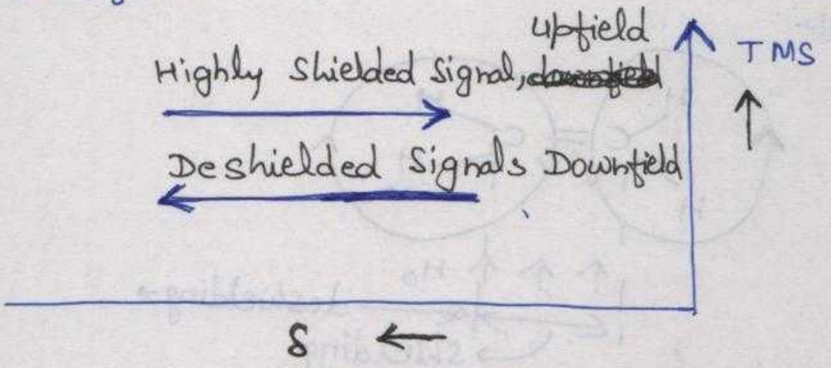
Nuclear Magnetic Resonance :→

- If Induced field opposes the applied field, the proton is said to be shielded. Shielding shifts the absorption upfield and δ value will be lowered.

- If the induced field ~~opposes~~ reinforces the applied field the proton feels a higher field strength and such a proton is said to be deshielded. Deshielding shifts the absorption downfield to get an effective field strength necessary for absorption. Greater the deshielding of protons, larger will be the value of δ.



- Presence of the electronegative atoms or groups cause reduction in electron density around the proton (deshielding) and thus, absorption is shifted downfield (δ increases).

→ It has been found that the absorption depends upon the manner in which the π electrons circulate under the influence of the applied field.

* protons adjacent to $-\overset{+}{N}\leq$ are very strongly deshielded while those near $>\overset{(-)}{C}-$ are powerfully shielded.

various aspects of NMR

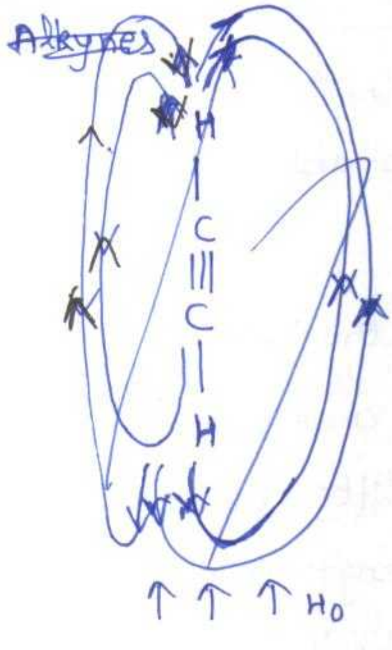
→ a.) No. of signals:- tells how many difft kinds of proton is there

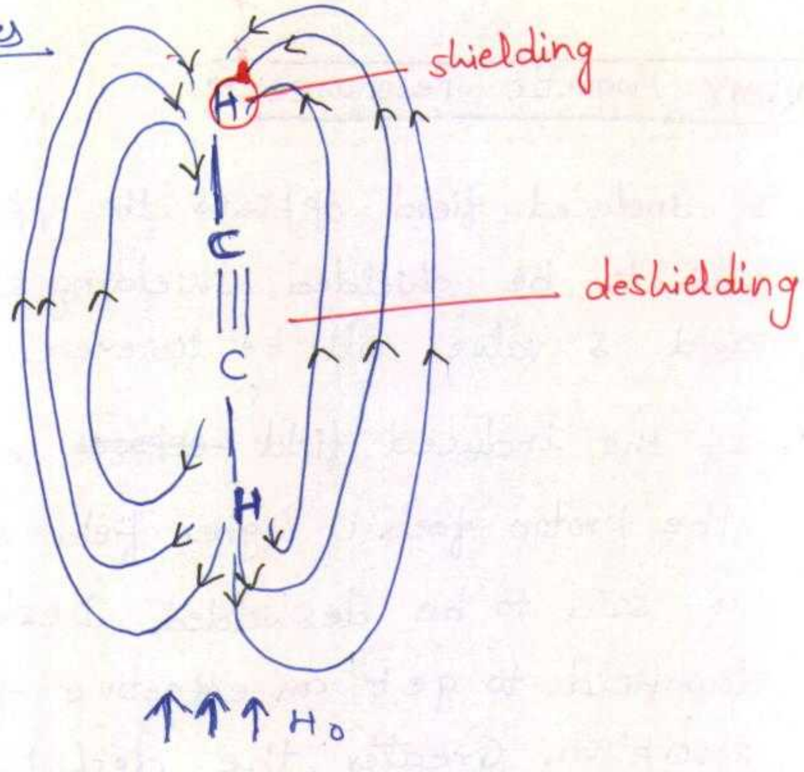
b.) position of signal:- tell us something abt electronic enviroment around each proton

c.) Intensity of signal → no. of protons of each kind

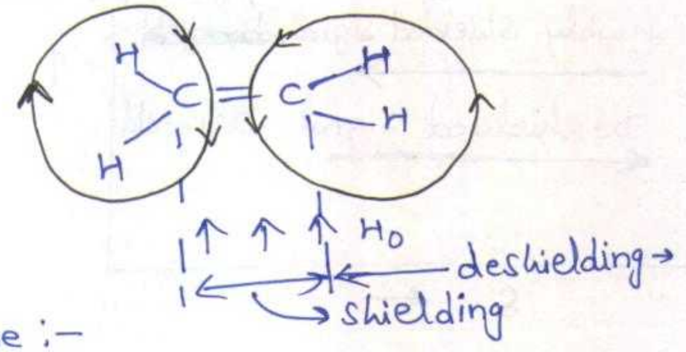
d.) Splitting of signal :- environment of a proton wrt nearby protons

Anisotropic effect:- i) Alkynes

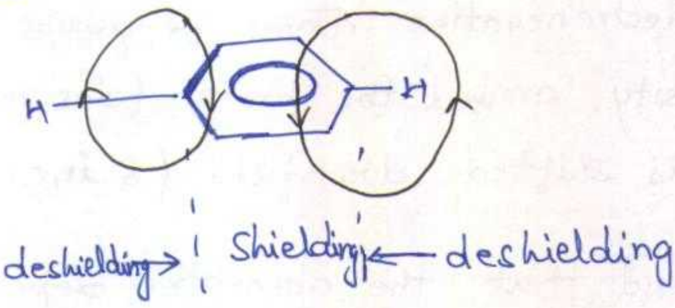




ii) Alkenes:-



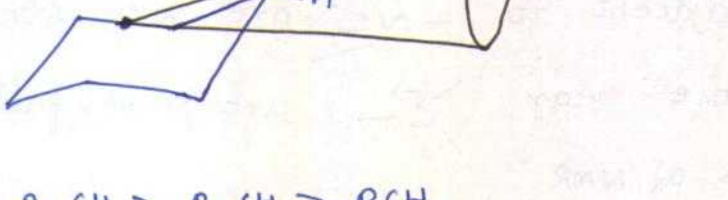
iii) Benzene :-



iv) Six membered ring

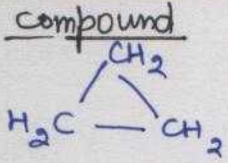
δ equitorial >

δ axial



→ δ values:- $R_3CH > R_2CH > RCH_3$

chemical shift :-

	compound		δ values
i)			0.2
ii)	primary	$R-CH_3$	0.9
iii)	vinylic	$C=C-H$	4.6 – 5.8
iv)	Acetylenic	$C\equiv C-H$	2 – 3.5
v.)	Aromatic	$Ar-H$	6 – 9.0
vi)	**Fluorides**	$H-C-F$	4 – 4.5
vii)	chlorides	$H-C-Cl$	3 – 4
viii)	alcohol	$H-C-OH$	3.4 – 4
ix)	Ethers	$H-C-OR$	3.3 – 4
x.)	Esters	$H-C-COOR$	2 – 2.2
xi)	Acids	$H-C-COOH$	2 – 2.5
xii)	Aldehydes	$RCHO$	9 – 10
xiii)	Hydroxy	$R-OH$	1 – 5.5
xiv)	Phenolic	$Ar-OH$	4 – 12
xv.)	Enolic	$C=C-OH$	15 – 17
xvi)	Carboxylic	$RCOOH$	10.5 – 12

Some points regarding the value of chemical shift

- → δ value for Methine > Methylene > Methyl
- → Greater the electronegativity of substituent, greater is value of δ.
- → Value of δ depends upon the type of hybrid orbital holding proton i.e. $sp^2 > sp > sp^3$.
- → For the aldehydic protons, δ values are 9.2 or above
- → δ value for protons in a cyclic compd is always lower than that of any other proton.
- → The chemical shift of protons in O–H groups and also in $-NH_2$ group depend upon temperature, solvent, conc^{n} and the neighbouring group.
- → The absorption due to $-COOH$ group appears at 10.5–12 δ.
- → If two singlets are observed then there are two kinds of protons and two carbon atoms carrying two sets of protons are not the adjacent carbons.
- → Formation of two triplets must be due to two methylene groups whose protons are in different chemical environments

$$X-CH_2-CH_2-Y$$

Hydrogen Bonding :-

- H-bonding proton being attached to a highly electronegative atom will have smaller electron density around it. Being less shielded, the field felt by such a proton will be more and hence resonance will occur downfield.

  So ~~high~~ hydrogen bonding → more δ value.

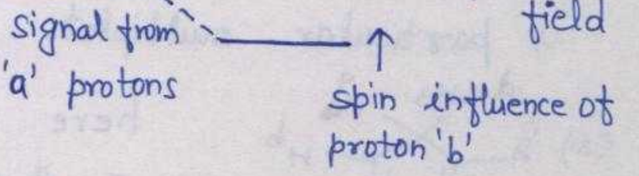
- Intermolecular and intramolecular hydrogen bonding can be easily distinguished

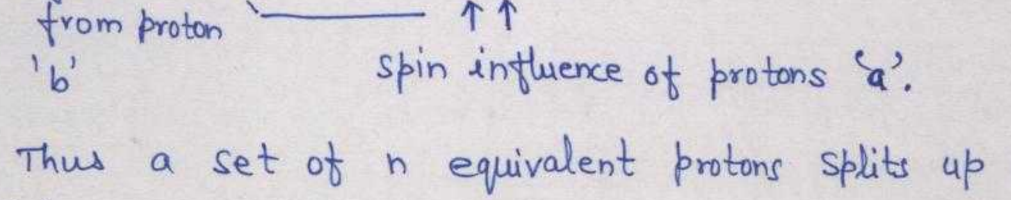
  → Intramolecular H-bonding is conc^n independent whereas Intermolecular H-bonding is conc^n dependent & δ value increases with ↑ in concentration.

Spin-Spin Coupling :-

- Splitting of a signal is due to the different environment of the absorbing proton with respect to the nearby protons.
- The relative intensities of the individual lines of a multiplet correspond to the ~~numbe~~ numerical coefficient of the lines of the binomial expansion of $(1+x)^n$.

For ex:- $Cl\overset{a}{C}H_2\overset{b}{C}HCl_2$



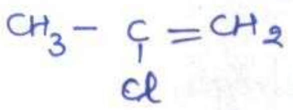


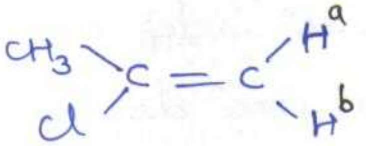
- Thus a set of n equivalent protons splits up a signal (due to neighbouring group) into a group of (n+1) peaks multiplet.

- It is important to remember that no splitting is caused if

i) all the protons in a molecule are equivalent. for ex. benzene, cyclobutane.

ii) a set of equivalent protons do not have another set of protons attached with the adjacent carbon atom. For ex: $CH_3CH_2COCH_3$.

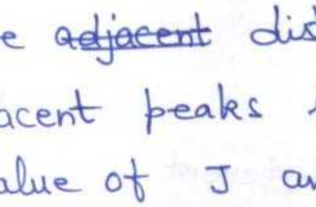
Ex.) 
$CH_3-\underset{Cl}{C}=CH_2$ here one will get 3 signals, which corresponds to three non-equivalent protons as follows



here H^a and H^b also cause splitting of signals and each appears as doublet.

- The ~~adjacent~~ distance between the centres of two adjacent peaks in a particular multiplet is shown by the value of J and is called Coupling Constant.
  → separation of peaks in a triplet is exactly the same as that observed in the doublet.

Some times the heights of the peaks in a particular multiplet are not always symmetrical. It is due to th fact that the separation between the two signals is not very large relative to the separation of peaks within a particular multiplet.

- Ex.) 

here H^a is under the influence of 3 sets of protons with different chemical environments.

Chemical Exchange:- (proton exchange)

* If a proton shuttles bet^n two magnetic enviroments at a rate which is much faster in comparison with the nmr transitions times then the resonance observed for that proton will be simply that of the avg effective field in the two environments.

→ pure anhydrous ethanol. CH_3CH_2OH → 3 signals are observed and a triplet will be observed for OH.

→ ethyl alcohol containing water, the OH signal appears as a singlet and its coupling with adjacent $-CH_2-$ does not take place.

→ proton exchange becomes faster as the water content is increased.

→ proton exchange does not occur
i) if sample is pure
ii) if the sample is recorded at a low temperature, and
iii) if the sample is dissolved in a highly polar solvent like dimethyl sulphoxide.

→ a proton undergoing chemical exchange does not show spin-spin coupling

→ Proton exchange also occurs rapidly in some other compds in which hydrogen is attached with nitrogen, sulphur and oxygen (carboxylic acids, thiols, amines etc.) and hence no coupling is observed between the protons of these functional groups with the protons on the adjacent carbon atoms.

Coupling Constant (J)

→ The distance betn the centres of two adjacent peaks in a multiplet is usually constant and is called coupling constant.

→ J is independent of the external field.

→ Unit:- Hz or in cps ; generally betn 0→20 Hz

→ Spectrum of a particular compound at different radio-freq. the separation of two adjacent peaks in a multiplet remains always **constant.**

→ From the value of coupling constant, one can distinguish between the two singlets and one doublet. How?

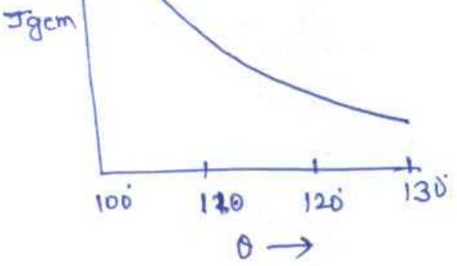
- If the separation betn the lines (ie value of J) does not change while changing the radio-frequencies then the signal is a doublet otherwise it will be two singlets.

→ If a signal is split due to the influence of two different sets of protons (protons with different chemical shifts), then the peak separations in the multiplet observed will not be equidistant.

ex:- $\overset{c}{C}H_3-\overset{b}{C}H_2\overset{a}{C}H_2I$ here $J_{ab}=6.8$ cps, $J_{bc}=7.3$ cps

→ J depends partly on the no. of covalent ~~compounds~~ bonds through which protons may interact and also upon the structural relationships between the coupled protons.

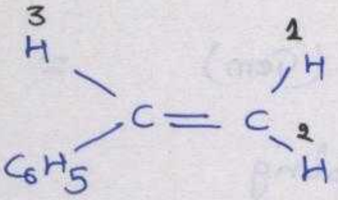
i) <u>Geminal Coupling</u>:- • protons attached on the same carbon having different chemical environment, of a saturated compound, the value of J will depend upon the bond angle $\left(-C{<}^{H}_{H}\right)$



- J value increases with increase in bond angle (increases in s- character)
- with ↑ in electronegativity of the atom, ↑ the value of J.
- The value of J decreases if an electronegative substituent withdraws electrons from the π-bonds.

- Geminal coupling constants for olefins, are quite small.
- For mono-substituted olefins $\boxed{J_{trans} > J_{cis} > J_{gem}.}$
- For isomeric olefins, it is found that J for gem cis protons is two-third of the value of gem trans protons.

For ex:-



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

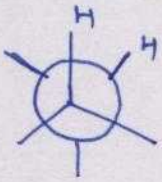
$J_{trans}(H^2, H^3) = 17.4$ cps

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

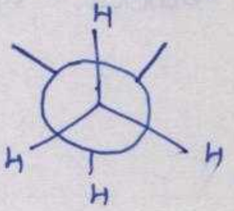
ii) Vicinal Coupling :-

- J varies with the dihedral angle.
- max J value, when dihedral angle is 0° or 180°
  min J value [slightly (−)ve] when dihedral angle is 90°.
- J value for gauche-protons

J varies from 0–4 cps



J value for anti-protons varies from 5–12 cps

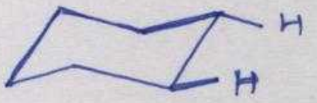


- Cyclopentanes :- Here dihedral angle in cis protons is zero so J value ≈ 8 cps
  In case of trans, dihedral angle is 90°
  so J value ≃ 0

- Cyclohexanes :- From the value of the J, it is possible to determine the configuration of a particular system.

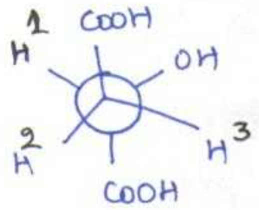
For axial-axial
dihedral angle ≃ 180°
J ≃ 8 cps

axial-equitorial interaction
dihedral angle = 60°
J ≃ 2 cps



equitorial-equitorial
dihedral angle = 60°
J ≈ 2 cps

Ex.)



J values for various types of interacting nuclei

$J(H^1, H^2)$ (vicinal gauche) = 4.4 cps

$J(H^1, H^3)$ (Vicinal – anti) = 7.1 cps

$J(H^2, H^3)$ (Gem) = 17.0 cps

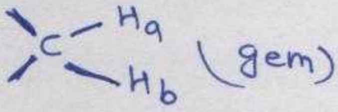
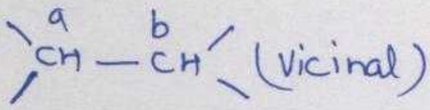
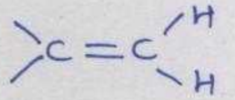
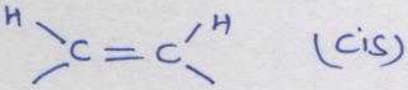
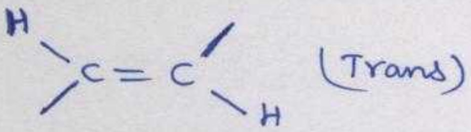
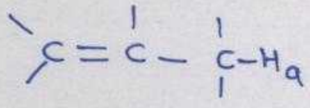
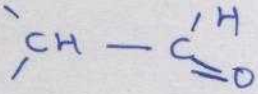
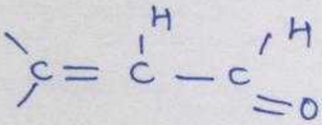
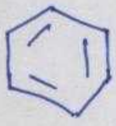
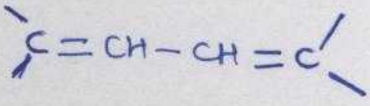
→ Important points for vicinal coupling

- J is always positive
- In olefinic compds J_{trans} is more than J_{cis}

iii) Long range coupling:-

- no coupling if distance betⁿ two absorbing nuclei is more than three covalent bonds.
- But in unsaturated and fluoro compounds, appreciable coupling is observed even if concerned nuclei are three bonds apart.

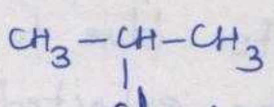
Coupling Constant due to geminal and vicinal groups

Function	J value (in cps)	
 (gem)	0-25	depending upon the electronegativity of the attached groups
 (vicinal)	2-9	depends upon dihedral angle.
	0.5-3.0	
 (cis)	7-12	
 (Trans)	13-18	
	4-10	
$H-C\equiv C-H$	9.1	
	1-3	
	6-8	
	i) ortho = 6-9 ii) meta = 1-3 iii) para = 0-1	
	9-13	

Applications of NMR Spectroscopy

i) Identification of structural isomers :-

$CH_3CH_2CH_2Cl$
(3 signals)



$CH_3-CH(Cl)-CH_3$
(2 signals)

ii) Detection of H-bonding :-

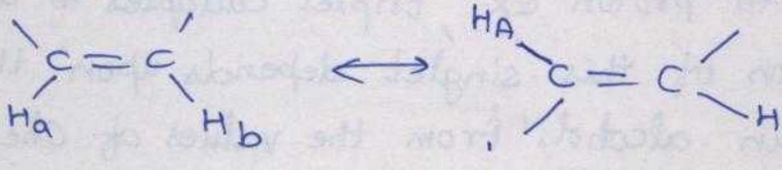
- Intermolecular hydrogen bonding shifts the absorption for a concerned proton downfield. The extent of hydrogen bonding varies as → solvent
  → conc^n of sol^n
  → temperature
- Intramolecular H-bonding is conc^n independent.

iii) Detection of aromaticity :→

- aromatic character of the compd can be investigated.

iv) Detection bet^h Cis-Trans isomers & Conformers :-

- The cis and trans isomers of a compd can be easily distinguished as the concerned protons having different chemical shifts as well as the coupling constants.



(cis) (trans)

$J_{cis} = 7\text{–}12$ cps

$J_{trans} = 13\text{–}18$ cps

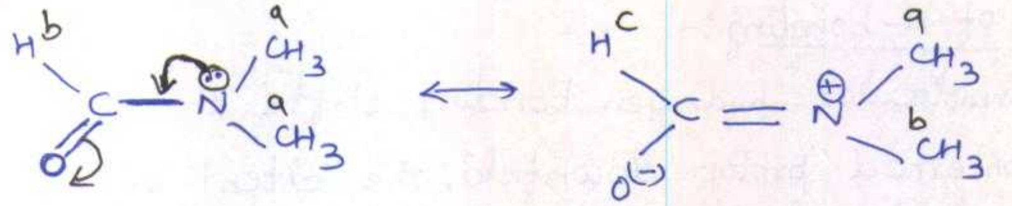
- Similarily, the various conformations of a compound, the axial and equitorial positions can be distinguished from their different values of the coupling constants.

v.) Detection of electronegative atom or group :-

presence of an electronegative atom causes deshielding and the signal is shifted downfield.

vi) Detection of some double bond character due to resonance:→

- In some compounds, the molecule acquires a little double bond character due to resonance. Due to this, two signals can be expected for apparently equivalent protons.



(two signal)

(three signal)

Here presence of double bond restricts rotation and two methyl groups remain no longer equivalent.

vii) Importance in Qualitative analysis:-

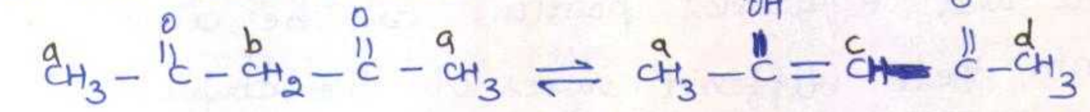
- Equilibrium mixture can be analyzed when the proton signals of the components are well separated.

estimation of water and alcohol in a mixture:→

→ In nmr spectrum of pure ethanol, a triplet is formed for OH proton but when water is added in alcohol then due to proton ex., triplet collapses to a singlet. The position of this singlet depends upon the water content in alcohol. From the values of chemical shift, the ratio of water and alcohol can be estimated by comparing with known results.

viii) Keto-enol Content:- Keto-enol tautomerism can be studied

in the same manner.



$$\overset{a}{CH_3}-\overset{\overset{O}{||}}{C}-\overset{b}{CH_2}-\overset{\overset{O}{||}}{C}-\overset{a}{CH_3} \rightleftharpoons \overset{a}{CH_3}-\overset{\overset{b}{OH}}{C}=\overset{c}{CH}-\overset{\overset{O}{||}}{C}-\overset{d}{CH_3}$$

a = 7.86 τ

b = 6.35 τ

A distinct two proton singlet at 6.35 τ appears due to ketonic form

a = 8.03 τ

b = -4.3 τ

c = 4.4 τ

d = 7.87 τ

all eight protons in the enolic form are observed as four signals.

So no. of enol protons relative to keto protons may give the ratio.

Misc

Deuterium labeling

1.) A particularily elegant way to simplify an NMR spectrum – and one that is easily understood by an organic chemist – is the use of Deuterium labeling.

Because a deutron has a much smaller magnetic moment than a proton, it absorbs at a much higher field and so gives no signal in the proton NMR spectrum. Furthermore, its coupling with a proton is weak and its ordinarily broadens, but does not split, a proton's signal.

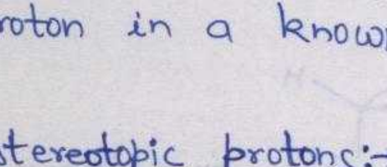
As a result, then, the replacement of a proton by a deutron removes from an NMR spectrum both the signal produced from that proton and the splitting by it of signals of other protons.

CH_3-	CH_2-	;	CH_2D-	CH_2-
Triplet	Quartet		Triplet	Triplet
3H	2H		2H	2H

→ One can use deuterium labeling to find out which signal is produced by which proton or protons: one observes the dissappearance of a particular signal when a proton in a known location is replaced by deuterium.

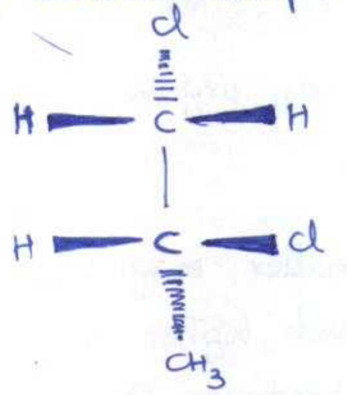
2.) Diastereotopic protons :→ Diastereotopic protons, are non-equivalent and no rotation will change this. Thus diastereotopic will produce different signals.

For ex: –

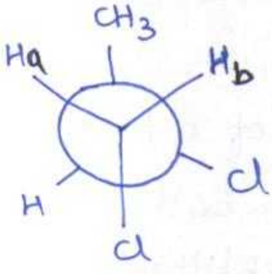


Here 3 signals will be observed.

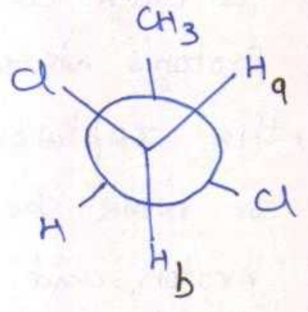
Ex.) The two protons of 1-2, dichloro propane $CH_3CH\,Cl\,CH_2Cl$ are diastereotopic.



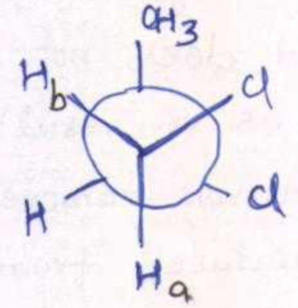
Here rotation can not interconvert the diastereoisomers, nor can it make the protons Ha and Hb equivalent. In none of the conformations (I, II and III) is the environment of the two protons are same.



(I)



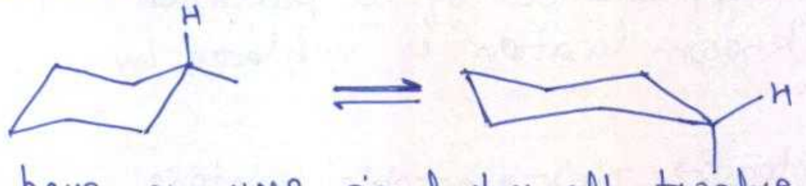
(II)



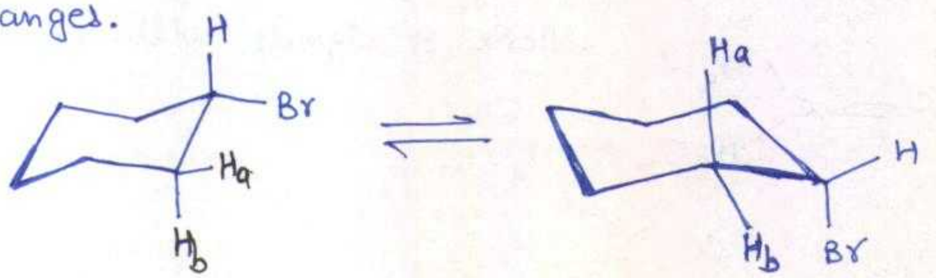
(III)

→ This thing holds good whether the compound is optically active or inactive; the presence or absence of an enatiomeric molecule has no effect on the environment of a proton in any individual molecule.

Ex.) Cyclohexane:→



We have one NMR signal for all twelve, since their avg environments are identical: half equitorial, half axial. However if we replace a proton by, say bromine, the picture changes.



Now the axial and equitorial protons on each carbon are diastereotopic protons.

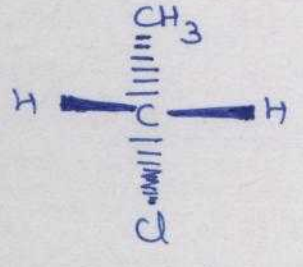
Protons H_a and H_b have different environments. Furthermore the stabilities and hence populations of the two conformations will, in general, be different, and H_a and H_b will spend different fractions of their time in axial and equitorial positions.

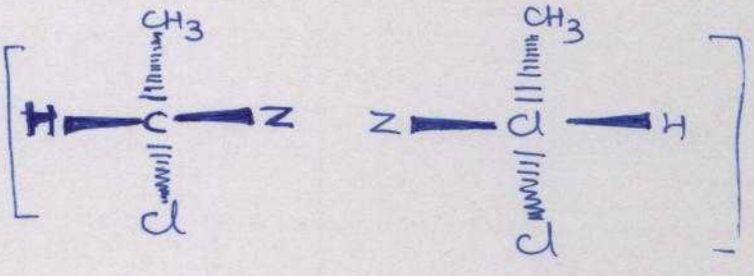
Concept :- By lowering the temperature – we could sufficiently slow down rotations about single bonds, we would expect an NMR spectrum that reflects the instantaneous environments of protons in each conformation.

For ex: If cyclohexane is cooled down, the single sharp peak observed at room temperature is seen to broaden and then, at about −70°c, to split into two peaks, which at −100°c are clearly separated: One peak is due to axial protons and the other peak is due to equitorial protons.

Note :- By study of the broadening of peak, or of the coalescence of the two peaks, it is possible to estimate the Eact for rotation.

3.) Enatiotopic Protons :-





Here replacement of either of two methylene protons would give one of a pair of enatiomers. Such pairs of protons are called enatiotopic protons. The environments of these two protons are mirror images of each other; in an achiral medium, these protons behave as if they were equivalent and we see one NMR signal for each pair.

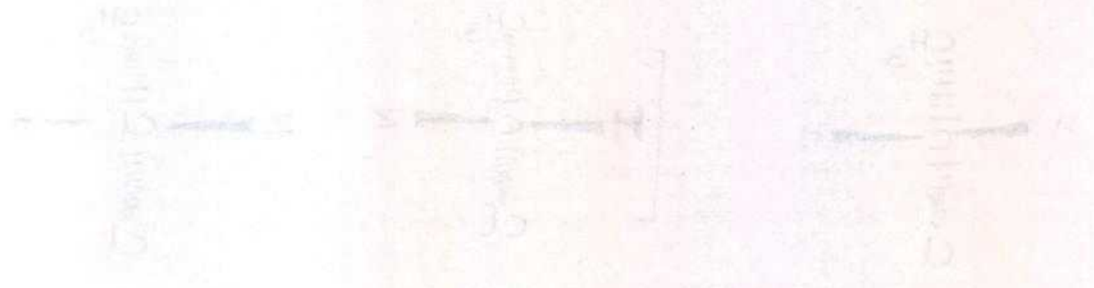
protons H_a and H_b have different chemical
shifted, and hence [illegible] of the
in general, be different and the coupling
fractions of their lifetime in any two

– By lowering the temperature we can
slow down rotations about single bond
expect an NMR spectrum that reflects the
environments of protons in each conformation.

– If a cyclohexane is cooled down, the single
observed at room temperature is seen
and then, at about −70°C, to split into
two – these are clearly separated, one for
axial protons and the other for equatorial
protons.

Note:
By study of the broadening of peaks
and coalescence of the two peaks, it is [illegible]
the Eact for rotation.

Enantiotopic Protons :-

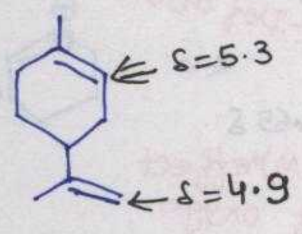


The replacement of either of the methylene
[illegible] give one of a pair of enantiomers. Such
protons are called enantiotopic protons. The environments of
these two protons are mirror images of each
(enantiomeric) these protons are equivalent [illegible] the
[illegible] we see one NMR signal for each pair.

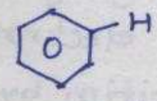
→ The sp^2 carbon of the double bond has high s-character and attracts electrons, there by removing electrons from the vicinity of the hydrogen and deshielding it. Thus the range for position of protons on alkene carbons (vinylic protons) is quite large

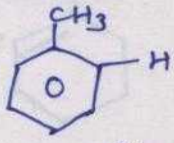
$C{=}C{-}H \qquad \delta = 4.6 - 5.9$

→ Terminal alkene hydrogen appear at higher fields than their internal counter parts.



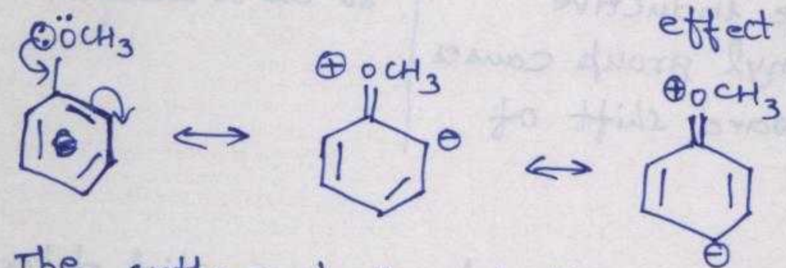
→ Benzene & substituted benzenes:-

 $\delta = 7.37$,



This is so becoz the electronic effect of methyl group is small.

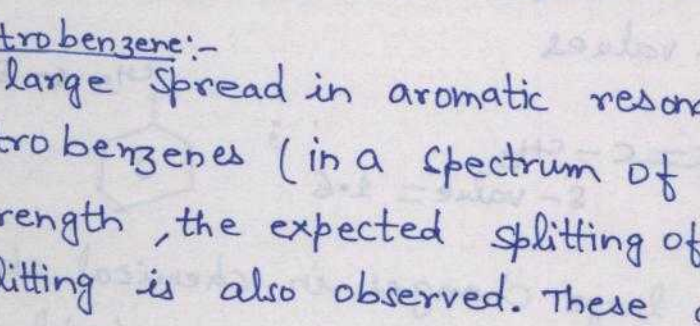
*

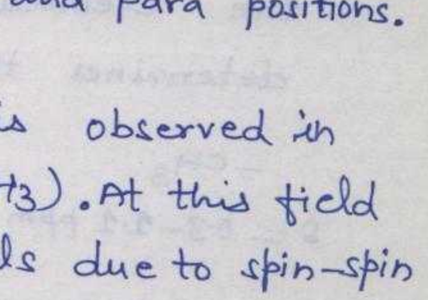


The ortho and para position of anisole are shielded becoz $-OCH_3$ group has (+) M effect at ortho and para positions.

Nitrobenzene:-

* A large spread in aromatic resonance is observed in nitrobenzenes (in a spectrum of 300 MH3). At this field strength, the expected splitting of signals due to spin-spin splitting is also observed. These details are however not clear in case of ^1H NMR at 60 MH3.

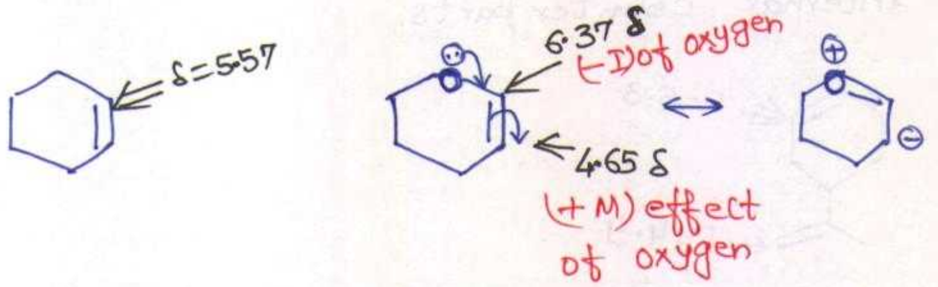




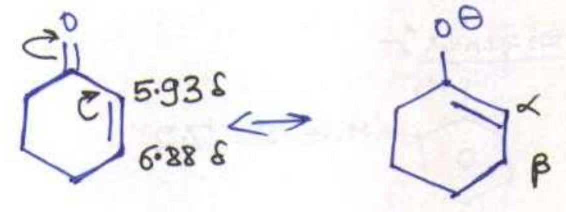
* When a substituent in a monosubstituted benzene is neutral, electronegative or electropositive relative to carbon. the ortho, meta and para hydrogens have significantly difft chemical shifts.

* The alkenic protons of cyclohexene has δ value = 5.57 but it may vary with the substituent in the ring

Ex.)



Ex.)



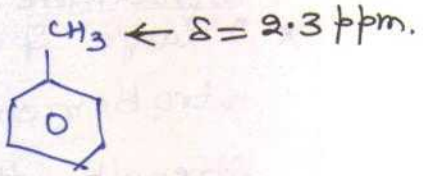
here carbonyl group withdraws electrons from the β-position by resonance so as to deshield this position

In this case the inductive effect of carbonyl group causes at little downward shift of C=O group.

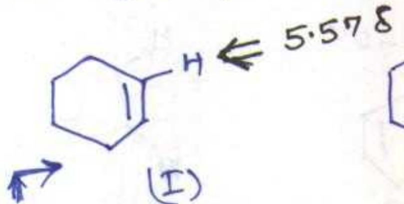
→ The electronic factor is not only factor which determines the chemical shift. These are other factors also which determines the δ-values

$-CH_3$; $-C{=}C-CH_3$;

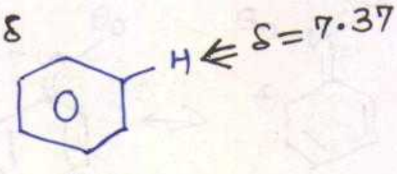
δ = 0.9–1.1 ppm   δ-value = 1.6



* on the other hand large changes in chemical shifts are seen for protons directly attached to double bonds.



(I)



(II)

$H-C{\equiv}C-H \Leftarrow 2.9\ \delta$

(III)

greater s-character in sp^2 orbital and greater electronegativity of sp^2-hybridised carbon may account for the downfield shift of protons in case of (I)

→ The propargylic methyl groups ($-C\equiv C-CH_3$) are found at higher field than the allylic methyl groups.

$-C\equiv C-\underset{\uparrow}{CH_3}$; $-C=C-\underset{\uparrow}{CH_3}$

$\delta = 1\cdot 3$; $\delta = 1\cdot 6$

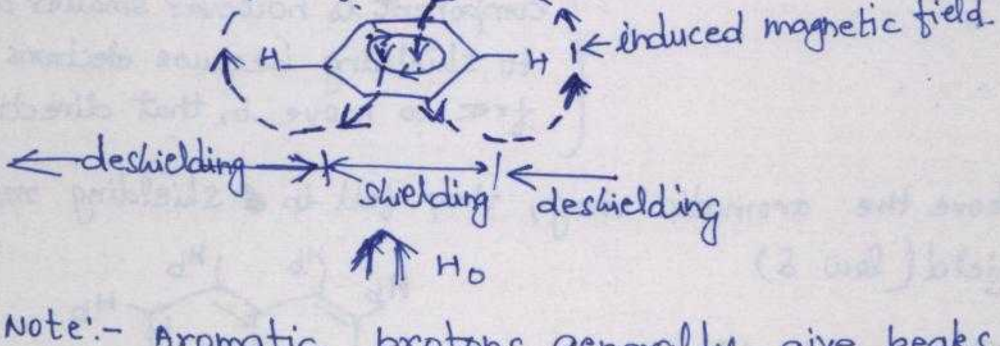
Anisotropic effects:-

- molecular mag. field induced by the action of applied field on pi-electrons.
- magnetic field induced by pi electrons are directional i.e. unsymmetrical.
- Becoz the effects of ~~molef~~ molecular fields induced by pi-electrons are direction dependent, these are, therefore termed anisotropic effects.

* The downward shift of aromatic protons, spectrum of p-xylene, alkenic proton and aldehydic proton all are explained by anisotropic effect.

* Since π-electrons are more polarisable than σ-electrons they are more free to move in response to a magnetic field.

* Aromatic deshielding & shielding



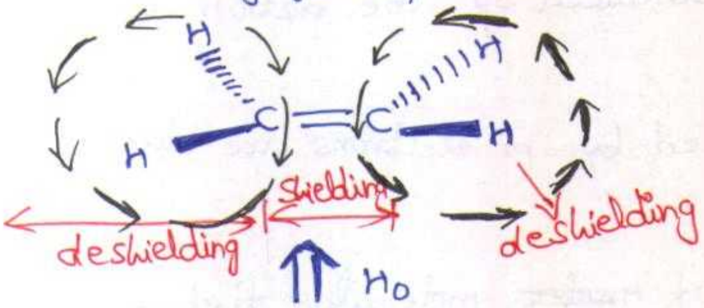
Note:- Aromatic protons generally give peaks at $\delta > 7$ ppm and benzylic methyl groups at $\delta \simeq 2\cdot 4$. These being significantly shifted downfield due to anisotropy of the aromatic ring. The shift of benzylic protons is less than the shift of aromatic protons becoz benzylic protons are further from the aromatic ring than are the protons attached to the ring.

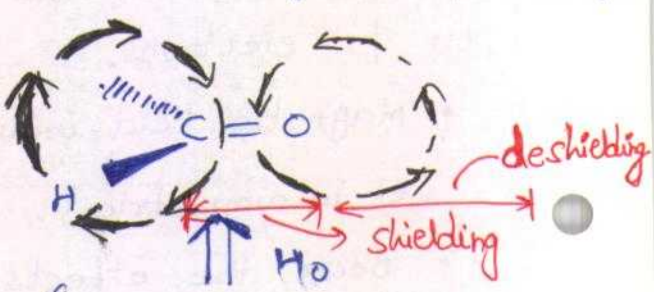
- When aromatic absorptions are farther downfield than those of benzene (δ 7.37) an electron withdrawing substituent may be attached.

→ When upfield of δ 7.37, an electron donating group may be present in the benzene.

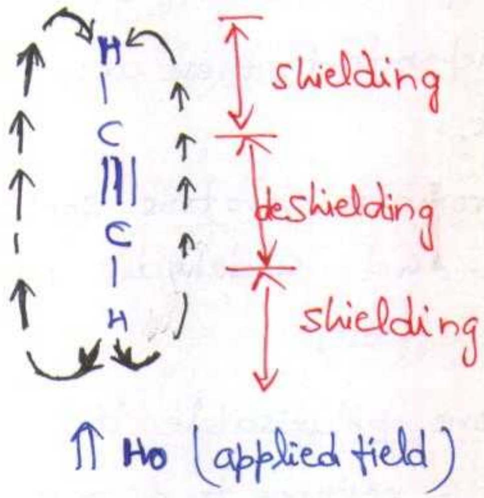
→ induced mag field by alkene

in duced mag field by an aldehyde



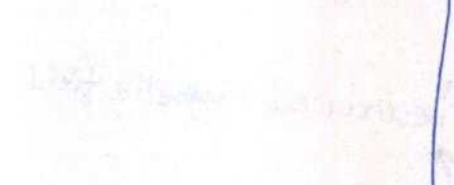


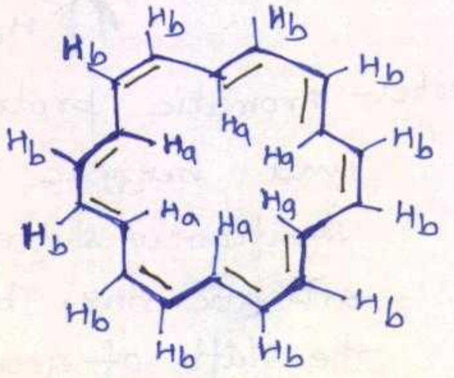
higher deshielding position of aldehyde is due to combination of strong inductive effect and the diamagnetic anisotropy of the carbonyl group.



here π-electrons are most free to circulate around the symmetry axis of the triple bond. When however one considers the molecule aligned ⊥r to the applied fi the acetylenic proton is deshielded as is so in the case of an alkene but deshielding component is however smaller when compared to shielding because electrons are not free to move in that direction.

* If protons above the aromatic ring, they fall in shielding region and so high field (low δ)





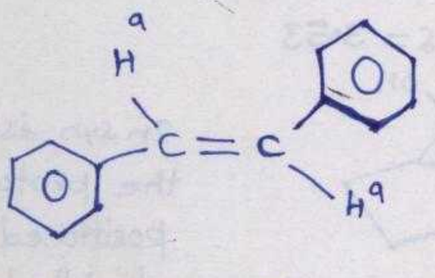
Ha → δ = -1.9
Hb ≃ 8.8 δ

[18] - Annulene

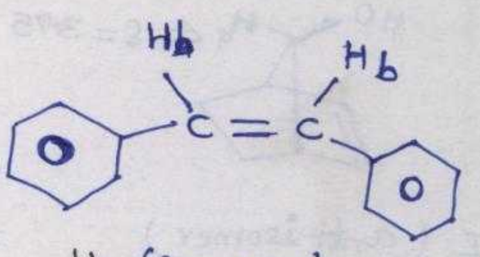
- This information is used in relating chemical shift with relative configuration. The relative stereochemistry of diastereomers can be determined from the chemical shift data.

→ Coplanarity or near coplanarity ~~with~~ of protons with groups like an aromatic ring, a C=C or C=O results in deshielding while protons which lie above these are shielded.

For ex:) Cis and trans-stilbene



Ha (δ = 6·99) (trans)

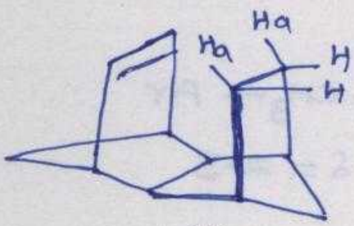


Hb (δ = 6·49) cis

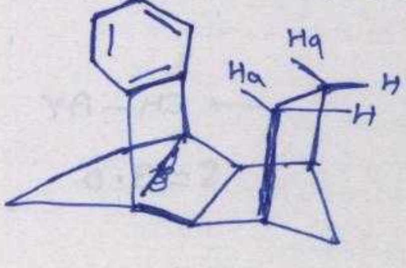
In trans isomer both alkene protons Ha are deshielded by both the aromatic rings

In cis isomers, each of the protons Hb is deshielded by only one adjacent aromatic ring.

→ The shielding and deshielding effects of benzenoid ring currents are more powerful than the π-electrons in alkenic bonds. As a result; protons attached to isolated double bonds are observed to resonate between δ 4.6 and 6.4 ppm and benzenoid protons usually resonate between δ 6.6 and 8.8 ppm.



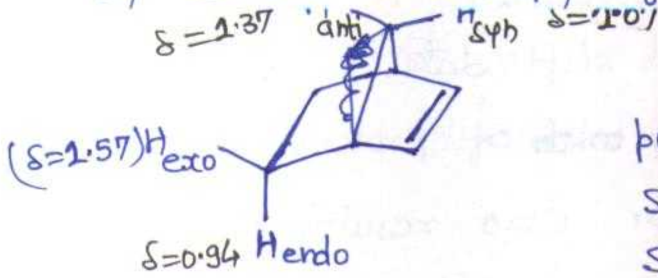
(1)



(2)

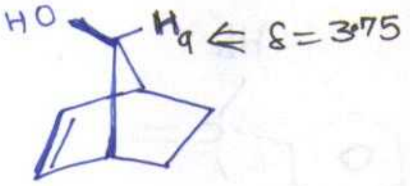
The protons Ha are in the shielding regions of the double bond and the aromatic ring. As the shielding effect of a benzenoid ring is stronger than the alkenic double bond, the protons ~~Ha~~ in 2 resonate at higher ~~[illegible]~~ field (lower δ) than in 1.

→ The position of methylene protons in norbornene can be explained by the anisotropy of double bonds.

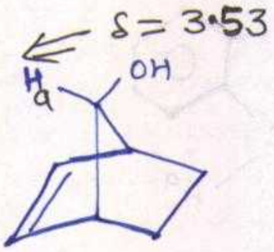


The syn and endo protons are positioned over the double bond (in the shielding region) and are therefore, more shielded than those which are in the plane of the double bond.

- Using this information one can assign stereostructures to compounds (I & II).



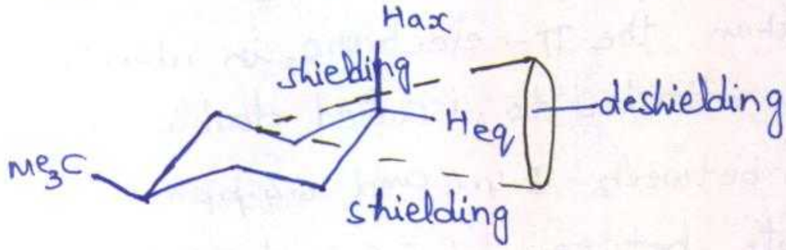
I (anti-isomer)



II (syn isomer)

In syn isomer (II) the proton (Ha) is positioned over the double bond and is thus shielded compared to proton (Ha) in anti compound.

- The anisotropic effect of σ electrons of C-C bond are small compared to the circulating π-electrons and the axis of the C-C bond is the axis of the deshielding cone.



The equitorial proton is always found downfield (by about δ 0.5) than the axial proton on the same carbon atom.

→ $-CH_2Ar$ $\delta_H = 2.7$ $\quad -\overset{|}{C}H-Ar$ $\delta = 3.0$ $\quad -CH_3-Ar$ $\delta = 2.3$

* The protons on cyclopropyl rings are also found at high field (~δ 0·2) due to the cyclopropane ring anisotrophy.

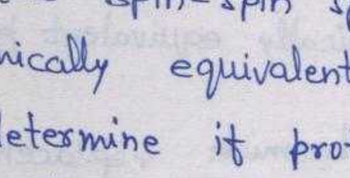
* The chemical shifts of hydrogen bonded protons, i.e. O-H protons in alcohols and N-H protons in amines, depend on concentration. In concentrated solutions these protons are deshielded by hydrogen bonded when these absorb at lower field (δ 3·5 amine N-H, δ 4·5 for an alcohol O-H). When the alcohol or amine is diluted with a non-hydrogen bonding solvent, hydrogen bonding becomes less imp & consequently these resonances are then observed at around δ 2.0.

→ Hydrogen bonding & proton exchange leads to broadening of the signal corresponding to the resonance of a O-H or N-H proton. A broad peak is observed since, protons are exchanging from one molecule to another during PMR resonance.

* The chemically equivalent protons are chemical shift equivalent and the spin-spin splitting is not observed for protons which are chemically equivalent.

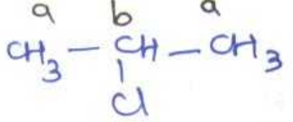
→ To determine it protons are equivalent, one may carryout a simple test. One inspects the structure and mentally replaces each proton by another atom. If the replacement results in only one product (not isomers), the protons are equivalent. If however, the replacement gives isomers, the protons are not equivalent.

→ In vinyl chloride, proton cis to the Cl atom is in a different environment than the trans-proton.



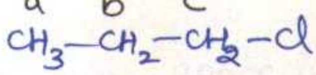
Three protons are non-equivalent so we get three signals.

→ The distinction beth isopropyl chloride and n-propyl chloride can be analyzed. ~~using the test~~



$CH_3-\underset{\displaystyle Cl}{CH}-CH_3$

2-PMR signals
(Iso propyl chloride)



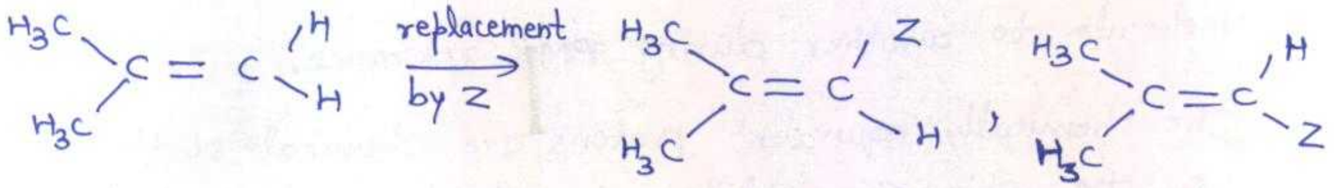
$CH_3-CH_2-CH_2-Cl$

3-PMR signals
(n-propyl chloride)

* Chemical shift Equivalence of Protons replacement test:→

i) Homotopic Hydrogen atoms:- A simple way to decide if or not two or more protons in a given compound are chemical shift equivalent i.e. homotopic is to replace each hydrogen in turn by some other group. ~~the group~~ ~~may~~ If, in making these replacements, one gets the same compound, then the hydrogens being replaced are said to be chemically equivalent or homotopic atoms.

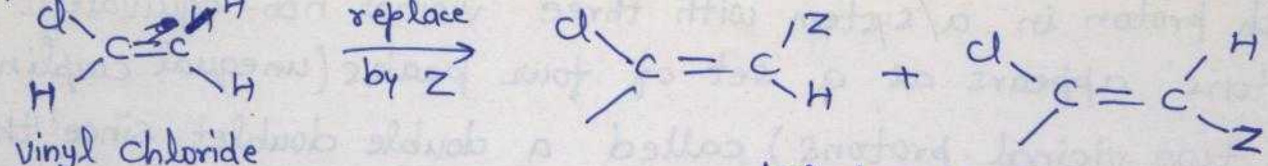
For ex:- In isobutylene (2-methyl propene) two protons are equivalent



(chemically equivalent protons)

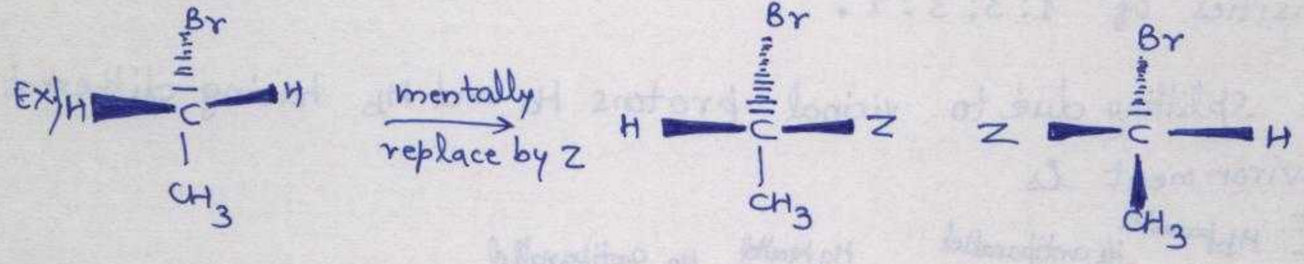
ii) Enantiotopic hydrogen atoms:- In ethyl bromide replacement of either of the two methylene protons by a group Z would afford a pair of enatiomers. These type of pairs of protons are termed enatiotopic protons. These will give only one 1H NMR signal. (Enatiotopic hydrogens may, however, not have the same chemical shift when dissolved in a chiral solvent. Since most 1H NMR spectra are determined using achiral solvents and in these situations enatiotopic protons have same chemical shift).
(see in the next page)

iii) Diastereotopic hydrogen bonding:- When one replaces either vinyl proton by a group Z, one gets compds that are diastereomers. These type of protons are termed "diastereostopic" which have different chemical shifts and give two signals in the 1H NMR spectrum.



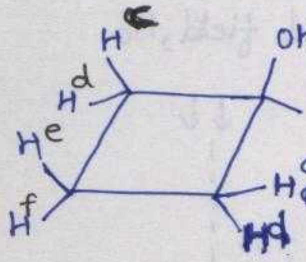
vinyl chloride
three non equivalent protons.

(Diastereomers)



(enatiomers) so only one proton signal.

* Cyclobutanol possesses an internal mirror plane of symmetry.



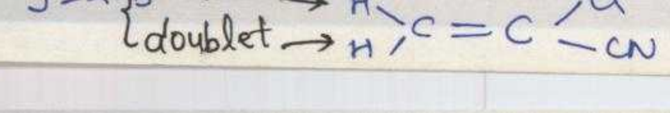
- The hydroxyl proton H^a absorbs betⁿ δ 3-5 depending on solvent & concⁿ.
- proton H^e and H^f are diastereotopic and will give different signals.
- protons H^c are enantiotopic and equivalent & so the protons H^d.

It will show six signals in its 1H NMR spectrum.

→ Not only do ~~diastereotom~~ diastereotopic protons have different chemical shifts but these often have different coupling constants with neighbouring protons and this leads to further complexities in the NMR spectra.

→ Spin- Spin Splitting :→

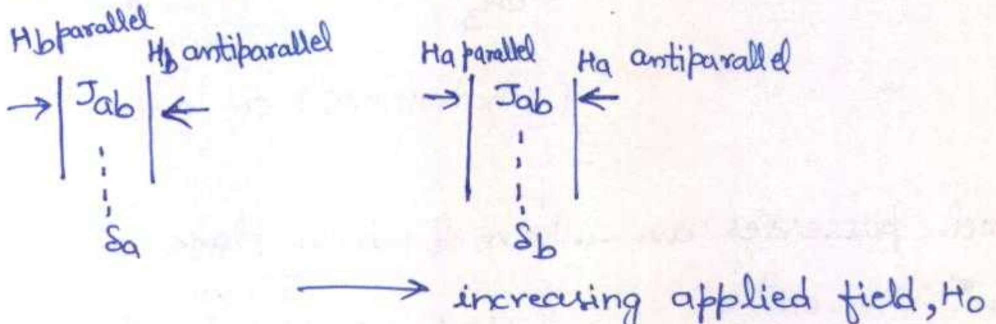
- The first order splitting arises betⁿ protons on adjacent or on the same atoms.
- Splitting occurs only between nuclei with different chemical shifts, that is chemically non-equivalent protons
- The geminal protons can also mutually coupled to give a pair of doublets. The splitting due to geminal coupling occurs only in CH_2 groups provided the two protons are diastereotopic.



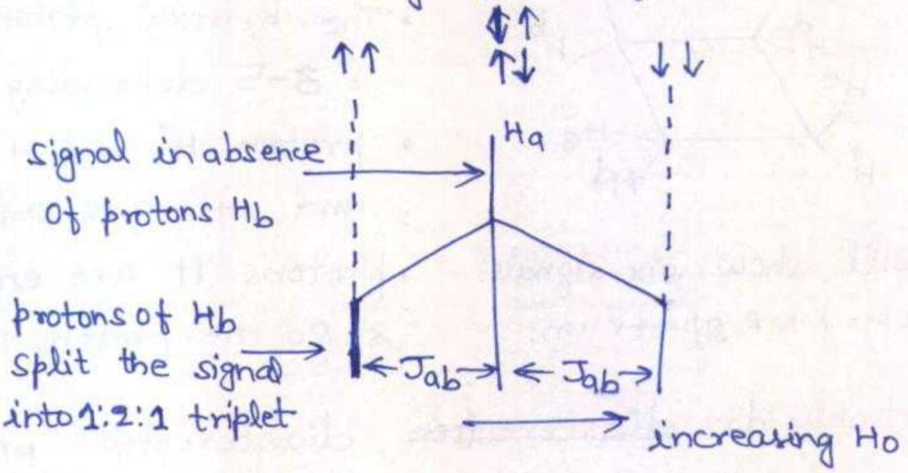
- Each proton in a system with three vicinal non-equivalent protons appears as a set of four peaks (unequal coupling to two vicinal protons) called a double doublet [illegible] four peaks are not evenly spaced and do not have relative intensities of 1:3:3:1.

- The splitting due to vicinal protons Ha and Hb having different environment is

i) doublet



ii) triplet :-



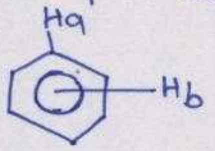
→ Some times the doublets are distorted (i.e. skewed) the intensity ratio of peaks in neither of the doublets is 1:1. The skewing is minimal when chemical shift diff betⁿ two coupled protons is much larger than their coupling constant.

→ Usually the symmetrical nature of the theoretically predicted peak intensities in a multiplet is not observed. The triplet and quartet are not symmetrical and give the apperance of leaning and slanting towards each other. The triplet is slanted in downward direction while the quartet is slanted in the upward direction. These shapes actually offer an advantage as these enable to pick our related multiplets from a complex spectrum.

→ The magnitude of J differs for cis and trans hydrogens. Although the ranges of both sets overlap, for a pair of isomeric cis and trans alkenes J_{trans} is invariably greater than J_{cis}. The difference betn J_{cis} and J_{trans} is an imp tool for distinguishing cis and trans alkenes.

→ In a mono-~~conjugated~~ substituted ethylene $CH_2=CHY$, all three hydrogens are non equivalent. They all split each other to yield a complex multiplet.

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



	J (Hz)
ortho	7–10
meta	2–3
para	0–1

→ For hydrogens to give first order spectra, the difference in Hz in their chemical shifts ($\Delta\delta$) must be at least 10 times greater than their coupling constant i.e. $\Delta\delta > 10 J_{ab}$

- Although the J does not depend on field strength but δ value does. The greater the field strength, the greater the chemical shift diff & thus greater the possibility of obtaining first order spectra.

→ The magnitude of J differs for cis and trans

although the ranges of both overlap, the

and trans isomers. J_{trans} is invariably gre

the difference between J_{cis} and J_{trans} in

coupling is max. trans planar.

→ In a mono-~~substituted~~ substituted phenylene

the hydrogens are non-equivalent, they

yield a complex multiplet.

→ Coupling depends on whether the

ortho, meta or para to each other.

→ For hydrogens to give first order spectra, the

in their chemical shifts ($\Delta\nu$) must at

greater than their coupling constant (J) & C

• Although the J does not depend on the

$\Delta\nu$ value does. The greater the field st

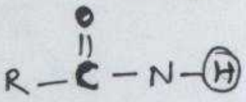
the chemical shift diff. & thus greater

of obtaining first order spectra.

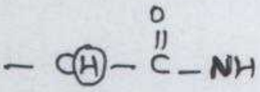
1.) Nitroalkanes — δ-values

$-CH-NO_2$ — 4.1 - 4.3 ppm

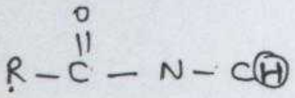
2.) Amides



$R-\overset{O}{\overset{\|}{C}}-N-\textcircled{H}$ — 5.0 - 9.0 ppm

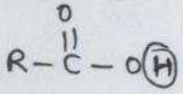


$-C\textcircled{H}-\overset{O}{\overset{\|}{C}}-NH$ — 2.1 - 2.5 ppm



$R-\overset{O}{\overset{\|}{C}}-N-C\textcircled{H}$ — 2.2 - 2.9 ppm

3.) Carboxylic Acid

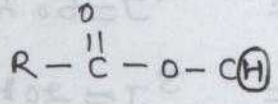


$R-\overset{O}{\overset{\|}{C}}-O\textcircled{H}$ — 11.0 - 12.0 ppm

$-C\textcircled{H}-COOH$ — 2.1 - 2.5 ppm

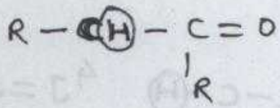
4.) Esters

$R-C\textcircled{H}-COOR$ — 2.1 - 2.5 ppm



$R-\overset{O}{\overset{\|}{C}}-O-C\textcircled{H}$ — 3.5 - 4.8 ppm

5.) Ketones



$R-C\textcircled{H}-\underset{R}{\underset{|}{C}}=O$ — 2.1 - 2.4 ppm

6.) Aldehydes

$R-C\textcircled{H}O$ — 9.0 - 10.0 ppm

$R-C\textcircled{H}-CH=O$ — 2.1 - 2.4 ppm $\quad {}^3J = 1-3\ H_3$

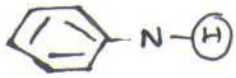
7.) Nitriles

$-C\textcircled{H}-C\equiv N$ — 2.1 - 3.0 ppm

8.) Amines

R−N−Ⓗ 0.5−4.0 ppm

−CⒽ−N− 2.2−2.9 ppm


3.0 − 5.0 ppm

9.) Ethers

R−O−CⒽ− 3.2−3.8 ppm

10.) Alcohols

C−OⒽ 0.5−5.0 ppm

CⒽ−OH 3.2−3.8 ppm

11.) Alkyl Halides

−CH−I 2.0−4.0 ppm

−CH−Br 2.7−4.1 ppm

−CH−Cl 3.1−4.1 ppm

−CH−F 4.2−4.8 ppm

−CH−F $^2J = 50$ Hz

−CH−CF $^3J \simeq 20$ Hz

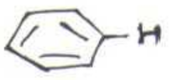
12.) Alkynes

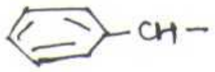
−C≡C−Ⓗ 1.7−2.7 ppm

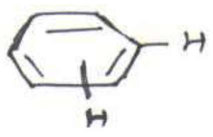
C≡C−CⒽ 1.6−2.6 ppm

Ⓗ−C≡C−C−Ⓗ $^4J = 2\text{-}3$ Hz

13.) Aromatic Compounds


6.5−8.0 ppm


2.3−2.7 ppm



$^3J_{ortho} \simeq$ 7−10 ~~ppm~~ Hz

$^4J_{meta} \simeq$ 2−3 Hz

$^5J_{para} \simeq$ 0−1 Hz

δ-values

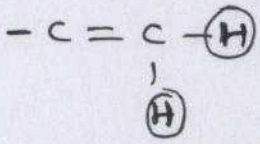
14.) Alkenes

$C=C-\textcircled{H}$ 4.5 – 6.5 ppm

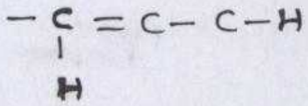
$C=C-C-\textcircled{H}$ 1.6 – 2.6 ppm

$\textcircled{H}-C=C-\textcircled{H}$ $^3J_{trans} = 11-18$ Hz

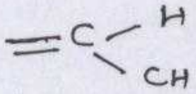
$^3J_{cis} = 6-15$ Hz



$-C=\underset{\textcircled{H}}{C}-\textcircled{H}$ $^2J \approx 0-1$ Hz.



$-\underset{H}{C}=C-C-H$ $^4J \approx 0-3$ Hz



$^3J = 4-10$ Hz

15.) Alkanes

$R-C\textcircled{H}_3$ 0.7 – 1.3 ppm

$R-C\textcircled{H}_2-R$ 1.2 – 1.4 ppm $-C\textcircled{H}-C\textcircled{H}$ $^3J = 7-8$ Hz

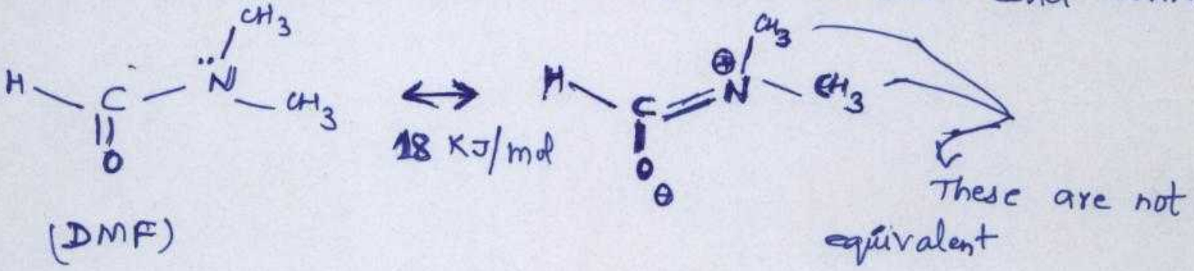
$R_3C\textcircled{H}$ 1.4 – 1.7 ppm

16.)

* protons attached to nitrogen in aliphatic or cyclic amines (0.5- 30)δ
aromatic amines δ 3.0-50

- depends upon → purity, temp, conc^n, nature of solvent
- because of H-bonding
- N-H protons of amides appear as δ 5.0- 8.0 (broad)
- at rapid exchange rates N-H is a sharp singlet.
- N-H proton never appears as multiplet.
- In most aliphatic amines R-NH_2 splitting (coupling due to N-H) is not observed.

* rotation about ~~double~~ single bond with partial double bond character

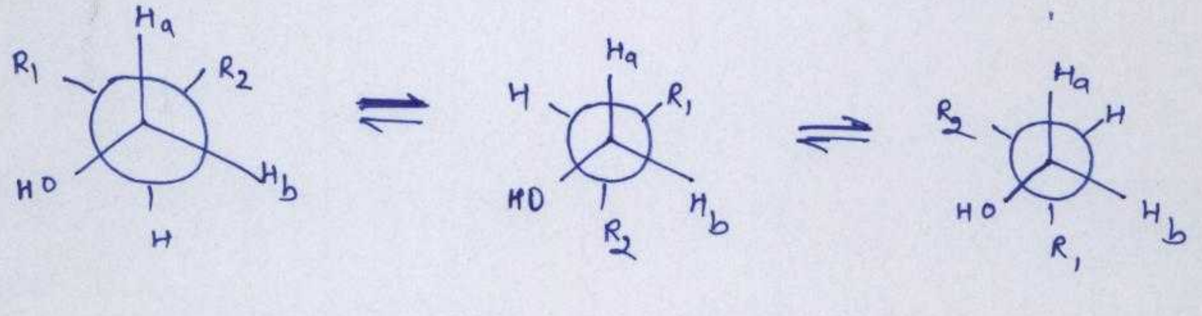


(DMF)

→ at 165°C only one ~~singl~~ signal for all 6- CH_3 hydrogens. due to ↑ rate of rotation.

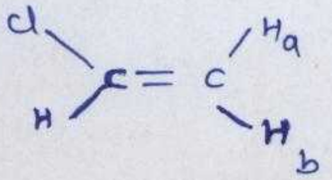
* diastereotopic protons.

a.)



Ha & Hb are diastereotopic
Ha & Hb are magnetically and chemically difft

b.)



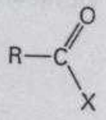
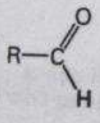
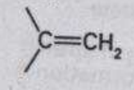
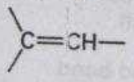
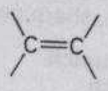
Ha & Hb diastereotopic

* Enantiotopic protons may have difft chemical shifts if the compd is dissolved in an optically active compound. otherwise they can't be distinguished in NMR.

* CX_2WY : the x atoms or groups in CX_2WY will be diastereotopic if either W or Y is chiral.

* protons which can not distinguished in NMR are termed isochronous.

An Alphabetical Listing of Some Functional Groups and Classes of Compounds with Their Absorption Frequencies in the Infrared

Groups or Class	Frequency Ranges (cm^{-1}) and Intensities*	Assignment and Remarks
Acid halides 		
Aliphatic	1810–1790 (s)	C=O stretch; fluorides 50 cm^{-1} higher
	965–920 (m)	C—C stretch
	440–420 (s)	Cl—C=O in-plane deformation
Aromatic	1785–1765 (s)	C=O stretch; also a weaker band (1750–1735 cm^{-1}) due to Fermi resonance
	890–850 (s)	C—C stretch (Ar—C) or C—Cl stretch
Alcohols		
Primary $-CH_2OH$	3640–3630 (s)	OH stretch, dil CCl_4 soln
	1060–1030 (s)	C—OH stretch; lowered by unsaturation
Secondary $-CHROH$	3630–3620 (s)	OH stretch, dil CCl_4 soln
	1120–1080 (s)	C—OH stretch; lower when R is a branched chain or cyclic
Tertiary $-CR_2OH$	3620–3610 (s)	OH stretch, dil CCl_4 soln
	1160–1120 (s)	C—OH stretch; lower when R is branched
General —OH	3350–3250 (s)	OH stretch; broad band in pure solids or liquids
	1440–1260 (m–s, br)	C—OH in-plane bend
	700–600 (m–s, br)	C—OH out-of-plane deformation
Aldehydes 	2830–2810 (m) 2740–2720 (m)	Fermi doublet; CH stretch with overtone of CH bend
	1725–1695 (vs)	C=O stretch; slightly higher in CCl_4 soln
	1440–1320 (s)	H—C=O bend in aliphatic aldehydes
	695–635 (s)	C—C—CHO bend
	565–520 (s)	C—C=O bend
Alkenes		
Monosubst $-CH=CH_2$	—	*See* Vinyl
Disubst $-CH=CH-$	—	*See* Vinylene
	—	*See* Vinylidene
Trisubst 	3050–3000 (w)	CH stretch
	1690–1655 (w–m)	C=C stretch
	850–790 (m)	CH out-of-plane bending
Tetrasubst 	1690–1670 (w)	C=C stretch, may be absent for symmetrical compounds
Alkyl	2980–2850 (m)	CH stretch, several bands
	1470–1450 (m)	CH_2 deformation
	1400–1360 (m)	CH_3 deformation
	740–720 (w)	CH_2 rocking
Alkynes $RC\equiv C-H$	3300–3250 (m–s)	Terminal $\equiv C-H$ stretch
	2250–2100 (w–m)	$C\equiv C$, frequency raised by conjugation
	680–580 (s)	$-C\equiv CH$ bend
Amides		
Primary $-CONH_2$	3540–3520 (m) 3400–3380 (m)	NH_2 stretch (dil solns); bands shift to 3360–3340 and 3200–3180 in solid
	1680–1660 (vs)	C=O stretch (Amide I band)
	1650–1610 (m)	NH_2 deformation; sometimes appears as a shoulder (Amide II band)
	1420–1400 (m–s)	C—N stretch (Amide III band)
Secondary $-CONHR$	3440–3420 (m)	NH stretch (dil soln); shifts to 3300–3280 in pure liquid or solid
	1680–1640 (vs)	C=O stretch (Amide I band)
	1560–1530 (vs)	NH bend (Amide II band)
	1310–1290 (m)	C—N stretch
	710–690 (m)	Assignment uncertain

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*Key: s = strong; m = medium; w = weak; v = very; br = broad.

Continued

TABLE 8-2
An Alphabetical Listing of Some Functional Groups and Classes of Compounds with Their Absorption Frequencies in the Infrared—cont'd

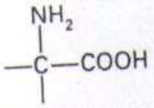
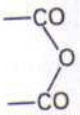
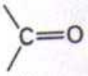
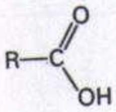
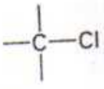
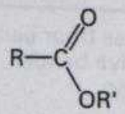
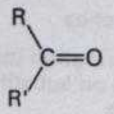
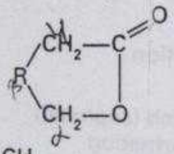
Groups or Class	*Frequency Ranges (cm^{-1}) and Intensities**	*Assignment and Remarks*
Amides—cont'd Tertiary —$CONR_2$	1670–1640 (vs)	C=O stretch
General —$CONR_2$	630–570 (s)	N—C=O bend
	615–535 (s)	C=O out-of-plane bend
	520–430 (m–s)	C—C=O bend
Amines Primary —NH_2	3460–3280 (m)	NH stretch; broad band, may have some structure
	2830–2810 (m)	CH stretch
	1650–1590 (s)	NH_2 deformation
Secondary —NHR	3350–3300 (vw)	NH stretch
	1190–1130 (m)	C—N stretch
	740–700 (m)	NH deformation
	450–400 (w, br)	C—N—C bend
Tertiary —NR_2	510–480 (s)	C—N—C bend
Amine hydrohalides $RNH_3^+X^-$ $R'\overset{+}{N}H_2R\ X^-$	2800–2300 (m–s)	NH_3^+ stretch, several peaks
	1600–1500 (m)	NH deformation (one or two bands)
Amino acids  $-\overset{NH_2}{\underset{\vert}{\overset{\vert}{C}}}-COOH$	3200–3000 (s)	H-bonded NH_2 and OH stretch; v broad band in solid state
(or $-C\overset{+}{N}H_3COO^-$)	1600–1590 (s)	COO^- antisym stretch
	1550–1480 (m–s)	$-NH_3^+$ deformation
	1425–1390 (w–m)	COO^- sym stretch
	560–500 (s)	COO^- rocking
Ammonium NH_4^+	3350–3050 (vs)	NH stretch; broad band
	1430–1390 (s)	NH_2 deformation; sharp peak
Anhydrides 	1850–1780 (variable)	Antisym C=O stretch
	1770–1710 (m–s)	Sym C=O stretch
	1220–1180 (vs)	C—O—C stretch (higher in cyclic anhydrides)
Aromatic compounds	3100–3000 (m)	CH stretch, several peaks
	2000–1660 (w)	Overtone and combination bands
	1630–1430 (variable)	Aromatic ring stretching (four bands)
Out of plane CH def.	900–650 (s)	Out-of-plane CH deformations (one or two bands depending on substitution)
	580–420 (m–s)	Ring deformations (two bands)
Azides $-\overset{-}{N}=\overset{+}{N}=N$	2160–2080 (s)	N=N=N stretch
Bromo —C—Br	650–500 (m)	C—Br stretch
tert-Butyl $(CH_3)_3C-$	2980–2850 (m)	CH stretch; several bands
	1400–1370 (m) and 1380–1360 (s)	CH_3 deformations
Carbodiimides —N=C=N—	2150–2100 (vs)	N=C=N antisym stretch
Carbonyl 	1870–1650 (vs, br)	C=O stretch
Carboxylic acids 	3550–3500 (s)	OH stretch (monomer, dil soln)
	3300–2400 (s, v br)	H-bonded OH stretch (solid and liquid states)
	1800–1740 (s)	C=O stretch of monomer (dil soln)
	1710–1680 (vs)	C=O stretch of dimer (solid and liquid states)
	960–910 (s)	C—OH deformation
	700–590 (s)	O—C=O bend
	550–465 (s)	C—C=O bend
Chloro  $-\underset{\vert}{\overset{\vert}{C}}-Cl$	850–550 (m)	C—Cl stretch
Cycloalkanes	580–430 (s)	Ring deformation

TABLE 8-2

An Alphabetical Listing of Some Functional Groups and Classes of Compounds with Their Absorption Frequencies in the Infrared—cont'd

Groups or Class	Frequency Ranges (cm^{-1}) and Intensities*	Assignment and Remarks
Diazonium salts $-\overset{+}{N}\equiv N$	2300–2240 (s)	$N\equiv N$ stretch
Esters  $R-C(=O)OR'$	1765–1720 (vs)	$C=O$ stretch
	1290–1180 (vs)	$C-O-C$ antisym stretch
	645–575 (s)	$O-C-O$ bend
Ethers $-C-O-C-$	1280–1220 (s)	$C-O-C$ stretch in alkyl aryl ethers
	1140–1110 (vs)	$C-O-C$ stretch in dialkyl ethers
	1275–1200 (vs)	$C-O-C$ stretch in vinyl ethers
	1250–1170 (s)	$C-O-C$ stretch in cyclic ethers
	1050–1000 (s)	R(alkyl)$-C-O$ stretch in alkyl aryl ethers
Fluoroalkyl $-CF_3$, $-CH_2-$, etc.	1400–1000 (vs)	$C-F$ stretch
Isocyanates $-N=C=O$	2280–2260 (vs)	$N=C=O$ stretch
Isothiocyanates $-N=C=S$	2140–2040 (vs, br)	$C=N=S$ antisym stretch
Ketones  $R(R')C=O$	1725–1705 (vs)	$C=O$ stretch in saturated aliphatic ketones
	1700–1650 (vs)	$C=O$ stretch in aromatic ketones
	1705–1665 (s)	$C=O$ and $C=C$ stretching in α,β-unsaturated ketones
	and 1650–1580 (m)	
Lactones 	1850–1830 (s)	$C=O$ stretch in β-lactones
	1780–1770 (s)	$C=O$ stretch in γ-lactones
	1750–1730 (s)	$C=O$ stretch in δ-lactones
Methyl $-CH_3$	2970–2850 (s)	CH stretch in $C-CH_3$ compounds
	2835–2815 (s)	CH stretch in methyl ethers ($O-CH_3$)
	2820–2780 (s)	CH stretch in $N-CH_3$ compounds
	1470–1440 (m)	CH_3 antisym deformation
	1390–1370 (m–s)	CH_3 sym deformation
Methylene $-CH_2-$	2940–2920 (m) and 2860–2850 (m)	CH stretches in alkanes
	3090–3070 (m) and 3020–2980 (m)	CH stretches in alkenes
	1470–1450 (m)	CH_2 deformation
Naphthalenes	645–615 (m–s) and 545–520 (s)	In-plane ring bending
	490–465 (variable)	Out-of-plane ring bending
Nitriles $-C\equiv N$	2260–2240 (w)	$C\equiv N$ stretch in aliphatic nitriles
	2240–2220 (m)	$C\equiv N$ stretch in aromatic nitriles
	580–530 (m–s)	$C-C-CN$ bend
Nitro $-NO_2$	1570–1550 (vs) and 1380–1360 (vs)	NO_2 stretches in aliphatic nitro compounds
	1480–1460 (vs) and 1360–1320 (vs)	NO_2 stretches in aromatic nitro compounds
	920–830 (m)	$C-N$ stretch
	650–600 (s)	NO_2 bend in aliphatic compounds
	580–520 (m)	NO_2 bend in aromatic compounds
	530–470 (m–s)	NO_2 rocking
Oximes $=NOH$	3600–3590 (vs)	OH stretch (dil soln)
	3260–3240 (vs)	OH stretch (solids)
	1680–1620 (w)	$C=N$ stretch; strong in Raman
Phenols $Ar-OH$	720–600 (s, br)	$O-H$ out-of-plane deformation
	450–375 (w)	$C-OH$ deformation
Phenyl C_6H_5-	3100–3000 (w–m)	CH stretch
	2000–1700 (w)	Four weak bands; overtones and combinations

Continued

TABLE 8-2

An Alphabetical Listing of Some Functional Groups and Classes of Compounds with Their Absorption Frequencies in the Infrared—cont'd

Groups or Class	*Frequency Ranges (cm^{-1}) and Intensities**	*Assignment and Remarks*
Phenyl—cont'd	1625–1430 (m-s)	Aromatic C=C stretches (four bands)
	1250–1025 (m-s)	CH in-plane bending (five bands)
	770–730 (vs)	CH out-of-plane bending
	710–690 (vs)	Ring deformation
	560–420 (m-s)	Ring deformation
Phosphates $(RO)_3P{=}O$		
R = alkyl	1285–1255 (vs)	P=O stretch
	1050–990 (vs)	P—O—C stretch
R = aryl	1315–1290 (vs)	P=O stretch
	1240–1190 (vs)	P—O—C stretch
Phosphines $—PH_2$, —PH	2410–2280 (m)	P—H stretch
	1100–1040 (w-m)	P—H deformation
	700–650 (m-s)	P—C stretch
Pyridyl $—C_5H_4N$	3080–3020 (m)	CH stretch
	1620–1580 (vs)	C—C and C—N stretches
	and 1590–1560 (vs)	
	840–720 (s)	CH out-of-plane deformation (one or two bands, depending on substitution)
	635–605 (m-s)	In-plane ring bending
Silanes $—SiH_3$	2160–2110 (m)	Si—H stretch
$—SiH_2—$	950–800 (s)	Si—H deformation
Silanes (fully substituted)	1280–1250 (m-s)	Si—C stretch
	1110–1050 (vs)	Si—O—C stretch (aliphatic)
	840–800 (m)	Si—O—C deformation
Sulfates $R—O—SO_2—O—R$	1140–1350 (s)	S—O stretches in covalent sulfates
	and 1230–1150 (s)	
$R—O—SO_3^-M^+$ ($M = Na^+, K^+$, etc.)	1260–1210 (vs)	S=O stretches in alkyl sulfate salts
	and 810–770 (s)	C—O—S stretch
Sulfides C—S—	710–570 (m)	C—S stretch
Sulfones $—SO_2—$	1360–1290 (vs)	SO_2 antisym stretch
	1170–1120 (vs)	SO_2 sym stretch
	610–545 (ms)	SO_2 scissor mode
Sulfonic acids $—SO_2OH$	1250–1150 (vs, br)	S=O stretch
Sulfoxides $>S{=}O$	1060–1030 (s, br)	S=O stretch
	610–545 (m-s)	SO_2 scissoring
Thiocyanates —S—C≡N	2175–2160 (m)	C≡N stretch
	650–600 (w)	S—CN stretch
	405–400 (s)	S—C≡N bend
Thiols —S—H	2590–2560 (w)	S—H stretch; strong in Raman
	700–550 (w)	C—S stretch; strong in Raman
Triazines $C_3N_2Y_3$ 1,3,4,5-trisubst	1600–1500 (vs)	Ring stretching
	1380–1350 (vs)	Ring stretching
	820–800 (s)	CH out-of-plane deformation
Vinyl $—CH{=}CH_2$	3095–3080 (m)	$=CH_2$ stretching
	and 3030–2980 (w-m)	=CH stretching
	1850–1800 (w-m)	Overtone of CH_2 out-of-plane wagging
	1645–1615 (m-s)	C=C stretch
	1000–950 (s)	CH out-of-plane deformation
	950–900 (vs)	CH_2 out-of-plane wagging
Vinylene —CH=CH—	3040–3010 (m)	$=CH_2$ stretching
	1665–1635 (w-m)	C=C stretch (cis isomer)
	1675–1665 (w-m)	C=C stretch (trans isomer)
	~~980–955 (s)~~	CH out-of-plane deformation (cis isomer)
	730–665 (s)	CH out-of-plane deformation (trans isomer)
Vinylidene $>C{=}CH_2$	3095–3075 (m)	$=CH_2$ stretching
	1665–1620 (w-m)	C=C stretch
	895–885 (s)	CH_2 out-of-plane wagging

TABLE 8-3

A Numerical Listing of Wavenumber Ranges in Which Some Functional Groups and Classes of Compounds Absorb in the Infrared

*Range (cm^{-1}) and Intensity**	*Group and Class*	*Assignment and Remarks*
3700–3600 (s)	—OH in alcohols and phenols	OH stretch (dil soln)
3520–3320 (m–s)	—NH_2 in aromatic amines, primary amines and amides	NH stretch (dil soln)
3420–3250 (s)	—OH in alcohols and phenols	OH stretch (solids and liquids)
3360–3340 (m)	—NH_2 in primary amides	NH_2 antisym stretch (solids)
3320–3250 (m)	—OH in oximes	O—H stretch
3300–3250 (m–s)	≡CH in acetylenes	≡C—H stretch
3300–3280 (s)	—NH in secondary amides	NH stretch (solids); also in polypeptides and proteins
3200–3180 (s)	—NH_2 in primary amides	NH_2 sym stretch (solids)
3200–3000 (v br)	—NH_3^+ in amino acids	NH_3^+ antisym stretch
3100–2400 (v br)	—OH in carboxylic acids	H-bonded OH stretch
3100–3000 (m)	=CH in aromatic and unsaturated hydrocarbons	=C—H stretch
2990–2850 (m–s)	—CH_3 and —CH_2— in aliphatic compounds	CH antisym and sym stretching
2850–2700 (m)	—CH_3 attached to O or N	CH stretching modes
2750–2650 (w–m)	—CHO in aldehydes	Overtone of CH bending (Fermi resonance)
2750–2350 (br)	—NH_3^+ in amine hydrohalides	NH stretching modes
2720–2560 (m)	—OH in phosphorus oxyacids	Associated OH stretching
2600–2540 (w)	—SH in alkyl mercaptans	S—H stretch; strong in Raman
2410–2280 (m)	—PH in phosphines	P—H stretch; sharp peak
2300–2230 (m)	N≡N in diazonium salts	N≡N stretch, aq soln
2285–2250 (s)	N=C=O in isocyanates	N=C=O antisym stretch
2260–2200 (m–s)	C≡N in nitriles	C≡N stretch
2260–2190 (w–m)	C≡C in alkynes (disubstitution)	C≡C stretch; stong in Raman
2190–2130 (m)	C≡N in thiocyanates	C≡N stretch
2175–2115 (s)	N≡C in isonitriles	N≡C stretch
2160–2080 (m)	N=N=N in azides	N=N=N antisym stretch
2140–2100 (w–m)	C≡C in alkynes (monosubstitution)	C≡C stretch
2000–1650 (w)	Substituted benzene rings	Several bands from overtones and combinations
1980–1950 (s)	C=C=C in allenes	C=C=C antisym stretch
1870–1650 (vs)	C=O in carbonyl compounds	C=O stretch
1870–1830 (s)	C=O in β-lactones	C=O stretch
1870–1790 (vs)	C=O in anhydrides	C=O antisym stretch; part of doublet
1820–1800 (s)	C=O in acid halides	C=O stretch; lower for aromatic acid halides
1780–1760 (s)	C=O in γ-lactones	C=O stretch
1765–1725 (vs)	C=O in anhydrides	C=O sym stretch; part of doublet
1760–1740 (vs)	C=O in α-keto esters	C=O stretch; enol form
1750–1730 (s)	C=O in δ-lactones	C=O stretch
1750–1740 (vs)	C=O in esters	C=O stretch; 20 cm^{-1} lower if unsaturated
1740–1720 (s)	C=O in aldehydes	C=O stretch; 30 cm^{-1} lower if unsaturated
1720–1700 (s)	C=O in ketones	C=O stretch; 20 cm^{-1} lower if unsaturated
1710–1690 (s)	C=O in carboxylic acids	C=O stretch; fairly broad
1690–1640 (s)	C=N in oximes	C=N stretch; also imines
1680–1620 (s)	C=O and NH_2 in primary amides	Two bands from C=O stretch and NH_2 deformation
1680–1635 (s)	C=O in ureas	C=O stretch; broad band
1680–1630 (m–s)	C=C in alkenes, etc.	C=C stretch
1680–1630 (vs)	C=O in secondary amides	C=O stretch (Amide I band)
1670–1640 (s–vs)	C=O in benzophenones	C=O stretch
1670–1650 (vs)	C=O in primary amides	C=O stretch (Amide I band)
1670–1630 (vs)	C=O in tertiary amides	C=O stretch

*KEY: s = strong, m = medium, w = weak, v = very, br = broad.

Continued

TABLE 8-3

A Numerical Listing of Wavenumber Ranges in Which Some Functional Groups and Classes of Compounds Absorb in the Infrared—cont'd

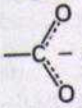
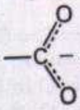
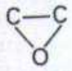
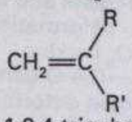
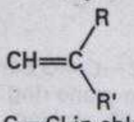
Range (cm^{-1}) *and Intensity**	*Group and Class*	*Assignment and Remarks*
1655–1635 (vs)	C═O in β-ketone esters	C═O stretch; enol form
1650–1620 (w–m)	N—H in primary amides	NH deformation (Amide II band)
1650–1580 (m–s)	NH_2 in primary amines	NH_2 deformation
1640–1580 (s)	NH_3^+ in amino acids	NH_3 deformation
1640–1580 (vs)	C═O in β-diketones	C═O stretch; enol form
1620–1610 (s)	C═C in vinyl ethers	C═C stretch; doublet due to rotational isomerism
1615–1590 (m)	Benzene ring in aromatic compounds	Ring stretch; sharp peak
1615–1565 (s)	Pyridine derivatives	Ring stretch; doublet
1610–1580 (s)	NH_2 in amino acids	NH_2 deformation; broad band
1610–1560 (vs)	COO^- in carboxylic acid salts	 – antisym stretch
1590–1580 (m)	NH_2 primary alkyl amide	NH_2 deformation (Amide II band)
1575–1545 (vs)	NO_2 in aliphatic nitro compounds	NO_2 antisym stretch
1565–1475 (vs)	NH in secondary amides	NH deformation (Amide II band)
1560–1510 (s)	Triazine compounds	Ring stretch; sharp band
1550–1490 (s)	NO_2 in aromatic nitro compounds	NO_2 antisym stretch
1530–1490 (s)	NH_3^+ in amino acids or hydrochlorides	NH_3^+ deformation
1530–1450 (m–s)	N═N—O in azoxy compounds	N═N—O antisym stretch
1515–1485 (m)	Benzene ring in aromatic compounds	Ring stretch, sharp band
1475–1450 (vs)	CH_2 in aliphatic compounds	CH_2 scissors vibration
1465–1440 (vs)	CH_3 in aliphatic compounds	CH_3 antisym deformation
1440–1400 (m)	OH in carboxylic acids	In-plane OH bending
1420–1400 (m)	C—N in primary amides	C—N stretch (Amide III band) ✓
1400–1370 (m)	*tert*-Butyl group	CH_3 deformations (two bands)
1400–1310 (s)	COO^- group in carboxylic acid salts	 – sym stretch; broad band
1390–1360 (vs)	SO_2 in sulfonyl chlorides	SO_2 antisym stretch
1380–1370 (s)	CH_3 in aliphatic compounds	CH_3 sym deformation
1380–1360 (m)	Isopropyl group	CH_3 deformations (two bands)
1375–1350 (s)	NO_2 in aliphatic nitro compounds	NO_2 sym stretch
1360–1335 (vs)	SO_2 in sulfonamides	SO_2 antisym stretch
1360–1320 (vs)	NO_2 in aromatic nitro compounds	NO_2 sym stretch
1350–1280 (m–s)	N═N—O in azoxy compounds	N═N—O sym stretch
1335–1295 (vs)	SO_2 in sulfones	SO_2 antisym stretch
1330–1310 (m–s)	CF_3 attached to a benzene ring	CF_3 antisym stretch
1300–1200 (vs)	$\overset{+}{N}—\overset{-}{O}$ in pyridine *N*-oxides	N—O stretch
1300–1175 (vs)	P═O in phosphorus oxyacids and phosphates	P═O stretch
1300–1000 (vs)	C—F in aliphatic fluoro compounds	C—F stretch
1285–1240 (vs)	Ar—O in alkyl aryl ethers	C—O stretch
1280–1250 (vs)	Si—CH_3 in silanes	CH_3 sym deformation
1280–1240 (m–s)	 in epoxides	C—O stretch
1280–1180 (s)	C—N in aromatic amines	C—N stretch
1280–1150 (vs)	C—O—C in esters, lactones	C—O—C antisym stretch
1255–1240 (m)	*tert*-Butyl in hydrocarbons	Skeletal vibration; second band near 1200 cm^{-1}
1245–1155 (vs)	SO_3H in sulfonic acids	S═O stretch
1240–1070 (s–vs)	C—O—C in ethers	C—O—C stretch; also in esters
1230–1100 (s)	C—C—N in amines	C—C—N bending
1225–1200 (s)	C—O—C in vinyl ethers	C—O—C antisym stretch
1200–1165 (s)	SO_2Cl in sulfonyl chlorides	SO_2 sym stretch
1200–1015 (vs)	C—OH in alcohols	C—O stretch
1170–1145 (s)	SO_2NH_2 in sulfonamides	SO_2 sym stretch
1170–1140 (s)	SO_2— in sulfones	SO_2 sym stretch

TABLE 8-3

A Numerical Listing of Wavenumber Ranges in Which Some Functional Groups and Classes of Compounds Absorb in the Infrared—cont'd

*Range (cm⁻¹) and Intensity**	*Group and Class*	*Assignment and Remarks*
1160–1100 (m)	C═S in thiocarbonyl compounds	C═S stretch; strong in Raman
1150–1070 (vs)	C—O—C in aliphatic ethers	C—O—C antisym stretch
1120–1080 (s)	C—OH in secondary or tertiary alcohols	C—O stretch
1120–1030 (s)	C—NH_2 in primary aliphatic amines	C—N stretch
1100–1000 (vs)	Si—O—Si in siloxanes	Si—O—Si antisym stretch
1080–1040 (s)	SO_3H in sulfonic acids	SO_3 sym stretch
1065–1015 (s)	CH—OH in cyclic alcohols	C—O stretch
1060–1025 (vs)	CH_2—OH in primary alcohols	C—O stretch
1060–1045 (vs)	S═O in alkyl sulfoxides	S═O stretch
1055–915 (vs)	P—O—C in organophosphorus compounds	P—O—C antisym stretch
1030–950 (w)	Carbon ring in cyclic compounds	Ring breathing mode; strong in Raman
1000–950 (s)	CH═CH_2 in vinyl compounds	═CH out-of-plane deformation
980–960 (vs)	CH═CH— in trans disubstituted alkenes	═CH out-of-plane deformation
950–900 (vs)	CH═CH_2 in vinyl compounds	CH_2 out-of-plane wag
900–865 (vs)	 $CH_2{=}C(R)(R')$ in vinylidenes	CH_2 out-of-plane wag
890–805 (vs)	1,2,4-trisubstituted benzenes	CH out-of-plane deformation (two bands)
860–760 (vs, br)	R—NH_2 primary amines	NH_2 wag
860–720 (vs)	Si—C in organosilicon compounds	Si—C stretch
850–830 (vs)	1,3,5-trisubstituted benzenes	CH out-of-plane deformation
850–810 (vs)	Si—CH_3 in silanes	Si—CH_3 rocking
850–790 (m)	 $CH{=}C(R)(R')$ in trisubstituted alkenes	CH out-of-plane deformation
850–550 (m)	C—Cl in chloro compounds	C—Cl stretch
830–810 (vs)	*p*-disubstituted benzenes	CH out-of-plane deformation ✓
825–805 (vs)	1,2,4-trisubstituted benzenes	CH out-of-plane deformation
820–800 (s)	Triazines	CH out-of-plane deformation
815–810 (s)	CH═CH_2 in vinyl ethers	CH_2 out-of-plane wag
810–790 (vs)	1,2,3,4-tetrasubstituted benzenes	CH out-of-plane deformation
800–690 (vs)	*m*-disubstituted benzenes	CH out-of-plane deformation (two bands)
785–680 (vs)	1,2,3-trisubstituted benzenes	CH out-of-plane deformation (two bands)
775–650 (m)	C—S in sulfonyl chlorides	C—S stretch; strong in Raman
770–690 (vs)	Monosubstituted benzenes	CH out-of-plane deformation (two bands)
~~760–740 (s)~~	~~*o*-disubstituted benzenes~~	~~CH out-of-plane deformation~~
760–510 (s)	C—Cl alkyl chlorides	C—Cl stretch
740–720 (w–m)	—$(CH_2)_n$— in hydrocarbons	CH_2 rocking in methylene chains; intensity depends on chain length
730–665 (s)	CH═CH in cis disubstituted alkenes	CH out-of-plane deformation
720–600 (s, br)	Ar—OH in phenols	OH out-of-plane deformation
710–570 (m)	C—S in sulfides	C—S stretch; strong in Raman
700–590 (s)	O—C═O in carboxylic acids	O—C═O bending
695–635 (s)	C—C—CHO in aldehydes	C—C—CHO bending
680–620 (s)	C—OH in alcohols	C—O—H bending
680–580 (s)	C≡C—H in alkynes	C≡C—H bending
650–600 (w)	S—C≡N in thiocyanates	S—C stretch; strong in Raman
650–600 (s)	NO_2 in aliphatic nitro compounds	NO_2 deformation
650–500 (s)	Ar—CF_3 in aromatic trifluoro-methyl compounds	CF_3 deformation (two or three bands)
650–500 (s)	C—Br in bromo compounds	C—Br stretch
645–615 (m–s)	Naphthalenes	In-plane ring deformation
645–575 (s)	O—C—O in esters	O—C—O bend
640–630 (s)	═CH_2 in vinyl compounds	═CH_2 twisting
635–605 (m–s)	Pyridines	In-plane ring deformation
630–570 (s)	N—C═O in amides	N—C═O bend

Continued

TABLE 8-3

A Numerical Listing of Wavenumber Ranges in Which Some Functional Groups and Classes of Compounds Absorb in the Infrared—cont'd

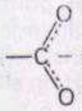
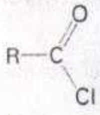
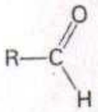
*Range (cm^{-1}) and Intensity**	*Group and Class*	*Assignment and Remarks*
630–565 (s)	C—CO—C in ketones	C—CO—C bend
615–535 (s)	C=O in amides	C=O out-of-plane bend
610–565 (vs)	SO_2 in sulfonyl chlorides	SO_2 deformation
610–545 (m–s)	SO_2 in sulfones	SO_2 scissoring
600–465 (s)	C—I in iodo compounds	C—I stretch
580–530 (m–s)	C—C—CN in nitriles	C—C—CN bend
580–520 (m)	NO_2 in aromatic nitro compounds	NO_2 deformation
580–430 (s)	Ring in cycloalkanes	Ring deformation
580–420 (m–s)	Ring in benzene derivatives	In-plane and out-of-plane ring deformations (two bands)
570–530 (vs)	SO_2 in sulfonyl chlorides	SO_2 rocking
565–520 (s)	C—C=O in aldehydes	C—C=O bend
565–440 (w–m)	C_nH_{2n+1} in alkyl groups	Chain deformation modes (two bands)
560–510 (s)	C—C=O in ketones	C—C=O bend
560–500 (s)	 – in amino acids	 – rocking
555–545 (s)		
=CH_2 in vinyl compounds	=CH_2 twisting	
550–465 (s)	C—C=O in carboxylic acids	C—C=O bend
545–520 (s)	Naphthalenes	In-plane ring deformation
530–470 (m–s)	NO_2 in nitro compounds	NO_2 rocking
520–430 (m–s)	C—O—C in ethers	C—O—C bend
510–400 (s)	C—N—C in amines	C—N—C bend
490–465 (variable)	Naphthalenes	Out-of-plane ring bending
440–420 (s)	Cl—C=O in acid chlorides	Cl—C=O in-plane deformation
405–400 (s)	S—C≡N in thiocyanates	S—C≡N bend

TABLE 8-4

Characteristic Frequencies of Functional Groups in the Raman Spectra of Complex Molecules

Groups or Class	*Frequency Ranges (cm^{-1}) and Intensities**	*Assignment and Remarks*
Acetylenes ≡CH (alkynes) R—C≡C—R	3340–3270 (s) 2300–2190 (s)	CH stretch C≡C stretch in disubstituted acetylenes, sometimes two bands (Fermi doublet)
R—C≡CH	2140–2100 (s) 650–600 (m)	C≡C stretch in monoalkyl acetylenes C—C≡CH deformation
Acid chlorides 	1800–1790 (s)	C=O stretch
Alcohols R—OH	3400–3300 (vw) 1450–1350 (m) 1150–1050 (m–s) 970–800 (s)	OH stretch; broad band OH in-plane bend C—O antisym stretch C—C—O sym stretch
Aldehydes 	1730–1700 (m)	C=O stretch
n-Alkanes (general)	2980–2800 (vs) 1475–1450 (s) 1350–1300 (m–s) 340–230 (s)	CH stretch CH_3 antisym deformation CH_2 bend ---C—C—C— bend

*Key: s = strong; m = medium; w = weak; v = very; br = broad.