B. Sc. III Year (Sem-VI)

PMR Spectroscopy

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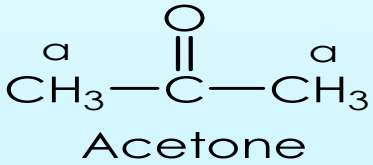
Introduction

- PMR spectroscopy is most useful method for detection of structure of organic compounds.
- **It is used for detection of nature of protons in organic compounds**.
- Most of the organic molecules deals with study of proton, hence called as PMR spectroscopy. Radio frequency 10^7 to 10^8 μ is required for this resonance.

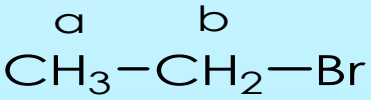
Types of protons

- There are two types of proton.
- **1) Equivalent protons :** A set of protons with same (identical) environment, such protons are called as equivalent protons.
- Ex.



Acetone

- In acetone, all six protons having same environment therefore they are called as equivalent protons.
- **2) Non-equivalent protons :** A set of protons with different environment, such protons are called as non-equivalent protons.
- Ex.

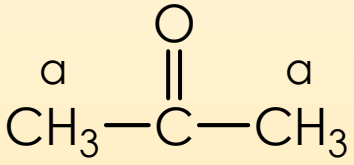


Ethyl bromide

- In ethyl bromide, a set of CH_3 protons having same environment and a set of CH_2 protons having same environment but set of CH_3 protons and set of CH_2 protons having different environment, therefore they are called as non equivalent protons.

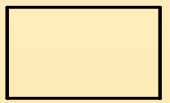
PMR signals of following compound

- 1) Acetone :

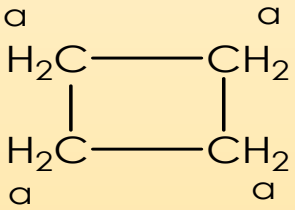


1 PMR signal

- 2) Cyclobutane :

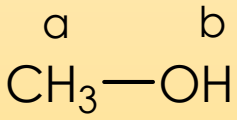


Or



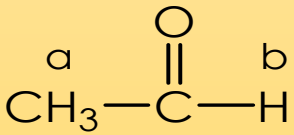
1 PMR signal

- 3) Methanol :



2 PMR signals

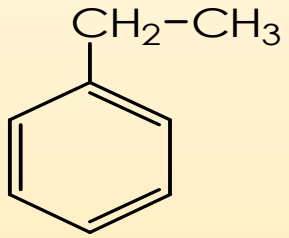
- 4) Acetaldehyde :



2 PMR signals

PMR signals of following compound

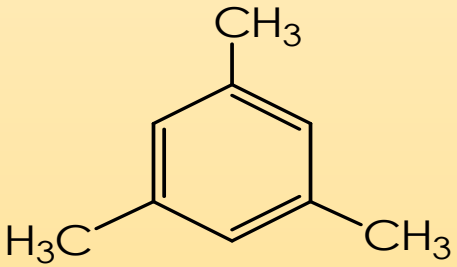
- 5) Ethyl benzene :



- 6) Ethyl amine :

$CH_3–CH_2–NH_2$

- 7) Mesitylene :

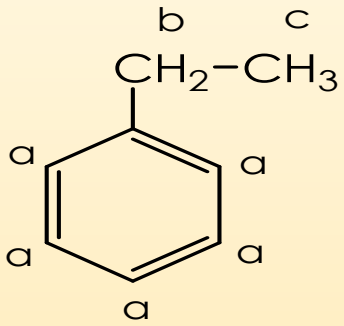


- 8) Diethyl ether :

$CH_3–CH_2–O–CH_2–CH_3$

PMR signals of following compound

- 5) Ethyl benzene :



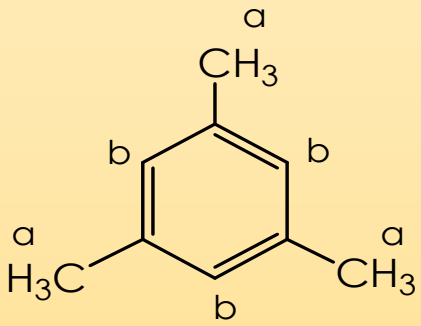
3 PMR signals

- 6) Ethyl amine :

a b c
$CH_3-CH_2-NH_2$

3 PMR signals

- 7) Mesitylene :



2 PMR signals

- 8) Diethyl ether :

a b b a
$CH_3-CH_2-O-CH_2-CH_3$

2 PMR signals

PMR signals of following compound

- 9) Ethyl bromide :

$$CH_3-CH_2-Br$$

PMR signals of following compound

- 9) Ethyl bromide :

a b

CH_3-CH_2-Br

2 PMR signals

Chemical Shift

- The difference in absorption position of proton with respect to TMS signal is called as chemical shift.
- Chemical shift is caused due to shielded and deshielded protons. It is measured in δppm.
- **a) Shielded protons in Acetylene :**

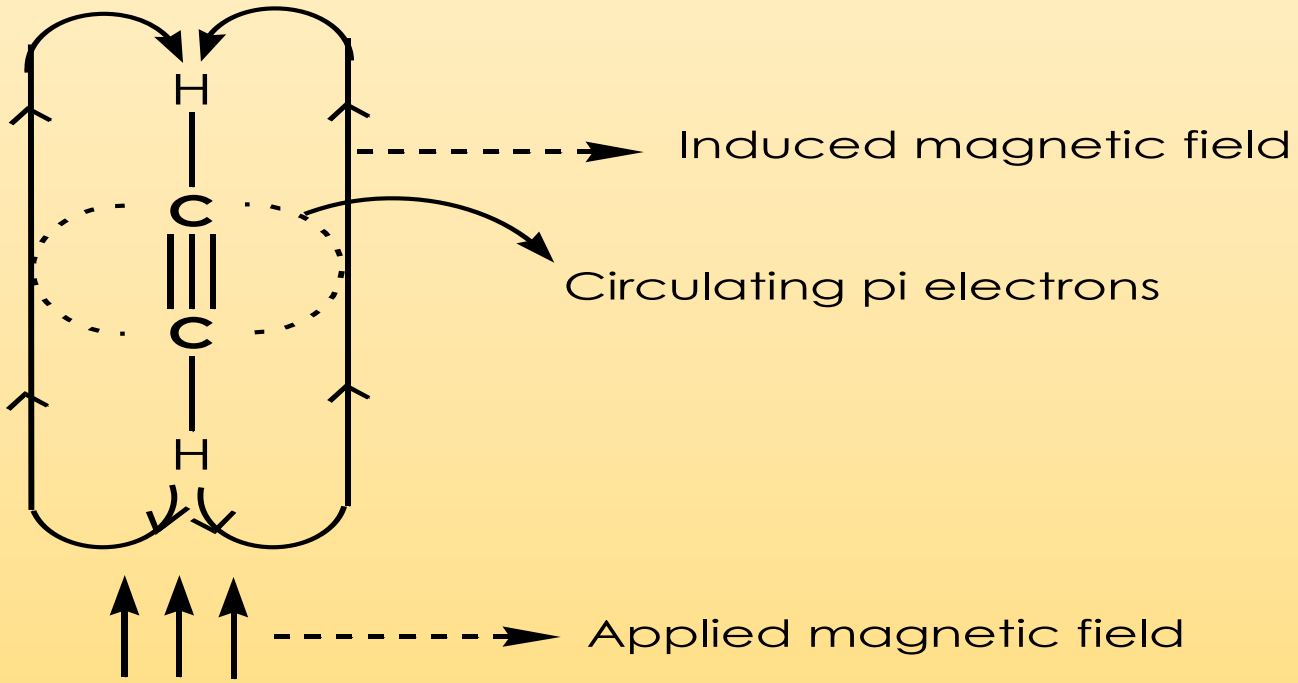


Fig. : Showing Shielded protons in Acetylene

- Acetylene molecule is linear and triple bond in acetylene molecule is symmetrical about axis.
- When acetylene molecule is placed in applied external magnetic field, the circulating π-electrons of triple bond generate its own magnetic field called as induced magnetic field.
- This induced magnetic field opposes to applied external magnetic field. Hence this effect is called as shielding effect.
- Therefore protons in acetylene appears towards upfield region and proton is said to be diamagnetic.

Deshielded protons in benzene

- Benzene is planner and hexagonal molecule. When benzene molecule is placed in applied external magnetic field, the circulating π-electrons of benzene generate its own magnetic field called as induced magnetic field.

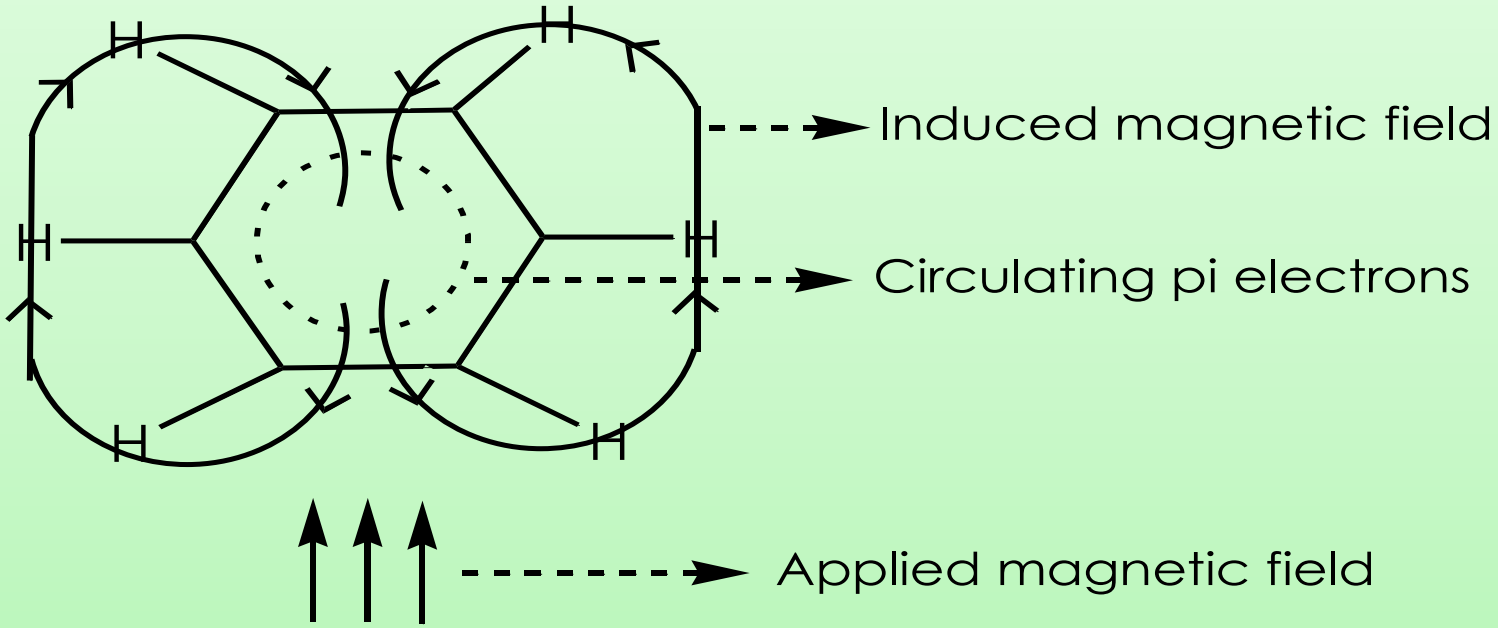
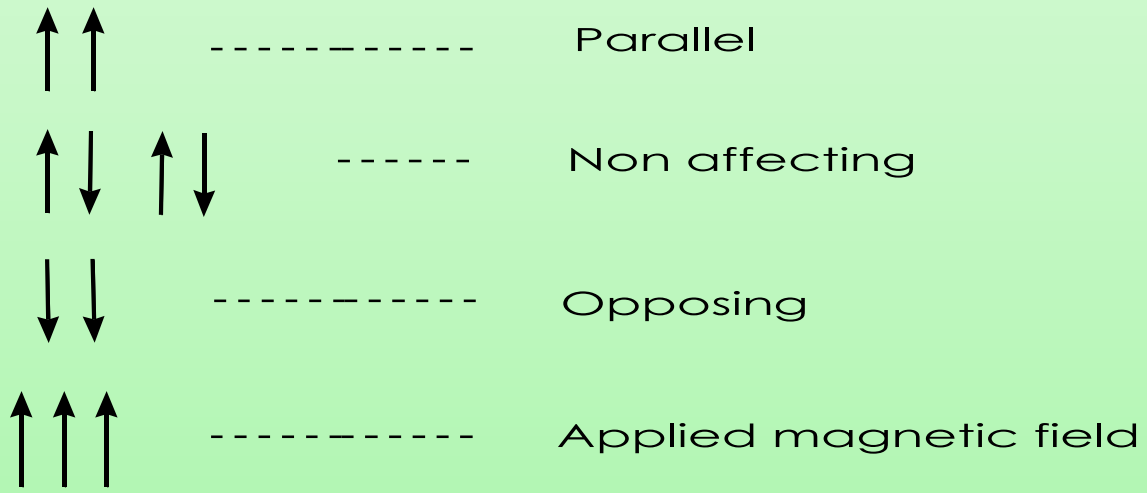


Fig. : Showing deshielded protons in Benzene

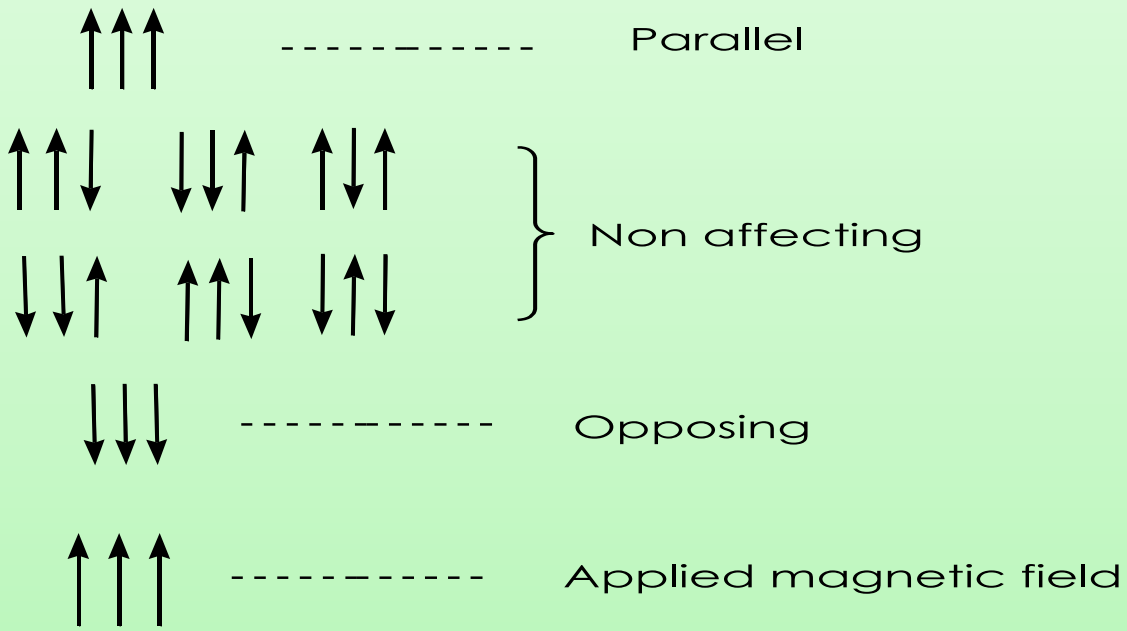
- Due to horizontal planner structure of benzene, protons lie in the region where direction of induced magnetic field and applied external magnetic field is same. Hence this effect is called as deshielding effect.
- Therefore protons in benzene appears towards downfield region and proton is said to be paramagnetic.

Spin-spin splitting

- Splitting of PMR signal is called spin-spin splitting.
- Splitting of signal caused due to magnetic influence of hydrogens on adjacent carbons.
- Spin –spin splitting is observed only in non equivalent protons present on adjacent carbons.
- Ex. In CH_3-CH_2-Br molecule.
- **Signal of –CH_3 group :**
- Spin of two protons of -CH_2 group couple with adjacent -CH_3 group in three different ways relative to external magnetic field as follows.



- Thus, signal of $-CH_3$ protons split into 3 peaks i.e. triplet (t) having intensity 1:2:1
- **Signal of $-CH_2$ group :**
- Similarly, spin of three protons of $-CH_3$ can couple with adjacent $-CH_2$ group in four different ways relative to external magnetic field as follows.



- Thus, signal of $-CH_2$ protons split into 4 peaks i.e. quartet (q) having intensity 1:3:3:1

TMS

- Tetramethyl silane (TMS) is used as reference point in NMR spectroscopy because all the protons in TMS absorbed radiofrequency towards upfield region at zero δ value.
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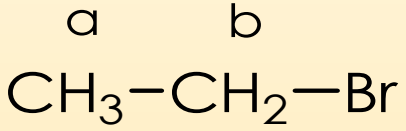
- Tetramethyl silane is known as TMS.
- **Advantages of TMS :**
- i) TMS is used as reference in NMR spectroscopy.
- ii) TMS gives only one band in upfield region relative to organic compound.
- iii) TMS is highly volatile and easily removable.
- iv) TMS gives sharp instance band at low concentration.

Coupling constant

- The distance between the centers of two adjacent bands in a multiplet is called as coupling constant. It is denoted by J. Generally J value is always observed in between 0-20 Hertz.

PMR signals of following compounds

- 1) Ethyl bromide :

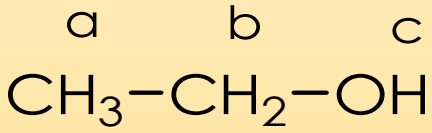


2 PMR signals

δ 1.5, t, 3H of $-CH_3$

δ 3.4, q, 2H of $-CH_2$

- 2) Ethyl alcohol :



3 PMR signals

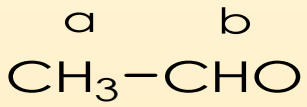
δ 1.3, t, 3H of $-CH_3$

δ 3.5, q, 2H of $-CH_2$

δ 4.5, s, 1H of –OH

PMR signals of following compounds

- 3) Acetaldehyde :

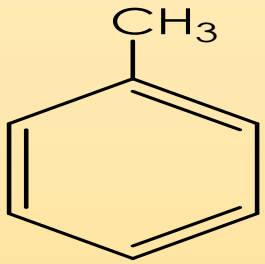


2 PMR signals

δ 2.33, d, 3H of $–CH_3$

δ 9.9, q, 1H of –CHO

- 4) Toluene :



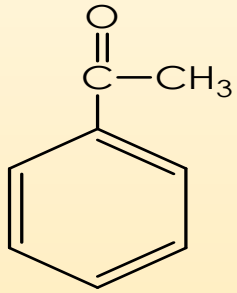
2 PMR signals

δ 2.3, s, 3H of $–CH_3$

δ 7.1, s, 5H of Ar-H

PMR signals of following compounds

- 5) Acetophenone :



2 PMR signals

δ 2.33, s, 3H of $-CH_3$

δ 7.1, m, 5H of Ar-H

- 6) Ethyl amine :

$CH_3-CH_2-NH_2$

3 PMR signals

δ 1.5, t, 3H of $-CH_3$

δ 2.5, q, 2H of $-CH_2$

δ 2.0, s, 2H of $-NH_2$

PMR signals of following compounds

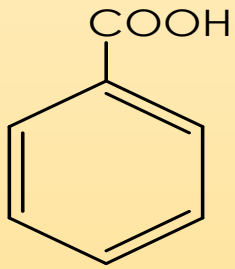
- 7) Acetic acid : CH_3-COOH

2 PMR signals

δ 2.1, s, 3H of $–CH_3$

δ 10.5, s, 1H of –COOH

- 8) Benzoic acid :



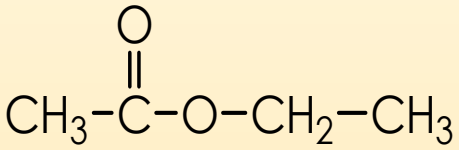
2 PMR signals

δ 7.1, s, 5H of Ar-H

δ 10.5, s, 1H of –COOH

PMR signals of following compounds

- 9) Ethyl acetate :



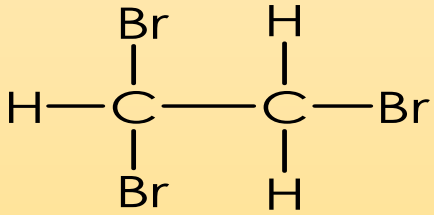
3 PMR signals

δ 1.5, t, 3H of $-CH_3$

δ 3.5, q, 2H of $-CH_2$

δ 2.3, s, 3H of $-CH_3$

- 10) 1,1,2-tribromo ethane :



2 PMR signals

δ 3.5, t, 1H of –CH

δ 3.5, d, 2H of $-CH_2$

Combine problems on UV, IR and PMR spectroscopy

1) A organic compound having molecular formula C_3H_8O gave the following spectral data :

UV : Transparent above λmax 210 nm.

IR : 3400, 2890, 1050 cm^{-1}

PMR (δppm) : δ 1.2 (t, J = 7.5 Hz, 3H)

δ 2.6 (sextet, J = 7.5 Hz, 2H)

δ 3.5 (t, J = 7.5 Hz, 2H)

δ 4.5 (s, 1H, exchangeable with D_2O)

Deduce the structure of following compound.

$$DBE = X + 1 - \frac{Y}{2}$$

$$= 3 + 1 - \frac{8}{2} = 4 - 4 = 0$$

X = No. of carbon atoms

Y = No. of hydrogen atoms

Shows absence of double bond.

UV : Transparent above λmax 210 nm, shows absence of conjugation.

IR : 3400 cm^{-1} due to O-H stretching.

2890 cm^{-1} due to C-H stretching.

1050 cm^{-1} due to C-O stretching of primary alcohol.

PMR : 4 PMR signals

δ 1.2, t, 3H, J = 7.5 Hz, due to $-CH_3$ group

δ 2.6, sextet, 2H, 7.5 Hz, due to $-CH_2$ group

δ 3.5, t, 2H, J = 7.5 Hz due to $-CH_2$ group

δ 4.5, s, 1H due to O-H group.

Hence, the structure of compound is,

$CH_3-CH_2-CH_2-OH$ 1-propanol

- 2) A organic compound having molecular formula C_3H_8O gave the
- following spectral data :
- UV : Transparent above λmax 215 nm.
- IR : 3500, 2910, 1100 cm^{-1}
- PMR (δppm) : δ 1.4 (d, J = 6 Hz, 6H)
- δ 3.8 (septet, J = 6 Hz, 1H)
- δ 4.5 (s, 1H, exchangeable with D_2O)
- Deduce the structure of following compound.
-

2) A organic compound having molecular formula C_3H_8O gave the following spectral data :

UV : Transparent above λmax 215 nm.

IR : 3500, 2910, 1100 cm^{-1}

PMR (δppm) : δ 1.4 (d, J = 6 Hz, 6H)

δ 3.8 (septet, J = 6 Hz, 1H)

δ 4.5 (s, 1H, exchangeable with D_2O)

Deduce the structure of following compound.

$$DBE = X + 1 - \frac{Y}{2}$$

$$= 3 + 1 - \frac{8}{2} \qquad = 4 - 4 \quad = 0$$

Shows absence of double bond.

UV : Transparent above λmax 215 nm, shows absence of conjugation.

IR : 3500 cm^{-1} due to O-H stretching.

2910 cm^{-1} due to C-H stretching.

1100 cm^{-1} due to C-O stretching of secondary alcohol.

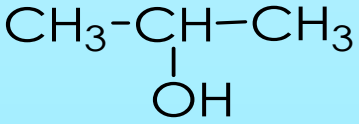
PMR : 3 PMR signals

δ 1.4, d, 6H due to $-CH_3$ group

δ 3.8, septet, 1H due to –CH group

δ 4.5, s, 1H due to O-H group.

Hence, the structure of compound is :



2-propanol

- 3) A organic compound having molecular formula $C_4H_{10}O$ gave the following spectral data :
- UV : Transparent above λmax 210 nm.
- IR : 3310, 2970, 1150 cm^{-1}
- PMR (δppm) : δ 1.3 (s, 9H)
- δ 4.5 (s, 1H, exchangeable with D_2O)
- Deduce the structure of following compound.

3) A organic compound having molecular formula $C_4H_{10}O$ gave the following spectral data :

UV : Transparent above λmax 210 nm.

IR : 3310, 2970, 1150 cm^{-1}

PMR (δppm) : δ 1.3 (s, 9H)

δ 4.5 (s, 1H, exchangeable with D_2O)

Deduce the structure of following compound.

$$DBE = X + 1 - \frac{Y}{2}$$

$$= 4 + 1 - \frac{10}{2} = 5 - 5 = 0$$

Shows absence of double bond.

UV : Transparent above λmax 210 nm, shows absence of conjugation.

IR : 3310 cm^{-1} due to O-H stretching.

2970 cm^{-1} due to C-H stretching.

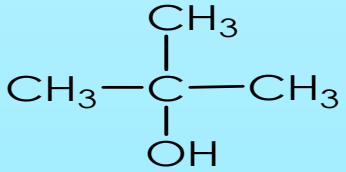
1150 cm^{-1} due to C-O stretching of tertiary alcohol.

PMR : 2 PMR signals

δ 1.3, s, 9H due to $-CH_3$ group

δ 4.5, s, 1H due to O-H group.

Hence, the structure of compound is :



2-methyl-2-propanol (t-butyl alcohol)

4) A organic compound having molecular formula C_4H_8O gave the following spectral data :

UV : λmax 283 nm.

IR : 2940, 1705 cm^{-1}

PMR (δppm) : δ 1.07 (t, J = 7.2 Hz, 3H)

δ 2.48 (q, J = 7.2 Hz, 2H)

δ 2.12 (s, 3H)

Deduce the structure of following compound.

4) A organic compound having molecular formula C_4H_8O gave the following spectral data :

UV : λmax 283 nm.

IR : 2940, 1705 cm^{-1}

PMR (δppm) : δ 1.07 (t, J = 7.2 Hz, 3H)

δ 2.48 (q, J = 7.2 Hz, 2H)

δ 2.12 (s, 3H)

Deduce the structure of following compound.

$$DBE = X + 1 - \frac{Y}{2}$$

$$= 4 + 1 - \frac{8}{2} \qquad = 5 - 4 \quad = 1$$

Shows one double bond.

UV : λmax 283 nm, due to n-π* transition .

IR : 2940 cm^{-1} due to C-H stretching.

1705 cm^{-1} due to C=O stretching.

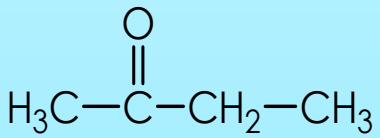
PMR : 3 PMR signals

δ 1.07, t, 3H due to $-CH_3$ group

δ 2.48, q, 2H due to $-CH_2$ group

δ 2.12, s, 3H due to $-CH_3$ group.

Hence, the structure of compound is :



2-butanone (Ethyl methyl ketone)

- 5) A organic compound having molecular formula C_3H_6O gave the
- following spectral data :
- UV : λmax 290 nm.
- IR : 2980, 2720, 1740 cm^{-1}
- PMR (δppm) : δ 1.1 (t, J = 6 Hz, 3H)
- δ 2.5 (q, J = 6 Hz, 2H)
- δ 9.6 (t, 1H)
- Deduce the structure of following compound.
-

- DBE = $X + 1 - \frac{Y}{2}$
- $= 3 + 1 - \frac{6}{2}$ $= 4 - 3 = 1$
- Shows presence of one double bond.
- **UV :** λmax 290 nm, due to n-π* transition .
- **IR :** 2980 cm^{-1} due to C-H stretching.
- 2720 cm^{-1} due to –CH of -CHO stretching.
- 1740 cm^{-1} due to C=O stretching.
- **PMR :** 3 PMR signals
- δ 1.1, t, 3H due to $-CH_3$ group
- δ 2.5, quintet, 2H due to $-CH_2$ group
- δ 9.6, t, 1H due to –CHO group.
- Hence, the structure of compound is,
- CH_3-CH_2-CHO
- Propanal (propionaldehyde)

6) A organic compound having molecular formula C_3H_5N gave the following spectral data :

UV : Transparent above λmax 210 nm.

IR : 2980, 2250 cm^{-1}

PMR (δppm) : δ 1.1 (t, J = 6 Hz, 3H)

δ 3.5 (q, J = 6 Hz, 2H)

Deduce the structure of following compound.

$$DBE = X + 1 - \frac{Y - Z}{2}$$

Z= No. of Nitrogen atoms.

$$= 3 + 1 - \frac{5 - 1}{2} \quad = 4 - 2 \quad = 2$$

Shows presence of two double bonds.

UV : Transparent above λmax 210 nm, shows absence of conjugation.

IR : 2980 cm^{-1} due to C-H stretching.

2250 cm^{-1} due to -CN stretching.

PMR : 2 PMR signals

δ 1.1, t, 3H due to $-CH_3$ group

δ 3.5, q, 2H due to $-CH_2$ group

Hence, the structure of compound is,

CH_3-CH_2-CN Ethyl cyanide (propionitrile)

- 7) A organic compound having molecular formula C_3H_8O gave
- the following spectral data :
- UV : Transparent above λmax 210 nm.
- IR : 2970, 2880, 1110 cm^{-1}
- PMR (δppm) : δ 1.1 (t, J = 6 Hz, 3H)
- δ 3.4 (q, J = 6 Hz, 2H)
- δ 2.4 (s, 3H)
- Deduce the structure of following compound.
-

- DBE = X + 1 - $\frac{Y}{2}$
- = 3 + 1 – $\frac{8}{2}$ = 4 – 4 = 0
- Shows absence of double bond.

- **UV :** Transparent above λmax 210 nm, shows absence of conjugation.

- **IR :** 2970, 2880 cm^{-1} due to C-H stretching.
  1110 cm^{-1} due to C-O-C stretching.

- **PMR :** 3 PMR signals
  δ 1.1, t, 3H due to $-CH_3$ group
  δ 3.4, q, 2H due to $-CH_2$ group
  δ 2.4, s, 3H due to $-CH_3$ group.

- Hence, the structure of compound is,

$$CH_3-CH_2-O-CH_3$$

- Ethyl methyl ether (Methoxy ethane)

- **8) A organic compound having molecular formula $C_2H_4O_2$ gave the following spectral data :**
- **UV : λmax 204 nm (Emax = 50)**
- **IR : Broad band between 3100 - 2700, 2940, 1720 cm^{-1}**
- **PMR (δppm) : δ 2.1 (s, 3H)**
- **δ 9.8 (s, 1H, exchangeable with D_2O)**
- **Deduce the structure of following compound.**

➢ $DBE = X + 1 - \frac{Y}{2}$

$= 2 + 1 - \frac{4}{2} \quad = 3 - 2 \quad = 1$

- Shows one double bond.

- **UV :** λmax 204 nm, shows n-π* transitions.
- **IR :** 3100-2700 cm^{-1} due to O-H stretching of -COOH.
- 2940 cm^{-1} due to C-H stretching.
- 1720 cm^{-1} due to C=O stretching.
- **PMR :** 2 PMR signals
- δ 2.1, s, 3H due to $-CH_3$ group
- δ 9.8, s, 1H due to –COOH group
- Hence, the structure of compound is,

CH_3-COOH Acetic acid (Ethanoic acid)

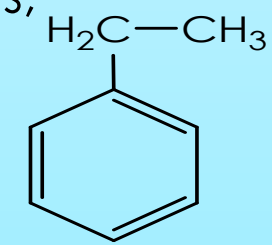
- 9) A organic compound having molecular formula C_8H_{10} gave
- the following spectral data :
- UV : λmax above 255 nm.
- IR : 2920, 3021, 1620, 1550, 1475 cm^{-1}
- PMR (δppm) : δ 1.5 (t, J = 7 Hz, 3H)
- δ 2.3 (q, J = 7 Hz, 2H)
- δ 7.4 (s, 5H)
- Deduce the structure of following compound.

- DBE = X + 1 - $\frac{Y}{2}$

- $= 8 + 1 - \frac{10}{2} = 9 - 5 = 4$

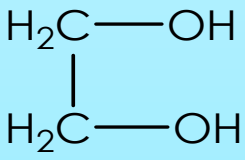
- Shows Four double bonds.
- **UV :** λmax 255 nm, shows conjugation.
- **IR :** 3021 cm^{-1} due to Ar-H stretching.
- 2920 cm^{-1} due to C-H stretching.
- 1620, 1550, 1475 cm^{-1} due to aromatic C=C stretching.
- **PMR :** 3 PMR signals
- δ 1.5, t, 3H due to $-CH_3$ group
- δ 2.3, q, 2H due to $-CH_2$ group
- δ 7.4, s, 5H due to Ar-H group

Hence, the structure of compound is,



Ethyl benzene

- 10) A organic compound having molecular formula $C_2H_6O_2$ gave the following spectral data :
- UV : Transparent above λmax above 210 nm.
- IR : 3400, 2920 cm^{-1}
- PMR (δppm) : δ 4.5 (s, 2H, exchangeable with D_2O)
- δ 3.5 (t, 4H)
- Deduce the structure of following compound.

- DBE = X + 1 - $\frac{Y}{2}$
-
- $= 2 + 1 - \frac{6}{2}$ $= 3 - 3$ $= 0$
- Shows absence of double bond.
- **UV :** Transparent above λmax above 210 nm, shows no
- conjugation.
- **IR :** 3400 cm^{-1} due to O-H stretching.
- 2920 cm^{-1} due to C-H stretching.
- **PMR :** 2 PMR signals
- δ 4.5, s, 2H due to -OH group
- δ 3.5, t, 4H due to $-CH_2$ group
- Hence, the structure of compound is,
- 
- Ethylene glycol (Ethane1,2-diol)

11) A organic compound having molecular formula C_2H_7N gave the following spectral data :

UV : Transparent above λmax above 210 nm.

IR : 3530, 2975 cm^{-1}

PMR (δppm) : δ 1.0 (t, 3H, J = 6 Hz)
δ 2.5 (q, 2H, J = 6 Hz)
δ 2.0 (s, 2H)

Deduce the structure of following compound.

➢ DBE = X + 1 - $\frac{Y-Z}{2}$ Z= No. of Nitrogen atoms.

= 2 + 1 – $\frac{7-1}{2}$ = 3 – 3 = 0

Shows absence of double bond.

UV : Transparent above λmax above 210 nm, shows no conjugation.

IR : 3530 cm^{-1} due to N-H stretching.
2975 cm^{-1} due to C-H stretching.

PMR : 3 PMR signals
δ 1.0, t, 3H due to $–CH_3$ group
δ 2.5, q, 2H due to $–CH_2$ group
δ 2.0, s, 2H due to $–NH_2$ group

Hence, the structure of compound is,

$$CH_3–CH_2–NH_2$$

Ethyl amine (Ethanamine)

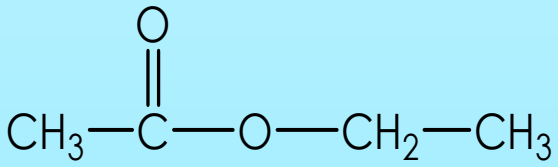
- 12) A organic compound having molecular formula $C_4H_8O_2$ gave
- the following spectral data :
- UV : λmax 211 nm (Emax 57).
- IR : 2983, 1743 , 1243 cm^{-1}
- PMR (δppm) : δ 4.12 (q, J 7.1 Hz, 2H)
- δ 1.26 (t, J 7.1 Hz, 3H)
- δ 2.04 (s, 3H)
- Deduce the structure of following compound.

- DBE = X + 1 - $\frac{Y}{2}$
- $= 4 + 1 - \frac{8}{2} = 5 - 4 = 1$
- Shows one double bond.

- **UV :** λmax above 285 nm, shows n-π* transition.

- **IR :** 2983 cm^{-1} due to C-H stretching.
- 1743 cm^{-1} due to C=O stretching.
- 1243 cm^{-1} due to C-O stretching.

- **PMR :** 3 PMR signals
- δ 4.12, q, 2H due to $-CH_2$ group
- δ 1.26, t, 3H due to $-CH_3$ group
- δ 2.04, s, 3H due to $-CH_3$ group
- Hence, the structure of compound is,



Ethyl acetate (Ethoxy ethanoate)

- 13) A organic compound having molecular formula C_8H_8O gave
- the following spectral data :
- UV : λmax 275 nm.
- IR : 3080, 2910, 2750, 1740, 1620, 1585 cm^{-1}
- PMR (δppm) : δ 2.1 (d, 2H)
- δ 7.1 (m, 5H)
- δ 9.9 (t, 1H)
- Deduce the structure of following compound.

- DBE = X + 1 - $\frac{Y}{2}$

= 8 + 1 – $\frac{8}{2}$ = 9 – 4 = 5

- Shows Five double bonds.

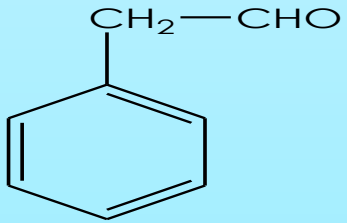
- **UV :** λmax 275 nm, due to n-π* transition.

- **IR :** 3080 cm^{-1} due to Ar-H stretching.
  2910 cm^{-1} due to C-H stretching.
  2750 cm^{-1} due to C-H stretching of –CHO group.
  1740 cm^{-1} due to C=O stretching.
  1620, 1585 cm^{-1} due to aromatic C=C stretching.

- **PMR :** 3 PMR signals
  δ 2.1, d, 2H due to $–CH_2$ group
  δ 7.1, m, 5H due to Ar-H group
  δ 9.9, t, 1H due to –CHO group

- Hence, the structure of compound is,

Phenyl acetaldehyde



- 14) A organic compound having molecular formula C_6H_6O gave
- the following spectral data :
- UV : λmax 280 nm.
- IR : 3395, 3035, 1625, 1540, 1200 cm^{-1}
- PMR (δppm) : δ 12.0 (s, 1H)
- δ 7.2 (m, 5H)
- Deduce the structure of following compound.

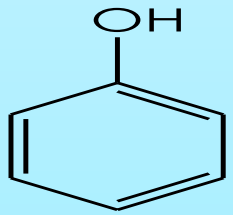
- DBE = $X + 1 - \frac{Y}{2}$

$= 6 + 1 - \frac{6}{2} = 7 - 3 = 4$

- Shows four double bonds.
- **UV :** λmax 280 nm, due to conjugation.

- **IR :** 3395 cm^{-1} due to O-H stretching.
- 3035 cm^{-1} due to Ar-H stretching.
- 1625, 1540 cm^{-1} due to aromatic C=C stretching.
- 1200 cm^{-1} due to C-O stretching.

- **PMR :** 2 PMR signals
- δ 12.0, s, 1H due to –OH group
- δ 7.2, s, 5H due to Ar-H protons.
- Hence, the structure of compound is,



Phenol

Thank You ……