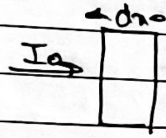
law? Derive its expression.

Unit-2
Spectroscopy

* Lambard's Bear law -
There are three absorption laws -
(i) lambard's Law
(ii) Lambard's Beard Law
(iii) Beard Law.

* Lambard's Law - " When monochromatic radiation is passed through a solution, the decrease in intensity of radiation with the thickness of Solution is directly proportional to the intensity of ~~monochromatic~~ incident radiation."



$$\boxed{-\frac{dI}{dx} \propto I}$$

$$\Rightarrow \quad -\frac{dI}{dx} = kI$$

$$\Rightarrow \quad -\frac{dI}{I} = k\,dx, \text{ now } [I_0 - I] \quad [x = 0 \text{ to } l]$$

$$\int_{I_0}^{I} +\frac{dI}{I} = -k\int_0^l dx$$

$$\Rightarrow \quad \ln\frac{I}{I_0} = -kl$$

$$2.303 \log_{10}\left(\frac{I}{I_0}\right) = -kl$$

$$\log_{10}\left(\frac{I_0}{I}\right) = \frac{+k}{2.303}\, l$$

$$\log_{10}\frac{I_0}{I} = \varepsilon l$$

$$\boxed{A = \varepsilon l}$$

Absorbence

Extinction Coefficient
Absorption coeffient
where $\varepsilon = \frac{k}{2.303}$

[l=cm]

* Transmittance, $T = \frac{I}{I_0}$ [unitless]

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

[T → always %].

* Transmittance is the ratio of intensity of transmitted beam to the intensity of incident beam.
It is always expressed in %.

* Lambard bear's law - " When monochromatic radiation is passed through a soln, the decrease in intensity of radiation with the thickness of solution is directly proportional to the intensity of incident radiation as well as to the concentration of solution."

$$-\frac{dI}{I} = kcI$$

$$\int_{I_0}^{I} \frac{dI}{I} = -kc\int_0^l dx$$

$$\Rightarrow \quad \ln\left[\frac{I}{I_0}\right] = -kcl$$

$$2.303 \log_{10}\left(\frac{I}{I_0}\right) = -kcl$$

$$\log_{10}\left(\frac{I_0}{I}\right) = \frac{k}{2.303}\, cl$$

$$A = \varepsilon \times c \times l$$

$$A = \varepsilon \times c \times l$$

Absorbence

Molar extinction coefficient.

Concentration → (g/dm³, mol/dm³)

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$\varepsilon = mol^{-1}\, dm^{3} \times cm^{-1}$

→ If concentration is in (mol/dm³), then ε is called molar extinction coefficient.

→ If conc – (g/dm³) → e. coefficient, absorbity, absorption coefficient).

Q. Calculate absorbance if %T = 80 %, <u>0.8</u> = T

Ans: $A = -\log(80)$

~~$A = -\log(8\times10)$~~

~~$A = -\log 8 - \log 10$~~

~~$A = -3\log 2 - 1$~~

~~$A = -3\times0.3 - 1$~~

~~$A = -0.9 - 1 = -1.9$~~

$A = -\log(0.8)$

$A = -\log(8\times10^{-1})$

$A = -\log 8 + \log 10$

$A = -3\log 2 + 1$

$A = -3\times0.3 + 1$

$A = 1 - 0.9$

$= +0.096$

Q. A solⁿ of thickness is 3cm transmits 30% incident light. Calculate conc. of solⁿ. If $\varepsilon = 4000\ dm^{3}\, mol^{-1}\, cm^{-1}$.

$l = 3cm$,

$\%T = 30\ \%$, $\varepsilon = 4000$

$T = 0.3$

$A = \varepsilon \times C \times l$

$A = -\log T$

$(0.3) = 0.522$

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$C = \frac{0.522}{4000\times3} = \frac{0.522}{12000}$

$C = 4.35\times10^{-5}$

Q. 10^{-4} M solⁿ, gives 63% T in 25 nm long tube. Calculate molar absorbity of solⁿ.

Ans: $L = 25\times10^{-9}m$, $T = 0.63$, $C = 10^{-4}$

$= 25\times10^{-6}m$

Q. Calculate value for ε_{max} for a given compound whose conc = 2×10^{-6} M, placed in a 1cm tube. has an absorbance of 0.63 at λ_{max} = 287 nm.

Q. The molar absorbity of a substance is 2×10^{4} $cm^{-1}\, mol^{-1}\, dm^{3}$. ($\varepsilon = 2\times10^{4}$). Calculate Transmit by using a cuvette of path length (5cm) containing 2×10^{-6} mol/dm³.

$A = \varepsilon \times C \times l$ $\quad C = 2\times10^{-6}$

$A = 2\times10^{4}\times2\times10^{-6}\times5$

~~$A = 10\times10^{-2} = 2\times10^{-6}$~~

~~$A = -\log(T)$~~

~~$2\times10^{-6} = -\log(T)$~~

~~$-2\times10^{-6} = \log(T)$~~

~~$e^{(-2\times10^{-6})} = T$~~

~~$e^{(-2\times10^{-6})} = T$~~

$\boxed{T = 0.65}$

$T =$ $T = 0.63\%$

$A = 10\times10^{4}\times2\times10^{-6} = 0.2$

$T = e^{-A}$

$T = e^{-0.2} = 0.81$

... is the basic principle of U.V visible spectroscopy? Explain all the type of electronic transition possible in acetone ($CH_3-\overset{O}{\overset{\|}{C}}-CH_3$).

$A = 0.63$

Ans = $C = \underline{2\times10^{-5}}$ M, $L = 1$ cm, $A = 0.63$

$$A = \varepsilon c l$$

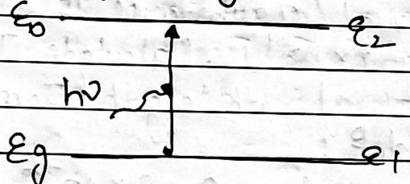
$$\varepsilon = \frac{A}{cl} = \frac{0.63}{2\times10^{-5}}$$

$$\varepsilon = \frac{0.63}{0.00002} = \underline{31500}$$

Imp

// * **UV visible Spectroscopy** –

When a molecule absorb U.V or visible light, its electrons get promoted from ground state to the higher energy state and the energy difference given by



$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$(E_2 - E_1) = \frac{hc}{\lambda\,(nm)}$$

* UV visible region ranges from 15–800nm.

Far U.V Region — Near UV Region — Visible region

15nm — 200 — 400 — 800

Main U.V

V ⟶ R

→ There are three types of electrons which are present in compounds –

(i) σ electron

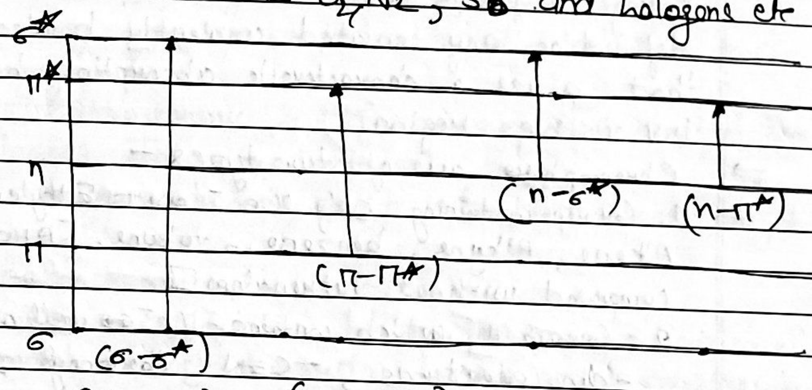
(ii) π electron

(iii) n electron

(i) σ electron – is the type of electron associated with formation of σ bond

with formation of π bond

→ n electron – The pair of e^- associated with hetero atom like O_2, N_2, S and halogens etc



(CH_3-CH_3) ($CH_2=CH_2$) CH_3OH CH_3CHO

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

* **σ-σ* transition** – electrons are involved in the formation of σ bond are present in all existi... compounds. And this type of transition shown by all saturated compounds without heteroatom.

* **π-π* transition** – This type of transition is shown by unsaturated compounds.

* **n-σ* transition** – If a saturated compound contain any hetero atom then this type of transition is posible – CH_3OH, CH_3Cl.

* **n-π* transition** – The compound having multiple bond with heteroatom like O, S, N, halo-ens. can give this type of transition.

Ex – acetyl halide, acetone.

* **Auxochrome & Chromophore** –

Q. Define Auxochrome & Chromophore. Using suitable example.
Q. Differentiate between Auxochrome & Chromophore.
Imp Q. Explain various absorption & Intensity shift using suitable example.

A. * Chromophore – The coloured substances ~~do~~ give their colour due to presence of one or more unsaturated linkage or groups are called chromophore. It is defined as any isolated covalently bonded group that gives a characteristic absorption band in U.V visible region.

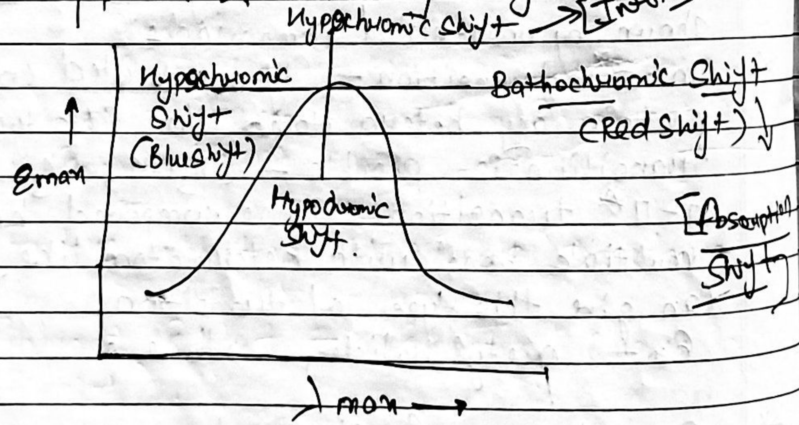
→ Chromophore are of two types –

1. Group containing only π e⁻ ex – Ethylene, Alkene, Alkyne, benzene, toluene. [Aromatic compound without heteroatom].
2. Group II which contains π e⁻ as well as non-bonding electrons, –C≡N, Carbonyl, Carbonyl

→ Auxochrome – These are not colour bearing groups but presence of these groups enhance the intensity of colour bearing group, or shift the absorption bands towards a longer wavelength. Examples – All functional group having lone pair – $-\ddot{O}H$, $-\ddot{O}R$, $-\dot{N}H_2$, $-\overset{O}{\overset{\|}{C}}-NH_2$, –C≡N, $-\ddot{X}:$

Imp

* Absorption & Intensity Shift –



Imp Q. Write the difference between ~~batho~~ bathochromic and hypsochromic shift.

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There are two type of shift in U.V visible region:–

1. Absorption Shift.
2. Intensity Shift.

Both of type of shifts are subdivided into two categories –

(i) Bathochromic & Hypsochromic [Absorption Shift]

Whereas Intensity Shift are –

(i) Hyperchromic shift (ii) Hypochromic shift.

* Bathochromic Shift –

It is an effect in which the absorption maximum shifted towards longer wavelength due to presence of an auxochrome OR by the change in the polarity of Solvent.

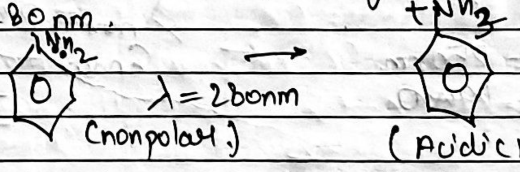
Example – benzene –  – λmax (255nm)

$\xrightarrow{NH_2}$  λmax (280nm) (non-polar solvent)

* Hypsochromic Shift –

It is an effect in which the absorption maximum shifted towards shorter wavelength may be due to removal of conjugation or the change in polarity of solvent. Example –

Aniline in non-polar gives its absorption at 280nm.



In acidic medium, anilinium ion ~~is~~ which has λ = 203nm. The shift is ~~hypso~~ hypsochromic shift.

In anilinium ion, the lone pair of e⁻ are not available, hence leads to less stability (increases destability.)

Q. Write a short note on Factors Affecting U.V. Visible Spectrum.

Imp Q. Write a short note on solvent effect.

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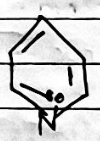
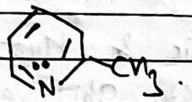
* **Hyperchromic effect** – It is an effect due to which the intensity of absorption maximum increases, usually due to introduction of an auxochrome.



Pyridine



2 methyl pyridine.

λ_{max} – 257 nm.

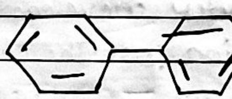
ε_{max} – 2750 $mol^{-1} cm^{-1} dm^3$.

λ_{max} – 262 nm.

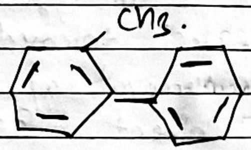
ε_{max} – 3560 $mol^{-1} dm^3 cm^{-1}$

(stability ↑, energy ↓, λ_{max} ↑)

* **Hypochromic effect** – It is an effect due to which the intensity of absorption maximum decrease usually due to removal of auxochrome or change in polarity of solvent or removal of conjugation as ring becomes unstable.



Biphenyl



λ_{max} = 250 nm.

ε_{max} = 19000

λ_{max} = 237 nm.

ε_{max} = 10,250

Imp

* **Factors affecting U.V visible spectrum** –

1. Solvent Effect – (Effect of change in polarity of solvent).

Q. Show that change in polarity of solvent affect U.V. Visible spectrum.

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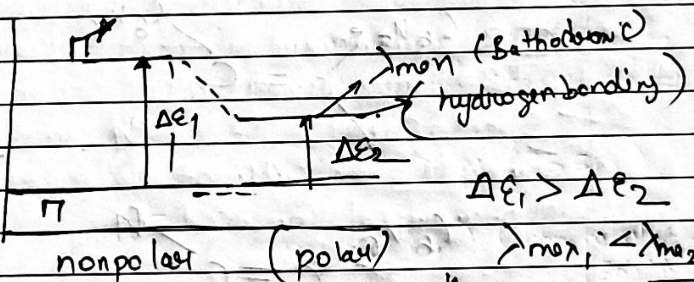
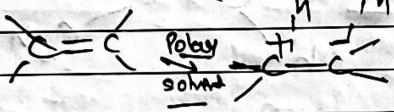
In general, 95% ethanol cyclohexane, n hexane and diethyl ether are common solvents used in U.V visible spectroscopy. There is no change with $\sigma - \sigma^*$ transition whereas remaining three transitions – $\pi - \pi^*$, $n - \pi^*$ & $n - \sigma^*$ show solvent effect.

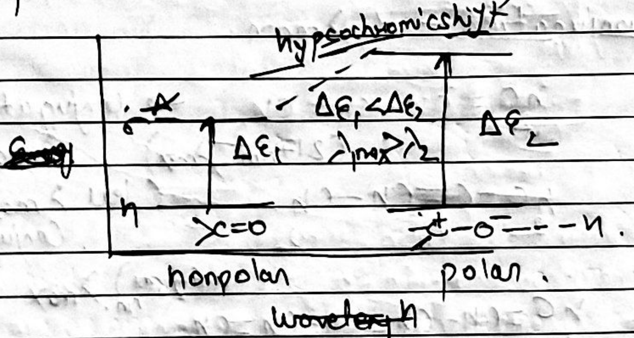
→ Group 1 ($\pi - \pi^*$) :- If group is more polar in excited state, then absorption band shifted towards longer wavelength with increase in polarity of solvent. (Bathochromic Shift).



Example –



* Group 2 – ($n - \sigma^*$ or $n - \pi^*$)



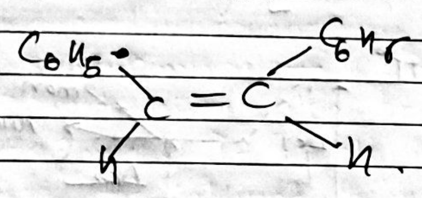
→ If group is more polar in ground state, then Stability increase in polarity of solvent stabilize molecule in ground state due to H bonding

Hence, absorption band shifted towards shorter wavelength.

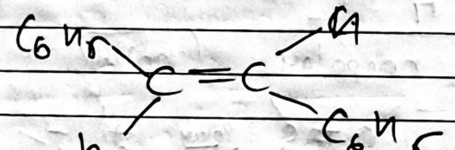
* Greater the hydrogen bonding lesser will be the λmax or it will show hypsochromic shift.

Imp. * Planarity of the molecule —

Cis-trans : Stillbene.



(less stable due to bulky groups will be more separate → more E, λ ↓ λmax = 283 nm.



(more stable as bulky are in trans) → less E, λ ↑ λmax = 295 nm

* Conjugation — ∝ λmax.

$H_2C=CH-CH=CH_2$ → conjugation, thus λmax more (217 nm, λmax)

$H_2C=C=CH-CH_2$ (less λmax, no conjugation).

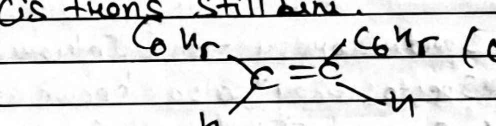
$H_2C=CH-CH=CH-CH=CH_2$ (264 nm) λmax (most λmax due to conjugation)
1,3,5 hexatriene

$H_2C=CH_2$ (λ_{max} = 170 nm).

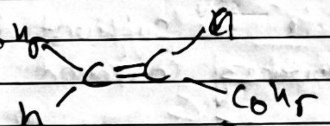
Q. Explain why acetone gives its absorption in hexane at 279 nm? while in water at 264 nm?

* Applications of U.V. Spectroscopy —

1. It is used for identification of unknown compound.
2. It is used for detect the impurity in the given compound.
3. It is used to distinguish conjugated and non-conjugated compounds.
4. Extent of conjugation — Higher the conjugation, greater will be the λmax, so we can determine the extent of conjugation by using it.
5. It is used to distinguish geometrical isomers. Ex — cis trans Stillbene.

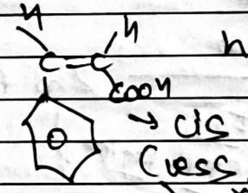


C_6H_5 (cis) (less λmax)

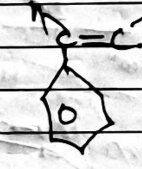


(Trans) ~~less~~ more λmax

And,

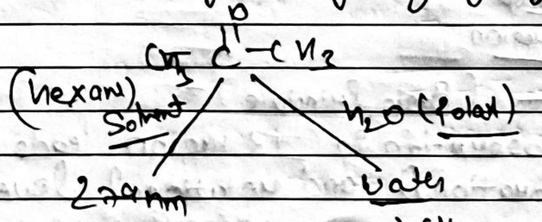


→ cis (less λmax) and



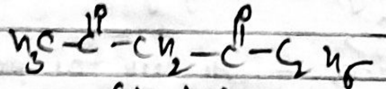
Trans (more λmax)

6. Detection of Absence or presence of chromophore it is very useful.
7. Determination of strength of hydrogen bonding.



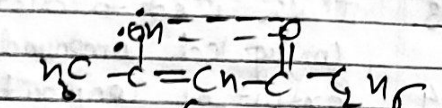
By measuring the va[illegible] of λmax for a compound in polar and non-p[illegible] solvent, the presence of hydrogen bonding and its extent is determined,

8. Study of keto-enol tautomerism –
keto form always gives its absorption at higher wavelength.



$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C_2H_5$

(keto)
($\lambda_{max} = 275\,nm$)

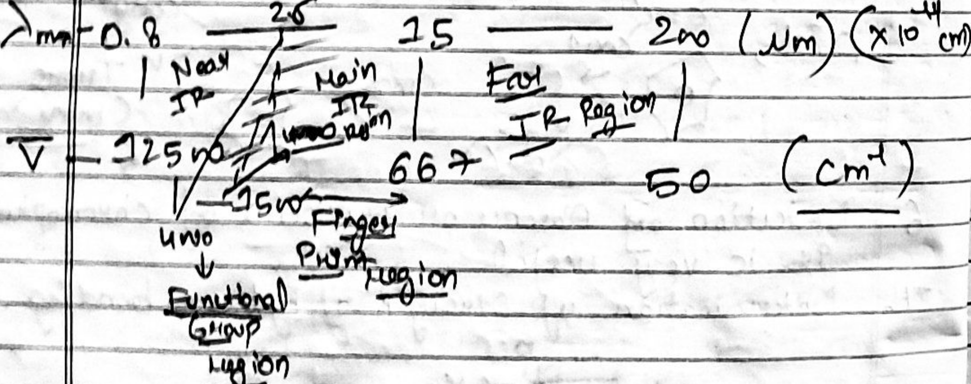


$H_3C-\overset{:\ddot{O}H}{C}=CH-\overset{O}{\overset{\|}{C}}-C_2H_5$

(enol)
(245 nm)

[due to hydrogen bonding.]

* IR spectroscopy — (Infrared)
IR spectroscopy also known as Infrared spectroscopy. It is an important tool to provide the sufficient information about the structure of compound.



* Theory – (Basic Principle) –
The absorption in IR region leads to changes in vibrational and rotational levels. And the changes depends upon following factors –

1. Masses of the atoms present in a molecule.
2. Strength of bond

Q. What is the basic principle of IR spectroscopy & Discuss various kinds of vibrations possible in a molecule like AB_2.

3. Arrangement of atoms within the molecule.
It has been found that no two compounds hav similar IR spectra except enantiomers.

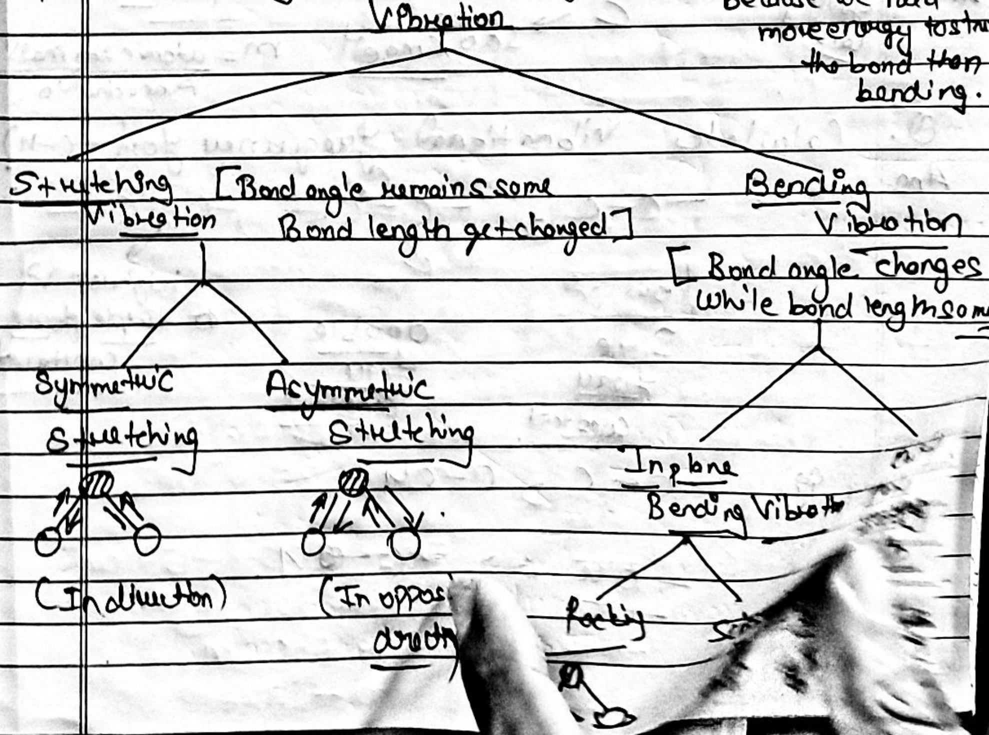
* Vibrations in IR –
Conditions for IR absorptions –

(i) The natural frequency of vibration of a molecule must be equal to the frequency of incident radiation.
(ii) Changes in vibration must stimulate changes in dipole moment.
(iii) The equation must be stastified. –

$$E = h\nu$$

(iv) The intensity of absorption must be proportional to the square of rate of change of dipole.

Imp → Stretching vibration always occur at higher frequen because we need more energy to str the bond than bending.



* Vibration modes –

For Linear (3n–5)

For non-linear (3n–6)

here n is total no. of atoms associate

* Vibrational Frequency by using Hook's law –

Single →

double = double force constant.

triple = triple force constant

$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ → force constant $(5\times10^{5}$ dyne/s) (gm/s^2)

→ reduced mass.

$\bar{v} = \frac{v}{c}$ cm^{-1}

$c \rightarrow 3\times10^{20}\ cm\,sec^{-1}$.

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

m = atomic mass / Avagadro No.

Q. Calculate vibrational frequency for (–C–H)

Ans. –C–C, –C=C=, –C≡C–

low v Single force constant.

v double force constant

highest v triple force constant

(ii) C–C > C–CH

(iii) –OH ⇔ –C–OH.

(4000 to 15)

Ans = $v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

–C–H

1) $m_1 = \frac{12}{6.02\times10^{23}}$, $m_2 = \frac{1}{6.02\times10^{23}}$

$\frac{m_1 m_2}{m_1+m_2} = \frac{\frac{12}{Na^2}}{\frac{12}{Na}+\frac{1}{Na}} = \frac{\frac{12}{Na^2}}{\frac{13}{Na}}$

$\mu = \frac{12}{13}\times\frac{\cancel{N_0}}{Na^{\cancel{2}}} = \frac{12}{13}\times\frac{1}{6.023\times10^{23}}$

$\mu = 0.92 \times \frac{\quad}{7.829\times10^{24}}$

2) $v = \frac{1}{2\times3.14}\times\sqrt{\frac{5\times10^{5}\times13\times6.02\times10^{23}}{12}}$

$v = \frac{1}{2\times3.14}\times\sqrt{\frac{65\times10^{28}\times\cancel{6.023}}{\cancel{12}\ 2}}$

$v = \frac{1}{2\times3.14}\sqrt{\frac{\overset{32.5}{\cancel{65}}\times10^{28}}{\cancel{2}}}$

$v = \frac{1}{2\times3.14}\sqrt{325\times10^{18}}$

5.70

$v = 1\cancel{0000}10\ \frac{18.02\times10^{9}}{2\times3.14}$

$v = \frac{5.7\times10^{9}}{6.28} = \frac{57\times10^{8}}{6.28}$

$v = 9.\cancel{07}6\times10^{8}$.

* ~~IR~~ (Wave no) —

1. C–H (alkane) $>C-H$ — 2850 – 2970 cm^{-1} (strong); 1350 – 1470 cm^{-1} (weak)

2. C–H (alkene) $>C=C(H)-$ — 3010 – 3095 cm^{-1}; 675 – 995 cm^{-1}.

3. C–H (alkyne) $-C\equiv C-H$ — 3300 cm^{-1}.

4. O–H — Monomeric alcohols & Phenols (3590 – 3650) cm^{-1}.

5. OH — hydrogen bonded alcohol & Phenol (3200 – 3600 cm^{-1})

6. OH — Monomeric carboxylic acid (3500 – 3650) cm^{-1}.

7. OH — H-bonded carboxylic acid. (2500 – 2700 cm^{-1})

8. N–H — Amines & Amides (3300 – 3500) cm^{-1}.

9. C–C — ~~150~~ 1560 – 1580 cm^{-1}

10. C=C — 1610 – 1680 cm^{-1}

11. C≡C — 2100 – 2260 cm^{-1}.

Q. What are the various factors which can affect IR Spectrum?

11 — C=O — Aldehyde, ketone, acid, Ester, Carboxylic acid, amide anhydride.

$>C=O$ — 1690 – 1760 cm^{-1}.

12 — C–O — Ether, Alcohol, Esters Carboxylic Acid, (1050 – 1300 cm^{-1})

13. $N-O_2$ — 1500 – 1570 cm^{-1}; 1300 – 1370 cm^{-1}

Q. How will you distinguish between hexane, 1-hexene, 1-hexyne?

Ans. 1-hexyne gives a strong signal due $-C\equiv C-H$ stretching at 3010 3300 cm^{-1} and a weaker signal due to C≡C at ~~2~~ 1610 cm^{-1}.

1-hexene gives ~~a~~ st characteristic absorption at 3095 cm^{-1} due to $>C=C-H$ stretching. and a weaker signal at 1620 / cm^{-1}. due to C=C stretching.

For Hexane — C–H stretching will appear below 2970 cm^{-1} and weaker signal ~~due~~ around 1560 cm^{-1} due to –C–C– stretching.

* Factors Affecting IR vibrations —

1. Physical State — In general, a compound in vapour state absorbs at higher frequency in comparison to solid & liquid state. Example — Cyclopentanone — vapour phase ($\bar{\nu}$ – 1772 cm^{-1}) Liquid state [$\bar{\nu}$ – 1746 cm^{-1}]

2. Effect of solven

Q. How will you differentiate between Intermolecular and Intramolecular H-bonding?

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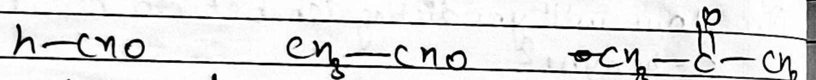
Change in polarity of solvent from non-polar to polar gives downward frequency shift. Example – ↓ Hexane, $CHCl_3$, C_2H_5OH, H_2O
1726 cm^{-1}, 1713 cm^{-1}, 1709 cm^{-1}, 1660 cm^{-1}

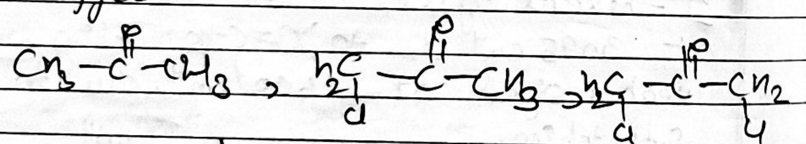
* Inductive effect –
+I effect is inversely proportional to frequency or wavenumber because it results in the lengthening of bond, hence force constant also get reduced.
–I effect is directly proportional to frequency or $\bar{\nu}$ because it results in less b.l, hence force constant increases.

* +I effect



H–CHO CH_3–CHO CH_3–C(=O)–CH_3
1745 cm^{-1} 1740 cm^{-1} 1715 cm^{-1}.

* –I effect –



CH_3–C(=O)–CH_3, $H_2C(Cl)$–C(=O)–CH_3, $H_2C(Cl)$–C(=O)–CH_2Cl
1715 cm^{-1} 1725 cm^{-1}. 1740 cm^{-1}.

* Hydrogen bonding –
Hydrogen bonding brings downward frequency shift. Stronger the hydrogen bonding lesser will be the wavenumber.
→ Intermolecular H-bonding gives a broadband on dilution, whereas
→ Intramolecular H-bonding gives a sharp and well defined absorption band which does not get effected by dilution.

Q. How will you distinguish between Aliphatic and aromatic compounds using IR spectography?

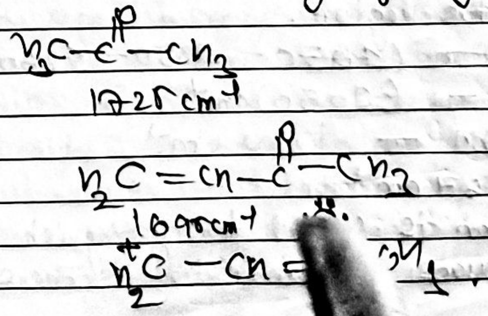
Date:- / /
Page:-

* Aromatic compounds shows many absorption band including characteristic –C=C– stretching at 1600 cm^{-1} (1500, 1580, 1450)

Imp
Q. Which one is expected to absorb at higher frequency and why?
Ans. (i) $\overset{✓}{C{\equiv}C}$, C–C ; (C=C) $\bar{\nu} \propto k$)
(ii) C≡C, C=C. (C≡C) $\nu \propto k$)
(iii) $\overset{✓}{O{-}H}$, C–C (O–H) ($\nu \propto \frac{1}{\mu}$)
(iv) HCHO, CH_3CHO. (due to $bl \propto \frac{1}{\nu}$, +I)
(v) CH_3CHO, CH_2ClCHO ✓ (–I ∝ , bl dec, ν inc).

Q. How will you distinguish between following pairs on the basis of IR spectroscopy?
Ans. CH_3COOH & $CH_3COOC_2H_5$ ⇒ due to COOH –OH → carboxylic
& C_2H_5OH & $C_2H_5OC_2H_5$ → –OH → (3600).
=

* Resonance Effect :–
If any group ~~undeg~~ undergoes resonance and gets partial ~~sign~~ single bond character due to decrease in ~~bond~~ force constant & this compound will absorb at lower frequency.



H_3C–C(=O)–CH_3
1725 cm^{-1}

H_2C=CH–C(=O)–CH_3
1690 cm^{-1}

$H_2\overset{+}{C}$–CH=

Q. Write a short note on finger print region.
Q. Give the significance of ~~st~~ finger print region in IR spectroscopy.

Imp

* Finger print region -

→ One of the important function of IR spectroscopy is to determine the identity of given compounds. If two compounds are identical and have similar spectra under similar conditions.

- The region below 1500 cm^{-1} is rich in many absorptions due to different stretching and bending vibrations. This region is known as finger print region. Except Enantiomers, all existing compound can be differentiated or identified in this ~~your~~ finger print region. It can further divided into three subregion
(i) 1500 - 1350 cm^{-1} (ii) 1350 cm^{-1} - 1000 cm^{-1}
(iii) 1000 - 667 cm^{-1}.

1. 1500 - 1350 cm^{-1} -

- Appearance of a doublet near (1380 - 1365) cm^{-1} confirms the presence of tertiary butyl group in the compound.
- The characteristic absorption band for NO_2 group will appear at 1350 cm^{-1}.

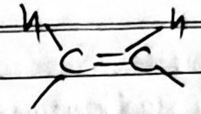
2. 1850 - 1000 cm^{-1}

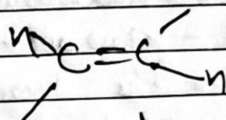
- Alcohols, acids, esters, ethers, acid anhydrides, lactones etc. gives characteristic due to C-O stretching in this region.

ROH - (~~1050~~ - 1350 - 1260) cm^{-1}
R_2OH - (1050) cm^{-1}
PhOH - 1200 cm^{-1}.

3. 1000 - 667 cm^{-1}

- This region is useful to distinguish between

Cis -

(700 cm^{-1})

trans -

(970 - 960 cm^{-1})

With ~~In~~ this region, we can also differentiate mono substituted, disubstituted and ~~or~~ ortho ~~para~~ metapara position in benzene. or in aromatic compound.

→ monosubstituded - (Aromatic) - ~~750~~ 750 - 700 cm^{-1}

→ disubstituted -
Ortho & Para - (770 - 735) cm^{-1}
(840 - 810) cm^{-1}.
meta - (720 - 690) cm^{-1}.
(800 - 750) cm^{-1}.

* Applications of IR -

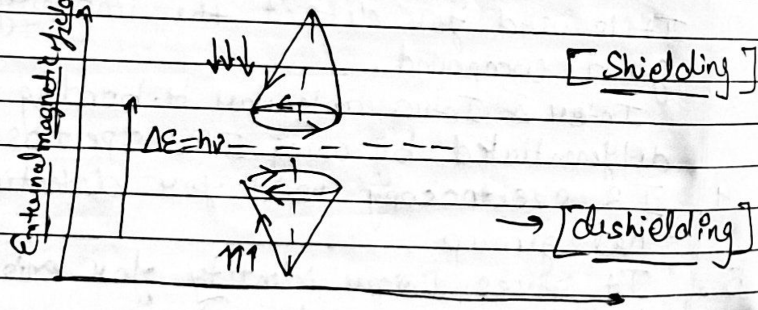
1. It is used for identification of unknown compound.
2. It is used for detect the impurity in the given compound.
3. Inter & Intra molecular H-bonding can be easily differentiated by using IR spectroscopy.
4. IR spectroscopy used for detection of functional group.
5. It gives unique identity for existing compound due to finger print region.
6. IR spectroscopy useful for detection to differentiate between cis & trans geometrical isomer.
7. With help of IR spectroscopy, we can identify, substitution in aromatic compound like mono or disubstituted (o & p and para).

[, H' → any one odd → spin active
otherwise, it is spin inactive.

* Nuclear Magnetic Resonance (NMR) —
NMR is in radiowave. It's wavelength ranges from 1 – 100 cm.
NMR involves the transistion of a nucleus from one spin state to another with the absorption of electromagnetic radiation by spin active nuclei. When such nuclei are placed in magnetic field, then they give two type of orientation —

1. Aligned with external magnetic field.
2. Opposition with magnetic field.

Ther nucleus of spin active nuclei behaves like a tiny magnetic as it possess both electric and magnetic spin. Ex— $_1H$.
The spinning of nucleus with the vertical axis is known as precessional motion.

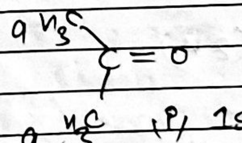


* The transition of nucleus from lower energy stable orientation to higher energy unstable orientation. If a proton is precessioning in aligned orientation it can pass into opposed orientation by absorbing energy from the high energy opposed orientation it come back to the low energy aligned orientation by loosing energy

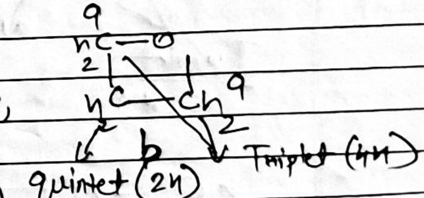
This transistion from one spin state to another is known as Flipping of proton.
The energy required for flipping is ΔE=hν.

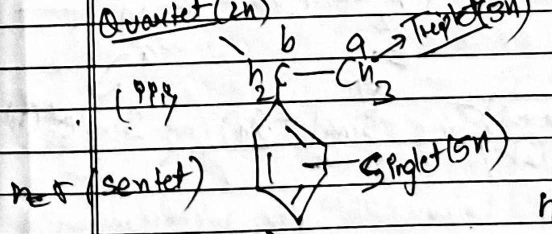
*→ **Spin active nuclei** —
All nuclei carry a charge, it means possess spin angular momentum and the moment is quantized only, the nuclei having a finite value of spin quantam number behaves like a spin active nuclei. The orientations given by the nucleus = (2I+1) where I = spin quantam no.
Ex— $_1H^1$, $_7N^{15}$, $_7N^{14}$, $_6C^{13}$, O^{17} [atomic no. or mass no. one should be odd].
[, H' possess higher sensitivity & vast occurence.

Imp * **Number of signals** —
The number of signals in NMR spectra provide us the information about the different sets of equivalent proton in a molecule. If chemical environment is different, then we get different signals due to non-equivalent sets of proton.



(i) 1 signal
Singlet (6H)

(ii)


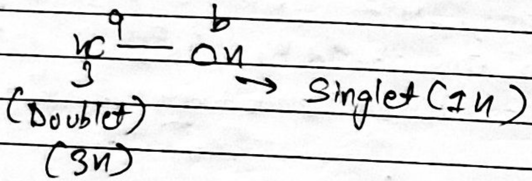
(iii)


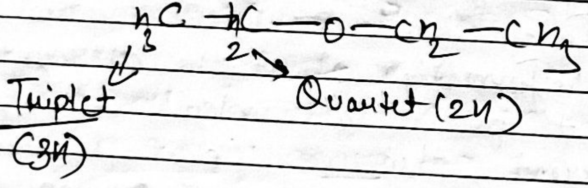
n = 0 → Singlet (1)
n = 1 → (1+1) = Doublet
n = 2 (2+1) = Triplet (1 : 2 : 1)
n = 3 (3+1) Quadruplet (1 : 3 : 3 : 1)
n = 4 (4+1) Quintet (1 : 4 : 6 : 4 : 1)

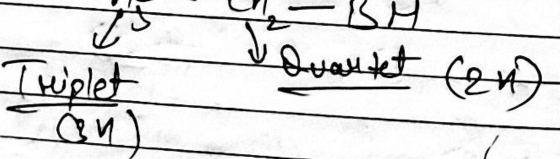
(1 : 5 : 10 : 10 : 5 : 1) → Intensity ratio

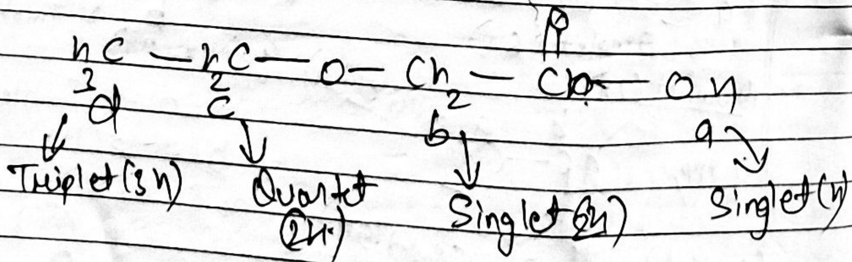
* In spectrum of NMR, each signal represents one kind or one set of proton in the molecule. In general, we get different multiplets or group of peaks for a given compound. It is due to spin coupling. The splitting of signal takes place. And splitting can be given by $(n+1)$, where n is no. of protons present in the neighbour atom. But in different chemical environment:—

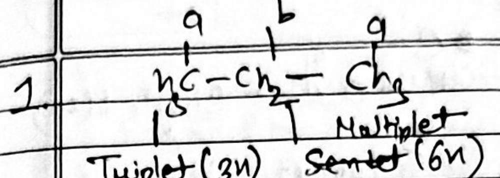
$(n+1)(n'+1)(n''+1)\ldots\ldots$

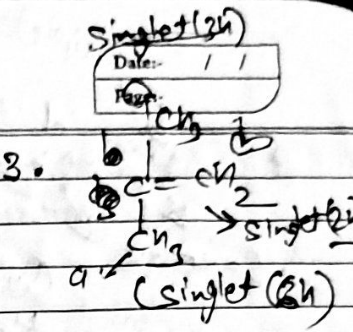

H_3C-OH

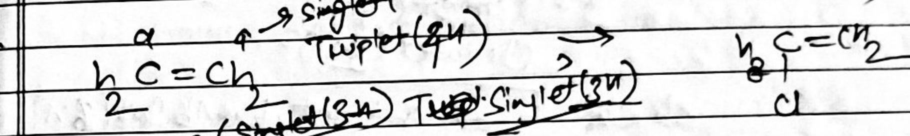

$H_3C-H_2C-O-CH_2-CH_3$

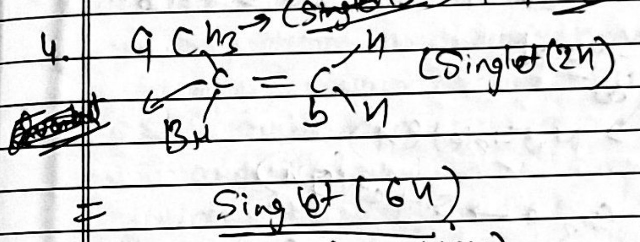

H_3C-CH_2-SH

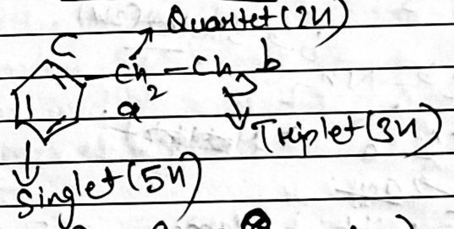

$H_3C-H_2C-O-CH_2-C(=O)-OH$

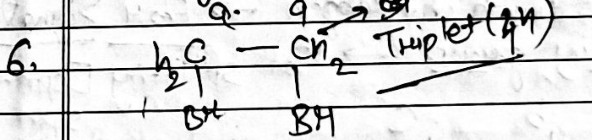
1.

$H_3C-CH_2-CH_3$

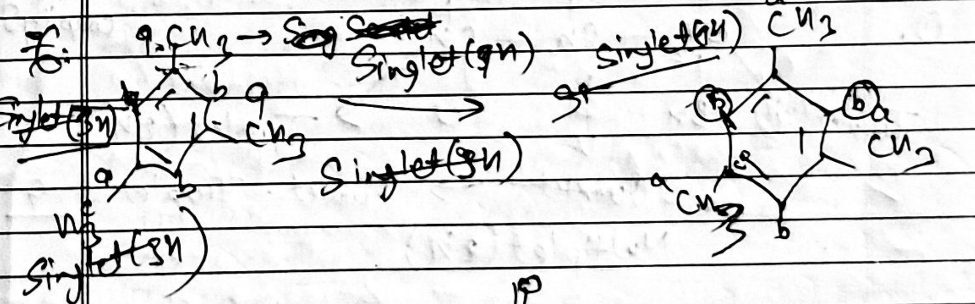
3.


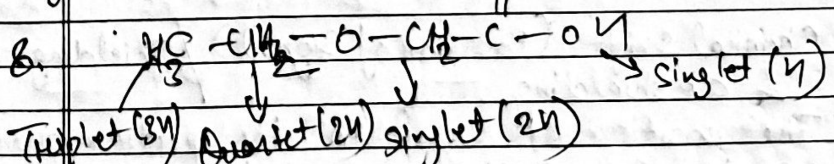
2.

$H_2C=CH_2$

4.


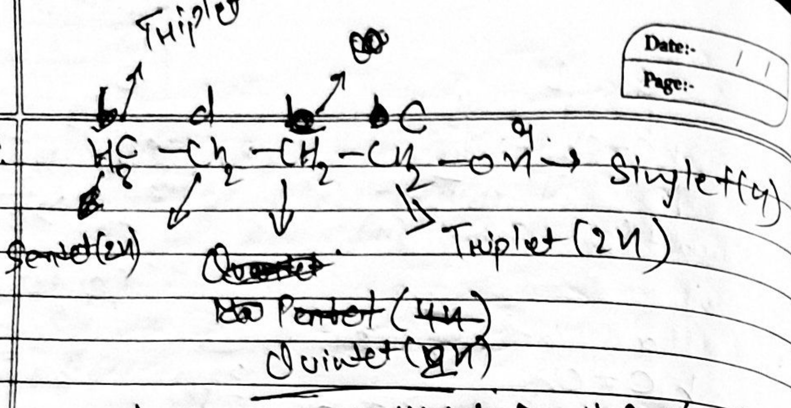
5.


6.

$H_2C(BH)-CH_2(BH)$

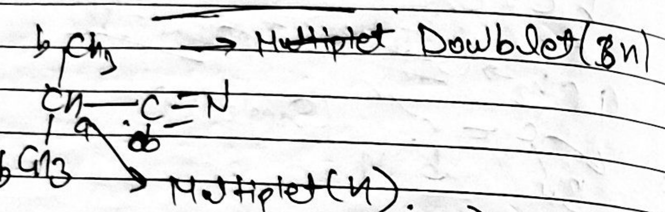
7.


8.

$H_3C-CH_2-O-CH_2-C(=O)-OH$

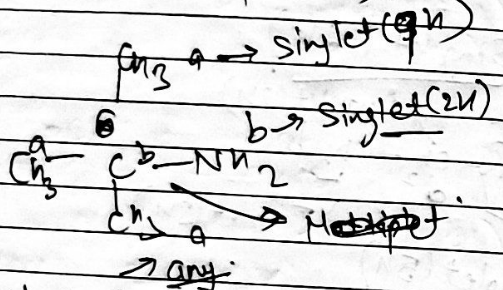
9.



10.

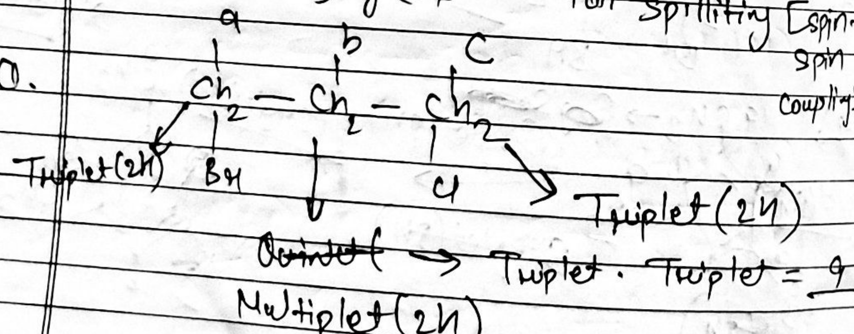


11.



* Only for. C with hydrogen → For Signal
neighbouring group → For spilliting [spin-spin coupling]

Q.



* Chemical shift (Position of Signal) / shielding & deshielding –

The position of signal in the spectrum provides us the information about the nature of

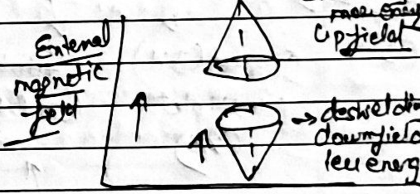
→ OH → Not → It cuts

→ C_6H_6 → It wts.

proton like aliphatic & aromatic, vinylic adjacent to any e⁻ donating group or withdrawing group.

→ Each type of proton will have different electronic environment, hence absorbed at different field.

→ When a molecule is placed in an external magnetic field, its e⁻ are promoted to circulate produces secondary magnetic field, ~~to~~ which also known as (induced magnetic field), the rotation of e⁻ around the proton generates magnetic field. If the generated field is in alignment or parallel, it the field felt by the proton get increases, and it is set to be deshielded and the phenomena is known as deshielding.



* But if it opposes, the external magnetic field, then, the field felt by the proton get decreases and it is said to be shielded. The phenomenon is known as Shielding

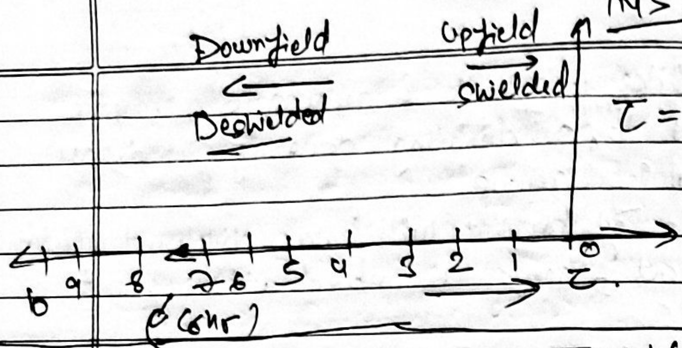
→ The shielded proton signal will absorb at upfield & while deshielded signal will be at downfield.

→ "The difference in the absorption position of proton with respect to TMS signal]. [Tetramethyl ~~sy~~ S.] unit.

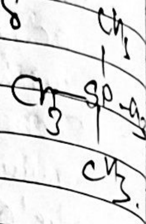
→ We use two scale in NMR spectrum – which is τ & δ.

$\tau = 10 - \delta$.

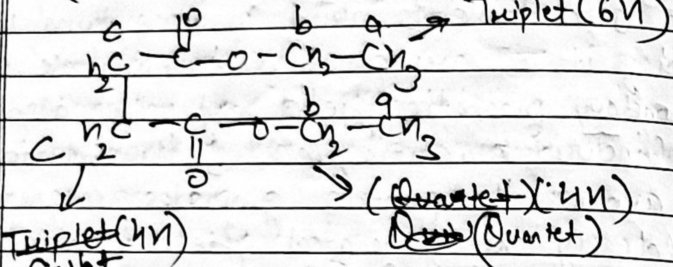
TMS → δ = 0



$\tau = 10 - \delta$



Q.

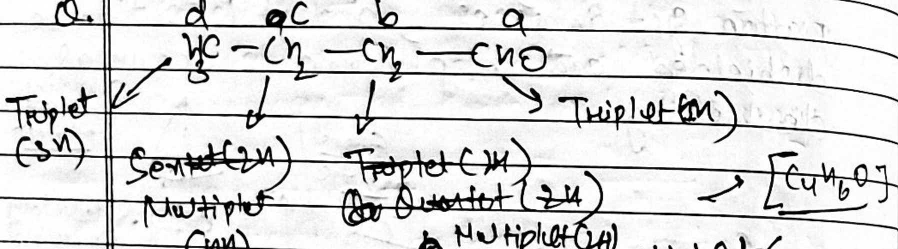


→ Triplet (6H)

→ (~~Quartet~~)(4H) (Quartet)

→ ~~Triplet~~(4H) Singlet

Q.



Triplet (3H)

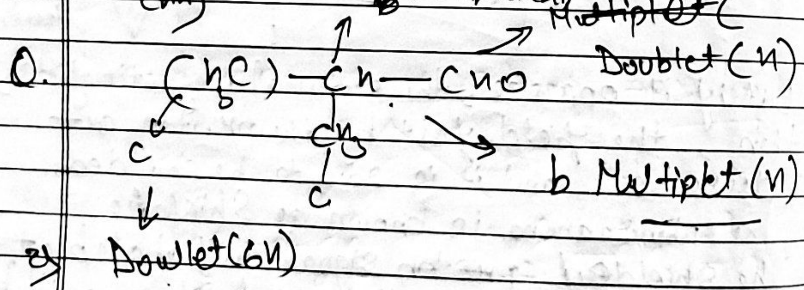
~~Sextet~~(2H) Multiplet (2H)

~~Triplet (2H)~~ ~~Quartet~~ (2H)

→ Triplet (1H)

→ [C_4H_8O]

Q.



Multiplet(2H) ~~Multiplet~~ (

Doublet (1H)

b Multiplet (1H)

→ Doublet (6H)

→ sample frequency

$$\delta = \frac{\nu_s - \nu_{TMS}}{\nu_0}$$

→ (Tms) frequency (Hz)

ν_0 → operating frequency

* Factors Affecting NMR Spectra –

→ Inter – Two different

Intra – Same

1. Inductive Effect
2. Hydrogen bonding
3. Anisotropic Effect
4. Van der waals deshielding.

* Inductive Effect –

I

+I effect ∝ ~~downfield~~ upfield

(~~greater~~ lower value of δ)

→ attached to higher δ

−I effect ∝ ~~upfield~~ downfield (~~less~~ higher value of δ)

→ attached to lower δ greater δ)

* Hydrogen bonding –

H-bonding ∝ deshielded, (higher value of δ)

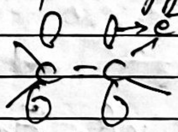
↓

downfield

more downfield ↗ same ↗

Imp → Inter, Intra.

* Anisotropic Effect –



→ e cloud – repulsion to e → deshielding

C≡C

∝ deshielding

downfield

greater value of δ.

C_6H_5 (5H) → Singlet

* Also known as space effect.

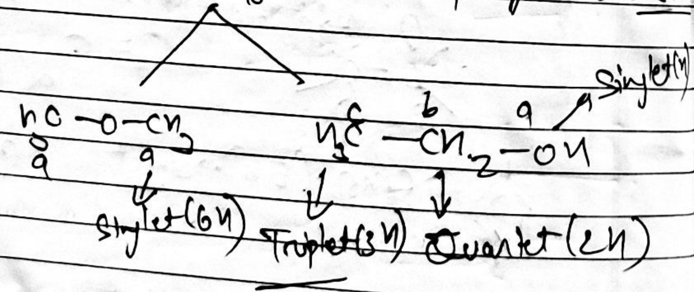
* The deshielding effect on proton attached to C=C, C≡C is more than that of inductive effect. Alkane, Alkynes and aeromatic protons

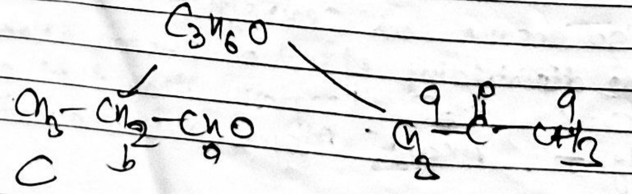
are much deshielded results in higher value on δ scale. gives deshielded signal and at downward frequency. It is due to presence of π e⁻ cloud. which causes repulsion between with the e⁻ moving around the nucleus. This is Anisotropic Effect.

* Van der waal's Deshielding – (hindrance effect)
Van der waal's deshielding also known as hindrance effect, in overcrowded molecule it is possible. that some protons may occupy stearically hindrance position and the e⁻ cloud of bulky group will repeal the e⁻ moving around the proton. Hence, the proton will be deshielded. The signal will appear at downward frequency.

* Applications –

1. Distinction between structural isomers.
2. Distinction C_2H_6O btw ~~ope~~ functional isom.



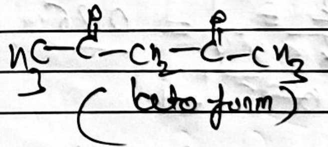


Q. Write short note on applications of NMR.
Q Discuss various factors effect on NMR Spectroscopy

3. Differentiation between inter & intra molecular hydrogen bonding –
NMR spectoscopy is useful to differentiate between inter & intra molecular hydrogen bonded compound with the help of ~~positional~~ NMR spectoscopy by the position of signals.
→ Intermolecular H bonded signal appear at downfield. And on dilution, it gives more downfield shift.
→ Wheras Intramolecular signal is concentration independent.

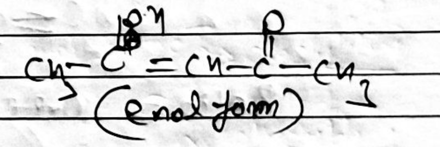
4. Detection of aromaticity –
In NMR spectoscopy due to anisotropic effect, it can easily identify whether the compound is aliphatic & aromatic because the signal of aromatic compound appear at higher value of δ. or downfield.

5. Differentiation between keto-enol isomerism.



$H_3C-C(=O)-CH_2-C(=O)-CH_3$

(keto form)

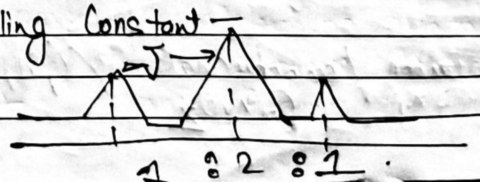


$CH_3-C(OH)=CH-C(=O)-CH_3$

(enol form)

6. Detection of e⁻ negative atom or group.
E⁻ negative atom on group gives deshielding to the proton, hence their presence shift the signal towards downfield.

* Coupling Constant –



* ~~Ratio of height~~ –
The distance between centres of two adjaunt peak in a signaletoH multiplet is a constant & known as Coupling constant. Denoted by J.

* Ratio of height –

$HC - CH_2 - OH$

HC → Triplet (3H)
CH_2 → Quartet (2H)
OH → Singlet (1H) → 1 unit

→ Siylet(1H) $\frac{1}{1} = 1$

→ Triplet – 1 : 2 : 1

$= \frac{3}{4} = \underline{0.75}$ → 0.75 : 1.5 : 0.75

→ Quartet – 1 : 3 : 3 : 1
(2H)

$= \frac{2}{8} = \frac{1}{4} = \underline{0.25}$

Ratio = ~~0.25~~ : 0.75 : 1

0.25 : 0.75 : 0.75 : 0.25

* Numericals based on spectroscopy –

1. Double bond equivalent (DBE) –

(i) hydrocarbon / carbohydrate / C, H, O
C_nH_y / $C_nH_yO_z$

$$D.BE = n+1-\frac{y}{2}$$

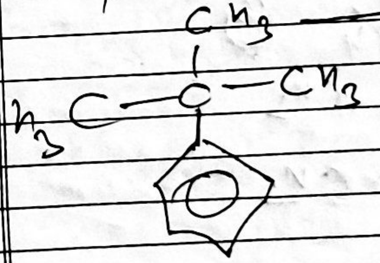
(ii) $C_nH_yN_z$ $D.BE = n+1-\frac{(y-z)}{2}$

(iii) $C_nH_yX_z$ $D.B.E = n+1-\frac{(y+z)}{2}$.

Q. A compound has molecular formula $C_{10}H_{14}$. It gives following NMR data –
i) 0.88 δ (9H) → Singlet → 3° butyl
ii) 7.26 (5H), singlet.

(i) $D.B.E = 10+1-\frac{14}{2} = \underline{4}$.

⇒ (ii) 7.26 (5H) → 4 → DBE confirms presence (C_6H_5) (C_4H_9)

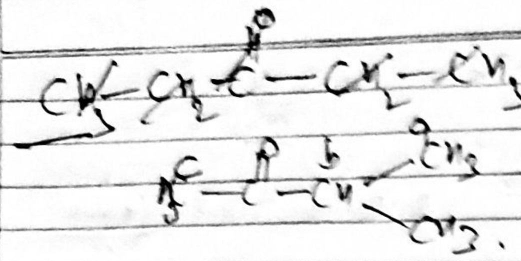


(i) 0.88 (9H) → Singlet
This confirms presence of tertiary butyl.

*Q. An organic compound with molecular formula $C_5H_{10}O$. gives following NMR Spectoscopy

$D.B.E = 5+1-\frac{10}{2} = \underline{1}$.

(i) 0.95 δ (6H) → doublet (Isopropyl)
(ii) 2.10 δ (3H) → singlet
(iii) 2.43 δ (1H) → Multiplet.

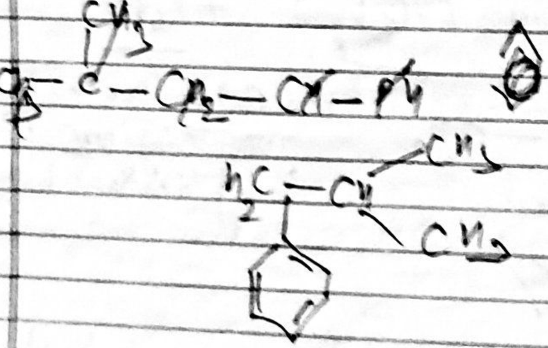


Q. A compound has molecular formula $C_{10}H_{14}$.

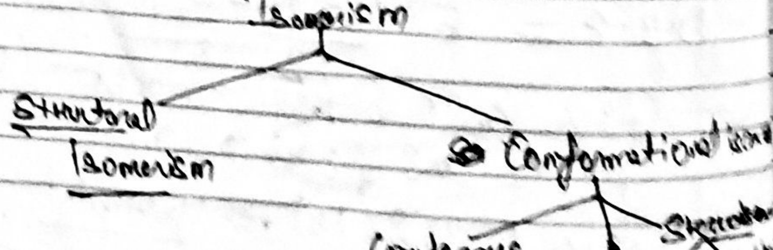
$D.B.E = 10 + 1 - \frac{14}{2} = 4$

gives following NMR data —

- i) 0.88 δ → (6H) doublet — Isopropyl
- ii) 2.45 δ → (2H) doublet —
- iii) 1.86 (1H) multiplet
- iv) 7.12 (5H) singlet → benzene



* Stereo Isomerism —

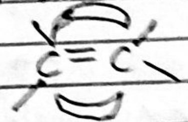


Q. What are Geometrical Isomers? Write the necessary Condition to be a geometrical isomer.

2. Assign cis-trans, syn-anti, E-Z

* Geometrical Isomerism —

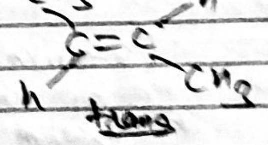
→ When the same molecular formula represents two Compounds having difference in the special arrangements of groups around $>C=C<$, such isomers are known as geometrical isomers. The phenomena is known as geometrical isomerism. It is due to restricted rotation around the double bond.



* Requirements —

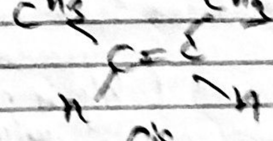
1. Presence of $>C=C<$ which prevents bond rotation.
2. Presence of ring structure to prevent bond rotation.
3. Carbon atom in double bond must be bonded with different atoms or groups.

Ex —

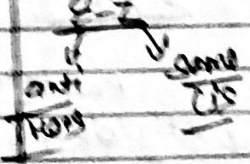


trans

(Stable trans) > cis



cis

* 

Priority → 1, 2, 3,

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Date:- / /

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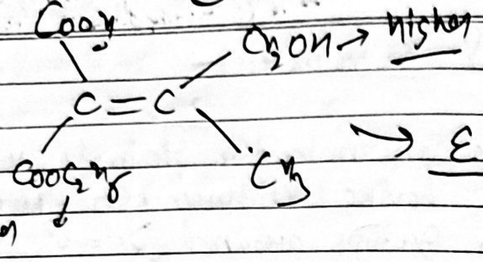
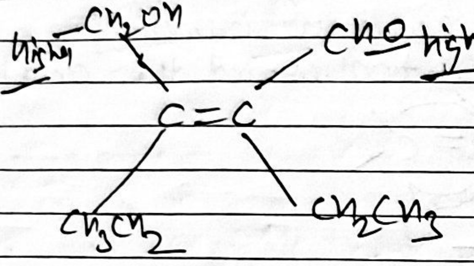
2.

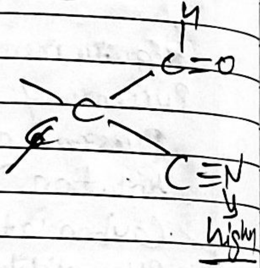


→ E form

3.

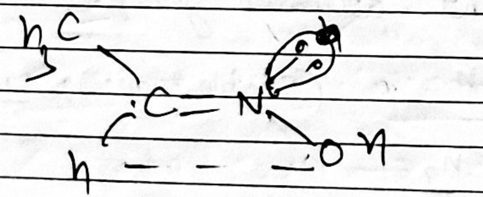


→ Z form



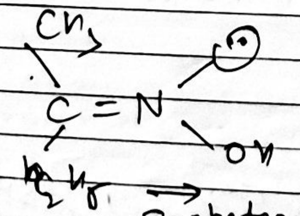
* Syn – Anti' – For oxime

$>C=NH_2$



Syn aldoxime

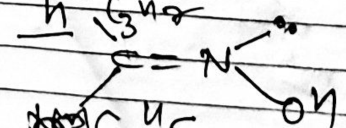
(H with OH) or Z form



→ Syn ketoxime

(Higher priority with OH) or Z form

Syn Aldoxime



Anti ketoxime

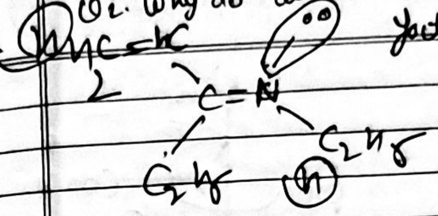
Antialdoxime

or

Q. What is Optical Isomerism? Discuss it with the help of compounds without chiral center.

Q2. Why do allenes show optical isomerism inspite of fact that they do not contain a chiral carbon center.

Date: / /



Anti ketoxime

Z

* Optical Isomerism –

The compounds having same molecular formula but different behaviour towards plane polarized light is called. Optical Isomerism.

* Optical Activity –

Many organic compounds when placed between polarizer and Analizer or in plane polarized light, they give rotation. Such substances are known as Optically Active compounds. And the phenomena is known as Optical Activity. The change in the angle of ppl is known as Optical rotation. If rotation is clockwise direction, it is called dextrorotatory. (+ve sign, d) whereas if its rotates in anticlockwise direction or leftside, then it is called leavorotatory (–ve, l).

→ If a compound does not possess plane of symmetry, center of symmetry or an alternating axis of symmetry, then compound will be optically active. Otherwise it will be optically inactive.

* Enantiomers –

Enantiomers are non-super imposable mirror images.

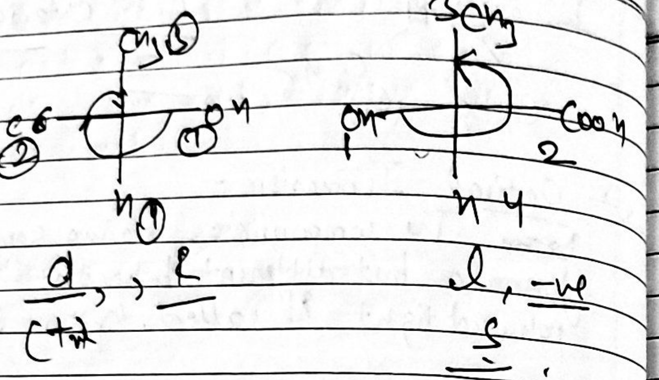
- Have identical physical ~~~~ rties but shows different behaviour towards

Q. Write the difference between Enantiomers & Diastereomers?

Q. Btw Racemic mixture & meso compounds.

Q. Write a short note on –

*



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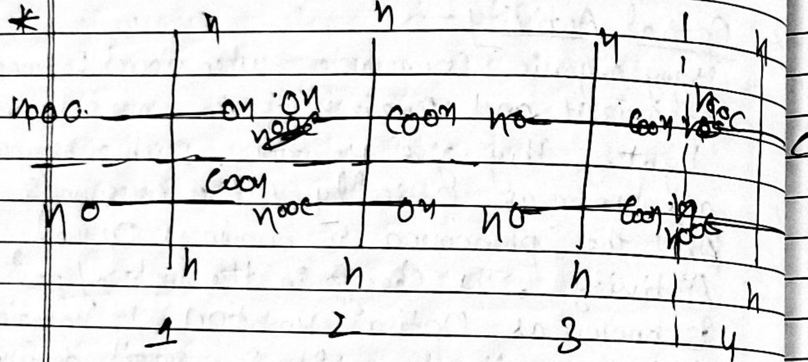


(3,4) 1, 2 – meso compounds (plane of symm)

(1,3) or (1,4) → disastero compounds (no mirror image.

(3,4) (1,2) → Enantiomer (non superimposable mirror)

* Diastereoisomers – Stereoisomers are not mirror images and have different physical & chemical properties are called diastereomers.

* Meso compounds –

If a compound is optically inactive due to internal compensation/ existence of

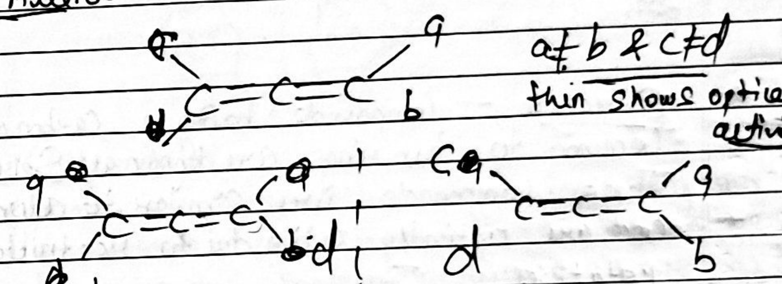
1. Optical activity
2. Optical Isomerism in Spirals
3. E2 system of configuration.

Symmetry.

→ Racemic mixture – A mixture of 50% d & 50% L form and it is optically inactive compounds due to external compensations.

* Compounds without chiral carbon centres.

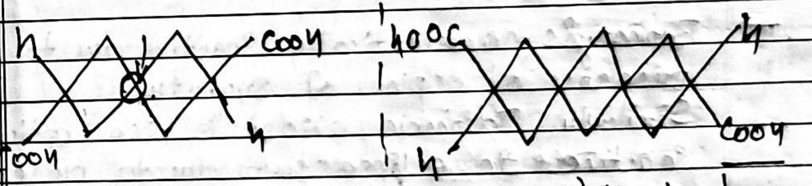
1 Allenes –



a≠b & c≠d then shows optically activity.

(1,1 diphenyl prop-dien

* Spiral –



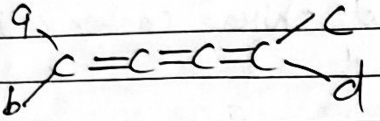
Spiranes. (1,7) dicarboxyl spiro-cyclo heptane

* Allenes –

The compound in which a singal carbon atom connected the carbon atom with the help of double bonds are allenes. Allenes with different substituent on end carbon are optically active. The central atom is Sp hybridised where as other two carbons are Sp2 hybridised and they form π bond which are ⊥ to each other.

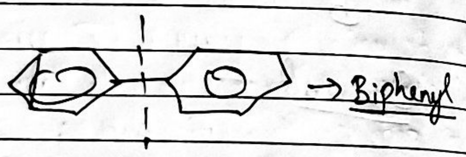
Q Identify which compound will be optically active! And why? 9n- Biphenyl, Diphenic acid, 7 ~~diphenyl~~ diphenyl ... 4: 6,6' dinitro diphenic acids.

* ~~Cum~~ Cumulenes ~~having~~ even are optically ~~a~~ active with even no. of ~~od~~ double bonds, and having three or more consecutive double bonds.



* Spiranes - Compounds having a carbon atom common to two rings are known as Spiranes. These compounds are similar to allenes and are optically active due to restricted rotation.

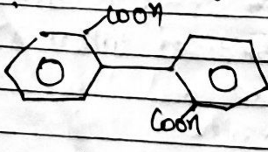
* Biphenyls -



→ Biphenyls are optically inactive due to presence of plane of symmetry. Similarly diphenic acids is also optically inactive in eclipse form due to presence of plane of symmetry.

2,2' diphenic acid

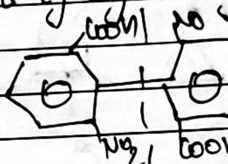
→ Due to presence of two bulky groups it prefers anti-configuration even though it is planar.



On introducing larger subsequents such as

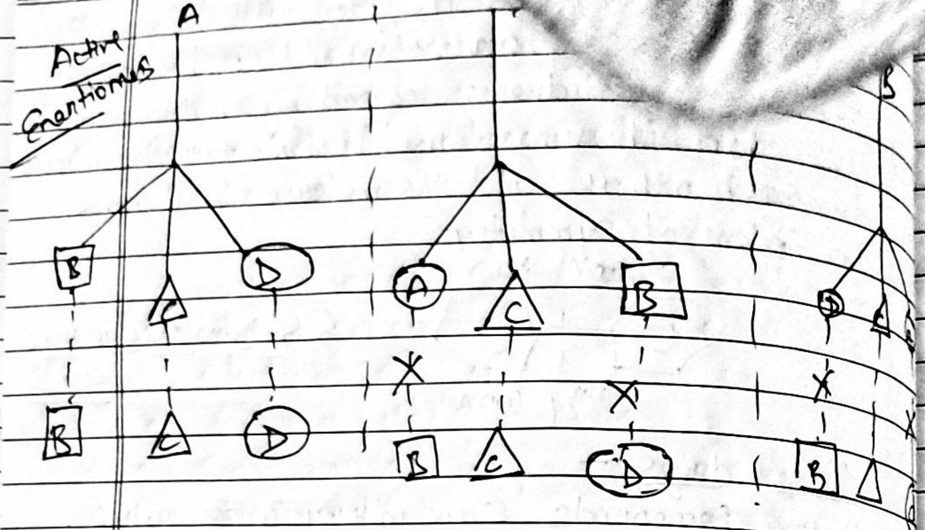
Q. Write a short note on Chiral drugs?

nitro at 6,6' position, it will be prevented from attaining planar structure because of Stearic hindrance caused by bulky groups ~~&~~ then the ringes will be almost perpendicular to each other and the molecule will have no plane of symmetry.



6,6' Dinitro diphenic acids

* Chiral drugs -
Chiral compounds show mirror image pairs (enantiomers) and compounds are known as chiral handed molecules. Drugs like Ketamine, Thiopentane, etropione ~~Dexzone~~. Ibuprofen, Thalidomide. Chirality plays an important role in the binding affinity & the interaction between the drug & its target.
In Pharmaceutical Industry, nearly 60% of the druge are chiral. And approximately 90% of them marked as racemic mixture.
Enantiomers of chiral druge have same chemical connectivity but differ in their interaction with enzymes, proteins & receptors. And this difference lead to the difference in ~~of~~ biological activities like toxicology, metabolism & immune response etc. The recognition of chiral drug explained by Easson and Stedman as three point interaction model.



* Only the Enantiomers which can interact with three binding sites of receptor is biologically active. The degree of purity of any chiral drug is measured by enantiomeric excess (ee) If a sample is having 70% R isomer and 30% S isomer then enantiomeric excess can be calculated?

$$ee = \frac{(\%\text{ of major enantiomer} - 50)}{50} \times 100$$

$$\underbrace{30\%\,R - 30\%\,S}_{} = \underline{40\%}$$

Racemic → 40% → R purity.

Example of chiral enatiomers —

1. R & S Enantiomer of Thalidomide - R forms is ~~used~~ used as sedlative to treat anxiety & causes drowsiness. Whereas S forms causes ~~tera~~ teratogenic defect. (birth & foetus defect)

2. Ibuprofen — Used as pain killer drug. S enantiomer has desired ~~biological~~ pharmacological activity whereas S is completely inactive.
3. ~~&~~ R is completely optically inactive.
3. Carvone — ~~[illegible]~~ In human olfactory system, R & S carvone enantiomer have different smell, R forms smell like spear mint leaves whereas ~~[illegible]~~ S-form smell like caraway seeds.