

* Paramagnetic & diamagnetic anisotropy :-

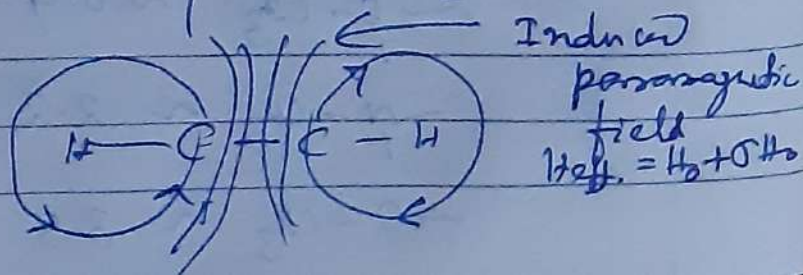
This is caused by the neighbouring atoms or group of atoms.

	<u>δ-value</u>	<u>Electronegativity</u>
CH_3-CH_3	~ 0.96	$\bullet \text{sp} > \bullet \text{sp}^2 > \text{sp}^3$
$\text{CH}_2=\text{CH}_2$	~ 5.84	
$\text{CH}\equiv\text{CH}$	~ 2.84 (why?)	

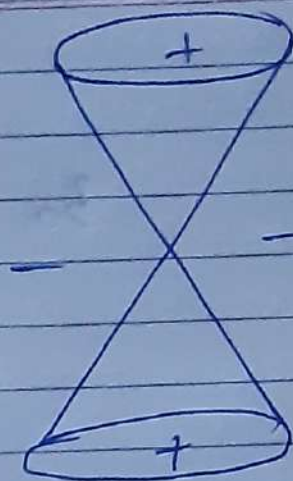
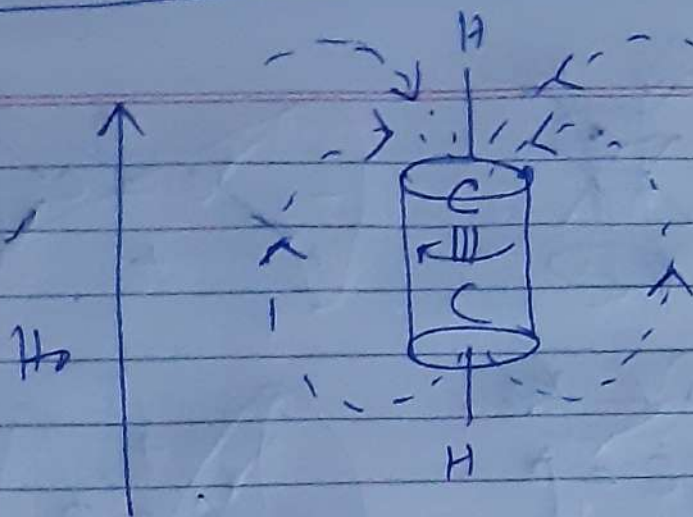
Order of inductive effect is not observed in acetylene and the difference of proton chemical shifts in ethane & ethylene is too large to be accounted for only by the electronegativity difference of sp^3 and sp^2 carbon atoms.

Reason for high field shift of acetylenic proton :-

In linear molecule like acetylene an important contribution to the total shielding that a proton experiences causing a paramagnetic shielding which arises from electronic circulation within a molecule, when it is specifically oriented w.r.t the applied magnetic field. For acetylene molecule when it is oriented perpendicular to the applied magnetic field, the induced field is paramagnetic at the carbon but diamagnetic at the proton as shown in the following figure -



When bond axis is parallel to the magnetic field.



** In addition, to the paramagnetic effect there exist a diamagnetic anisotropic effect when the bond axis is parallel to the magnetic field. That results in diamagnetic shielding in the π -electron system.

$\oplus \rightarrow$ Region of shielding

$\ominus \rightarrow$ Region of deshielding

For ethylene and aldehyde case:-

The situation is more complicated for $C=C$ and $C=O$ double bonds, since these groups does not have cylindrical symmetry. In this non-linear group, the applied field can induce a paramagnetic current when it is parallel to the $C=O$ or $C=C$. When an alkene group is oriented such that the plane of the double bond is perpendicular to the direction of the applied magnetic field, the induced circulation of π -electrons generates a secondary magnetic field that is diamagnetic, which opposes the applied magnetic field B_0 around the carbon atoms. But in the region of alkene protons, the secondary field is paramagnetic. Thus the alkene proton resonates at lower field (higher δ value).

