

UNIT → 2.

SPECTROSCOPIC ANALYSIS

- Spectroscopy :

physical

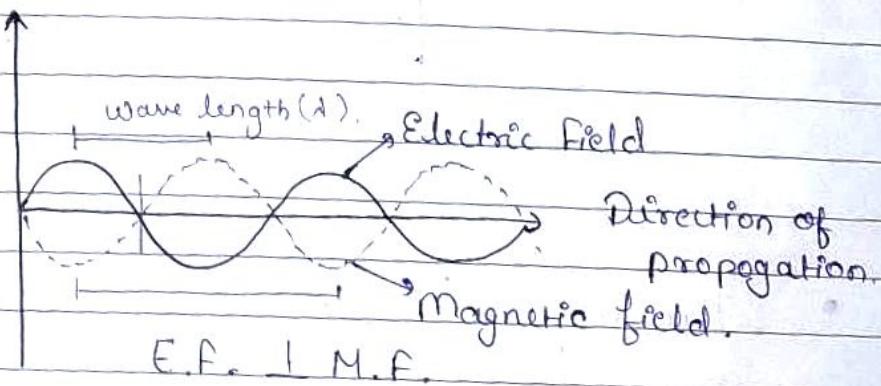
The branch of Chemistry which deals with the interaction of Electromagnetic radiation and matter is called Spectroscopy.

- Spectrophotometer :

The instrument which is used to study interaction of electromagnetic radiation and matter is called Spectrophotometer.

- Electromagnetic Radiation :

The radiation which propagates in such a way that electric field is perpendicular to the magnetic field is called Electromagnetic Radiation.

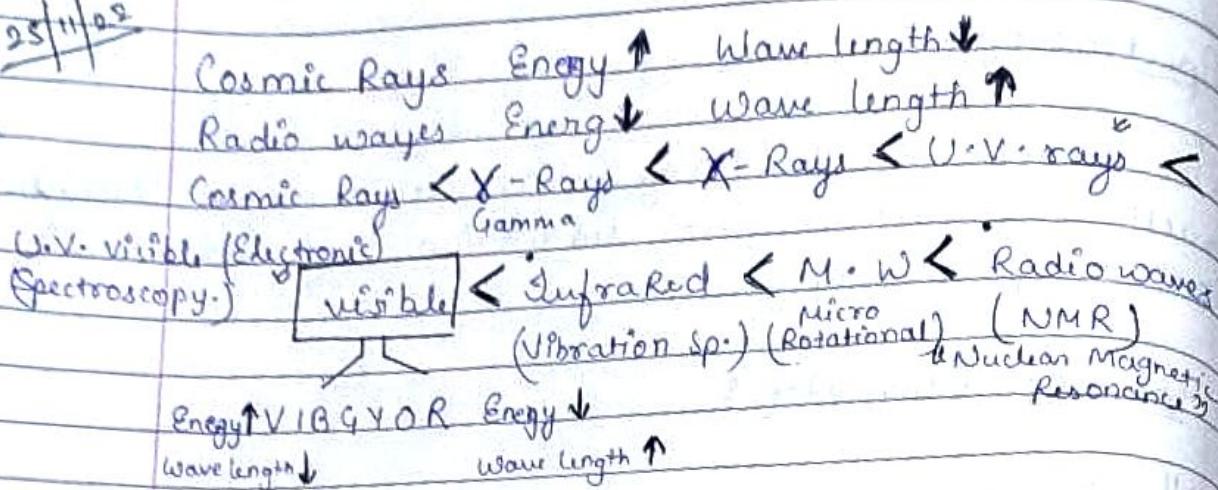


- Electromagnetic Spectrum :

When all electromagnetic radiation arranged in

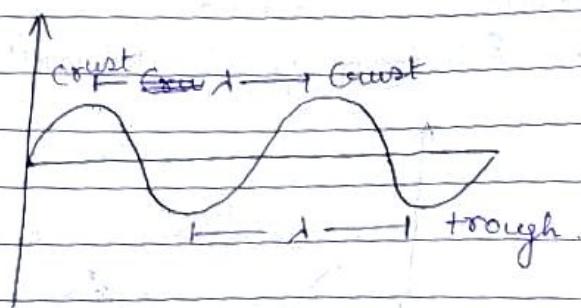
or decreasing order
increasing order of wavelength, thus spectrum
Obtain it called Electromagnetic Spectrum.

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Characteristics of Electromagnetic Radiation:

- **Wavelength (λ):** The distance b/w two adjacent crest or trough is called wavelength.
It is represented by λ and its S.I. unit is meter, nanometer, picometer.



- **Frequency (ν):** The number of waves passes through a given point in a unit time is called frequency
'OR'

It is known as the no. of cycles per second.

It is denoted by Greek word ν (nu)

It's unit is cycle s^{-1} or Hertz 'Hz'.

- Wave number (\bar{v}) : It is defined as the reciprocal of wave length , it is represented by nu bar (\bar{v}). It's unit is m^{-1} , cm^{-1} , nm^{-1} etc.

$$\bar{v} = \frac{1}{\lambda}$$

- Energy (E) : According to Planck's Quantum theory the energy of radiation is directly proportional to the frequency of radiation.

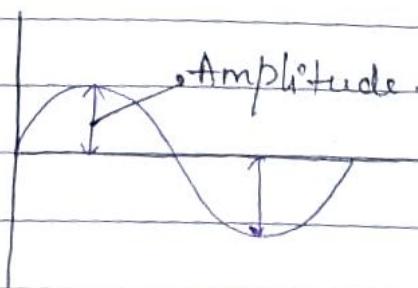
$$E \propto v$$

$$E = h v$$

where h = Planck's Constant $= 6.626 \times 10^{-34}$ Js.

- Amplitude (A) : The maximum height of crest or maximum depth of trough is called Amplitude.

It is represented by 'A'.



ULTRA VIOLET - VISIBLE SPECTROSCOPY

The branch of Spectroscopy which takes place by absorption of ultra-violet and visible radiation of EMR is called UV Visible Spectroscopy.

- Principle: When a molecule absorbs ultra-violet visible radiation it undergoes changes in electronic transition that is Electron excited from ground state to higher Energy State.

Therefore, it is also called Electronic Transition Spectroscopy.

- U.V. Visible Region: In the Electromagnetic Radiation which lies wave length 150 nm to 800 nm is called U.V. Visible Region.

It is further divided into two parts:

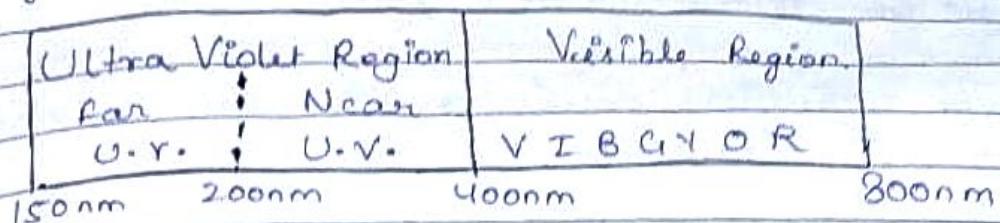
- ★ UltraViolet Region: The part of EMR (Electromagnetic Radiation) which have wavelength b/w 150 nm to 400 nm is called Ultra Violet Region.

It is further divided into 2 parts:

Near UltraViolet Region: The radiation which have wave length b/w 200 nm to 400 nm is called Near UltraViolet Region.

Far U.V. Region : The radiation which have wave length b/w 150nm to 200nm is called Far U.V. Region.

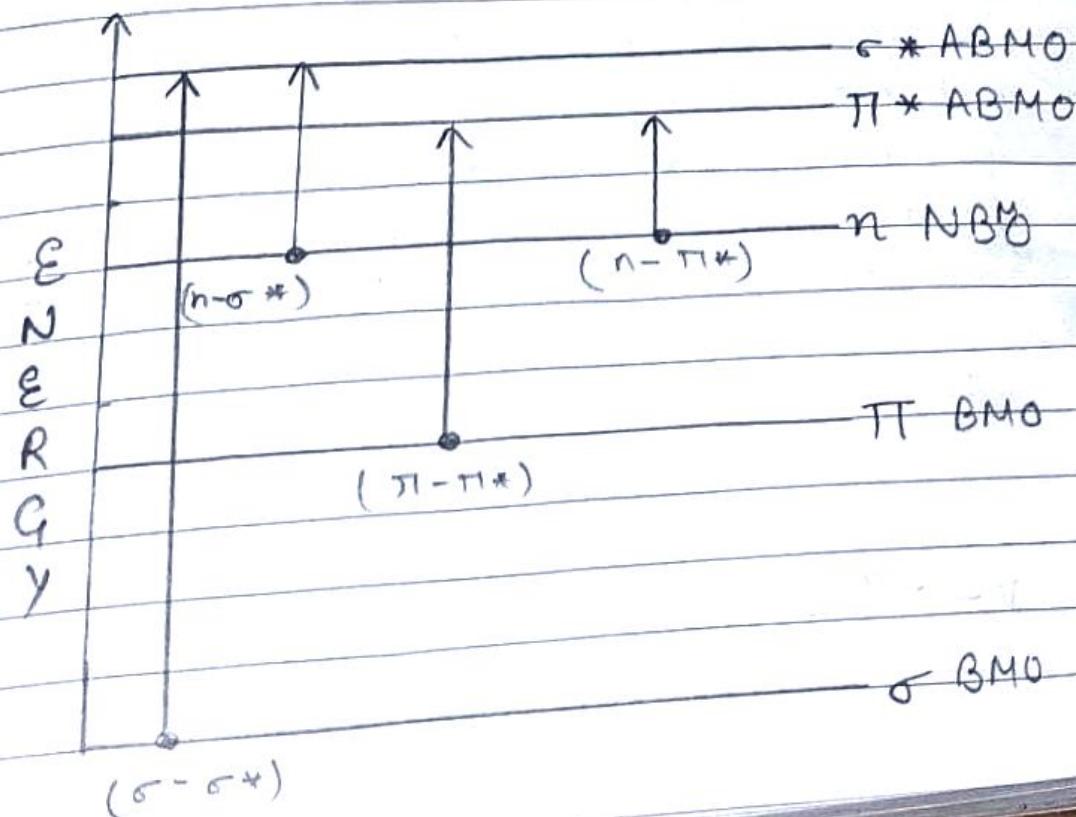
* Visible Region : The part of EMR which have wave length b/w 400nm to 800nm is called Visible Region.



Electronic transitions in U.V. - VISIBLE Spectroscopy

When a molecule absorbs ultra-violet & visible radiation it undergoes several electronic transition.

Generally there are 4 types of Electronic transitions (allowed) in a U.V. visible spectroscopy



① $\sigma - \sigma^*$ Transition: The excitation of electrons from Sigma bonding Molecular Orbital (σ BMO) to Sigma star Anti-bonding Molecular Orbital (σ^* ABMO) is called $\sigma - \sigma^*$ Transition.

- It requires very high energy so it takes place in Far-Ultra Violette Region.
- The molecules containing only sigma bonds show $\sigma - \sigma^*$ Transition.
- For example: H_2 , Saturated hydrocarbons. CH_4 , C_2H_6 , C_3H_8 etc.
& cyclic hydrocarbons Δ , \square , , .

② $n - \sigma^*$ Transition: The excitation of electrons from Non-Bonding Molecular Orbital (NBMO) to Sigma star Anti-Bonding Molecular Orbital (σ^* ABMO) is called $n - \sigma^*$ Transition

- It requires energy less than $\sigma + \sigma^*$ Transition but more than $\pi - \pi^*$ transition.
- It takes place in near U.V. region
- It is shown by the compounds having sigma bond and lone pair of electrons

For example: H_2O , H_2S , NH_3 , RNH_2 , $R-OH$, RSH , RX , HX , $R-O-R$, $R-S-R$.

$\pi - \pi^*$ Transition: The excitation of electrons from pi Bonding Molecular Orbital to pi

star Anti Bonding molecular orbital (π^*) i.e. called $\pi - \pi^*$ Transition.

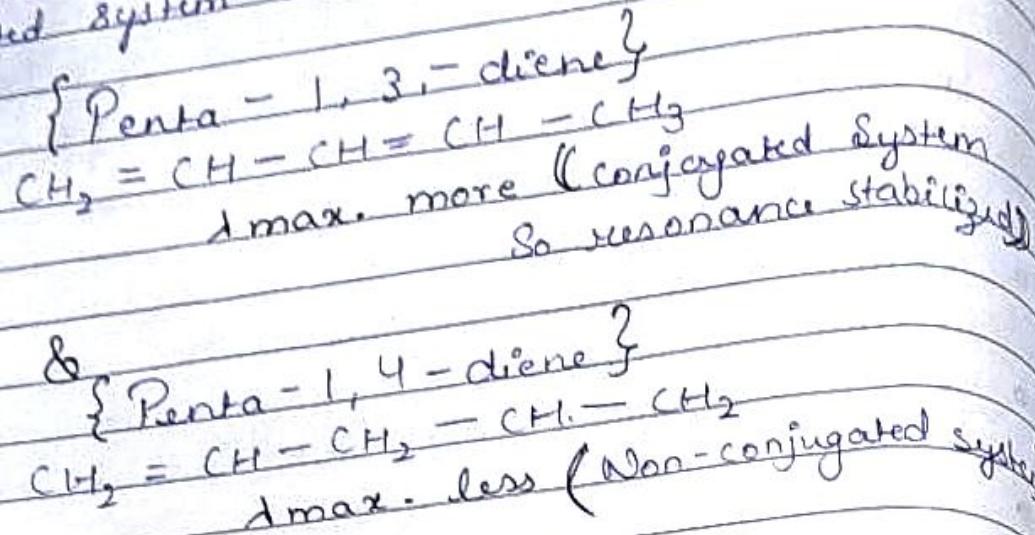
- It requires less energy than $n - \sigma^*$ Transition but $n - \pi^*$ more than $n - \pi^*$ Transition
- It takes place in Blue region of Visible Radiation.
- For example :- Alkenes, Alkynes, CycloAlkene, CycloAlkyne
- It is shown by the compounds containing multiple Bonds.

(4) $n - \pi^*$ Transition: The excitation of electrons from Non Bonding Molecular Orbital to π star Anti Bonding Molecular orbital (π^*) is called $n - \pi^*$ Transition

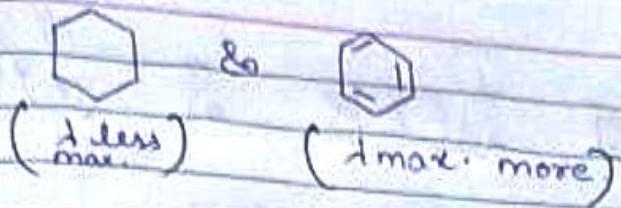
- It requires very low energy.
- It takes place in Red Visible Region.
- It is shown by the compounds containing multip bond and lone pair of electrons.
- For example :- O_2 , N_2 , HCN, R-CN, RCHO, R₂COOH, R COOR', R CONH₂, R COX.

APPLICATIONS OF U.V. VISIBLE SPECTROSCOPY

- Differentiate b/w Conjugated and non conjugated:
U.V. visible Spectroscopy is used to differentiate b/w conjugated & Non-Conjugated system
It is because a conjugated sys. item is resonance stabilize hence absorbed more value of absorption maximum (λ_{max}) than non-conjugated system



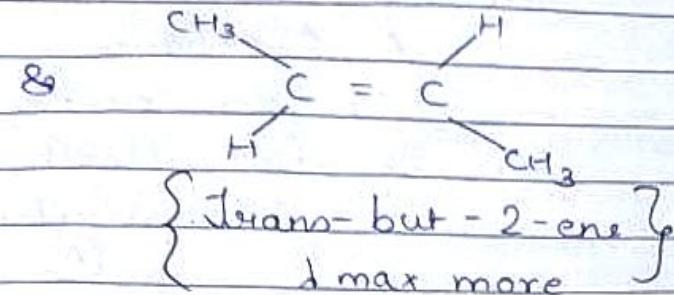
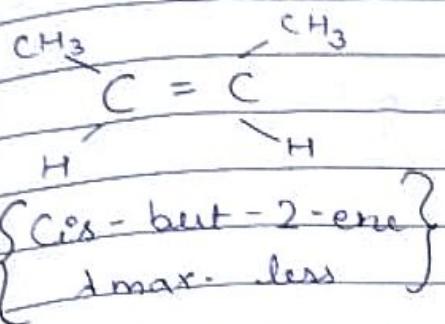
- 11/22
- Differentiation b/w Aromatic & Non-Aromatic compounds.
U.V. visible Spectroscopy is also used to differentiate b/w Aromatic & Non-Aromatic compounds
It is because Aromatic compounds are resonance stabilized and have less energy
Hence absorb more λ_{max} .
While Non-Aromatic compounds are not resonance stabilized Hence, absorb less λ_{max} .



- Differentiation b/w Geometrical Isomers:

It is also used to differentiate b/w Geometrical Isomers.

"Cis-Isomer" is less stable so absorbs less value of d_{max}. While "Trans-Isomer" is more stable hence absorbs more value of d_{max}.



- Identification of Impurity :

It is also used to detect the impurity present in a substance.

A impure compound absorbs more

- Inquantitative Analysis :

It is also used to determine the concentration of solution with the help of "Lambert - Beer's Law".

LAMBERT BEER'S LAW

Lambert Beer's law states that "When a beam of monochromatic radiation is passing through a homogeneous solution (the Absorbance is directly proportional to the product of concentration and Path length)."

$$A \propto C \times l$$

$$A = ECl$$

80

where:

A = Absorbance

C = Concentration in g/l

l = Path length in cm.

E = Absorptivity.



ABSORPTIVITY: It is define as the absorbance of solⁿ having concentration 1gm/l and path length 1cm

It is denoted by "E"

Molar ABSORPTIVITY: It is define as the absorbance of a solⁿ having conc. 1 mole per litre and length is 1 cm.

It is denoted by E_m^6

$$A = E_m^6 \times C_m \times l$$

where • A = Absorbance

• ϵ_m = Molar absorptivity

• C_m = Molar concentration

• l = Path length in cm.

Formulae :

Let I_0 is the intensity of incident radiation and T is the intensity of Transmitted radiation.

Transmittance is the ratio of Intensity of Transmitted light (Radiation) to the Intensity of Incident Radiation.

It is represented by T°

$$\left\{ T = \frac{I}{I_0} \right\}$$

$$\% T = T \times 100$$

$$\therefore T = \frac{\% T}{100}$$

~~30/11/22~~ Relation b/w Absorption And Transmittance:

Absorbance is the logarithm of reciprocal of Transmittance.

$$A = \log \left(\frac{1}{T} \right) \quad \& \quad A = \log \frac{I_0}{I}$$

$$A = \log \left(\frac{100}{\% T} \right)$$

$$\boxed{A = 2 - \log \% T.}$$

Q A solⁿ of tryptophan has an absorbance at 280 nm is 0.54. In a 0.5 cm length cuvette. If absor (A)

bance coefficient of ab Tryptophan $6.4 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$
 Calculate the conc. of solⁿ

$$A = E_m C_m l$$

$$0.54 = 6.4 \times 10^3 C_m \times 0.5$$

$$\frac{0.54}{6.4 \times 10^3 \times 0.5} = C_m$$

$$6400 \quad 1.68 \times 10^{-4} \text{ mol l}^{-1} = C_m$$

Q A solⁿ of thickness 2cm transmit 40% of incident light. Calculate the absorbance of the solⁿ if Molar absorptivity constant is $6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Also calculate the concentration of the solⁿ

$$A = 2 - \log \% \text{ transm.}$$

$$A = 2 - 1.60$$

$$A = 0.4$$

$$E_m = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$A = E_m C_m l$$

$$0.4 = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \times C_m \times 2$$

$$\frac{0.4}{6000 \times 2} = C_m$$

$$C_m = 3.33 \times 10^{-5} \text{ mol dm}^{-3}$$

Q A solⁿ shows a transmittance of 20% when taken in a cell of 2.5 cm length Calculate its conc and absorbtion if molar absorptivity is $12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

A₂₀₀₀

$$A = 2 - \log \% 20$$

$$A = 2 - 1.30$$

$$A = 0.7$$

$$2.33 \times 10^{-5}$$

$$A = E_m C_m l$$

$$C_m = \frac{A}{E_m \times l}$$

$$C_m = \frac{0.7}{12000 \times 2.5}$$

$$C_m = 2.33 \times 10^{-5} \text{ mol dm}^{-3}$$

Calculate the molar absorptivity of a solⁿ having conc. $1 \times 10^{-4} \text{ M}$ which has an absorbance of 0.20 and path length is 2.5 cm.

$$A = E_m C_m l$$

$$0.20 = E_m \times 1 \times 10^{-4} \times 2.5$$

$$\frac{0.20}{1 \times 10^{-4} \times 2.5} = E_m$$

$$\frac{20000}{25} = E_m$$

$$800 \text{ L mol}^{-1} \text{ cm}^{-1} = E_m$$

- (Q) The conc. of yeast transfer RNA (t-RNA) in an aqueous solⁿ is 10m if the absorbance is found to be 0.209 when this solⁿ is placed in 1cm length cuvette & 258 nm radiation are passed through it
- Calculate the Specific absorptivity.
 - What will be the absorbance if the solⁿ conc. 5cm
 - What will be the absorbance if path length increase to 5cm

(i) $\epsilon_m = ?$

$$A = \epsilon_m \times C_m \times l$$

$$0.209 = \epsilon_m \times 10 \times 1 \text{ cm}$$

$$\frac{0.209}{10 \times 1} = \epsilon_m$$

$$0.0209 \text{ L mol}^{-1} \text{ cm}^{-1} = \epsilon_m$$

(ii) $A = ?$

$$A = \epsilon_m \times C_m \times l$$

$$A = 0.0209 \times 5 \times 1$$

$$A = 0.1045$$

(iii) $A = ?$ if $l = 5$

$$A = \epsilon_m \times C_m \times l$$

$$A = 0.0209 \times 10 \times 5$$

$$A = 1.045$$

Q A compound having conc. ~~$\times 10^{-4}$~~ g/L, measured absorbance value is 0.20 at 510 nm. Using 1cm length in cuvette. $\epsilon_m = ?$ calculate it. Absorptivity & molar ϵ_m if the molecular weight of compound is 400 g/mol.

$\epsilon_m = ?$ & $E = ?$

$$A = \epsilon_m \times C_m \times l$$

$$0.20 = \epsilon_m \times 10^{-4} \times 1$$

$$\frac{0.20}{10^{-4} \times 1} = \epsilon_m$$

$$2000 = \epsilon_m$$

$$2000 \text{ L mol}^{-1} \text{ cm}^{-1} = \epsilon_m$$

$$C_M = \frac{C}{M_w} \rightarrow \text{Molecular}$$

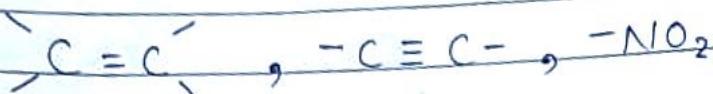
$$\Delta \sigma E = A$$

$$E_m = \frac{\Delta \sigma E \times l}{A \times M_w}$$

$$E_m = \Delta \sigma E \times M_w$$

$$E_m = 2000 \times 400 \\ = 80,000 \text{ L mol}^{-1} \text{ cm}^{-1}$$

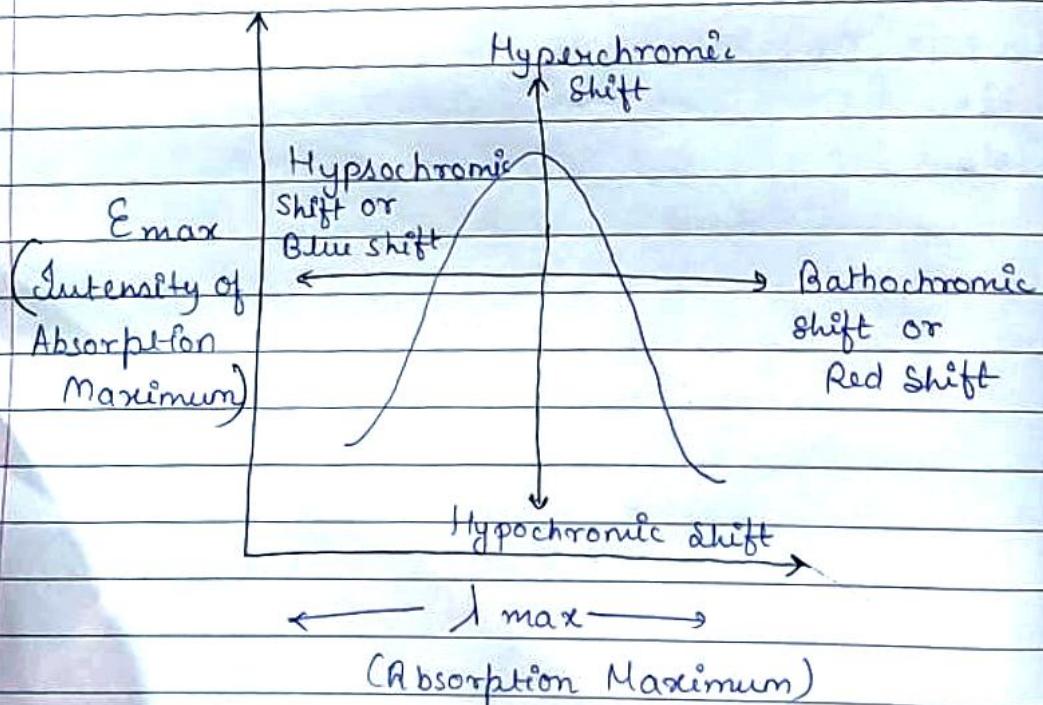
- Chromophores: The atoms or group of atoms or functional groups which are responsible for colour of compounds are called chromophores.



- Auxochromes: Those atoms or group of atoms or functional groups which do not produce colour but their presence increase the intensity of colour are called auxochrome.

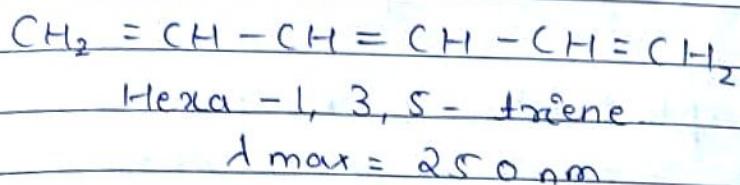
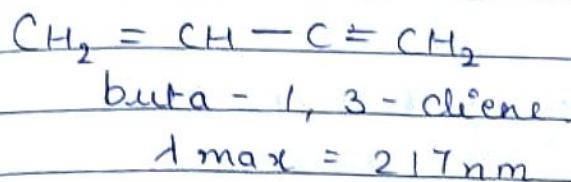


- Intensity & Absorption Shifts:



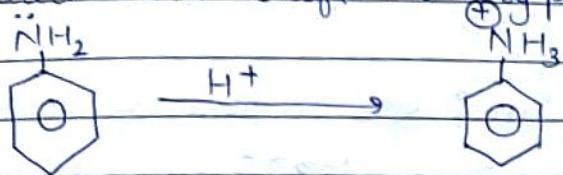
Absorption Shifts:

① Red Shift OR Bathochromic Shift: The shifting of absorption max. (λ_{max}) towards longer wave length is called Red Shift or Bathochromic shift.



{Resonance \uparrow = $\lambda_{\text{max.}} \uparrow$ = Energy ↓. = Stable ↑}

② Blue Shift OR Hypsochromic Shift: The shifting of absorption max. (λ_{max}) towards shorter wave length is called Blue shift or Hypsochromic shift.



aniline

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

anilinium ion

$\lambda_{\text{max.}} = 265 \text{ nm}$

{Resonance \downarrow = $\lambda_{\text{max.}} \downarrow$ = Energy ↑ = less stable ↓?}

Intensity Shifts:

① Hyperchromic Shift: The increase in intensity of absorption maximum ($E_{\text{max.}}$) is called Hyperchromic shift.

② Hypochromic Shift : The decrease in intensity of Absorption Maximum (E_{max}) is called Hypochromic Shift.

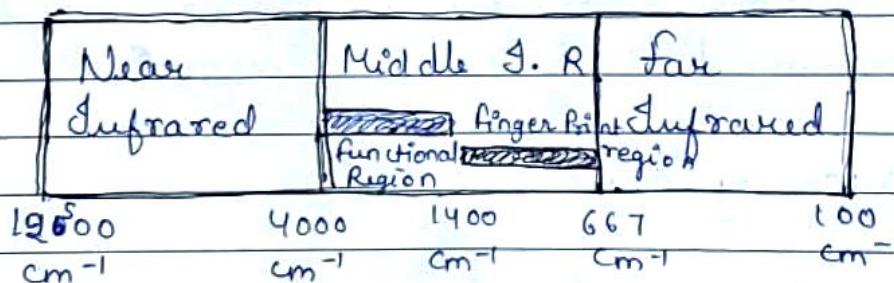
Infra Red SPECTROSCOPY

The branch of spectroscopy which deals with the interaction of I.R. radiation and matter is called Infrared Spectroscopy.

Principle : When a molecule having permanent dipole moment or shows change in dipole moment in any one of vibrational Energy level by the absorption of Infrared Radiation are called I.R. active molecules.

And this branch of spectroscopy is called Vibrational Spectroscopy.

Infrared Region : The region of E.M.R which lies wave no. from 12500 cm^{-1} to 100 cm^{-1} is called Infrared Region.



It is further divided into 3 parts :

- Near I.R. Region : Having $\rightarrow 12500\text{ cm}^{-1}$ to 4000 cm^{-1} .

- Middle I.R. Region : The region of I.R. radiation having $\bar{\nu}$ from 4000 cm^{-1} to 667 cm^{-1} is called Middle I.R. Region.

It is further divided into 2 parts:-

- Functional Group Region : The region of I.R. radiation which have wave no. ($\bar{\nu}$) b/w 4000 cm^{-1} to 1400 cm^{-1} is called Functional Group Region.

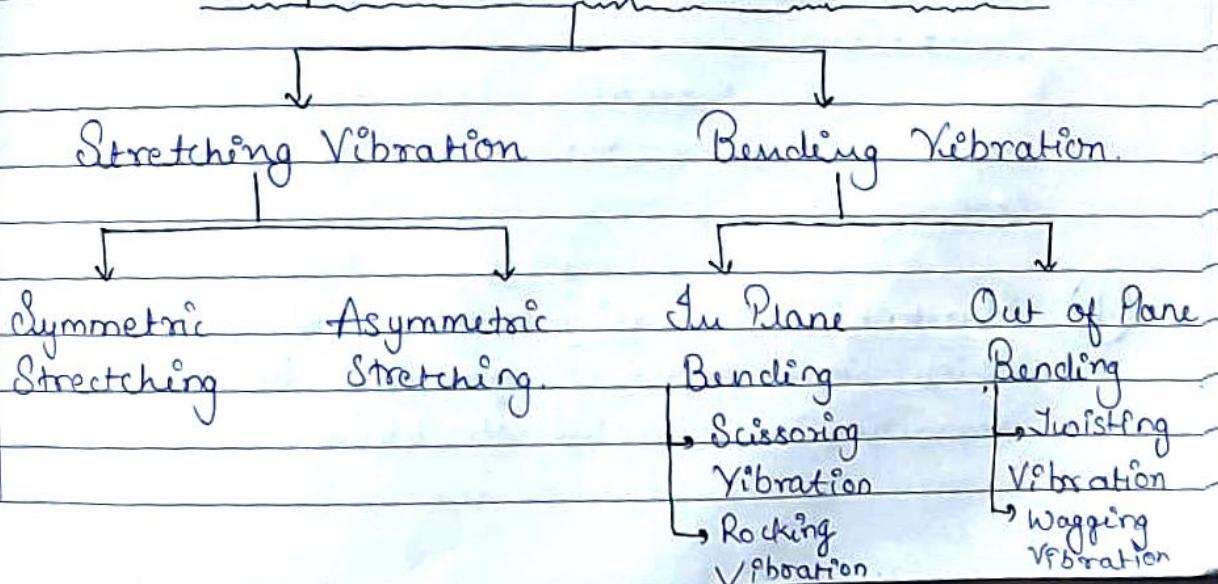
It is used to detect the functional group present in a molecule because different functional groups absorbs different wave numbers ($\bar{\nu}$).

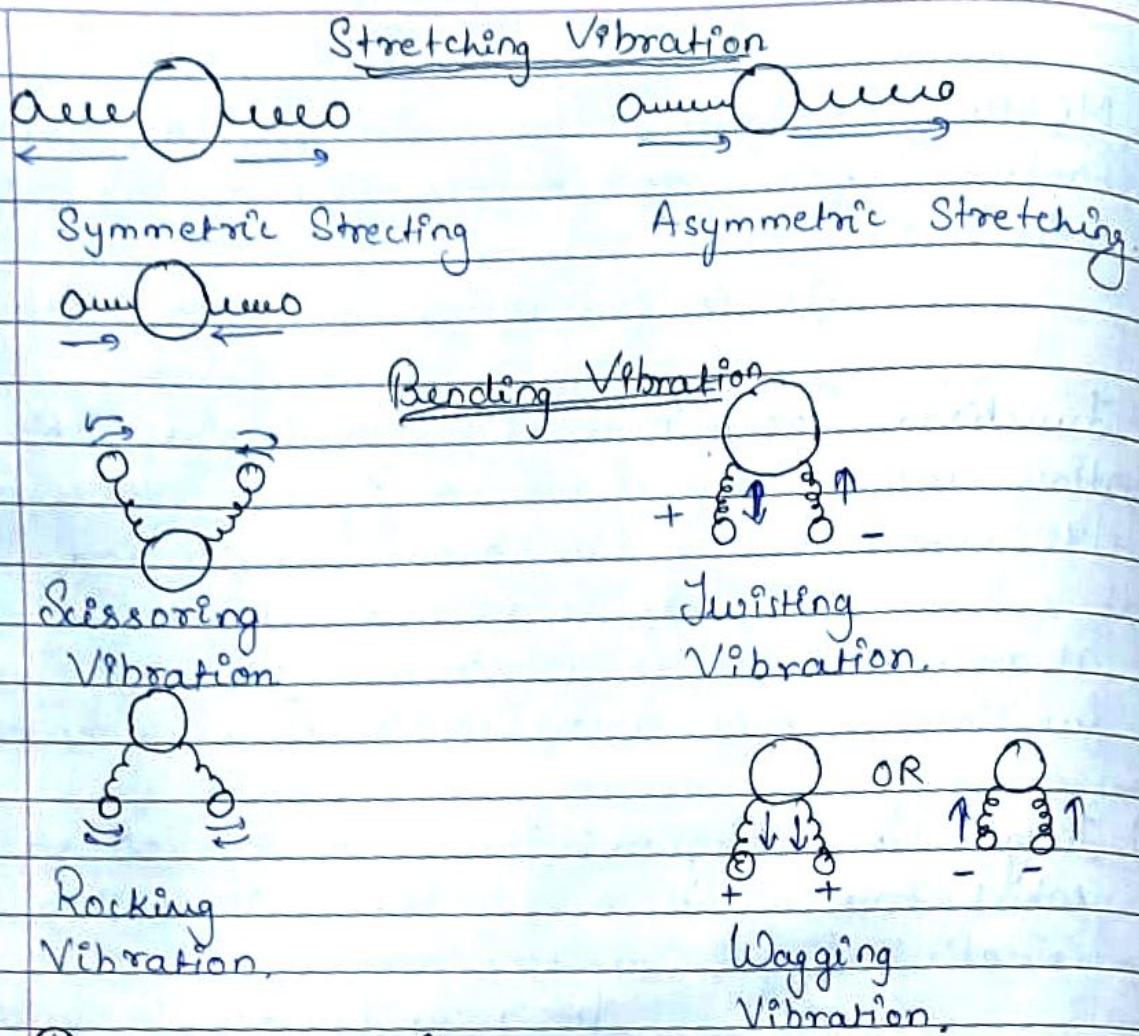
- Finger Print Region : The region of I.R. radiation which have wave no. ($\bar{\nu}$) b/w 1400 cm^{-1} to 667 cm^{-1} is called Finger Print Region.

It is unique for individual compounds. Two compounds never give same peak in finger print region.

- Far I.R. Region : Having $\bar{\nu} 667 \text{ cm}^{-1}$ to 100 cm^{-1} .

MOLECULAR VIBRATIONS





P. Molecular Vibrations:

When a molecule either having permanent dipole moment or shows change in dipole moment in any vibrational Energy level by the absorption of I.R. radiation undergoes vibrational transitions.

Generally there are two types of molecular vibrations takes place in I.R. spectroscopy.

① Stretching Vibration: Those molecular vibration in which bond length changes but bond angle remains unchanged are called stretching vibration.

These are further divided into two parts:

- (A) Symmetric Stretching: Those stretching vibration in which both the bonds either stretched or compressed are called Symmetric Stretching.
- (B) Asymmetric Stretching: Those stretching vibration in which one bond stretched and another bond compressed are called Asymmetric Stretching.
- (2) Bending Vibrations: Those molecular vibrations in which bond angle changes are called bending Vibrations.

These are further divided into two parts:

- ~~02/12/22~~
- (A) In Plane bending: Those bending vibration in which plane does not change are called In Plane bending.
 - (i) Scissoring Vibration: Those bending vibration in which both the bonds either approach each other or apart from each other are called scissoring vibration.
 - (ii) Rocking Vibration: Those bending vibration in which both the bonds either go left side or right side is called Rocking vibration.
 - (B) Out of Plane bending: Those bending vibration which takes place by the change in plane are called Out of Plane bendings.

These are further divided into two parts.

- ① Twisting Vibration :- Those bending vibrations in which one bond moves above the plane and other bonds moves below the plane are called twisting vibration.
- ② Wagging Vibration :- Those bending vibrations in which both the bonds either move above the plane or below the plane are called wagging vibration.

Applications of I.R. Spectroscopy

- Identification of functional group : I.R. Spectroscopy is a powerful analytical tool to identify the functional group present in a molecule. It is because diff. functional group absorbs diff. I.R. radiation & gives different signals in functional group region.
- To detect or Identify of Compound : It is used to identify a compound because different compound absorb different I.R. radiation and gives different signals in fingerprint region.
- Identification of Isotopes : It is used to detect Isotope because different isotopes of same element gives different signals in fingerprint region.
- Detection of Optical Isomers : I.R. Spectroscopy is also used to detect optical Isomers if it is because d and l Isomers gives different signals in

finger print region.

- Identification of Impurity: It is used to detect impurity in compound because impure compound gives different signals than pure compounds in Infrared spectroscopy.

Infrared Active Compounds:

Those molecule which have either permanent dipole moment or show change in dipole moment in any vibrational energy level are called IR active compounds.
for example: NO, HCl, HF.

Exception = $\text{CO}_2 \rightarrow \text{CO}_2$ having zero dipole moment, so it is IR inactive in stretching vibration, but it shows change in dipole moment in bending vibration.
 $\therefore \text{CO}_2$ is IR active in bending vibration.

$\text{H}-\text{C}\equiv\text{C}-\text{H}$ is also exceptional as same as CO_2 .

Infrared Inactive molecules:

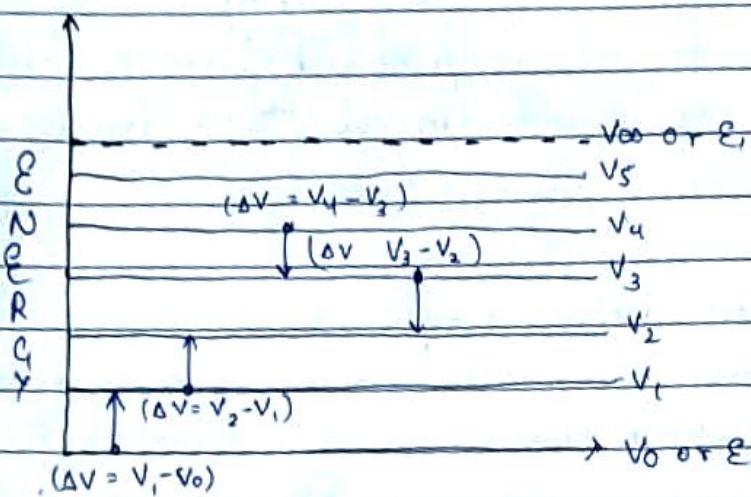
Those molecules which have no permanent dipole moment or does not show change in dipole moment in any vibrational transition are called IR inactive molecules.

for example: H_2 , N_2 , O_2 , Cl_2 .

Selection rule for IR Spectroscopy:

It state that when a molecule either having permanent dipole moment or show change in dipole moment by the absorption of IR radiation undergoes vi-

Irrational transitions, only those vibrational transitions are allowed for which $\Delta v = \pm 1$



6/12/22

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR Spectroscopy)

The branch of Spectroscopy which takes place in radio frequency region of EMR is called nuclear magnetic resonance spectroscopy.

Principle : Nuclear magnetic resonance spectroscopy involves the transition of a nucleus from 1 spin state to another spin state with the absorption of radio frequency radiation by spin active nuclei when they are placed in external magnetic field.

Radio frequency region : The electromagnetic radiation (EMR) which have very long wavelength

$\lambda = 10^7 \text{ nm to } 10^8 \text{ nm}$

$\lambda = 10 \text{ m to } 100 \text{ m}$.

They have extremely low energy.

- Spin Active Nuclei :- Nuclei that exhibit NMR phenomenon due to presence of odd ~~electron~~ protons are known as Spin Active Nucleus.

Only those nuclei will exhibit the NMR for which spin quantum number (I) is greater than zero.

For example : H^1 , C^{13} , F^{19} etc.

- Spin Inactive Nuclei :- These Nuclei for which Spin Quantum number (I) is zero due to presence of even no. number of protons are called Spin Inactive Nucleus.

They does not show NMR

Spectra.

For example : O^{16} , S^{32} , C^{12} etc.

P

Types of NMR Spectroscopy

Generally there are two types of NMR spectroscopy.

nuclear

- PNMR : (H-NMR) : It stands for proton magnetic resonance.

- C^{13} NMR : C^{13} NMR is called Carbon 13 Nuclear magnetic resonance.

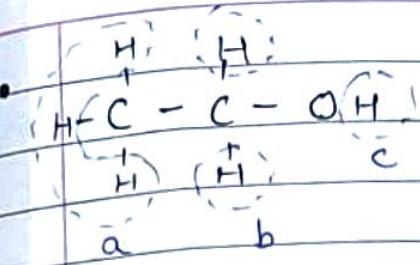
• Proton Signals : When a molecule is placed in the influence of external magnetic field in radio frequency region then it gives proton signals.

Generally there are two types of protons in NMR Spectroscopy.

① Equivalent Protons : The protons with same environment gives one signal that is they absorb same applied field strength are called Magnetically Equivalent Protons.

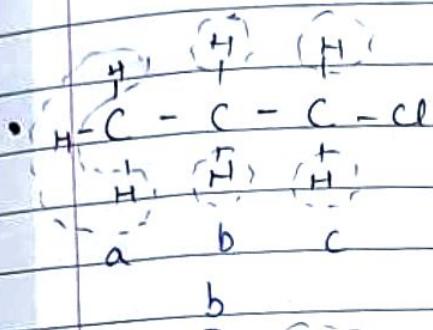
② Non-Equivalent Protons : The protons with different environment gives different signal that is they absorb different applied field strength are called Magnetically Non-Equivalent Protons.

Compounds	Types of protons	No. of signal
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \\ \text{a} \end{array}$	4 protons of same environment type a	1
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \\ \text{a} \quad \text{a} \end{array}$	6 protons of same environment type a	1
$\begin{array}{c} \text{H} \quad \text{H}^b \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H}^b \quad \text{H} \\ \text{a} \quad \text{a} \quad \text{a} \end{array}$	6 protons of same environment type a 2 protons of same environment type b	2.



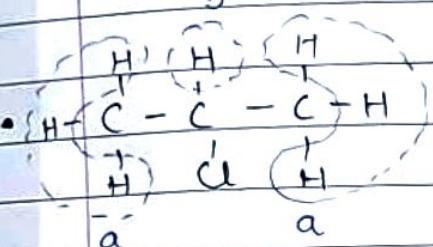
3 equivalent proton
 of type a
 2 equivalent proton
 of type b
 1 equivalent proton
 of type c

3.



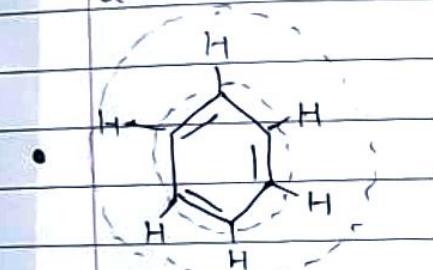
3 equivalent protons of type a
 2 equivalent protons of type b
 2 equivalent protons of type c

3



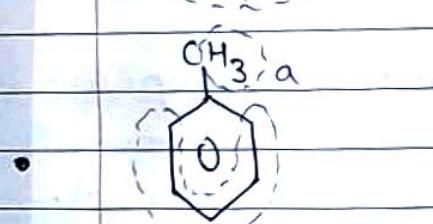
6 equivalent protons of type a
 1 equivalent protons of type b

2



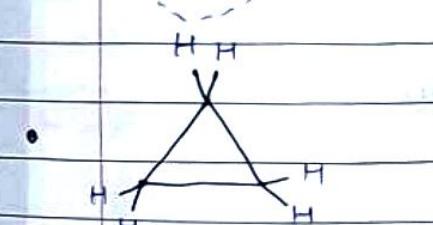
6 equivalent protons
 of type a

1.



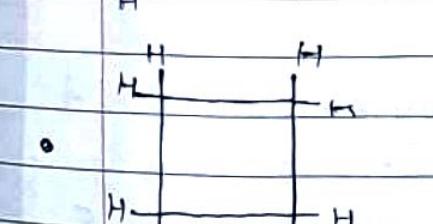
3 equivalent protons of type a
 5 equivalent protons of type b

2.



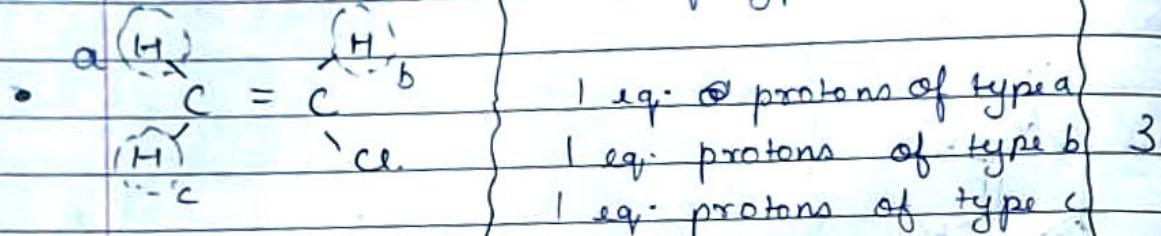
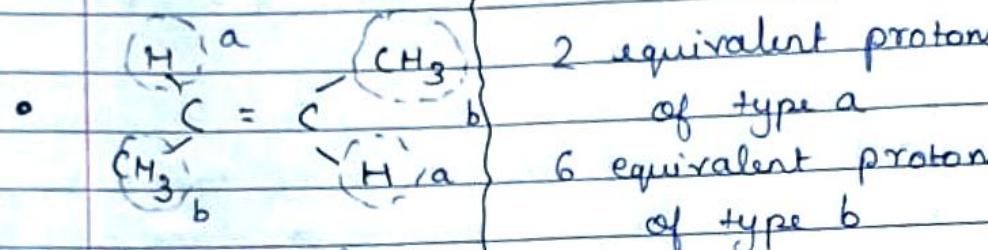
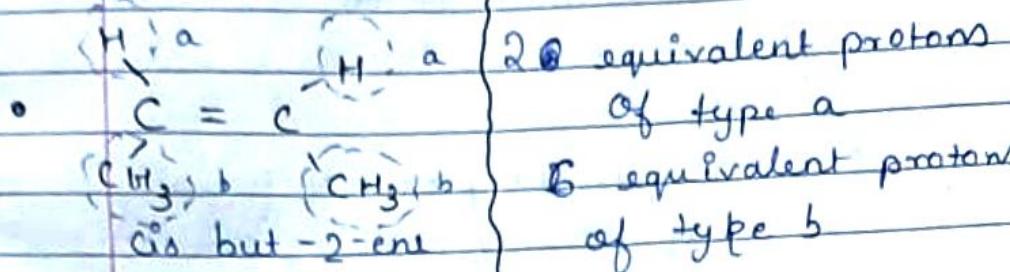
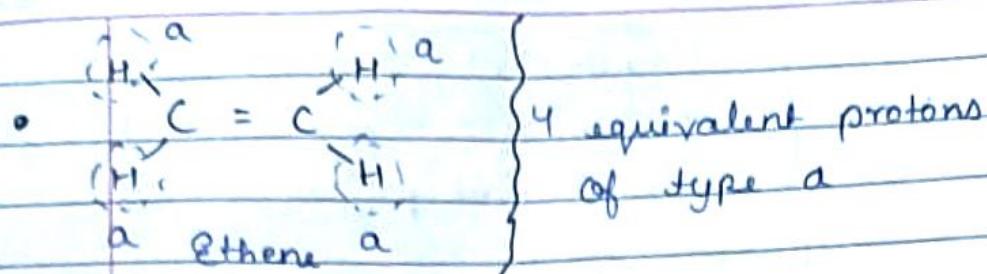
6 equivalent protons of type
 a

1.



8 equivalent protons of
 type a

1



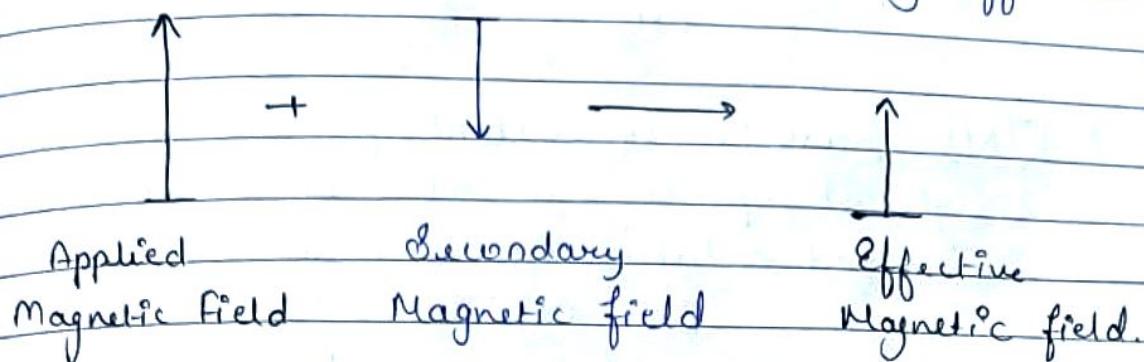
~~01/12/22~~ Chemical Shifts: When a molecule (spin-active nuclei) is placed in an external magnetic field its electrons are circulate in a manner producing secondary magnetic field.

This is also called Induced magnetic field.

It may causes following situations:

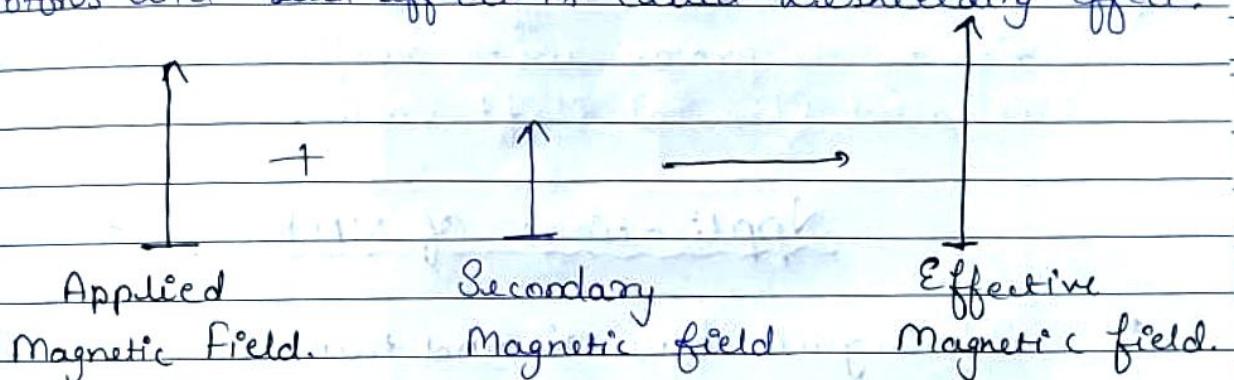
(i) Shielding Effect: If the secondary magnetic field / Shielding of Proton: produced by the circulation of electrons opposes the applied magnetic field at a proton the effective field experienced by the

proton is decrease. Such protons are called shielding protons and this effect is called shielding effect.



(ii) Deshielding Effect / Deshielding of Proton : If the secondary magnetic field produced by the circulation of electrons is reinforced by the applied magnetic field the effective magnetic field experienced by the proton is more than the applied field.

Such protons are said to be deshielding protons and such effect is called deshielding effect.



Measurements of Chemical Shift

The measurement of frequency of a group of nuclei in absolute frequency unit is extremely difficult and it is not required also.

The chemical shift value of the protons in a particular compound can determine with respect to universally accepted standard TMS (tetra methyl silane).



(12 equivalent protons)

TMS have 12 equivalent protons and give a single sharp signal also it is chemically inert and soluble in organic solvents.
It can be added to the sample solution as an internal standard.

The NMR signal value for a particular proton in a molecule will appear at different field strengths compared with a signal of TMS.

~~18 | 12 | 20~~
This difference in absorption position of the proton with respect to TMS signal is called Chemical shift value.

Applications of NMR Spectroscopy

- Distinguish b/w cis and trans isomers:

NMR spectroscopy is used to differentiate b/w cis & trans isomers. It is because it gives different signals or peaks for cis & trans isomers.

- Differentiate b/w inter-molecular and intra-molecular hydrogen bonding.

It is very useful to differentiate b/w inter-

molecular and intermolecular Hydrogen Bonding. It is because in NMR spectroscopy stronger peak is obtain for intermolecular hydrogen Bonding than intera molecular Hydrogen Bonding.

- Identification of Structural Isomers

It is used to identify the different structural isomers because it gives different peaks or signals for different isomers.

- Detection of Aromaticity

NMR Spectroscopy is also used to identify the aromatic nature of compounds. It is because the protons attached to the aromatic rings are highly deshielded. as a result signals for aromatic protons appears at a very low field.

SPLITTING Of SIGNALS

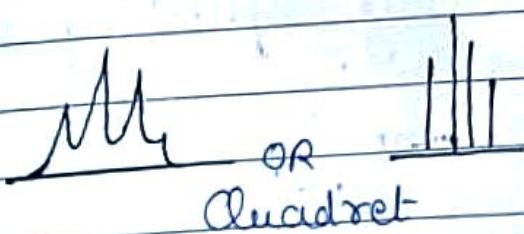
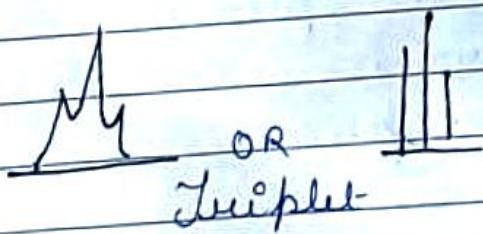
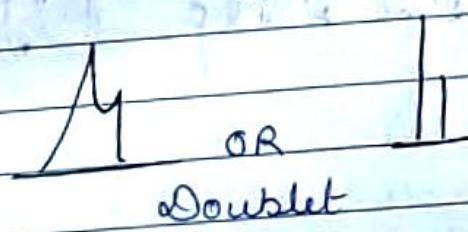
The interaction b/w spins of two or more neighbouring protons most often through the bond resulting in the splitting of signals or spectral lines. This process is called splitting of signals or Spin-Spin coupling.

Rules for Covering splitting of signals :-

- Splitting of a proton signals is caused only by the neibouring proton and if Protons are non-

equivalent.

- Splitting of one proton by another proton present on same carbon atom is very rare because such protons are equivalent.
- The mutual splitting of protons separated by more than two carbon atoms is very uncommon.
- The number of peaks (N) is equal to the $(n+1)$ where $n = \text{no. of neighbouring protons (non-equivalent)}$.
- All the peaks of a multiplet are non-symmetrical



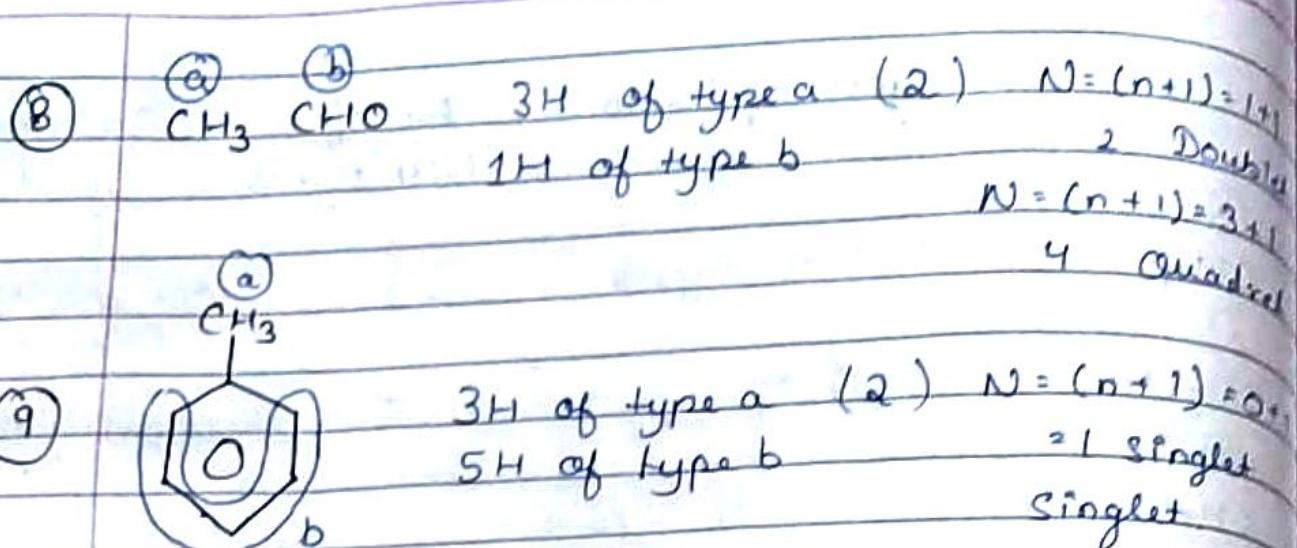
Types of Protons No. of Splitting of
NMR signals Signals.

(1) CH_4	$4(\text{H})$ of type a	1	No splitting (singlet)
(2) $(\text{CH}_3)_2$	$6(\text{H})$ of type a	1	No splitting (singlet)
(3) $\text{CH}_3\text{CH}_2\text{OH}$	3H of type a 2H of type b 1H of type c	3	$N = (n+1) = 2+1 = 3$ Triplet $N = (n+1) = 3+1 = 4$ Quadruplet $N = (n+1) = 1$ singlet

(4) $\text{CH}_3 - \overset{\textcircled{a}}{\underset{\textcircled{b}}{\text{C}}} - \text{CH}_3$	6H of type a	1	$N = (n+1) = (0+1) = 1$ singlet
---------------------------------------------------------------------------------------------------	--------------	---	------------------------------------

(5) $\text{CH}_3 - \overset{\textcircled{a}}{\underset{\textcircled{b}}{\text{O}}} - \overset{\textcircled{c}}{\text{CH}_3}$	3H of type a 2H of type b 3H of type c	3	$N = (n+1) = 0+1 = 1$ singlet $N = (n+1) = 3+1 = 4$ Quadruplet $N = (n+1) = 2+1 = 3$ Triplet.
------------------------------------------------------------------------------------------------------------------------------	----------------------------------------------	---	--------------------------------------------------------------------------------------------------------------

(6) O	6H of type a	1	Singlet
(7) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	3H of type a 2H of type b 2H of type c 1H of type d	4	$N = (n+1) = 2+1 = 3$ Triplet $N = (n+1) = 5+1 = 6$ Septuplet $N = (n+1) = 2+1 = 3$ Triplet $N = (n+1) = 0+1 = 1$ Singlet



~~10 | 12 | 22~~

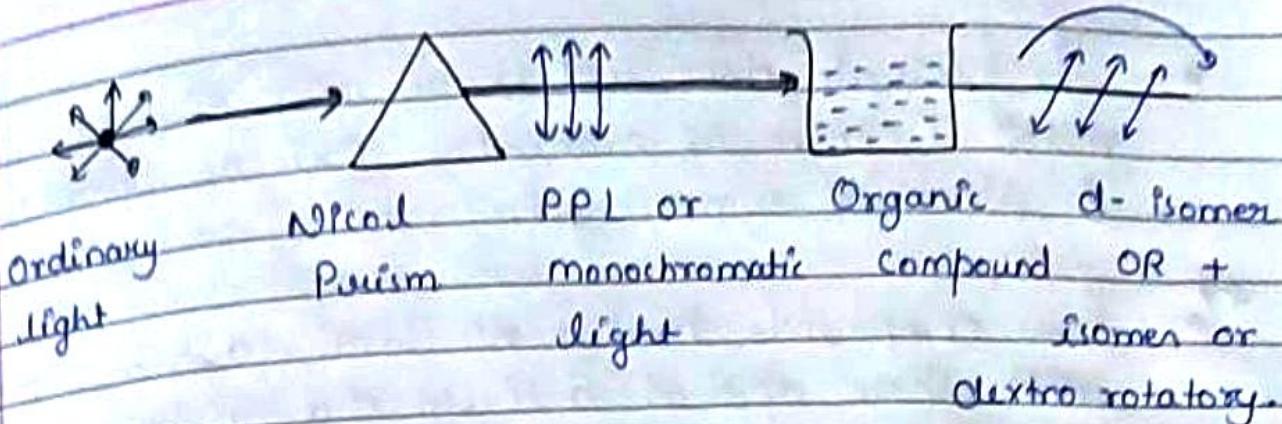
OPTICAL ISOMERISM:

When two or more compounds having same molecular formula, same structural formula, same physical and chemical properties except their behaviour towards plane polarised light (PPL) are called Optical Isomers and this phenomenon is called Optical Isomerism.

Generally there are two types of optical isomers :

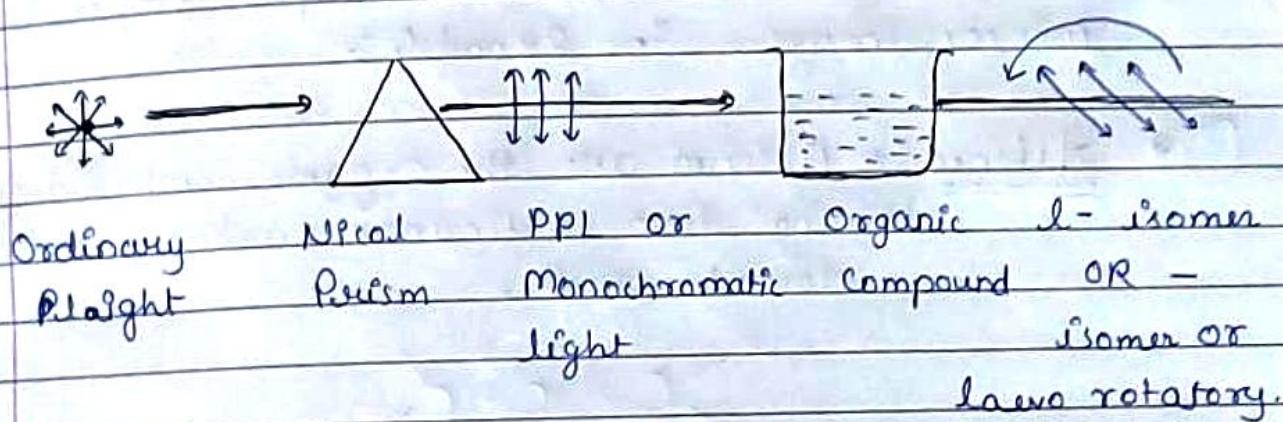
① d-Isomers : The optical isomers which rotate plane polarised light (PPL) into clockwise direction (+) are called d-isomers or + isomers.
 These are also called ~~dextro~~ dextrorotatory compounds.

For these compounds the optical rotation value is always positive.



② L -Isomers: The optical isomers which rotate plane polarised light (PPL) into anticlockwise or counter clockwise (\leftarrow) are called L -isomers or $-$ -isomers. These are also called laevorotatory compounds.

For these compounds the optical rotation value is always negative.



Conditions for a molecule to be Optical active

The molecule contains atleast one chiral (asymmetric) carbon atom.

The compounds must have non-superimposable mirror image.

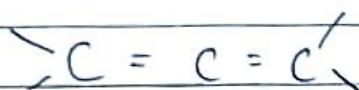
- The molecule does not have any kind of symmetry (centre of symmetry, Axis of symmetry & plane of symmetry).

Some compounds having no chiral carbon atom ~~will~~ show optical activity due to their overall asymmetric structure and non-superimposable mirror image.

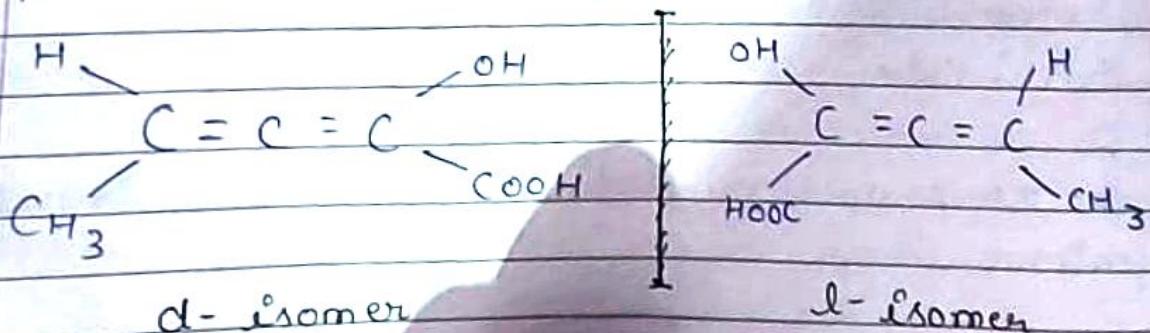
Examples of optical active compounds having no chiral carbon atom...

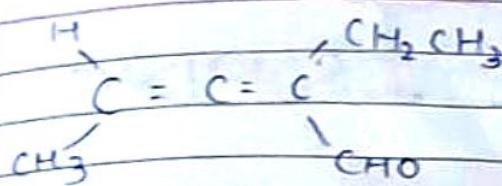
Some compounds having no chiral carbon atom show optical activity due to their overall asymmetric structure and non-superimposable mirror image. For Example :-

- ① Allenes :- Allenes are the organic compound containing two continuous carbon-carbon double bonds.

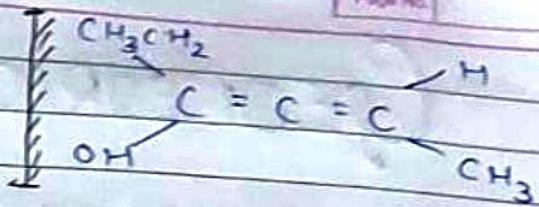


The allenes with different groups at terminal positions will show optical activity



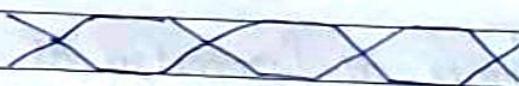


d-isomer

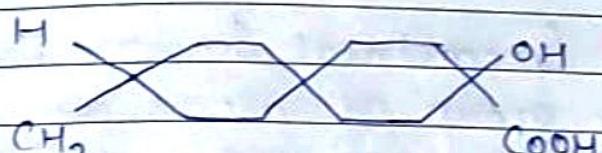


l-isomer

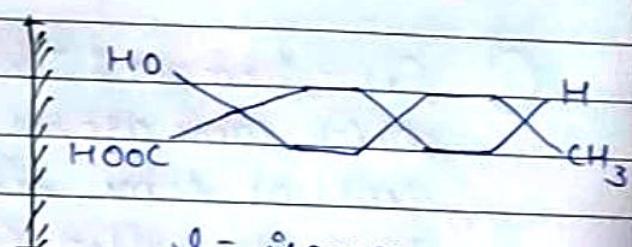
- ② Spiro Compounds or Spiran: Those compounds in which two rings are fused with single carbon atom are called Spiro compound or spiro.



If Spiroane contains different atoms or group of atoms at terminal position it will show optical isomerism



d-isomer

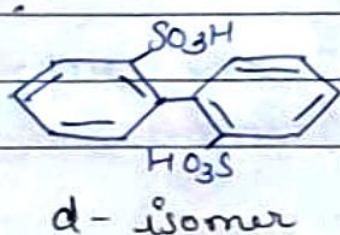


l-isomer

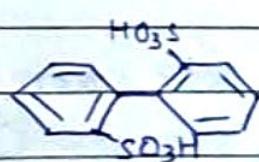
- ③ Biphenyl Derivatives: Those compound in which two benzene rings are fused with a single covalent bond are called Biphenyl derivatives.



Some of the Biphenyl derivatives represent non superimposable mirror image due to their overall asymmetric structure will show optical activity.



d-isomer



l-isomer

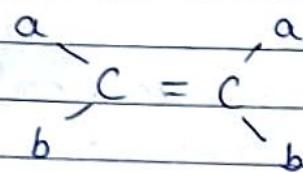
GEOMETRICAL ISOMERISM

When two or more compounds having same molecular formula, same structural formula but different arrangement of atoms or group of atoms along carbon-carbon double bond are called Geometrical Isomers and this phenomenon is called Geometrical Isomerism.

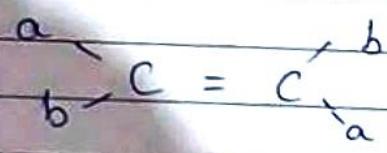
Types of Geometrical Isomers:

Generally there are two types of Geometrical Isomers:

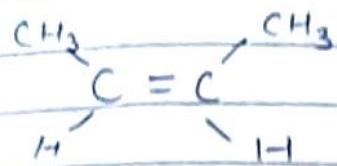
- ① Cis - Isomers : Those Geometrical Isomers in which same atoms or group of atoms are present at same site of carbon-carbon double bond are called Cis Isomers.



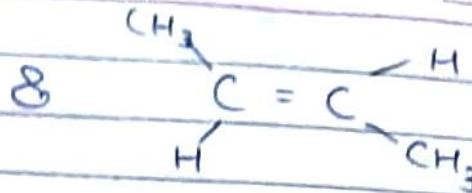
- ② Trans - Isomers : Those Geometrical Isomers in which same atoms or group of atoms are present at different site of carbon-carbon double bond are called Trans - Isomers.



For example : But - 2ene represent 2 Geometrical Isomers



cis-but-2-ene

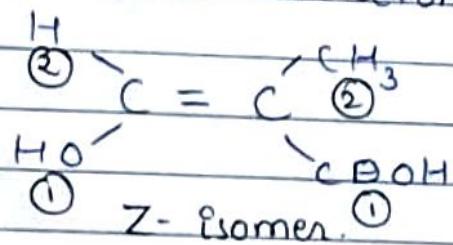


trans-but-2-ene

E-Z nomenclature of Geometrical Isomers: When Geometrical Isomers contains 4 different atoms or group of atoms they are assigned as E isomers and Z isomers.

According to CIP rule (Cahn, Ingold & Prelog) there are two types of Geometrical Isomers:

- Z-Isomers: The word Z is taken from the Greek word Zusammen which means all together. If the same priority groups are present at same side of carbon-carbon double bond the isomer is called Z isomer.



- E-Isomers: The word E is taken from the Greek word Entgegen which means opposite. If the same priority groups are present at the different side of carbon-carbon double bond such isomer is called E isomers.

