B.L.D.E. Association's

S. B. Arts & K.C.P. Science College, VIJAYAPUR- 586 103.

ASSIGNMENT

For B.A./B.Sc. ...II..... Semester

2022 - 2023

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Roll No. 06 R.C.U. Seat No. P15KM22S032020

Subject Spectroscopy -II

Assignment No.	Date	Marks Assigned	Marks Obtained	Name and Signature of Teacher	Remarks
1					
2					
3					
4					

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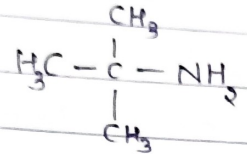
PART - I

1) Define Karmar precissional frequency

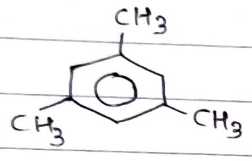
→ The rate of precission of the magnetic moment of the proton around the external magnetic field

2) Write the Number of signal for the following Compound (^{1}H NMR)

i) Tert-butyl amine



ii) Mesitylene



3) What is dihedral angle in NMR spectroscopy? Give one example

The angle between two planes both of which pass through the same bond

ex :- Karplus equation

$$J(\phi) = A\cos^2\phi + B\cos\phi + C$$

PART - II

1) Discuss the factors affecting on chemical shifts

1) Inductive effect :-

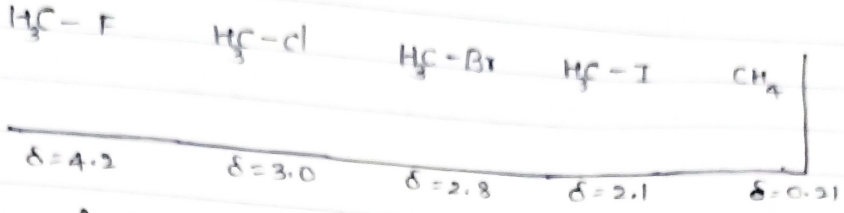
The presence of electronegative atom will leads to dishield the proton. Such that absorption occurs at atom field in the Spectrum greater or More the electronegativity character of atom attached to a any gp or proton. More the deshielding & More the deshielding more the δ value

Consider

H_3C-F, H_3C-Cl, H_3C-Br, H_3C-I, CH_4

In the above compounds F is more electronegative than Cl & Cl > Br > I > H therefore H_3C-F has more value Compound to H_3C-Cl & IIIrd other compound

Since the electronegative atom withdraw the $e^{\ominus}$ & makes the proton from shielded to deshielded Hence less magnetic field strength required for absorption of atom proton



& also, if the distance between electronegative atom & the proton is more than lesser the deshielding occurs. lesser the deshielding. More MF required for absorption of proton.

→ If $e^{\ominus}$ releasing group present more shielding occurs more the shielding, large MF required to resonate the proton or to absorption of proton from α-spin state to β-spin state

2) Vanderwall deshielding

In the above example deshielding occurs more in ② than ① bcz due to the presence of bulky group. Since the bulky group contain more electron i.e it is shielded This group will repel the neighbouring H-atom so H get deshielded by bulky group More the no of bulky group more is the deshielding then δ value shifts to higher value

3 Anisotropic effect:

The deshielding effect on protons attached to C=C is higher than that can be accounted for by the inductive alone. Aldehyde & aromatic pressure are much more deshielded. Alkyne protons appear at relatively low value of δ. The values of δ in each case can be justified by explaining the manner in which the π-electron calculate under the influence of the applied field

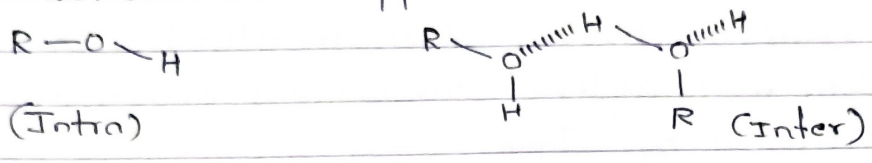
4 Hydrogen bonding:

If the Compounds which contain H-atom Then there may be a formation of H-bonding with more electronegative atom. This $e^{\ominus}$ negative atom will withdrawn the $e^{\ominus}$ from H & H got deshielded & absorption occurs downfield. these are two

types of H-bonding

1) Inter molecular H-bonding
2) Intramolecular H-bonding

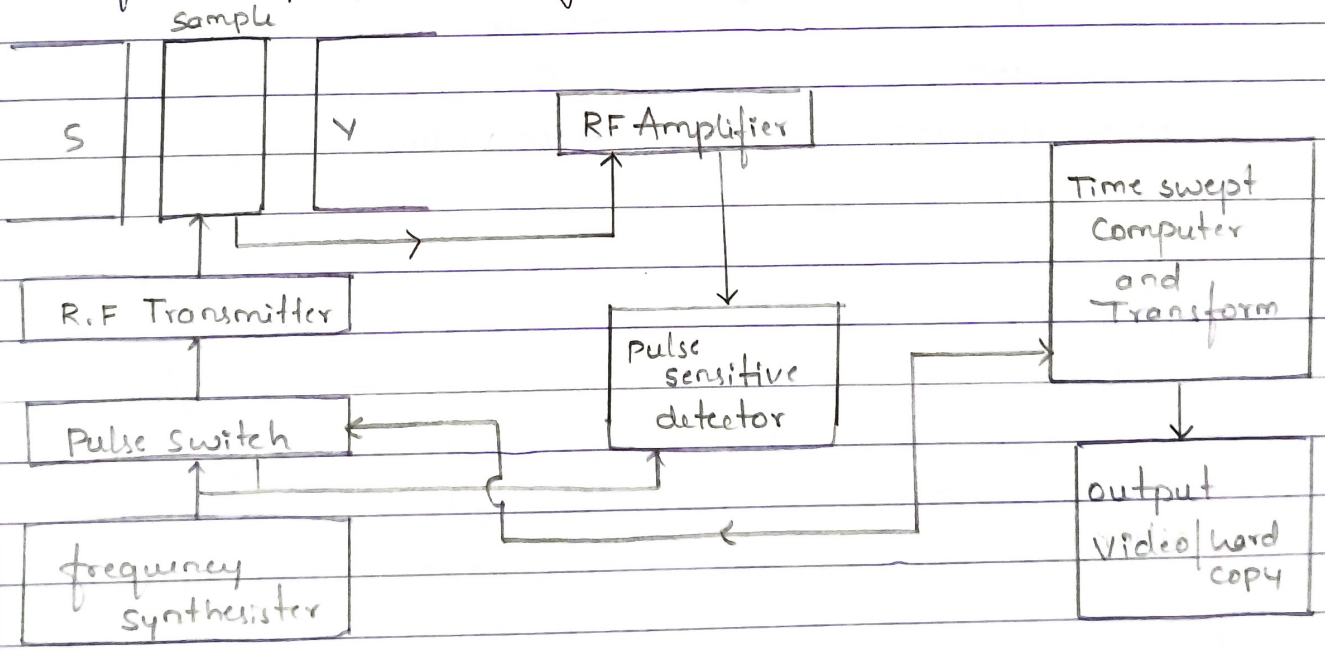
→ More the conc^n of sol^n more the molecules can come in contact with each other & more the hydrogen bonding i.e the proton or H-get deshielded more & chemical shift value is high
→ at less concentration there is no of H bonding
→ Concentrated sol^{n}s absorption is 4-5 ppm & dilute sol^n absorption sol^n between 0.5 - 1.0 ppm



2) Discuss the instrumentation of pulsed FT-NMR spectroscopy

FT-NMR or pulse NMR the sample is irradiated periodically with brief. high intense pulses of radiofrequency radiation following which the free induction decay signal - a characterstic radio frequency emission signal stimulated by the irradiated is recorded as a function of time.

The frequency domain Spectrum Can be obtained by a fourier transform employing a digital Computer.



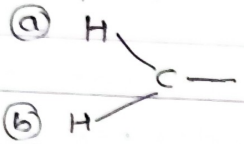
In FT-NMR or pulse-NMR

→ The radio transmitter coil that produces a short powerful pulse of radio waves
→ A powerful magnet that produces strong Magnetic fields magnets.

& probes are similar to those of Continuous wave instruments
→ The Sample is placed in a glass tube that spins so that test material is subjected to uniform magnetic field
→ A radio recieves coil that detects radio frequencies emitted as nuclei relax to a lower energy level
→ A computer that analyses & record the data

3) What are the types of coupling ? discuss their effects on J-value

→ Geminal Coupling :- protons which are attached to same Carbon atom with different environment known as Geminal Coupling denoted by J_{gem}

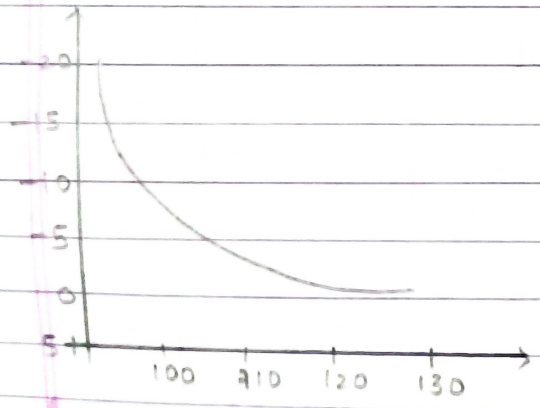


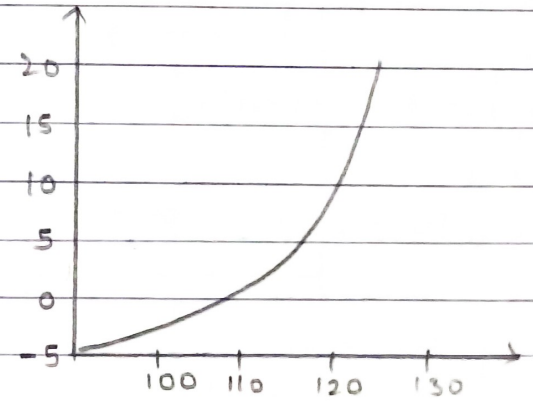
Where @ & ⓑ are geminal protons

Charectristics

* Value of J_{gem} depend upon bond angle between two geminal protons of saturated Compounds

Bond Angle	J_{gem}	
105	-25 Hz	i.e bondangle ∝ J_{gem}
109	-12 Hz	
125	0	
More than 125	+ve values	





→ J_{gem} value also increases with electronegative atom

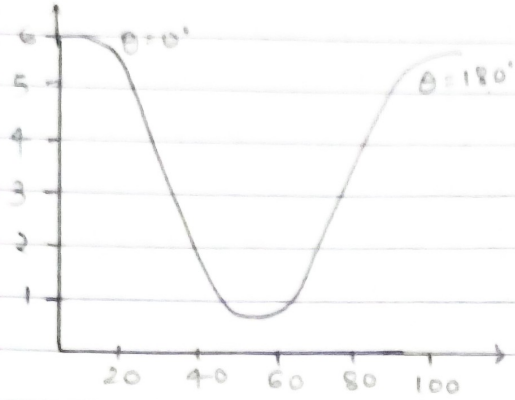
→ Vicinal coupling :-
Protons are separated by 3 -bonds

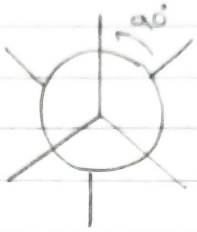
Characteristics

→ Value J Vicinal varies with dihedral angle

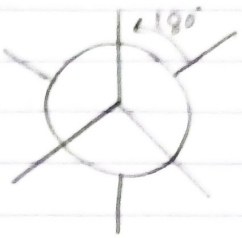
→ when θ is 0° or 180° J value Increases

→ When θ = 90° Then J value is negative





J = 2-4 Hz



J = 5-12 Hz

→ For galic proton the values of J - varies from 2-4 Hz & for anti proton 5-12 Hz

→ J-value can be Calculated by Karplus eq?

$J = 8.5\cos^2\theta - 0.28$ Where $\theta = 0° - 90°$

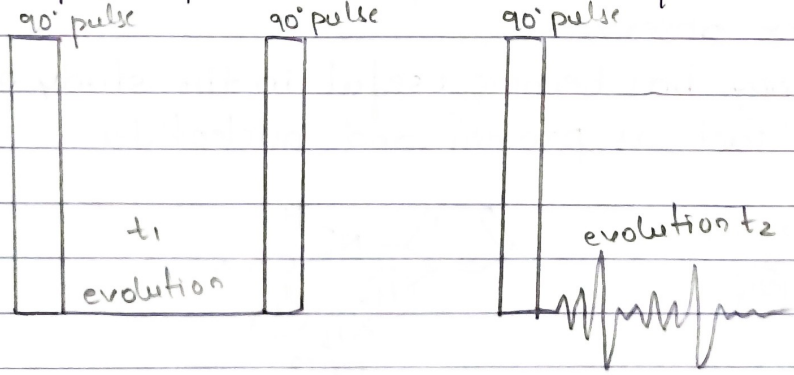
$J = 9.5\cos^2\theta - 0.28$ Where $\theta = 0° - 180°$

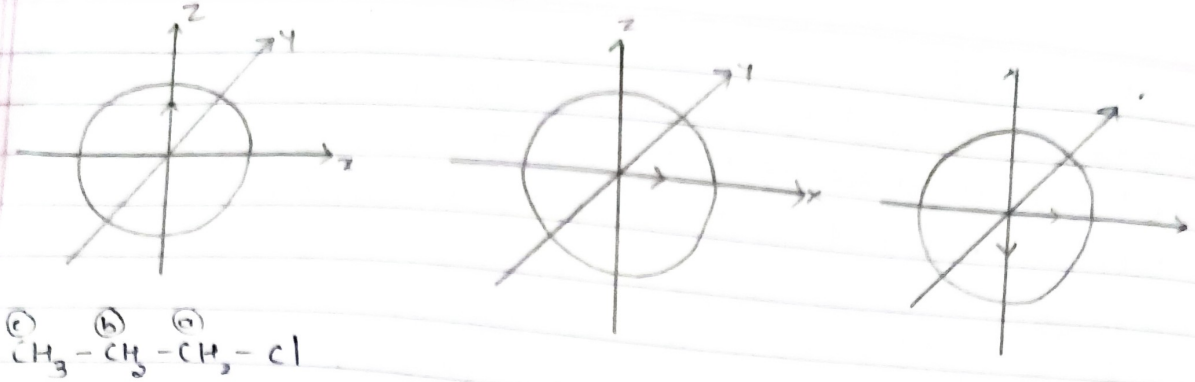
→ Long range Coupling:

If the distance between two protons is more than 3 Co-valent bonds then there is no Coupling. But If the Compound is unsaturated or flouro Compound then Coupling observed with the help of high reduction spectrometer even the protons are Seperated by Three bonds known as long range Coupling & the spectrometer has high resolution

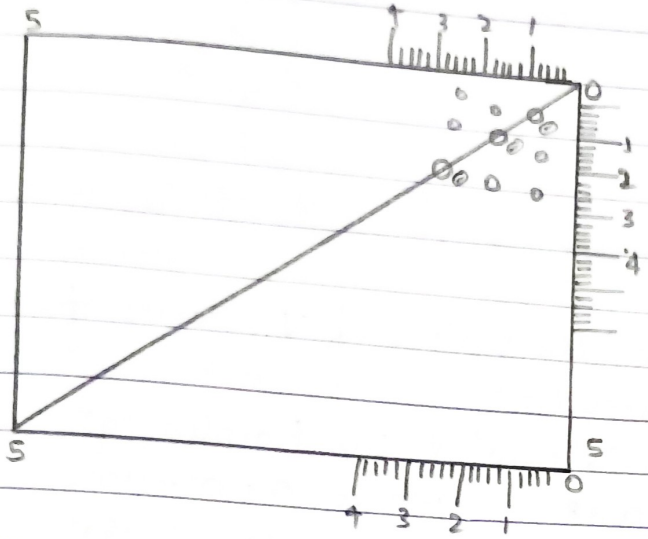
ex:- $CH_3-CH=CH$ (H below CH)

4) Briefly explain on NOESY technique





(a) (b) (c)
$CH_3 - CH_2 - CH_2 - Cl$



A two dimensional NMR experiment that takes advantage of nucleus overhouser effect is known as NOESY

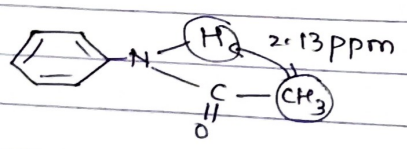
→ Any proton nuclei that means interact with one another through a bipolar relaxation process will appear has cross peaks in a nosey sprectrum

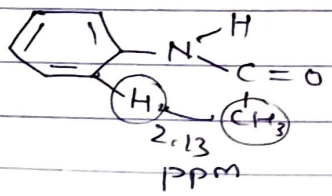
→ This type of interaction includes nuclei that are directly Coupled to one another but not directly Coupled to one another through space or close in space

→ The result is a two dimensional spectrum that looks very much like cosy spectrum but includes besides many of the expected nuclei that interact through space

→ The nuclei must be within 5A° of each other then only interaction to be observed

→ NOESY spectroscopy has become useful in the study of large molecules such as protons and nucleotides



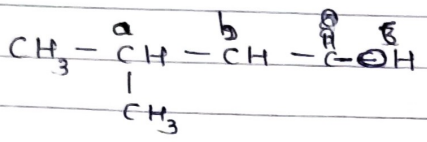


The two Conformations are shown with circle drawn around the protons that are close to each other & could be expected to show nuclear overhouser effect

5) Calculate & draw the number of signals splitting & peak area ratio for the following Compounds:

i) $(CH_3)_2CHCOH$ ii) $CH_3C(H_2)_2CN$

1) $(CH_3)_2CHCOH$



Number of Signals = 3

a) CH = n + 1 = 6 + 1 = 7 Heptate

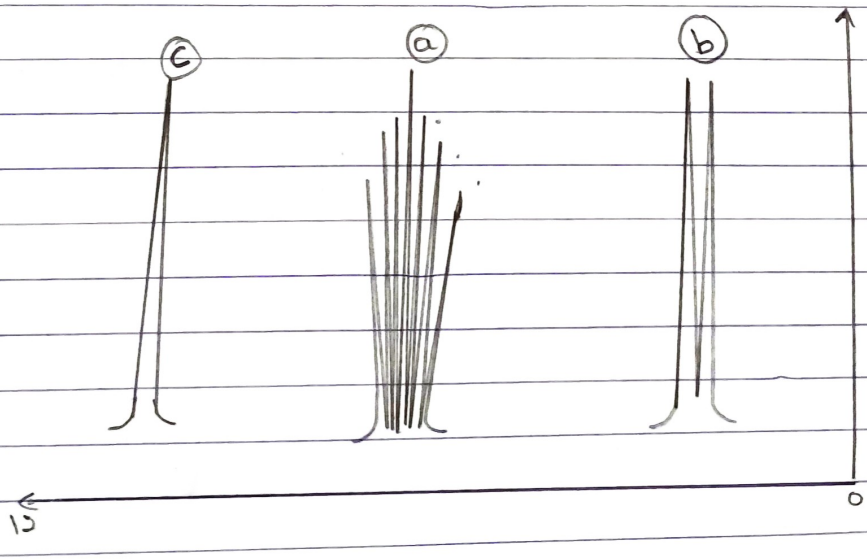
c) −OH = Singlet

b) CH_3 = n + 1 = 1 + 1 = 2 doublet

peak area c) OH = 9.17

a) −CH = 2.39

b) −CH = 1.06



2) $CH_3(CH_2)_2CN$

$\underset{(c)}{CH_3}-\underset{(b)}{CH_2}-\underset{(a)}{CH_2}-CN$

Number of signals - 3

a) CH_2 = 2 + 1 → triplet → 3
b) CH_2 = 5 + 1 → 6 → Sexel
c) CH_3 = 2 + 1 → 3 triplet

peak area (a) CH_2 = 2.07
(b) CH_2 = 1.39
(c) $-CH_3$ = 0.810