Mitali Dewan/B.Sc Chem(H)/SEM-IV/

Number of signals in NMR spectrum.

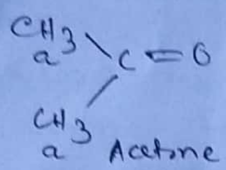
NMR spectroscopy.

- It tells us the number of different sets of equivalent protons.

- Each ~~set~~ signal corresponds to a set of equivalent protons.

- Magnetically equivalent protons are chemically equivalent.

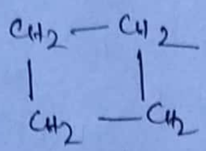
e.g



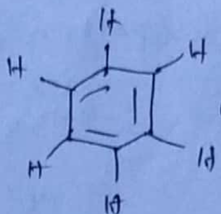
Acetone

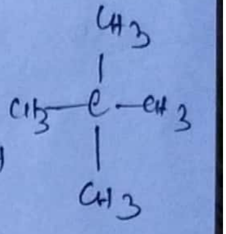
one set of proton

so one signal is observed.



one-signal





one-signal.

- Here all the protons of each compounds are equivalent that means they are in the similar environment.

Therefore one signal is obtained.

- Some compounds showing more than one signal are as follows.

(i) $\underset{ⓑ}{CH_3}-\underset{ⓐ}{OH}$

2. nmr signals (Proton signals) as two types of protons.

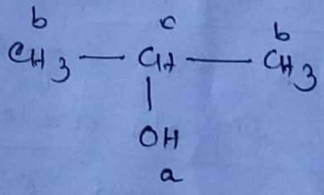
(ii) $\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{NH_2}$

3 nmr signals.

(iii) $\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{CH_2}-Cl$

3 nmr signals.

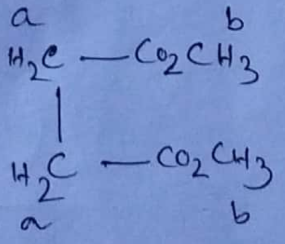
(iv)



$\overset{b}{CH_3}-\underset{\underset{a}{OH}}{\overset{c}{CH}}-\overset{b}{CH_3}$

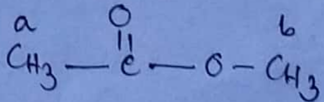
Three nmr signals as three types (a, b & c) of protons.

(v)



(Two signals)

(vi)



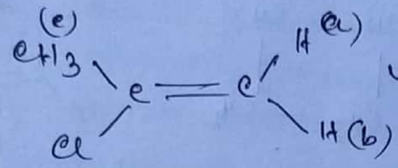
$\overset{a}{CH_3}-\overset{O}{\overset{\|}{C}}-O-\overset{b}{CH_3}$

Methyl acetate

(Two signals)

⊛ chemically equivalent protons must also be stereo-chemically equivalent.

∴ Stereochemical formula of the molecule under consideration is written. eg. (i) $CH_3-C(Cl)=CH_2$ → Two sets of protons is expected, but if we draw steriochemical formula

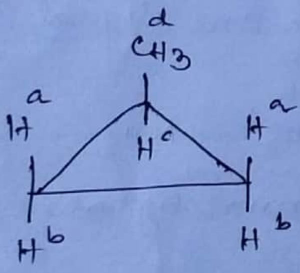


we can see that there are three sets of protons. (a, b & c) so three signals.

Here ~~Ha~~ H^a and H^b are not in exactly similar environment.

(ii) methyl cyclopropane: How many sets of proton & how many nmr signal is obtained.

Ans: we have to draw stereochemical formula also

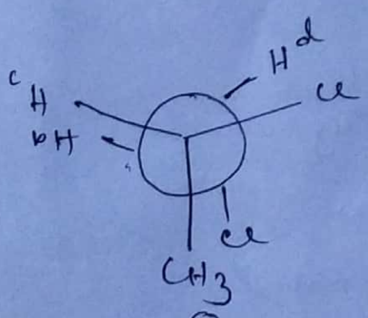


four sets of ~~sigma~~ protons so four signals (Proton nmr signal).

(iii) 1, 2 dichloropropane: $\overset{3}{C}H_3-\overset{2}{C}H(Cl)-\overset{1}{C}H_2Cl$

Here we can expect three types of protons. But four signals are obtained

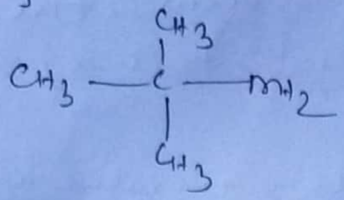
Here rotation around C—C single bond in this molecule can not bring similar environment for the said hydrogen.



ⓐ

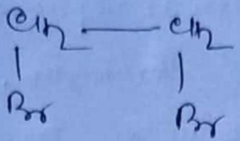
How many number of nmr signals for the following compounds:

(i)



$CH_3-C(CH_3)_2-NH_2$

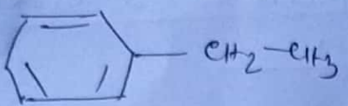
(ii)



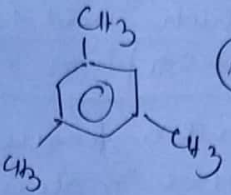
$CH_2(Br)-CH_2(Br)$

(iii) CH_3CHBr_2

(iv)



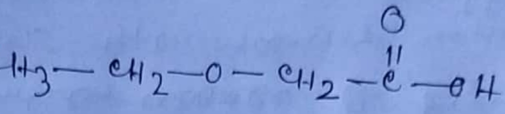
(v)



(vi) $CH_3-CH_2-O-CH_2CH_3$

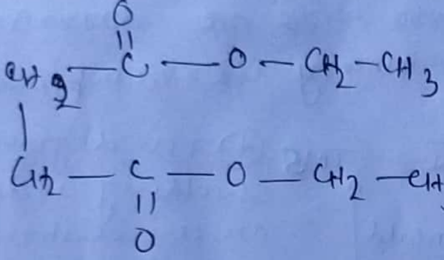
(vii) CH_3-CH_2CHO

(viii)



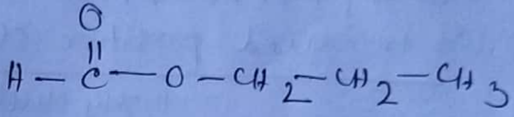
$CH_3-CH_2-O-CH_2-\overset{O}{\overset{\|}{C}}-OH$

(ix)



$CH_2(-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3)-CH_2-\underset{O}{\underset{\|}{C}}-O-CH_2-CH_3$

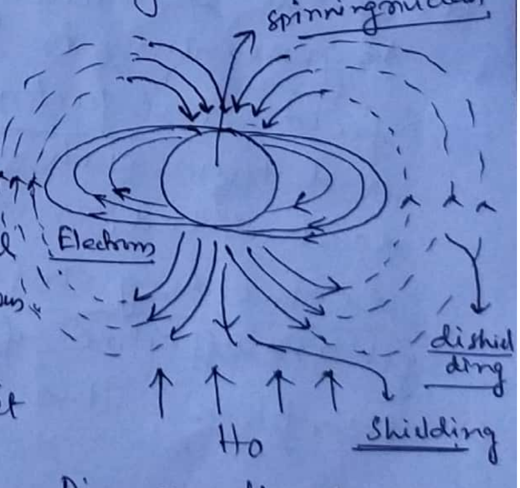
(x)



$H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$

Shielding and Deshielding effect:

Hydrogen nuclei in a molecule are surrounded by the electronic charge which shields the nucleus from the influence of applied field. ~~To overcome the~~ shid under the influence of applied magnetic field electrons sorrounds the nucleus start to rotate ⊥ to the applied (external) magnetic field. So an induced secondary magnetic field ↑↑↑ is generated which oppose the external magnetic field in the region of nucleus. Thus the nucleus experience a weaker magnetic field(Ho) and it is said to be shilded. This type of shilding is called diamagnetic shidding and it is termed as shillding effect.



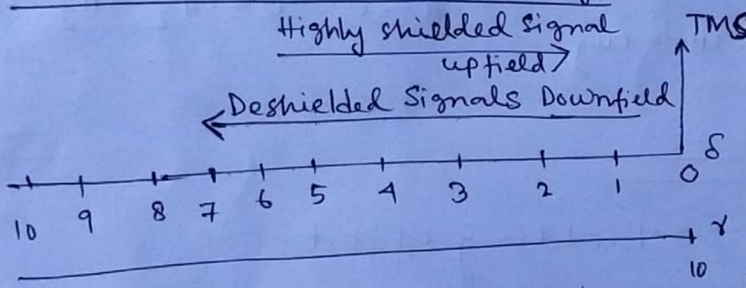
Diamagnetic Shielding about the nucleus

The extent of shielding is represented interms of Shillding parameters(α). When absorption occurs, the field H felt by the proton is represented as, $H = H_0(1-\alpha)$

H_0 is applied field strength.

Greater the value of α, greater will be the value of applied field strength which has to be applied to get effective field required for absorption and viceversa.

(*) At constant radio-frequency, shielding shift the absorption upfield in the molecules. became the field experience by proton decreases with shillding ~~[illegible]~~ [illegible] ~~frequency of~~ [illegible] ~~and absorption occurs at~~ [illegible] ~~frequency~~ [illegible]. It is called positive shillding.



(*) The degree of such shielding is dependent on the electron density around the proton. Higher the electron density around proton, higher the field and lower the δ value at which proton absorps.

(*) Presence of electronegative atoms or groups reduces e^- density around the proton (deshielding) and thus absorption is shifted downfield. (higher δ value of absorption).

(*) If the secondary induced magnetic field (which is generated) reinforces the applied magnetic field, the protons feels a higher field ~~str~~ strength and thus such a proton is said to be deshielded.

deshielding shift the absorption downfield to get an effective field strength necessary for absorption. This is Called paramagnetic effect.

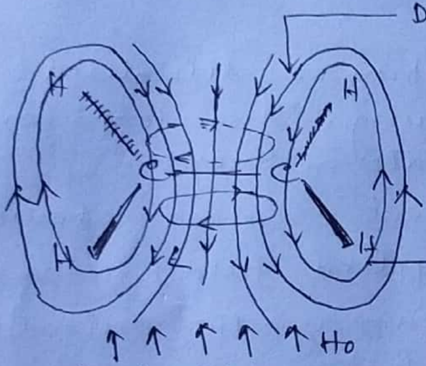
In this case the field H, felt by the proton is represented as $H = H_0(1+\alpha)$

Mitali Dewan/B.sc chem(H)/SEM IV/CC-10

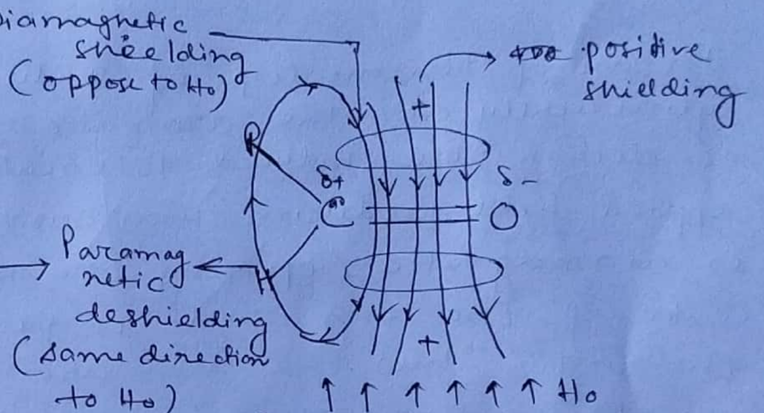
NMR- spectrosopy

(*) Absorption depends upon the manner in which the π electrons circulate under the influence of applied field.

(*) In ethylene, orientation of π-electrons is at right angle to the direction of applied magnetic field, and induced magnetic field due to circulation of π-electrons is diamagnetic (opposes external field) around the carbon atoms and paramagnetic (in the direction of applied field) in the region of protons. Thus proton feels more magnetic field (Deshielding) and hence adsorption occurs at low field.



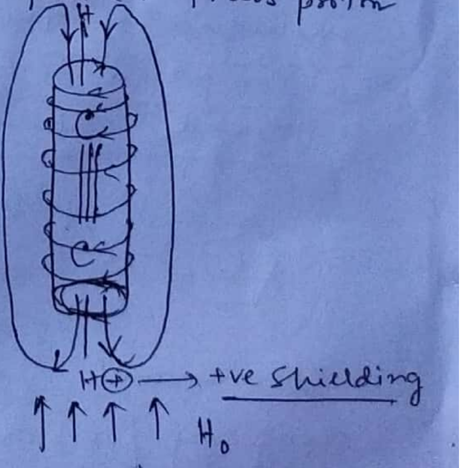
Deshielding of Ethylenic protons



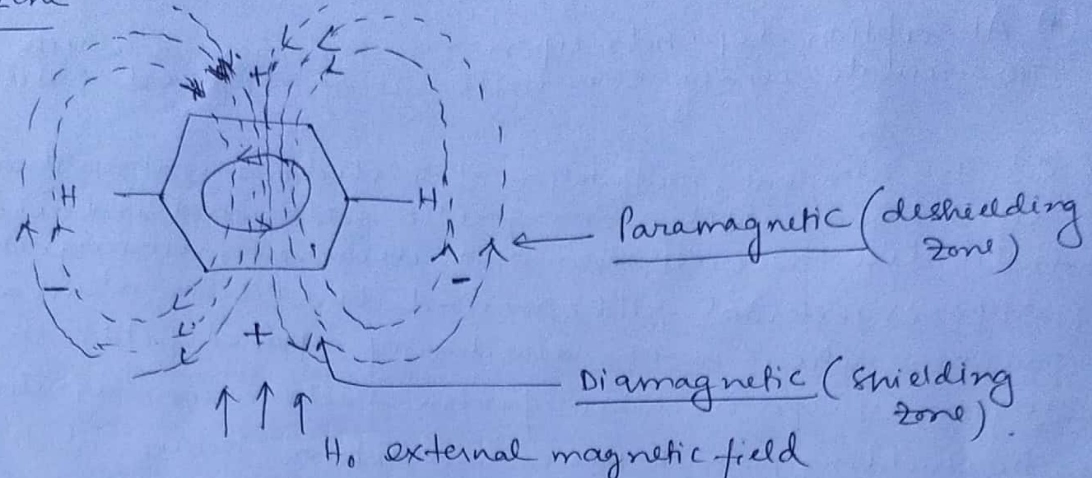
Deshielding of aldehydic proton.

Similarly, aldehydic protons appear at low field.

In case of acetylene, the protons experience a diamagnetic shielding effect. Here circulation of around triple bond takes place in such a way that the proton experience diamagnetic shielding. when the axis of alkyne group lies parallel to the direction of the applied field, the π electrons are induced to circulate around the axis in such a way that induced field opposes the applied field. Thus proton feel smaller field strength (shielding) and hence resonance occur at higher applied field. (low δ value).



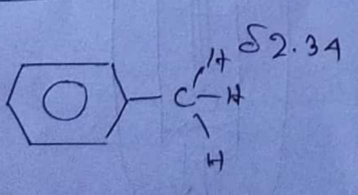
Benzene

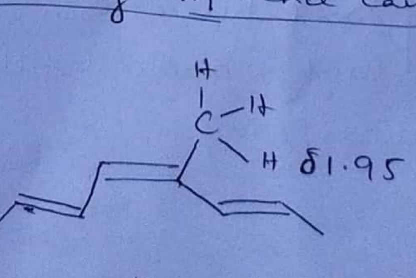


In case of benzene loops of π-electrons are delocalised cylindrically over the aromatic ring. These loops ~~are~~ of electrons are induced to circulate in presence of applied field producing ring current. The induced current is diamagnetic (opposing the applied field) in the centre of the ring and is paramagnetic outside the ring. Thus the aromatic proton (around the peripheri of the ring) experience a magnetic field greater in magnetude than the applied field. Such protons are said to be ~~de~~ deshielded and hence smaller applied magnetic field (higher value of δ) will be required to bring them to resonance.

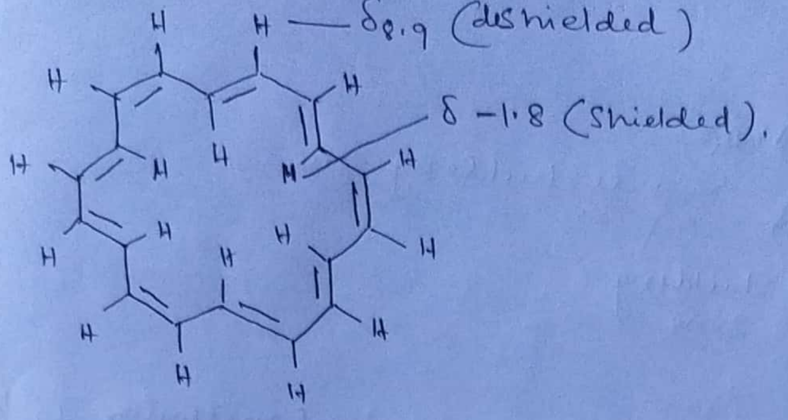
(*) The protons held above and below the ring (plane) resonate at lower value.

(*) In toluene, the methyl protons resonate at δ 2.34, whereas a methyl gr. attached to an acyclic alkene appear at 1.95 δ. (*) This is due to greater deshielding influence of the ring current in an aromatic compound as compared to the deshielding influence caused by conjugated alkene gr.



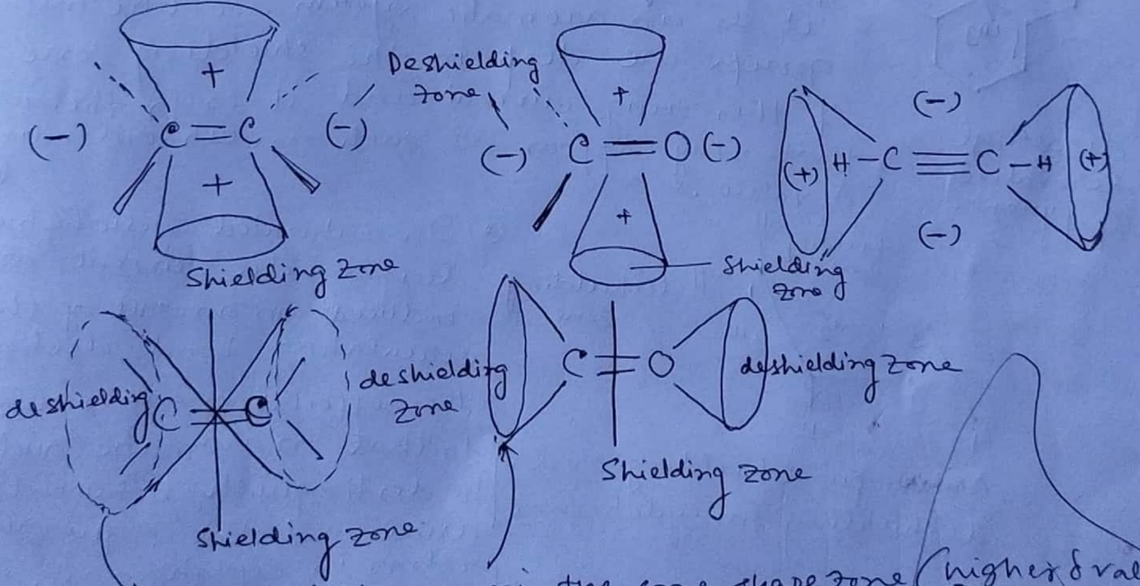


(*) ~~Bz aromat~~ In annulene, the protons outside the ring of [18] annulenes are strongly deshielded & those inside the ring are shielded.



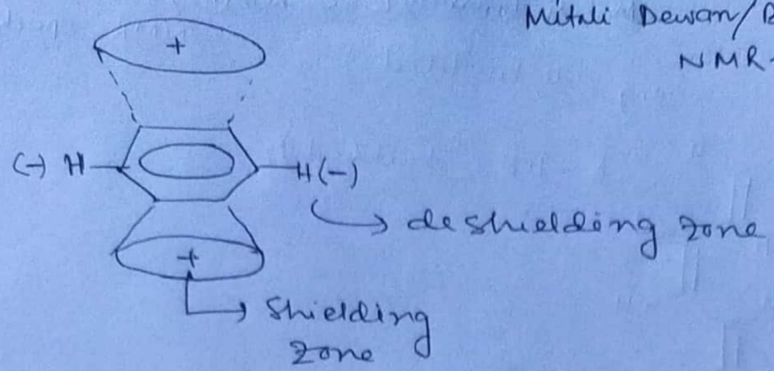
[18] Annulene

from the cases discussed earlier (π electron systems), the effect circulation of π electrons under the influence of applied field, can lead to shifts to higher frequency (downfield shifts or paramagnetic shift) or to lower frequency (upfield shift or diamagnetic shift). In addition, the effects are paramagnetic in certain direction around the π- clouds and diamagnetic in others, so that these effects are described as anisotropic, as opposed to isotropic (operating equally through space).

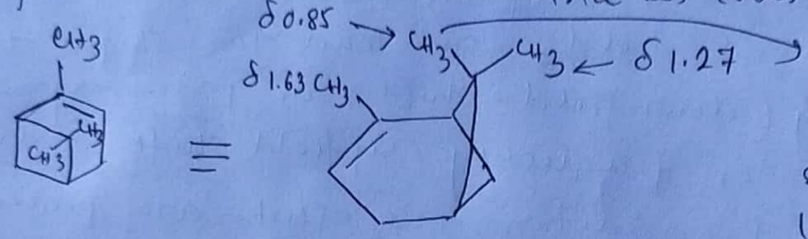


deshielding occur in the cone shape zone (higher δ value).

✱ Any group held above or below the plane of the double bond will experience a shielding effect.

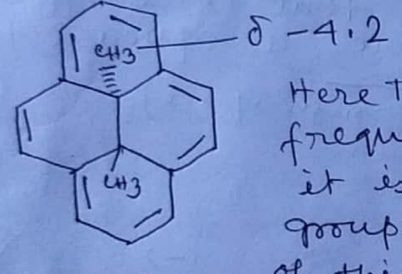


Q In α-pinene one of the geminal methyl gr. is held in just such a shielded position, and comes to resonance at significantly lower δ (frequency), since it lies in the plane of the double bond and is thus deshielded.



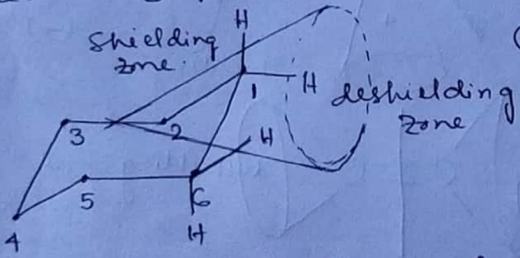
These hydrogens are in shielded position. So δ value is lower than other.

⊛



dimethyl derivative of pyrene.

Here the -Me grs appear at δ -4.2, lower in frequency than TMS. This is because as it is an aromatic system, so the methyl groups are deep in the shielding zone of this ring current and it is for this reason that they appear at such an extraordinary δ value.



Anisotropic shielding and deshielding in cyclohexane

⊛ In saturated cyclic hydrocarbon diamagnetic currents are induced as a result of the circulating bond electrons. This effect is weaker relative to that in aromatic nuclei to distinguish between the axial and the equitorial protons in cyclohexane.

Axial protons are comparatively shielded and such protons absorbs 0.5 ppm upfield as compared to those of equitorial protons.