19/08/2025

Unit - 3

Interaction of IR radiation with matter vibrational changes is called IR spectroscopy (or) vibrational spectroscopy.

Use:-

To find out the functional group.

vibrational frequancy is calculated $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$

c = light velocity 3×10^8 m/s

K = Force constant (or) bond strength

μ = reduced mass. $\mu = \frac{m_1 m_2}{m_1 + m_2}$

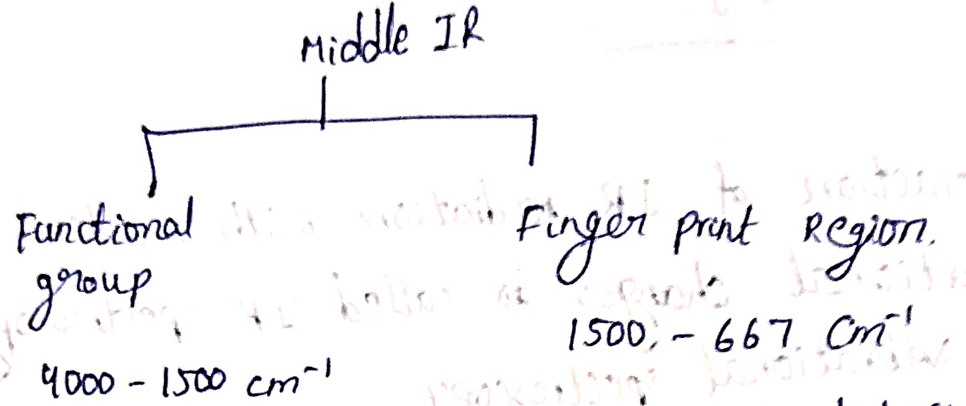
Range of IR radiation:-

13000 - 50 cm^{-1}

- 13000 - 4000 cm^{-1} near IR
- 4000 - 667 cm^{-1} Middle IR
- 667 - 50 cm^{-1} Far IR

In this middle IR most important because all the organic compounds must be obserbed in this region.

It is again classified into two types

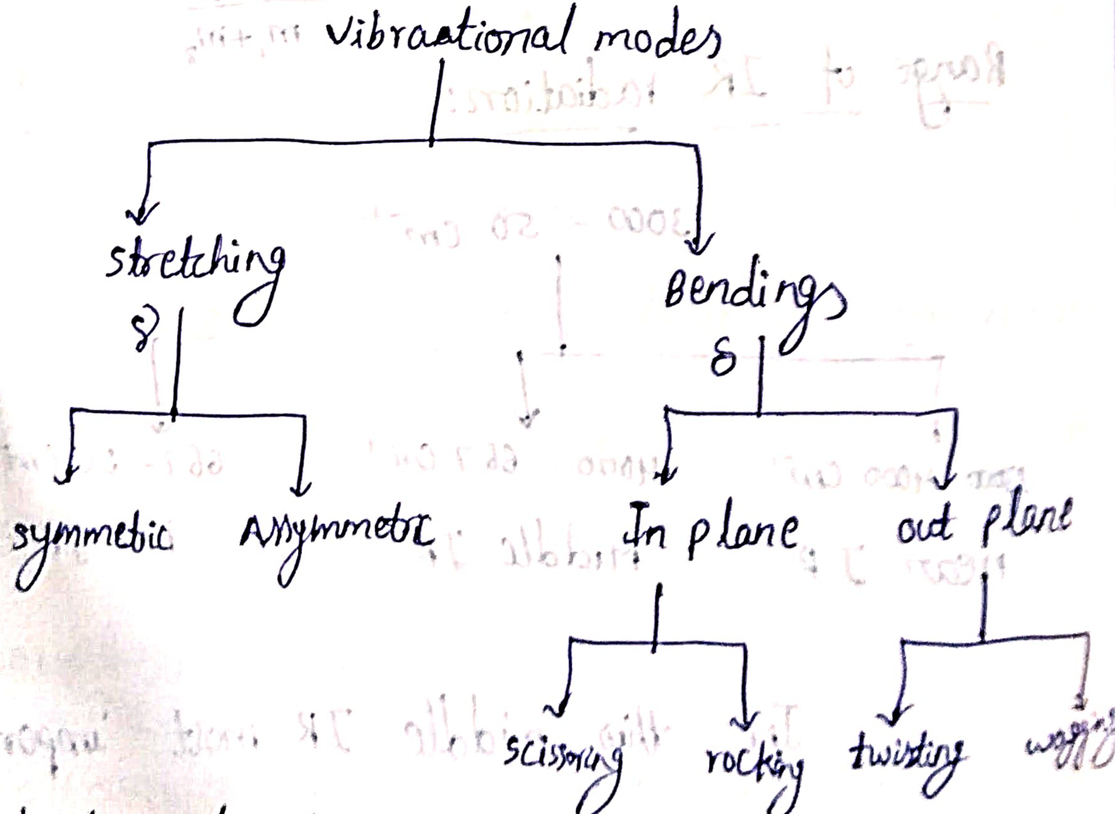


To find functional group

To distinguish identical compounds.
like cis, trans
ortho, meta, para.

Vibrational modes :-

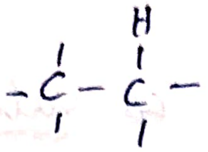
vibrational modes can be depends on bond length & bond angle.



Vibrational frequancy values of Different functional groups :-

Alkane

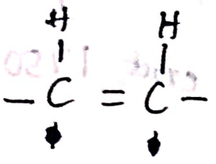
Alkanes :-



ϑ_{C-C} : 1100 - 1300 cm^{-1}

ϑ_{C-CH} : 2850 - 3000 cm^{-1}

Alkene :-



$\vartheta_{C=C}$: 1640 - 1670 cm^{-1}

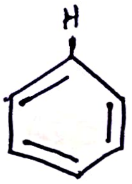
$\vartheta_{C=C-H}$: ~~2850 - 3000 cm^{-1}~~ 3000 - 3100 cm^{-1}

Alkyne :- $C \equiv C - H$

$\vartheta_{C\equiv C}$: 2140 - 2200 cm^{-1}

$\vartheta_{C\equiv C-H}$: 3333 cm^{-1}

Benzene :-



$\vartheta_{C{\parallel\parallel}C}$: 1600, 1580, 1500, 1450 cm^{-1}

$\vartheta_{C{\parallel\parallel}C-H}$: 3030 cm^{-1}

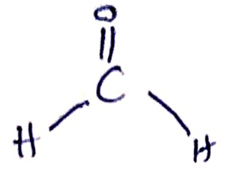
Mono sub Benzene : 690, 710 cm^{-1}

ortho : 735 cm^{-1}

Meta : 700, 770 cm^{-1}

Para : 840 cm^{-1}

Vibrational frequency of co values of carbonyl compounds :

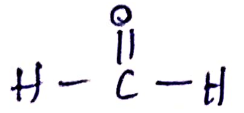


1650 - 1850 cm⁻¹

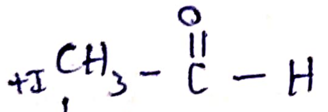
↓

exact 1750 cm⁻¹

Aldehyde :

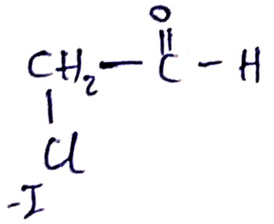


$H-\overset{\overset{O}{\|}}{C}-H$: ϑ C=O 1750 cm⁻¹



$+I\ CH_3-\overset{\overset{O}{\|}}{C}-H$: ϑ C=O 1745 cm⁻¹

↓ Its a little influenced



$\underset{\underset{Cl}{|}}{CH_2}-\overset{\overset{O}{\|}}{C}-H$: ϑ C=O 1770 cm⁻¹

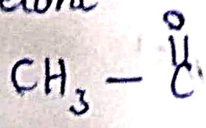
-I

+M

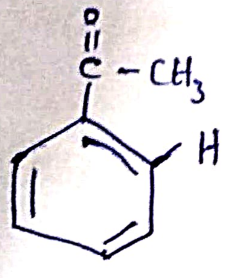
: ϑ C=O 1680 cm⁻¹

Ketone :

Acetone



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$: ϑ C=O 1718 cm⁻¹



Acid :

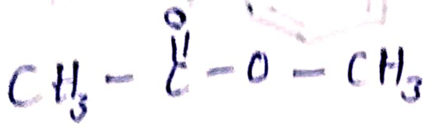
$CH_3-\overset{O}{\overset{\|}{C}}-OH$

$\vartheta_{C=O}$: 1720 cm^{-1}

ϑ_{O-H} (Acid) : 2500 - 3000 cm^{-1} (B.S) Broad singlet

$\vartheta\ \overset{O}{\overset{\|}{C}}-O$: 1330 - 1250 cm^{-1}

Ester :



$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

ϑ C=O : 735 cm^{-1}

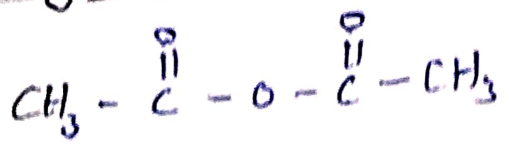
$\overset{O}{\overset{\|}{C}}-O$: 1330 - 1250 cm^{-1}

Amide :

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

$\vartheta_{C=O}$: 1650 dil
1690 con

Anhydride :



$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$

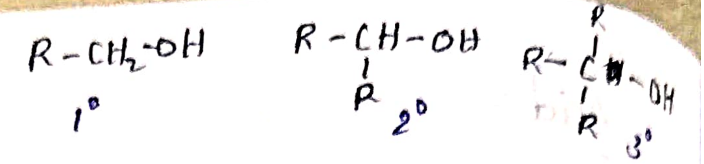
ϑ C=O : 1760 } doublet
1820

Alcohols :

~~$CH_3-\overset{O}{\overset{\|}{C}}$~~ - R-OH

Alcohol :

$R-O-H$



$R-CH_2-OH$ 1° $R-\underset{R}{CH}-OH$ 2° $R-\underset{R}{\overset{R}{C}}-OH$ 3°

ν_{O-H} (free) : 3650 cm^{-1}

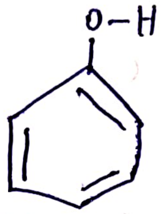
ν_{C-O} : 1° = 1050

2° = 1100

3° = 1150

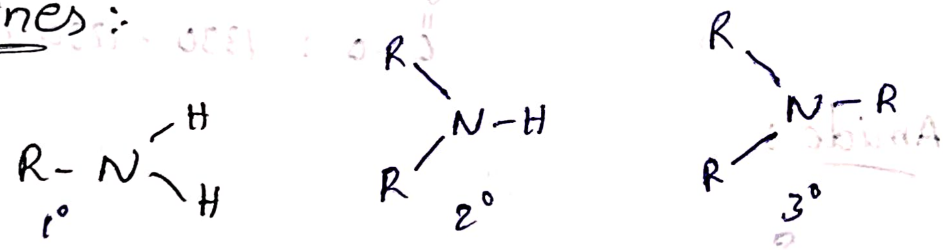
ν_{O-H} Inter M.H.B : 3350 cm^{-1}

ν_{O-H} Intra M.H.B : 3600 cm^{-1}



phenol = 1200 cm^{-1}

Amines :



1° ν_{N-H} : 3500, 3300 } doublet

2° ν_{N-H} : 3400 cm^{-1} singlet

3° ν_{N-H} : Absent

ν_{C-N} : 1240 - 1300 cm^{-1}

Ether :

$R-O-R$

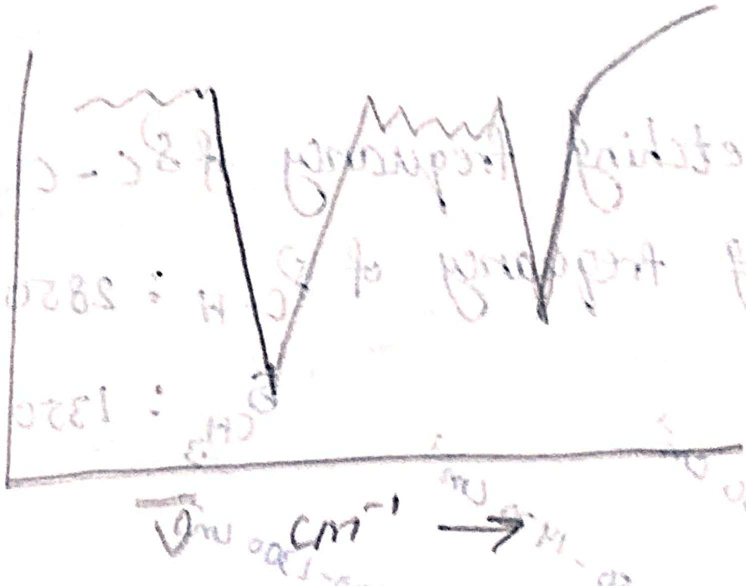
ν_{O-C} : 1330 - 1250 cm^{-1}

ν_{C-H} : 3650 cm^{-1}

$R-C\equiv N$

$\bar{\nu}_{C\equiv N}$: 2240 cm^{-1}

IR spectra



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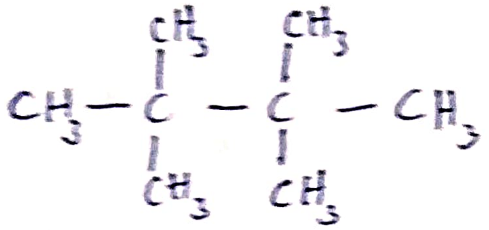
2,2,3,3 - tetramethyl Butane



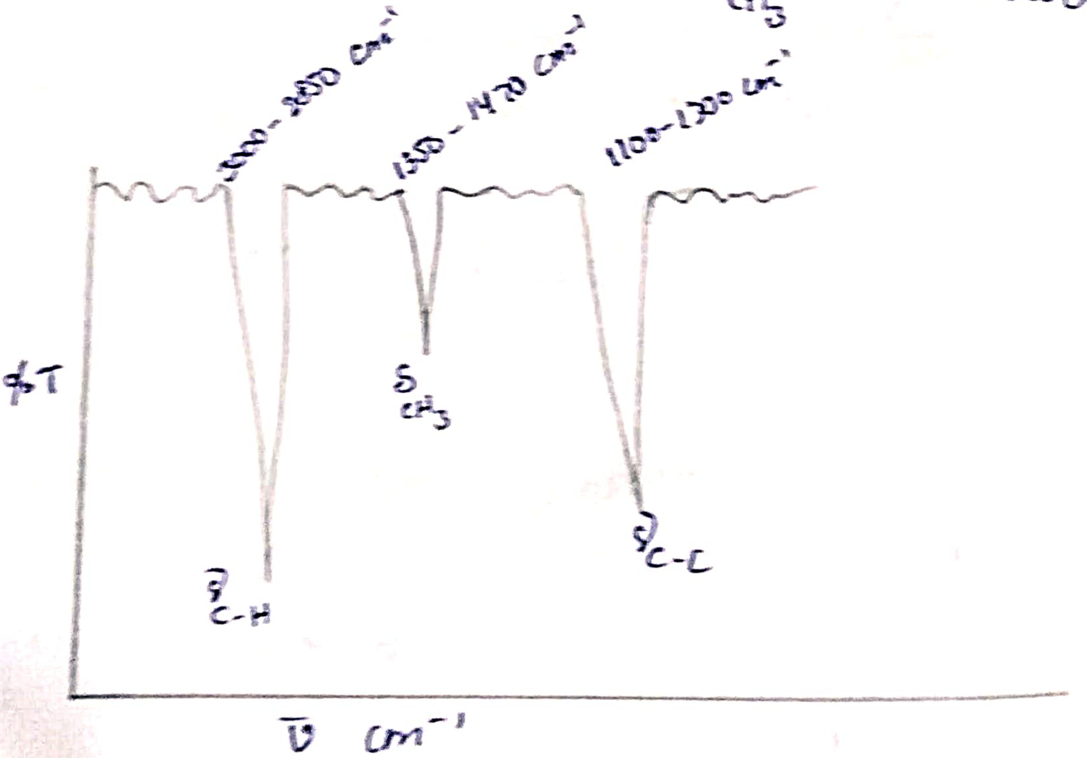
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

IR spectral :-

vibration stretching frequancy of ϑ_{C-C} : 1100-1300 cm^{-1}

vibration stretching frequancy of ϑ_{C-H} : 2850-3000 cm^{-1}

δ_{CH_3} : 1350 - 1470 cm^{-1}

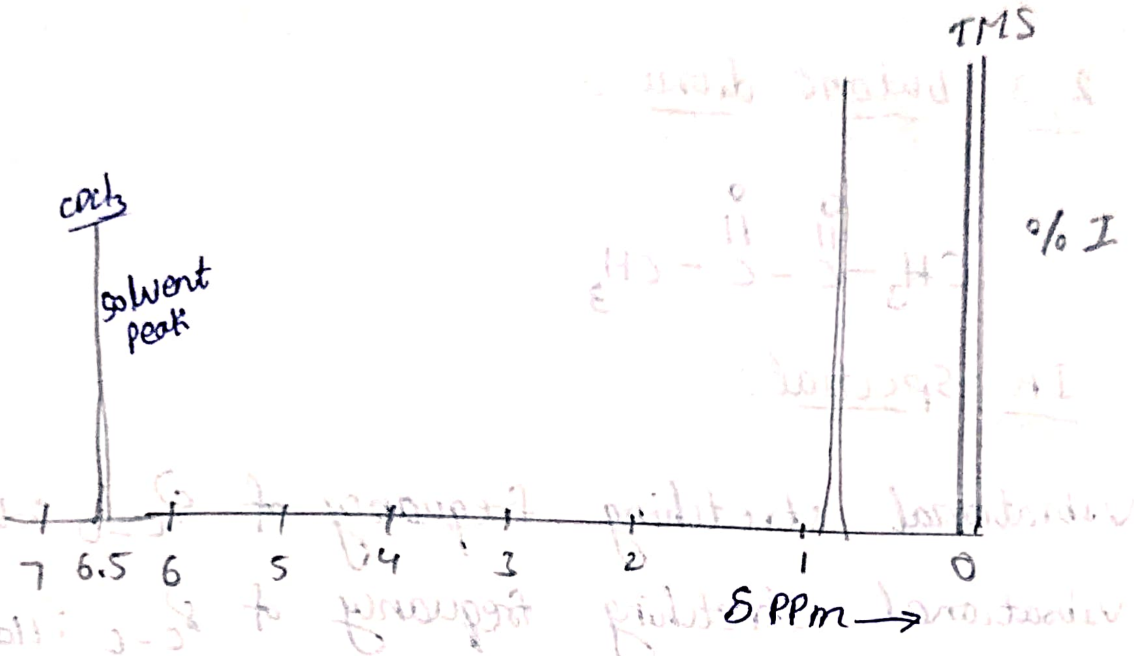


N

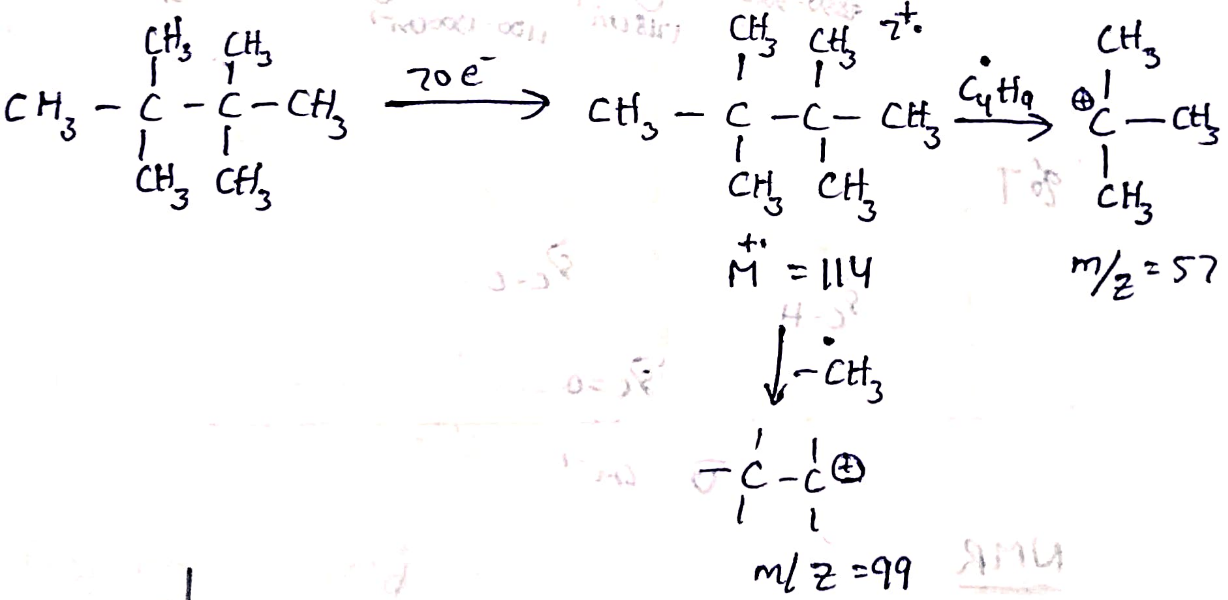
This compound gives only one signal because all the 18 protons present in same environment.

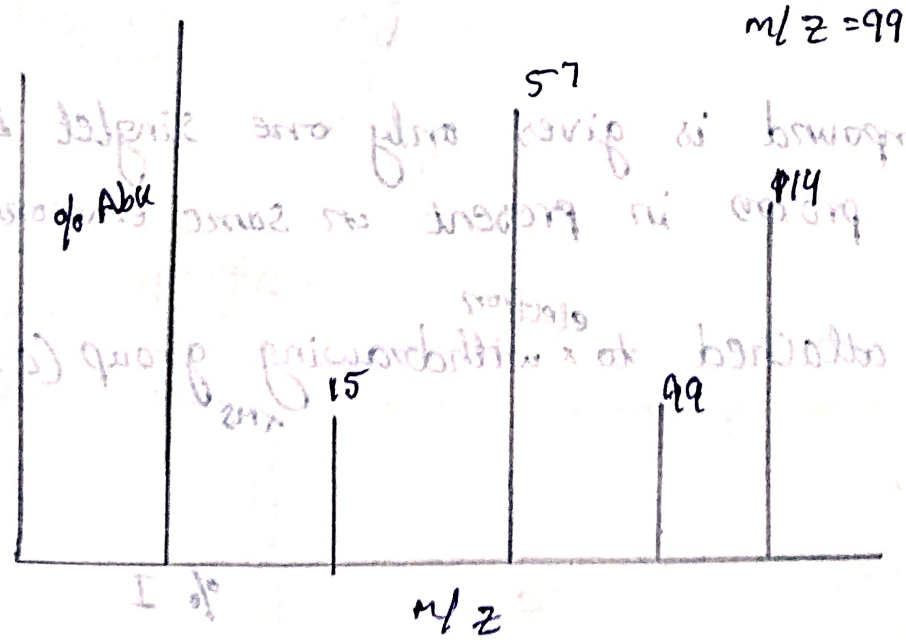
chemical shift :-

CH_3 : 0.9 PPm (singlet - 18 H)

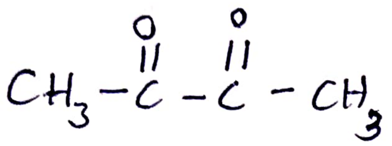


Mass spectra :-





2,3 butane dione :-



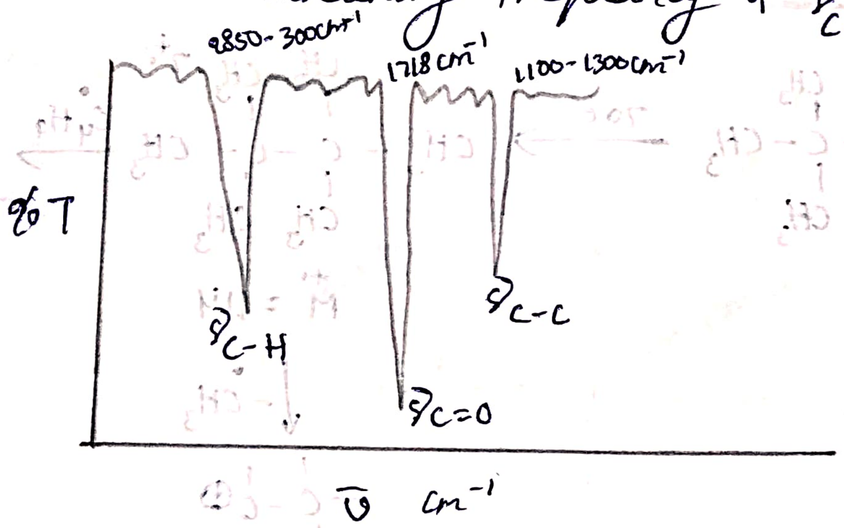
$CH_3-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-CH_3$

IR Spectral :-

vibrational stretching frequancy of $\nu_{C=O}$: 1718 cm⁻¹

Vibrational stretching frequancy of ν_{C-C} : 1100-1300 cm⁻¹

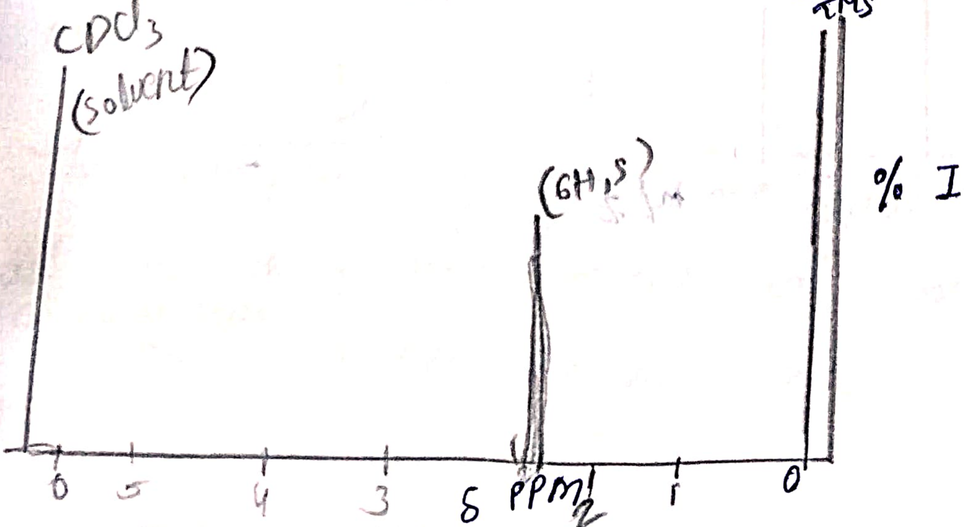
vibrational stretching frequancy of ν_{C-H} : 2850 - 3000 cm⁻¹



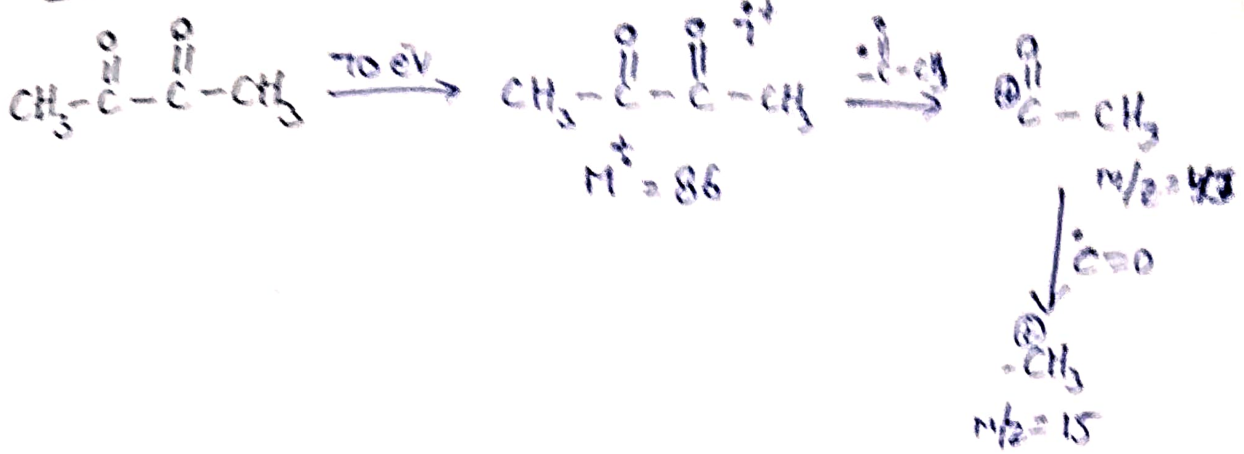
NMR

This compound is gives only one singlet because all the protons in present in same environment.

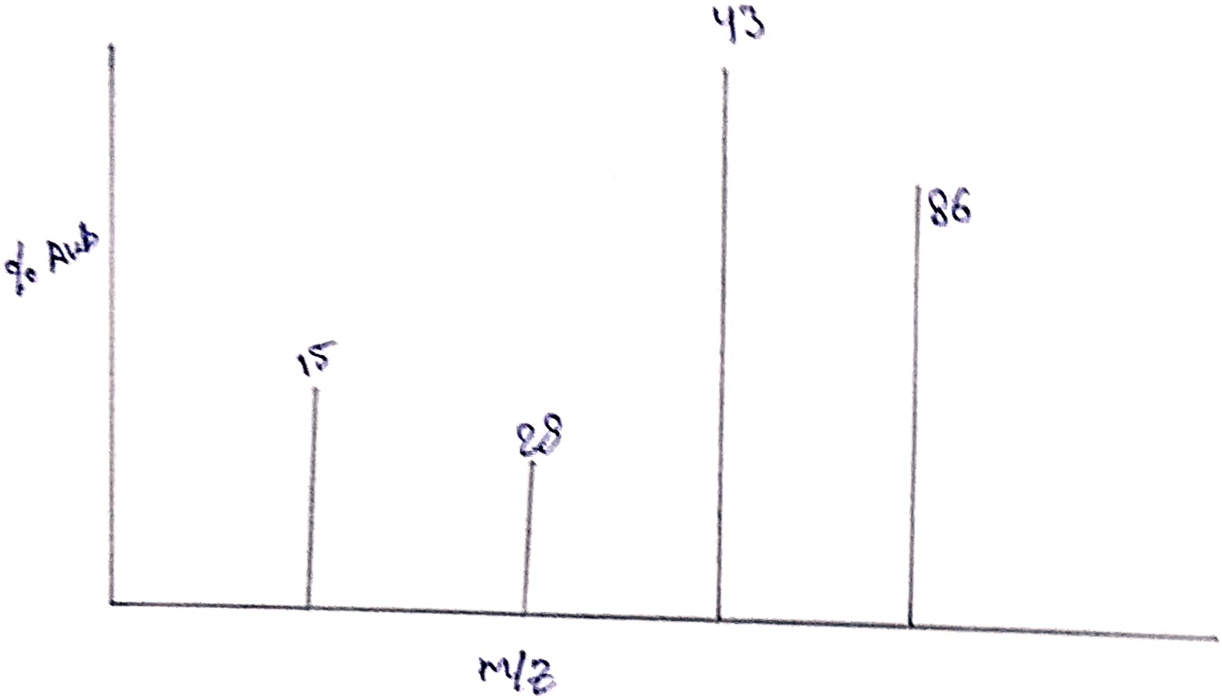
It is attached to electron withdrawing group (C=O)



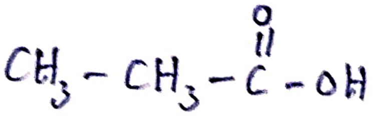
Mass spectra :-



$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{70\ eV} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3^{+\bullet} \longrightarrow \overset{\oplus}{\overset{O}{\overset{\|}{C}}}-CH_3 \xrightarrow{-\dot{C}=O} \overset{\oplus}{C}H_3$$



Propanoic acid :-



$$CH_3-CH_3-\overset{O}{\overset{\|}{C}}-OH$$

IR spectral :-

vibrational stretching frequancy of $\overset{O}{\overset{\|}{C}}$ is 1720 cm^{-1}

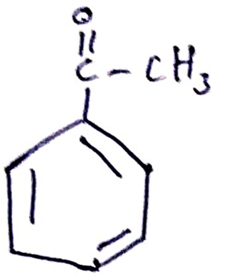
O–H is 2500–3000 cm^{-1}

$\overset{O}{\overset{\|}{C}}-O$ is 1330–1250 cm^{-1}

C–C is 1100–1300 cm^{-1}

C–H is 2850–3000 cm^{-1}

Aceto phenone :



IR spectrum :

$\vartheta_{C=O}$: 1670 cm^{-1}

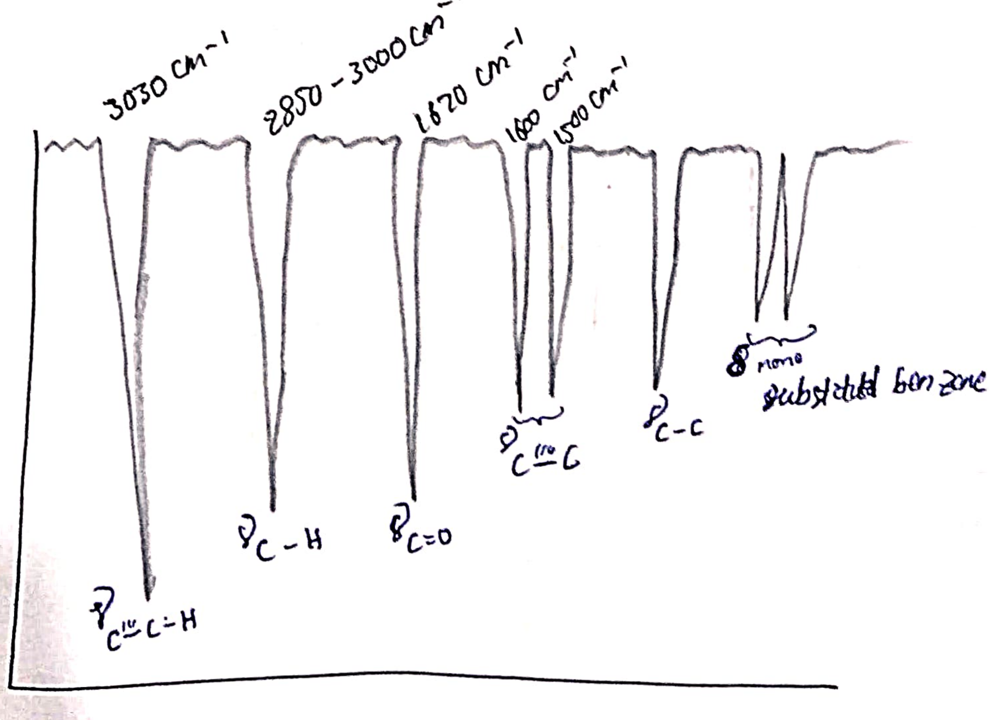
$\vartheta_{C \overset{...}{=} C}$: 1600, 1580, 1500, 1450 cm^{-1}

$\vartheta_{C \overset{...}{=} C-H}$: 3030 cm^{-1}

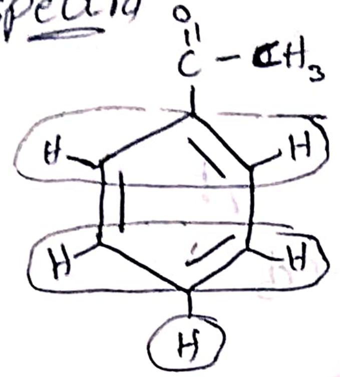
ϑ_{C-H} : 2850 - 3000 cm^{-1}

ϑ_{C-C} : 1100 - 1300 cm^{-1}

$\delta_{\text{mon sub Benzene}}$: 690 cm^{-1}, 710 cm^{-1} } doublet



NMR spectra



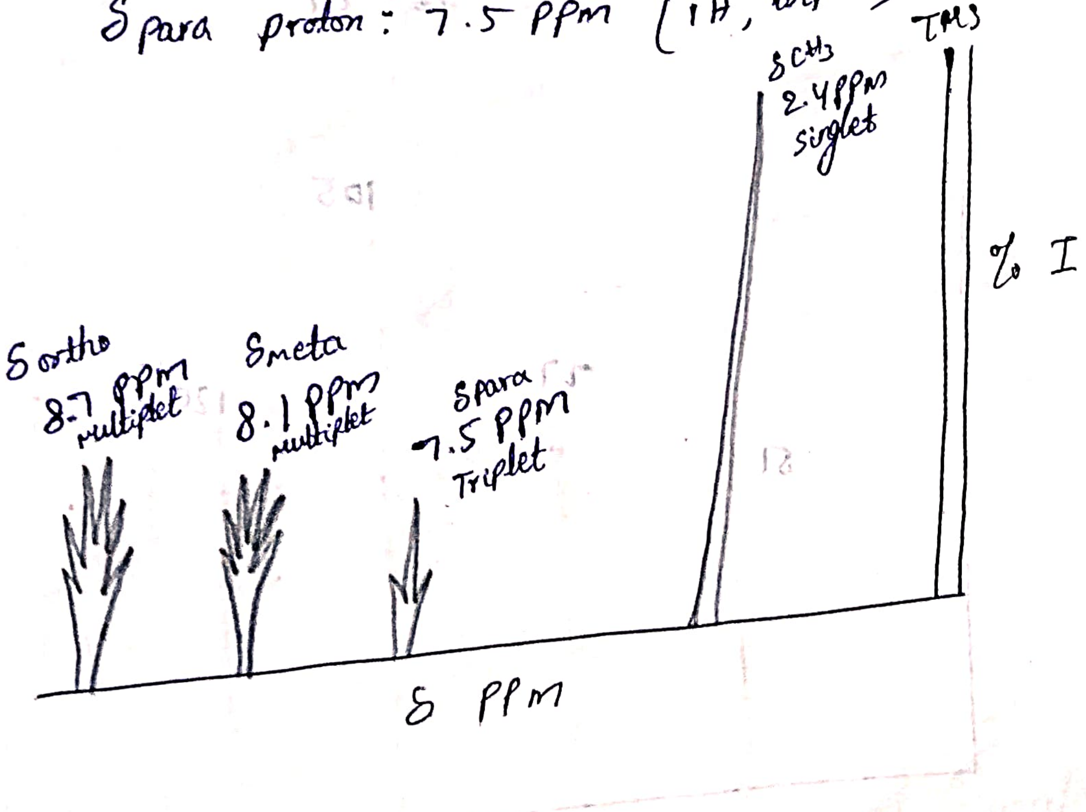
δ_{CH_3} : 2.4 ppm

chemical shift value of methyl is δ_{CH_3} : 2.4 PPM because it is attached to the withdrawing group $\overset{O}{\overset{\|}{C}}$. it is 3H protons and singlet.

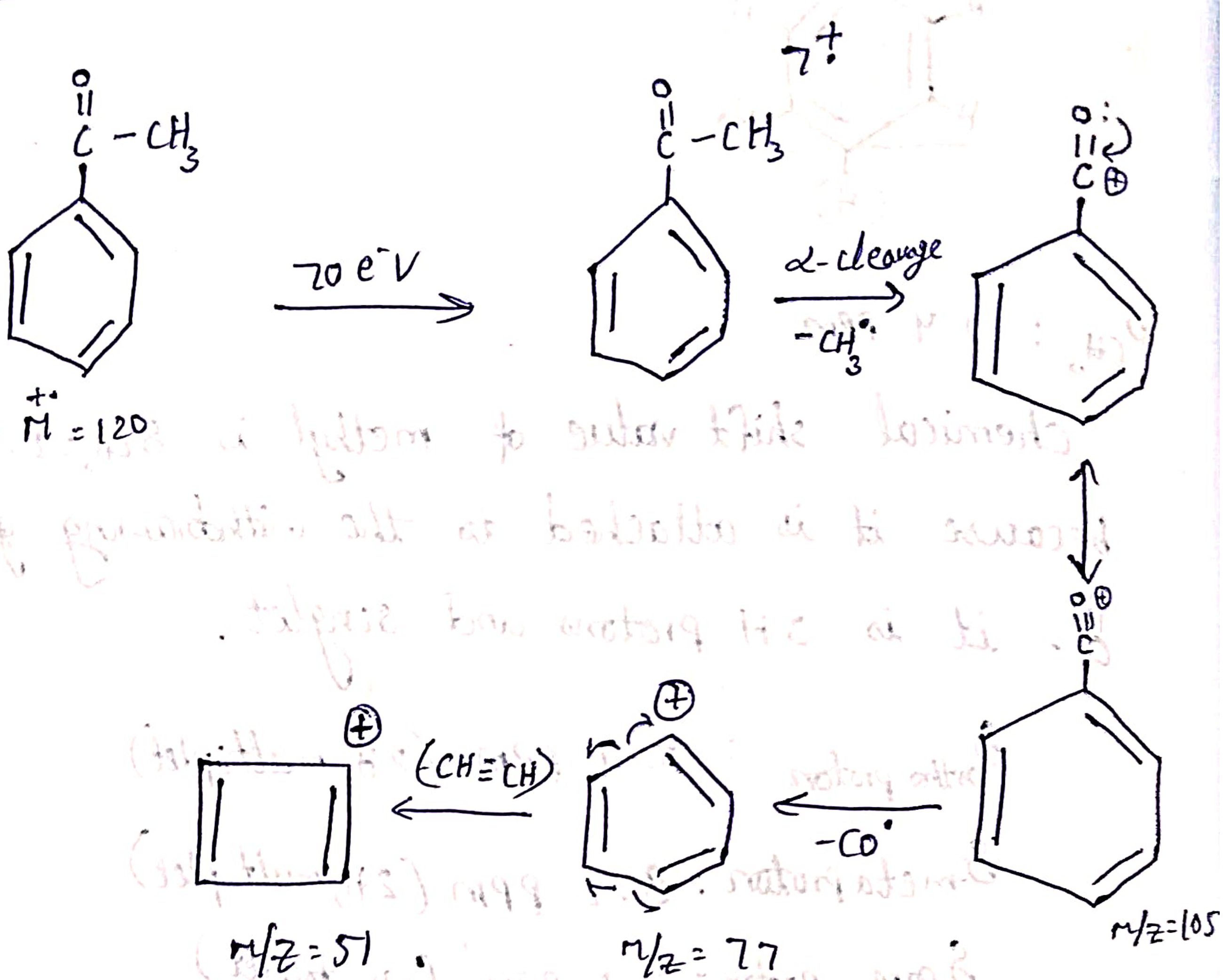
$\delta_{\text{ortho proton}}$: 8.7 PPM (2H, multiplet)

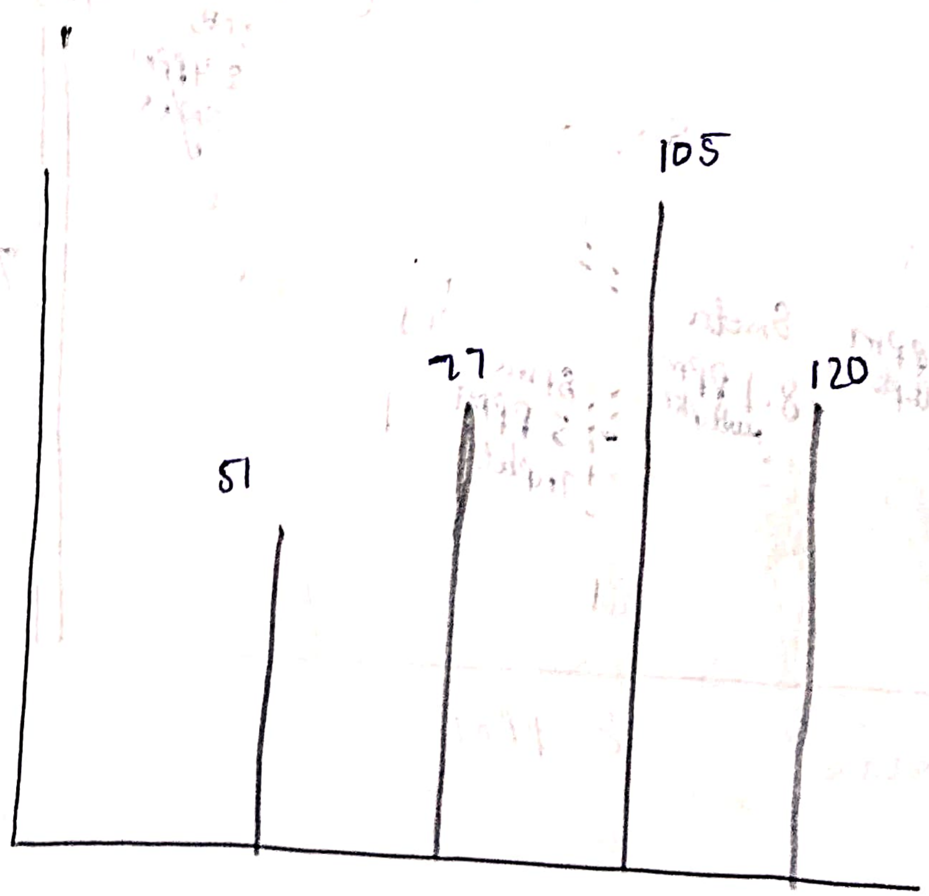
$\delta_{\text{meta proton}}$: 8.1 PPM (2H, multiplet)

$\delta_{\text{para proton}}$: 7.5 PPM (1H, triplet)

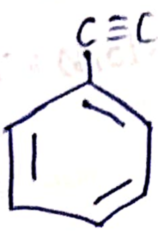


Mass spectra :





Phenyl Acetalene :



IR spectrum :

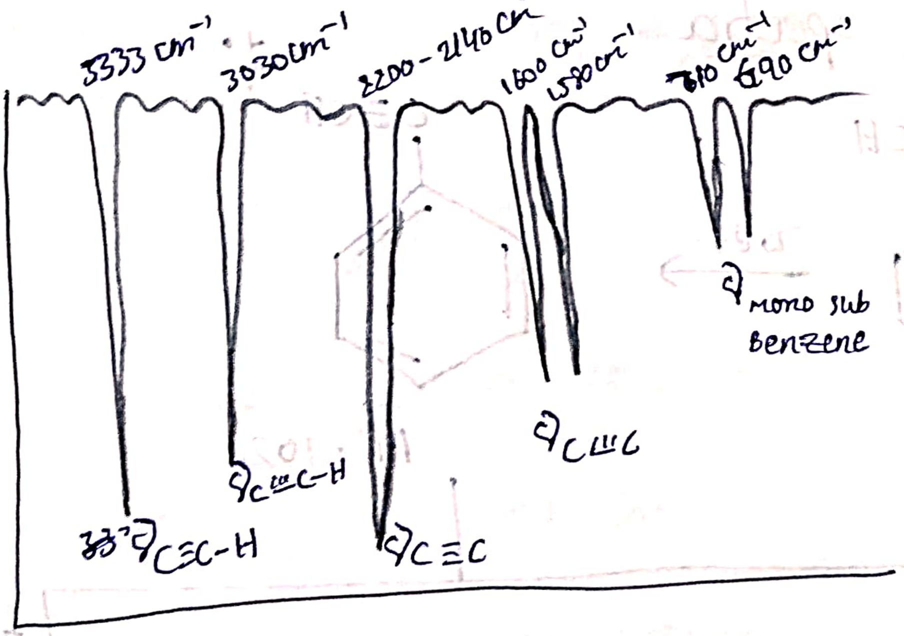
$\vartheta_{C\equiv C}$: 2140 - 2200 cm^{-1}

$\vartheta_{C\equiv C-H}$: 3333 cm^{-1}

$\vartheta_{C \overset{\cdots}{=} C}$: 1600, 1580, 1500, 1450 cm^{-1}

$\vartheta_{C \overset{\cdots}{=} C-H}$: 3030 cm^{-1}

$\vartheta_{\text{mono sub Benzen}}$: $\left.\begin{matrix}690\\710\end{matrix}\right\}$ doublet

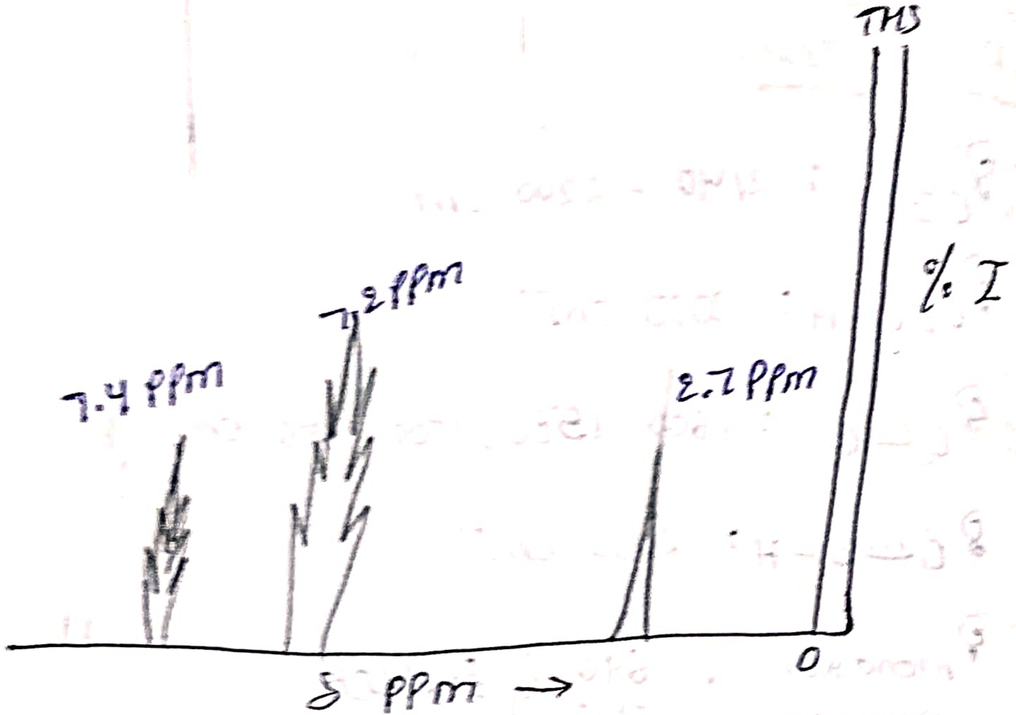


NMR spectrum

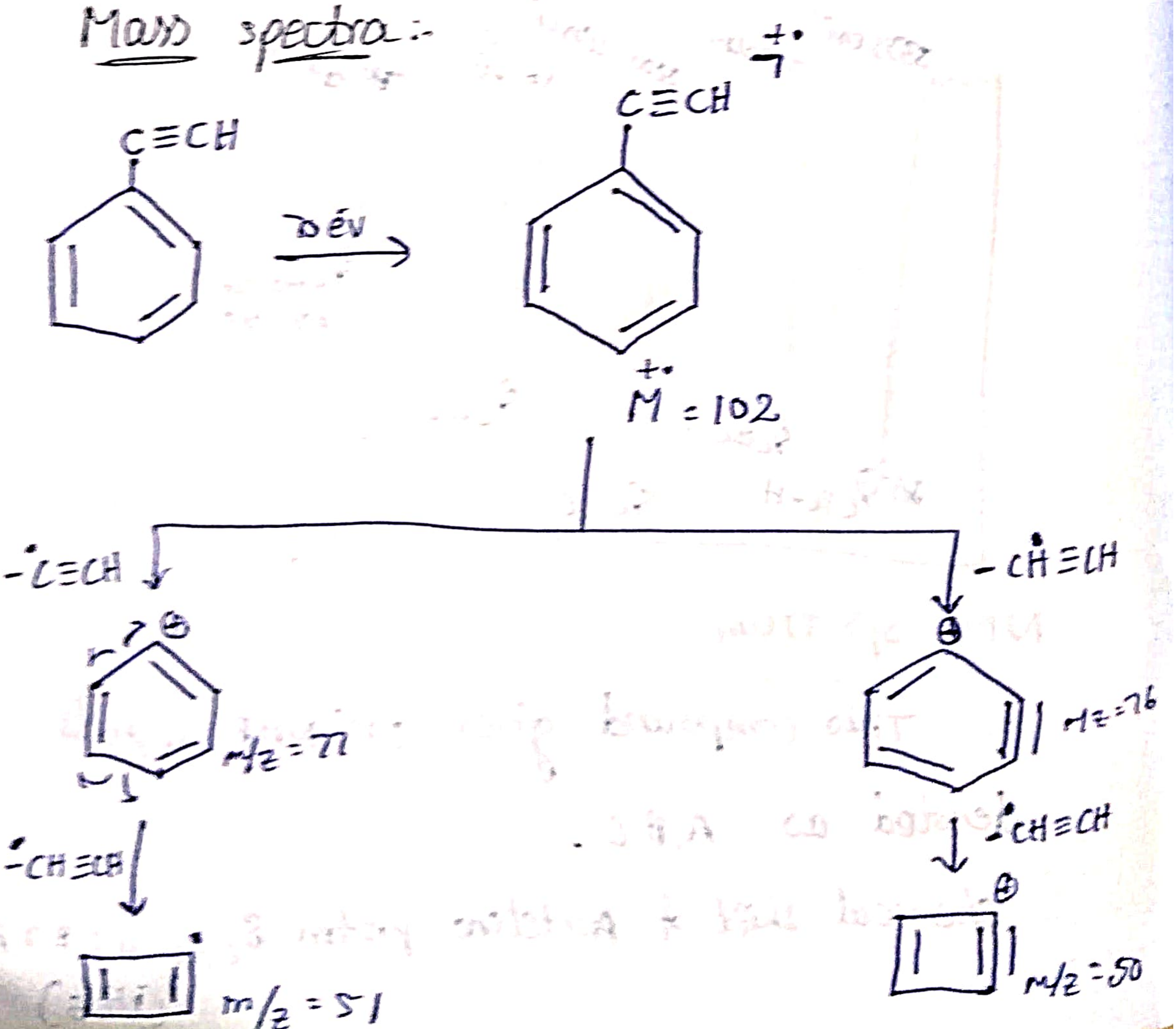
This compound gives 3 H' NMR signals denoted as A, B, C.

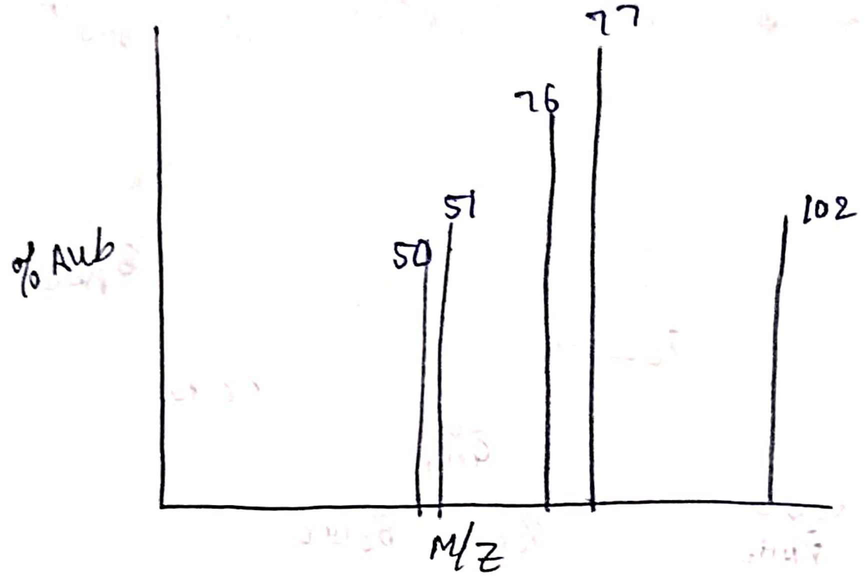
Chemical shift of Acetelene proton $\delta_{C\equiv C-H}$: 2.7 PPm (1H, S) chemical shift of ortho protons is 7.4 ppm (2H, multi)

chemical shift of meta & para protons : 7.2 ppm (3H, multiplet)

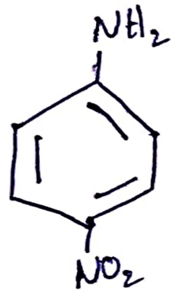


Mass spectra :-





Para-nitro aniline :-



Vibrational stretching frequancy of NH gives 3500-3300 cm^{-1} indicates 1° amine.

ϑ_{-NH_2} : $\left.\begin{matrix}3500\\3300\end{matrix}\right\}$ doublet

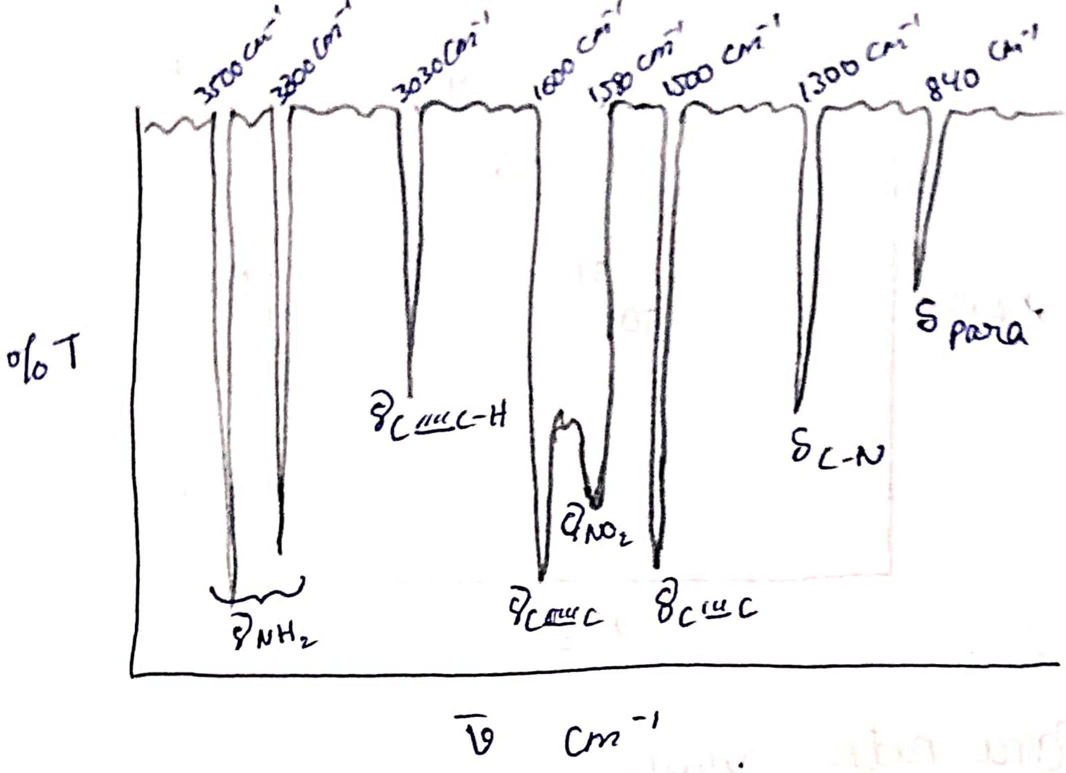
$\delta_{C \overset{...}{=} C}$: 1600, 1580, 1500, 1450 cm^{-1}

$\vartheta_{C \overset{...}{=} C-H}$: 3030 cm^{-1}

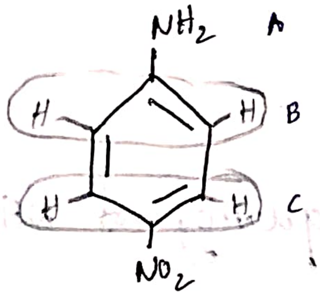
ϑ_{N-O} : 1530 - 1580 cm^{-1}

ϑ_{C-N} : 1310 - 1200 cm^{-1}

$\delta_{\text{Para disub}}$: 840 cm^{-1}

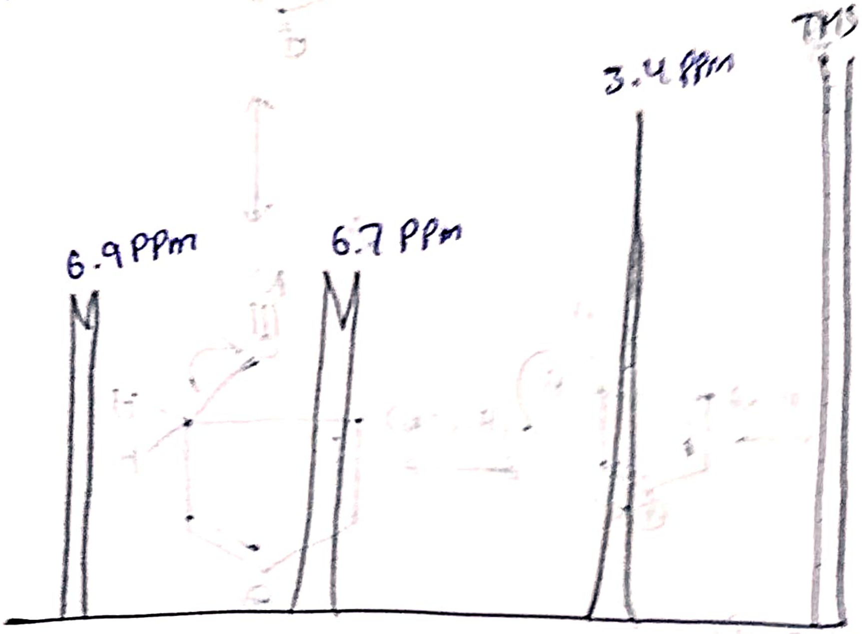


NMR spectrum :-

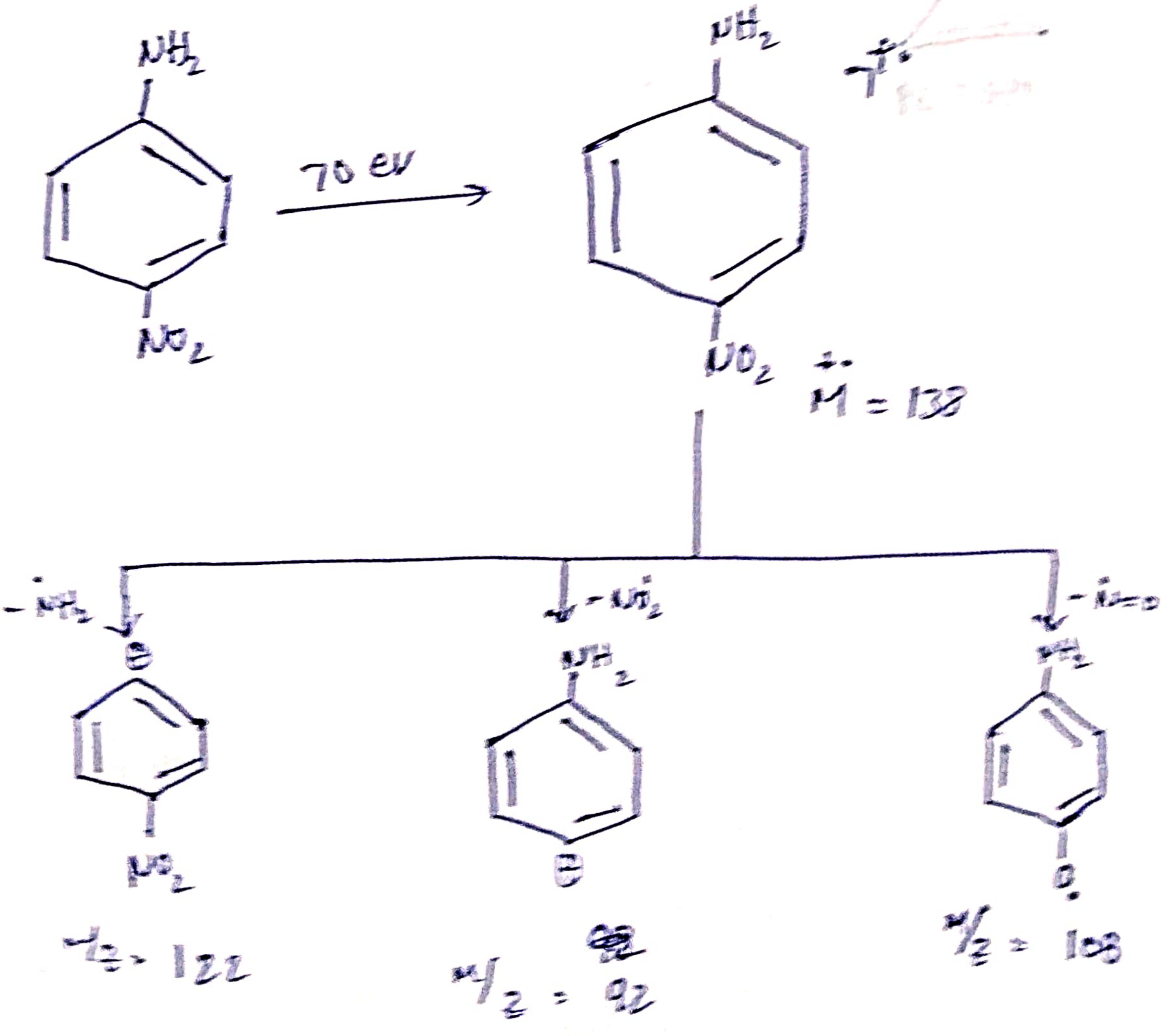


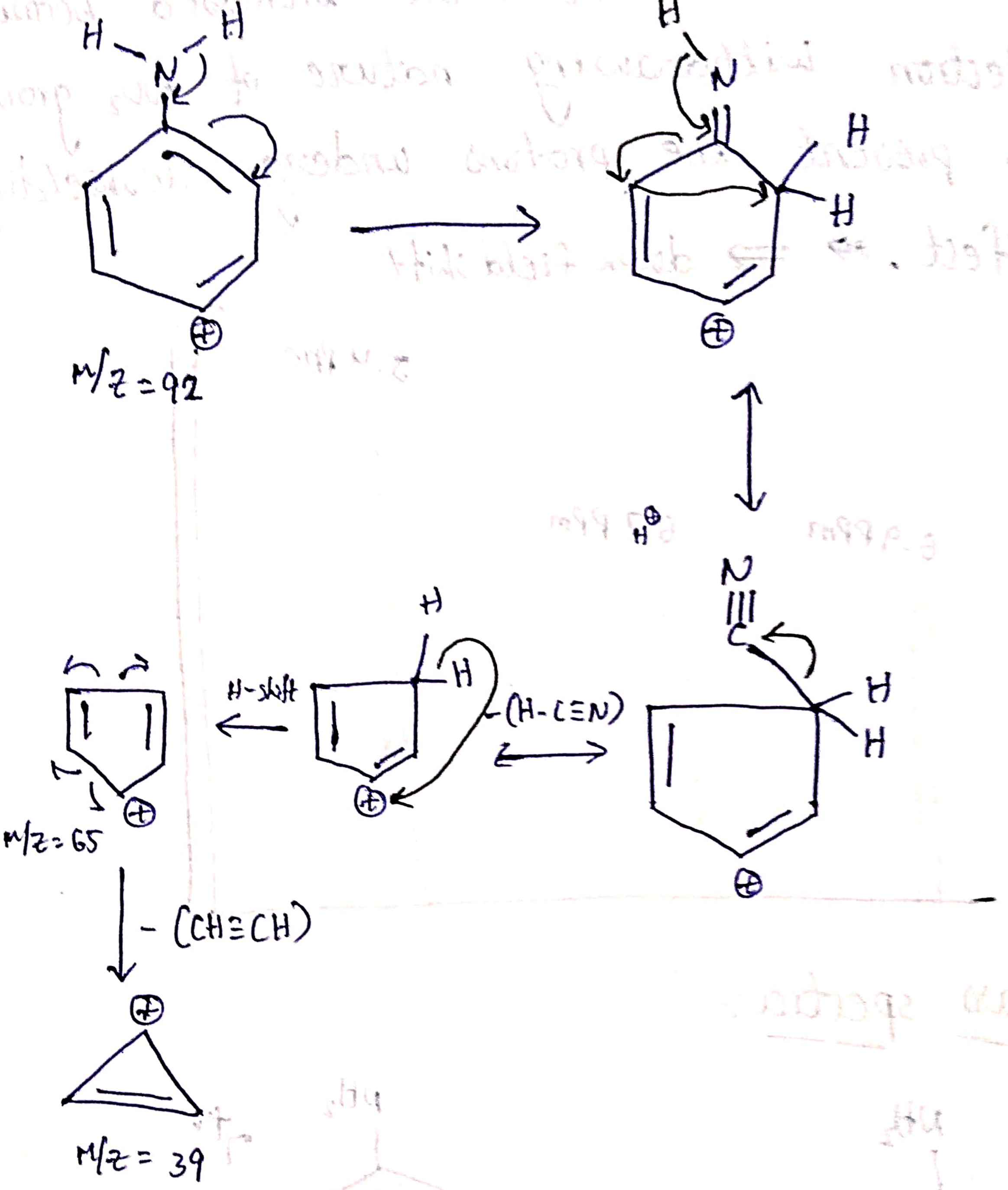
- In this compound 3 signals are present in H^1 NMR spectrum.
- chemical shift of amine Protons $\delta_{NH_2} = 3.4$ PPm, s
- chemical shift of ortho protons nearer to amine group is $\delta_{CH_2} = 6.7$ PPm doublet with 1:1 integral multiple ration
- The chemical shift is presented due to presence electrone donating nature of amine group then protons undergo shielding effect. ⇒ upfield shift.
- The chemical shift of ortho protons nearer to Nitro group is 8.9 PPm, doublet, with 1:1 ratio.

* The chemical shift value increased because electron withdrawing nature of NO_2 group is present, the protons undergo deshielding effect. ⇒ down field shift



Mass spectra:




m/z = 92
H-shift
-(H-C≡N)
m/z = 65
-(CH≡CH)
m/z = 39