WELCOME TO THE SPECTROSCOPY TUTORIAL

This tutorial is developed for students pursuing their Master degree in Chemistry. During teaching at University of Delhi, I realized that there is a great need to develop a teaching methodology by which students can learn how to interpret the structure of an unknown compound whose spectra is given. This tutorial is developed in such a way that any student can learn the art of structure determination by spectroscopic techniques.

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Nuclear Magnetic Resonance Spectroscopy

Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy is a powerful method used in the determination of the structure of unknown organic compounds.

The most challenging task of a chemist is to identify structure of unknown organic compound. There are many ways to obtain the identity of an unknown substance. A person can use physical methods such as boiling point, infrared spectroscopy, or several other chemical methods for determination of structure of organic compounds. However, I think that spectroscopy is one of the best ways to identify a substance and Nuclear Magnetic Resonance (NMR) spectroscopy plays an important role in this process. It not only provides an accurate identification, but its fun to solve the NMR spectrum. NMR spectrum is like a good puzzle and it provides a challenge, but with a little thought, and understanding of the concepts, it can be solved. NMR provides an "information" about number of hydrogen or carbon present in the given molecule. Many kinds of nuclei act like tiny magnets and therefore interact with an external magnetic field. Depending, the electron density around the proton, protons said to be shielded (up filed, low δ value) or deshielded (down filed, high δ value). Each peak in the ^{1}H NMR spectrum tells about different kind of proton as well as total number of proton present in a molecule. This tutorial is being developed for any chemist who wishes to play with the spectroscopy related problems. Efforts are being made, to understand the concept based on problems, and at the end how to solve the structure of the complex organic compound is described.

The ^{1}H NMR spectrum of an organic compound provides information concerning:

- the different types of hydrogen's present in the molecule
- the relative number of the different types of hydrogen's
- the electronic environment of the different types of hydrogen's
- the number of hydrogen "neighbor" a hydrogen has

Proton Chemical Shifts of Methyl Derivatives

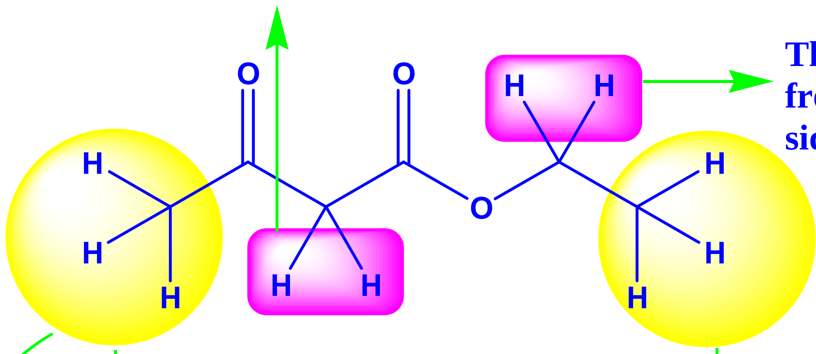
Compound	$(CH_3)_4C$	$(CH_3)_3N$	$(CH_3)_2O$	CH_3F
δ	0.9	2.1	3.2	4.1
Compound	$(CH_3)_4Si$	$(CH_3)_3P$	$(CH_3)_2S$	CH_3Cl
δ	0.0	0.9	2.1	3.0

Proton Chemical Shifts (ppm)

Comp / Sub.	X=Cl	X=Br	X=I	X=OR	X=SR
CH_3X	3.0	2.7	2.1	3.1	2.1
CH_2X_2	5.3	5.0	3.9	4.4	3.7
CHX_3	7.3	6.8	4.9	5.0	

Let us see how many ^{1}H NMR signals you will get for ethyl-3-oxobutanoate [$CH_3COCH_2COOCH_2CH_3$], see structure of this compound as depicted below:

This CH_2 group is flanked between two CO groups



This CH_2 group is attached with oxygen from one end, and CH_3 group from other side

Ethyl 3-oxobutanoate

See these two CH_3 groups, both of these groups have different environment.

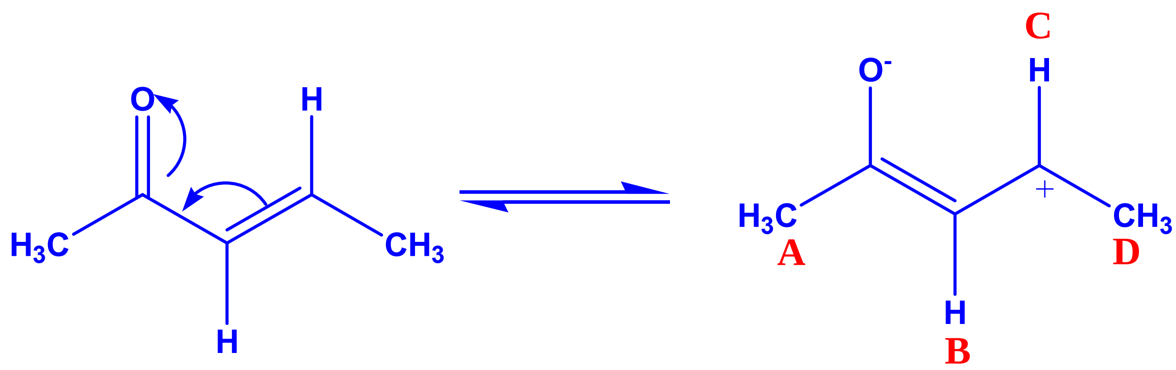
This CH_3 group is attached with CO group

This CH_3 group is attached with CH_2 group

As you can see ethyl 3-oxobutanoate has four different kind of protons, so this compound will give you four signals in the NMR.

It means you can count how many different kinds of protons you have in a given compound. If you can visualize the electron density at each of the carbon/hydrogen in a given compound, you can easily tell how many signals you should expect in a given compound. Can you tell me how many signals you will expect for compound (E)-pent-3-

en-2-one. First write down the resonating structure of the compound. Now try to find out the electron density around each of the carbon in the given compound.

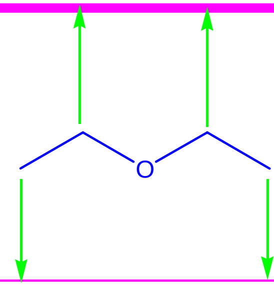


By inspecting above structure CH_3 group labeled as A is attached with CO group, while other CH_3 group labeled as D is attached with vinylic carbon, so both of these CH_3 groups will have different electron density. It means in another word, both of these CH_3 groups will give you different NMR signals. Now if you see both of the vinylic hydrogen's labeled as B and C, both of these hydrogen's are under different chemical environment. H labeled as B is attached with a carbon having double bond, while H labeled as C is attached with a carbon having + charge on it. So both of these hydrogen's will give you two different ^{1}H NMR signals. So this compound will give you four NMR signals.

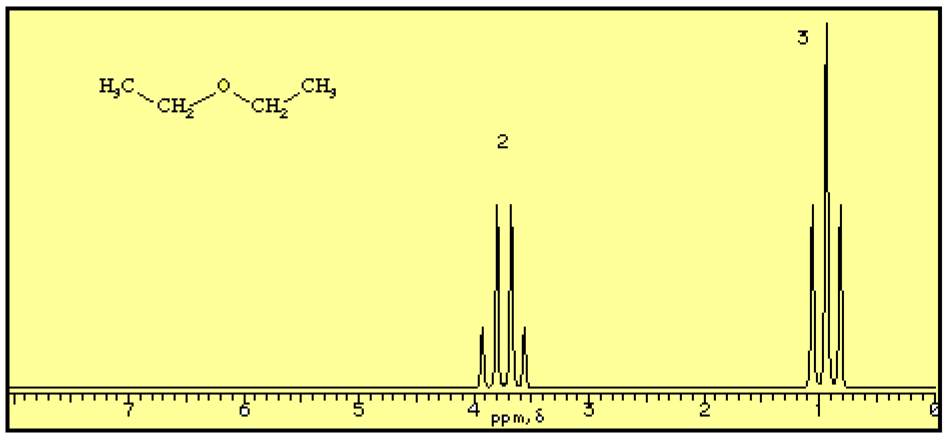
Spin-Spin Coupling/Splitting:

Splitting of signals depends on the number of hydrogen present on the neighboring carbon atom. Consider the example of diethyl ether ($CH_3CH_2OCH_2CH_3$).

See these CH_2 groups are attached with a carbon having three protons, so this signal will appear as quartet (2nI+1)



See these CH_3 groups are attached with a carbon having two protons, so this signal will appear as triplet (2nI+1)



This multiplicity depends on the phenomena called *spin coupling* and this arises because of interaction of the proton magnetic field with bonding electrons. In essence, each proton can have one of two possible spin orientations in the applied magnetic field, so that the magnetic field sensed by adjacent protons can have one of two possible values. The result is that *n* protons will split adjacent protons into (*n* + 1) peaks. The intensities of these peaks are simply a result of the possible spin orientations, thus, the protons of a CH_2 group can have the following possible spins:

↑↑ ↑↓ ↓↑ ↓↓

The middle pair is degenerate, therefore a proton adjacent to a CH_2 group will be split into three separate peaks in the ratio 1:2:1.

The separation between these peaks is referred to as the *coupling constant*, *J* which is measured in Hz; typical values for *J* seldom exceed 20 Hz and it is important to note that sets of coupled protons will display exactly the same coupling constant.

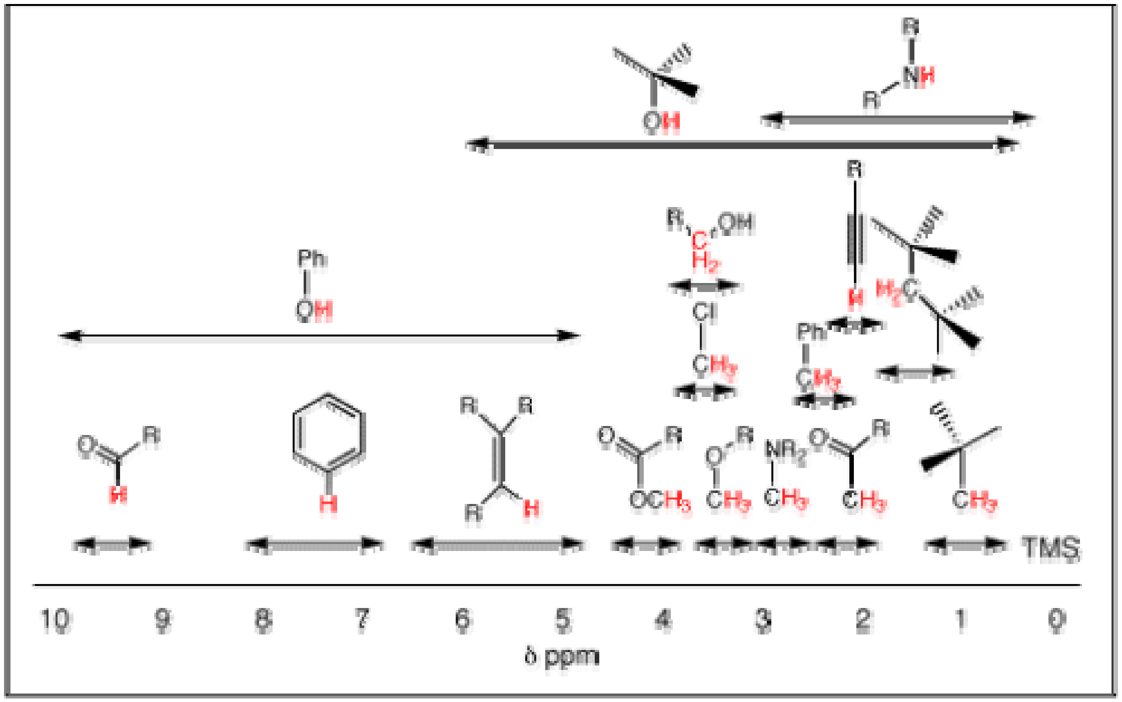
In the spectrum for diethyl ether, the CH_3 group is split by the two protons on the adjacent CH_2 group into three peaks (a **triplet**) and the absorbance for the CH_2 is split by the three protons on the methyl group into (*n* + 1) = 4 peaks (a **quartet**). The two ethyl groups in diethyl ether show as a single absorbance since the molecule has a plane of symmetry, that is, both ethyl groups are chemically and magnetically equivalent.

Proton NMR Chemical Shifts for Common Functional Groups

- Electronegative groups are "deshielding" and tend to move NMR signals from neighboring protons further "downfield" (to higher δ values).

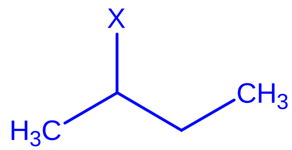
- Protons on oxygen or nitrogen have highly variable chemical shifts which are sensitive to concentration, solvent, temperature, etc.
- The π-system of alkenes, aromatic compounds and carbonyls strongly deshield attached protons and move them "downfield" to higher ppm values.

Figure 8. Approximate proton chemical shifts.

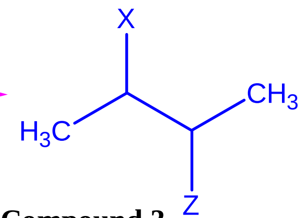


Speculate how many signals each of the following compounds will give in their proton NMR spectra.

This compound becomes enatiomer;
So this CH_2 is known as enantiotopic
proton, and enatiotopic protons are chemically
or magnetically equivalent, so will not couple
each other, so this compound will give two signals only
(one for two CH_3, and other for two CH_2 groups



Compound 2

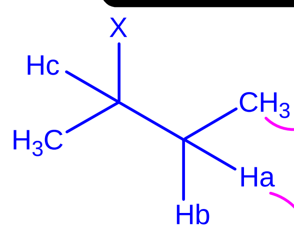


Compound 3

Substitute one H from
CH_2 group by X

Compound 1

This compound becomes distereoiomer;
So this CH_2 is known as distereotopic
proton, and distereotopic protons are chemically or
magnetically non equivalent, so will couple
each other



This CH_3 has different environment than other CH_3, so two signals will be observed for these two CH_3

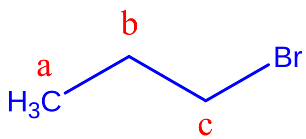
Non equivalent, so will give two NMR signals

So this compound will give five NMR signals (explanation is in the next page

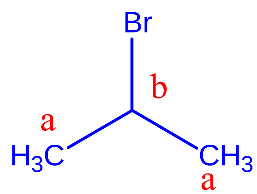
Compound 1: There are two CH_3 groups attached with two CH_2 groups, so there are two kinds of protons. So this compound will give you only two NMR signals.

Compound 2: One of the CH_3 group is attached with CHX group while other with CH_2 group, so both of the CH_3 groups are non equivalent, so will show two different signals. There is one CH2 group which is attached with a carbon that is chiral, remember: CH_2 group attached with chiral center is chemically and magnetically non equivalent, so the proton attached of this CH_2 group are non equivalent, so will give two signals. One signal will be by the CH. So there will be total five NMR signals in this compound.

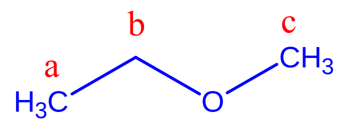
<u>Find out number of NMR signals in the following compounds</u>



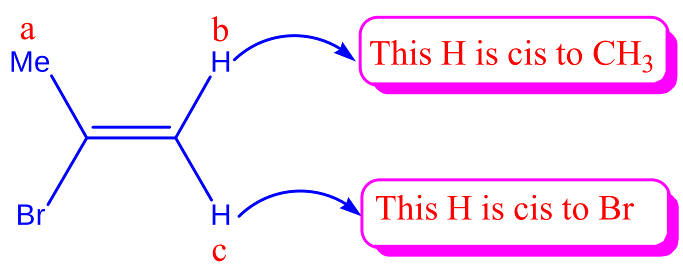
3 NMR Signal



2 NMR Signal

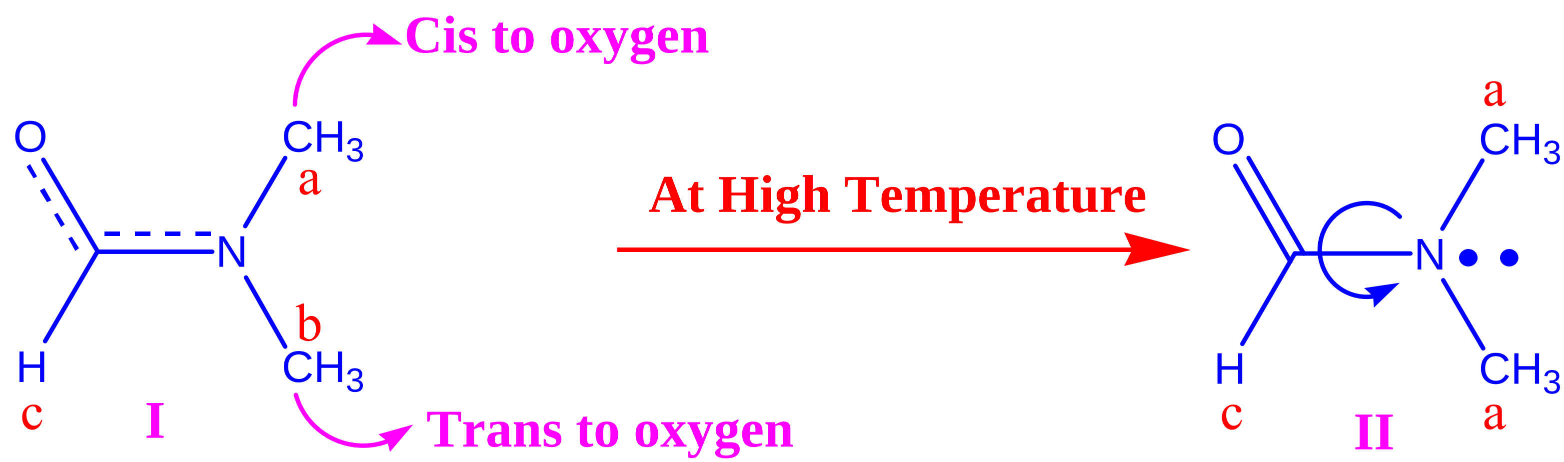


3 NMR Signal



3 NMR Signal

<u>N,N-Dimethyl formamide (DMF):</u>



DMF exist as structure I at room temperature, so one of the CH_3 group is Cis to oxygen, and other in Trans to oxygen. Since the bond order between N and C is 1.5 so there is no free rotation. Hence both of the CH_3 will give you different signals. As a result compound I will show three signals.

At higher temperature DMF exist as compound II, and there will be a free rotation between N and C bond, hence, both of these CH_3 groups will show one signal. This compound will show two signals in all.

Problems: The chemical shift scale on a NMR spectrum is typically given in dimensionless units termed "parts per million" (ppm) from some reference compound. What is the relationship between a chemical shift scale in Hz and a scale in "ppm" ?

Solution: The resonance frequency of a nucleus (expressed in Hz) is directly proportional to the strength of the applied magnetic field and *changes from spectrometer to spectrometer*, depending on the strength of the magnet. It is more convenient

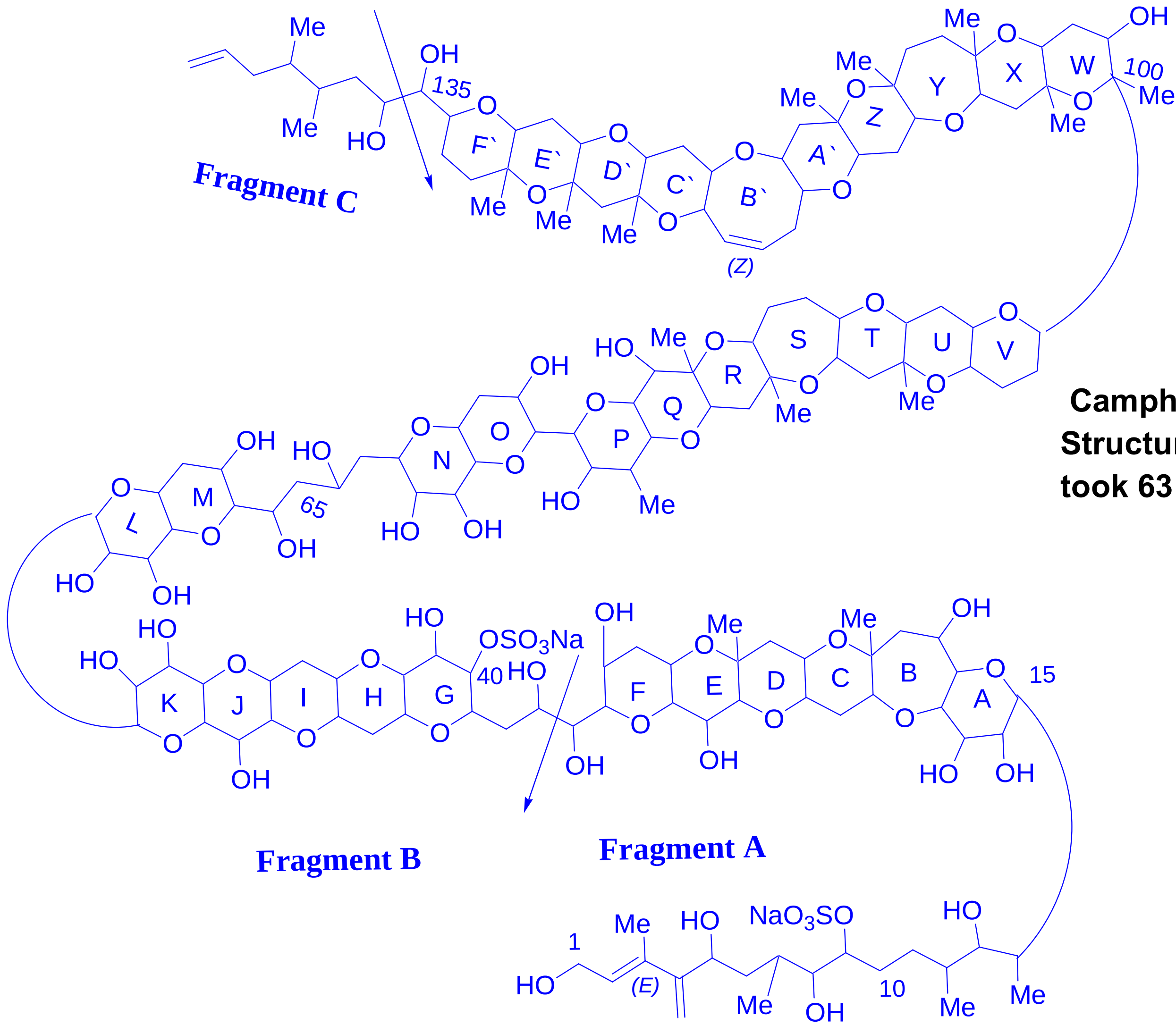
to express the resonance frequency in dimensionless units (termed "parts per million" or "ppm") by dividing the actual resonance frequency of the nucleus by the Larmor frequency of the type of nucleus being observed. In this way, all chemical shifts are effectively "normalized" to take account of the fact that each different spectrometer may have a different magnetic field strength. Chemical shifts are typically measured relative to the frequency of some standard compound, taken by convention as a reference, and chemical shifts are usually expressed in units of ppm from the resonance of the reference compound. Chemical shifts expressed in ppm are independent of B_o and are tabulated as characteristic molecular properties. If the Larmor frequency for observing a nucleus in particular spectrometer is 400 MHz then 1 ppm corresponds to 400Hz.

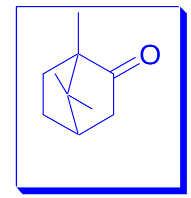
Problem: The magnetogyric ratio of the deuterium (^{2}H) nucleus is approximately 6.5 times smaller than that of the proton. In a magnet where a ^{1}H spectrum can be observed at about 400 MHz, what is the approximate frequency of Rf. radiation you would need to observe the ^{2}H NMR spectrum ?

Solution: The answer to this question is very similar to the answer to Question 4. The question asks for a comparison between the frequencies required for the observation of protons (^{1}H) and deuterium (^{2}H) in the same magnet. The magnetogyric ratio of ^{1}H is 6.5 times that of ^{2}H, so the frequency required to observe ^{2}H will be 1/6.5 that required to observe ^{1}H.

^{2}H frequency = ^{1}H frequency / 6.5
= (400 / 6.6) MHz
= 61.54 MHz.

See the following two structures, and you will realize what is the role of spectroscopy in the structure elucidation of an organic compound !!





Camphor ($C_{10}H_{16}O$)
Structure determination took 63 years

Maitotoxin ($C_{163}H_{260}Na_2O_{68}S_2$: Structure elucidation was acheived within five years

Problem 1: An organic compound having molecular formula $C_5H_{12}O$ gave following spectral data.

- IR: 3400 cm^{-1}; 1H NMR (CDCl3): 0.95 (d, 6H), 1.8 (m, 3H), 2.7 (brs, 1H), 3.9 (t, 2H). Find out structure of the compound.

Problem 2: An organic compound having molecular formula $C_{13}H_{20}N_2O_2$ gave following spectral data.

- IR: 3500, 3400, 1765, 13342 cm-1; 1H NMR (400 MHz, CDCl3): 1.15 (t, 6H), 2.4-2.8 (m, 6H), 4.1 (t, 2H), 6.8 (d, J = 9Hz, 2H), 7.8 (d, J = 9Hz, 2H). Determine structure of given compound.

Problem 3: An organic of molecular formula C_9H_{12} showed following spectral data.

- ^{1}H NMR: 1.2 (d, J = 8Hz, 6H), 2.87 (sept, 1H), 7.2 (s, 5H). Determine the structure of given compound.

Solution of problem 1:

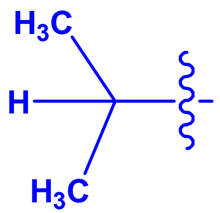
- If MF of the compound is given, you MUST calculate DBE first. Double Bond Equivalence (DBE) gives you an idea about the nature of the compound, if the compound is acyclic, cyclic, unsaturated or aromatic.

- (DBE) = [(2a+2)-(b-d)]/2; Where: a = No of Carbon atom; b = Hydrogen or monovalent atom; d = Nitrogen.

- DBE of given compound ($C_5H_{12}O$), so DBE = [(2X5+2)-(12-0)]/2 = 0

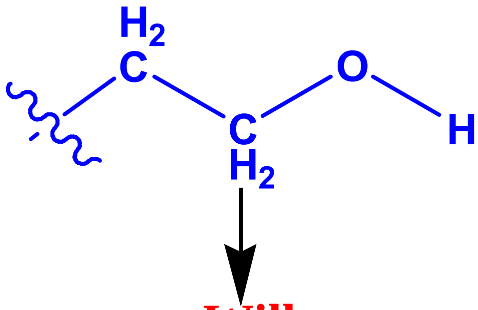
- It means the given compound is saturated acyclic. If DBE is greater than zero, than compound may be cyclic, unsaturated or aromatic.

- IR of given compound shows presence of a stretch at 3400 cm^{-1}, typical for OH group (see the given IR spectral data).
- ^{1}H NMR gives four signals, indicates the presence of four sets of non-equivalent protons (see the given spectral data).
- A doublet at 0.95 ppm of six protons indicates the presence of one $(CH_3)_2CH$ group. Remember the multiplicity depends on the number of protons present at the neighbouring carbon atom.



See these two CH_3 groups are attached with CH, so these CH_3 groups will give a doublet

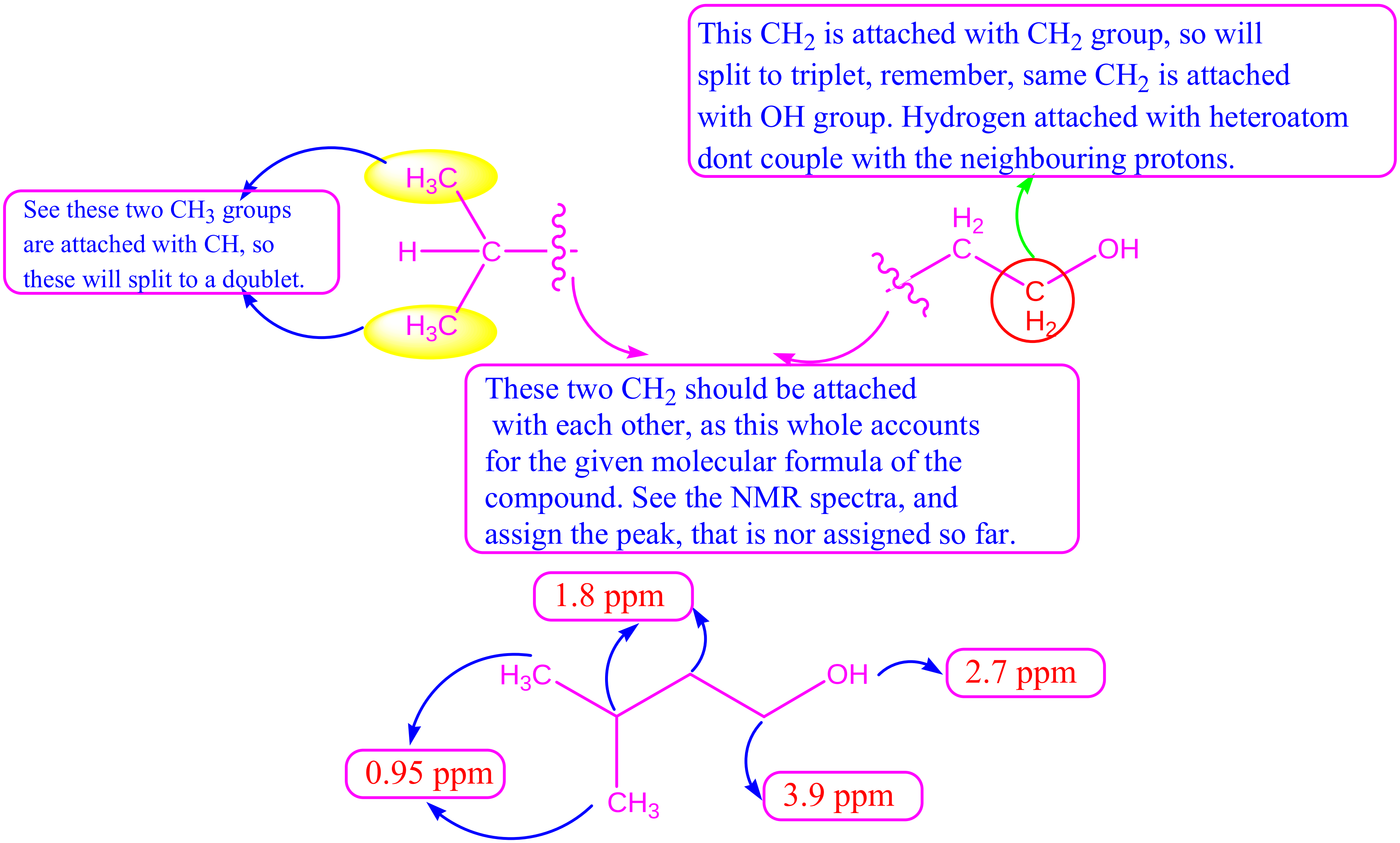
- Presence of a triplet at 3.9 ppm of two protons confirms the presence of CH_2CH_2-O functionality, because you can see triplet only if next carbon have two hydrogens. Resonance around 3.5-4.3 is typical for OCH functionality.



Remember you have one Oxygen in your molecule, and nature of oxygen is hydroxyl as confirmed by its IR, and OH does not participate in coupling

Will appear as triplet as this CH_2 group is attached with CH_2 group

- Presence of a broad singlet at 2.7 for one proton is typical for OH group, which is further confirmed by IR. Based on this discussion the structure of the given compound is:


This CH2 is attached with CH2 group, so will split to triplet, remember, same CH2 is attached with OH group. Hydrogen attached with heteroatom dont couple with the neighbouring protons.
See these two CH3 groups are attached with CH, so these will split to a doublet.
H3C
H
C
H3C
H2
C
OH
C
H2
These two CH2 should be attached with each other, as this whole accounts for the given molecular formula of the compound. See the NMR spectra, and assign the peak, that is nor assigned so far.
1.8 ppm
H3C
OH
2.7 ppm
0.95 ppm
CH3
3.9 ppm

Solution of problem 2

- MF of the given compound is: $C_{13}H_{20}N_2O_2$

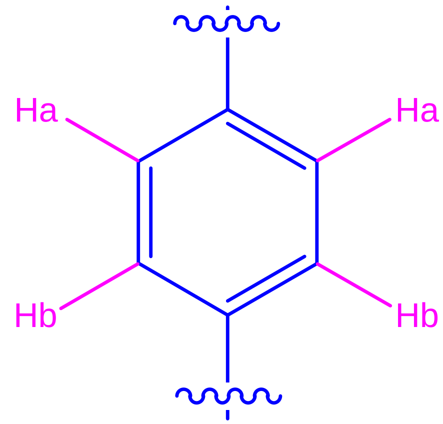
- DBE of given compound = [(2a+2)-(b-d)]/2

- DBE = [(2X13+2)-(20-2)]/2 = 5; it means the given compound contains five degree of unsaturation, that menas: it can contain five double bonds, one aromatic ring (remember benzene has one ring, and three double bonds, so benzene accounts for four DBE), and one double bond etc.

- IR of given compound shows presence of a stretch at 3500, 3400, 1765, and 1342 cm^{-1}, the data suggest the presence of primary amine (two peaks at 3500, 3400 cm^{-1}, typical for primary amines), and one stretch as 1765 cm^{-1} indicates the presence of carbonyl group, that's too should be of ester functionality (remember CO group of ester requires more energy than isolated carbonyl group).

- ^{1}H NMR gives six signals, indicates the presence of six sets of non-equivalent protons (see the given spectral data).

- Two doublets at 6.8 and 7.8 ppm of two protons each with coupling constant 8Hz is typical for p-disubstituted benzenes (protons of benzene appears from 6.5 to 7.5 ppm, and if it is substituted, the pattern of substitution can be confirmed by the coupling constant. Ortho copuling is 8Hz, meta coupling is 2-3 Hz, and para coupling is 1 Hz).



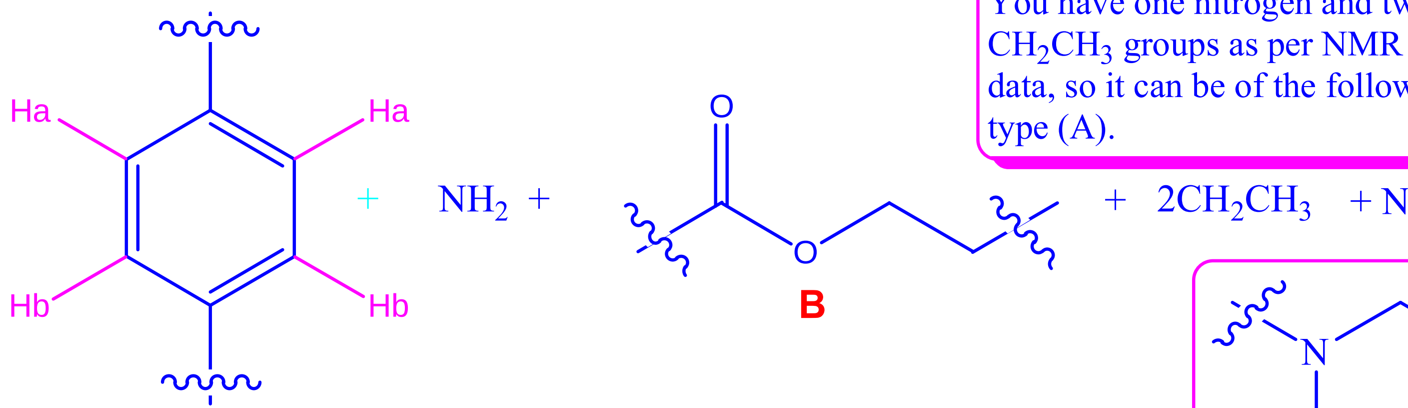
- As mentioned before we have already confirmed the presence of CO group, so one side of the aromatic ring should be attached with CO group, and it will deactivate the aromatic ring in such a way that hydrogen at ortho position to the CO group will be deshielded (downfield, high δ values) while proton at para position will be shielded (upfield, low δ values).

- This accounts the four DBE, and one is for CO group, so all five DBE is accounted for.

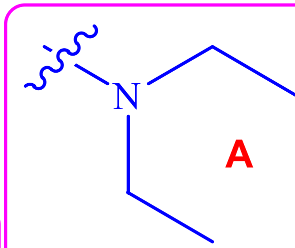
- Presence of a triplet at 1.15 ppm of six protons indicates the presence of two CH_2CH_3 groups, because you can see triplet only if next carbon have two hydrogens.

- Presence of a broad singlet (typical for hydrogen attached with heteroatom) at 3.7 ppm for two proton is typical for NH_2 group, which is further confirmed by IR.

- Presence of one triplet of two protons at 4.1 ppm is typical for OCH_2CH_2 functionality.

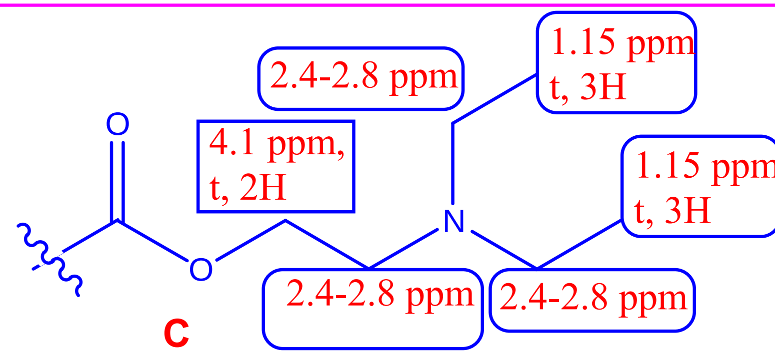


You have one nitrogen and two CH_2CH_3 groups as per NMR data, so it can be of the following type (A).



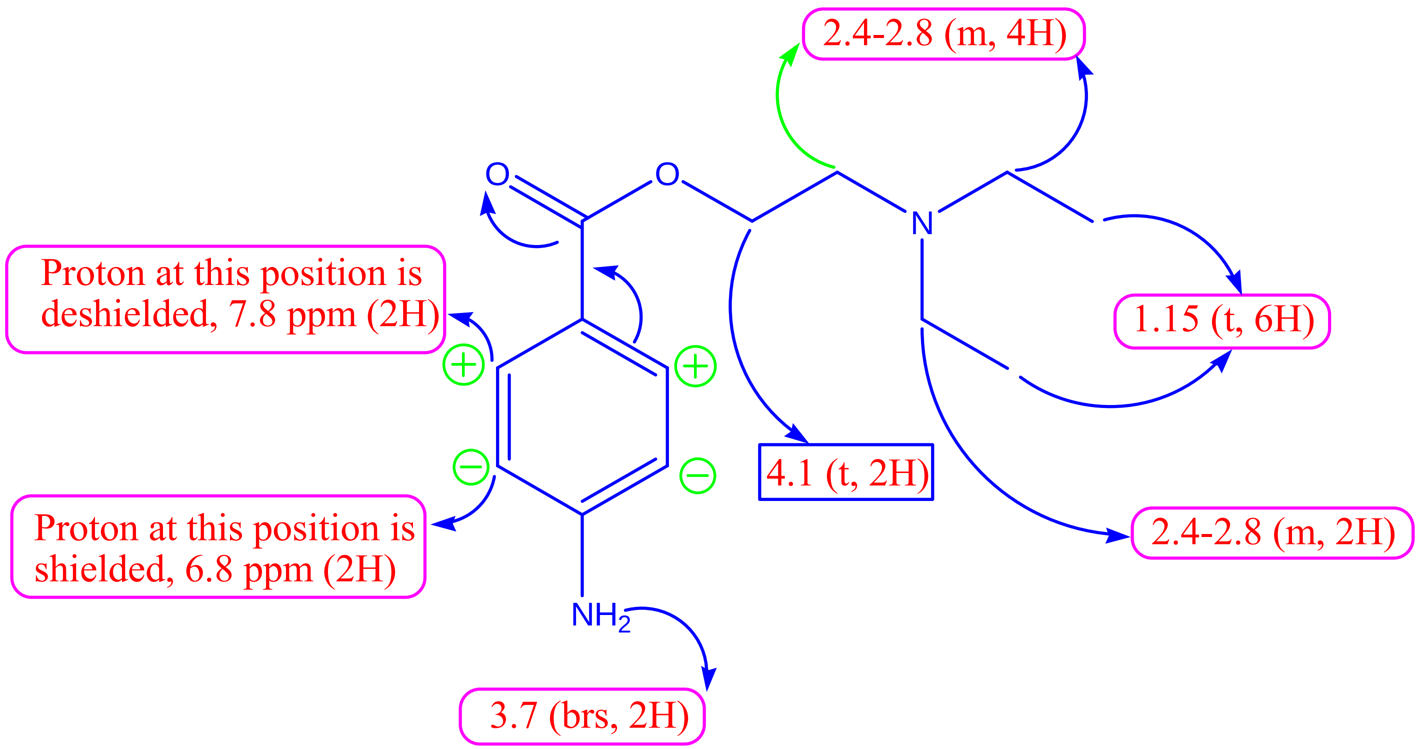
Benzene ring must be 1,4-disubstituted since we see two doublets of two protons each in the aromatic region. Ha must be desheilded than Hb as chemical shift difference between two doublets is about 1 ppm, it indicates a deactivating group is directly attached with the ring.
See, you have an ester functionality, so ester functionality should be attached at one position of the ring, while at other position NH_2 group should be attached.

A and B can be attached with each other, and one complete frgment can be constructed.



Fragment C should be attached with
Benzens ring and at other position
NH_2 group should be attached. The final structure is shown in next slide.

Structure of the given compound



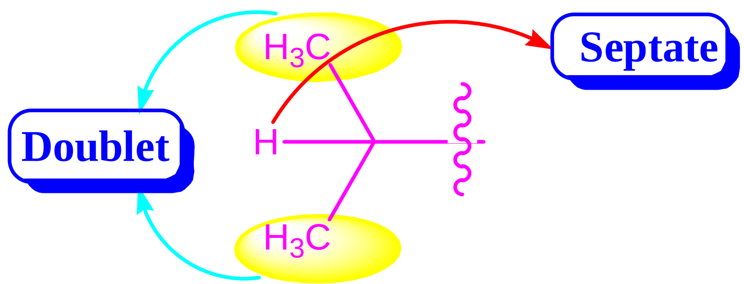
Solution of problem 3

- MF of the given compound is: C_9H_{12}

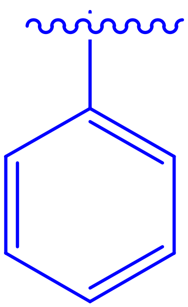
- DBE of given compound = [(2a+2)-(b-d)]/2; [(2X9+2)-(12-2)]/2 = 4; it means the given compound is aromatic.

- [1]H NMR gives three signals, indicates the presence of three sets of non-equivalent protons (see the given spectral data).

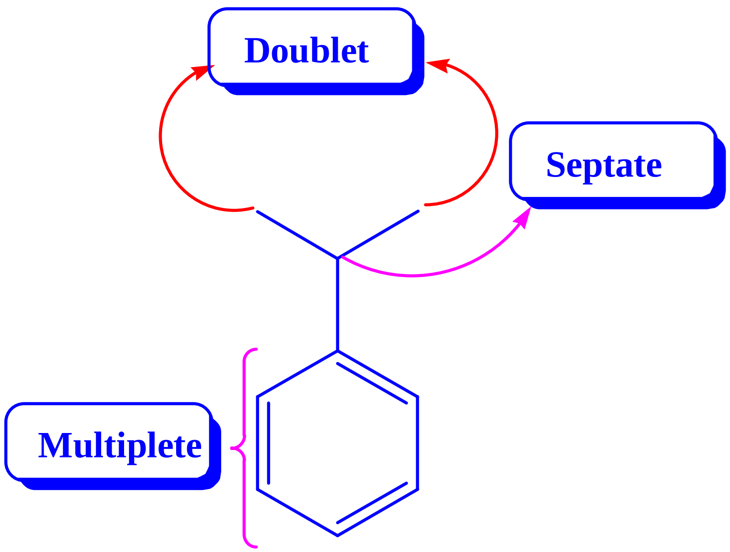
- A doublets at 1.2 ppm of six protons indicates the presence of $(CH_3)_2CH$. This also confirms the presence of a septate of one proton.



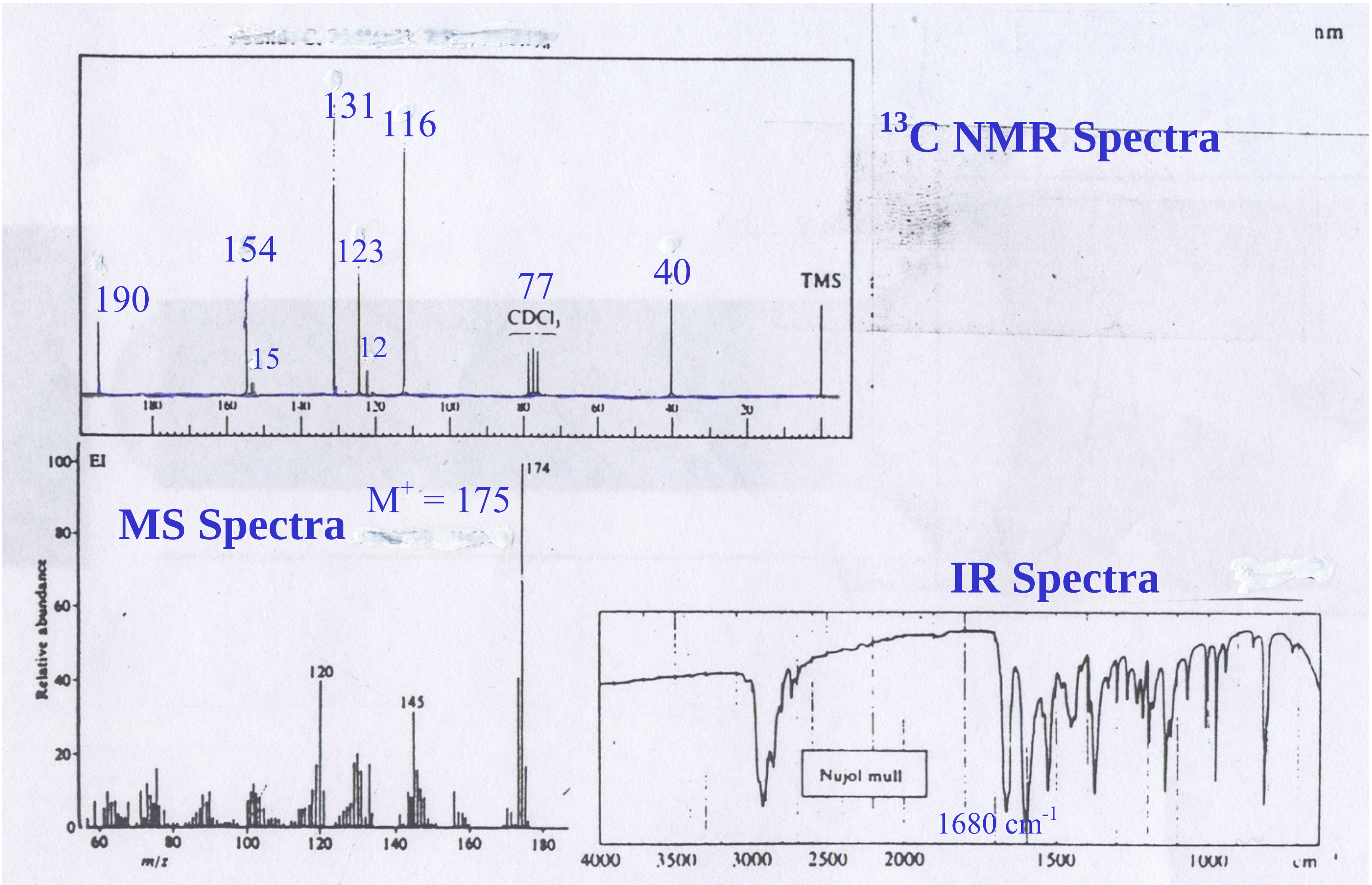
- Presence of multiplete of five protons at 7.2 ppm indicates the presence of aromatic ring.



Based on this discussion, final structure of the compound is as below:

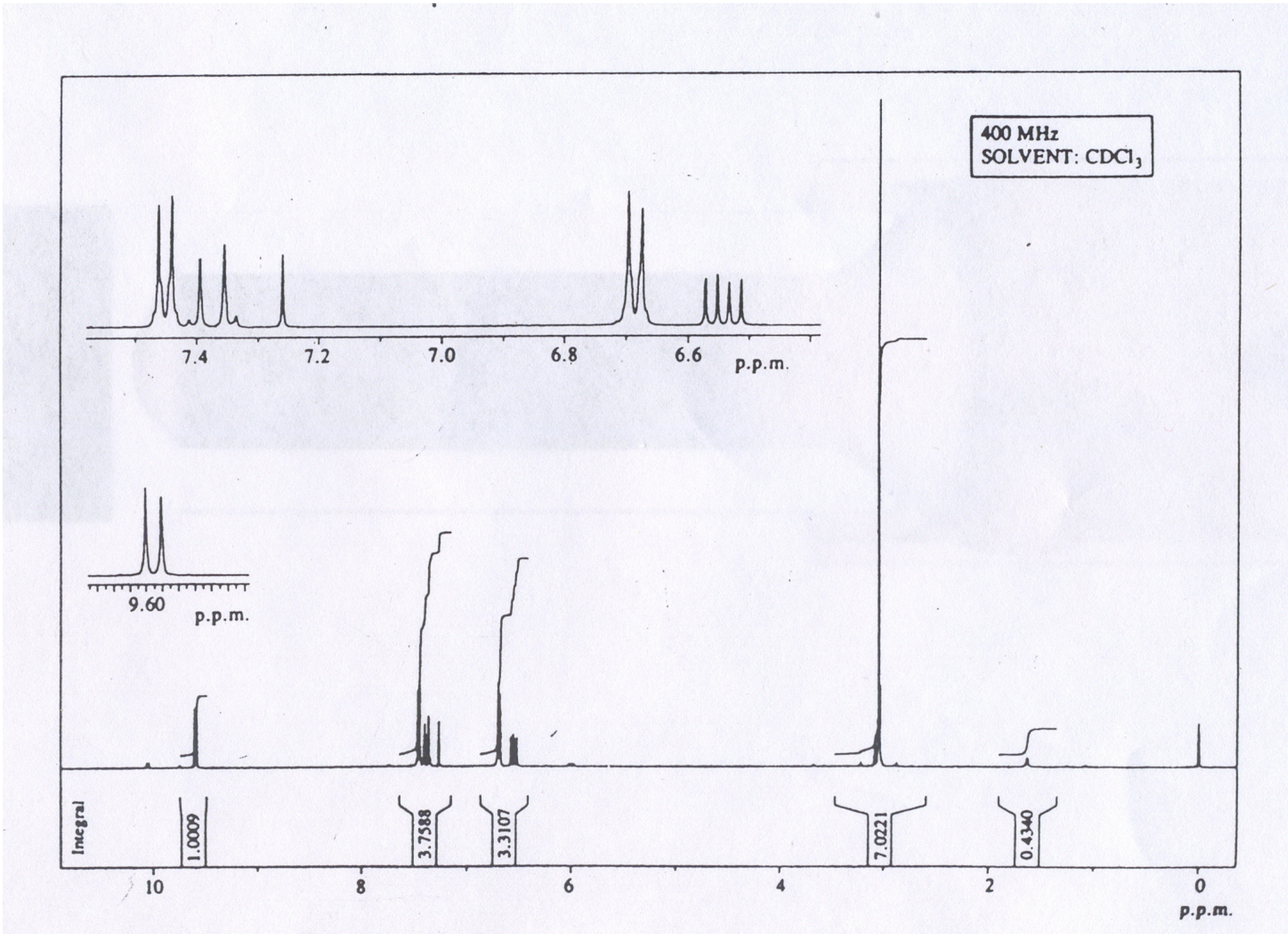


Problem 4: Assign the structure if the compound whose ^{1}H NMR, ^{13}C NMR, MS, and IR spectra is given below (see next page).



13C NMR Spectra
190
154
15
131
116
123
12
77
CDCl3
40
TMS
MS Spectra
EI
M+ = 175
174
120
145
Relative abundance
m/z
IR Spectra
Nujol mull
1680 cm-1
4000
3500
3000
2500
2000
1500
1000
cm
nm

[1]H NMR


400 MHz
SOLVENT: $CDCl_3$
7.4
7.2
7.0
6.8
6.6
p.p.m.
9.60
p.p.m.
Integral
1.0009
3.7588
3.3107
7.0221
0.4340
10
8
6
4
2
0
p.p.m.

Spectral Analysis

Before rushing to solve the problem please remember, for such kind of problem, you need to be careful, and should try to find out basic information from each kind of spectroscopy (for example, see the MS, to know the molecular weight of the compiound. MS will also give you information about the presence of isotopes [if you have Cl, Br or S in your compound there must be a M+2 peak with 33%, 100% or 4.5% respectively of the molecular ion peak]. IR gives you an idea about the functional group present, while ^{1}H NMR tell you how many protons you have in your compound.

- Molecular ion peak at (m/z) 175, tells us there ***MUST*** be odd number of ***Nitrogen*** present in the compound.
- IR (ν = 1680 cm^{-1}) clearly indicates the presence of CO group in resonance with aromatic ring or with a double bond.
- ^{1}H NMR clearly indicates that there is an aldehydic proton present in the compound, and nearly 14 protons.
- ^{13}C NMR spectra confirmed the presence of CHO group as there is a resonance around 190 ppm.
- $_{13}$C NMR spectra confirmed the presence atleast EIGHT carbon in the compound.

Tentative MF from given spectrum

- The compound consist atleast one NITROGEN, and on OXYGEN apart from carbon and hydrogen.
- **According to Rule 13**, tentative MF of the compound:

No of Carbon atom present in the compound = [M+]/13

C = 175/13 = 13 (Reminder = 6)

No of H = No of carbon + Reminder

H = 19

- **If compound consist only C and H then MF of the compound = $C_{13}H_{19}$**

MF from given spectrum

- But as mentioned before, the compound contain atleast one **NITROGEN** and one **OXYGEN**.

- N and O are equivalent to CH_2, and CH_4 respectively.

- So tentative MF of the compound = $C_{13}H_{19}$ + N - CH_2 + O - CH_4 = **$C_{11}H_{13}NO$**

- This compound contains only one Nitrogen and one Oxygen as ^{1}H NMR confirmed the presence of AROUND 14 protons in the compound. So MF of the compound = **$C_{11}H_{13}NO$**

Spectral Analysis of $C_{11}H_{13}NO$

- **Double Bond Equivalence**

(DBE) = [(2a+2) -(b-d)]/2

a = No of carbon atom

b = No of hydrogen or monovalent atom

d = Nitrogen or any trivalent atom

- DBE = [(2 x 11 +2) – (13 – 1)]/2 = 6
- It means this compound contains six degree of unsaturation.

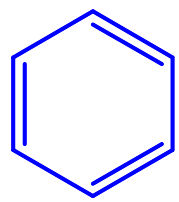
Spectral Analysis of $C_{11}H_{13}NO$: Contd.

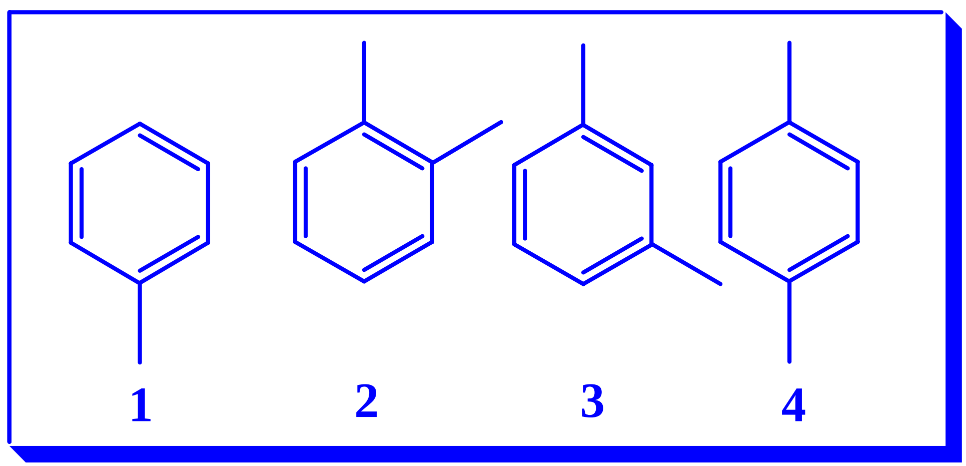
- ^{1}H NMR and ^{13}C NMR clearly indicates the presence of an aromatic ring (6.6 – 7.4 ppm, and 116-154 ppm) , and CHO group.

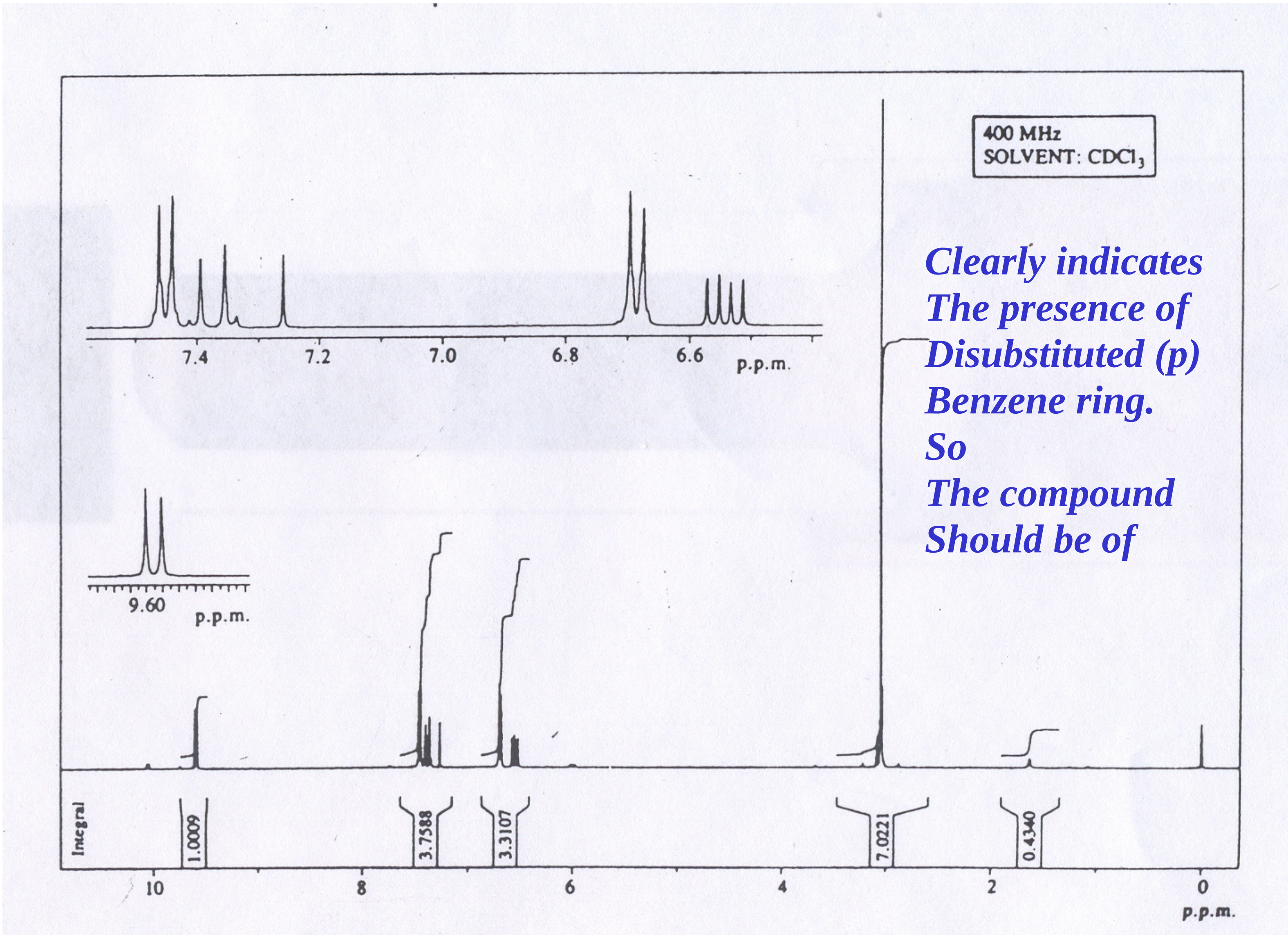
- Aromatic ring means DBE 4, and CHO means One DBE.
- Presence of double doublet (dd) at 6.5 ppm and doublet at 7.35 ppm confirms the presence of a vinylic group in the compound.
- It means the compound is aromatic which is attached with a vinylic, and aldehydic group.

Spectral Analysis of $C_{11}H_{13}NO$: Contd.

- So tentative structure of the compound:

 + Vinylic group + CHO + N



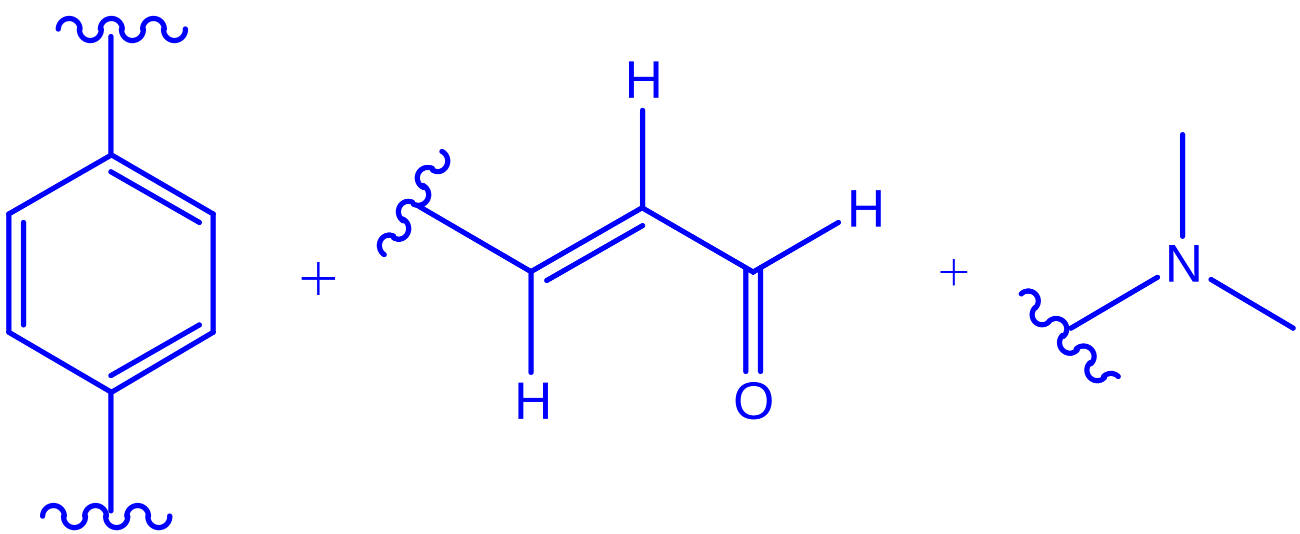


Clearly indicates
The presence of
Disubstituted (p)
Benzene ring.
So
The compound
Should be of

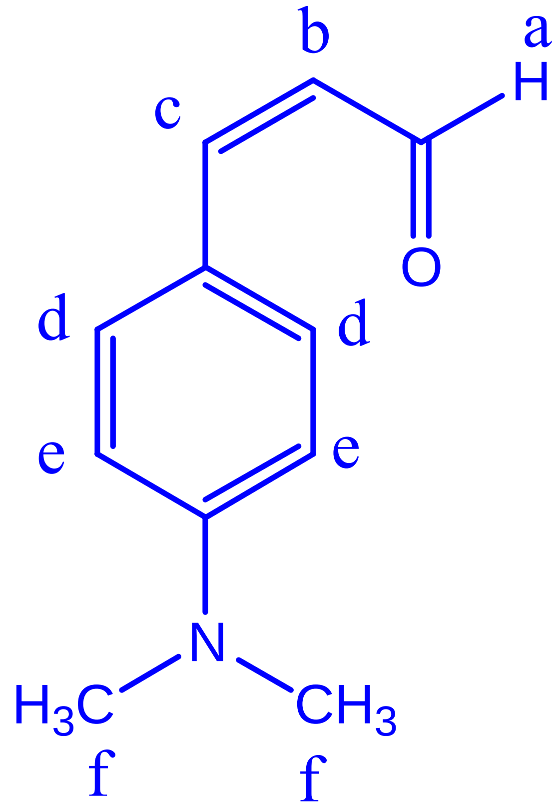
Spectral Analysis of $C_{11}H_{13}NO$: Contd.

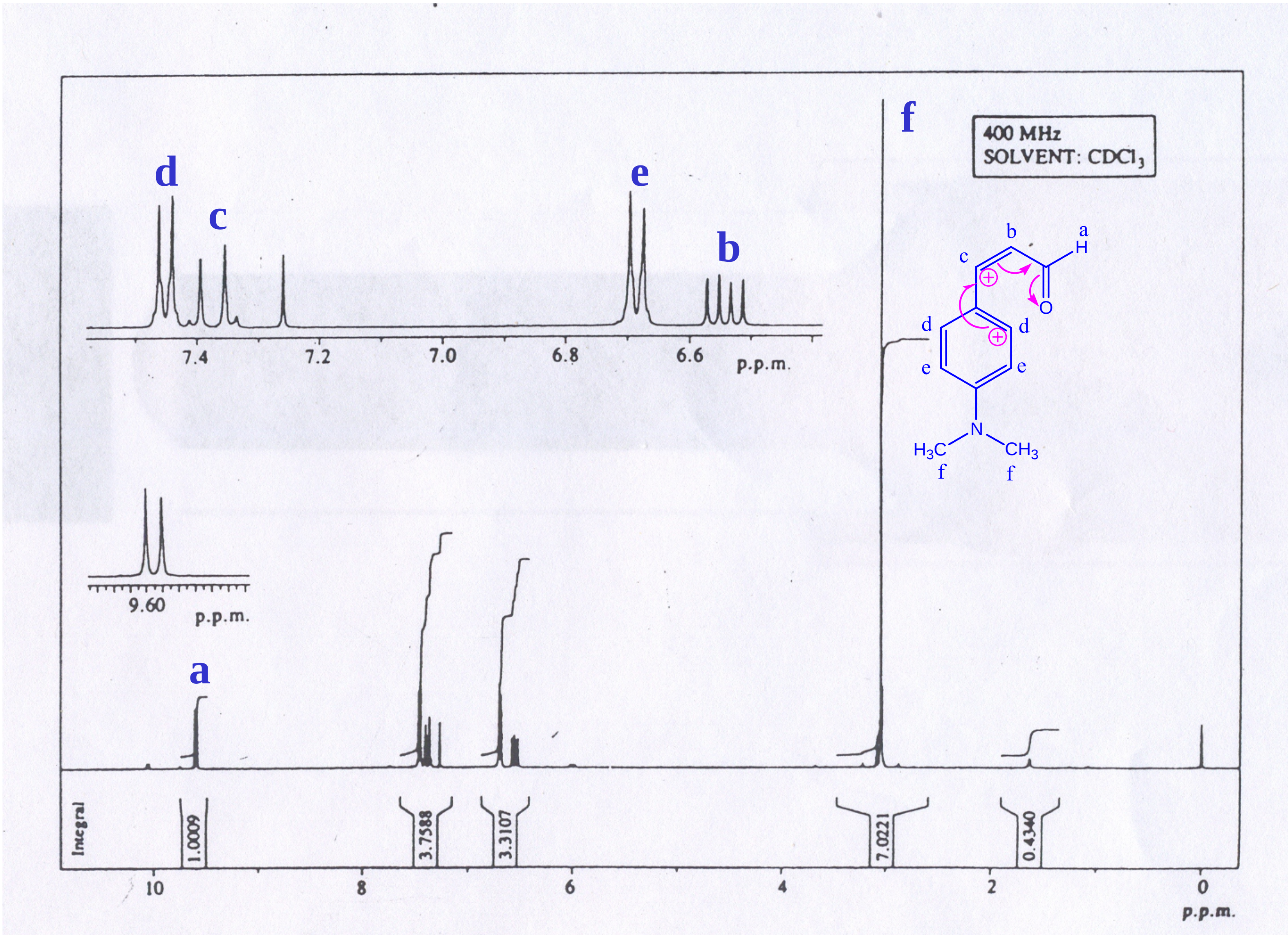
- We have accounted so far: C_9H_7NO from MF $C_{11}H_{13}NO$
- Remaining part = C_2H_6 or ($2CH_3$)
- ^{1}H NMR indicates presence of atleast 6 proton at 3 ppm, and a peak at 40 ppm indicates the presence of Methyl group attached with heteroatom (N).

- So tentative structure of the compound:
- Disubstituted benzene ring + Aldehydic group attached with vinylic group + two methyl groups attached with Nitrogen



- ***Combining all these information together, we get the following structure.***


b
a
H
c
O
d
d
e
e
N
H_3C
CH_3
f
f



d
c
e
b
f
400 MHz
SOLVENT: $CDCl_3$
a
b
c
d
d
e
e
H
O
N
H_3C
CH_3
f
f
7.4
7.2
7.0
6.8
6.6
p.p.m.
9.60
p.p.m.
a
Integral
1.0009
3.7588
3.3107
7.0221
0.4340
10
8
6
4
2
0
p.p.m.

Under construction (please visit again).
Any suggestion, comments will be highly appreciated