

4. Nuclear Magnetic Resonance (NMR) Spectroscopy.



Imp

* Chemical shift

The difference in peak or resonance position of proton with respect to an arbitrary standard is called chemical shift.

The difference in peak position is due to difference in electron density around the proton of sample as compared with electron density around the proton standard chosen. Chemical shift is measured in equivalent frequency unit and not in gauss.

Chemical shift signifies the exact position of resonance signals of different types of protons for an arbitrarily chosen standard.

Protons which are in identical electronic environment have same chemical shift. These are called equivalent protons. Then the protons are in different electronic environments have different chemical shifts. These are called non-equivalent protons.

Measurement of chemical shift (peak position)

The non-equivalent protons of a compound absorb at different field strengths but field differences could be small at 600 gauss, and NMR instruments producing 1400 gauss can't accurately measure field strength differences of the order of 10^{-2} gauss, so, absolute peak position cannot

be determined and it is not essential also. A standard proton reference TMS is used with the sample. TMS protons resonate and absorb if arbitrarily fixed to be zero, so we really measure a relative field strength to get required accuracy. The TMS is always higher peak or frequency and commonly peaks due to anilid protons remains at lower (or down peak) and those of TMS protons.

a) Delta scale (δ):

It is most commonly used scale. A delta unit is the ratio of freqⁿ shift to the operating freqⁿ instrument, if ν is the freqⁿ symbol then chemical shift is mathematically given as under:

$$\delta = \frac{(\nu_{\text{sample}} - \nu_{\text{TMS}}) \text{ in Hz}}{\text{operating } \nu_{\text{instrument}} \text{ in MHz}} \quad \text{--- (1)}$$

In this eqⁿ freqⁿ of sample and TMS are expressed in Hz, where freqⁿ of is expressed in MHz, so δ has units part per million - (PPM)

Now, $\nu_{\text{sample}} - \nu_{\text{TMS}} = \Delta \nu$ and
 $1 \text{ MHz} = 10^6 \text{ Hz}$

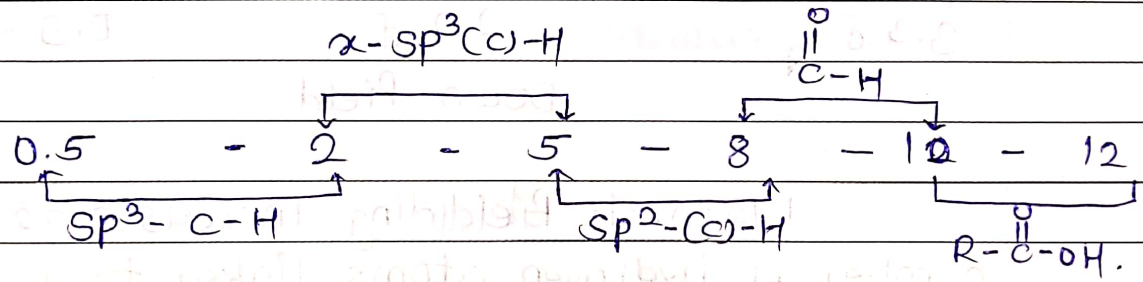
So, eqⁿ (1) can be written as.

b) Tau (τ) scale :

A larger δ value signifies lower field strength and lesser shielding i.e down field. A smaller δ value signifies higher field strength, greater shielding i.e up field. so values expressed in δ scale are misleading. To overcome this difficulty a direct tau scale is introduced. It is related to δ -value by the equation,

$$\tau = (10 - \delta)$$

The protons having same δ or τ value are equivalent protons. The protons having different δ or τ values are non-equivalent protons.



* Factors affecting chemical shift δ values:

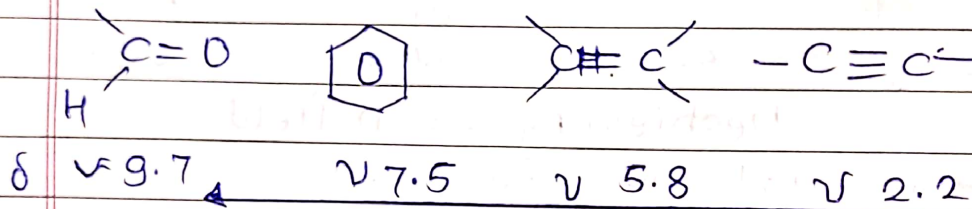
Many factors modify electron environment around a proton by influencing its local field and thereby affect the δ values.

Prominent factors are discussed below with common examples.

i) Electronegativity and inductive effect:

Presence of an electron withdrawing atom or group in near proximity de-shields the proton and increases the δ value (down field shift). eg. increasing δ value of

the influence of applied field circulate and generate magnetic field. But the field generated by pi-electrons is unsymmetric or does not operate equally in space. That is, it may exert paramagnetic effect causing up field shift in certain area. In some other area it exerts diamagnetic effect causing down field shift. eg. consider the δ values of series of compounds.



Anisotropic deshielding.

a) Aldehyde proton :

Electronegative nature of 'O' de-shields aldehyde proton. further, the induced field generated by circulating π -electrons of C=O bond reinforce the applied field around aldehyde proton as shown in fig. The shift caused is too down field so raises δ values to ≈ 9.7 .

b) Benzene :

Induced force reinforces the centered on π and staying par applied field around the aromatic protons so they get de-shielded greatly this raises their δ -value.

c) Alkene:

The vinyl protons experience paramagnetic de-shielding due to parallel alignment of applied field and the induced field. This causes down field shift giving higher δ value.

d) Alkynes:

In alkynes the pi-electrons freely circulate around the triple bond symmetry axis. The acetylene protons experience diamagnetic shielding and cause further up field shift.

* Shielding and De-shielding:

An electron is a spinning charge, so, electron circulation under the influence of external applied field generates its own magnetic field called secondary or induced magnetic field.

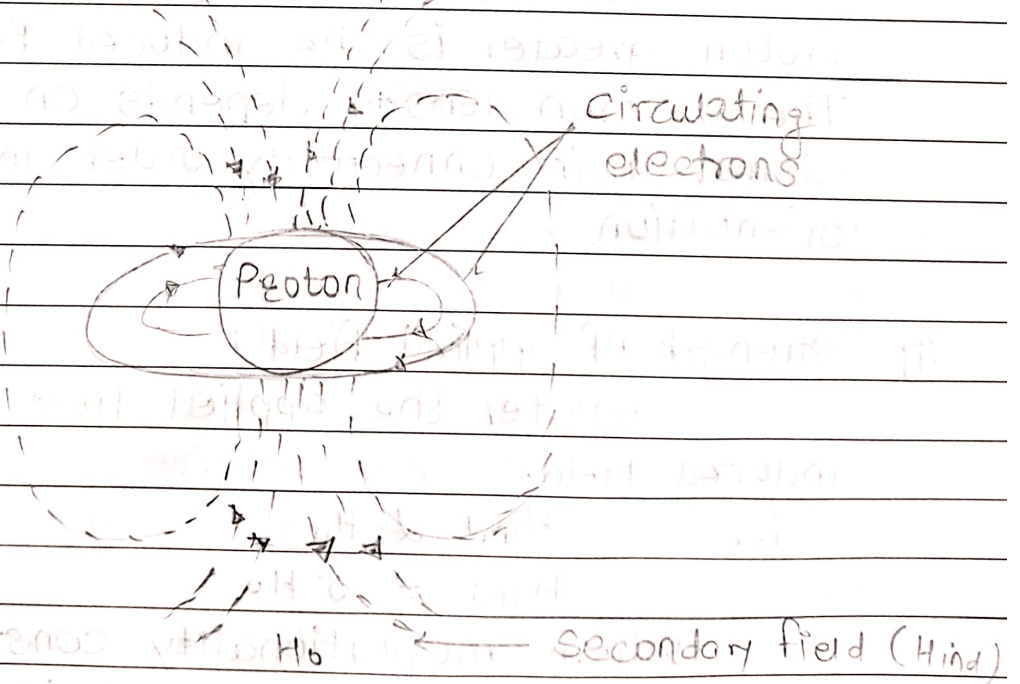


Fig. Shielding by induced field due to circulating electrons.

The induced field generated around the proton may either oppose or reinforce the external applied field. so, the actual field felt by the protons is not same as that of applied field strength (H_0) and called as local field (H)

When the induced field opposes the external field ($\uparrow\downarrow$). The protons experience a field which is slightly less than the applied field. such protons are said to be protected or shielded. This phenomenon of partially protecting the protons from the applied field is called shielding or diamagnetic shielding. The extent of shielding depends on the strength of induced magnetic field (H_{ind}) generated. Two factors control H_{ind} value and they are as under.

i) Electron density around the proton:

Greater the electron density around the proton greater is the induced field generated. The electron density depends on the nature of atoms, their connectivity order and even spatial orientation

ii) strength of applied field:

Greater the applied field greater is the induced field.

i.e. $H_{ind} \propto H_0$

$$H_{ind} = \sigma H_0$$

Where proportionality constant σ is called shielding parameter. It is a measure of

degree of shielding or de-shielding. Larger the σ value greater is the shielding and smaller the σ value lesser the shielding.

When the induced field opposes the applied field around proton it is called diamagnetic shielding and σ value is positive. When induced field the applied field it is called para-magnetic de-shielding and σ value is negative. Thus σ value influences the local field (H) around proton.

$$H = H_0 (1 - \sigma)$$

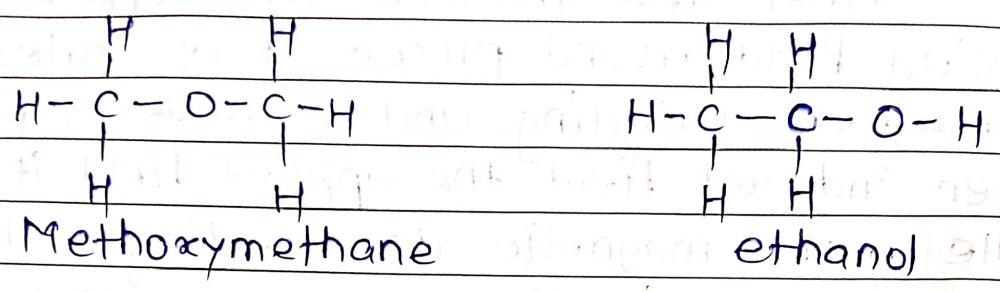
The total field ' H ' is related to precessional frequency by eqⁿ

$$\nu = \frac{\nu}{2\pi} H_0 (1 - \sigma)$$

The ν and π are constants and if applied field strength is fixed, it means the ' ν ' value is depends only on σ . As σ value increases shielding increases, and as σ value decreases shielding decreases.

At a given applied field protons under identical electronic environments have same σ value and are called equivalent protons. Protons under different electronic environment differ in σ value and are called as non-equivalent protons.

The compound ($C_2H_6O_2$) can exist in two isomeric forms depending on atomic connectivity and their structure are as under.



All six protons of methoxy methane are in identical chemical environment, so they have same δ , H or ν values. They are equally shielding process with same so they all form only one set of equivalent protons.

Six protons of ethanol are in three different chemical environments. so they have different values of δ , H or ν . They are unequal shielded, have so they form three sets of non-equivalent protons.

a) Van der Waals de-shielding: The proton occupying a sterically hindered position in a rigid molecules is de-shielded. Because, the electron cloud of hindering group will tend to repel the electron cloud surrounding proton. eg. the highly substituted steroids and alkaloid.

b) Anisotropic effects: The circulation of pi-electrons under

right angle to the direction of the applied field, the induced field due to π -electrons forms two cone shape lobe. One on either side of $C=C$ bond the lobes stay parallel bond axis as shown in fig below.

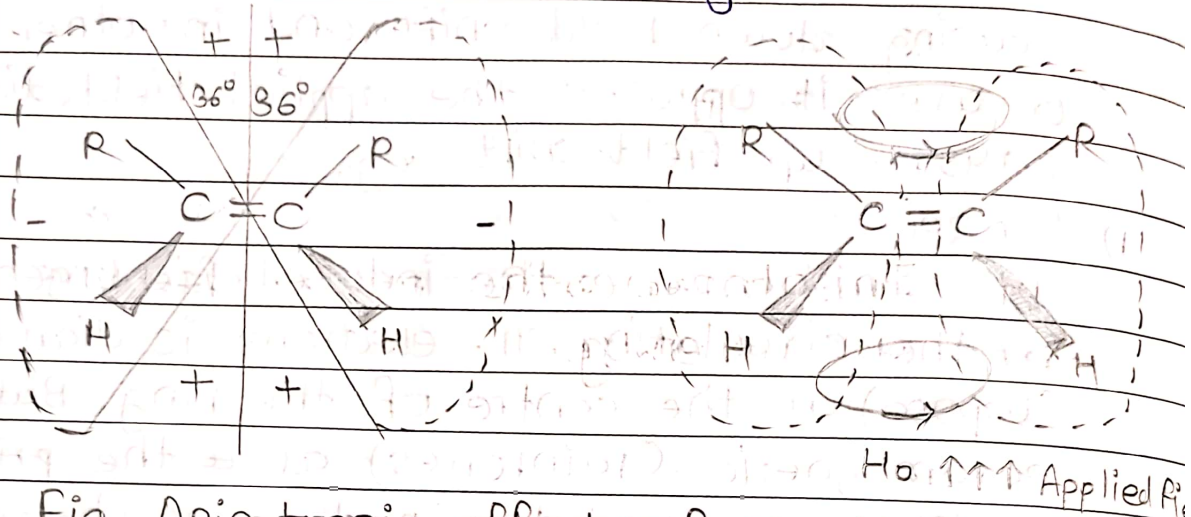


Fig. Anisotropic effect of π -electrons in an alkene.

The protons coming within cone are experience paramagnetic effect and de-shield (higher δ value). But around the C bond axis diamagnetic effect is felt. This dual effect of induced field is anisotropic effect.

3) Aldehyde:

In aldehydes the shielding and de-shielding zone around $C=O$ group is slightly differs from alkene. The two cone shape volumes are centered on 'O' atom, They stay parallel to the $C=O$ bond axis, The protons within the zone experience de-shielding but protons held above or below the cone are shielded.

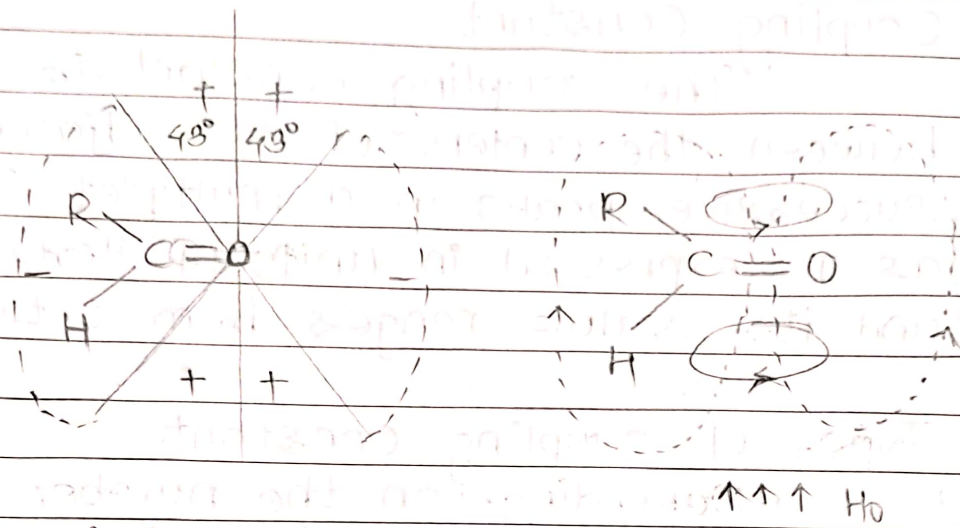


Fig. Anisotropic effect of pi-electrons in an aldehyde.

4] Alkyne:

The electron distribution at acetylene triple bond axis is symmetric. When triple bond axis remains parallel to applied field, electronic circulation induced is perpendicular. so acetylene protons get shielded hence absorb further up field than vinylic protons. as shown in below.

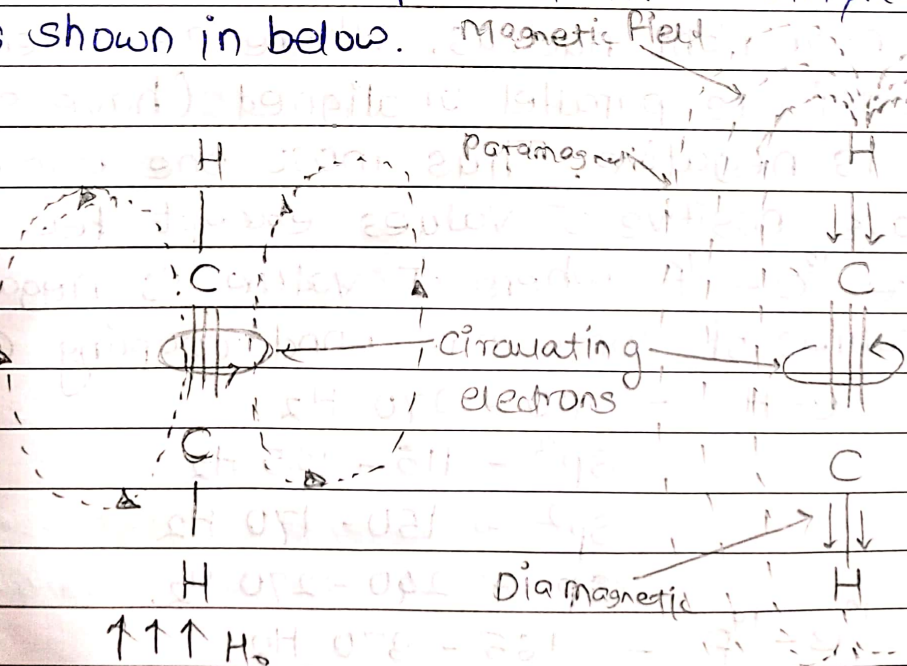


Fig. Shielding of acetylenic proton in alkyne

* Coupling constant

The coupling constant is distance between the centers of two adjacent or successive peaks in a multiplet. It is denoted as J , expressed in units of Hertz or cps and its value ranges from 0 to 20.

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Types of coupling constant -

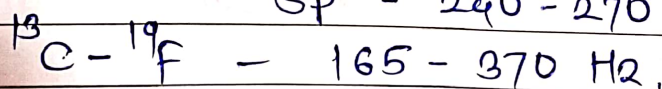
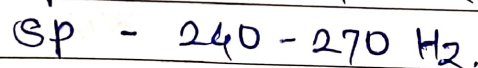
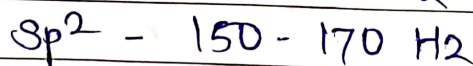
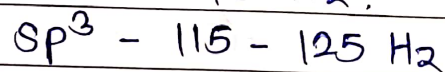
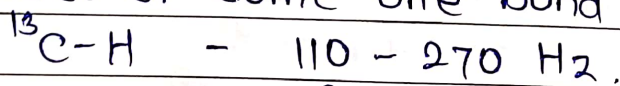
Depending on the number of bond involved in the coupling different types of couplings are recognised and they are as under.

I 1 bond coupling ($1J$) -

This type of coupling occurs between two spin active nuclei joined by a single bond eg. $^{13}\text{C}-\text{H}$ - 110 - 270 Hz

The bonding electrons in a single bond are assumed to avoid each other so that one electron is near left nucleus and other electron is near right nucleus. Where as when the nuclei are parallel or aligned (have same spin) J is negative. Thus most one bond coupling have positive J values except few exceptions like $^{13}\text{C}-^{19}\text{F}$ where J value is negative.

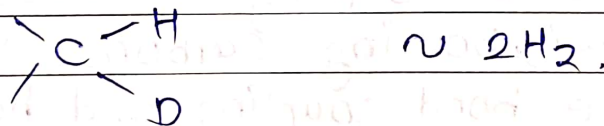
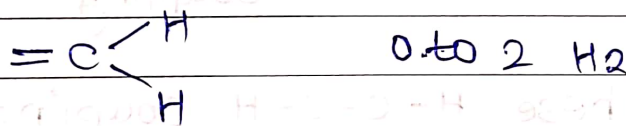
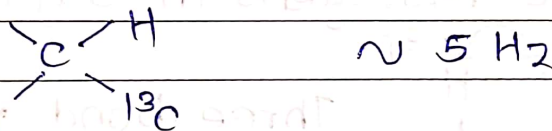
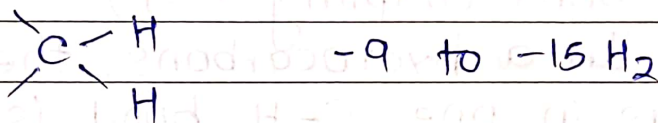
values of some one bond coupling constants (J)



2] Two bond coupling ($2J$) -

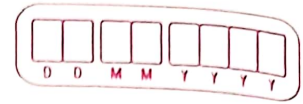
These type of couplings are common in NMR. These are sometimes called geminal couplings because the two nuclei that interact are attached to the same central atom. The two bond coupling constants are represented as $2J$.

They occurs in carbon compounds when two spin active atoms are attached to the same carbon atom, typically smaller in magnitude than one bond coupling. In majority cases the two bond couplings are those of HCH and are found to be negative.



The values of $2J$ depends upon the bond angle ($\text{-C}-\text{H}$) in case of geminal protons of a saturated compound.

$\equiv sp$
 $= sp^2$
 $- sp^3$



Characteristics of two bond or geminal coupling constants.

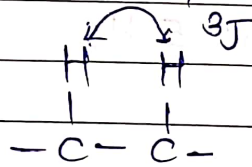
1) The value of coupling constant increases with increase in bond angle.
eg. Methane $2J = -12.4 \text{ Hz}$, Ethene $2J = +2.5 \text{ Hz}$

2) The value of coupling constant increases with increase in atom or group.

3) The value of coupling constant decreases if an electron negative substituent withdraws electron from the π bond. eg. Ethane - $2J = +2.1 \text{ Hz}$. vinyl Fluoride - $2J = -3.3 \text{ Hz}$.

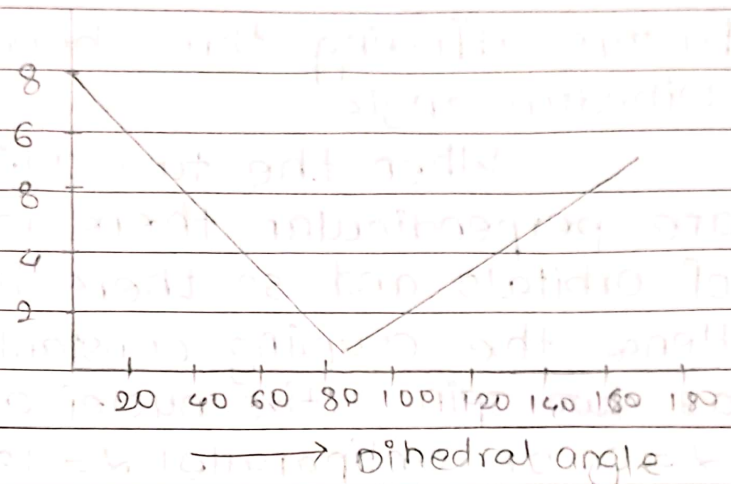
3) Three bond coupling ($3J$) -

In a hydrocarbons, the spin of hydrogen nucleus in one C-H bond is coupled to the spins of the hydrogens in adjacent C-H bond

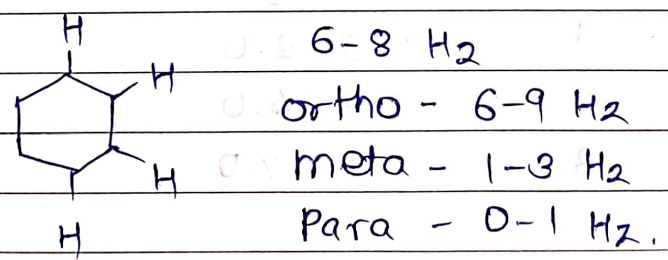
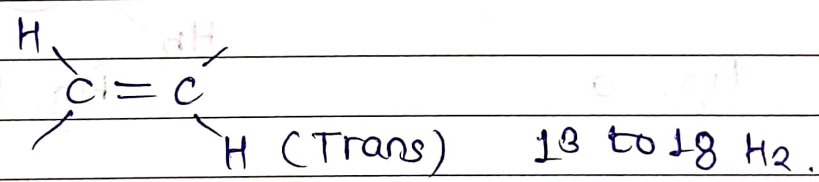
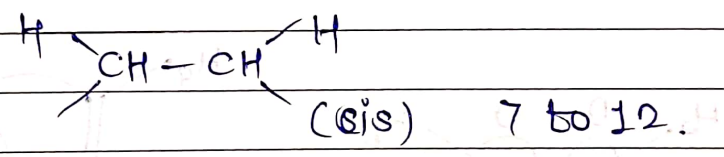
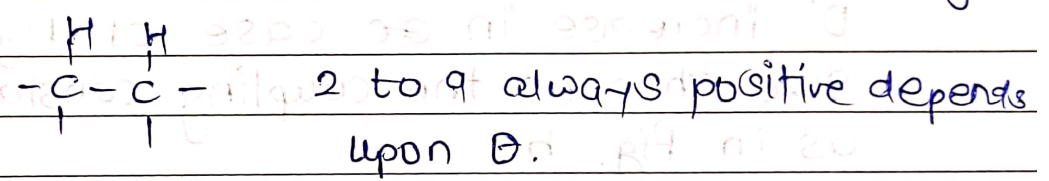


Three bond vicinal coupling.

These H-C-C-H couplings are also called vicinal coupling because the hydrogens are on neighbouring carbons. Vicinal couplings are three bond coupling and have a coupling constant designated as $3J$. These coupling produce spin-spin coupling patterns that follow $n+1$ rule in simple aliphatic hydrocarbon chains. For vicinal protons the value of coupling dihedral angle as shown in fig



Coupling constant maximum values with when dihedral angle is 0° or 180° . The value of J is slightly negative when dihedral angle is 90° . The values are some coupling are.



Factors affecting three bond couplings.

i) Dihedral angle -

When the two adjacent C-H bonds are perpendicular there is minimum overlap of orbitals and so there is no spin interaction. Hence the coupling constant $^3J_{H-H} = 0$. Where as two spin active nuclei are parallel i.e. $\alpha = 0$ or antiparallel $\alpha = 180^\circ$. The coupling constant has maximum value $^3J_{H-H} = \text{maximum}$.

ii) Valance angle -

The value to J decreases as θ and θ' increase in the case of Fig. a. The ring size changes the coupling constant changes as in Fig. b.

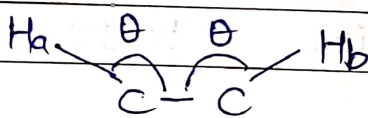


Fig. a

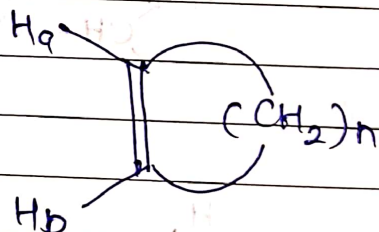


Fig. b.

n	J_{ab} Hz
1	0.5 - 2.0
2	2.5 - 4.0
3	5.1 - 7.0

iii) Bond length -

The value of coupling constant are dependent on whether the coupling nuclei

on adjacent carbons are joined by a single or double bond. Hence ortho coupling constant are nearly 8 Hz slightly lower than cis olefinic coupling constant in cyclohexane $8.8 - 10.5 \text{ Hz}$.

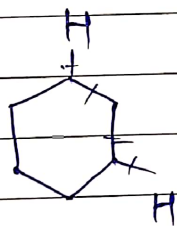
iv) Presence of electronegative or electropositive substituents -

When electronegative elements are directly attached to the same carbon atoms as vicinal couple protons the coupling constant is decreases, whereas attached electronegative elements increases.

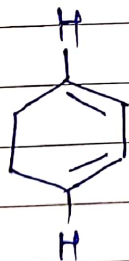
4) Long range coupling ($4J - {}^nJ$) -

These involve more than 3 bonds and its common in allylic hydrogens or aromatic ring hydrogen.

eg



meta
1 to 3 Hz



Para
0-1 Hz