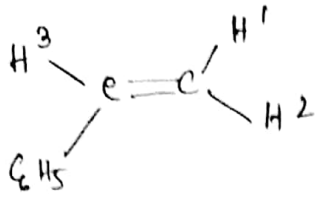


For monosubstituted olefins,  $J_{trans} > J_{cis} > J_{gem}$ .

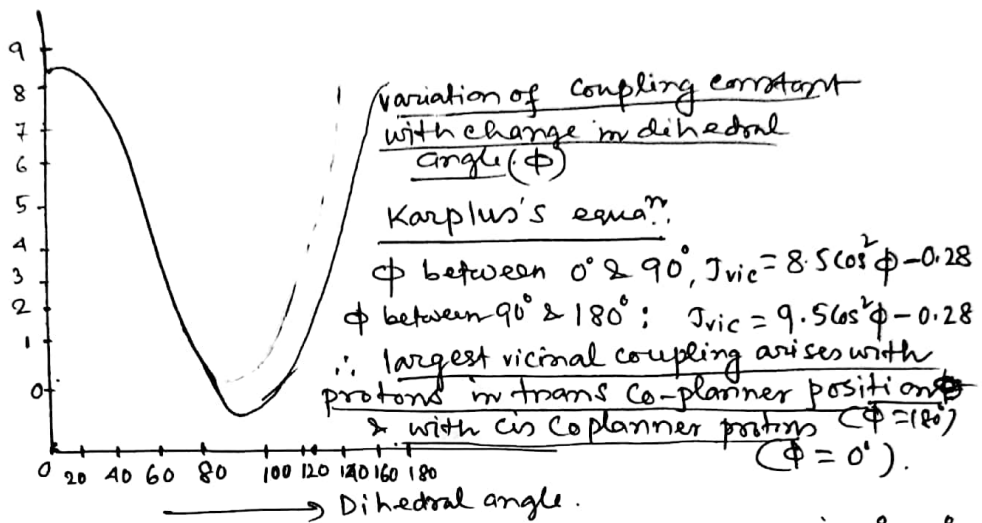


$$J_{cis}(H^1, H^3) = 10.6 \text{ cps.}$$

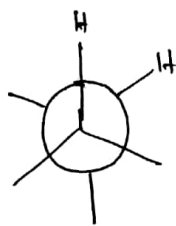
$$J_{trans}(H^2, H^3) = 17.4 \text{ cps.}$$

$$J_{gem}(H^1, H^2) = -1.4 \text{ cps.}$$

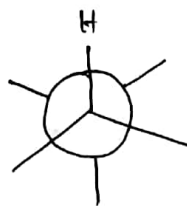
(b) Vicinal Coupling: For vicinal protons, the value of coupling constant varies with the dihedral angle. vicinal protons are the protons which are separated by three bonds.



- \* From the graph it is found that when the dihedral angle is  $0^\circ$  or  $180^\circ$  we observe largest values for the coupling constants.
- \* The value of  $J$  is slightly negative when the dihedral angle is  $90^\circ$ .



Gauche

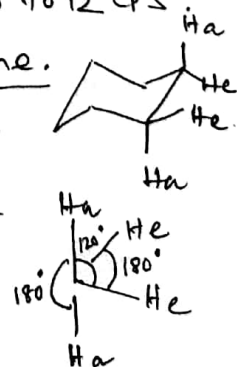


H Anti

In the signal (multiplet) for gauche proton (dihedral angle  $60^\circ$ )  $J$  varies from 2 to 4 cps and that for anti protons (dihedral angle  $180^\circ$ ),  $J$  varies from 5 to 12 cps.

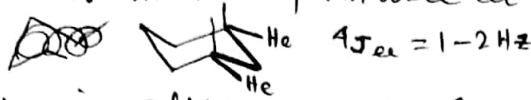
\* We can consider the protons in chair cyclohexane.

Here diaxial protons have coupling constant around 10-13 Hz ( $\phi = 180^\circ$ ), But diequatorial protons or those with axial/equatorial have coupling constant 2-5 Hz, corresponding to about  $60^\circ$  orientation.



② Long range coupling:

Usually no coupling is observed if the distance between the two absorbing nuclei is more than three covalent bonds. But is observed within rigid system where the w-shaped zig-zag of bonds is near to being ~~coplanar~~ coplanar, as indicated by heavy bonds in the formulae at the bottom of the table.



Trans coupling in alkene groups ( $J = 11-19$  Hz) is stronger than cis coupling ( $J, 5-14$  Hz), Typical values, 16 Hz and 8 Hz.

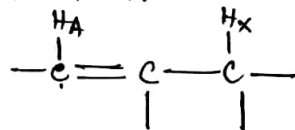
Aromatic coupling depends on whether the coupling protons are ortho, meta or para to each other.

$^3J_{ortho} = 7-10$  Hz,  $^4J_{meta} = 2-3$  Hz,  $^5J_{para} = 0-1$  Hz.

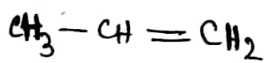
In  $\pi$  bonds system, appreciable coupling are frequently observed between protons separated by even four or five bonds. The effect of the nuclear spin are transmitted from C-H bond ( $\sigma$ -bond) by coupling of the resultant electron spin on carbon atom with  $\pi$  electrons.

In 2,4 dichlorobenzaldehyde, long range coupling takes place between the aldehydic protons and a ring protons.

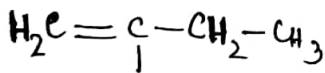
Allylic coupling, as in allylbenzene, is the most likely four-bond coupling to be met in non-aromatic system and is very small ( $J$  0-2 Hz)



$J_{AX}$  (allylic coupling), 0-2 Hz.

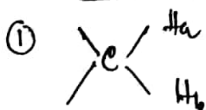


$\Rightarrow -1.7$  cps.

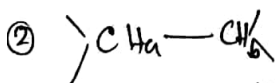


$\Rightarrow -2.3$  cps.

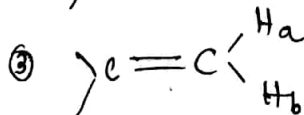
Proton-Proton Spin-Spin Coupling Constant.



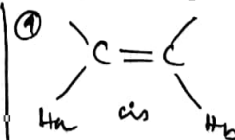
10-18 Hz



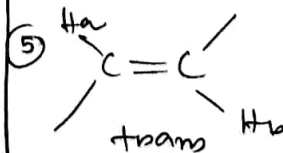
depends on dihedral angle.



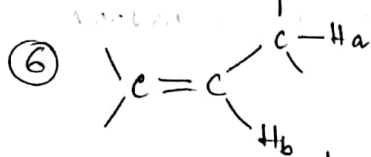
1-4



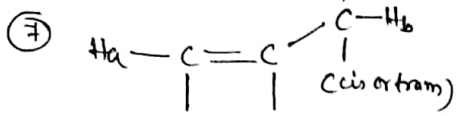
5-14 Hz  
Commonly around (6-8 Hz).



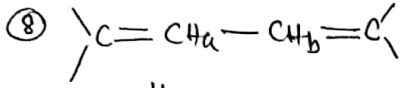
11-19  
(Commonly around 6-8 Hz)



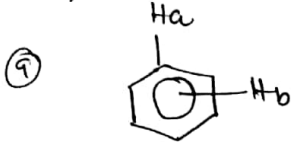
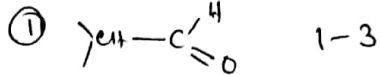
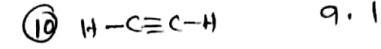
4-10 Hz



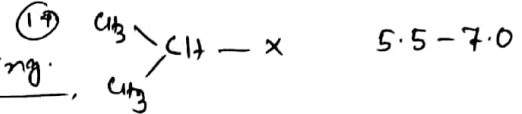
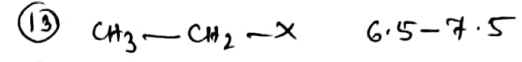
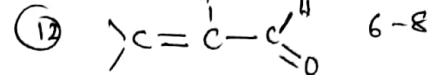
0-2 (for aromatic system, 0-1)



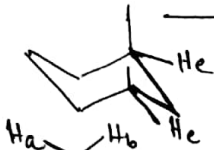
10-13



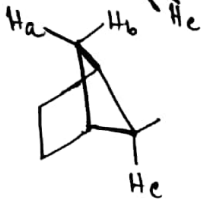
ortho 7-10  
meta 2-3  
para 0-1



Long range ( $4J$ ) Coupling.



$4J_{ee}$  1-2 Hz



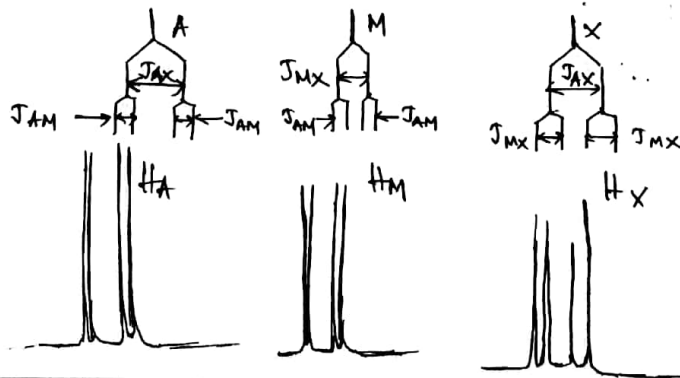
$4J_{ac}$  8 Hz

$4J_{bc}$  0.2 Hz



$4J_{ab}$  18 Hz.

\* In unsaturated systems (and aromatic system) it is frequently possible to observe three groups of protons A, M, X, each of which couples with the other two. For such a system to be first order, the chemical shift position of the proton must be relatively well separated, just as A, M & X are separated in the alphabet. The NMR spectrum of ~~furan-2-al~~ furan-2-aldehyde show such an AMX system. The coupling pattern involves interaction between protons separated by four bonds.

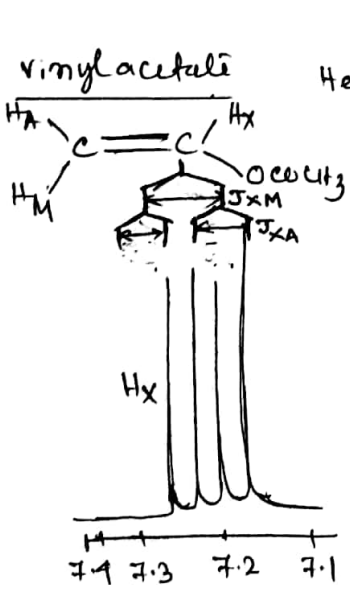
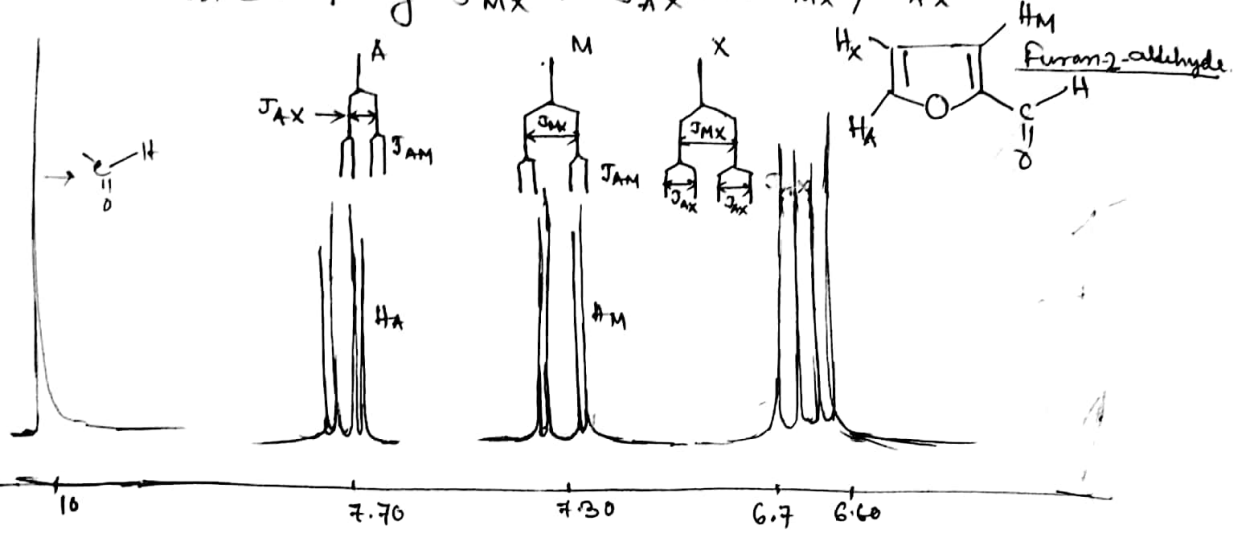


coupling constant in an AMX system.

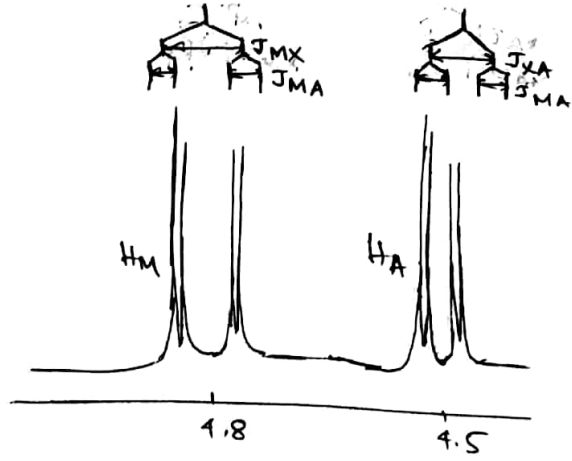
Here proton A couples with X, which split A signal into doublet. But A also couple with M, (four bond coupling) so that each line of A is further split into two giving four lines in all. The signal for proton A shows two splittings,  $J_{AM}$  and  $J_{AX}$ , and is therefore a double doublet, and  $J_{AX} > J_{AM}$ .

Similarly M signal into two coupling with X, and each line is further split into two by coupling with A, two coupling constant are again seen  $J_{MX}$  and  $J_{AM}$ . and M appear as double doublet.  $J_{MX} > J_{AM}$ .

Lastly, X signal is split into a double doublet by two successive coupling  $J_{MX}$  &  $J_{AX}$ . &  $J_{MX} > J_{AX}$



Here  $J_{XM}$  (From coupling) = 14-16 cps,  $J_{AM} = 1-4$  cps.  
 $J_{XA}$  (cis coupling) = 6-8 cps.

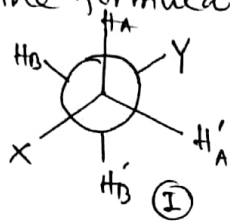


Chemical and Magnetic Equivalence in NMR Spectra.

Two protons are defined as being chemically equivalent if, by virtue of symmetry within the molecule, their electronic environments are indistinguishable and, therefore, they possess the same value of chemical shift.

Two protons are defined as being magnetically equivalent if each couples equally to a third neighboring proton; otherwise they are magnetically nonequivalent.

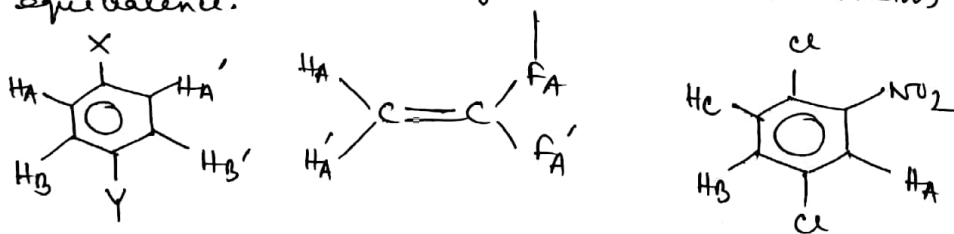
Consider that the formula I which is the most stable conform<sup>n</sup> of  $XCH_2-CH_2Y$ .



Because of symmetry,  $H_A$  and  $H_{A'}$  will have the same chemical shift values, as will  $H_B$  &  $H_{B'}$ . Now  $H_A$  will undergo spin-spin coupling  $H_B$ , but this will be different from the

Coupling of  $H_A$  to  $H_B$ . Because the dihedral angle ( $\Phi$ ) between  $H_A$  &  $H_B$  are different ~~with~~ from the  $\Phi$  of  $H_A$  &  $H_{B'}$ . Here we say that  $H_A$  &  $H_{A'}$  are chemically equivalent but magnetically non-equivalent.

\* Chemical equivalence means simply chemical shift equivalence, and magnetic equivalence means coupling equivalence.



The Labels A, B, c and so on are allocated to each separate group of chemically equivalent nuclei.

If two protons  $H_A$  are magnetically non-equivalent, this is indicated by the use prime (thus  $H_A$  &  $H_{A'}$ )

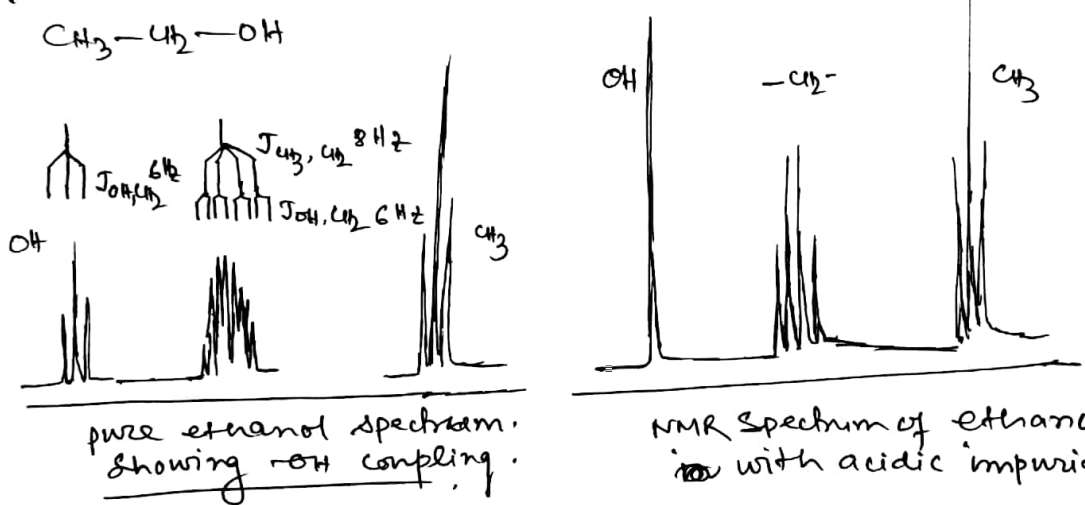
Similarly, protons  $H_B$  &  $H_{B'}$  must be chemically equivalent but magnetically nonequivalent.

Proton-exchange Reaction.

If the  $^1\text{H}$  NMR spectrum of ethanol is recorded on a slightly impure sample and then compare with the spectrum of a high-purity sample, we become faced with another problem.

Earlier we have seen the spectrum of pure ethanol: A triplet is obtained for  $-\text{CH}_3$  gr. because of coupling with  $-\text{CH}_2$ . The  $-\text{OH}$  signal is a triplet because of coupling to  $\text{CH}_2$ . The  $-\text{CH}_2-$  is split into a quartet by  $\text{CH}_3$  gr, and each line further split into two by  $-\text{OH}$  protons. (There are two different coupling constant involved (8 Hz & 6 Hz), so all eight predicted lines are reasonably clear.

⊛ But this OH coupling not observed in the spectrum recorded on the contaminated sample of ethanol - why?



Ans: Exchange of the OH protons among ethanol molecule is normally so rapid that one particular proton does not reside for a sufficiently long time on a particular oxygen atom so that nuclear coupling to be observed.



we know that  $\Delta\nu \approx \frac{1}{2}\pi$ , Here  $\Delta t$  is time needed to resolve accurately the multiplicity in the  $\text{CH}_2$  and  $\text{OH}$  groups brought about by their coupling &  $\Delta\nu$  is the coupling constant. when resident time for a particular proton on oxygen is sufficiently long, we can record coupling. (greater than  $\Delta t$ )

Mitali Dewan/B.Sc Chem(H)/SEM-IV/CC-10/NMR Spectra

If there is rapid proton exchange, the residence time will be shorter than  $\tau_c$  and the coupling will not be resolved. The rate of exchange is related to the coupling constant (6 Hz in this case) and if we are unable to resolve the coupling, the rate of exchange must be greater than  $6 \text{ s}^{-1}$ . This proton exchange phenomenon is acid and base catalyzed and if the samples are acid and base free, the residence time will be sufficiently long for the coupling to be observed between OH and  $\text{CH}_2$ .

⊛ Rapid proton exchange occur in carboxylic acids, phenols, amines, thiols, etc, so that in general no coupling is observable between the protons on these functions and their neighbors.

⊛ In case of alcohols it is relatively easy to see the OH coupling if the sample is pure, or if the spectrum is recorded with a low temperature sample (when the exchange is retarded), or if the sample is dissolved in a highly polar solvent such as DMSO, ( $\text{Me}_2\text{SO}$ ), when strong solvation stabilizes individual alcohol molecules and reduces the exchange.