**Study Material**

M.Sc. Part-I (Chemistry)
Course - Org. chem. B (CCTR-61/CHO-250)
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Simple problems based on 13C-NMR

1. Deduce the structure of the following.

   - MP = (C6H10O)
   - N.S.U = (Cn+1) - HO12
   - 10 + 1 = 11
   - 11 / 2 = 5.5
   - 7 - 5 = 02

   - CMR:
     - δ 204 (s) = presence of 1 of ketone (SP2)
       (s = its quaternary carbon)
     - 26 (t, strong) = -CH2- (SP3) x 2
       (strong = it is appeared due to more than one carbon)
     - 28 (t, strong) = -CH2- (SP3) x 2
       (strong = it is appeared due to more than one carbon)
     - 24 (t) = -CH2- (SP3 hybridized)

   The correct structure is -

   ![Structure Diagram]

   - 36
   - 204
   - 28
   - 24
   - Cyclohexanone,
2. \( MF = C_4H_8O \)

N.S.O. = \((4+1) - 8/2 = 5 - 4 = 0\) for Iodoform test

Chemical Information: A positive iodoform test implies:

- Presence of methyl ketone.

**CMR Data:**

a) 207 \( \delta(\delta) \) \(-\text{C} = \text{ketone}(\text{SP}^2)\) carbon.

b) 35 \( \delta(\delta) \) \(-\text{CH}_3\) \((\text{SP}^3)\) carbon

c) 32 \((t)\) \(-\text{CH}_2\) \((\text{SP}^3\) carbon)

d) 28 \( \delta(\delta) \) \(-\text{CH}_2\) \((\text{SP}^3)\) carbon

The correct structure is: \(-\text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3\)
3. \( MF = \text{C}_3\text{H}_7\text{I} \)

For calculating NSU replace I by H then MF becomes \( \text{C}_6\text{H}_8 \)

\[ \text{N.S.U} = (3+1) - 8/2 = 4 - 4 = 0 \]

**CMR data:**

(a) \( 9:2 \text{ (t)} \Rightarrow \) presence of \(-\text{CH}_2-\) (sp\(^3\) hybridised)

(b) \( 15:2 \text{ (q)} \Rightarrow \) presence of \(-\text{CH}_3\) (sp\(^3\) carbon)

(c) \( 27 \text{ (t)} \Rightarrow \) presence of \(-\text{CH}_2-\) (sp\(^3\) carbon)

The correct structure is:

\[ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I} \]

4. \( MF = \text{C}_6\text{H}_{12}\text{N}_2 \)

Replace N by 'CH' then MF becomes \( \text{C}_6\text{H}_{14} \)

\[ \text{N.S.U} = (6+1) - 14/2 = 7 - 7 = 0 \]

**CMR data:**

(a) \( 35 \text{ (t)} \Rightarrow \) \(-\text{CH}_2-\) (sp\(^3\) carbon) \( \times 2 \)

(b) \( 52 \text{ (t)} \Rightarrow \) \(-\text{CH}_2-\) (sp\(^3\) carbon) \( \times 2 \)

The number of signals given in CMR data are two while no. of carbons in MF are four.

\[ \Rightarrow \) each signal is appeared due to two carbons.

The correct structure is:

\[ \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 \]

1,4-butane dianmine
5) **MF:** C₆H₄NO

\[ \text{N.S.U} = (3+1) - 4/2 = 4 - 2 = 2 \]

(CMR Data):

a) 50 (t) = Presence of -CH₂- (sp³ carbon)

b) 74 (d) = Presence of \( \text{CH}_2 \) (sp² carbon)

c) 84 (s) = Presence of \( \text{C}=\text{O} \) (Quaternary carbon)

The probable structure is:

\[ \text{H-C=O-C-CH}_2\text{-OH} \]

6) **MF:** C₄H₅NO₂

\[ \text{NSU} = (5+1) - 16/2 = 6 - 3 = 3 \]

(CMR Data):

a) 60.3 (t) = Presence of -CH₂- (sp³ carbon)

b) 183.6 (s) = Presence of -\( \text{C}=\text{O} \) (sp² carbon)

In CMR only two signals are given, so each signal appeared due to more than one carbon.

The correct structure is:

Three s.u.

- 183.6 \( \Rightarrow \) two satisfied
- 80.3 (t) \( \Rightarrow \) in \( \text{CH}_2 \) group at 1,3
- 183.6

Succinamide.
7. \[ MF = \text{C}_5\text{H}_{11}\text{N} \]
   replace N by CH then \[ MF = \text{C}_6\text{H}_{12} \]
   \[ NSU = (6+1) - (12/2) \]
   \[ = 7 - 6 \]
   \[ = 0 \]

   \[ \text{CMR data:} \]
   (a) \[ 25.5 \text{ (t)} \] \[ \Rightarrow \] presence of \(-\text{CH}_2\) \(\text{ (sp}^3\text{ carbon)}\)
   (b) \[ 27.6 \text{ (t, strong)} \] \[ \Rightarrow \] presence of \(-\text{CH}_2\) \(\text{ (sp}^3\text{ carbon)}\)
   strong \(\Rightarrow\) it is appeared due to more than one 'C'
   (c) \[ 47.8 \text{ (t, strong)} \] \[ \Rightarrow \] presence of \(-\text{CH}_2\) \(\text{ (sp}^3\text{ carbon)}\)
   strong \(\Rightarrow\) it also appeared due to more than one 'C'

   All carbon atoms are \text{sp}^3 hybridised, so we have show size site of unsaturation in the form of ring (aliphatic)

   The probable structure is:

8. \[ MF = \text{C}_6\text{H}_{12}\text{O}_3 \]
   \[ NSU = (6+1) - 2/2 = 5 - 1 = 04 \]

   \[ \text{CMR data:} \]
   (a) \[ 136.6 \text{ (d)} \] \[ \Rightarrow \] presence of \(-\text{CH} \) \(\text{ (sp}^2\text{ carbon)}\)
   (b) \[ 164.3 \text{ (s)} \] \[ \Rightarrow \] presence of \(-\text{C} = \text{O} \) \(\text{sp}^2\text{ quaternary} \)

   In this example each signal appeared due to more than one carbon (two C)

   The correct structure is

   \[ \text{maleic anhydride} \]
8) MF = C8H12
NSU = (9+1) - \( \frac{12}{2} \) = 04
CMR data:
(a) 21.2 (q) = -CH₃ (sp³ carbon) \times 3
(b) 127.2 (d) = =CH (sp² carbon) \times 3
(c) 137.5 (s) = =C- (sp² quaternary C) \times 3

Only three signals are given so each signal appeared due to (more than one carbon) three carbons

The correct structure is:

![Structure](attachment:image.png)

10) MF = C4H8O
NSU = (4+1) - \( \frac{8}{2} \) = 5 - 4 = 01
CMR:
(a) 52 (t) = presence of -CH₂-X₂ (sp³ carbon)
(b) 33 (t) = presence of -CH₂-X₂ (sp³ carbon)

each signal appeared due to two carbons

The probable structure is:

![Structure](attachment:image.png)

Tetrahydrofuran
11 MF = C₄H₈O₂

NSU = (4+1) – 8/2 = 5 - 4 = 0

\textbf{CmR data: –}

\textbf{a)} \$8.85\ (t) \Rightarrow \text{presence of } -\text{CH₂-}

\text{only one signal appeared in CmR, from this we can say that all the carbon atoms are equivalent} \Rightarrow \text{presence of } (4-\text{CH₂-) groups}

The probable structure is:

\[ \text{1,4-dioxane} \]

12 MF = C₃H₇NO

\[ \text{replace N by CH then MF = C₄H₈O} \]

NSU = (4+1) – 8/2 = 5 - 4 = 0

\textbf{CmR data: –}

\textbf{a)} \$34.9\ (q) \Rightarrow -\text{CH₃} \ (\text{SP}^3 \ \text{carbon})

\textbf{b)} \$41.5\ (q) \Rightarrow -\text{CH₃} \ (\text{SP}^3 \ \text{carbon})

\textbf{c)} \$165.2\ (s) \Rightarrow -\text{C} = \text{O} \ (\text{SP}^2 \ \text{carbon}) \Rightarrow \text{amide}

The correct structure is:

\[ \text{CH₃} - \text{C} = \text{NH} - \text{CH₃} \]
13. **MF = C₃H₇NO**
   - Replace N by \(-\text{CH-}\) then MF = C₄H₈O₂N

   **NSD = \((4+1)-8/2 = 5-4 = 1\)**

   **CMR:**
   a) 168 (s) \(\Rightarrow\) presence of \(-\text{C-}\) (Sp² Quaternary C)
   b) 35 (t) \(\Rightarrow\) presence of \(-\text{CH}_2-\) (Sp³)
   c) 22 (q) \(\Rightarrow\) presence of \(-\text{CH}_3\) (Sp³ Carbon)

   The correct structure is:

   \[
   \text{CH₃-CH₂-C-NH₂} \quad \text{168}
   \]

   \[
   \text{22(q)} \quad \text{35(t)}
   \]

14. **Two isomorphic alcohols A & B with following data**

   **Isomer A**
   ④ 11 (q) \(\Rightarrow\) \(-\text{CH}_3\)
   ⑤ 23 (q) \(\Rightarrow\) \(-\text{CH}_3\)
   ⑥ 68 (d) \(\Rightarrow\) \(-\text{CH}-\)
   ⑦ 33 (t) \(\Rightarrow\) \(-\text{CH}_2-\)

   Correct structure is:

   \[
   \text{11(q) → CH₃-CH₂-CH-OH} \quad \text{68(d)}
   \]

   \[
   \text{33(t)} \quad \text{23(q)}
   \]

   **Isomer B**
   ⑤ 18 (q) \(\Rightarrow\) \(-\text{CH}_2\)
   ⑥ 32 (d) \(\Rightarrow\) \(-\text{CH}-\)
   ⑦ 67 (t) \(\Rightarrow\) \(-\text{CH}_2-\)

   \[
   \text{18(q)} \quad \text{67(t)} \quad \text{32(d)}
   \]
MF = C₈H₁₂O
NSU = \( (8 + 1) - \frac{12}{2} = 9 - 6 = 03 \)

CMR data:

- 23.5 (t) \( \Rightarrow \) presence of \(-\text{CH}_2-\) (sp³ carbon)
- 25.6 (t) \( \Rightarrow \) presence of \(-\text{CH}_{2}-\) (sp³ carbon)
- 40.1 (t) \( \Rightarrow \) presence of \(-\text{CH}_2-\) (sp³ carbon)
- 68.7 (s) \( \Rightarrow \) presence of \(-\text{C}=\text{C}-\) (sp³ quaternary carbon)
- 72.8 (d) \( \Rightarrow \) presence of \(-\text{C}=-\text{H}\) (sp carbon)
- 88.4 (s) \( \Rightarrow \) presence of \(-\text{C}=-\text{C}\) (sp quaternary carbon)

Out of these six signals, two are appears due to more than one carbon.

The correct structure is:

\[
\begin{align*}
\text{HO} & \quad \text{C} = \text{C} - \text{H} \\
\text{H} & \quad \text{C} = \text{C} - \text{H} \\
\text{HO} & \quad \text{C} = \text{C} - \text{C}
\end{align*}
\]

Mass:
- 124 (m/z), 123, 109, 85, 81, 68, 53, 39

\[
\begin{align*}
\text{HO} & \quad \text{C} = \text{C} - \text{H} \\
\text{HO} & \quad \text{C} = \text{C} - \text{H}
\end{align*}
\]

\[\text{m/e} = 124\]
\[\text{m/e} = 123\]
MF = C8H7OCl

Replace KI by H, then MF becomes C8H8O

N.S.O = (8+1) - 8/2 = 9 - 4 = 5

IR =

(a) 1750 cm\(^{-1}\) -> presence of \(\text{C}=\text{O}\) at ketone/Acid Chloride
(b) 1600 cm\(^{-1}\) -> presence of \(\text{C} = \text{C}\) of aromatic ring
(c) 1500 cm\(^{-1}\) ->

cmr data
(a) 28 (s) -> presence of \(-\text{CH}_3\) (sp\(^3\) carbons)
(b) 128 (d) -> presence of \(-\text{C} = \text{C}\) (sp\(^2\) carbons)
(c) 129 (d) -> presence of \(-\text{C} = \text{C}\) (sp\(^2\) hybridised)
(d) 135 (s) -> presence of \(-\text{C} = \text{O}\) (sp\(^2\) hybridised)
(e) 140 (s) ->

The probable structure is:

\[ \begin{align*}
  &\begin{array}{cc}
  \text{O} & \text{Cl} \\
  & \text{Cl}
  \end{array} \\
  &\begin{array}{cc}
  \text{O} & \text{Cl} \\
  & \text{Cl}
  \end{array} \\
\end{align*} \]

Mass: 154/156 \((\text{m}^+ : 3:1), 139/141, 111/113\)

If 35\(^{Cl}\) -> m/e = 154
37\(^{Cl}\) -> m/e = 156

\[ \begin{align*}
  &\begin{array}{cc}
  \text{O} & \text{Cl} \\
  & \text{Cl}
  \end{array} \\
  &\begin{array}{cc}
  \text{O} & \text{Cl} \\
  & \text{Cl}
  \end{array} \\
\end{align*} \]

\[ \text{O=C-Cl} \]

Not possible

\[ \text{[Diagram]} \]

\[ \text{[Diagram]} \]

\[ \text{[Diagram]} \]

\[ \text{[Diagram]} \]
Two isomeric hydrocarbons A and B of C5H10 show the following cnmr data. Deduce the structure from given data.

**Isomer A:**

1. $13(q) = -\text{CH}_3 (\text{sp}^3)$
2. $17(q) = -\text{CH}_3$
3. $26(q) = -\text{CH}_3$
4. $118(d) = -\text{CH}_2 (\text{sp}^2)$
5. $132(s) = -\text{C} = \text{C} - \text{CSp}^2 (\text{Quaternary carbon})$

The probable structure is:

![Structure of Isomer A]

**Isomer B:**

1. $13(q) = -\text{CH}_3$
2. $22(q) = -\text{CH}_3$
3. $31(t) = -\text{CH}_2 -$
4. $108(t) = -\text{CH}_2 - (\text{sp}^2 \text{ carbon})$
5. $147(s) = -\text{C} - \text{H} - (\text{sp}^2 \text{ Quaternary C})$

![Structure of Isomer B]
MF = C₄H₇NO
replace 'N' by 'CH' then MF becomes C₅H₁₀O
NSU = (5+1) - 10/2
= 6 - 5 = 01

CMR data:
(a) 47.4 (t) = -CH₂- (sp³ carbon)
(b) 68.2 (t) = -CH₂- (sp³ carbon)

Only two signals are given in CMR data, so each signal appears due to two carbons.

The correct structure is:

![Chemical structure diagram]

MF = C₁₂H₁₈
NSU = (12+1) - 18/2 = 13 - 9 = 04

CMR data:
6 × 4 20.9 (q, strong) = -CH₃ (sp³ carbon)
6 × 5 132.7 (s, strong) = =C- (sp²-hybridized quaternary carbon)

Only two signals are given, so each signal appeared due to six carbons.

The correct structure is:

![Chemical structure diagram]