NMR Spectroscopy

Semester – VI US06CCHE24

Material for Sardar Patel University Examination

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MCQs

1. **How many CMR signals would you expect from p-ethyl toluene?**

(a) 5 (b) 7 (c) 6 (d) 9

Answer: (b) 7

2. **How many NMR signals would you expect from $CH_2=CHCH_2OH$?**

(a) 5 (b) 4 (c) 3 (d) 6

Answer: (b) 4

3. **How many CMR signals would you expect from m-xylene?**

(a) 5 (b) 7 (c) 6 (d) 9

Answer: (a) 5

4. **Which of the following compound have largest proton chemical shift value?**

(a) CH_3Cl (b) R_2CHCl (c) R_3C-H (d) RCH_3

Answer: (b) R_2CHCl

5. **The correct relative order of CMR chemical shift for various hybridized carbons of an (i) alkane (ii) alkene and (iii) alkyne is:**

(a) i > ii > iii (b) ii > i > iii (c) ii > iii > i (d) iii > ii > i

Answer: (c) ii > iii > i

6. **Which of the following compound have smallest proton chemical shift value?**

(a) CH_3CI (b) R_2CHCI (c) R_3C-H (d) RCH_3

Answer: (d) RCH_3

7. **How many NMR signals would you expect from methyl cyclohexane?**

(a) 5 (b) 4 (c) 3 (d) 6

Answer: (a) 5

8. **In what region of the CMR spectrum, you find the signal of a carboxylic acid and their derivatives?**

(a) 150-185 (b) 190-220 (c) 1-5 (d) None of these

Answer: (a) 150-185

9. **The scale of δ ppm in CMR is __________.**

(a) 0-50 (b) 0-100 (c) 0-beyond 200 (d) 0-150

Answer: (c) 0-beyond 200

10. Which of the following is used as reference in NMR spectroscopy?

(a) Tetramethylsilane (b) Tetrahydrofuran (c) Dimethylformamide

(d) Benzenehexachloride

Answer: (a) Tetramethylsilane

11. How many CMR signals would you expect from 1,2-dimethyl cyclopropane?

(a) 2 (b) 3 (c) 5 (d) 6

Answer: (b) 3 (It has two isomeric formula, one gives 3 signals other gives four signals, so wisely see the option)

12. Which of the following alkylbenzene have smallest δ ppm value for the ring protons (Aromatic protons)?

(a) Toluene (b) p-xylene (c) Mesitylene (d) p-tert-butyltoluene

Answer: (c) Mesitylene

13. How many NMR signals would you expect from chloroethene?

(a) 1 (b) 2 (c) 3 (d) 4

Answer: (c) 3

Questions

1. **Why TMS is use as a standard for reference point in NMR spectroscopy?**

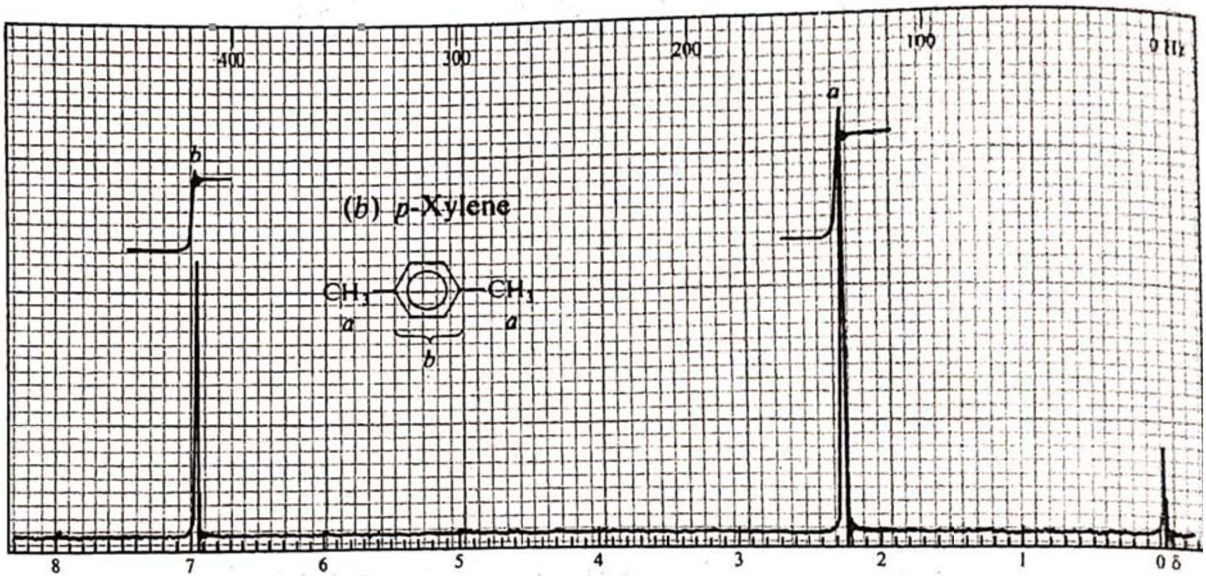
TMS is used as reference standard in NMR spectroscopy due to following reasons.

- TMS gives only one peak for 12H at high field position for its protons relative to those in most organic molecules.
- Due to low electronegativity of silicone, the protons are highly shielded as compare to most organic compounds.
- The signal of TMS is considered to be 0 δ ppm and all signals appeared left to TMS.
- TMS is highly volatile and inert.
- It gives intense peak even at low concentration so its peak can be recognized easily.

2. **Define the term chemical shift. Sketch the NMR spectrum of p-xylene with respect to δ value.**

- In NMR spectroscopy, shielded proton absorbs at higher magnetic field (lower δ value) and deshielded protons absorb at low magnetic field (higher δ value).
- Higher δ value is called upfield and lower δ value is called downfield.
- Shielded protons shift absorption in upfield and deshielded protons shift absorption in downfield.
- Such shift of the absorption in the NMR spectroscopy is referred as chemical shift.
- Mathematically chemical shift can be shown as below:

$$\delta = \frac{Shift\ from\ reference\ frequency\ (Hz)}{Probe\ Frequency}$$

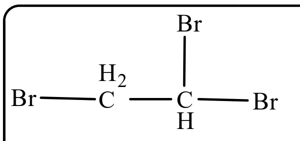


3. **Give the various aspects of NMR spectroscopy.**

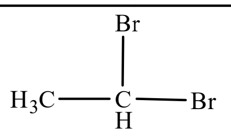
- The number of signals: it tells us how many different kinds of protons there are in a molecule.
- The position of signals: It tells us something about the electronic environment of each kind of proton.
- The intensity of signals: It tells us how many protons of each kind there are.
- The splitting of signal into several peaks, which tells us about the environment of a proton with respect to each other.

4. **Write a note on phenomenon of the splitting of NMR signals indicating clearly how the multiplicity of splitting reflects the number of protons adjacent to the absorbing protons.**

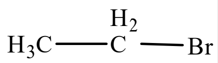
- NMR spectrum shows signal for each kind of protons in a molecule.
- Let's take examples of following compounds


$\mathrm{Br-CH_2-CH(Br)-Br}$

1,1,2-tribromoethane

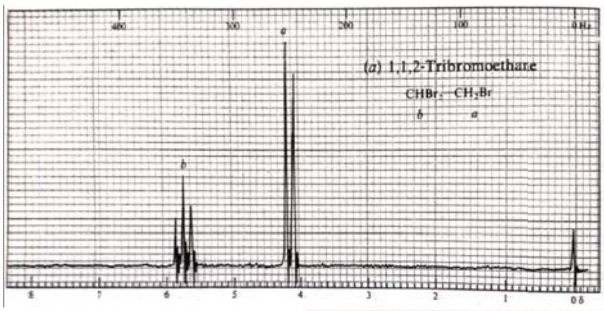

$\mathrm{H_3C-CH(Br)-Br}$

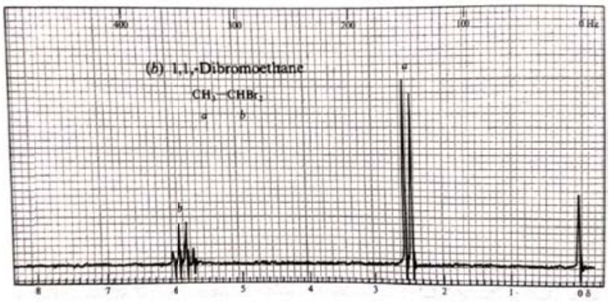
1,1-dibromoethane

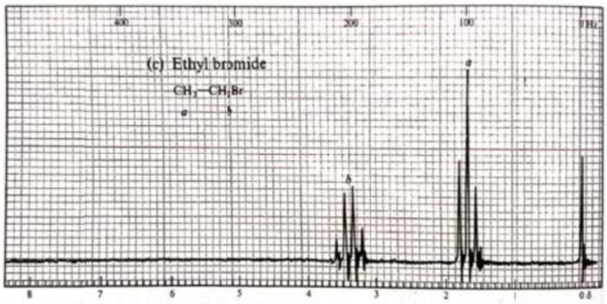

$\mathrm{H_3C-CH_2-Br}$

bromoethane

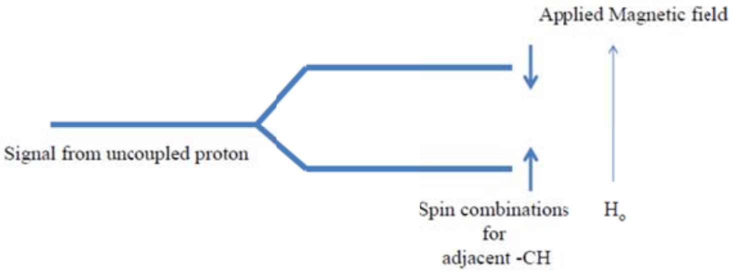
- All above compounds contain two types of protons but upon looking at spectra of such compounds we can observe 5, 6 and 7 peaks respectively.



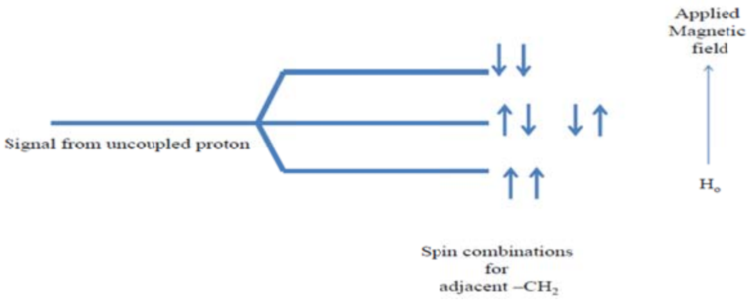




- Spin-spin coupling cause splitting of NMR signals.
- The signals we expect from each set of equivalent protons appear not as single peak but as a group of peaks.
- Splitting reflects the environment of the absorbing protons with respect to neighbouring protons.
- The secondary protons in –CH-CH$_2$ feels the magnetic field is slightly higher or lower due to orientation of spin of neighbouring protons.
- If tertiary protons aligned in line of external magnetic field the magnetic field for secondary proton will be increased.
- If tertiary protons aligned against the external magnetic field the magnetic field for secondary proton will be decreased.
- For secondary proton (-CH$_2$) the absorption is shifted slightly downfield and slightly upfield. The signal split into two peaks; doublet, with equal peak intensities.



- For tertiary proton (-CH) in –CH-CH$_2$ has two neighbouring protons.
- So, the –CH proton feel any one of three fields and its signal is split into three equal peaks (triplet) with relative intensity of 1:2:.1.

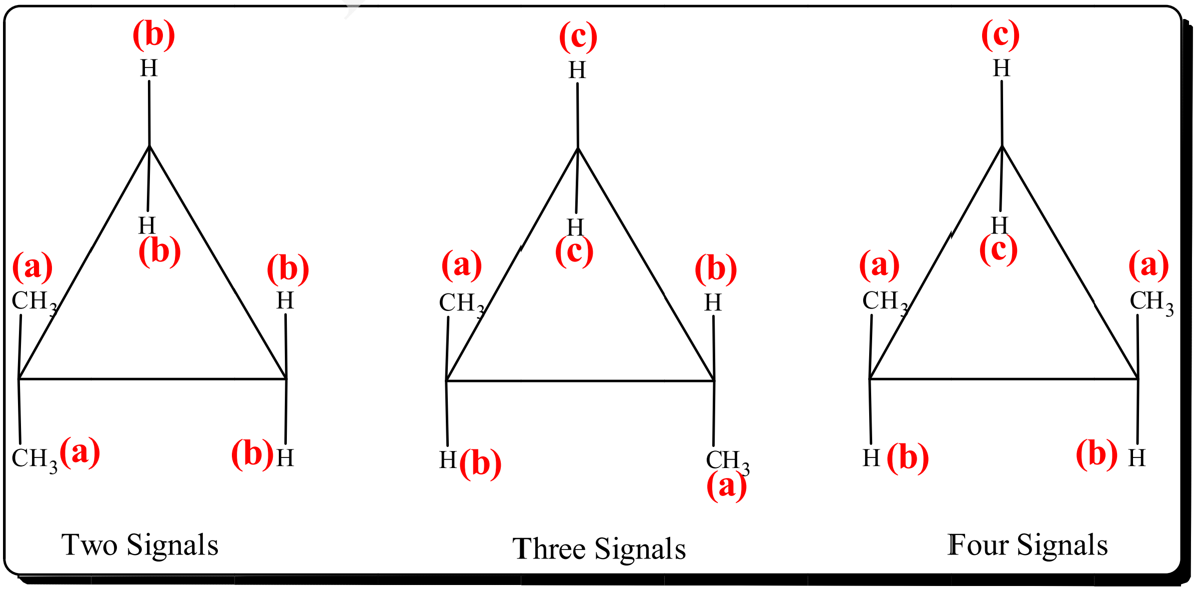


- The signal for –CH_2 split into doublet due to adjacent –CH and signal for –CH split into triplet due to adjacent –CH_2.
- In short, the number of splitting can be predicted by n + 1 rule, where n = number of non-equivalent protons on neighbouring carbon.

5. Define coupling constant and give various aspects of CMR spectroscopy.

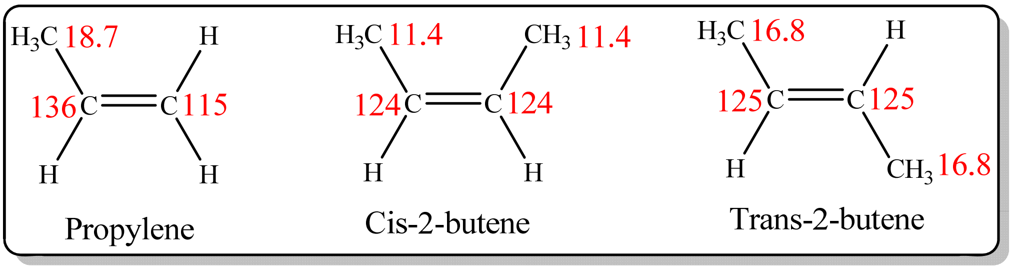
- Coupling constant: The distance between two consecutive peaks in multiplet is called coupling constant. It is denoted by ***J***. The unit for coupling constant is Hz.
- Number of signals: Different carbons or different sets of equivalent carbons absorbs at different magnetic field hence give signal at different chemical shift.
- Splitting of signals: The splitting is dependent upon hydrogen atoms attached to that carbon.
- Chemical shift: chemical shift is dependent upon hybridisation and electronic environment.

6. Three isomeric dimethylcyclopropane give respectively two, three and four NMR signals. Draw a stereo isomeric formula for the isomer giving rise to each number of signals.

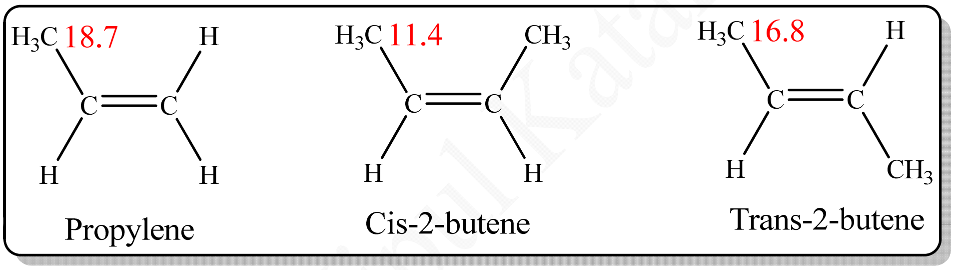


7. How will you assign the configuration of geometric isomers by using CMR spectroscopy, explain by considering suitable example.

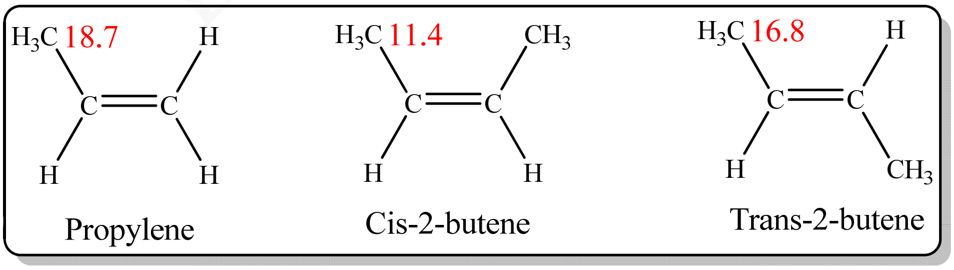
- The presence of carbon-carbon double bond may give rise to geometrical isomers.
- Such isomers have important effect on absorption by sp^3 hybridised carbons.
- Let's take example of propylene and compare it with cis and trans 2-butene.



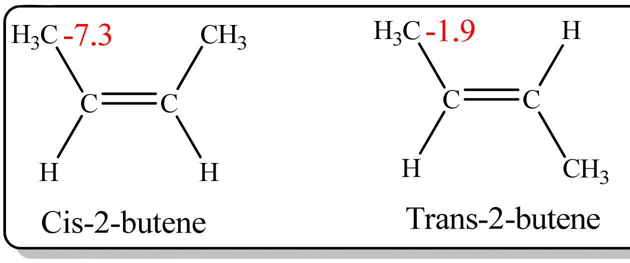
- Focus on methyl carbon of propylene and see how its absorption is affected by the substitution of a methyl group on or the other of the vinylic hydrogens. Here we are checking γ-effect.



- The γ-effect decreases the δ ppm (absorption to upfield) value for both carbon atoms.
- For cis isomer the δ ppm value goes down by -7.3 and for trans isomer the δ ppm value goes down by -1.9 ppm.



- Hence γ-effect for cis isomer is stronger than trans isomer.



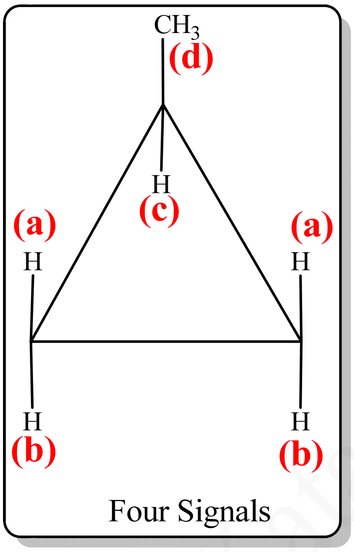
Size of γ - effects

cis > trans

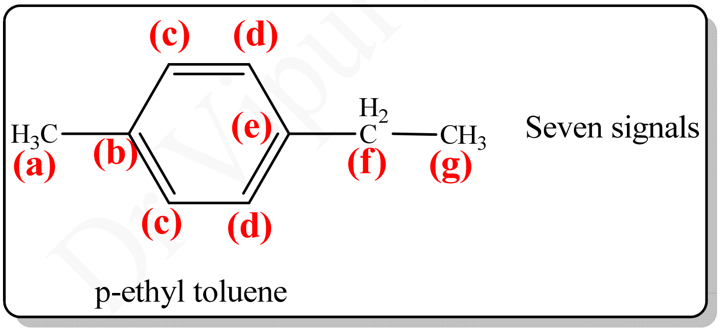
- ➢ The stereo chemical influence of γ-effect in alkenes is extremely useful in assigning configuration to geometric isomers.

8. Predict the number of (i) NMR signals from methyl cyclopropane and (ii) CMR signals from p-ethyl toluene.

(i) Methyl cyclopropane



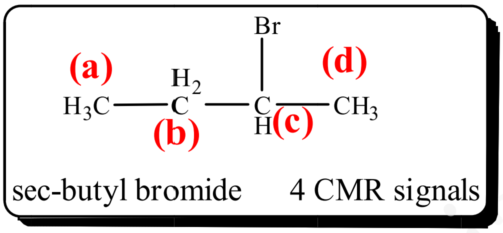
(ii) p-ethyl toluene

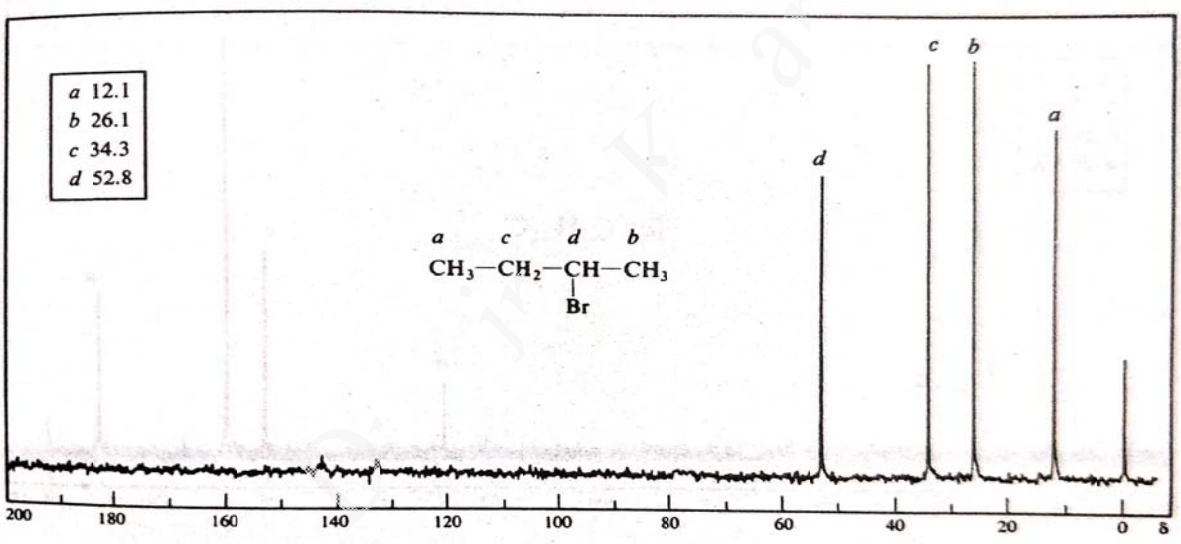


9. Discuss proton-coupled and proton-decoupled spectrum with suitable example.

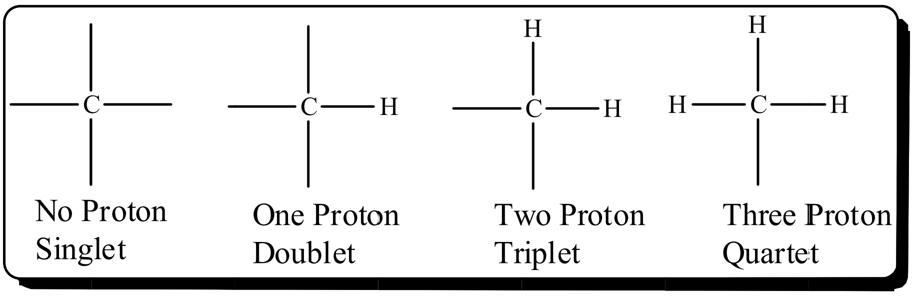
- ➢ The main issue with CMR is too much splitting that makes spectra complicated to interpret.
- ➢ However, this problem is removed at some extent due to low abundance ration of ^{13}C (1.1 %).
- ➢ ^{13}C rarely adjacent to ^{13}C hence it don't get split due to adjacent carbon which is generally ^{12}C (nuclear spin is zero hence NMR inactive).
- ➢ ^{13}C signal can be split by adjacent H.
- ➢ In CMR, we cannot see signals by H as the range is far away from proton range, however the signal of ^{13}C can be split by adjacent proton.

- Due to high number of H in organic compounds, the splitting can be so high that can complicate the spectra that make it almost impossible to interpret.
- The complication can be rectified by **proton decoupled** spectrum.
- Such spectrum shows no splitting at all.
- It consist of a set of single peaks one for each set of equivalent carbons present in the molecule.
- Let's take an example of sec-butyl bromide in which all carbons are non-equivalent and shows the proton-decoupled spectrum of sec-butyl bromide.

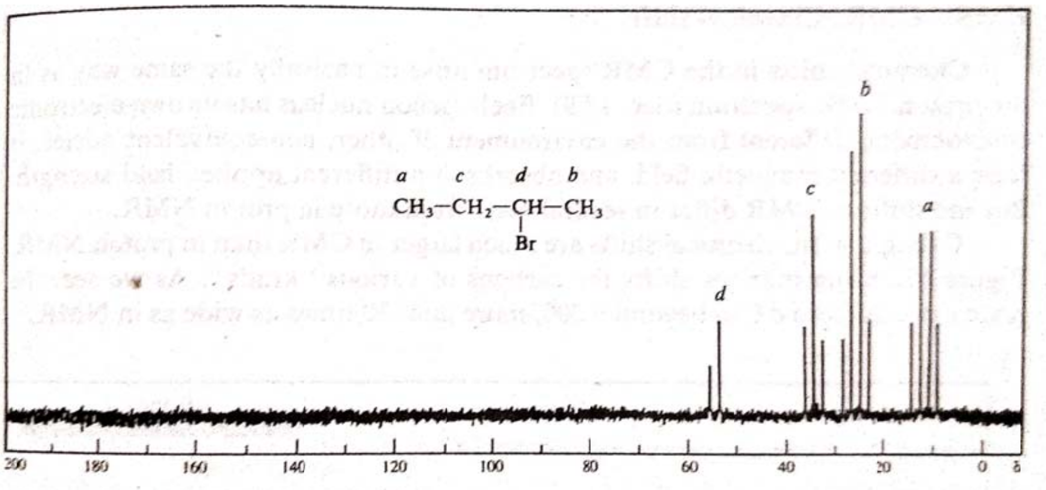




- Another method of decoupling that is also referred as off resonance method in which spectrum shows splitting of carbon signal by adjacent proton attached to that carbon itself.
- It shows ^{13}C-H coupling and not ^{13}C-C-H or ^{13}C-C-C-H coupling.
- Such spectrum is referred as proton-coupled spectrum. Splitting will occur as below.



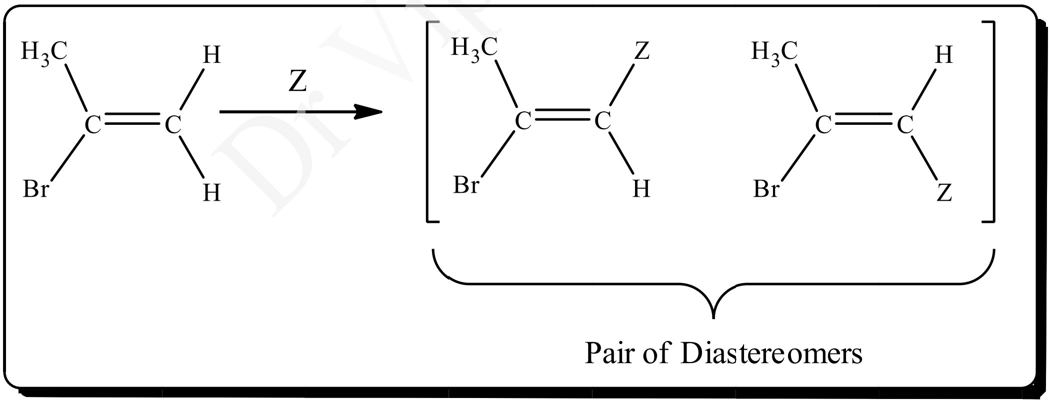
- In following proton-coupled spectrum of sec-butyl bromide we can observe on doublet, one triplet and two quartets.



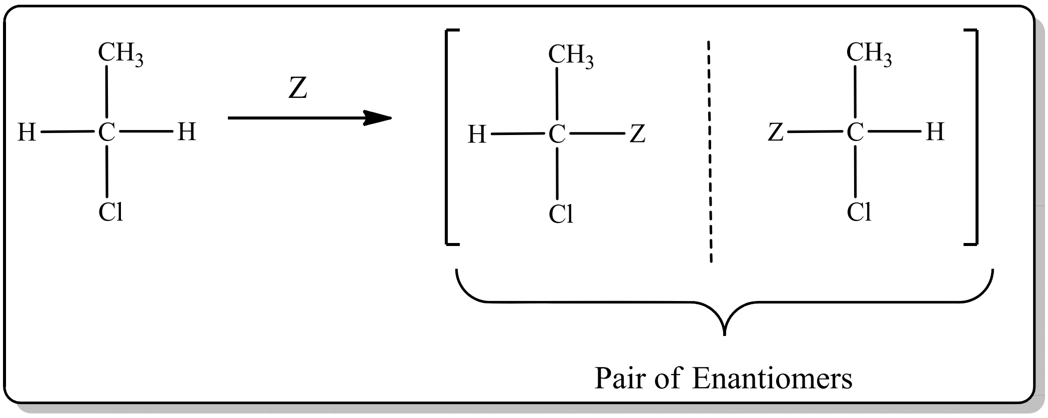
- The two types of spectrum; proton decoupled spectrum tells us about number of different carbon atoms and proton coupled spectrum tells about number of protons attached to each of these carbons.
- With use of both the spectrum we can have clear picture of the molecule.

10. Differentiate between Diastereotopic proton and Enantiotopic proton.

- **Diastereotopic Proton:** Upon replacement of one of proton by one imaginary group if we lead to pair of diastereomer such protons are called distereotopic protons.



- Such protons are non-equivalent proton and absorb at different δ ppm values; however signals are too near due to very minor difference in chemical shift.
- They will split each other’s signal however splitting will be negligible.
- Enantiotopic protons: Upon replacement of one of proton by one imaginary group if we lead to pair of enantiomer such protons are called enantiotopic protons.



- Such protons are equivalent and absorbs at same chemical shift,
- They do not split each other's signal.

11. Explain shielded and deshielded protons.

- When a molecule is placed under influence of magnetic field for NMR, the nucleus start to spin in either of the direction.
- The electron within the nucleus also rotates in circular motion that produce tiny magnetic field which is called induced magnetic field.
- This induced magnetic field can be in line with the external magnetic field or against the external magnetic field.
- If the induced magnetic field is in line with the external magnetic field, the actual magnetic field feel by the corresponding proton will be higher than external magnetic field. Such protons absorb at lower magnetic field and at higher δ ppm value (in downfield) that makes such protons the deshielded protons.
- If the induced magnetic field is against the external magnetic field, the actual magnetic field feel by the corresponding proton will be lower than external magnetic field. Such protons absorb at higher magnetic field and at lower δ ppm value (in upfield) that makes such protons the shielded protons.

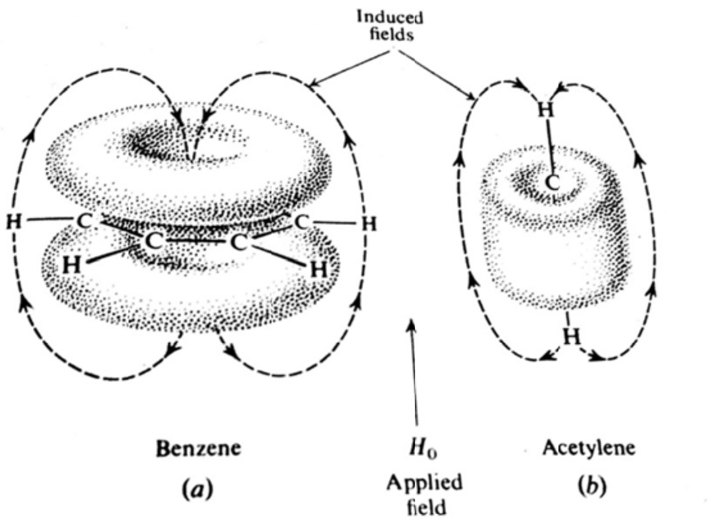
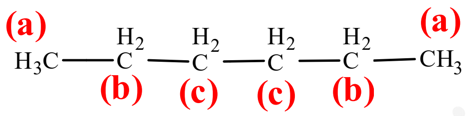


Figure 17.9 Induced field (*a*) reinforces the applied field at the aromatic protons, and (*b*) opposes the applied field at the acetylenic protons. Aromatic protons are deshielded; acetylenic protons are shielded.

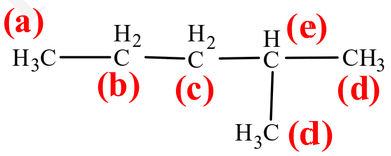
12. **Draw all possible isomers of for the formula C_6H_{14} and tell how many CMR signals do you expect from each isomer?**

Isomer:1



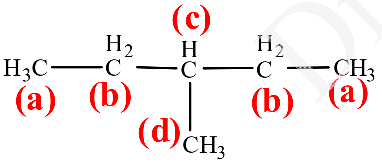
n-Hexane 3 CMR Signals

Isomer:2



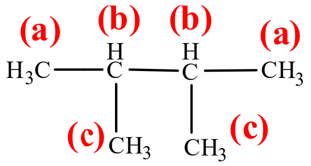
2-methyl Pentane 5 CMR Signals

Isomer:3



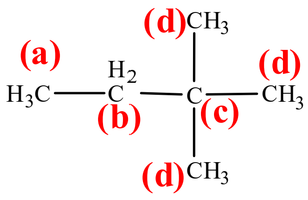
3-methyl Pentane 4 CMR Signals

Isomer:4



2,3-Dimethyl Butane 3 CMR Signals

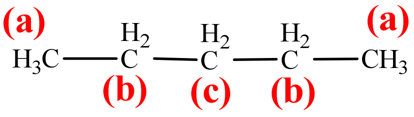
Isomer:5



2,2-Dimethyl Butane 4 CMR Signals

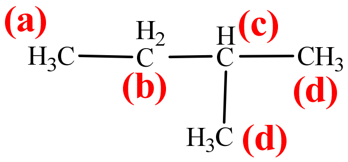
13. Draw all possible isomers of for the formula C_5H_{12} and tell how many CMR signals do you expect from each isomer?

Isomer:1



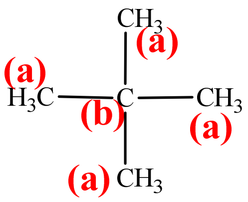
n-Pentane 3 CMR Signals

Isomer:2



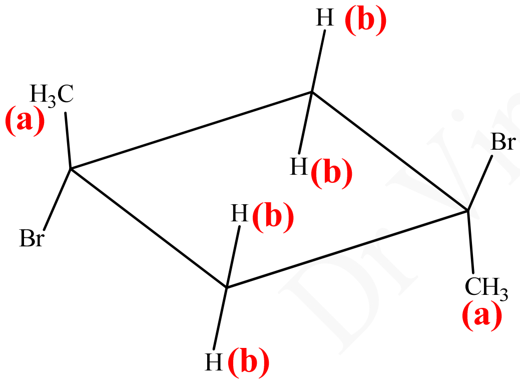
2-methyl Butane 4 CMR Signals

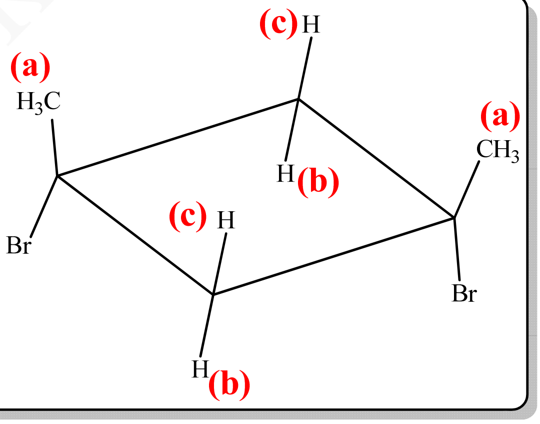
Isomer:3



2,3-Dimethyl Propane 2 CMR Signals

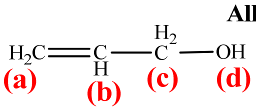
14. Identify stereoisomers of 1,3-dibromo, 1,3-dimethyl cyclobutane.



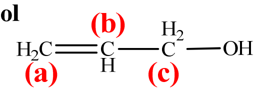


15. Predict number of signals from allyl alcohol and vinyl chloride for NMR and CMR

Allyl Alcohol



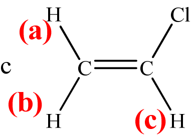
NMR: 4 signals



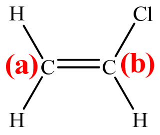
CMR: 3 signals

Vinyl Chloride

a & b are diastereotopic protons



NMR: 3 signals

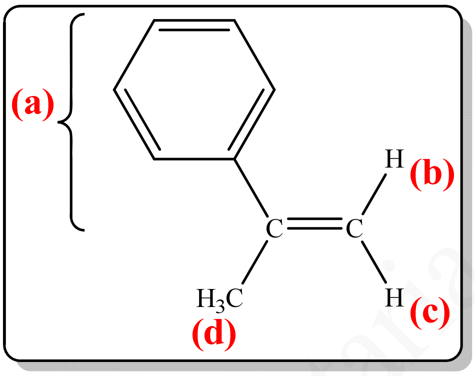


CMR: 2 signals

Examples: Deduce the structure of compound having following spectral data. Label all kinds of carbons/protons and give appropriate explanation for the structure. (Example number 1-23 have been asked in Sardar Patel University examination since 2012-2020)

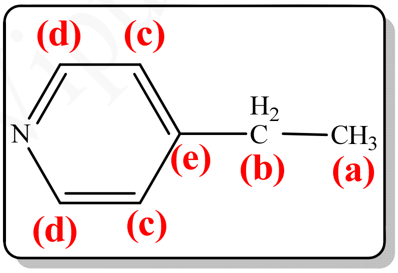
1. **Molecular formula: C_9H_{10}**

   NMR (δ ppm): (a) 7.4, 5H, Complex (b) 5.35, 1H, Singlet (c) 5.1, 1H, Singlet (d) 2.10, 3H, Singlet.



2. **Molecular formula: C_7H_9N**

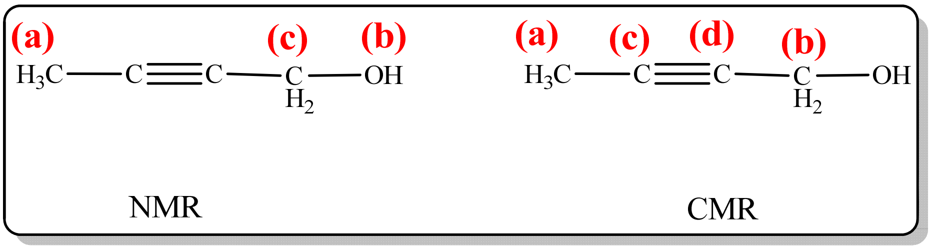
   CMR (δ ppm): (a) 14.3, Quartet (b) 28.2, Triplet (c) 123.4, Doublet (d) 149.8, Doublet (e) 152.8, Singlet.



3. **Molecular formula: C_4H_6O**

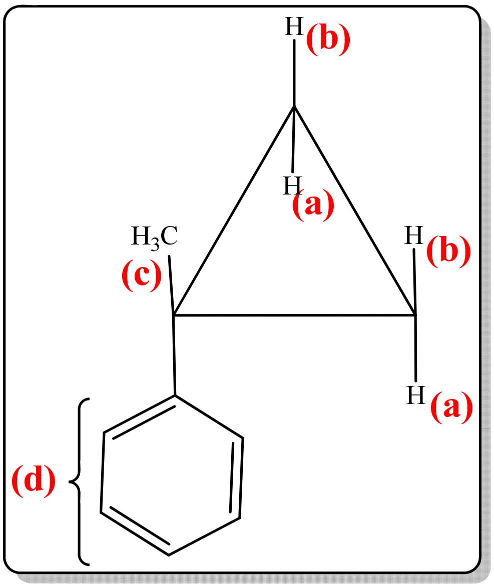
   CMR (δ ppm) : (a) 3.4, Quartet (b) 50.8, Triplet (c) 77.9, Singlet (d) 81 .6, Singlet.

   NMR (δ ppm): (a) 2.0, 3H , Singlet (b) 1.8, 1 H, Singlet (c) 4.1, 2H , Singlet.



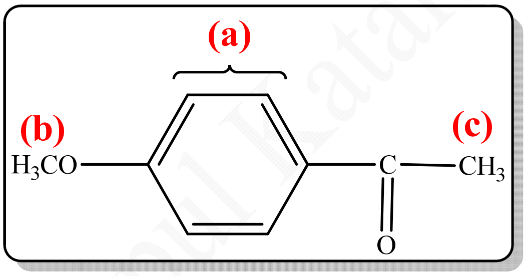
4. **Molecular formula: $C_{10}H_{12}$**

   NMR (δ ppm): (a) 0.65, 2H, Multiplet (b) 0.81, 2H, Multiplet (c) 1.37, 3H , Singlet (d) 7.17, 5H, Singlet



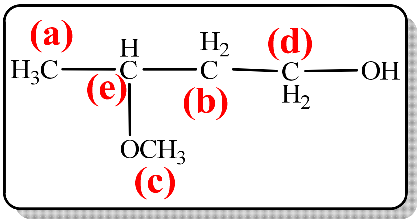
5. Molecular formula: $C_9H_{10}O_2$

NMR (δ ppm) : (a) 7.5, 4H, Quartet (b) 3.9, 3H, Singlet (c) 2.5, 3 H, Singlet



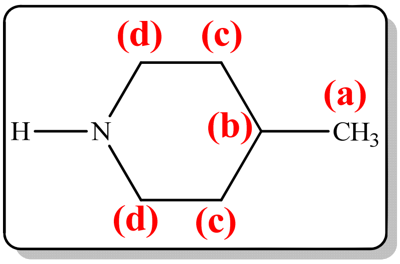
6. Molecular formula: $C_5H_{12}O_2$

CMR (δ ppm): (a) 19.0, Quartet (b) 39.4, Triplet (c) 55.8, Quartet (d) 59.3, Triplet (e) 75.1, Doublet



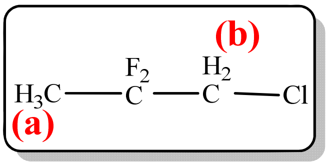
7. Molecular formula: $C_6H_{13}N$

CMR (δ ppm): (a) 22.7, Quartet (b) 31.5, Doublet (c) 35.8, Triplet (d) 46.9, Triplet.



8. Molecular formula $C_3H_5ClF_2$

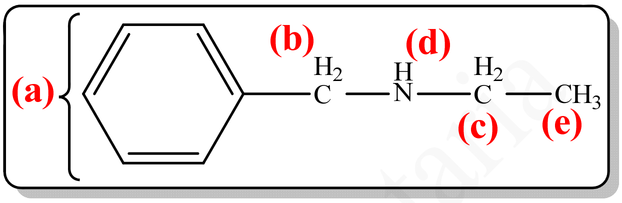
NMR (δ ppm): (a) 1.75, 3H, Triplet (b) 3.63, 2H, Triplet.



Most IMP Trick: *Fluorine doesn't give signal in range of PMR but it can split signal of adjacent proton.

9. Molecular formula: $C_9H_{13}N$

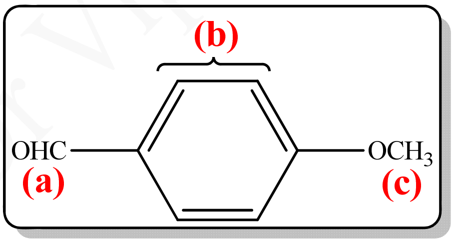
NMR (δ ppm): (a) 7.3, 5H, Singlet (b) 3.7, 2H, Singlet (c) 2.5, 2H, Quartet (d) 1.25, 1H, Singlet (e) 1.1, 3H, Triplet.



Most IMP Trick: 3H triplet and 2H quartet always represents ethyl ($-CH_2-CH_3$) group.

10. Molecular formula: $C_8H_8O_2$

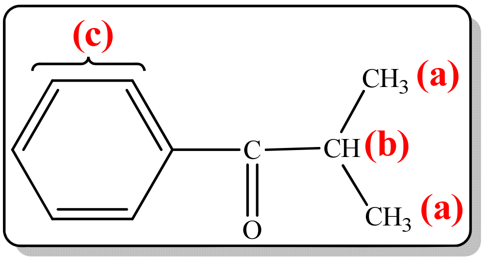
NMR (δ ppm): (a) 8.35, 1H, Singlet (b) 7.5, 4H, Quartet (c) 3.85, 3H, Singlet



Most IMP Trick: 1H singlet between 8 and 9 always represents aldehyde proton.

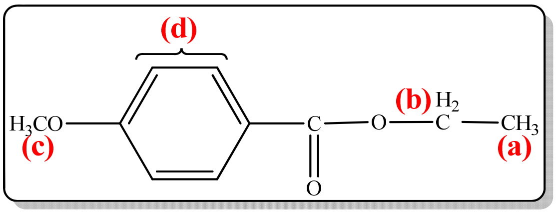
11. Molecular formula: $C_{10}H_{12}O$

NMR (δ ppm): (a) Doublet, 6H, 1.25 (b) Multiplet, 1H, 3.4 (c) Singlet, 5H, 7.67



12. Molecular formula: $C_{10}H_{12}O_3$

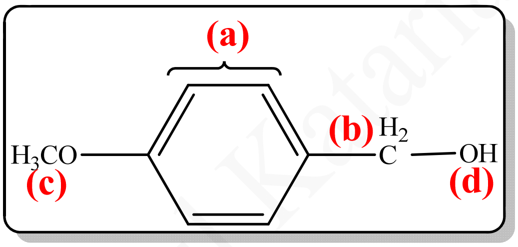
NMR (δ ppm): (a) 1.35, 3H, Triplet (b) 4.35, 2H, Quartet (c) 3.8, 3H, Singlet (d) 7.5, 4H, Quartet



Most IMP Trick: 3H triplet and 2H quartet always represents ethyl (-CH_2-CH_3) group.

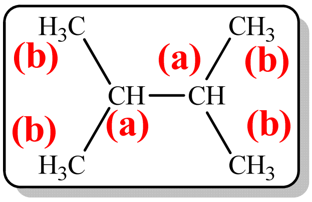
13. Molecular formula: $C_8H_{10}O_2$

NMR (δ ppm): (a) 7.2, 4H, Quartet (b) 4.4, 2H, Singlet (c) 3.8, 3H, Singlet (d) 3.6, 1H, Singlet



14. Molecular formula: C_9H_{14}

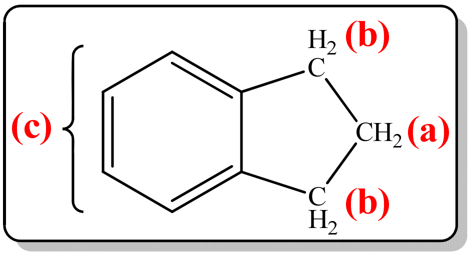
NMR (δ ppm): (a) 3.35, 2H, Septet (b) 1.18, 12H, Doublet



Most IMP Trick: 1H multiplet and 6H doublet always represents isopropyl group (in this case it is dimer of isopropyl so 12H doublet and 2H multiplet).

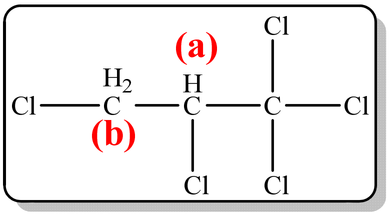
15. Molecular formula: C_9H_{10}

NMR (δ ppm): (a) 2.04, 2H, Quintet (b) 2.91, 4H, Triplet (c) 7.17, 4H, Singlet/M/DD



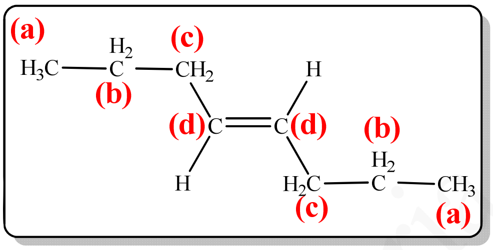
16. Molecular formula: $C_3H_3Cl_5$

NMR (δ ppm): (a) 4.52, 1H, Triplet (b) 6.07, 2H, Doublet



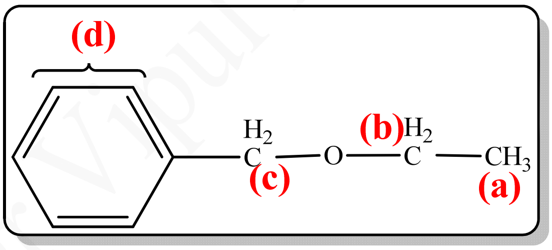
17. Molecular formula: C_8H_{16}

CMR (δ ppm): (a) 13.7 Quartet (b) 23.1, Triplet (c) 35.1, Triplet (d) 130.6, Doublet



18. Molecular formula: $C_9H_{12}O$

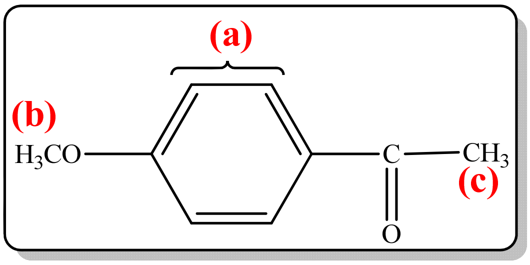
NMR (δ ppm): (a) 1.28, 3H, Triplet (b) 3.48, 2H, Quartet (c) 4.58, 2H, Singlet (d) 7.38, 5H, Singlet



Most IMP Trick: 3H triplet and 2H quartet always represents ethyl (-CH_2-CH_3) group.

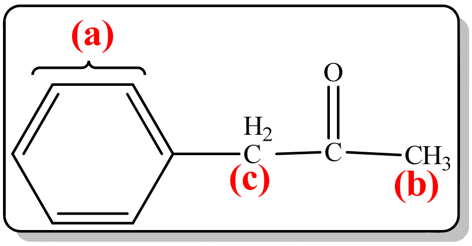
19. Molecular formula: $C_9H_{10}O_2$

NMR (δ ppm): (a) 7.5, 4H, Quartet (b) 3.9, 3H, Singlet (c) 2.5, 3H, Singlet



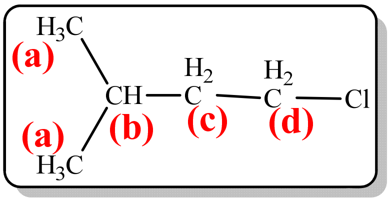
20. Molecular formula: $C_9H_{10}O$

NMR (δ ppm): (a) 7.3, 5H, Singlet (b) 2.0, 3H, Singlet (c) 5.0, 2H, Singlet



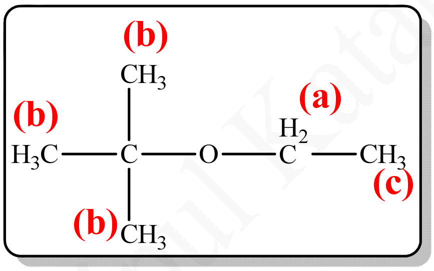
21. Molecular formula: $C_5H_{11}Cl$

CMR (δ ppm): (a) 22.1 Quartet (b) 25.8, Doublet (c) 41.8, Triplet (d) 43.2, Triplet



22. Molecular formula: $C_6H_{14}O$

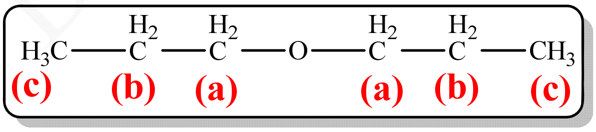
NMR (δ ppm): (a) 3.4, 2H, Quartet (b) 1.3, 9H, Singlet (c) 1.2, 3H, Triplet



Most IMP Trick: 9H singlet always represents t-butyl group.

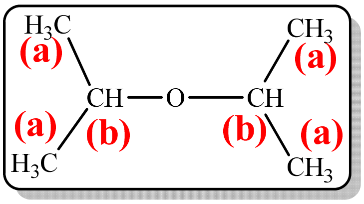
23. Molecular formula: $C_6H_{14}O$

NMR (δ ppm): (a) 3.35, 4H, Triplet (b) 1.56, 4H, Multiplet (c) 0.9, 6H, Triplet



24. Molecular formula: $C_6H_{14}O$

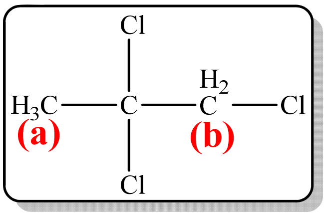
NMR (δ ppm): (a) 3.6, 12H, Doublet (b) 1.1, 2H, Multiplet



Most IMP Trick: 1H multiplet and 6H doublet always represents isopropyl group.

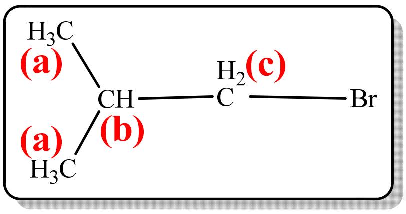
25. Molecular formula: $C_3H_5Cl_5$

NMR (δ ppm): (a) 2.20, 3H, Singlet (b) 4.02, 2H, Singlet



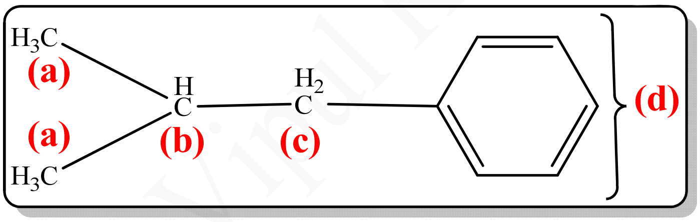
26. Molecular formula: C_4H_9Br

NMR (δ ppm): (a) 1.04, 6H, Doublet (b) 1.95, 1H, Multiplet (c) 3.33, 2H, Doublet



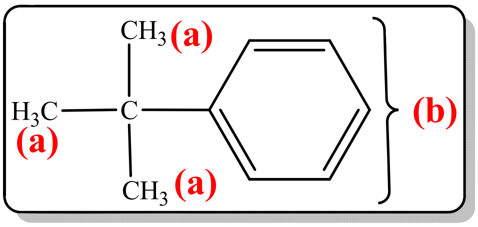
27. Molecular formula: $C_{10}H_{14}$

NMR (δ ppm): (a) 0.88, 6H, Doublet (b) 1.86, 1H, Multiplet (c) 2.45, 2H, Doublet (d) 7.12, 5H, Singlet



28. Molecular formula: $C_{10}H_{14}$

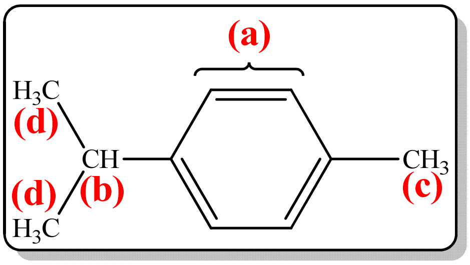
NMR (δ ppm): (a) 1.38, 9H, Singlet (b) 7.28, 5H, Singlet



Most IMP Trick: 9H singlet always represents t-butyl group.

29. Molecular formula: $C_{10}H_{14}$

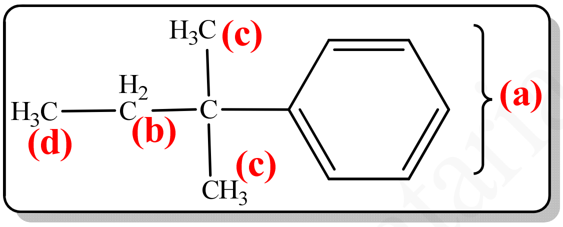
NMR (δ ppm): (a) 7.05, 4H, Singlet/Q/M/DD (b) 2.70, 1H, Multiplet (c) 2.25, 3H, Singlet (c) 1.25, 6H, Doublet



Most IMP Trick: 1H multiplet and 6H doublet always represents isopropyl group.

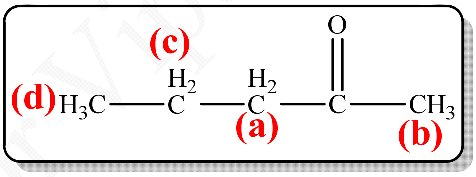
30 Molecular formula: $C_{11}H_{16}$

NMR (δ ppm): (a) 7.3, 5H, Singlet (b) 1.6, 2H, Quartet (c) 1.3, 6H, Singlet (d) 0.7, 3H, Triplet



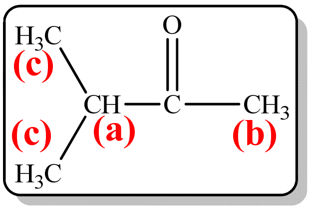
31. Molecular formula: $C_5H_{10}O$

NMR (δ ppm): (a) 2.4, 2H, Triplet (b) 2.1, 3H, Singlet (c) 2.6, 2H, Sixtet/Multiplet (d) 0.9, 3H, Triplet



32. Molecular formula: $C_5H_{10}O$

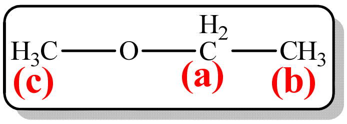
NMR (δ ppm): (a) 2.5, 1H, Multiplet (b) 2.1, 3H, Singlet (c) 1.1, 6H, Doublet



Most IMP Trick: 1H multiplet and 6H doublet always represents isopropyl group.

33. **Molecular formula: C_3H_8O**

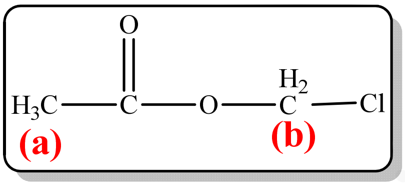
NMR (δ ppm): (a) 2.4, 2H, Quartet (b) 2.0, 3H, Singlet (c) 1.0, 3H, Triplet



Most IMP Trick: 3H triplet and 2H quartet always represents ethyl ($-CH_2-CH_3$) group.

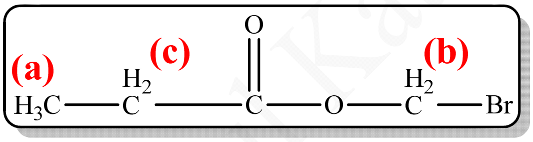
34. **Molecular formula: $C_3H_5ClO_2$**

NMR (δ ppm): (a) 3.81, 3H, Singlet (b) 4.08, 2H, Singlet



35. **Molecular formula: $C_4H_7BrO_2$**

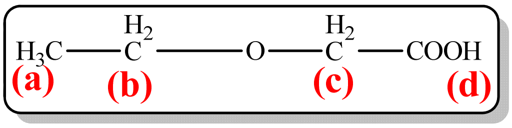
NMR (δ ppm): (a) 1.3, 3H, Triplet (b) 3.7, 2H, Singlet (c) 4.2, 2H, Quartet



Most IMP Trick: 3H triplet and 2H quartet always represents ethyl ($-CH_2-CH_3$) group.

36. **Molecular formula: $C_4H_8O_3$**

NMR (δ ppm): (a) 1.27, 3H, Triplet (b) 3.66, 2H, Quartet (c) 4.13, 2H, Singlet (d) 10.95, 1H, Singlet

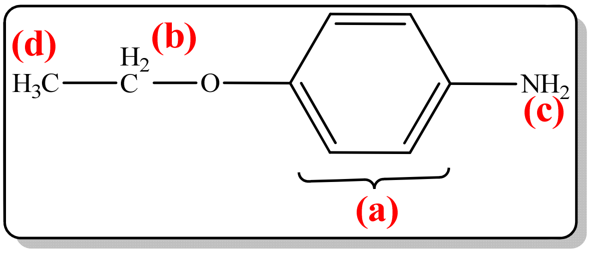


Most IMP Trick: 3H triplet and 2H quartet always represents ethyl ($-CH_2-CH_3$) group.

1H between 10 and 11 always represents acidic proton.

37. **Molecular formula: $C_8H_{11}NO$**

NMR (δ ppm): (a) 6.68, 4H, Quartet/DD (b) 3.88, 2H, Quartet (c) 3.31, 2H, Singlet (d) 1.32, 3H, Triplet



Most IMP Trick: 3H triplet and 2H quartet always represents ethyl (-CH_2-CH_3) group.

38. Molecular formula: $C_{11}H_{16}$

	δ Value		Square	calculated No. Of Protons
(a)	1.38	S	8.8	9H
(b)	2.25	S	2.9	3H
(c)	7.15	S	3.8	4H

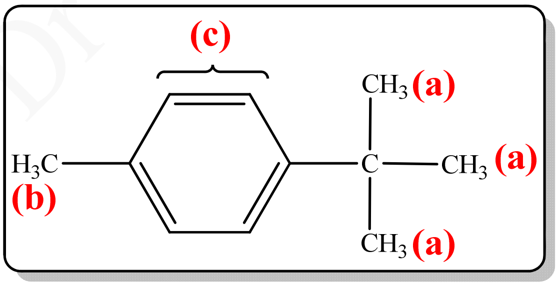
First of all sum of all the squares: 8.8 + 2.9 + 3.8 = 15.5 squares. Now total protons are 16 so divide 16/15.5 = 1.03 proton per square

Now,

(a) 1.38 x 1.03 = 9.1 = 9H

(b) 2.25 x 1.03 = 3.0 = 3H

(c) 7.15 x 1.03 = 3.9 = 4H



39. Molecular formula: $C_3H_7NO_2$

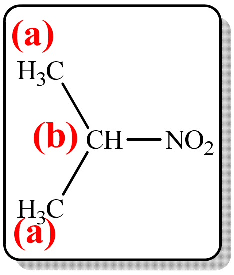
	δ Value		Square	calculated No. Of Protons
(a)	1.50	D	37.3	6H
(b)	3.30	M	6.2	1H

First of all sum of all the squares: 37.3 + 6.2 = 43.5 squares. Now total protons are 7 so divide 7/43.5 = 0.16 proton per square

Now,

(a) 37.3 x 0.16 = 5.9 = 6H

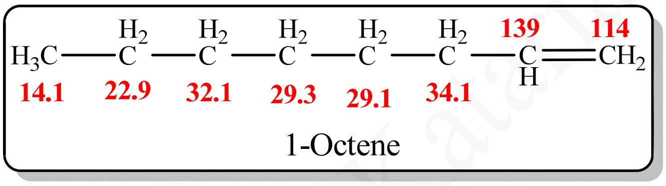
(b) 6.2 x 0.16 = 0.99 = 1H



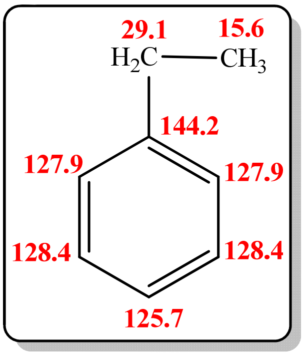
Topics not asked yet in any Sardar Patel University Examination

CMR Chemical shift

- CMR chemical shift phenomenon is almost same to proton chemical shift however the scale of chemical shift (0-200 δ ppm) is much larger than proton.
- Each carbon nucleus has its own electronic environment that makes it non-equivalent to other carbons having different electronic environment.
- Every non-equivalent set of carbon atoms absorbs at different magnetic field and accordingly have different δ ppm.
- The most important factor for having different chemical shift is hybridization. Let's look at following example to understand different chemical shift for different types of carbons.

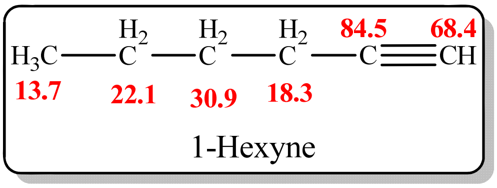


- The sp^3 hybridized carbons absorb in upfield (lower δ ppm) ranging from 14.1 to 34.1 and sp^2 hybridized carbons absorb in downfield (higher δ ppm) in the range of 114 to 139.
- Aromatic carbons are also sp^3 hybridized and also absorb in downfield (higher δ ppm) as similar to alkene carbons.
- Let's see below example of ethyl benzene.

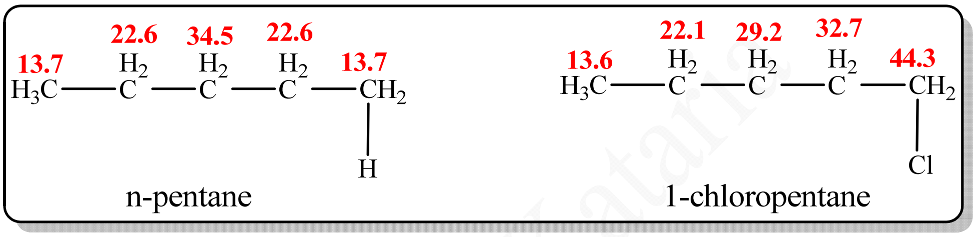


- The alkyl part of ethyl benzene (sp^3 carbons) absorb at upfield (lower δ ppm) in range of 15.6 to 29.1. The aromatic part of ethyl benzene (sp^2 carbons) absorb at downfield (higher δ ppm) in range of 125 to 144 (in range of alkene carbons).
- Triply bonded carbon (alkyne carbons) is sp hybridized and absorb in between region of alkane (sp^3) and alkene (sp^2).

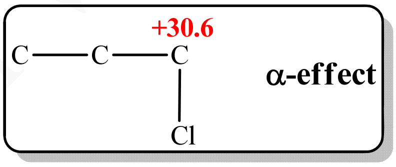
- Let us see example of 1-hexyne.



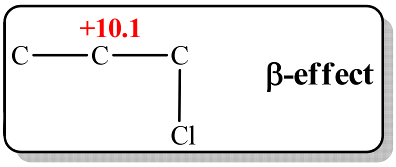
- The second factor for chemical shift is effect of substituents.
- As similar to ^{1}H NMR most of the substituents deshield the nucleus however these effects are much larger in case of ^{13}C NMR spectroscopy, in addition to these such effects are felt from far away in different patterns.
- Let us take an example of n-pentane and 1-chloro pentane to understand the effect of substituents.



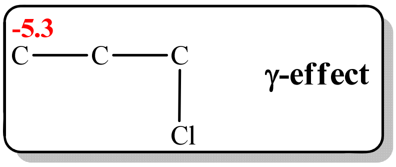
- Let us compare the δ ppm value carbon by carbon for both compounds.
- α-effect: In the signal for C-1, large download shift occurs due to effect of chlorine. The shift moves from 13.7 to 44.3 δ ppm causing difference of +30.6. Such a shift for the carbon bearing the substituent is called an α-effect.



- β-effect: In the signal for C-2, large download shift occurs due to effect of chlorine. The shift moves from 22.6 to 32.7 δ ppm causing difference of +10.1. Such a shift for the carbon bearing the substituent is called β-effect.



- γ-effect: In the signal for C-3, upfield shift occurs due to effect of chlorine. The shift moves from 34.5 to 29.2 δ ppm causing difference of -5.3. Such a shift for the carbon bearing the substituent is called γ-effect.



- Beyond the γ-effect, effect of chlorine on other carbons is very small.

NMR and CMR spectra of hydrocarbons

- Alkane and alkane like saturated compounds absorb at lower δ ppm in both NMR and CMR. ($R-CH_3$ 0-35 δ ppm, R_2-CH_2 15-40 δ ppm, R_3-CH 25-40 δ ppm, $R-CH_2-Br$ 20-40 δ ppm, $R-CH_2-Cl$ 25-50 δ ppm, $R-CH_2-NH_2$ 35-50 δ ppm, $R-CH_2-OH$ 50-65 δ ppm).
- Aromatic compounds would absorb at higher δ ppm. Alkene and vinylic compounds will also absorb at higher δ ppm ($C=C$ 100-150 δ ppm, $C\equiv C$ 65-90 δ ppm, Aromatic 110-175 δ ppm, $C=O$ 190-220 δ ppm).
- In short the δ ppm values for different class are; Alkane (sp^3 0-65 δ ppm), Alkene (sp^2 95-150 δ ppm), alkyne (sp 70-100 δ ppm), Aromatic (sp^2 110-135 δ ppm).

NMR and CMR spectra of alcohol and ether

- In ^1H NMR, the proton of –OH shift to downfield due to hydrogen bonding.
- The effect on chemical shift is proportional to the degree of hydrogen bonding.
- As a result of this, the signal for –OH can be seen anywhere between 1-5 δ ppm.
- The downfield shift can be justified by inductive effect of oxygen atom.
- In CMR, hydroxyl group exerts strong effects just like electronegative substituents; α-effect in range of +40 to +50 δ ppm; β-effect in range of +7 to 10 δ ppm; γ-effect -2 to -6 δ ppm.

Spectroscopic analysis of aldehyde and ketone

- In ^1H NMR, the aldehydic proton absorb much at downfield at 8-10 δ ppm. The signal of aldehydic proton neither split adjacent proton signal nor got splitted.
- CMR for carbonyl carbon of aldehyde or ketone absorb much at downfield at around 190 -220 δ ppm hence makes it highly deshielded.
- The shift to downfield owes to sp^2 hybridisation and electronegativity of oxygen atom.

Spectroscopic analysis of carboxylic acid

- In ^{1}H NMR, the acidic proton absorb much at downfield at 9-12 δ ppm. The signal of acidic proton neither split adjacent proton signal nor got splitted.
- CMR for carbonyl carbon of carboxylic acid absorb much at downfield at around 165 - 185 δ ppm hence makes it highly deshielded.
- The shift to downfield owes to sp^2 hybridisation and electronegativity of oxygen atom however somewhat upfield from the absorption by aldehydes and ketones.

Spectroscopic analysis of carboxylic acid derivatives

- In ^{1}H NMR, the alkyl proton attached to ester group (R-CH_2-COOR') absorb at downfield at 5-8 δ ppm as broad signal.
- CMR for carbonyl carbon of carboxylic acid absorb much at downfield at around 150 - 185 δ ppm hence makes it highly deshielded.
- The shift to downfield owes to sp^2 hybridisation and electronegativity of oxygen atom.

Spectroscopic analysis of amines and substituted amides

- In ^{1}H NMR, the proton of NH_2 absorb in region of 1 – 5 δ ppm.
- In ^{1}H NMR, the proton of –$CONH_2$ absorb in region of 5 – 8 δ ppm.
- CMR for carbon attached to nitrogen deshield the chemical shift.

I have work hard preparing this material……

You also work hard preparing from this material!!!!

Best Luck….