

## Unit-2 Spectroscopy and its techniques

### ⇒ Spectroscopy

The study of analysing the given unknown compound.

### \* Advantages

- small amount of sample is required.
- <sup>Less</sup> time consuming.
- cost effective.

### \* Study of Spectroscopy

Electromagnetic radiation (EMR)



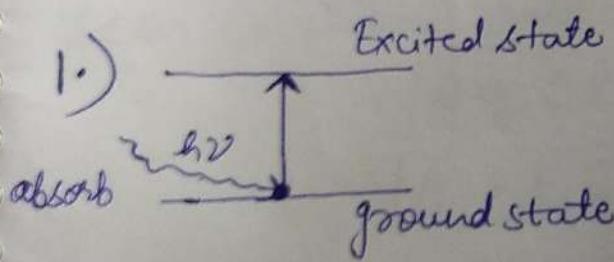
change in energy observed.

Matter/Particle

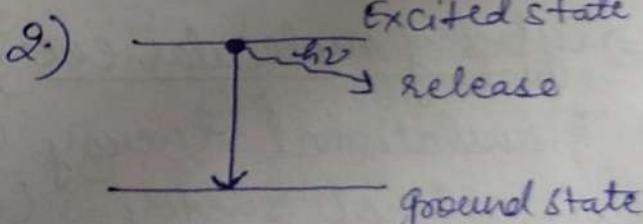
record in the form  
of spectra..

Spectrum

} known as  
spectroscopy.



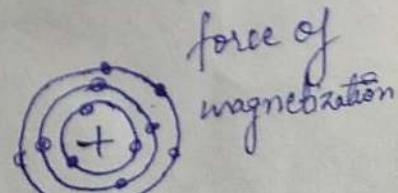
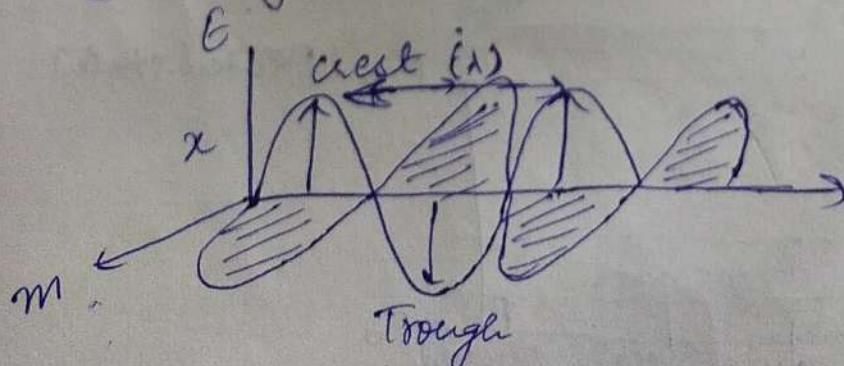
Absorption



Emission

### ⇒ Electromagnetic Radiation

The radiations made up of electric field and magnetic field are known as EMR.



## $\Rightarrow$ Electromagnetic Spectrum

The arrangement of electromagnetic radiation in the decreasing or increasing order of wavelength.  
(order)

Microwave radiation	Infrared radiation	Ultraviolet radiation	X-Rays
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$$\lambda(\text{m}) \quad 10^{-2} \quad 10^{-4} \quad 10^{-8} \quad 10^{-10}$$

\* Longer wavelength  
\* Lower energy

\* Shorter wavelength  
\* Higher energy.

\* Energy of photon,  $E = h\nu$  - ①

$$\nu = \frac{c}{\lambda} \quad \text{--- ②}$$

Put ② in ①

$$E = \frac{hc}{\lambda}$$

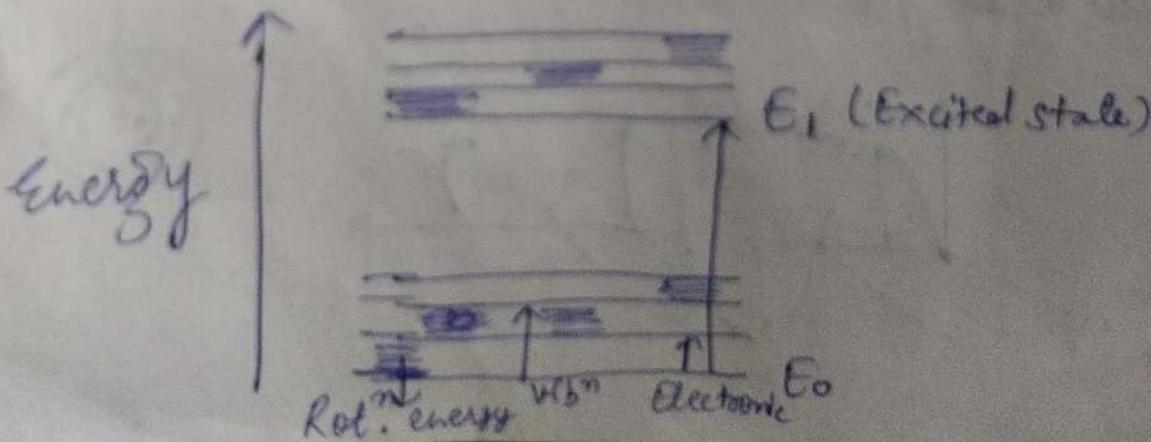
where  $h = \text{Planck's constant}$   
 $= 6.63 \times 10^{-3} \text{ Js}$

$$c = 3 \times 10^8 \text{ m/s}$$

## $\Rightarrow$ Types of molecular energies

- 1.) Translational energy ( $E_T$ )
- 2.) Rotational energy ( $E_R$ )
- 3.) Vibrational energy ( $E_V$ )
- 4.) Electronic energy ( $E_e$ )

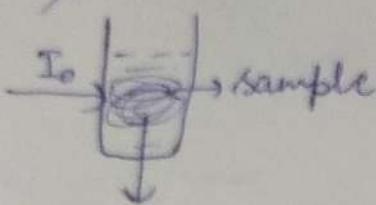
$$\therefore E_{\text{Total}} = E_T + E_R + E_V + E_e$$



Order of energy :-

$$\text{Electronic} \gg \text{Vibration} > \text{Rotation}$$

1.)



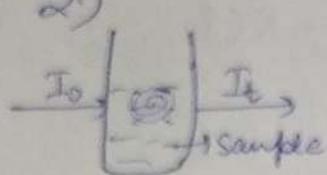
Absorbance (A)

Ans:

$$A = -\log_{10} T$$

Relation b/w A & T.

2.)



Transmittance (T)

Ans:

$$T = \frac{I_t}{I_0}$$

(Transmitted intensity)  
(Incident Intensity)

3.)



Scattered

Ans:

Raman scattering

⇒ Law of Absorbance

Ans:

Beer - Lambert's law :- According to Beer-Lambert law, absorbance of sample depends upon the concentration of the solution and path length of the sample.

$$A \propto Cl$$

$$A = ECl$$

where,  $A$  = absorbance  
 $C$  = concentration (M/L)  
 $l$  = Path length (cm)

$E$  = absorptivity coefficient  
( $\text{Lmol}^{-1}\text{cm}^{-1}$ ) (Liter mol<sup>-1</sup> cm<sup>-1</sup>)

⇒ Derivation of Beer - Lambert's law

$$-dI \propto I C dl \quad \text{--- (1)}$$

Decrease in intensity depends upon incident intensity, concentration of solution and path length.

$$-dI = K I C dl \quad \text{--- (2)}$$

$$\frac{I_t}{I_0} \int_0^l \frac{dI}{I} = - \int_0^l K C dl \quad \text{--- (3)}$$

$$\ln \left[ \frac{I}{I_0} \right]_0^{I_t} = - K C [l]$$

$$\ln(I_t - I_0) = -Kt \quad \text{--- (4)}$$

$$\ln \frac{I_t}{I_0} = -Kt \quad \text{--- (5)}$$

$$2.303 \log_{10} \frac{I_t}{I_0} = -Kt$$

$$\log_{10} \frac{I_t}{I_0} = \frac{-K}{2.303} t$$

$$\log_{10} \frac{I_t}{I_0} = -\epsilon ct \quad \left( \because \epsilon = \frac{K}{2.303} \right)$$

$$A = \epsilon ct = \log_{10} \frac{I_t}{I_0}$$

~~Ans.~~  $A = \epsilon ct = -\log_{10} T$

Ques A compound having concentration  $10^{-3} \text{ g/L}$  resulted absorbance value 0.20 at  $\lambda_{\text{max}} 510 \text{ nm}$  using 1 cm cell. Calculate absorptivity? Given molecular weight of compound is 400.

$$E_m = \frac{Cm}{M \cdot \text{wt}}$$

$$\frac{10^{-3}}{400}$$

$$A = \epsilon ct$$

$$0.20 = \epsilon \times 10^{-3} \times 1$$

$$\epsilon = \frac{0.20}{10^{-3} \times 1}$$

$$\epsilon = \frac{2 \times 10^3}{10} = 200 \text{ L g}^{-1} \text{ cm}^{-1}$$

$$\theta A = E_m C m l$$

$$= 200 \times 10^{-3} \times 1$$

$$A = E_m \times \frac{C}{M \cdot \text{wt}} \times l$$

$$0.20 = E_m \times \frac{10^{-3} \times 1}{400}$$

$$\frac{0.20 \times 400}{100} = 10^{-3} \times E_m$$

$$80 = 10^{-3} \times E_m$$

$$E_m = \frac{80}{10^{-3}} = 80,000 \text{ L mol}^{-1} \text{ cm}^{-1}$$

Ques The molar absorption coefficient of a molecule in water sample is  $1280 \text{ M}^{-1}\text{cm}^{-1}$  at  $280\text{nm}$ . Calculate the conc.<sup>n</sup> of solution in water if the absorbance of the sol<sup>n</sup> is  $0.34$  in a  $1\text{cm}$  cell.

$$E_{m \text{ Abs}} = 1280 \text{ M}^{-1}\text{cm}^{-1}, C = ?$$

$$A = 0.34, l = 1\text{ cm}$$

$$\frac{C}{A_m} = \frac{0.34}{1280}$$

$$A = ECl$$

$$0.34 = 1280 \times C \times 1$$

$$C = \frac{0.34}{1280 \times 100} = 0.000265$$

$$2.65 \times 10^{-4} \text{ mol/l cm}^{-1}$$

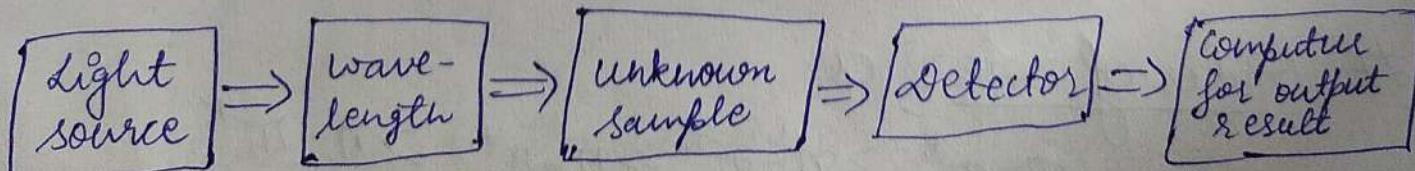
$$C = 250 \mu\text{M}$$

## ⇒ U.V visible Spectroscopy

wavelength range =  $200-800\text{nm}$

Near U.V.	$250-400\text{ nm}$
Far U.V.	$190-250\text{ nm}$
Vaccum U.V	$< 190\text{nm}$

## ⇒ Instrumentation of UV-visible Spectroscopy

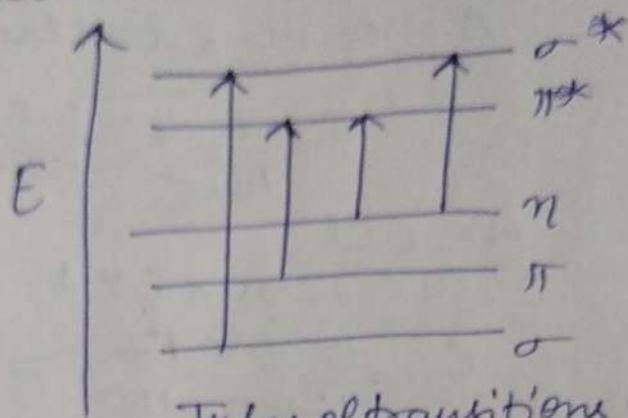


(W-lamp)  $\rightarrow$  (Tungsten lamp)

Main components of Spectrophotometer

## Types of electrons present in molecule

- 1.)  $\sigma$  electrons
- 2.)  $\pi$  electrons
- 3.) Non-bonded electrons



Types of transitions depending upon the

### # Allowed Transitions

- 1.)  $\sigma - \sigma^*$  transition
- 2.)  $\pi - \pi^*$  transition
- 3.)  $n - \sigma^*$  transition
- 4.)  $n - \pi^*$  transition

### # Forbidden transition or 'not allowed transition'

- 1.)  $\sigma - \pi^*$  transition
- 2.)  $\pi - \sigma^*$  transition

### # Order of Energies

$$\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$$

### # Types of transitions (Allowed)

- 1.)  $\sigma - \sigma^*$  - Molecules containing only sigma bond.
    - Saturated molecules (only single bond)
    - High energy transition
- Ex: Alkanes,  $\text{CH}_4$ , Ethane, Propane .

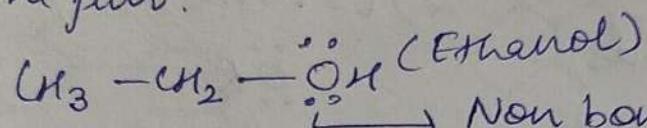
## 2.) $\pi - \pi^*$ transition

- Unsaturated molecules
- presence of  $\pi$ -bond

Ex.: Alkene,  $\text{CH}_2 = \text{CH}_2$  (ethene),  $\text{CH}_3 - \text{CH} = \text{CH}_2$  (propene)

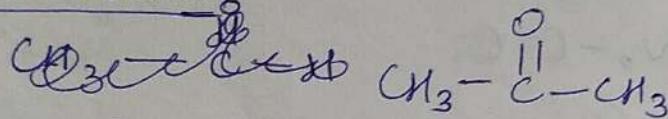
## 3.) $n - \sigma^*$ transition

- Saturated molecules containing heteroatom with lone pair.



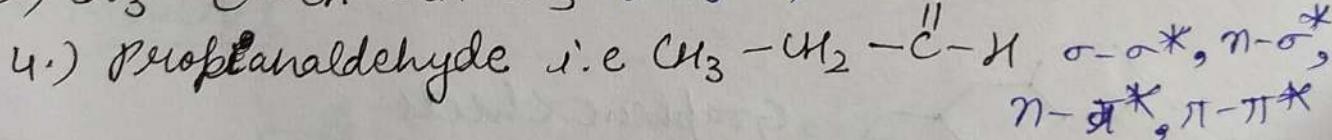
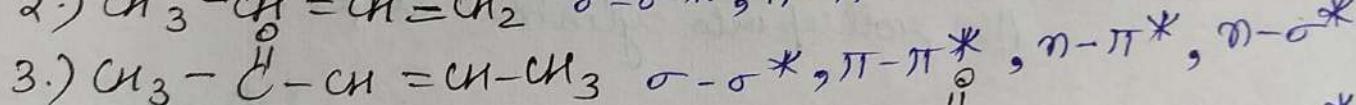
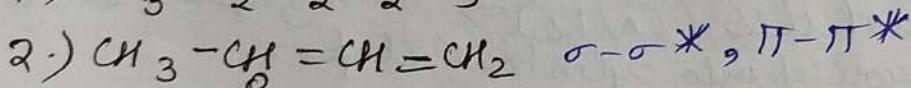
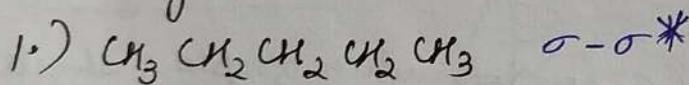
(Ethanol) Non bonded  $e^-$  or lone pair

## 4.) $n - \pi^*$ transition

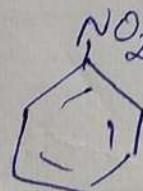


Ex: - CN

Ques: Give the possible electronic transitions in the given molecules.

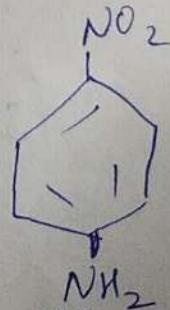


(Benzene)



(Nitrobenzene)  
(Yellow)

$\lambda = 255 \text{ nm}$



Dark Yellow

$\lambda = 280 \text{ nm}$

## Chromophores

- 1.) Chromo means colour & phores means bearing. i.e colour bearing.
- 2.) which impart colour to the molecule.
- 3.) by shifting towards longer wavelength
- 4.) Ex:  $-NO_2$ ,  $-NO$ ,  $-CO$ ,  $-CN$ ,  $-C=C$

## Auxochromes

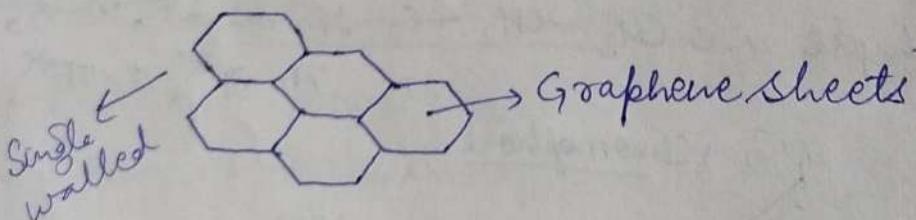
- 1.) does not itself impart colour but enhance the intensity of colour by attaching to the chromophore molecule.
- 2.) Ex:  $\text{--NH}_2$ ,  $\text{--NR}_2$ ,  $\text{--O}^{\cdot\cdot}\text{H}$ ,  $\text{--O}^{\cdot\cdot}\text{R}$

## Unit - 1

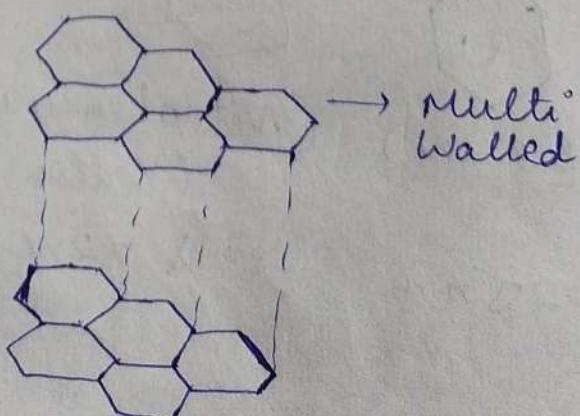
⇒ Nanomaterials



Carbon nanotubes (CNTs) ⇒ when Graphene sheets roll up into cylindrical shape.



Sheet 1

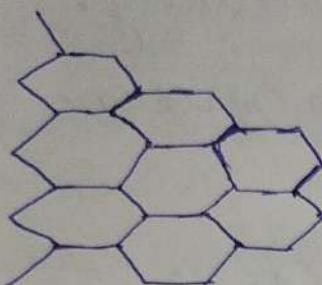


There are two types of carbon nanotubes:-

- 1.) Single walled carbon nanotubes (SWCNT)
- 2.) Multi walled carbon nanotubes (MWCNT)

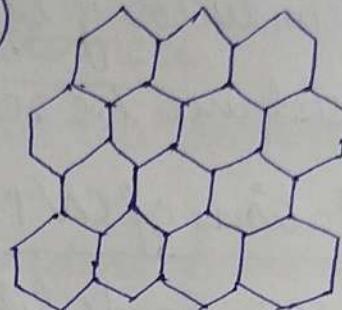
### # Types of Single walled CNT

1.)



Arm Chair  
(SWCNT)

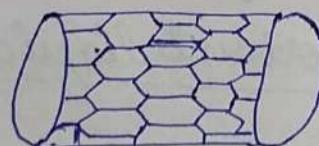
2.)



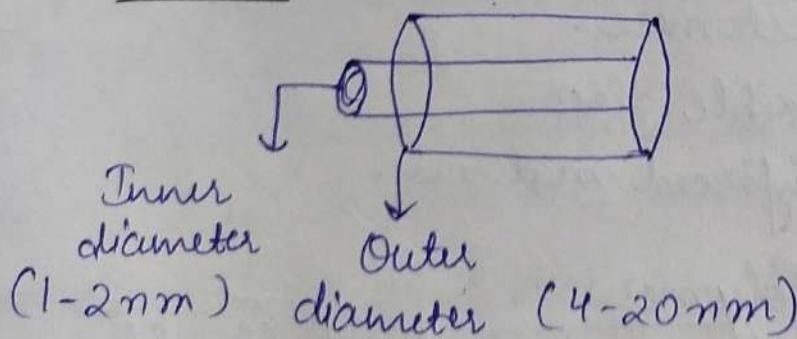
Zig - Zag  
(SWCNT)

Diameter  $\approx 1\text{nm}$

### Arrangement



### # MWCNT



### Important points about CNTs

- 1.) They are stiffer as diamond.
- 2.) They are light weighted materials.
- 3.) High thermal capacity.
- 4.) One carbon atom is attached with other three carbon atoms.

⇒ Application of CNTs ⇒ Properties of CNTs  
⇒ Applications of CNTs

- 1.) Used as elastomers i.e can be easily stretched.  
One can even tie a knot.
- 2.) Used as good conductor of heat and electricity.
- 3.) Chemical resistance i.e resistant to corrosion.

⇒ Uses/Applications of CNT

- 1.) Used in sporting goods like bicycle tennis, racket etc.
- 2.) Used in bullet proof jackets.
- 3.) Used to prepare electrode as they are good conductor of electricity.

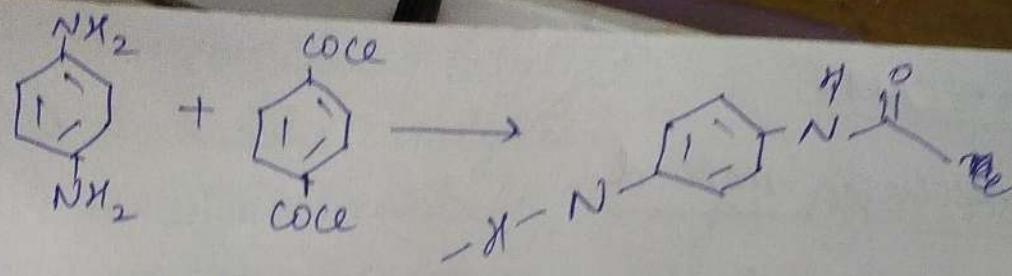
⇒ Industrially important liquid Crystal Classification

- 1.) Liquid crystal polymers.
- 2.) Liquid crystal Elastomers.
- 3.) Liquid crystal flexible glass.
- 4.) Liquid crystal reinforced material.

# Liquid crystal Polymer

Polymer which shows the property of liquid crystal.

- containing specially aromatic ring.
- They provide excellent mechanical and electrical properties.
- Ex: Kevlar polymer



- Used in making bullet proof jackets.

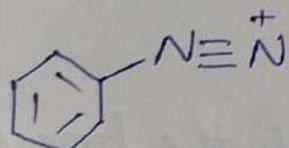
## # Liquid Crystal Elastomers

Elastomers which shows the property of liquid crystal.

- work as optical retarders because of their anisotropic nature.

(Optical retarders controls the deviation of light.)

Ex :- Azobenzene liquid crystal



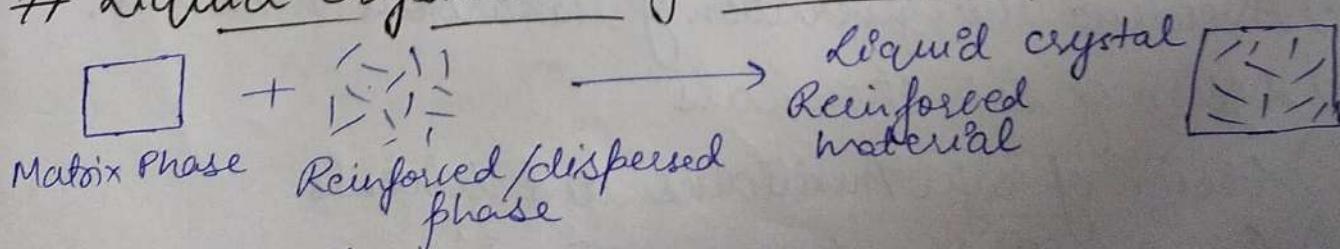
- Used ~~to~~ to make flat LCDs.

# Liquid crystal flexible glass

It is a laminated smart glass with liquid crystal film.

- Ex: Amorphous Silicon active matrix.
  - Used in digital electronic devices.

# Liquid crystal Reinforced material



- Ex: 

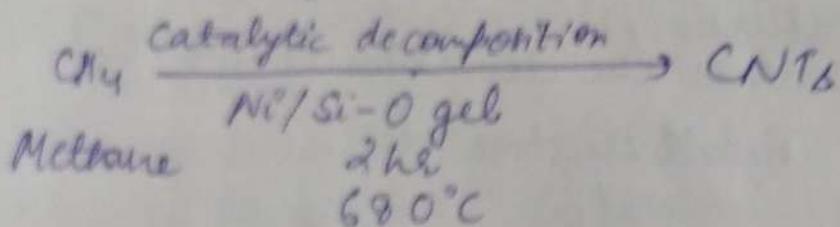
- Used in fillers.

## $\Rightarrow$ Preparation of CNTs

### 1.) By Arc discharge method

Graphite electrode    He atom  $\rightarrow$  CNT  
                            500 torr  
                            Electric current  
                             $\approx 0.25\text{ A}$

### 2.) By catalytic decomposition of methane



## $\Rightarrow$ Green Chemistry

It is the chemistry which deals with the process which minimize the use of toxic chemical.

Green chemistry is not same as environment chemistry.

~~and~~

### The 12 principles of Green chemistry

- 1.) Prevention of waste (Prevent waste from increasing)
- 2.) Atom Economy
- 3.) Avoiding the generation of hazardous chemicals.
- 4.) Design of safe chemicals.
- 5.) Design of safer Auxiliaries and solvents
- 6.) Energy Efficiency ( $A+B \rightarrow C + \text{⑤} - X$ )
- 7.) Incorporation of renewable material.
- 8.) Reduce the generation of derivatives.

9.) Incorporation of Catalyst.

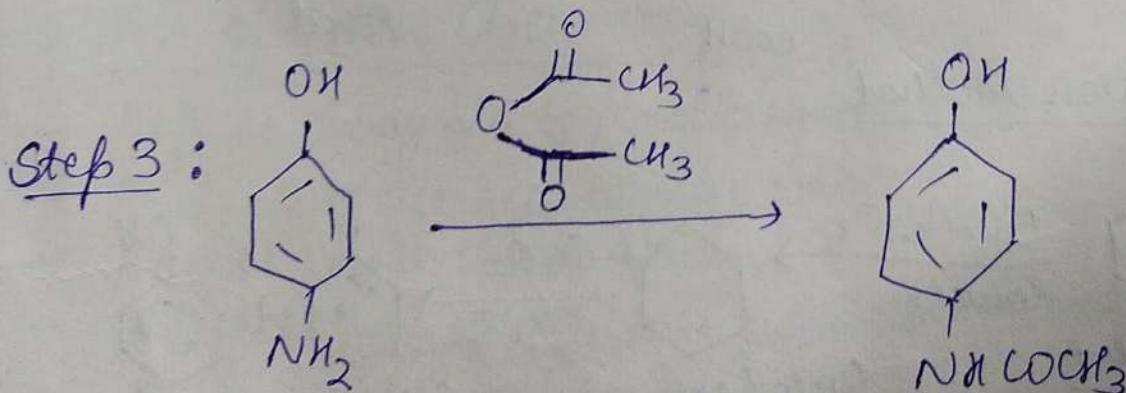
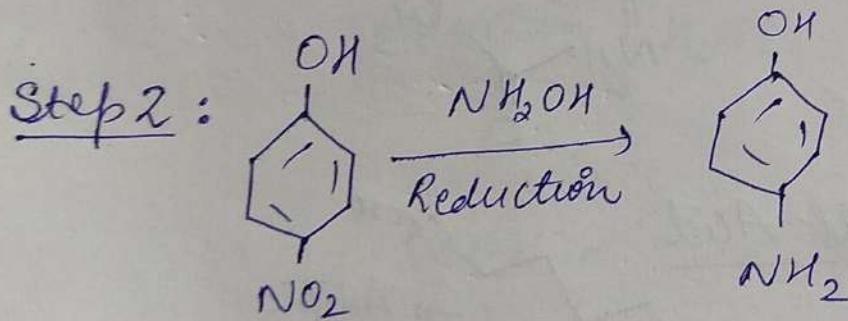
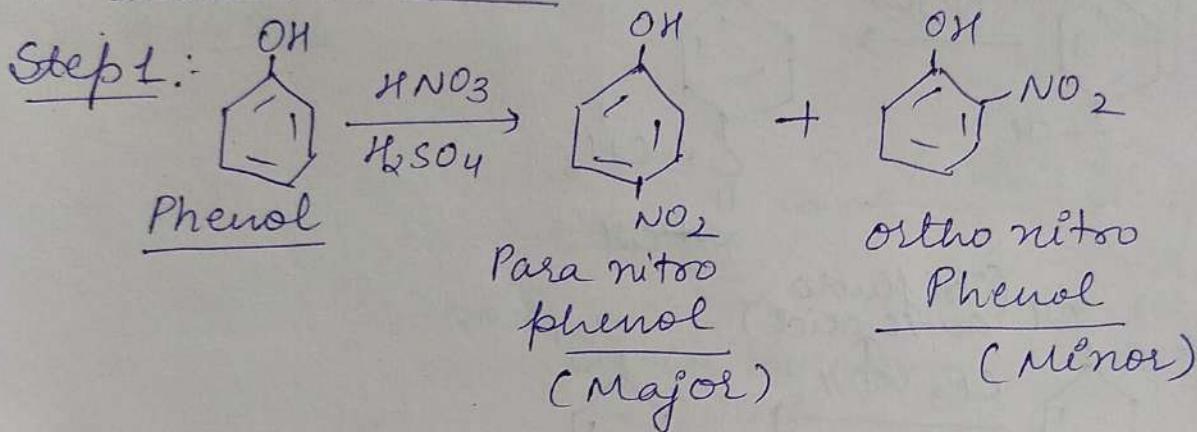
10.) Real time analysis.

11.) Design chemicals for safer degradation.

12.) Design of safer chemistry to prevent accident.

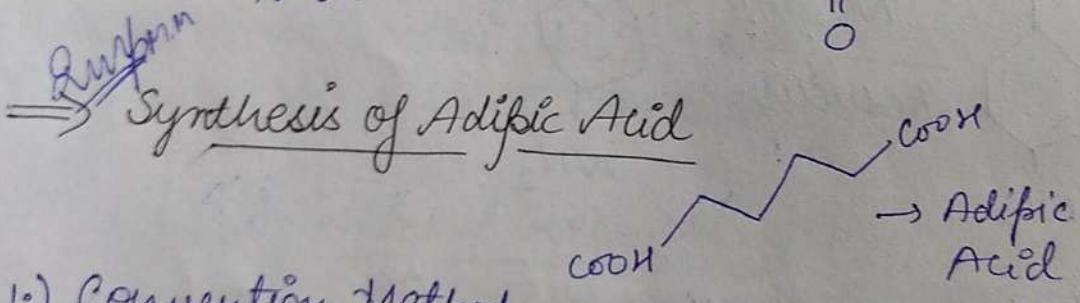
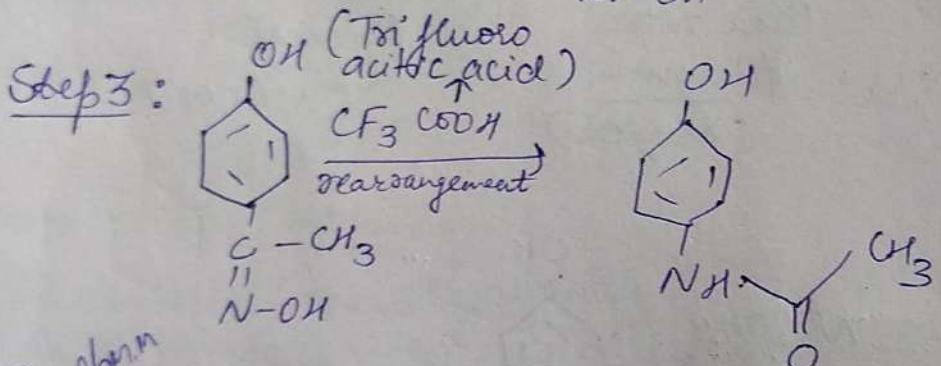
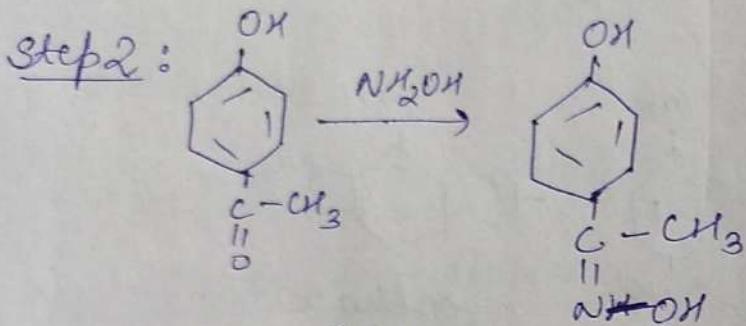
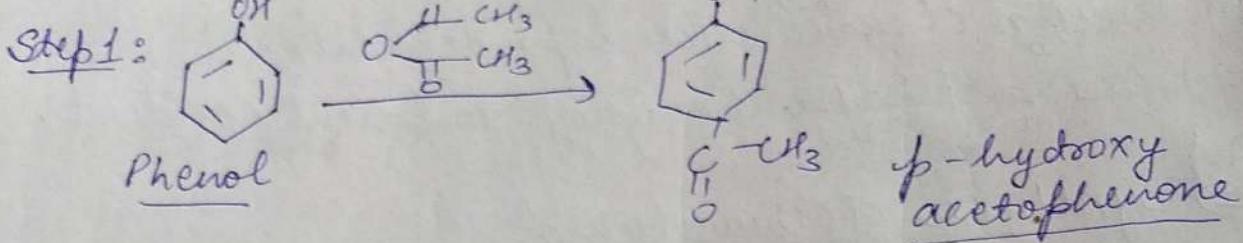
⇒ Synthesis of Paracetamol

1.) Conventional Method

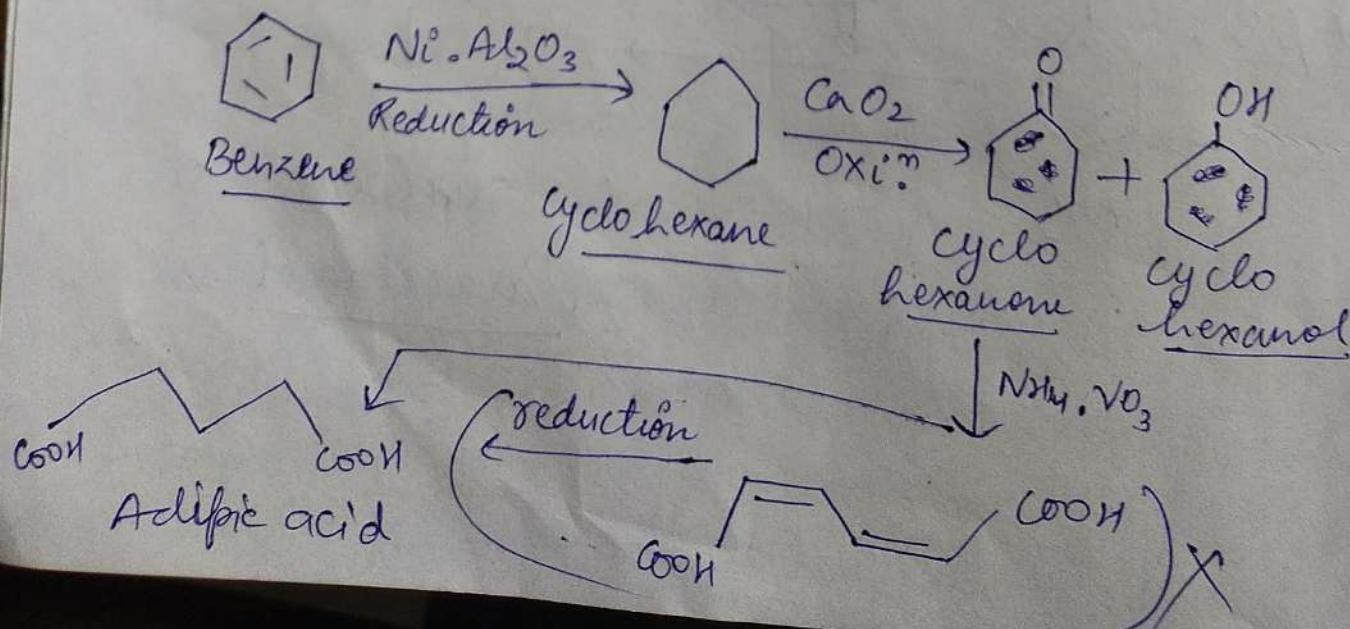


Paracetamol

## Q. 2) Green synthesis of Paracetamol

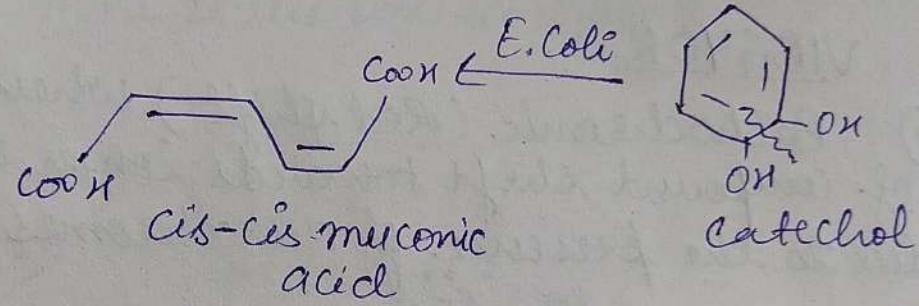
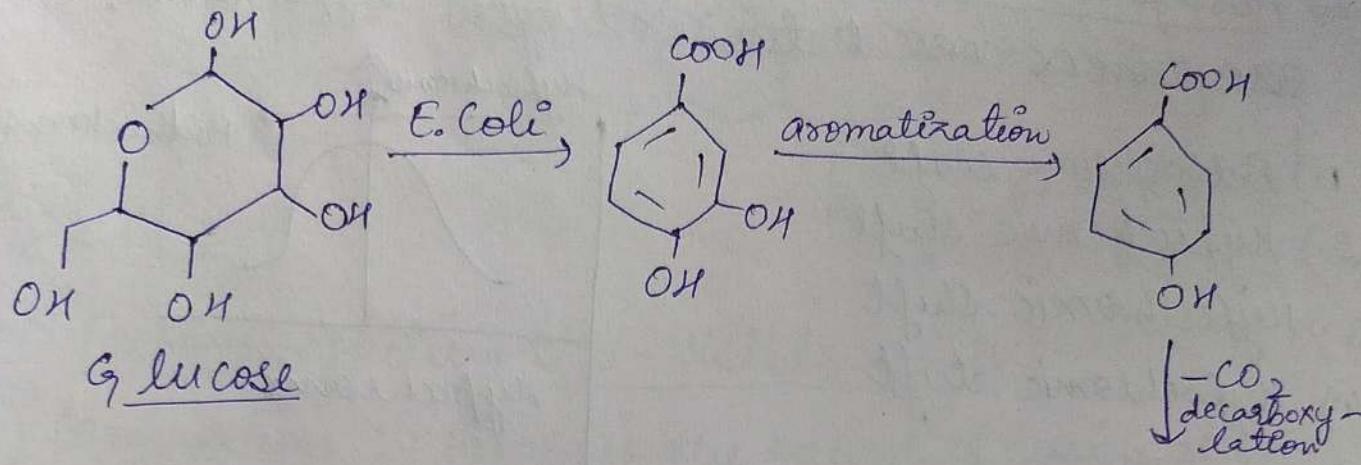


## 1.) Conventional Method

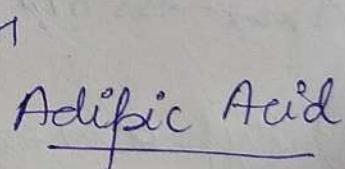


Q.) Green Synthesis of Adipic Acid

M.M. Green route



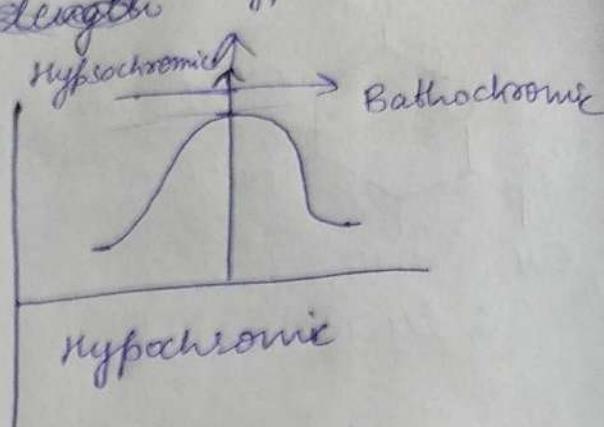
Reduction  $\downarrow \text{H}_2/\text{Pt}$



4R's of Green Chemistry

- Refuse (Say NO to plastic materials) YM X
- Reduce (Use acc. to your needs)
- Reuse (Use things again)
- Recycle (Make the things that can be used after recycling)

Unit-2 ....  
⇒ Absorption and Intensity shifts

- ~~Absorption concentration × length~~
- 1.) Bathochromic shift  
2.) Hypsochromic shift  
3.) Hyperchromic shift  
4.) Hypochromic shift
- 

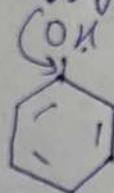
### VIBGYOR

1.) Bathochromic (Red shift) when wavelength of compound shift towards longer wavelength due to the presence of auxochromes.



Benzene

$$\lambda_{\text{max}} = 255 \text{ nm}$$



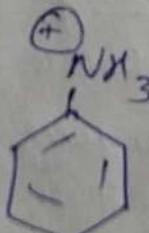
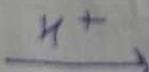
Phenol

$$\lambda_{\text{max}} = 280 \text{ nm}$$

2.) Hypsochromic : when wavelength of the compound shifts towards shorter wavelength due to the removal of auxochromes.

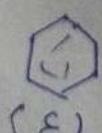


Aniline  
(More  $\lambda_{\text{max}}$ )

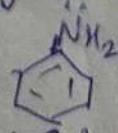


Anilinium Ion  
(Less  $\lambda_{\text{max}}$ )

3.) Hyperchromic : when wavelength of the compound shifts towards longer intensity due to presence of conjugation.



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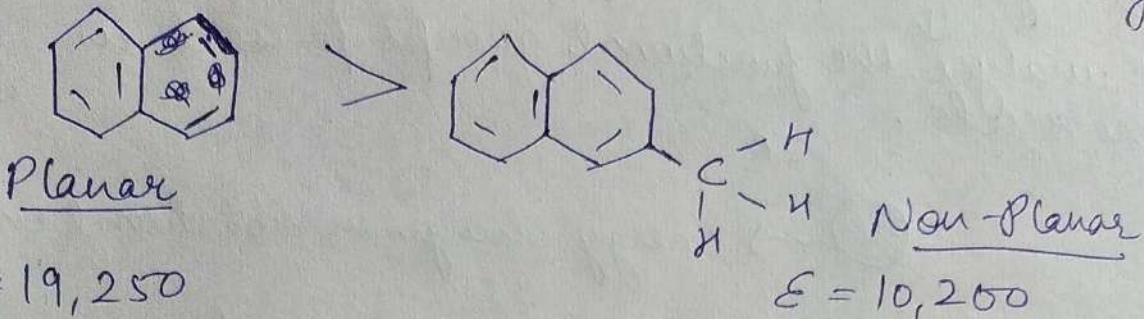


(E)

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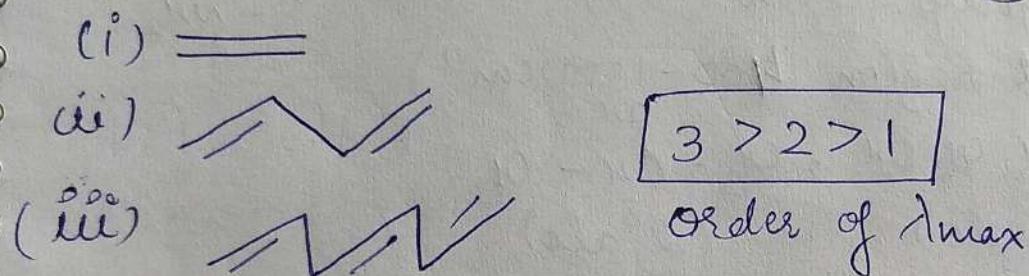
(E) → Intensity.

4.) Hypochromic : shift towards shorter intensity.



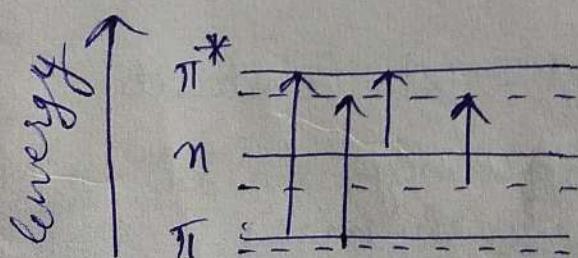
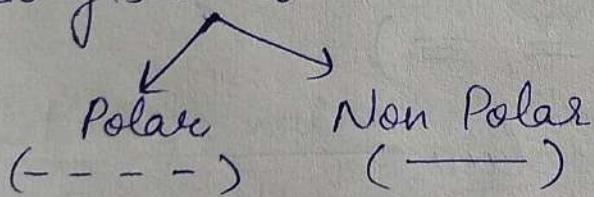
$\Rightarrow$  Factors affecting UV-visible shifts

1.) Conjugation :- More is the extent of conjugation more is the wavelength.



2.) Auxochrome :- due to the presence of auxochromes wavelength increases ( $\lambda_{\max} \uparrow$ )

3.) Effect of solvent



$$\pi < \pi^* < n$$

order of stability in Polar.

$$n - \pi^* < \pi - \pi^*$$

$$E_{N.P} < E_P \quad E_P < E_{N.P}$$

$$\lambda_{N.P} > \lambda_P \quad \lambda_P > \lambda_{N.P}$$

⇒ Infrared Spectroscopy or Vibrational Spectroscopy  
to analyse the functional groups present in molecule.

IR

→ Energy change in vibrational energy.

IR region exists between  $400 - 4000 \text{ cm}^{-1}$ .

⇒ Types of IR region

Ex: -OH  
-COOH  
-CHO  
-NH<sub>2</sub>

1.) Functional Group region ( $1500 - 4000 \text{ cm}^{-1}$ )

2.) Finger Print Region ( $400 - 1500 \text{ cm}^{-1}$ )

Ex:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_3-\overset{\text{OH}}{\underset{\text{(1° alc)}}{\text{CH}}}-\text{CH}_3$  (2° alc)

⇒ Energy change/change in frequency depends upon:

- 1.) mass of atom present in molecule.
- 2.) arrangement of atom.
- 3.) Bond Strength (-, =, ≡)

According to Hooke's law:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

where, K = force constant

$\nu$  = frequency

$\mu$  = reduced mass

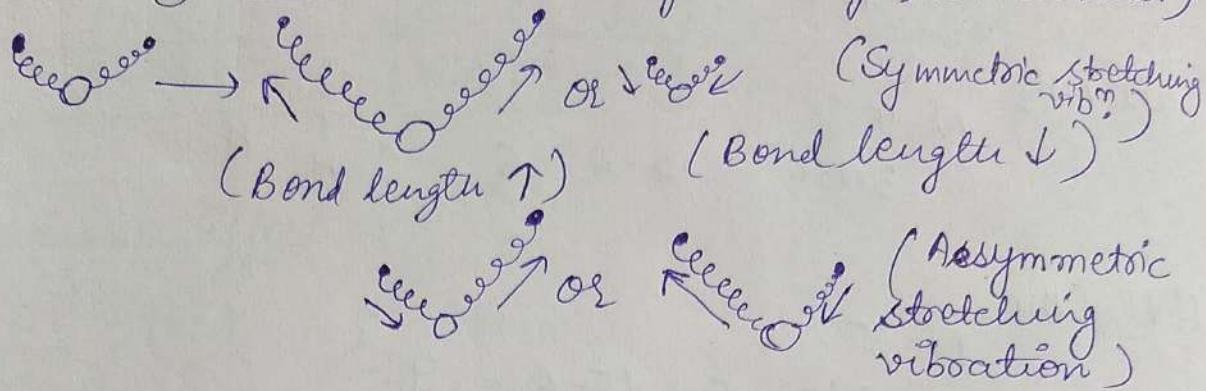
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$K \propto \nu$$

$$K \propto \nu \propto \text{Bond strength}$$

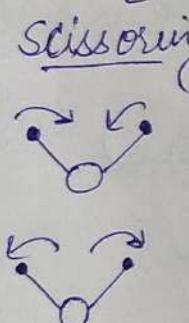
## $\Rightarrow$ Types of Vibrations (Ans)

1.) Stretching vibration (Bond length change i.e. inc. or dec.)

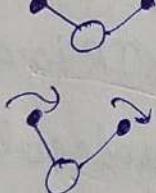


2.) Bending vibration (Bond angle changes)

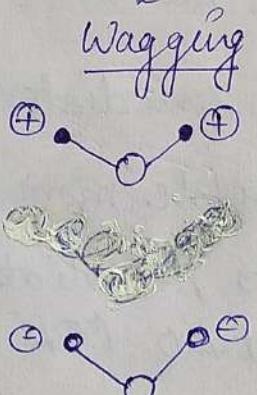
In plane



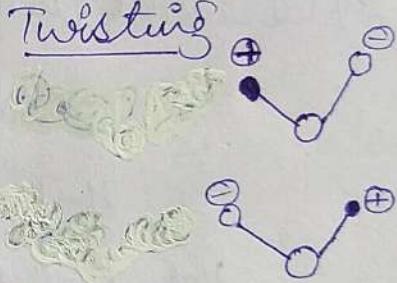
Rocking



out plane



Twisting



$\Rightarrow$  Calculation of total no. of vibration

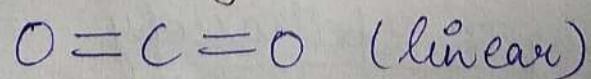
( $N$  = total no. of atoms)

1.) For a linear molecule =  $3N - 5$

2.) For a non linear molecule =  $3N - 6$

Ques calculate total no. of vibrations in  $^{(1)}\text{CO}_2$ .

Ans:



$$3N - 5$$

$$= 3(3) - 5 \Rightarrow 9 - 5$$

$$= 4.$$

(ii)  $H_2O$

$$N = 3$$

$$3N-6 + 3-6 = 3$$

(iii)  $NH_3$

$$N = 4$$

$$3N-6 = 12-6 = 6$$



(iv)  $CH_4$

$$N = 5$$

$$3(5)-6 = 15-6 = 9$$

~~Defn~~ Selection rule for IR Spectroscopy

- 1) Molecule must possess dipole moment.
- 2) Vibrational quantum number ( $\Delta V$ ) =  $\pm 1$ .

$H_2, F_2, O_2 \Rightarrow$  Homodiatomic molecules

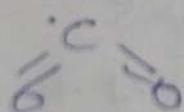
$H-H \Rightarrow$  Dipole moment = 0 (IR inactive)

$H-F, H_2O, NH_3 \Rightarrow$  Heterodiatomic molecules

Dipole moment  $\neq 0$  (IR active)

~~CO<sub>2</sub>~~ \*  $CO_2 \Rightarrow O=C=O$

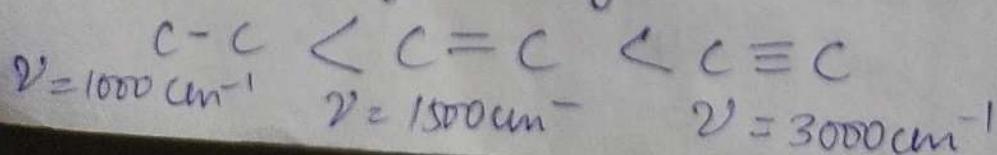
$\boxed{\mu = 0} \rightarrow$  IR inactive



$\boxed{\mu \neq 0} \rightarrow$  IR active

Factors affecting IR Spectroscopy

- 1) Bond Order: More is the bond order more will be the frequency.

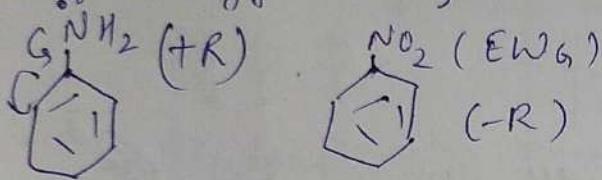


## 2.) Inductive Effect

+I	ERG	B.L ↑	B.O ↓	$\nu \downarrow$
-I	EWG	B.L ↓	B.O ↑	$\nu \uparrow$

ERG → e<sup>-</sup> releasing group  
 EWG → e<sup>-</sup> withdrawing group

## 3.) Resonance Effect



+R	ERG	B.L ↑	B.O ↓	$\nu \downarrow$
-R	EWG	B.L ↓	B.O ↑	$\nu \uparrow$

Ques A compound having

Ques If the stretching frequency of HF molecule is  $1.2 \times 10^{14} \text{ sec}^{-1}$ . Calculate the wave no. of molecule.

Sol<sup>n</sup>:  $\nu = 1.2 \times 10^{14} \text{ sec}^{-1}$

$C = 3 \times 10^{10} \text{ cm/s}$

wave no. (cm<sup>-1</sup>)  $\leftarrow \bar{\nu} = \frac{\nu}{C} = \frac{1.2 \times 10^{14}}{3 \times 10^{10} \times 10} = 4 \times 10^3 \text{ cm}^{-1}$

Ques One of the fundamental vib.<sup>n</sup> of H<sub>2</sub>O  $\bar{\nu}_{H_2O} = 3652 \text{ cm}^{-1}$

Assuming  $K_{H_2O} = K_{D_2O}$ .

$$\bar{\nu}_{D_2O} = ?$$

Sol<sup>n</sup>:  $\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$

$$\bar{\nu}_{H_2O} = \frac{\nu}{C} = \frac{1}{2\pi C} \sqrt{\frac{K_{H_2O}}{\mu_{H_2O}}} \quad \textcircled{1}$$

$$\bar{\nu}_{D_2O} = \frac{1}{2\pi C} \sqrt{\frac{K_{D_2O}}{\mu_{D_2O}}} \quad \textcircled{2}$$

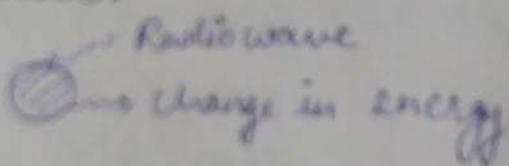
$$\mu_{H_2O} = \frac{m_H m_O}{m_H + m_O} = \frac{1416}{1416 + 16} = \frac{16}{17} = 0.94$$

$$\mu_{D_2O} = \frac{2416}{2416 + 16} = \frac{2416 - 16}{2416 + 16} = \frac{32}{18} = 1.78$$

divide eq? ② by ①

$$T_{D_2O} = \bar{\nu}_{H_2O} \sqrt{\frac{\mu_{H_2O}}{\mu_{D_2O}}} \\ = 3652 \times \sqrt{\frac{0.94}{1.78}} = \underline{\quad \quad \quad} \\ = 3652 \sqrt{0.52} \\ = 3652 \times 0.72 \\ \approx 2654.9 \text{ cm}^{-1}$$

$\Rightarrow$  Nuclear Magnetic Resonance (NMR) (Absorbs in radio frequency region). It determines the number of protons ( $H$ ) present in molecule.



All the molecules are not NMR active. Only few are NMR active.

Ex:  $^1H$ ,  $^{13}C$ ,  $^{15}N$ ,  $^{31}P$  etc.

### NMR active

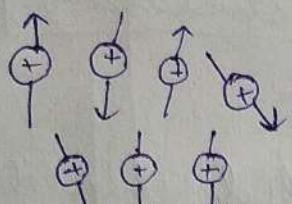
- |            |   |               |
|------------|---|---------------|
| Atomic No. | { | Atomic mass   |
| 1) odd     |   | odd = $^1H$ , |
- 
- |         |   |                 |
|---------|---|-----------------|
| 2) odd  | { | even = $^{14}N$ |
| 3) even |   | odd = $^{13}C$  |

### NMR inactive

- |            |   |             |
|------------|---|-------------|
| Atomic No. | { | Atomic Mass |
| even       |   | even        |
- 
- Ex.  $^{12}C$ ,  $^{16}O$

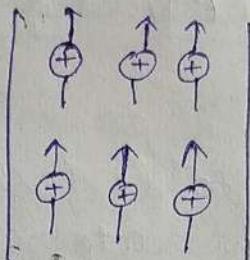
## $\Rightarrow$ Principle of NMR

Nuclear Magnetic Resonance  
 ↓                      ↓  
 Nucleus + magnetic field + matches frequency



random orientation

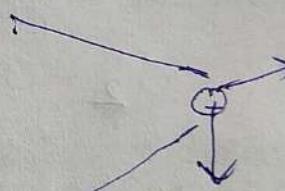
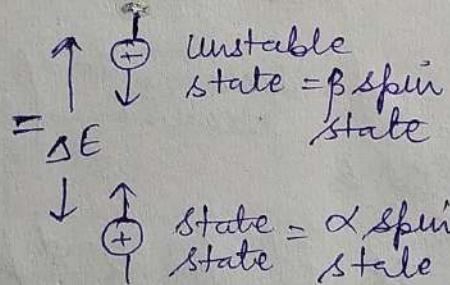
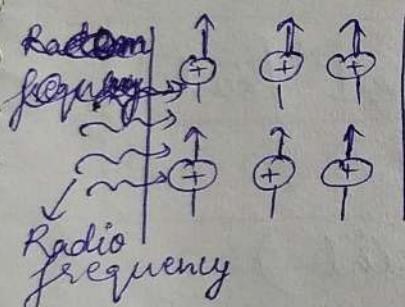
(without external magnetic field)



Most Stable =  $\alpha$ -spin state

$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$  → magnetic field

(In the presence of applied external magnetic field)



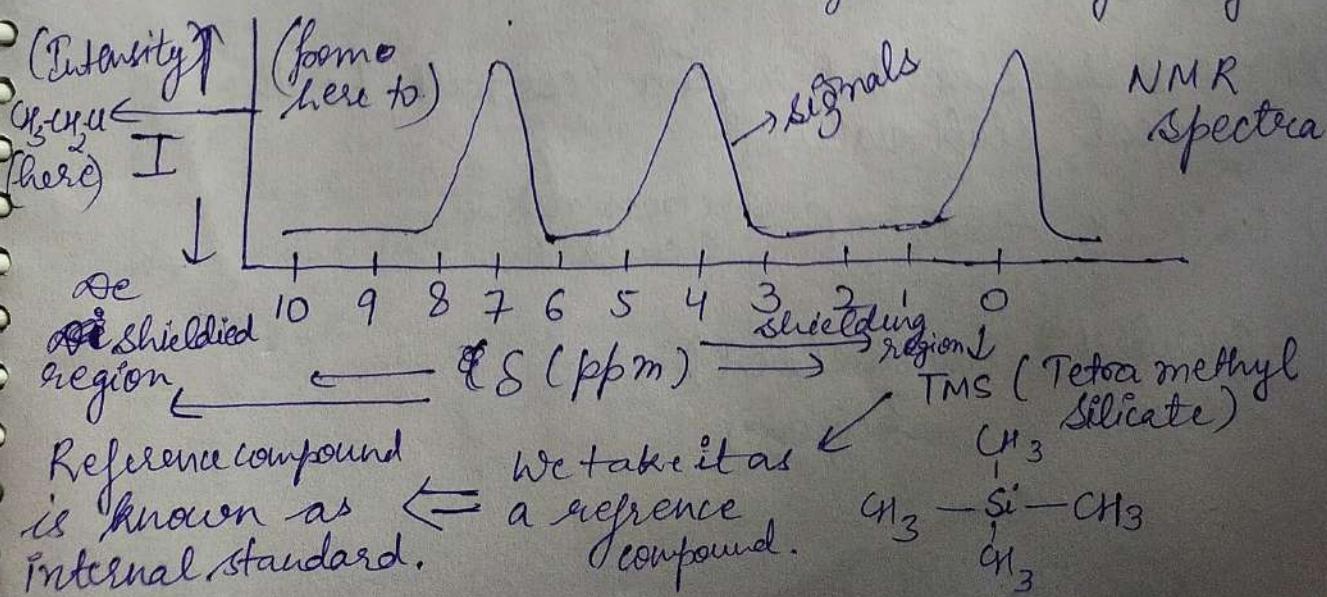
Random orientation of Nucleus

$$\boxed{\Delta E = h\nu}$$

## $\Rightarrow$ Chemical Shift ( $\delta$ )

Shielded region (upfield region)

Deshielded region (downfield region)



## Chemical shift in NMR spectra

The shift of signals from the signal of TMS.  
Chemical shift is generally given in PPM.

### Difference b/w deshielded and shielded region.

#### \* Deshielded Region

- 1.) A proton is said to be deshielded when it is attached with an electronegative element.
- 2.) More is the electronegativity, more will be the deshielding.
- 3.) More is the deshielding, more will be the chemical shift.

4.) Ex:  $\text{CH}_3 - \underset{\substack{\text{More} \\ \text{electro-} \\ \text{ve.} \\ \text{element}}}{\text{CH}_2} - \text{Cl}$   $\rightarrow$  Electronegative element (for 1<sup>st</sup> point)  
 $\text{deshielded}$

$\text{F} - \underset{\substack{\text{More} \\ \text{electro-} \\ \text{ve.} \\ \text{element}}}{\text{CH}_2} - \text{CH}_2 - \text{Cl}$  (for 2<sup>nd</sup> point)  
 $\text{deshielded}$

#### \* Shielded Region

- 1.) A proton is said to be shielded if it is away from electronegative element.
- 2.) More is the shielded region less will be the chemical shift value.

3.) Ex:  $\text{CH}_3 - \underset{\substack{\text{S} \\ \text{D}}}{\text{CH}_3} - \text{F}$  Electronegative element  
(shielded region) (deshielded region)

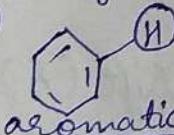
⇒ NMR spectra gives us valuable information

- Number of Signals → Tells about the no. of H (hydrogen).
- Position of signals → Tells about type of H having diff. environment.
- Intensity of signals → Tells about total no. of H w.r.t. to signal.
- Splitting of signals → Tells about the type of neighbouring H.

Ques Why only TMS is taken as ~~standard~~ compound?

- Ans:- 1.) TMS is highly shielded as compared to other organic compounds.
- 2.) Chemically inert.
- 3.) It does not interfere with other signals of compound.

⇒ Some important chemical shift values ( $\delta$ ) ppm.

Compounds	$\delta$ (PPM)
1.) $R - \text{CH}_2 - \text{H}$	~ 1
2.) $\text{C} = \text{C} - \text{H}$ vinyl	4.6 - 5.9
3.) $\text{C}' \equiv \text{C} - \text{H}$ acetylene	2 - 3
4.)  aromatic	6 - 8.5
5.) $\text{C} = \text{C} - \text{CH}_3$ Allyl	1.8 - 2.0
6.) $R - \text{O} - \text{H}$ Alcohol	3 - 4
7.) $R - \overset{\text{O}}{\underset{\text{C}}{\text{  }}} - \text{O} - \text{H}$ carboxylic	10 - 12
8.) $R - \overset{\text{O}}{\underset{\text{C}}{\text{  }}} - \text{H}$ Aldehyde	9 - 10

\* Calculation of chemical shift ( $\delta$ ):

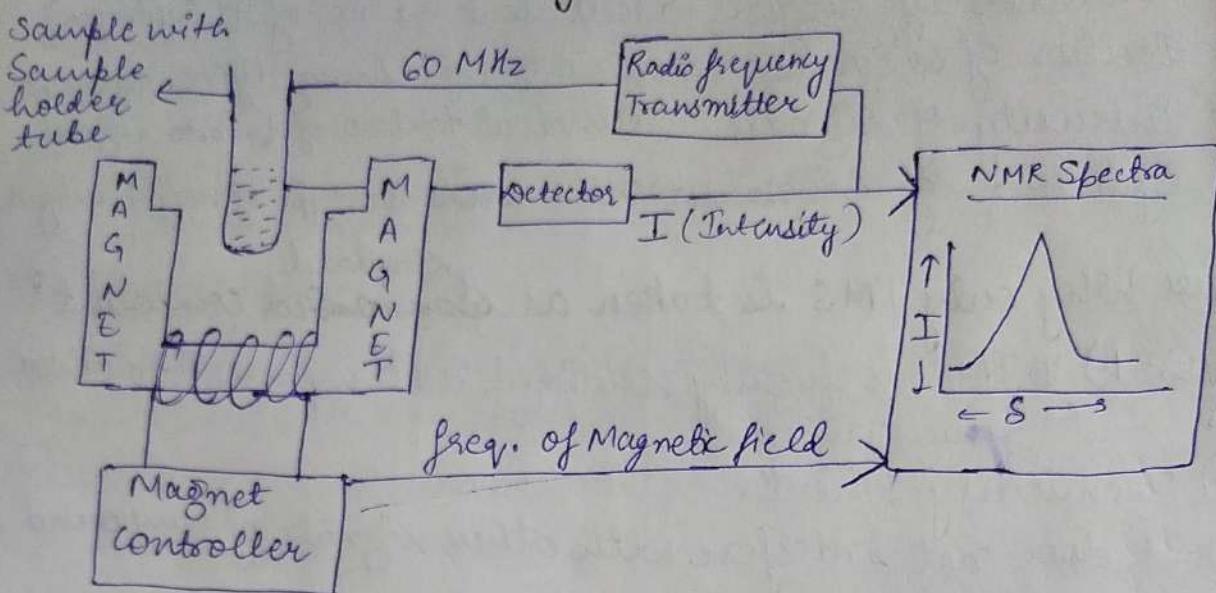
$$\delta = \frac{v_s - v_{\text{TMS}}}{v_0} \times 10^6$$

$v_s$  = frequency of sample.

$v_{\text{TMS}}$  = frequency of TMS.

$v_0$  = frequency of magnetic field.

## Instrumentation of NMR

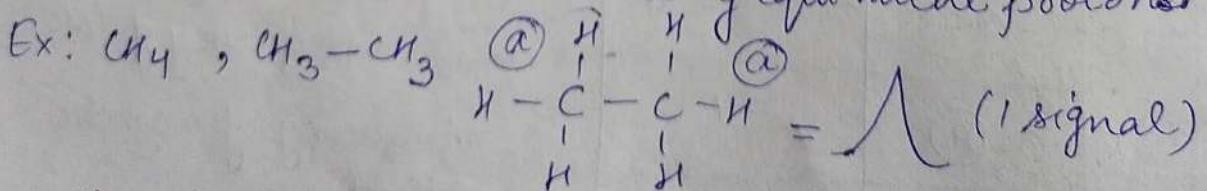


## NMR Spectrophotometer

\* Solvents like  $D_2O$ ,  $CDCl_3$  are used as in sample. Solvents containing 'H' like  $H_2O$  is not used in sample because it will give two peak but we need only one peak.

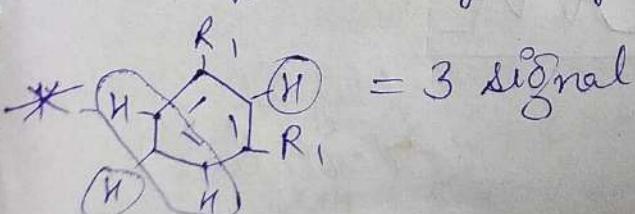
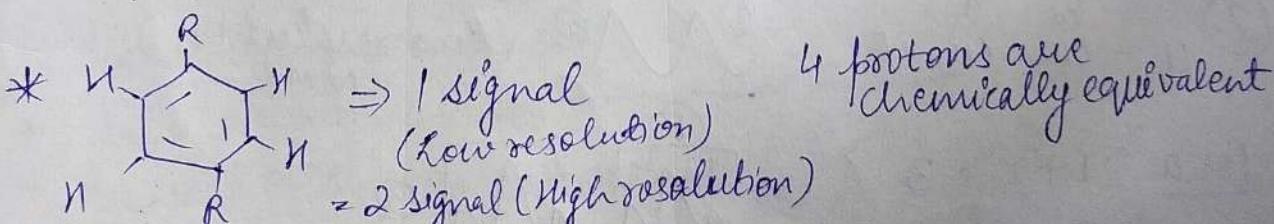
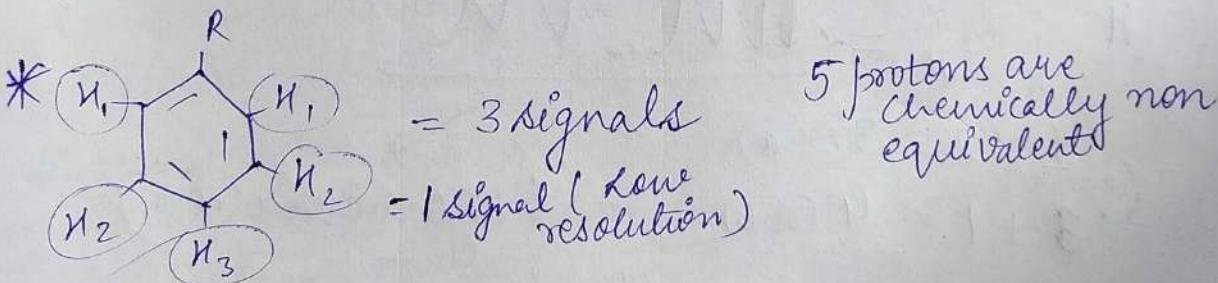
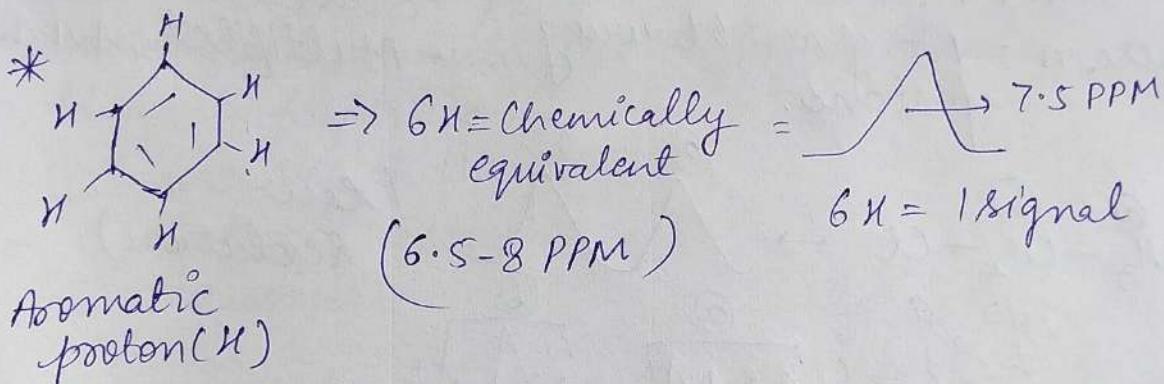
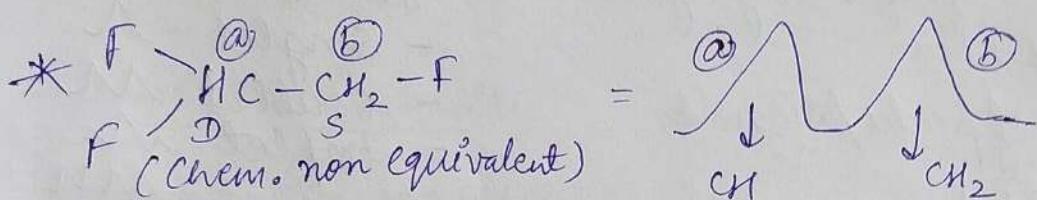
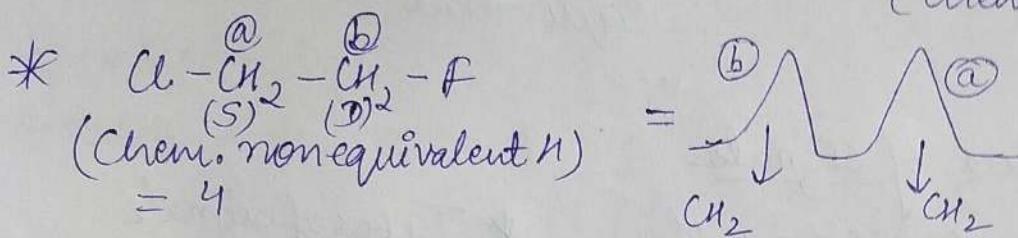
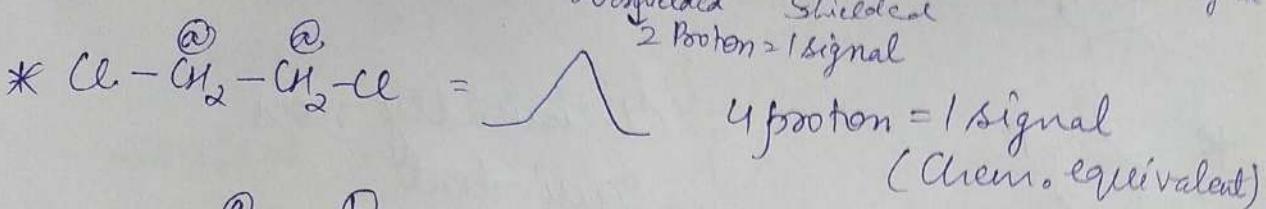
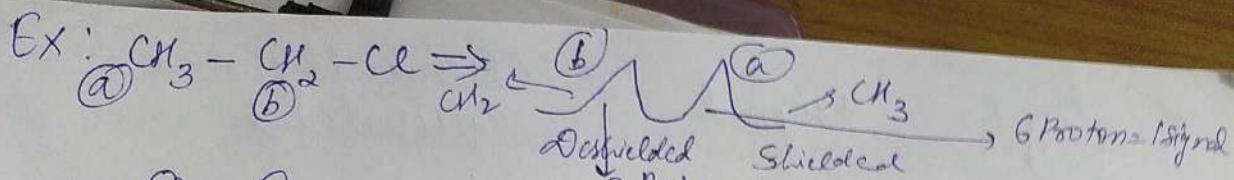
$\Rightarrow$  Chemically equivalent proton<sup>(4)</sup>

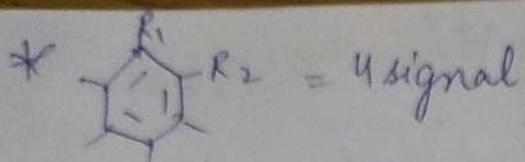
Those protons having same chemical shift ( $\delta$ ) value are known as chemically equivalent protons.



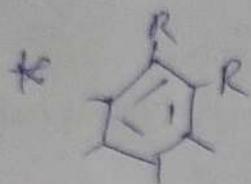
$\Rightarrow$  Chemically non-equivalent proton

Those protons having different chemical shift ( $\delta$ ) value are known as chemically non-equivalent protons.





Chemically non equivalent



Chemically non equivalent

⇒ Splitting of signals

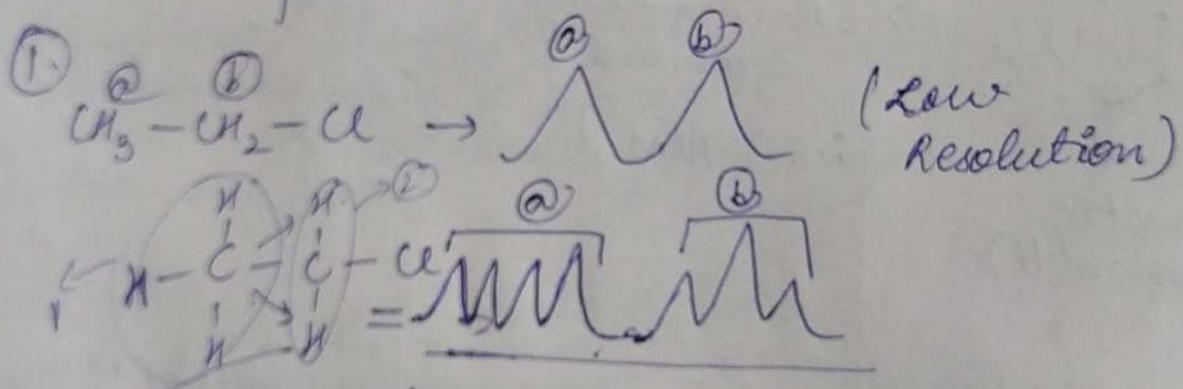
\* Calculation of splitting of signals.

Total no. of peaks/signals  
=  $n + 1$

where,  $n$  = No. of neighbouring protons.

\* Types of Signals

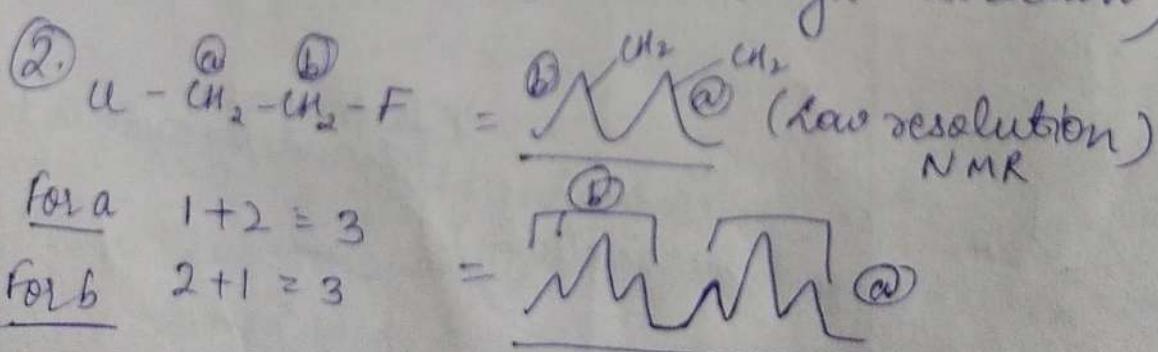
- Singlet = 1
- Doublet = M
- Triplet = MM
- Quartet = MMM
- Multiplet = MMMM



$$1 + 2 = 3 \text{ (for a)}$$

$$3 + 1 = 4 \text{ (for b)}$$

(High resolution)



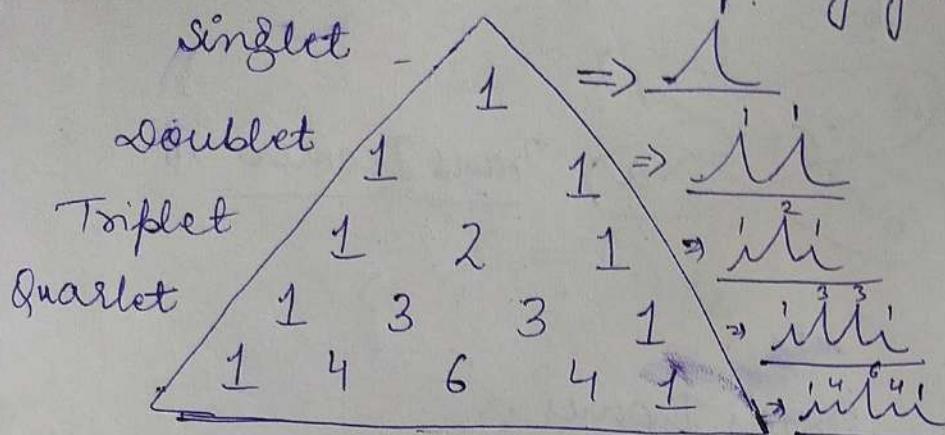
For a  $1 + 2 = 3$

For b  $2 + 1 = 3$

(High Resolution NMR)

⇒ Pascal's law of triangle

It tells us about the intensity of signal.



⇒ Stereochemistry

Isomer :- Those compounds which are having same molecular formula but different chemical and physical properties.

Isomers are of two types:-

- Structural Isomer
- Stereoisomers

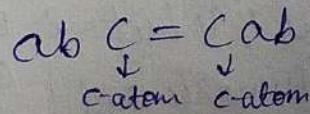
↓  
compounds having same molecular formula but different spatial arrangement.

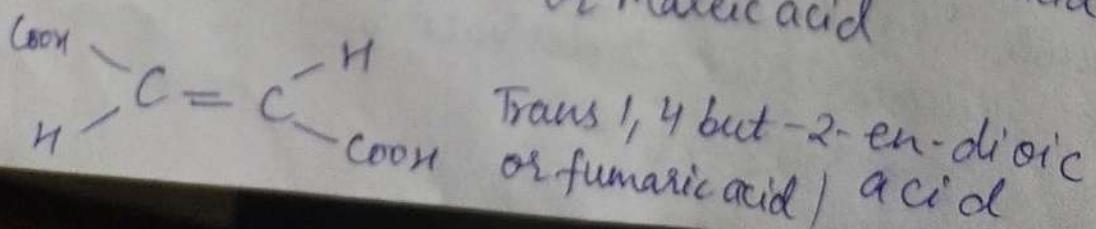
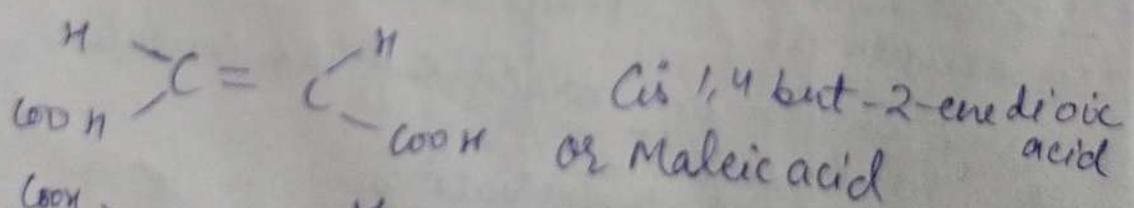
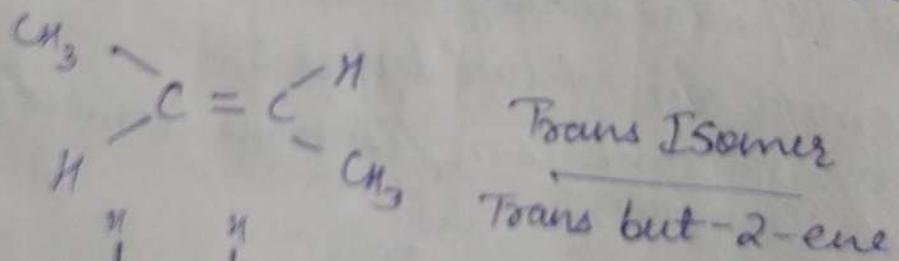
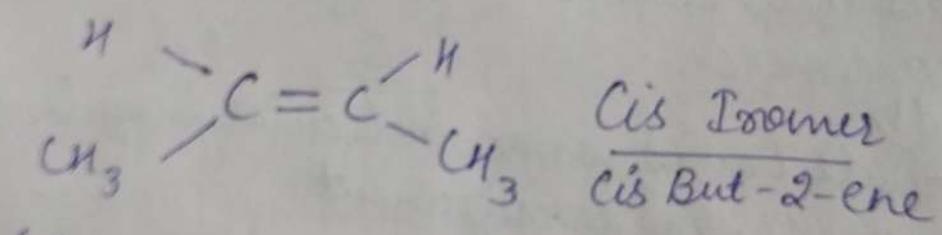
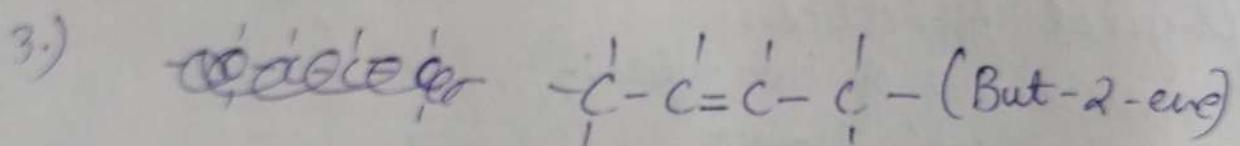
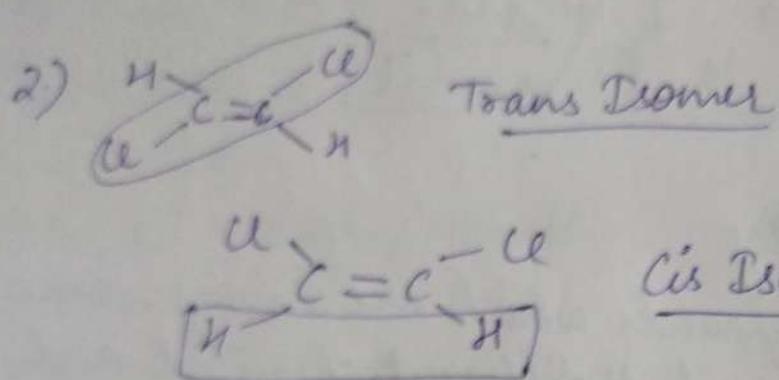
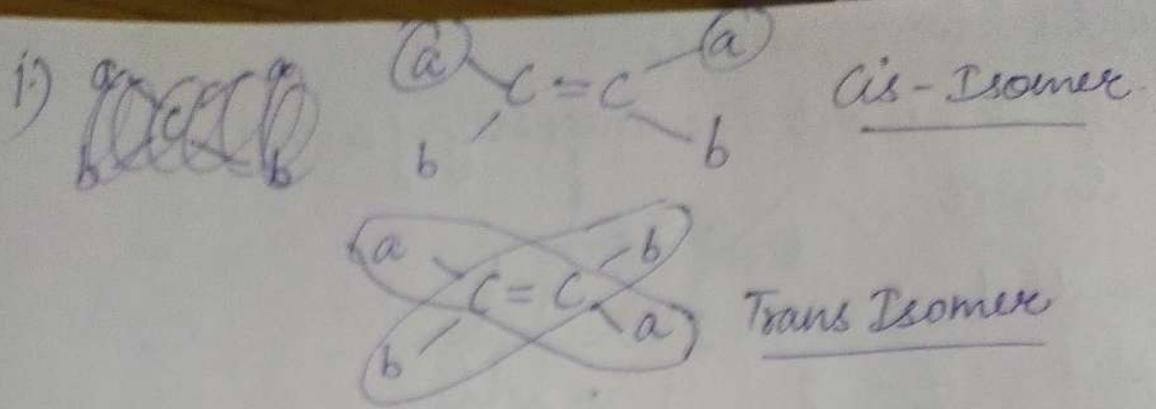
Stereoisomers are of two types :-

- Geometrical Isomerism / cis-trans Isomerism
- Optical Isomerism

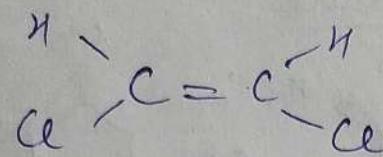
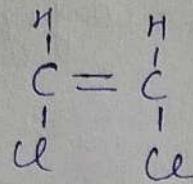
### 1.) Geometrical Isomerism

- also known as cis-trans isomerism
- Generally shown by molecule which contains double bond.
- Ex: Alkenes and its derivatives.

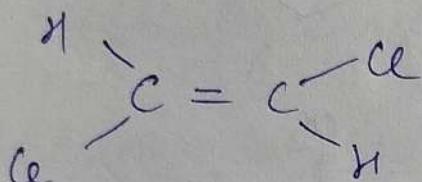




4.) 1,2 dichloro ethene

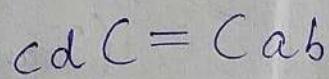


cis 1,2 dichloro ethene



trans 1,2 dichloro ethene

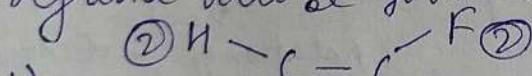
### ④ E/Z configuration



E = opposite side

Z = same side

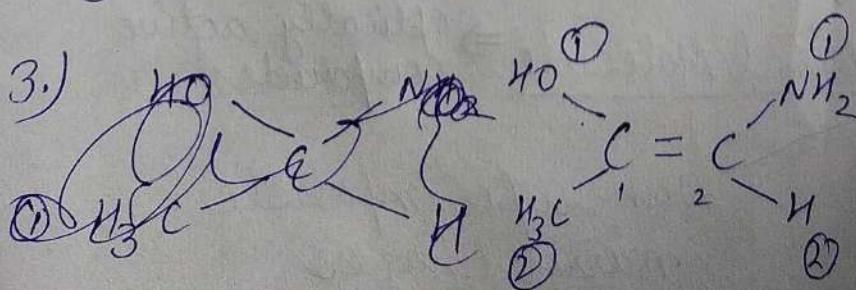
Higher the atomic no. higher will be the priority OR'  
Preference will be given to the higher atomic no. element



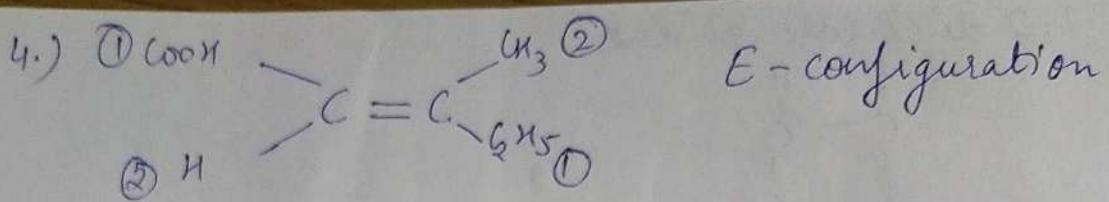
Z configuration



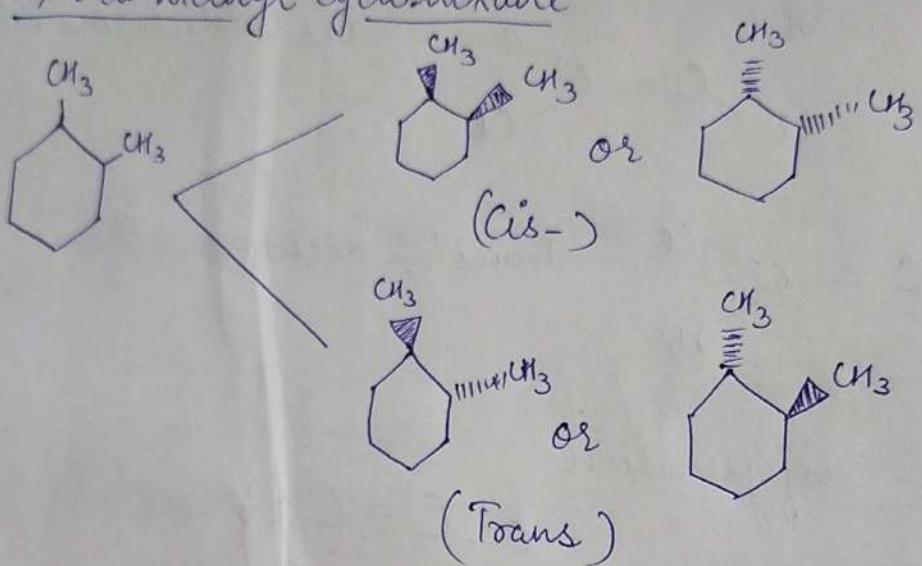
Z-configuration



Z-configuration

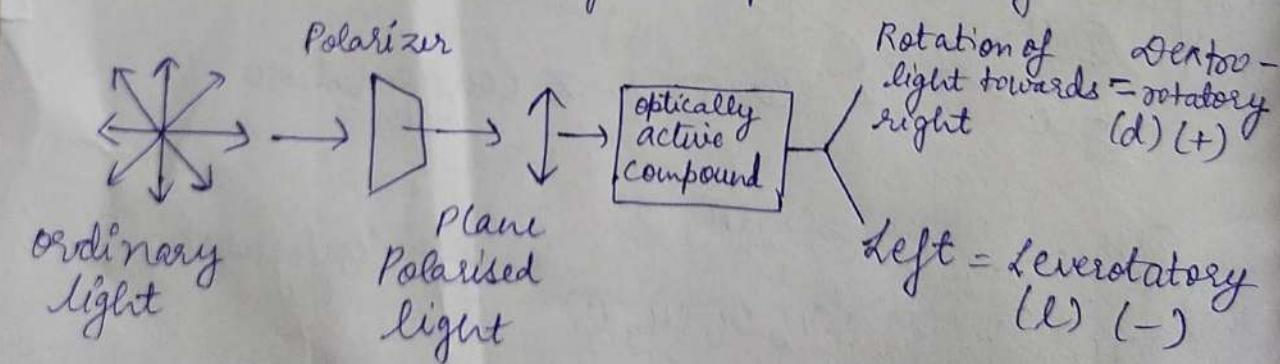


1, 2 di methyl cyclohexane



## 2.) Optical Isomerism

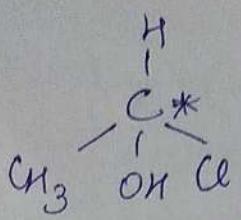
Isomers having same all the chemical properties except their action on plane polarized light.



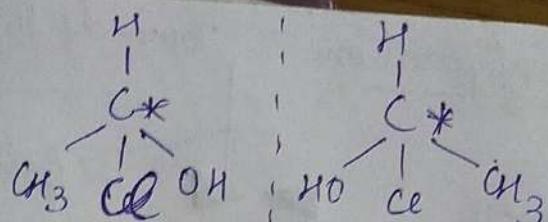
$\Rightarrow$  Asymmetric / Chiral Molecule  $\Rightarrow$  optically active compounds

C-atom having all the 4 groups different.

Non-superimposable mirror images



Asymmetric / Chiral



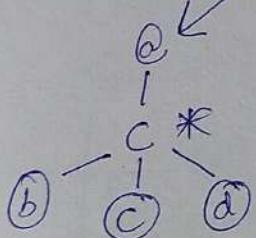
Mirror

$\Rightarrow$  Symmetric / Achiral molecules

$\Downarrow$   
Optically Inactive

$\Rightarrow$  Asymmetric / Chiral

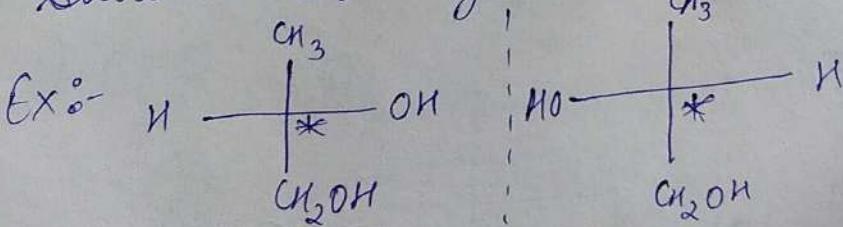
$\Downarrow$   
Optically active



Non-Superimposable  
Mirror Images

$\Rightarrow$  Enantiomers

Those molecules which are non superimposable and show mirror images to each other.



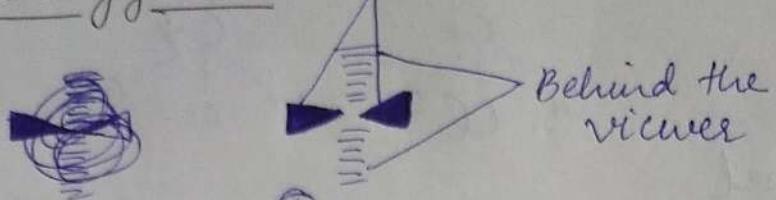
$\Rightarrow$  Sister Isomers

- Neither mirror images
- Nor superimposable

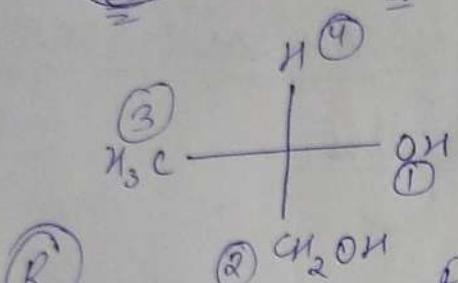
Those molecules which are neither mirror images nor superimposable to each other are called sister isomers.

$\Rightarrow R-S$  configuration

Towards the viewer



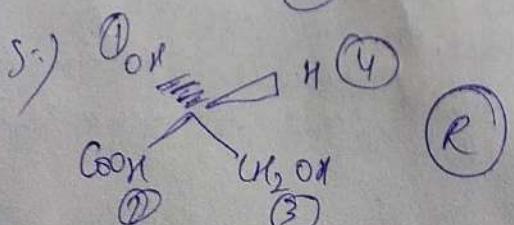
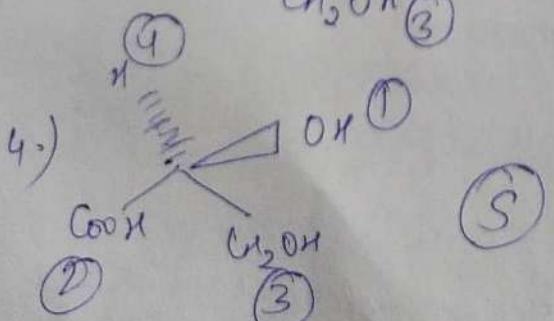
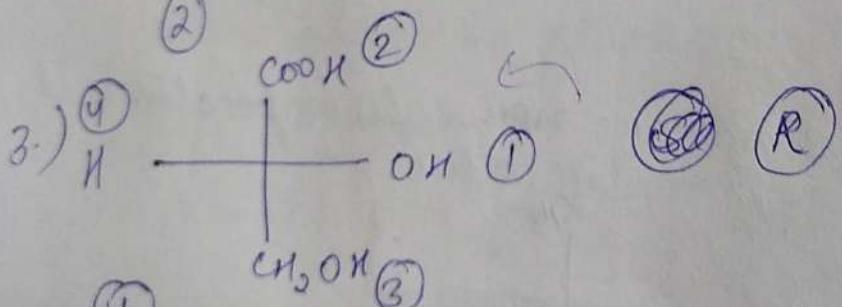
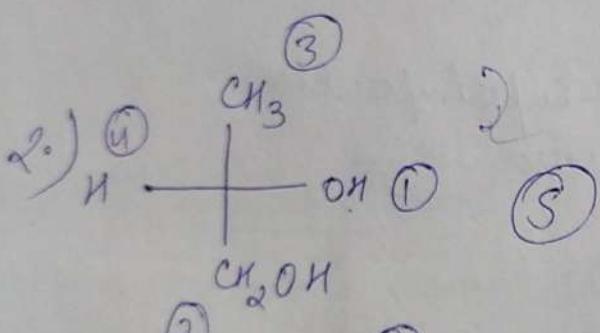
1.)

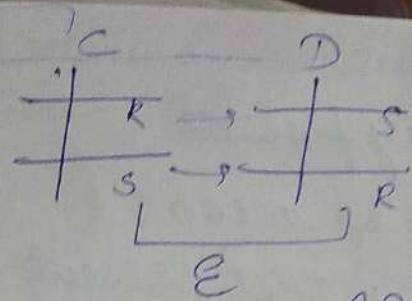
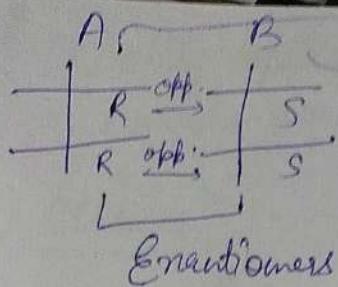


1 = highest priority  
4 = lowest priority

8 O 6 C 1 H

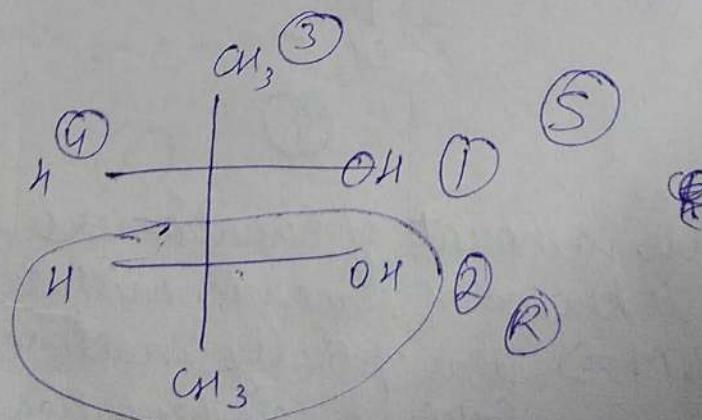
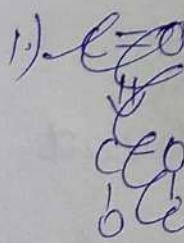
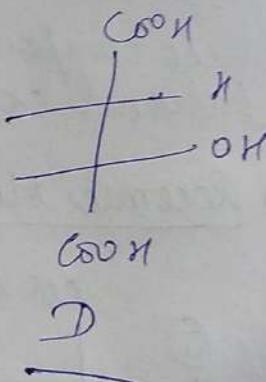
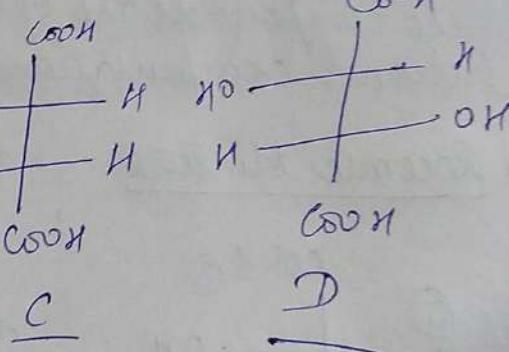
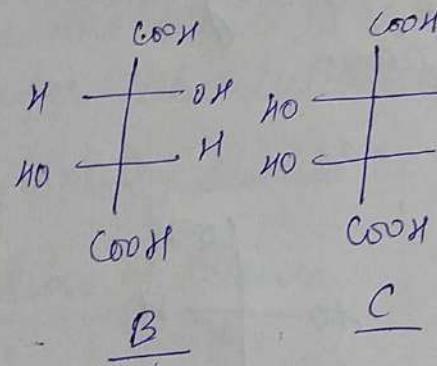
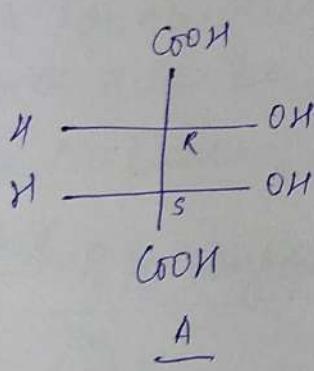
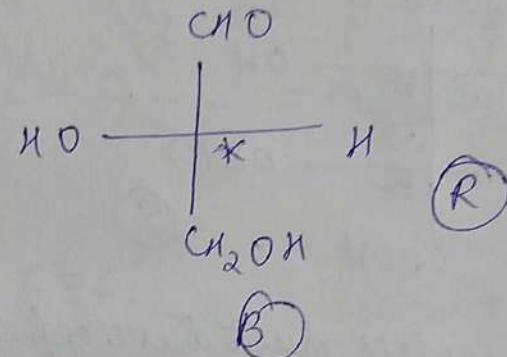
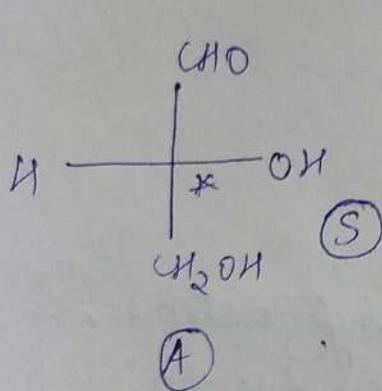
1  $\rightarrow$  2  $\rightarrow$  3  
clockwise = R  
Anticlockwise = S





$A \& C$   
 $B \& D$  =  $\alpha$ -Distereomers

$A \& B$   
 $C \& D$  = Enantiomers



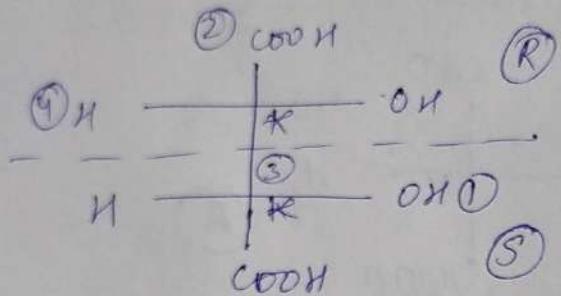
## $\Rightarrow$ Meso Compounds

- plane of symmetry present

for a compound to be meso :-

- plane of symmetry must present.

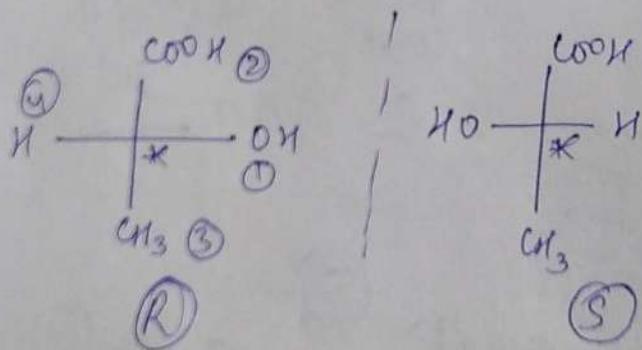
- Molecule must possess <sup>two</sup> chiral centres.



- Both chiral centres must have opp. configuration.

~~Meso compounds are optically inactive due to internal compensation.~~

## $\Rightarrow$ Racemic Mixture

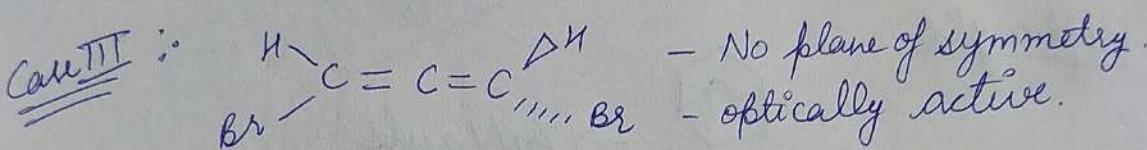
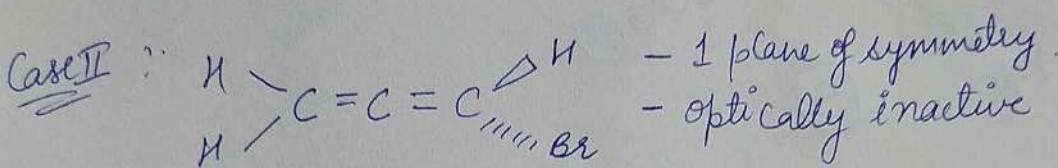
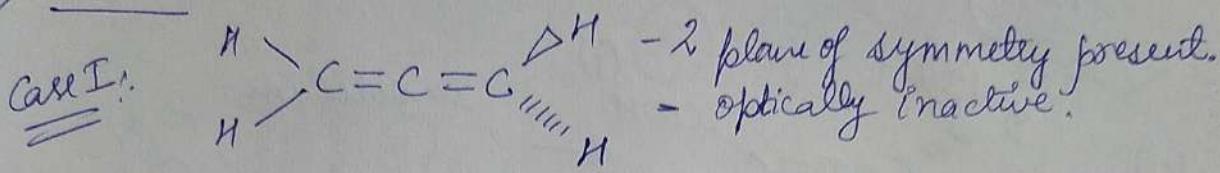


When equimolar amount of Enantiomers is present in mixture is known as Racemic mixture.

$A + B \Rightarrow R.M \Rightarrow$  It is optically inactive due to external compensation.

~~Ques~~ Chirality / optical activity in molecules having no chiral centre.

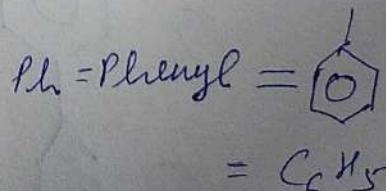
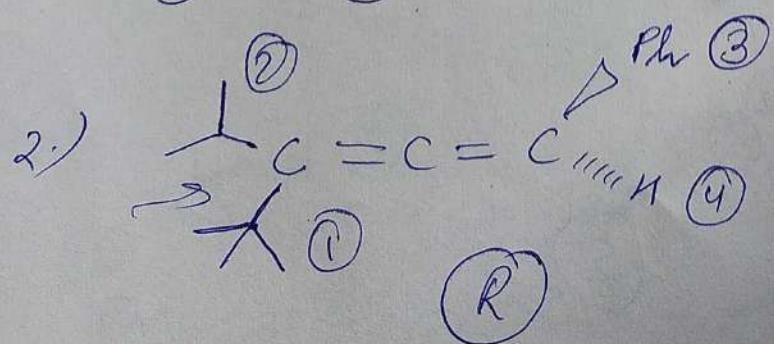
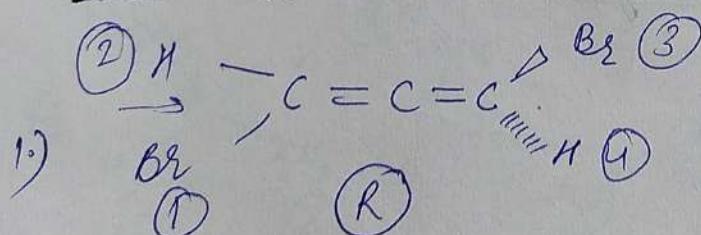
### 1.) Allenes

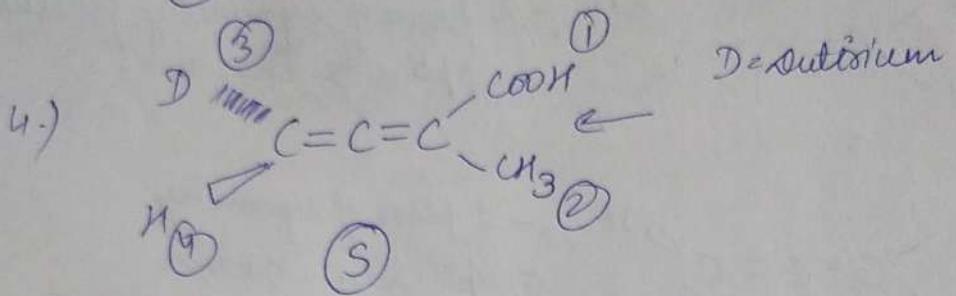
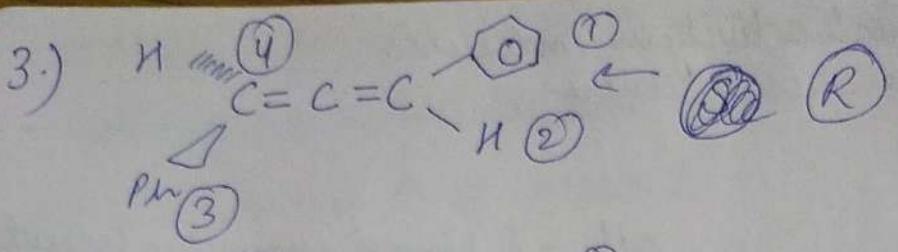


\* For an Allene molecule to be optically active there should be proper substitution at C-1 & C-3.

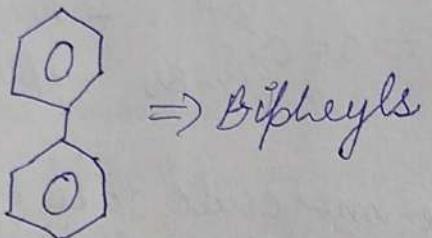
\* No plane of symmetry should be there.

### ~~Ques~~ R/S configuration of Allenes





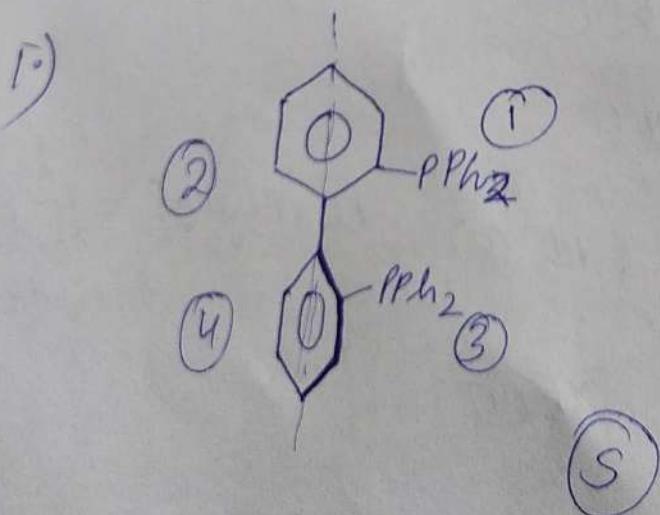
## 2.) Biphenyls



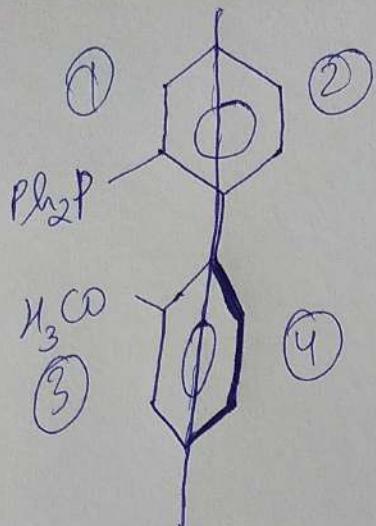
\* P.O.S is similar to alkenes.

\* 2 P.O.S, optically inactive

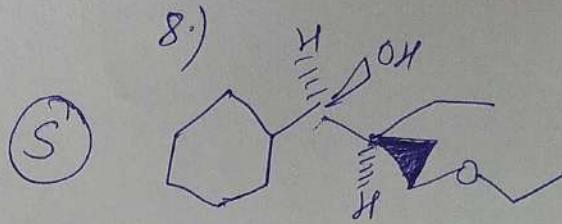
$\Rightarrow$  R/S configuration Biphenyls



2.)



8.)



3.)

