to each carbon atom are different, two stereo isomers are possible.

This restriction of rotation about the carbon - carbon double bond is responsible for the geometrical isomerism in alkenes.



The two geometrical isomers corresponding to the formula $\text{abC}=\text{Cab}$ can be represented by the following projection formula.

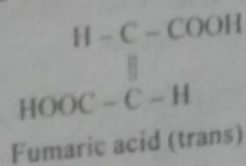
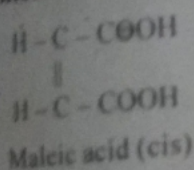


The cis isomer is one in which two similar groups are on the same side of the double bond. The trans isomer is that in which two similar groups are on the opposite sides of the double bond.

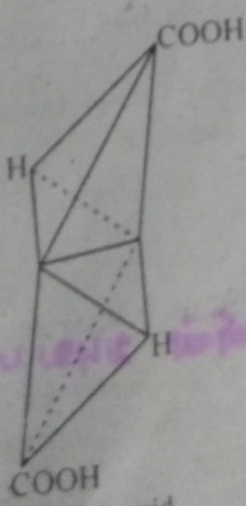
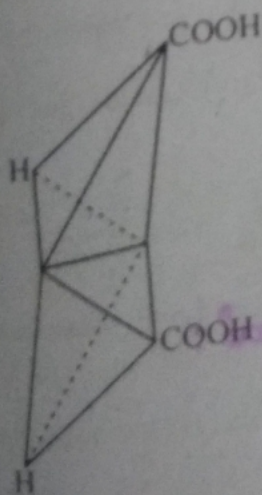
This type of isomerism is also called cis - trans isomerism.

The classical example of cis - trans isomerism is that of fumaric and maleic acids.

Geometrical isomerisms in Maleic and Fumaric acids:



The maleic acid and fumaric acid can be represented in tetrahedral forms as shown below.



Maleic acid

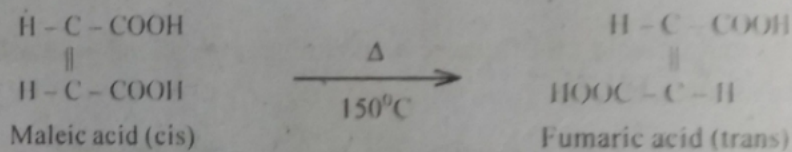
Fumaric acid

Tetrahedral models of maleic acid and fumaric acid

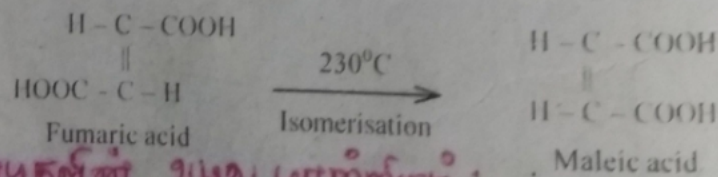
However, the two carbon atoms are united by a double bond, the tetrahedral representing them must necessarily be in contact at corners. In such a case all free rotation of the tetrahedral cases and groups attached to the two carbon atoms are fixed relative to each other. Thus, different spatial arrangements of the groups about the double bonded carbon atoms now become possible. For example, the tetrahedral models representing maleic acid and fumaric acid as shown before.

It is clearly noted that maleic acid and fumaric acid have quite different arrangements of groups about the double bond. While in one case similar groups are on the same side, in the other they lie on opposite sides. This is a type of isomerism due to the different geometrical arrangements of groups about the doubly bonded carbon atoms. When similar groups lie on the same side i.e., two carboxyl group and two hydrogen are at same side is called **maleic acid**, if they are opposite to each other is called **fumaric acid**. Consequently this type of isomerism is often spoken of as cis-trans isomerism.

When on prolonged heating at 150°C maleic acid isomerises to fumaric acid.



When fumaric acid is heated about 230°C it undergoes isomerisation to give maleic acid.



പ്രധാന ഗുണങ്ങൾ: **Properties of geometrical isomers:**

1. The melting point and stability of the cis are lower than those of trans isomer.
2. The density, refractive index, solubility, dipole moment heat of combustion and the dissociation constant (if the compound is an acid) of the cis are greater than those of trans isomer.

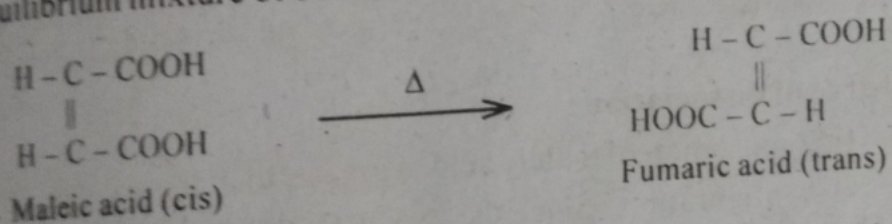
Based on these facts rule has been given and this rule is known as Marks-Skita rule. *2M-X*

Rule: In a pair of geometrical isomers the cis has the higher boiling point, density and refractive index.

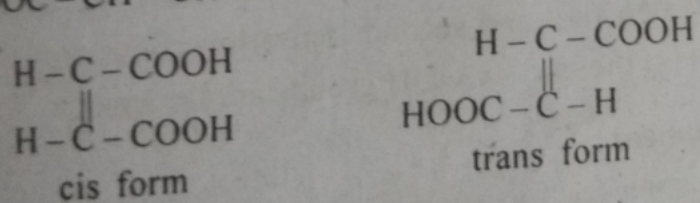
This rule is used to predict whether a compound is cis or trans. But there are exceptions to this rule.

Inter conversions

The cis isomer which is labile can be converted into the stable trans isomer. E.g., Maleic acid may be converted into fumaric acid by heating it above its melting point. It is more difficult to convert the trans isomer into cis isomer. Usually the best method is to irradiate the trans isomer with UV light in the presence of a trace of bromine; the product is generally an equilibrium mixture of both isomers.



These two compounds are unsaturated dicarboxylic acids of the formula $\text{HOOC} - \text{CH} = \text{CH} - \text{COOH}$. They may be represented as follows.



It has been shown that maleic acid is the cis isomer in which the two carboxyl groups are on the same side.

The fumaric acid is the trans isomer in which the two carboxyl groups are on the opposite sides.

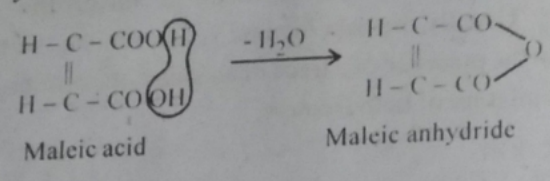
The following are the evidences to show that maleic acid is the cis-isomer and fumaric acid is the trans isomer.

2m 5m 10m v.v. Imp

**Methods of distinguishing geometrical isomers
(Distinguishing maleic acid and fumaric acid)**

1. Formation of cyclic anhydride :

Maleic acid on heating readily loses water to give the anhydride while fumaric acid gives the anhydride only at high temperatures. From this we infer that in maleic acid the two COOH groups must be on same side (As stated above, fumaric acid also gives cyclic anhydride only on strong heating. Both anhydrides are found to be identical maleic anhydride. Hence it is suggested that fumaric acid when heated isomerises into maleic acid and then eliminates a molecule of water to give the anhydride)



2. Degree of dissociation :

The first ionisation of maleic acid is greater than the second. It may be so in cis-configuration. Since the two -COOH groups lie on the same side the liberation of first hydrogen ion (H⁺) leaves a negative group. This the removal of the second H⁺ becomes difficult. In fumaric acid, the difference between first and second ionisation constants is very small. This is possible if the two -COOH groups are far apart.

3. Dipole moment :

The cis-isomer has unsymmetrical structure while trans-isomer has symmetrical structure. Therefore the cis-isomer is expected to show dipole moment. Actually maleic acid only has dipole moment while the dipole moment of fumaric acid is Zero. Therefore the cis form must be maleic acid.

4. Stability and heat of combustion :

Fumaric acid is stabler than maleic acid and it must be so for a trans-isomer in which the two identical groups are balanced on the opposite sides of the molecule. The unstable or "labile" maleic acid has therefore

greater energy content, hence it releases more energy on combustion. Evidently the heat of combustion of the cis - isomer must be greater than that of the trans - isomer and experimentally it is found to be so.

5. By X - ray analyses :

By examining the X-ray diffraction pattern of crystals, it is possible to determine the shape of the molecules and the position of various atoms and groups which constitute the molecule. This is probably the best method of deciding the configuration.

6. Melting point :

In the trans isomer, the carboxyl groups being on opposite sides, the molecules fit in more closely in the crystal lattice, hence intermolecular attraction is greatly increased. On the other hand, the arrangement of molecules of cis - isomer in the crystal lattice is less close, hence intermolecular attraction is comparatively less. Since the melting point is the temperature at which the crystal lattice collapses, the greater the intermolecular attraction, the higher will be the melting point. Hence trans - isomer will have a higher melting point than the cis - isomer.

7. Other physical constants :

Determination of other physical constants like density, boiling point etc., may be used in deciding the configuration of cis - trans isomers. Thus it has been found that as a rule, the boiling point, solubility and refractive index of the cis - isomer are greater than those of the trans.