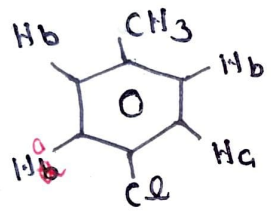


to the O-H and N-H protons. The protons pass through different environments during this exchange and give absorptions over a wide range of frequencies and field strengths.

Magnetic equivalence

chemical equivalence ^{requires} same chemical shift. Magnetic equivalence means coupling equivalence. In order to determine the equivalence of protons we will replace each proton by another atom. If replacement results only one product, then the protons are equivalent. If however replacement gives isomers, the protons are not equivalent.



The three methyl protons are equivalent
The two Ha protons are equivalent.
The two Hb protons are equivalent

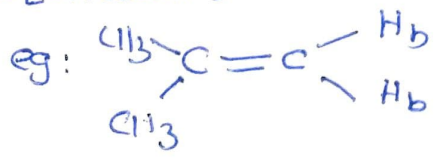
p-chlorotoluene (3 ¹H NMR signals).

→ To be magnetically equivalent, the nuclei must be chemically equivalent, and magnetically equivalent nuclei must have same coupling constant to any other nucleus in the molecule. Two nuclei are said to be magnetically equivalent if they exhibit the same chemical shift and the same coupling constant to every other nucleus in the molecule.

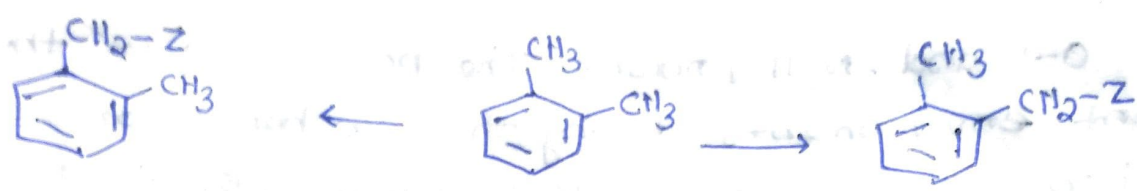
→ Chemically equivalent protons may not be magnetically equivalent always.

Homotopic protons

Homotopic hydrogen atoms on replacement gives same compounds with same chemical shift. (i.e. H' are chemically equivalent).

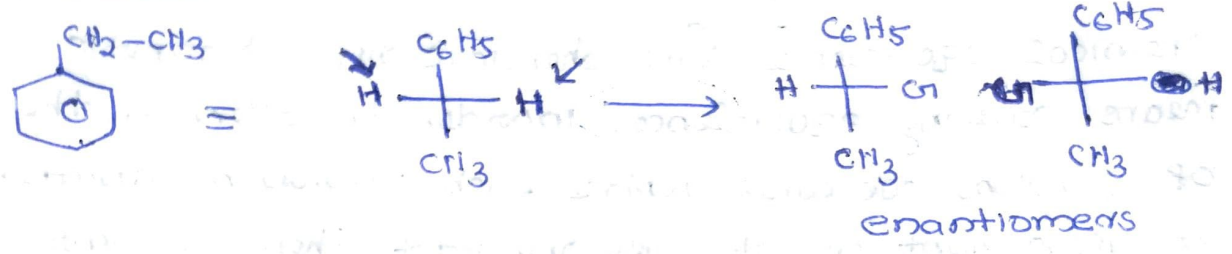


the two protons are homotopic

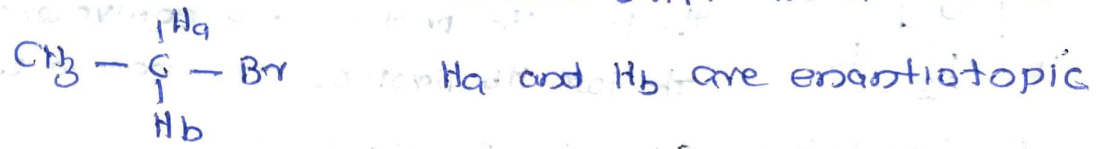


Methyl protons are homotopic.

Enantiotopic protons

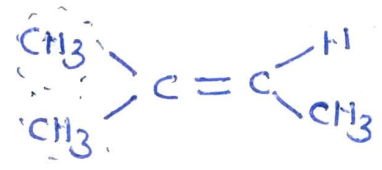
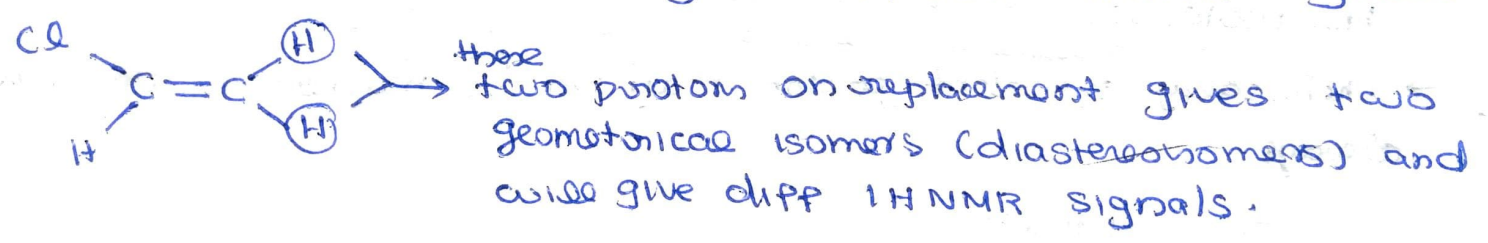


Methylene protons of ethylbenzene are enantiotopic since replacement by group like 'G' gives enantiomers. These enantiotopic protons have same chemical shift in an achiral solvent but will have different chemical shift in a chiral solvent.



Diastereotopic protons

Diastereotopic protons on replacement will give diastereoisomers. Diastereotopic hydrogen do not have the same chemical shift and will give different 1H NMR signals.



The two geminal methyl groups are diastereotopic and gives separate signals (2 singlets), CH3-C methylene group gives doublet. Alkenyl protons resonate at most downfield region.

Spin-spin splitting

Each proton as well as each bonding electron behave as a tiny spinning magnet and create its own magnetic field. A bonding electron has some tendency to pair its spin with the spin of the nearest proton. This electron, the spin of which has been affected by the neighbouring proton will affect the spin of another bonding electron, which then transmits this small magnetic polarization effect to another proton. This indirect spin interaction between neighbouring protons is called spin-spin coupling. This spin-spin coupling causes the splitting of the many of the lines in the NMR spectrum into multiplets. This is known as spin-spin splitting and is observable when high resolution spectrometers are used. So the indirect interaction between the spins of the neighbouring magnetic nuclei that is transmitted through intervening bonding electrons is called spin-spin coupling.

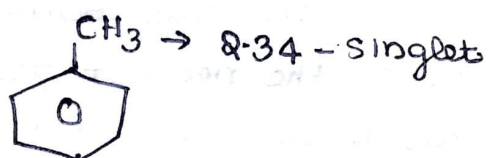
General rules

- ① Equivalent protons (i.e. protons with the same chemical shift) do not give observable splitting.
- ② A signal in the PMR spectrum for a set of equivalent protons is split into $(n+1)$ component lines, where 'n' is the number of equivalent protons in the adjacent set.
- ③ Suppose n_A equivalent protons and n_B equivalent protons couple with n_M equivalent protons; then the signal for M is split into $(n_A+1)(n_B+1)$ component lines.
- ④ The relative line intensities of a multiplet are given by Pascal triangle i.e. $(1+x)^n$.
 Singlet - 1 doublet - 1:1, triplet - 1:2:1, quartet - 1:3:3:1
 quintet - 1:4:6:4:1 sextet - 1:5:10:10:5:1

Problems

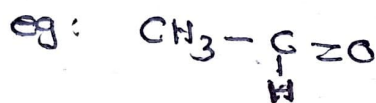
CU-Jan-2014 - D 52716

- ① p-OMe C₆H₄-Me shows in its ¹H NMR spectrum two peaks at δ (2.34, s, 3H), δ (3.75, s, 3H). Assign these two signals - CU-Jan 2014, D 52716



O-CH₃ → 3.75, -singlet (due to attachment of electronegative oxygen)

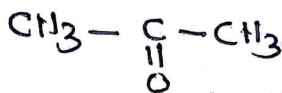
- ② How can aldehyde be distinguished from ketone by ¹H NMR.



2 signals

aldehydic proton

δ - 9-11



one signal

CH₃ - δ ~ 2.5

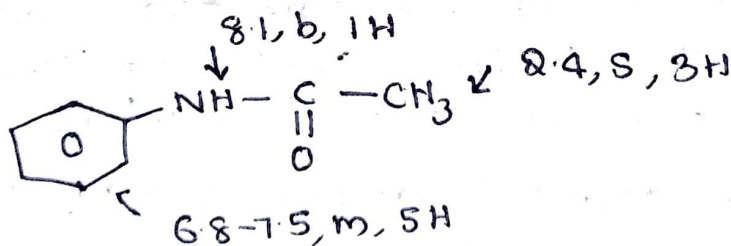
- ③ Explain the use of ¹H NMR spectroscopy in the structure elucidation of organic compounds?

④ IR - 3210 (b), 1685 (m)

¹H NMR - 2.4, s, 3H, 6.8-7.5, m, 5H, 8.1, b, 1H,

Mass - ~~M~~ - m/z 105

Find the structure of A C₈H₉NO from above details?

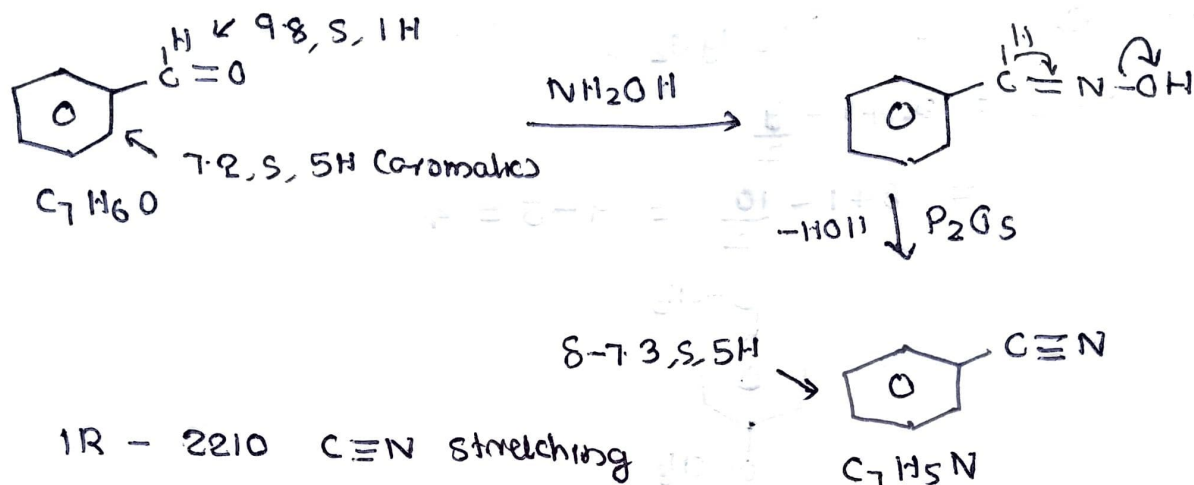


- ⑤ Explain simplification of complex NMR spectra?

⑥ A compound with molecular composition C₇H₆O

shows in its ¹H NMR spectrum peaks at δ - 9.8, s, 1H, 7.2, s, 5H. It reacted with hydroxylamine and the products so obtained was reacted with P₂O₅ to obtain another compound.

C_7H_5N which showed a peak at $\sim 2210\text{ cm}^{-1}$ in its IR and a signal at $\delta = 7.3, s, 5H$ in its 1H NMR spectrum. What are these two compounds? CU- Dec-2012 - D-31623

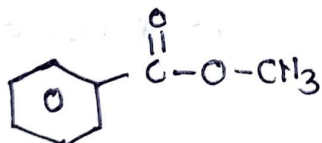


⑦ A compound shows a stretching band in its IR at 1710 cm^{-1} and its 1H NMR spectrum shows peak at $\delta = 9.8$. Identify the functional group responsible for the above.



⑧ Explain the effect of high field strength in the order of 1H NMR spectra?

⑨ Considering the structure of methyl benzoate predict the δ values of its methyl hydrogen in 1H NMR.



⑩ Identify the structure of the following comp

Mol. Formula - $C_8H_{10}O_2$

IR bands - 3000, 2951, 2936, 1509, 1464, 1233, 1060, 827 cm^{-1}

1H NMR - δ 3.75, s, 6H δ 8.3-8.4H

^{13}C NMR - (off resonance splitting in parenthesis) 66 (s), 114 (d), 153 (s) ppm

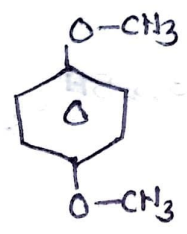
EI MS - 138 (Base peak), 123, 95, 41

Heating with HI gave CH_3I and an alkali soluble compound

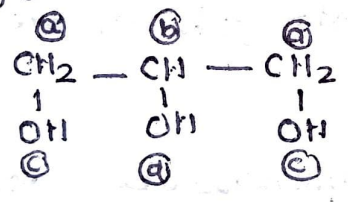
Ans - $\text{C}_8\text{H}_{10}\text{O}_2$ ($\text{C}_x\text{H}_y\text{O}_z$)

$$\text{DBE} = x + 1 - \frac{y}{2}$$

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



* (11) Predict the number of proton NMR signals with their multiplicity for glycerol?



- a → doublet
- b → quartet
- c → singlet
- d → singlet

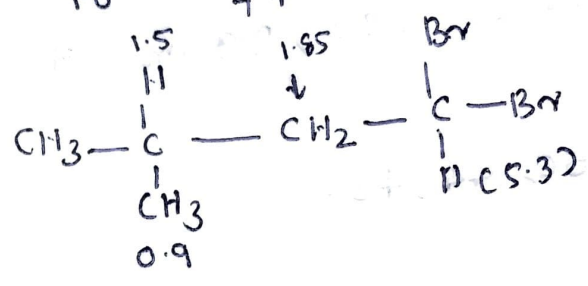
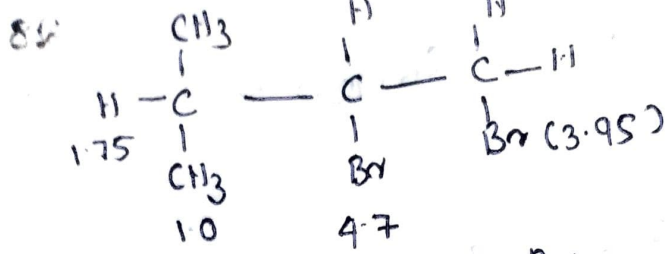
(12) Two isomers of $\text{C}_5\text{H}_{10}\text{Br}_2$ show the following PMR spectral data. Assign suitable structures

- a) 1.0, d (6H), 1.75 m (1H), 3.95 d (2H), 4.7 m (1H)
- b) 0.9 d (6H), 1.75 m (1H), 1.85 m (2H), 5.3 t (1H)

$$\text{DBE} = \text{C}_5\text{H}_{10}\text{Br}_2 \quad (\text{C}_x\text{H}_y\text{X}_z)$$

$$= x + 1 - \frac{y}{2}$$

$$= 5 + 1 - \frac{10}{2} = 6 - 5 = 1$$



check it well.

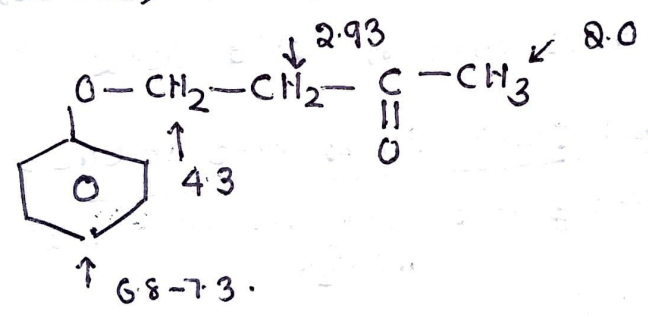
13) An organic compd with the mol. formula $\text{C}_{10}\text{H}_{12}\text{O}_2$ has the following spectral data

IR (cm^{-1}) - 1730, 3000 cm^{-1}

$^1\text{H NMR}$ - 2.0 (s, 3H), 2.93 (t, 2H), 4.3 (t, 2H),

6.8 - 7.3 m (5H)

Mass - 73, 91, 149, 164

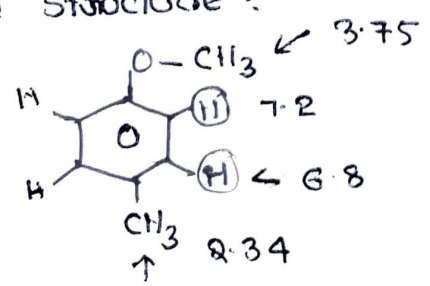


14) Explain why the $^1\text{H NMR}$ chemical shift values in δ ^{is the given order} ~~for~~ ^{order} alkene hydrogen < alkyne hydrogens < alkane hydrogens?

15) A compound on heating with HI gives $\text{CH}_3\text{-I}$ has the following $^1\text{H NMR}$ data

$\text{C}_8\text{H}_{10}\text{O}$
 δ 2.34 (s, 3H), 3.75 (s, 3H), 6.8 (dd, 2H), 7.2 (dd, 2H)

Identify the structure?



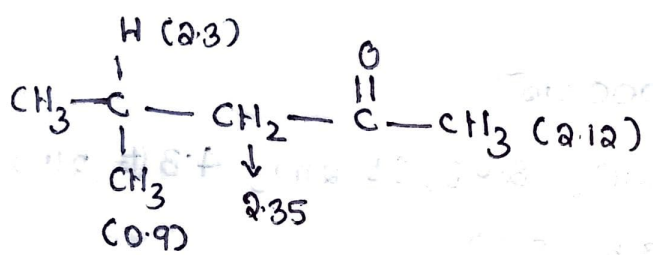
16) The Spectral data for a compound $C_6H_{12}O$ is as follows

IR - 2988-2880, 1718, 1450

1H NMR - δ 0.9 (d, 6H), 2.12 (s, 3H), 2.3, 1m (1H), 2.35, d (2H)

EMS - 100 (M^+), 85, 57, 56, 44, 43.

Ans. DBE = $C_6H_{12}O$
 $= 6 + 1 - \frac{12}{2} = 7 - 6 = 1$

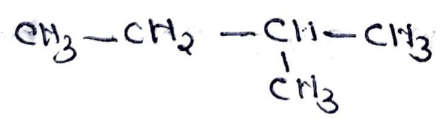


17) On a 60 MHz instrument a proton resonates at 210 Hz from TMS. Express this in delta scale

$$\delta = \frac{\text{Observed shift from TMS in (Hz)}}{\text{operating frequency of spectrometer in (Hz)}} \times 10^6$$

$$= \frac{210 \text{ Hz}}{60 \times 10^6 \text{ Hz}} \times 10^6 = 3.5 \text{ ppm}$$

18) what is pascal's triangle. Explain its use in predicting the PMR spectrum of the following compd



19) Deduce the structure of the compound having M.F $C_9H_8N_2O_2$.

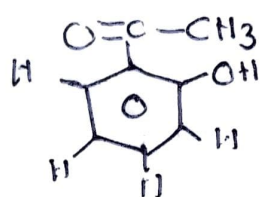
The spectral details are

IR - 3654, 2202, 1683 cm^{-1}

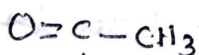
PMR - δ 4.5 (s, 2H), 6.0 (bs, 2H), 7.1-8.1 (m, 4H)

Mass = m/z , 176 ($M^+ - 1$), 132, 118, 102, 77

- 20) Base on $^1\text{H NMR}$ spectra, how will you differentiate between o-hydroxyacetophenone and p-hydroxyacetophenone?

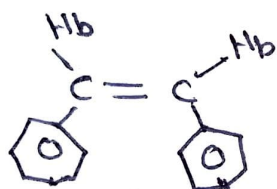


6 signals



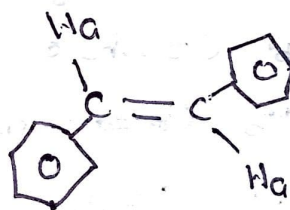
4 signals

- 21) What aspect of $^1\text{H NMR}$ spectroscopy will help you to differentiate between the cis-stilbene and trans-stilbene? Justify your answer?



$\delta_{\text{Hb}} = 6.49$

(cis)



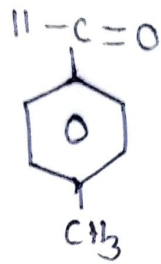
$\delta_{\text{Ha}} = 6.99$

(trans)

In trans stilbene both the vinylic protons are deshielded by both the aromatic rings thus have high δ value, while in cis stilbene protons are deshielded only by adjacent aromatic ring, thus have comparatively low δ value.

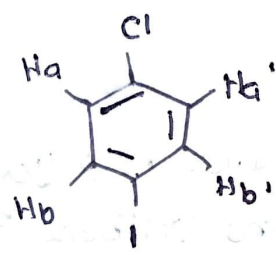
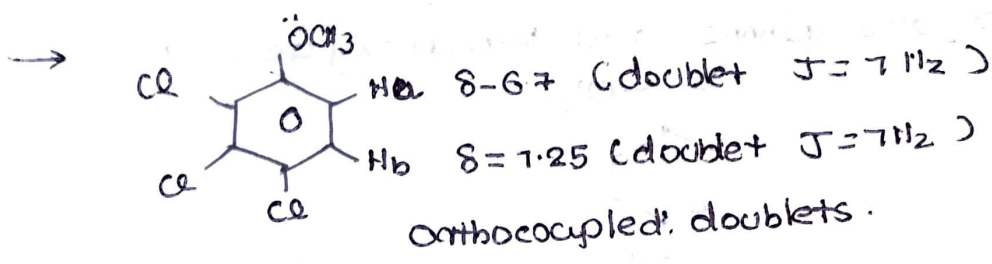
- 22) Proton attached to nitrogen appear as broad signal in the $^1\text{H NMR}$ spectrum. Explain?

- 23) $^1\text{H NMR}$ - 8-9.6 (s, 1H), 7.5 (d, $J = 7.5 \text{ Hz}$, 2H), 6.7 (d, $J = 7.5 \text{ Hz}$, 2H), 3.6 (s, 3H).



24) Give the splitting pattern in $\text{CH}_2 = \text{CH} - \text{Br}$

25) predict the number and multiplicity of signals observed in the $^1\text{H NMR}$ spectrum of 1,4-difluorobenzene?



The protons H_a and H_a' , also H_b and H_b' are chemically equivalent but magnetically non equivalent bec^z they have different coupling constants

$$J_{\text{H}_a \text{H}_b} = J_{\text{H}_a' \text{H}_b'} \quad (\text{ortho coupling})$$

$$J_{\text{H}_a \text{H}_b'} = J_{\text{H}_a' \text{H}_b} \quad (\text{meta para coupling})$$

$$J_{\text{H}_a' \text{H}_b'} \neq J_{\text{H}_a' \text{H}_b} \quad (\text{ortho coupling} \neq \text{para coupling})$$

$$J_{\text{H}_a \text{H}_b} \neq J_{\text{H}_a \text{H}_b'} \quad (\quad) \neq (\quad)$$

Thus protons H_a and H_a' have finite coupling constant $J_{\text{H}_a \text{H}_a'}$, also protons H_b and H_b' (magnetically non equivalent) have a coupling constant $J_{\text{H}_b \text{H}_b'}$.

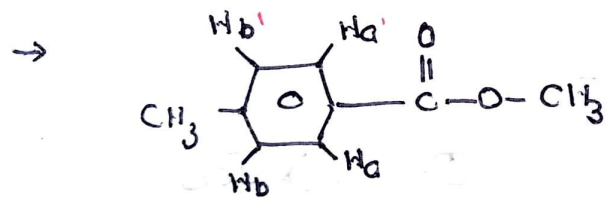
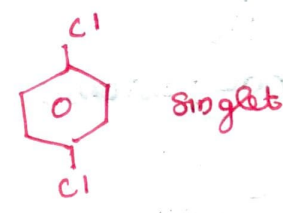
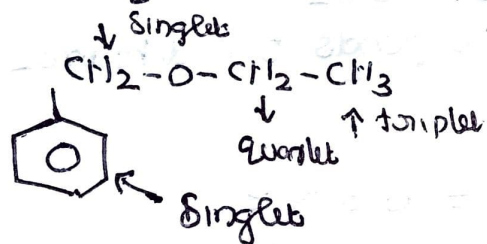
→ Distance b/w the centres of the peaks of the resonance multiplets doublet is called coupling constant J_{ab} . It is measured in Hertz. The magnitude of coupling constants are not dependent upon the magnitude of the applied field and their values in Hertz. It will be same regardless of the operating frequency of the spectrometer.

The code J_{ab} means the coupling constant for H_a split by H_b or for H_b split by H_a .

Reg: 4.7, 8 (211), d, J = 7

chemical shift in δ No of hydrogens No of peaks (d-doubles) coupling constant

→ In monosubstituted benzene, when the substituent is an alkyl group or some other group with about the same electronegativity as carbon all five benzenoid H's have almost same chemical shift thus appear as a singlet in the region δ 6-8.5. when the substituent in a monosubstituted benzene is electronegative or electropositive, then the o, m and p hydrogens & vice have different chemical shifts. eg: Nitrobenzene, disubstituted benzenes etc. In p-dichlorobenzene and p-xylene, the 4 benzenoid hydrogens are equivalent and display sharp singlet.



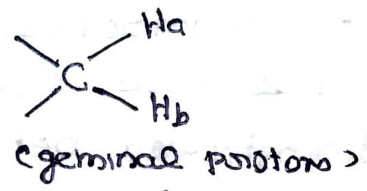
In a p-disubstituted benzene with different substituents, the aromatic protons appear as a pair of doublets. However one can detect additional lines within each doublet. This is bec² the two chemically equivalent protons H_a (with same chemical shift) are magnetically non equivalent (ie $H_a \neq H_a'$ & similarly $H_b \neq H_b'$) since their coupling constant to other nuclei is not same. Magnetically equivalent nuclei give first order spectra. while magnetically non equivalent nuclei will lead to non-first order pattern. Two protons are magnetically equivalent if they have the same chemical shift and the same coupling constant to every other nucleus in the molecule.

→ So in general ^{spectra} $^1\text{H NMR}$ spectrum with features of first order will have proton H_a displaying $n+1$ splitting pattern ($n = \text{equivalent adjacent hydrogen atoms}$). The separation of lines is designated by J Hz. The intensity of lines in a multiplet can be determined by using pascals triangle etc.

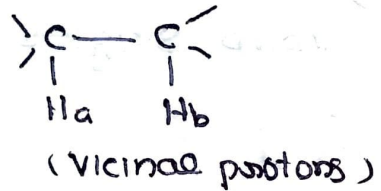
Magnitude of coupling constant, J

Structure

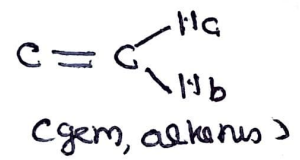
J in Hz



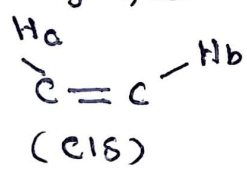
$J = 10-18 \text{ Hz}$
(Depends on E/N of attached groups)



$J \approx 8 \text{ Hz}$
(Depends on dihedral angle)

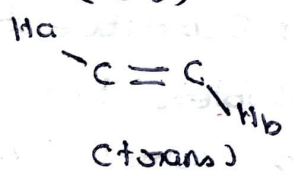


$J = 0.3 \sim 2$

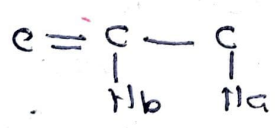


$J = 5-14$

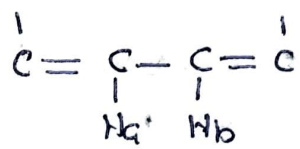
$J_{\text{trans}} > J_{\text{cis}}$



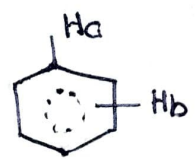
$J = 11-19$
(Trans coupling in alkenes is stronger than cis coupling.)




$J = 4-10$



$J = 10-13$



ortho - 7-10
meta - 2-3
para - 0-1

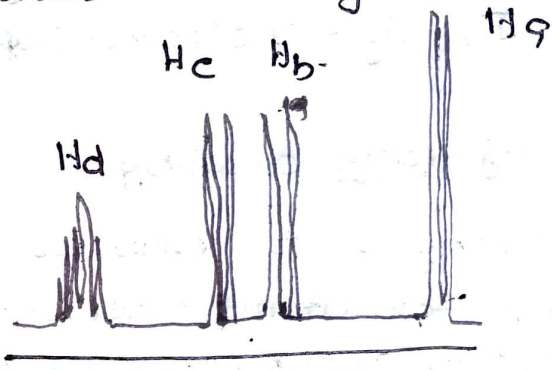
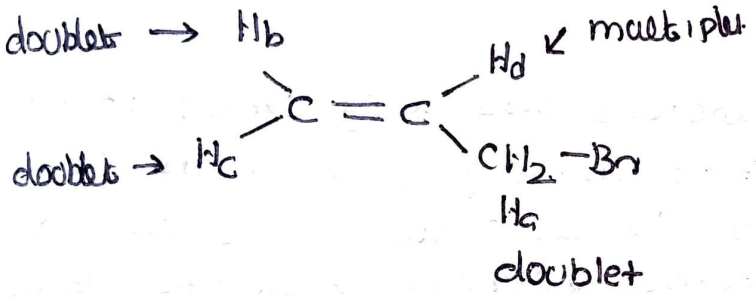
$10''$  Spin-spin splitting is normally observed if the two protons are nonequivalent, diastereotopic in geminal protons (2J). Value is small if two protons are bonded to an sp^2 carbon.

H_1 H
 $C^2 - C^3$ → Spin-spin splitting is normally observed protons separated by 3 σ bonds (3J)

H H
 $C^2 - C^3 - C^4$ → Spin-spin splitting is not normally observed for protons separated by 4 σ bonds

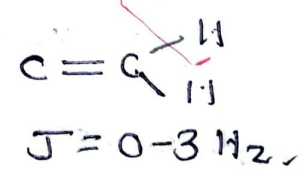
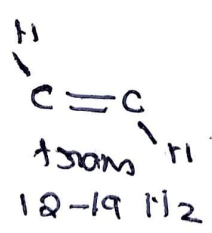
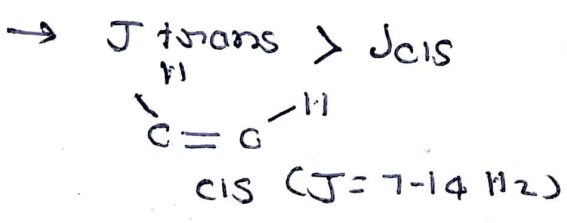
H
 $C - C = C - H$ → Spin-spin splitting is observed protons separated by 4 bonds including a π bond.

eg: 3-bromo-1-propene



→ CH_2 -methylene proton is most shielded, H_d protons is most deshielded. ($sp^2C + EN-Br$).

→ H_b and H_c are diastereotopic and non equivalent, but geminal coupling b/wn them is much smaller, so not observed well, but it will couple with H_d proton and forms doublet



→ H_d appears as multiplet, since it splits by all the three different protons H_a , H_b and H_c .

n-Butyl acrylate