Unit-III:

Structural elucidation of organic compounds using IR, NMR & mass spectral data-

1.Structural Elucidation of 2,2,3,3-Tetramethylbutane Using Integrated Spectroscopic Techniques

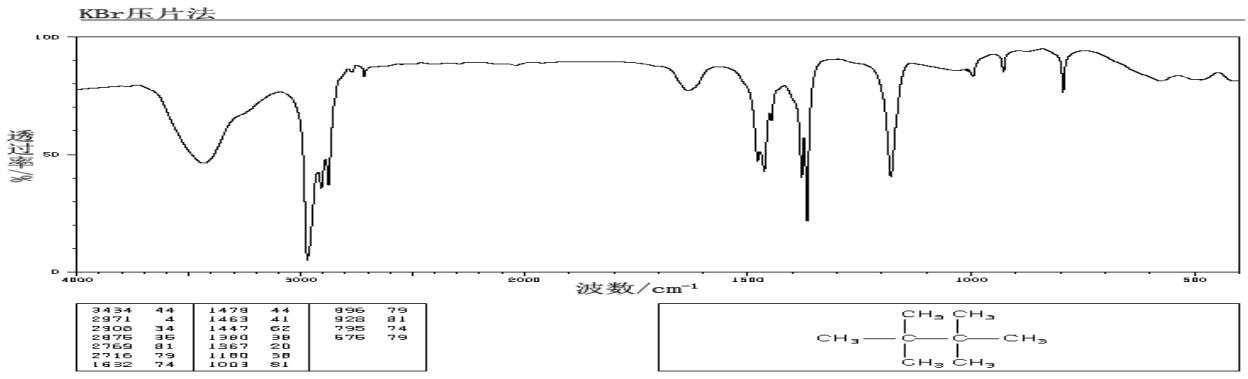
2,2,3,3-Tetramethylbutane (C_8H_{18}) is a highly branched alkane, sometimes referred to as neopentane. It consists of a central butane chain with four methyl groups attached symmetrically to the 2nd and 3rd carbon atoms. To elucidate its structure, we can use a combination of IR, NMR, MS, and UV-Vis spectroscopy.

The spectral data of 2,2,3,3-tetramethylbutane indicates a highly symmetric and saturated hydrocarbon structure. The IR spectrum confirms the presence of only C-H bonds, the NMR spectra (^1H and ^{13}C) show a high degree of symmetry with just two signals, and mass spectrometry reveals a molecular ion peak at m/z 114 with characteristic alkane fragmentation. These combined techniques confirm the structure of this molecule as a fully saturated, highly branched alkane with no unsaturation or functional groups.

1. Infrared (IR) Spectroscopy

Since 2,2,3,3-tetramethylbutane is a saturated alkane, its IR spectrum will show characteristic peaks of C-H bonds in alkanes.

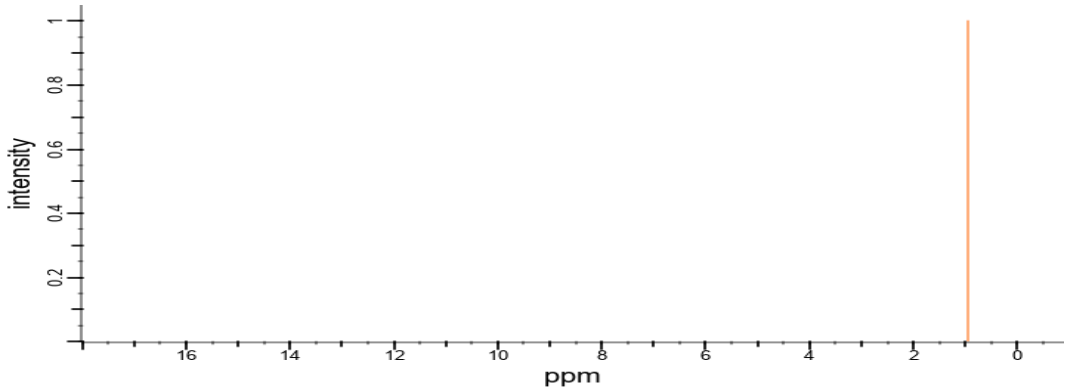
- *C-H Stretch (sp^3 hybridized): A series of peaks between 2850-2960 cm^{-1}, typical of the C-H stretching in methyl (CH_3) groups.*
- *C-H Bending (Methyl group): Medium intensity bands around 1375-1475 cm^{-1} corresponding to the bending vibrations of the methyl (CH_3) groups.*
- *No significant peaks around 1600-1800 cm^{-1}, which indicates the absence of any double or triple bonds (C=C or C≡C) or carbonyl groups (C=O).*
- *Overall, the IR spectrum suggests a completely saturated hydrocarbon structure without any polar functional groups or unsaturation.*



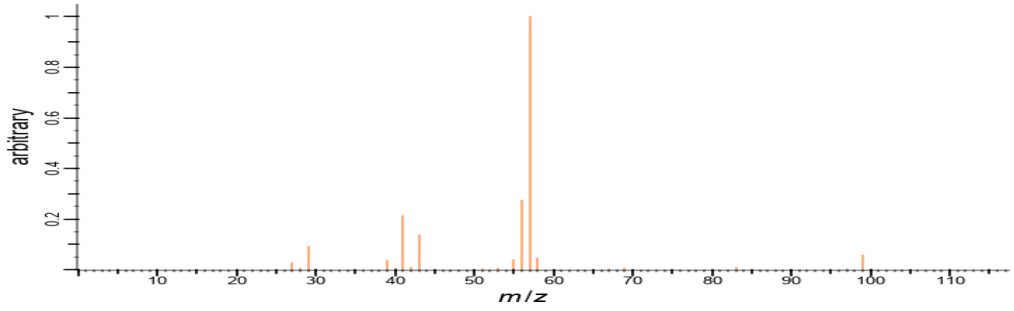
2. Nuclear Magnetic Resonance (NMR) Spectroscopy

1H NMR (Proton NMR)

Methyl Protons (CH_3 groups): In the ^1H NMR spectrum, we would observe a single, sharp singlet around δ 0.85-1.0 ppm. This corresponds to the 18 equivalent protons of the six methyl groups. All the methyl groups are chemically equivalent due to the high symmetry of the molecule, resulting in just one signal.

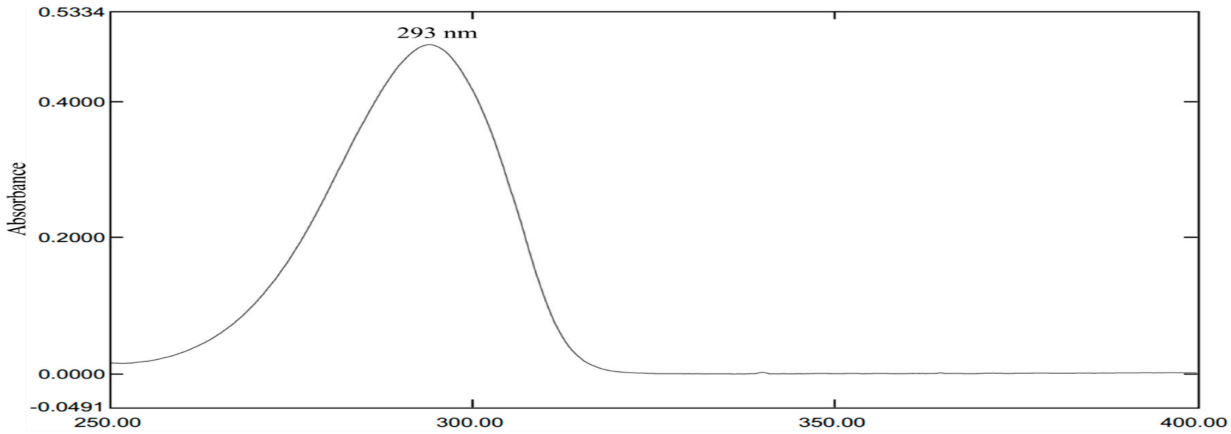


- *3. Mass Spectrometry (MS)*
- *Molecular Ion Peak (M^+): The molecular ion peak should be observed at m/z 114, which corresponds to the molecular weight of 2,2,3,3-tetramethylbutane (114 g/mol).*
- *Fragmentation Pattern:*
- *m/z 57: This peak is due to the loss of a neutral methyl radical (CH_3), resulting in a tertiary butyl cation ($C_4H_9^+$), which is a common and stable fragment.*
- *m/z 43: This peak corresponds to the propyl cation ($C_3H_7^+$), another common fragmentation product in branched alkanes.*
- *The absence of prominent peaks for functional groups like alcohols, carbonyls, or aromatic systems further supports the aliphatic hydrocarbon structure.*



4. Ultraviolet-Visible (UV-Vis) Spectroscopy

Alkanes like 2,2,3,3-tetramethylbutane do not absorb significantly in the UV-Vis range because they lack conjugated systems. The spectrum would show minimal absorbance in the 200-300 nm region, if at all, corresponding to any minor transitions from sigma to sigma-star ($\sigma \rightarrow \sigma^*$) bonds.



2.Structural Elucidation of Butane-2,3-dione ($C_4H_6O_2$) Using Integrated Spectroscopic Techniques

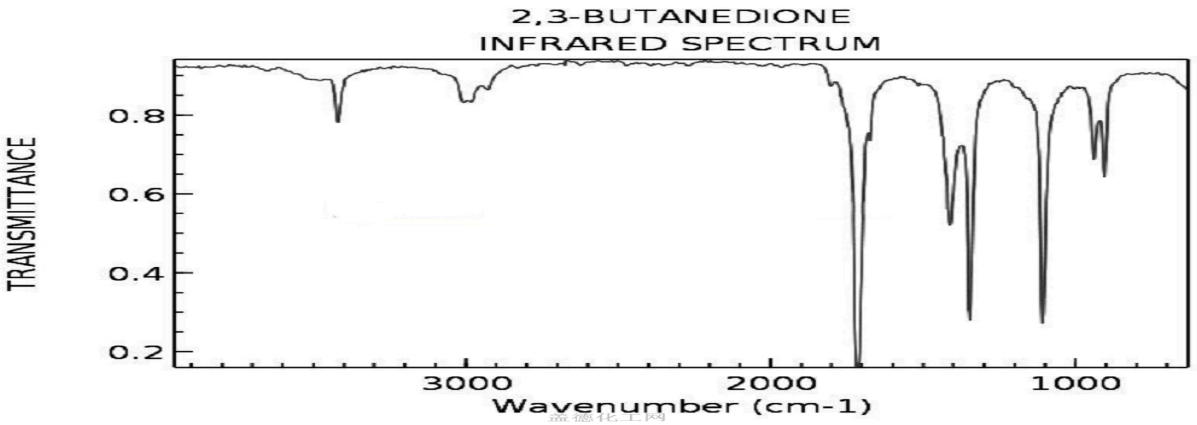
Butane-2,3-dione (commonly known as diacetyl) is a diketone, with the structure consisting of two adjacent carbonyl groups (-C=O) on the 2nd and 3rd carbon atoms of the butane chain. This compound can be analyzed using various spectroscopic techniques like IR, NMR, MS, and UV-Vis to confirm its structure.

1. Infrared (IR) Spectroscopy

The IR spectrum of butane-2,3-dione will exhibit key absorption bands related to the carbonyl functional groups and C-H bonds.

- *Carbonyl Stretch (C=O): Strong absorption bands are expected around 1725-1750 cm^{-1} due to the symmetric and asymmetric stretching of the carbonyl (C=O) groups. Since this is a diketone, there will be two carbonyl peaks, but they might overlap or appear as a single broad peak depending on their symmetry.*
- *C-H Stretch (Alkyl groups): Peaks around 2850-2960 cm^{-1} corresponding to the C-H stretching vibrations of the alkyl groups (CH_3) attached to the carbon backbone.*
- *C-H Bending (Methyl group): Medium intensity bands around 1375-1450 cm^{-1}, characteristic of the bending vibrations of the methyl groups (CH_3).*

These IR absorption patterns confirm the presence of two carbonyl groups and alkyl groups, indicating a diketone structure.

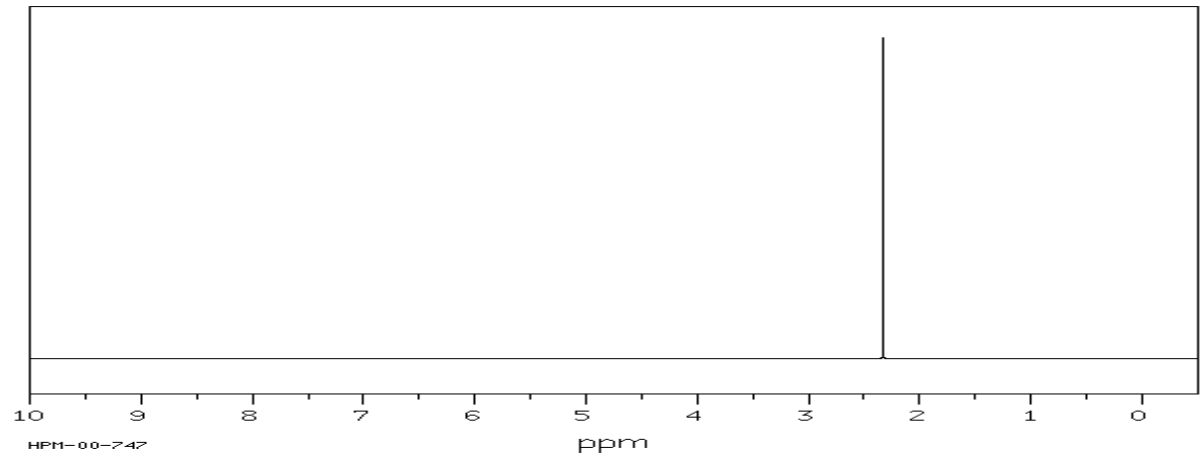


2. Nuclear Magnetic Resonance (NMR) Spectroscopy

1H NMR (Proton NMR)

- *Methyl Protons (CH_3 groups): The two methyl groups attached to the carbonyl carbons (CH_3-C=O) will appear as a singlet around δ 2.1-2.4 ppm. Since these two methyl groups are adjacent to carbonyl groups, they are slightly downfield.*

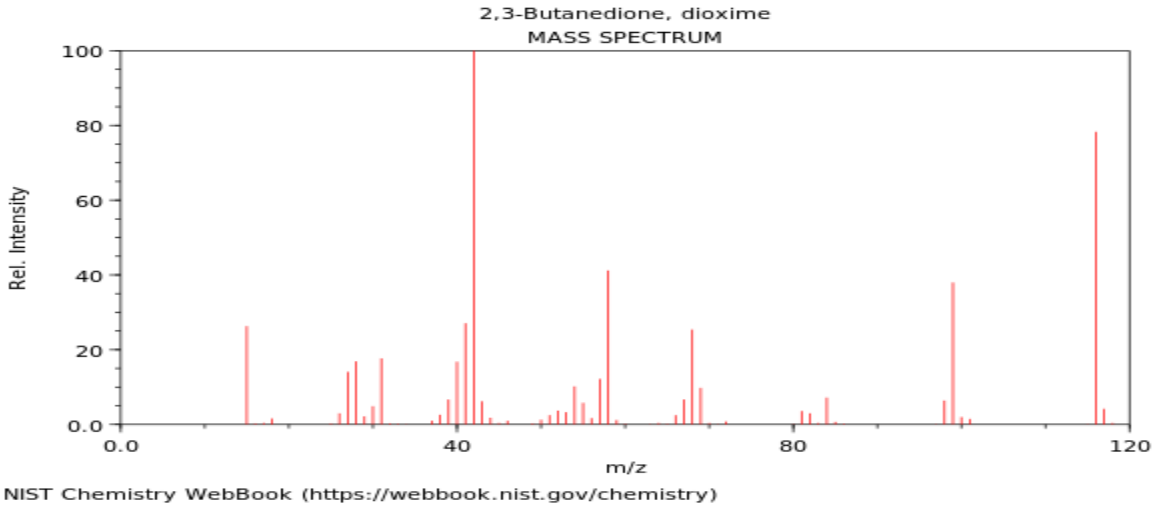
The spectrum is relatively simple due to the high symmetry of the molecule, resulting in just one signal for the two equivalent methyl groups.



3. Mass Spectrometry (MS)

- *Molecular Ion Peak (M^+): The molecular ion peak is expected at m/z 86, corresponding to the molecular weight of butane-2,3-dione (86 g/mol).*
- *Fragmentation Pattern:*
- *m/z 43: A common peak, resulting from the loss of one carbonyl group (-CO), leaving behind a methyl cation (CH_3^+) or acetyl fragment.*
- *m/z 29: This corresponds to the loss of an ethyl group ($C_2H_5^+$), a common fragmentation in smaller alkyl chains.*

- *The molecular ion peak and the fragmentation pattern support the structure of butane-2,3-dione as a small alkyl chain with two adjacent carbonyl groups.*

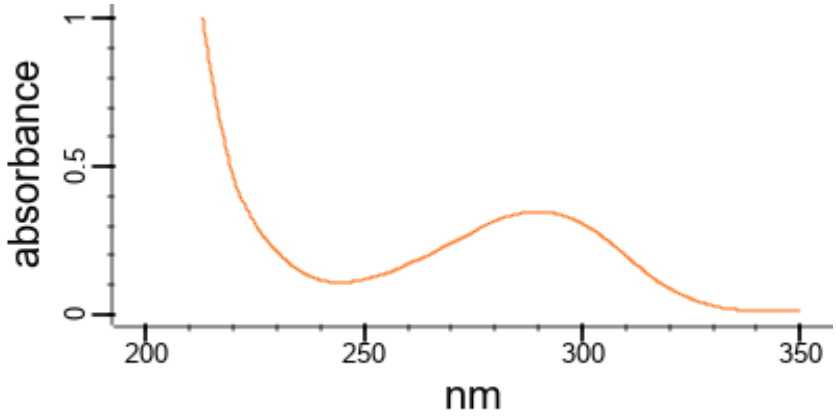


4. Ultraviolet-Visible (UV-Vis) Spectroscopy

Because butane-2,3-dione contains conjugated carbonyl groups, it may show some absorption in the UV region due to $n \rightarrow \pi^*$ transitions.

- *$n \rightarrow \pi$ Transition*: A weak absorption band is expected in the 270-300 nm region, which corresponds to the non-bonding electron transition from the oxygen atom in the carbonyl groups to the antibonding π^* orbital.*

The UV-Vis spectrum confirms the presence of conjugated carbonyl groups, consistent with the diketone structure.



Conclusion

- *The structure of butane-2,3-dione is confirmed by the combination of spectroscopic techniques:*
- *IR Spectroscopy shows the presence of two carbonyl groups (C=O) and alkyl (CH_3) groups.*

- *^{1}H NMR reveals a single signal corresponding to the two equivalent methyl groups adjacent to carbonyl carbons.*
- *^{13}C NMR confirms the presence of carbonyl and methyl carbons, showing two downfield signals for the carbonyl carbons.*
- *Mass Spectrometry provides a molecular ion peak at m/z 86 with characteristic fragment ions, confirming the molecular weight and structure.*
- *UV-Vis Spectroscopy supports the presence of conjugated carbonyl groups with weak absorption bands in the UV region.*

- *These data confirm the structure of butane-2,3-dione as a diketone with two adjacent carbonyl groups and methyl groups on a butane backbone.*

3.Structural Elucidation of Propanoic Acid Using Integrated Spectroscopic Techniques

Propanoic acid (CH_3CH_2COOH) is a simple carboxylic acid, and its structure can be elucidated using multiple spectroscopic techniques such as IR, NMR, MS, and UV-Vis. Here is an integrated description of its spectral data. Propanoic acid (CH_3CH_2COOH) can be fully characterized using integrated spectroscopic techniques. The IR spectrum clearly identifies the O-H and C=O stretches of the carboxylic acid group. The NMR data (both ^{1}H and ^{13}C) provide detailed information about the aliphatic chain and the carboxyl group, while the mass spectrometry confirms the molecular weight and provides fragmentation patterns supporting the structure.

1. Infrared (IR) Spectroscopy

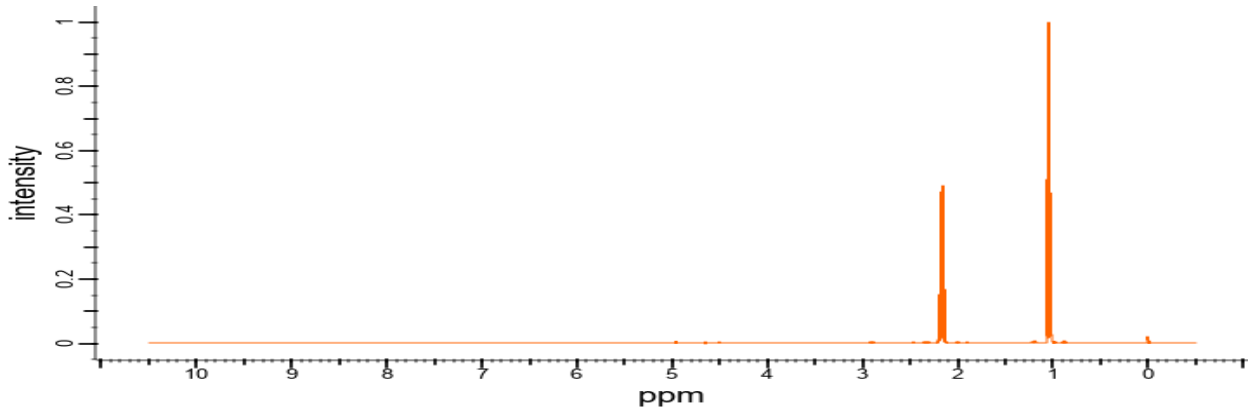
Functional Group Identification:

- *O-H Stretch (Carboxyl group): A broad, strong band around 2500-3300 cm^{-1} indicates the presence of the carboxylic acid (O-H stretch) group, characteristic of hydrogen-bonded carboxylic acids.*
- *C=O Stretch (Carbonyl group): A strong, sharp peak around 1700-1725 cm^{-1} confirms the presence of a carbonyl (C=O) group, typical for carboxylic acids.*
- *C-O Stretch: A band around 1200-1300 cm^{-1} represents the C-O stretch of the carboxyl group.*
- *C-H Stretch (Aliphatic chain): Peaks between 2850-2960 cm^{-1} indicate the C-H stretching from the methyl (CH_3) and methylene (CH_2) groups.*

2. Nuclear Magnetic Resonance (NMR) Spectroscopy

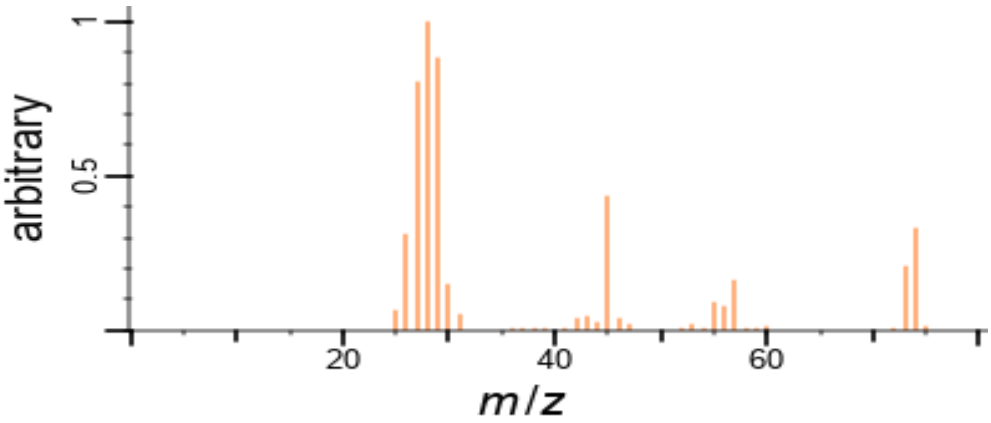
1H NMR (Proton NMR):

- *Methyl Protons (CH_3 group): A triplet at δ 1.0-1.2 ppm due to the three protons of the CH_3 group, which are adjacent to a CH_2 group.*
- *Methylene Protons (CH_2 group): A quartet around δ 2.2-2.4 ppm arises from the two protons of the CH_2 group adjacent to the CH_3 group and the carbonyl carbon (COOH).*
- *Carboxylic Proton (COOH group): A broad singlet around δ 10-12 ppm corresponds to the acidic proton of the carboxylic acid group.*



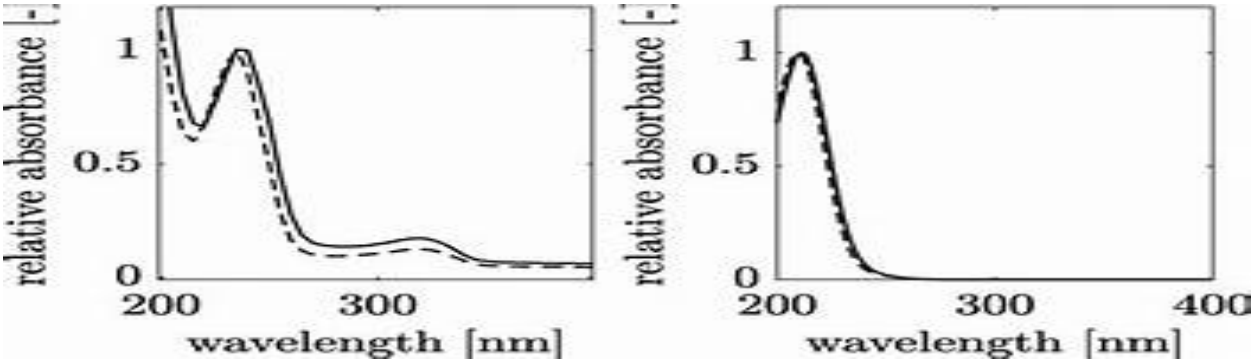
3. Mass Spectrometry (MS)

- *Molecular Ion Peak (M^+): The molecular ion peak at m/z 74 confirms the molecular weight of propanoic acid (74 g/mol).*
- *Fragmentation Patterns:*
  - *m/z 45: This peak is attributed to the loss of a carboxyl group (COOH, 29 mass units), yielding the ethyl fragment ($CH_3CH_2^+$).*
  - *m/z 29: This peak is due to the ethyl cation ($CH_3CH_2^+$), confirming the presence of the aliphatic chain.*



4. Ultraviolet-Visible (UV-Vis) Spectroscopy

$n \rightarrow \pi$ Transition: The UV spectrum typically shows weak absorption in the range of 200-210 nm, corresponding to the $n \rightarrow \pi^*$ transition associated with the carboxyl group. However, this is a minor contributor to structure elucidation for this compound, as carboxylic acids show minimal absorbance in the UV-Vis range.*



4.Structural Elucidation of Methyl Propionate ($C_4H_8O_2$) Using Integrated Spectroscopic Techniques

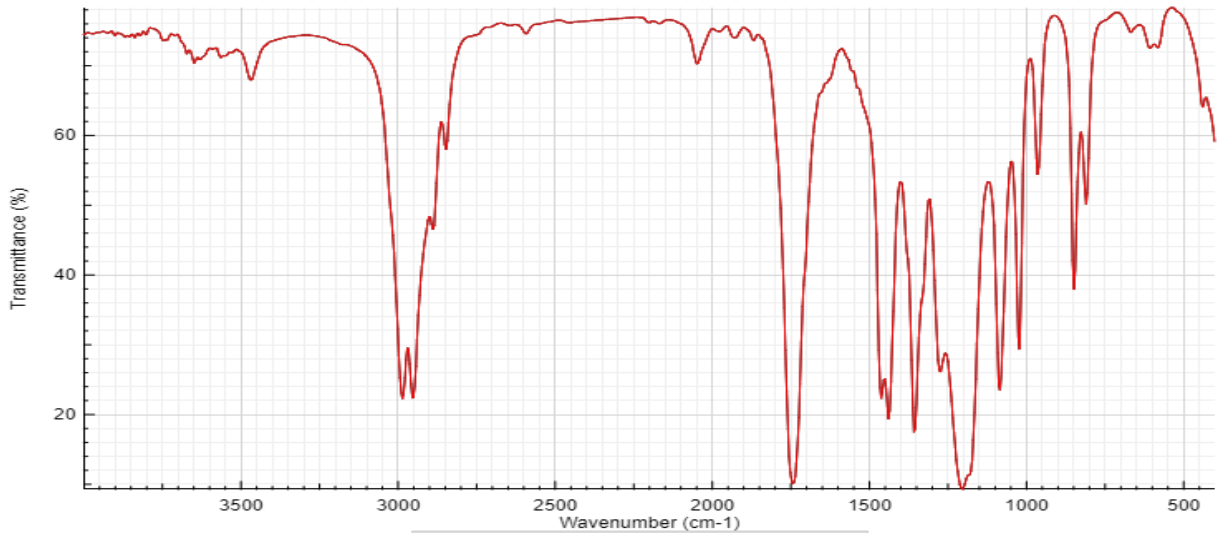
Methyl propionate is an ester with the molecular formula $C_4H_8O_2$. It consists of a propionate group ($CH_3CH_2COO–$) attached to a methyl group ($-OCH_3$). The combination of the ester functionality and alkyl chains can be elucidated using techniques such as IR, NMR, MS, and UV-Vis spectroscopy.

1. Infrared (IR) Spectroscopy

The IR spectrum of methyl propionate will show characteristic absorption bands for the ester functional group as well as alkyl groups:

- *C=O Stretch (Ester Carbonyl): A strong, sharp absorption band around 1735-1750 cm^{-1}, typical of the carbonyl stretch in esters.*
- *C-O Stretch (Ester Bond): A medium-intensity peak between 1050-1300 cm^{-1}, corresponding to the C-O single bond in the ester.*
- *C-H Stretch (Alkyl Groups): Absorption bands between 2850-3000 cm^{-1}, corresponding to the C-H stretching vibrations of the methyl (CH_3) and methylene (CH_2) groups.*
- *C-H Bending (Methyl Group): Medium peaks around 1370-1450 cm^{-1}, typical for C-H bending in the CH_3 group.*

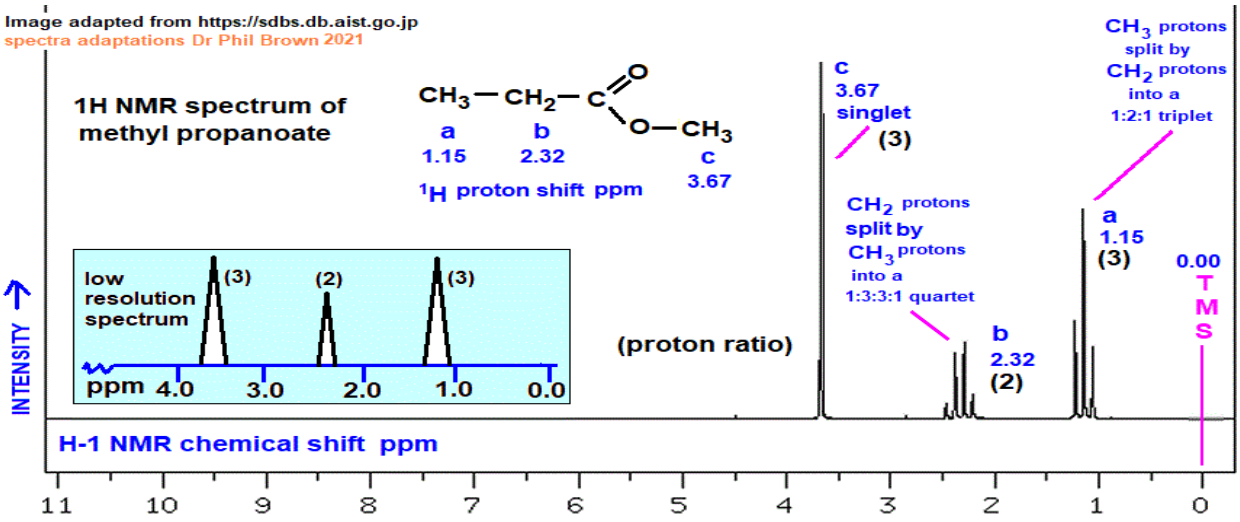
The IR spectrum confirms the presence of an ester functional group and alkyl chains based on the C=O and C-O absorption bands.



2. Nuclear Magnetic Resonance (NMR) Spectroscopy

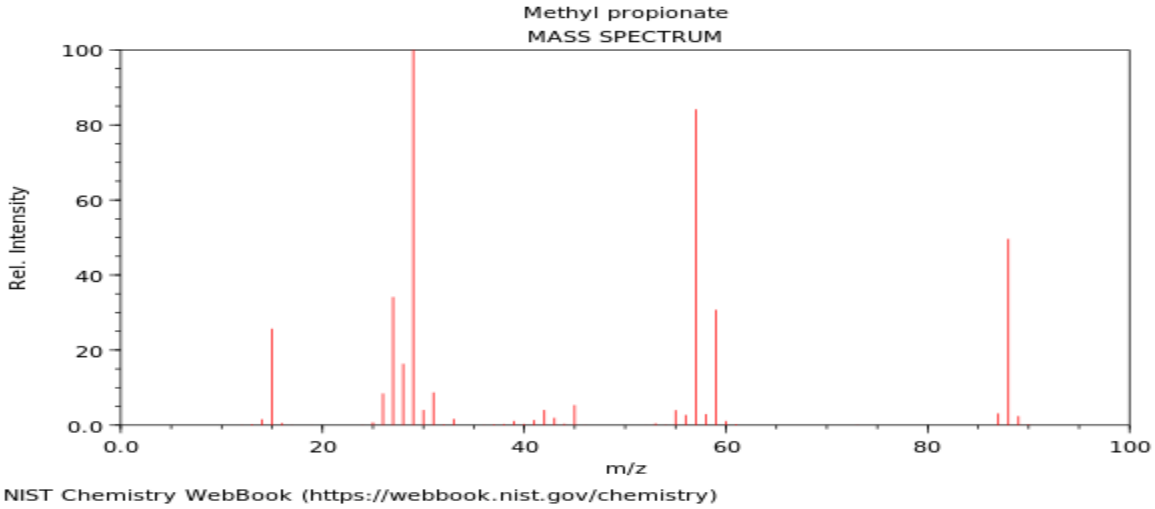
1H NMR (Proton NMR)

- *Methyl Protons (OCH_3 group): The methyl group attached to the oxygen atom ($-OCH_3$) will appear as a singlet around δ 3.6-3.7 ppm. The singlet nature is due to the absence of neighboring protons to couple with.*
- *Methylene Protons (CH_2 adjacent to C=O): The methylene protons (CH_2) adjacent to the carbonyl group (C=O) will appear as a triplet around δ 2.2-2.4 ppm. The triplet arises due to coupling with the neighboring CH_3 group.*
- *Methyl Protons (CH_3 group): The terminal methyl group (CH_3) of the propionate chain will show up as a quartet around δ 1.0-1.2 ppm, caused by coupling with the neighboring methylene group (CH_2).*



3. Mass Spectrometry (MS)

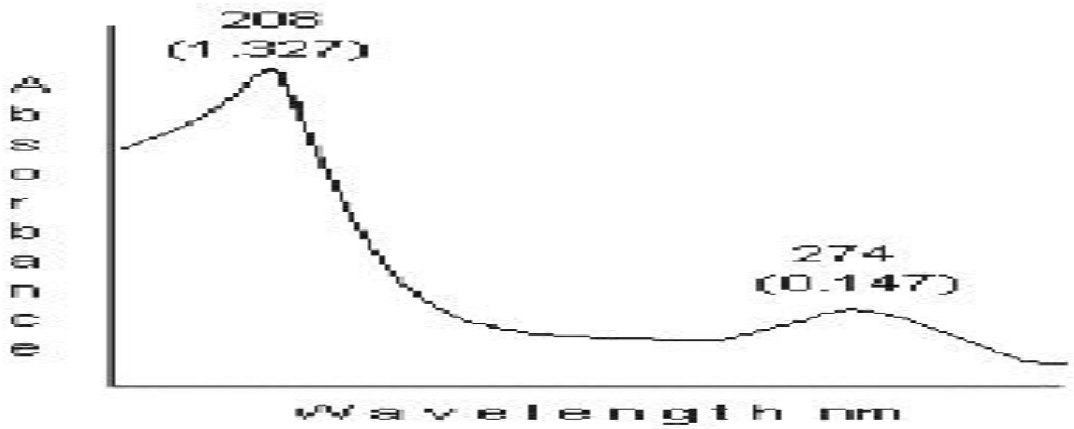
- *Molecular Ion Peak (M^+): The molecular ion peak should be observed at m/z 88, corresponding to the molecular weight of methyl propionate (88 g/mol).*
- *Fragmentation Pattern:*
- *m/z 59: A peak corresponding to the loss of the methoxy group (-OCH_3), leaving behind a propionyl fragment ($CH_3CH_2CO^+$).*
- *m/z 43: This peak is due to the formation of the acylium ion ($CH_3CH_2C^+$), a common fragment in esters.*
- *The molecular ion peak at m/z 88 and the characteristic fragment ions provide strong evidence for the structure of methyl propionate.*



4. Ultraviolet-Visible (UV-Vis) Spectroscopy

Since methyl propionate is a simple ester without conjugated systems, it will not absorb significantly in the UV-Vis range. Esters typically show weak absorption bands due to n → π transitions in the carbonyl group.*

- *n → π Transition*: A weak absorption may be seen around 190-220 nm, corresponding to the transition from non-bonding electrons on oxygen to the antibonding π* orbital of the carbonyl group.*



Conclusion

The structure of methyl propionate is confirmed by the combination of these spectroscopic techniques:

- *IR Spectroscopy shows the presence of a carbonyl (C=O) and ester (C-O) functional groups, as well as alkyl groups.*
- *^{1}H NMR reveals signals for the methyl (OCH_3), methylene (CH_2), and methyl (CH_3) protons, with characteristic coupling patterns.*
- *^{13}C NMR confirms the presence of carbonyl, methoxy, methylene, and methyl carbons with expected chemical shifts.*
- *Mass Spectrometry provides a molecular ion peak at m/z 88 with characteristic fragment ions.*
- *UV-Vis Spectroscopy indicates weak absorption bands for non-conjugated esters.*
- *These data collectively confirm the structure of methyl propionate as an ester with a propionate chain and a methoxy group attached to the oxygen.*

5.Structural Elucidation of Phenylacetylene (C_8H_6) Using Integrated Spectroscopic Techniques

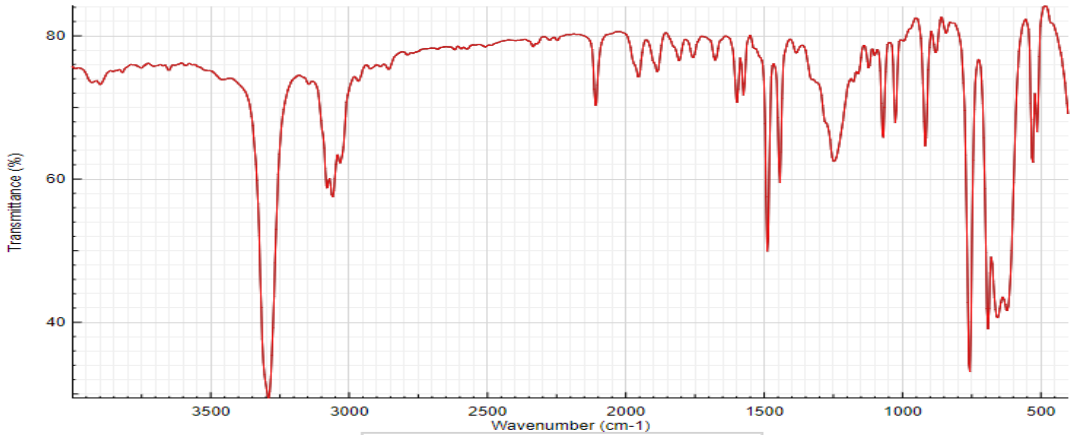
Phenylacetylene is an aromatic alkyne, consisting of a benzene ring attached to an acetylene group (-C≡CH). The combination of aromatic and alkyne functional groups can be elucidated using various spectroscopic techniques such as IR, NMR, MS, and UV-Vis spectroscopy.

1. Infrared (IR) Spectroscopy

Phenylacetylene contains both an aromatic ring and an alkyne group, each of which contributes characteristic absorption bands in the IR spectrum:

- *Alkyne (C≡C) Stretch: A strong, sharp peak around 2100-2200 cm^{-1} due to the stretching of the carbon-carbon triple bond (C≡C).*
- *Terminal Alkyne (C-H) Stretch: A sharp peak around 3300 cm^{-1} characteristic of the stretching vibration of the terminal alkyne C-H bond. This peak is usually sharper and more intense than typical alkane C-H stretches.*
- *Aromatic C-H Stretch: Peaks between 3000-3100 cm^{-1}, characteristic of the C-H stretching in the aromatic ring.*
- *Aromatic C=C Stretch: Weak to medium-intensity peaks between 1500-1600 cm^{-1}, which correspond to the C=C stretching vibrations in the benzene ring.*

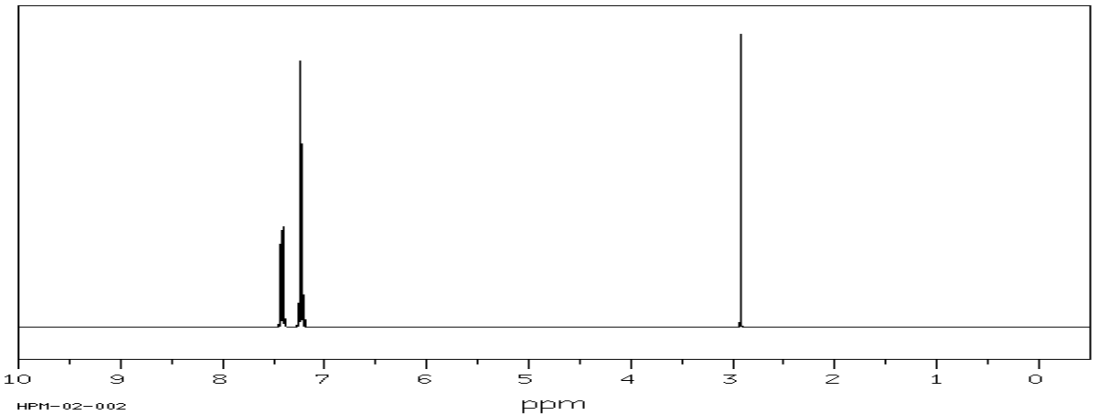
These peaks indicate the presence of both an aromatic system and a terminal alkyne group.



2. Nuclear Magnetic Resonance (NMR) Spectroscopy

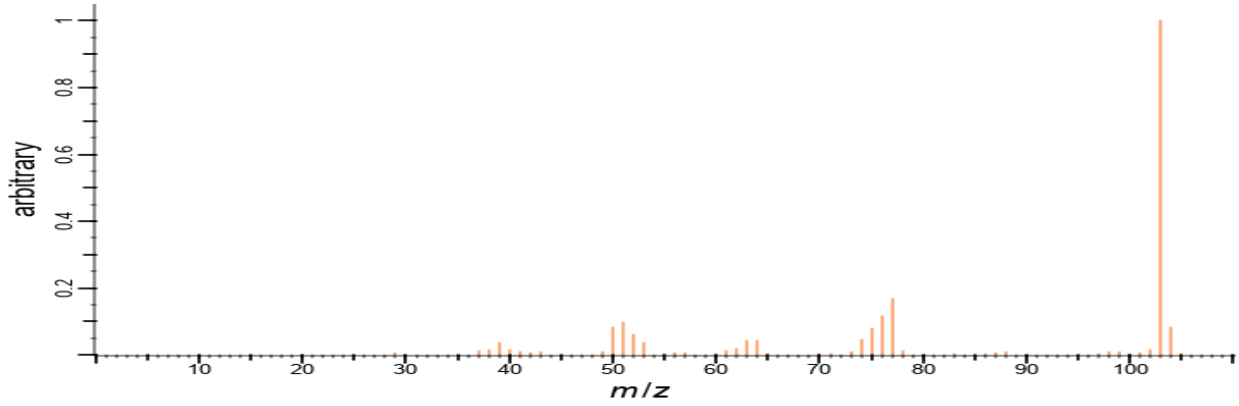
1H NMR (Proton NMR)

- *Alkyne Proton (C≡C-H): The proton attached to the terminal alkyne group (C≡CH) will appear as a sharp singlet around δ 3.0-3.2 ppm. This signal is downfield due to the electronegative nature of the sp-hybridized carbon in the alkyne.*
- *Aromatic Protons: The five protons on the phenyl ring (benzene) will show up between δ 7.2-7.5 ppm as a multiplet. These protons are in different electronic environments due to the influence of the alkyne group, leading to complex splitting patterns that may appear as overlapping signals.*



3. Mass Spectrometry (MS)

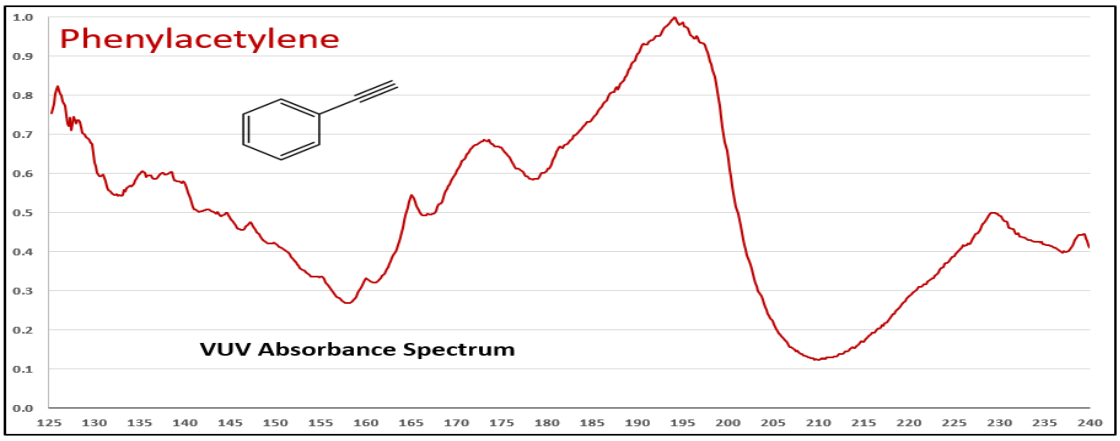
- *Molecular Ion Peak (M^+): The molecular ion peak would be observed at m/z 102, corresponding to the molecular weight of phenylacetylene (102 g/mol).*
- *Fragmentation Pattern:*
- *m/z 77: A common peak resulting from the loss of the acetylene group (-C≡CH), which corresponds to the phenyl cation ($C_6H_5^+$).*
- *m/z 51 and m/z 39: Additional peaks can be seen due to further fragmentation of the phenyl group or the loss of small fragments such as acetylene or benzene.*
- *This fragmentation pattern supports the presence of both an aromatic ring and an alkyne group in the molecule.*



4. Ultraviolet-Visible (UV-Vis) Spectroscopy

Phenylacetylene contains a conjugated system due to the interaction between the benzene ring and the alkyne group. This conjugation causes absorption in the UV region.

- *$\pi \rightarrow \pi^*$ Transitions: The aromatic system of the benzene ring shows absorption around 200-250 nm.*
- *$n \rightarrow \pi^*$ Transitions: Due to the conjugation between the alkyne group and the benzene ring, some weak absorption may occur at higher wavelengths (around 250-280 nm).*
- *This indicates the presence of conjugated π-systems, confirming the aromatic and alkyne nature of the molecule.*



Conclusion

The structure of phenylacetylene is confirmed by the combination of spectroscopic techniques:

- *IR Spectroscopy shows the presence of a carbon-carbon triple bond (C≡C) and terminal alkyne C-H bond.*
- *^{1}H NMR reveals signals for the alkyne proton (C≡CH) and aromatic protons in the phenyl group, with characteristic shifts.*
- *^{13}C NMR confirms the presence of sp-hybridized carbons (C≡C) and aromatic carbons.*
- *Mass Spectrometry gives a molecular ion peak at m/z 102 and fragmentation patterns corresponding to both the alkyne and phenyl groups.*

- *UV-Vis Spectroscopy shows absorption characteristic of $\pi \rightarrow \pi^*$ transitions in a conjugated system.*
- *These data collectively confirm the structure of phenylacetylene ($C_6H_5C{\equiv}CH$).*

6.Structural Elucidation of Acetophenone Using Integrated Spectroscopic Techniques

Acetophenone ($C_6H_5COCH_3$) is a simple aromatic ketone and its structure can be elucidated using several spectroscopic techniques, including IR, NMR, and MS. Here is a summary of the spectral data and the key points that help in structure elucidation:

Using integrated spectroscopic techniques, acetophenone is confirmed as an aromatic ketone ($C_6H_5COCH_3$). The IR spectrum provides key insights into the functional groups, the NMR spectrum confirms the structural framework with details on the proton and carbon environment, and mass spectrometry validates the molecular weight and fragmentation pattern. UV-Vis helps identify the electronic transitions in the molecule.

1. Infrared (IR) Spectroscopy

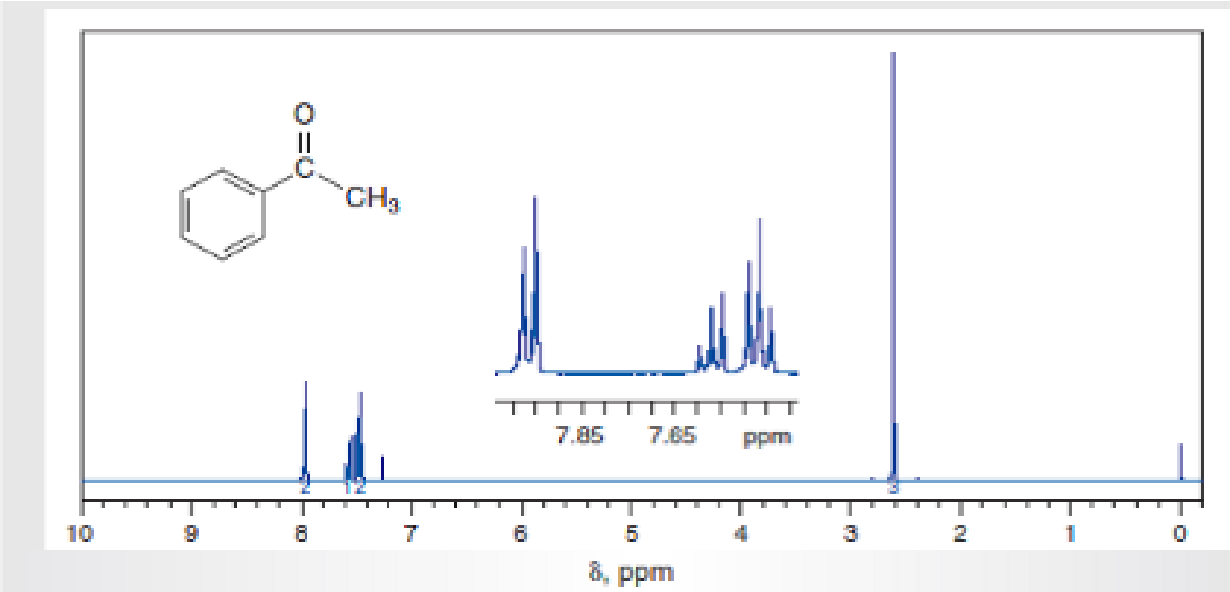
Functional Group Identification:

- *C=O Stretch (Carbonyl group): A strong absorption band around 1680-1700 cm^{-1} indicates the presence of a carbonyl (C=O) group, typical for ketones.*
- *C-H Stretch (Aromatic ring): Peaks in the region of 3000-3100 cm^{-1} suggest aromatic C-H stretching, characteristic of the phenyl group.*
- *C-H Stretch (Methyl group): Peaks near 2850-2960 cm^{-1} correspond to the C-H stretching of the methyl group (CH_3).*
- *C=C Stretch (Aromatic ring): Weak to medium-intensity bands around 1600 cm^{-1} and 1500 cm^{-1} indicate the presence of an aromatic ring.*

2. Nuclear Magnetic Resonance (NMR) Spectroscopy

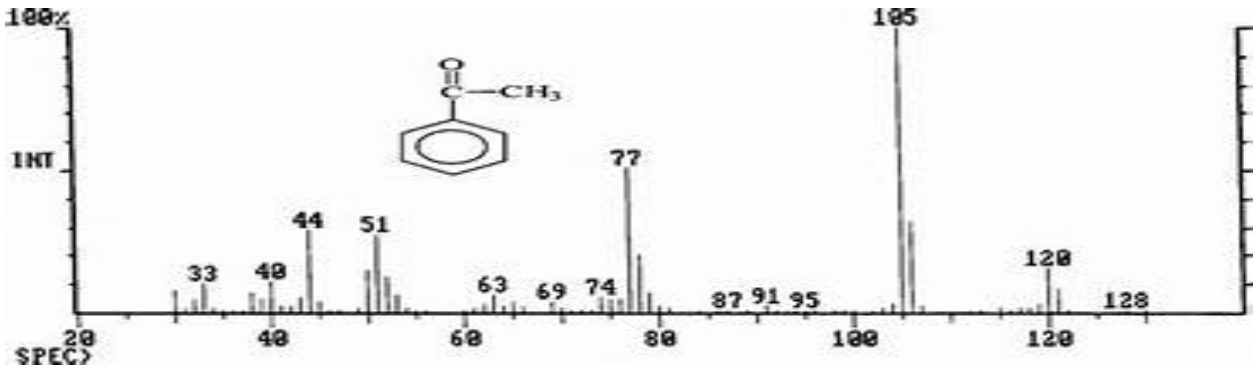
1H NMR (Proton NMR):

- *Methyl Protons (CH_3 group): A singlet around δ 2.6-2.7 ppm is attributed to the three equivalent protons of the methyl group (CH_3) attached to the carbonyl carbon.*
- *Aromatic Protons (C_6H_5 group): A set of multiplets between δ 7.2-7.8 ppm arises from the five aromatic protons of the phenyl ring (C_6H_5), showing characteristic splitting patterns based on their positions (ortho, meta, para) relative to the carbonyl group.*



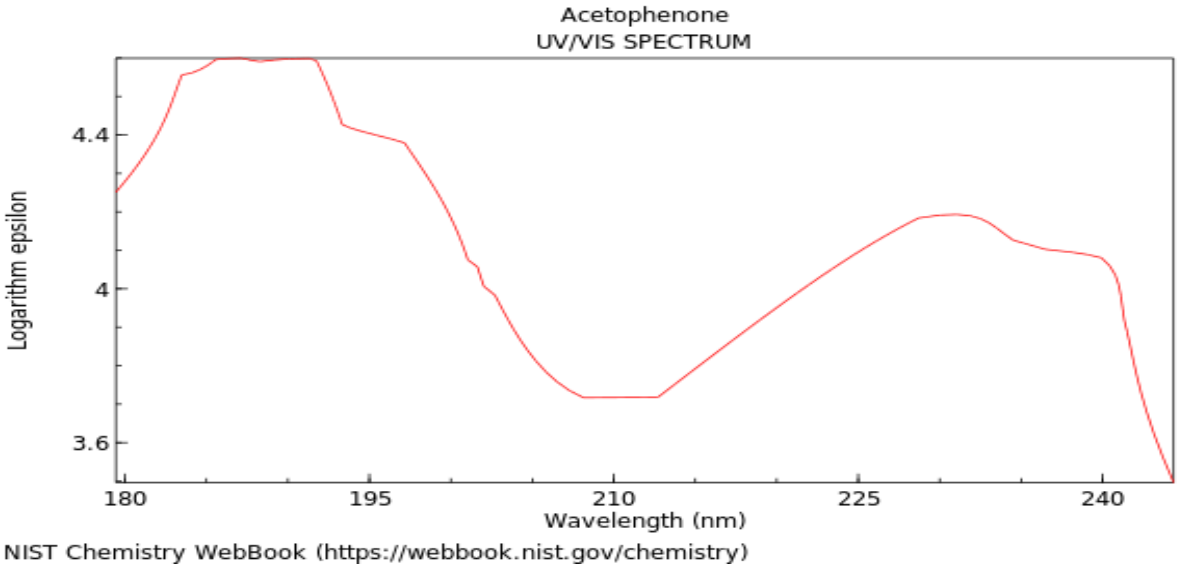
3. Mass Spectrometry (MS)

- *Molecular Ion Peak (M^+): The molecular ion peak at m/z 120 confirms the molecular weight of acetophenone (120 g/mol).*
- *Base Peak: A base peak at m/z 105 is due to the loss of a methyl group (CH_3, 15 mass units), yielding the phenyl ketone fragment ($C_6H_5CO^+$).*
- *Other Fragmentation Patterns: Additional peaks such as m/z 77 (benzyl cation, $C_6H_5^+$) and m/z 43 (acetyl cation, CH_3CO^+) support the presence of the phenyl group and the carbonyl methyl fragment.*

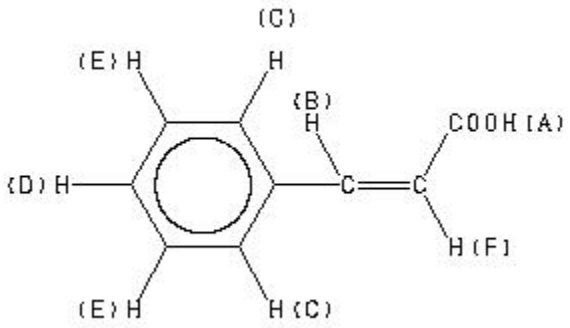


4. Ultraviolet-Visible (UV-Vis) Spectroscopy

- *$\pi \rightarrow \pi$ Transition*: The UV-Vis spectrum shows an absorption maximum (λmax) around 240-250 nm, which corresponds to the $\pi \rightarrow \pi^*$ transition in the conjugated system of the phenyl ring.*
- *$n \rightarrow \pi$ Transition*: A weaker absorption band near 300 nm is due to the $n \rightarrow \pi^*$ transition of the carbonyl group.*



7.Cinnamic acid



- Molecular formula: $C_9H_8O_2$
- Molecular weight: 148 g/mol
- Functional groups: Aromatic ring, alkene (–CH=CH–), and carboxylic acid (–COOH).
-
- 1. Infrared (IR) Spectroscopy
- O–H Stretch (Carboxylic acid –COOH):
  Very broad band in the region 2500–3300 cm^{-1} (overlaps with C–H stretching).

- C=O Stretch (Carboxylic acid):
  Strong absorption around 1680–1710 cm^{-1}.

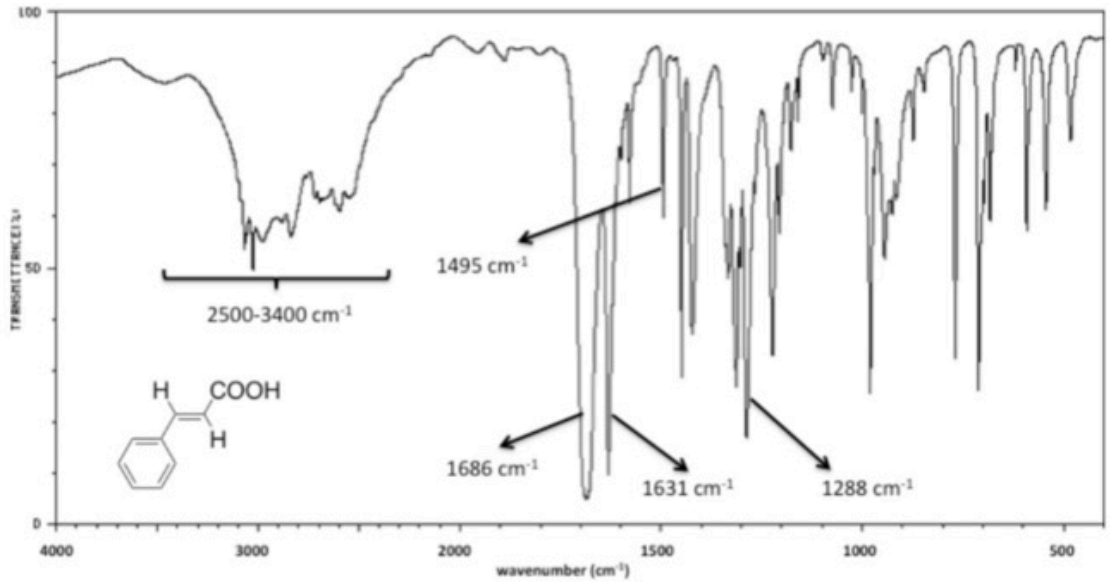
- C=C Stretch (Aromatic ring):
  Peaks in the 1450–1600 cm^{-1} region.

- C=C Stretch (Alkene):
  Medium absorption around 1620–1640 cm^{-1}.

- Aromatic C–H Stretch:
  Peaks at 3050–3100 cm^{-1}.

- C–O Stretch (COOH):
  Band near 1200–1300 cm^{-1}.

- Confirms aromatic ring, alkene group, and carboxylic acid group.



2. Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy

- **Aromatic Protons (C_6H_5):**
  Multiplet at **δ 7.2–7.6 ppm**, integrating for 5 protons.

- **Vinyl Protons (–CH=CH–):**

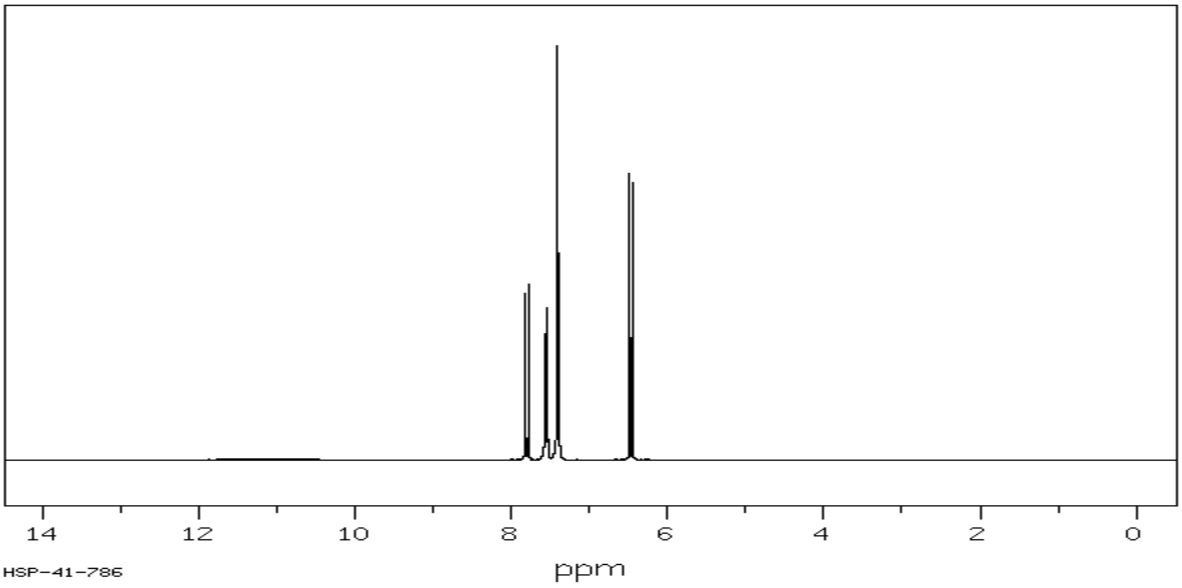
  - One proton at **δ 6.3–6.8 ppm** (cis proton).

  - One proton at **δ 7.4–7.6 ppm** (trans proton, deshielded by conjugation).

  - They show **coupling (J ~16 Hz)** confirming **trans geometry**.

- **Carboxylic Acid Proton (–COOH):**
  Broad singlet around **δ 11–12 ppm**.

- Confirms **alkene with trans coupling, aromatic system, and COOH group**.



3. Mass Spectrometry (MS)

- **Molecular ion peak (M^+):** m/z **148** (confirms molecular weight).

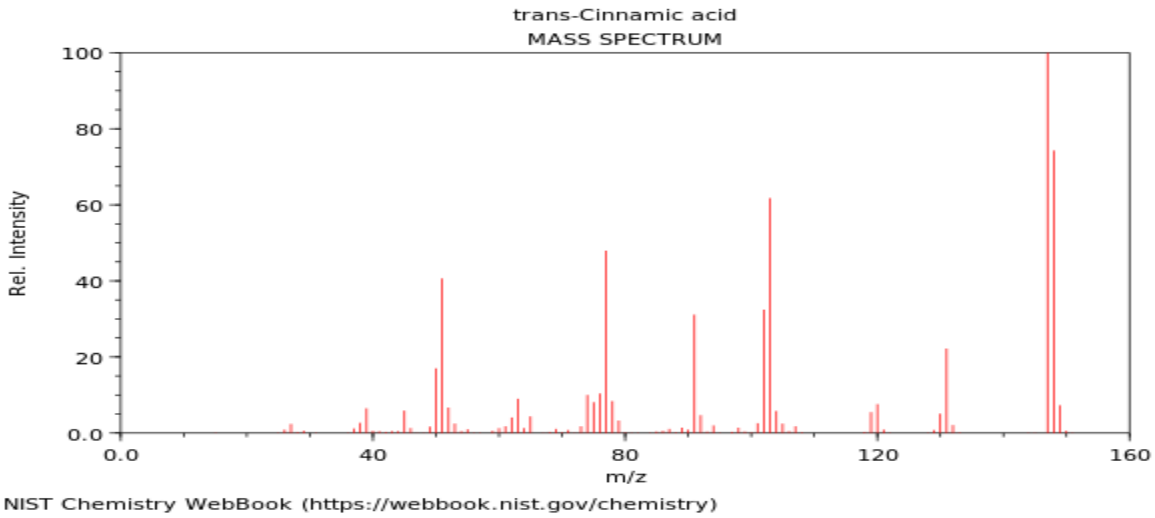
- **Key fragments:**

  - Loss of –OH → peak at **m/z 131**.

  - Loss of –COOH → peak at **m/z 103** (styrene cation).

  - Phenyl cation at **m/z 77** (strong fragment, common in aromatics).

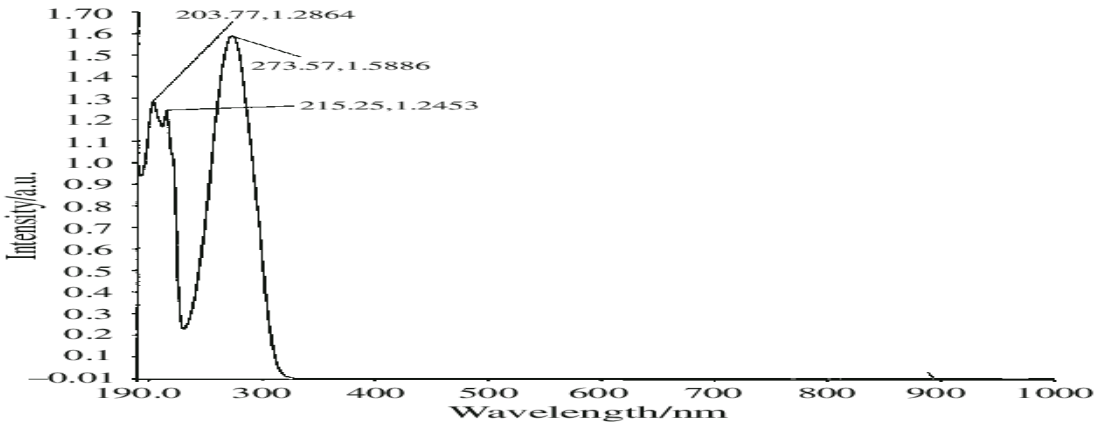
- Supports cinnamic acid structure.



4. UV–Visible Spectroscopy (UV-Vis)

- **π → π*** transitions (aromatic + conjugated double bond): absorption around **270–280 nm**.
- **Extended conjugation (Ph–CH=CH–COOH):** Shows a **bathochromic shift** (red shift) due to conjugation between benzene ring and alkene group.

Indicates **conjugated aromatic-alkene system**.



Final Structural Confirmation

- **IR:** Shows COOH, aromatic ring, and alkene group.

- **^{1}H NMR:** Confirms aromatic protons (5H), trans-alkene protons (J ~16 Hz), and COOH proton (~11–12 ppm).
- **MS:** Molecular ion m/z 148 with expected fragments.
- **UV-Vis:** Confirms conjugated aromatic + alkene chromophore.
- **Thus, the structure is confirmed as *Cinnamic Acid*.**

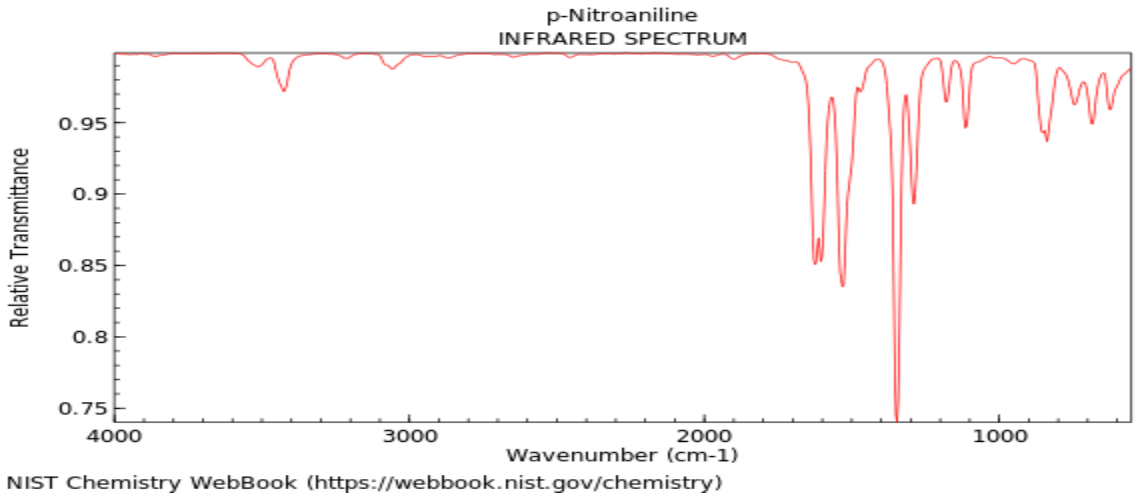
8.Structural Elucidation of p-Nitroaniline ($C_6H_6N_2O_2$) Using Integrated Spectroscopic Techniques

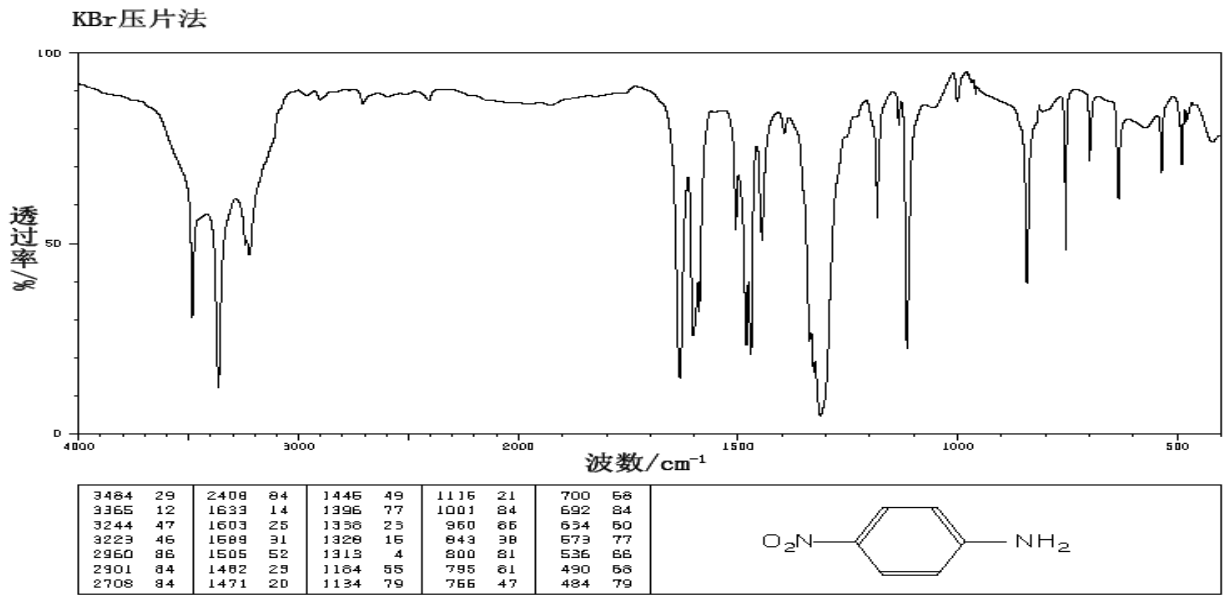
p-Nitroaniline is an aromatic compound with a nitro group (-NO_2) at the para position relative to an amino group (-NH_2) on a benzene ring. The structure of p-nitroaniline can be elucidated using IR, NMR, MS, and UV-Vis spectroscopy.

1. Infrared (IR) Spectroscopy

The IR spectrum of p-nitroaniline provides clear evidence for the presence of both the nitro group and the amino group, as well as the aromatic ring:

- *N-H Stretch (Amino Group, -NH_2): A pair of broad absorption bands in the range 3300-3500 cm^{-1} due to asymmetric and symmetric stretching of the N-H bonds in the amino group.*
- *NO_2 Stretch (Nitro Group): The nitro group (-NO_2) exhibits two characteristic strong bands:*
- *Asymmetric Stretch: A strong band around 1510-1550 cm^{-1}.*
- *Symmetric Stretch: Another strong band between 1330-1370 cm^{-1}.*
- *Aromatic C=C Stretch: Peaks in the range of 1450-1600 cm^{-1} correspond to the stretching vibrations of the C=C bonds in the aromatic ring.*
- *C-H Stretch (Aromatic Ring): Peaks around 3050-3100 cm^{-1} due to the C-H stretching vibrations of the aromatic system.*
- *These features confirm the presence of both nitro and amino groups on the benzene ring.*

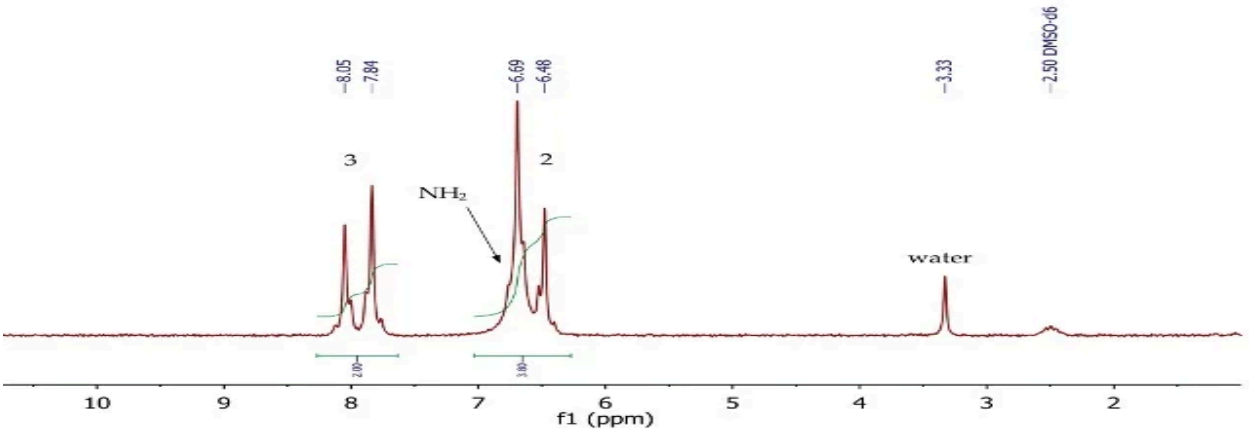




2. Nuclear Magnetic Resonance (NMR) Spectroscopy

1H NMR (Proton NMR)

- *Aromatic Protons: The protons on the benzene ring (C_6H_6) will appear as two doublets in the range of δ 6.5-8.0 ppm. These doublets arise due to the splitting from the neighboring protons, with the typical coupling constant for an aromatic system. The splitting is indicative of the para-substitution pattern of the nitro and amino groups on the ring, with two sets of equivalent protons.*
- *Amino Protons (NH_2 group): The protons of the -NH_2 group appear as a singlet around δ 4.5-5.5 ppm. This signal may be broad due to the ex-changeable nature of the amino protons.*

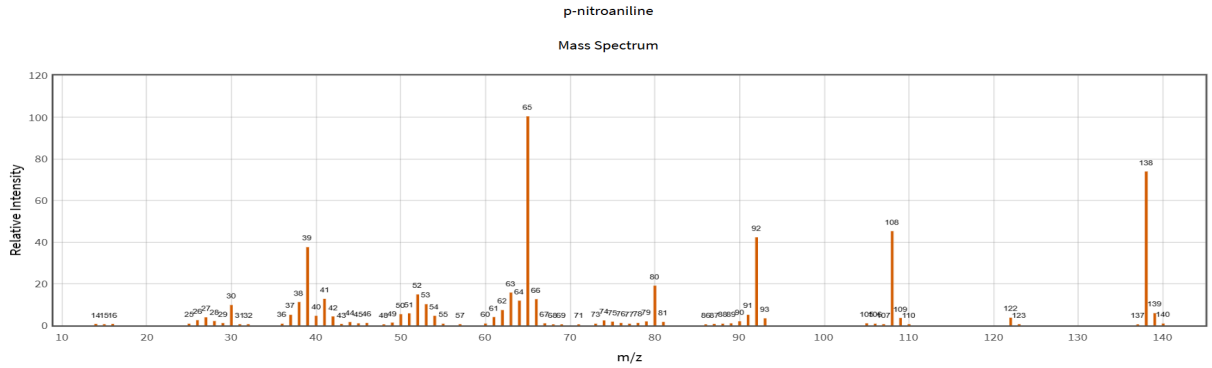


3. Mass Spectrometry (MS)

- *Molecular Ion Peak (M^+): The molecular ion peak is observed at m/z 138, which corresponds to the molecular weight of p-nitroaniline (138 g/mol).*

- *Fragmentation Pattern:*
  - *m/z 121: This peak corresponds to the loss of a hydroxyl group (-OH) from the nitro group.*
  - *m/z 65: A significant fragment due to the presence of the nitro group or a resonance-stabilized fragment of the benzene ring.*

The molecular ion peak at m/z 138 and the characteristic fragment ions confirm the structure of p-nitroaniline.

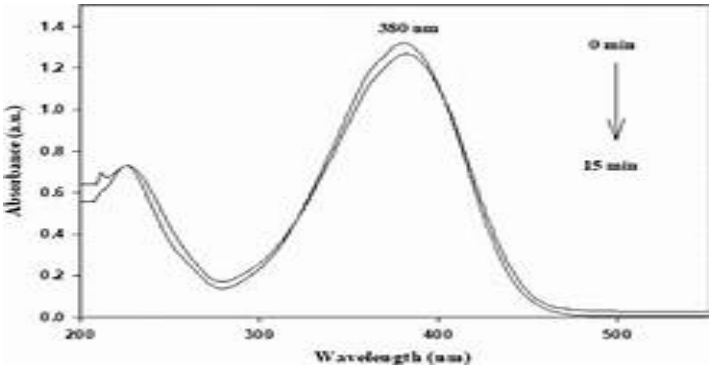


4. Ultraviolet-Visible (UV-Vis) Spectroscopy

The UV-Vis spectrum of p-nitroaniline shows absorptions due to the conjugation between the amino group (-NH_2) and the nitro group (-NO_2) through the aromatic ring:

- *$\pi \rightarrow \pi$ Transition*: An absorption band in the 230-270 nm range corresponds to $\pi \rightarrow \pi^*$ transitions within the aromatic system.*
- *$n \rightarrow \pi$ Transition (Nitro Group)**: The nitro group contributes an additional weak absorption band around 300-350 nm, due to $n \rightarrow \pi$ transitions involving the lone pair electrons on the nitrogen of the nitro group.*

These absorption bands are characteristic of the conjugated system involving the nitro and amino groups.



Conclusion

The structure of p-nitroaniline is confirmed by the combination of these spectroscopic techniques:

- *IR Spectroscopy: Shows characteristic peaks for the nitro group (-NO_2), amino group (-NH_2), and the aromatic ring.*
- *^1H NMR: Reveals doublets for the aromatic protons and a singlet for the amino protons, consistent with para-substitution.*
- *^{13}C NMR: Confirms the presence of aromatic carbons, with deshielding effects from the nitro and amino groups.*
- *Mass Spectrometry: Provides a molecular ion peak at m/z 138 and fragment ions that support the structure.*
- *UV-Vis Spectroscopy: Shows absorption bands typical of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the conjugated system.*

These data collectively confirm the structure of p-nitroaniline as a para-substituted aromatic compound with a nitro group and an amino group on opposite ends of the benzene ring.