NMR SPECTROSCOPY

SEM-4, CC-8
PART-3, PPT-15

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Significance of the Terms: Upfield/Downfield Protons

To generate an NMR spectrum, magnetic field strength (B_0) is increased from left to right. The signal for the reference compound TMS appears at the extreme right of the spectrum with $\delta = 0$ ppm. Due to the low electronegativity of silicon, the shielding of equivalent protons in TMS is greater than most of the organic compounds. Consequently, for most of the organic molecules, signals of the protons appear to the left of TMS signal in the NMR spectra.

The more deshielded proton signals appear at the higher δ value, lower field (downfield) which is towards the left side of the plot. The more shielded proton signals appear at the lower δ value, higher field (upfield) which is towards the right side of the plot.

Figure 1: Chemical Shift
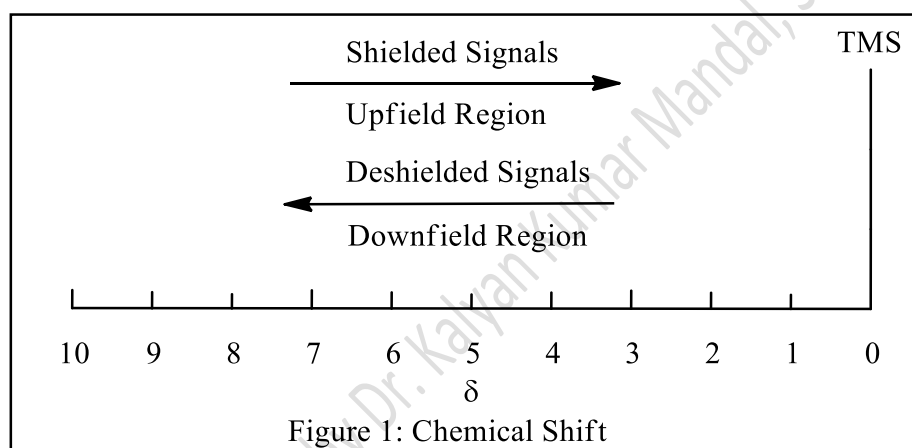
Hence, highly shielded protons appear to the right of this plot, and less shielded, or deshielded protons appear to the left. The region of the plot to the left is sometimes said to be downfield (or at low field), and that to the right, upfield (or at high field). Figure 1 is a typical chemical shift scale with the sequence of δ values that would be found on an NMR spectrum.

Shielded and Deshielded Protons

The valence-shell electron densities vary from one proton to another. In an applied magnetic field, i.e., when the molecule is placed in a uniform external magnetic field, the valence electrons around the protons are induced to circulate and this circulation, in turn, generates a secondary magnetic field, i.e., induced magnetic field. Circulation of electrons (specially π-electrons) about the nearby nuclei generates a field that can either oppose or reinforce the applied field at that proton.

If the induced field opposes the applied field, the proton feels a lower field strength, and then the proton is said to be shielded. But if the induced field reinforces the applied field, the proton feels a higher field strength, and thus, such a proton is said to be deshielded.

Therefore, the different protons in a molecule do not have resonance at exactly the same frequency. This variability is due to the fact that the protons in a molecule are surrounded by electrons and exist in slightly different electronic (magnetic) environments from one another. The protons are shielded or deshielded by the electrons that surround them.

As each proton in a molecule is in a slightly different chemical environment and consequently has a slightly different amount of electronic shielding, the precessional frequencies of different protons are different which results in a slightly different resonance frequency. Shielding shifts the absorption upfield and deshielding shifts the absorption downfield to get an effective field strength necessary for absorption.

Mechanism of Shielding and Deshielding of Protoms

Only a single peak should be obtainable from the interaction of radiofrequency energy and a strong magnetic field on a proton in accordance with the basic NMR equation as follows.
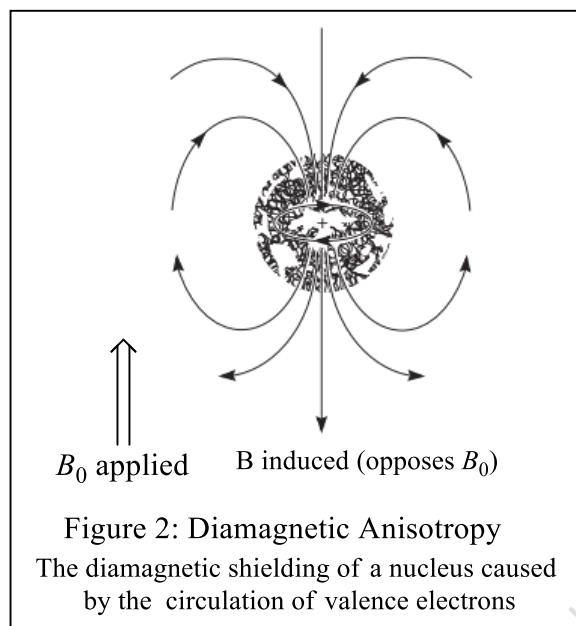
$$\nu_L \; = \; \nu_1 \; = \; \frac{\gamma B_0}{2\pi}$$

Different protons in a molecule have different chemical shifts, and different types of electronic circulation is responsible for this. The shielding or deshielding that a proton experiences in a magnetic field is a combination of the following factors:

- Local diamagnetic effect
- Diamagnetic and paramagnetic effects due to neighbouring atoms or groups of atoms
- Effects from interatomic ring current

Local Diamagnetic Effect

The H-atom bonded to a sp^3 hybridised carbon atom is surrounded by a pair of electrons. In an applied magnetic field this electron pair would undergo circulation in a plane perpendicular to the applied magnetic field. This diamagnetic circulation (Figure 2), in turn, produces a small magnetic field (induced magnetic field) which in the immediate vicinity of the proton opposed the external magnetic field. The induced field is directly proportional to the applied field: $B_{induced} = \sigma B_{applied}$ and $B_{effective} = B_{applied} \; - \; B_{induced}$

Figure 2: Diamagnetic Anisotropy
The diamagnetic shielding of a nucleus caused
by the circulation of valence electrons

B_0 applied   B induced (opposes B_0)

As a result, the apparent magnetic field (local magnetic field) at the proton becomes somewhat less than the applied magnetic field ($B_{eff} = B_0 - \sigma B_0$), where σ is the shielding constant. So, in order to bring the proton in the resonance condition one has to increase the strength of the field and such proton has lower δ value. This shielding effect of diamagnetic circulation of bonded electrons is known as the local diamagnetic effect.

As a result of diamagnetic anisotropy, each proton in a molecule is shielded from the applied magnetic field to an extent that depends on the electron density surrounding it. The greater is the electron density around the proton, the greater is the induced counter field that opposes the applied field and greater is the degree of shielding. The greater is the shielding, the higher is the magnitude of σ. Therefore, the induced magnetic field that shields a nucleus diminishes the net applied magnetic field (B_{eff}) that the nucleus experiences when it is placed in an external magnetic field, B_0.

The extent of this shielding influences the precessional frequency of the nucleus. The greater is the shielding, the lower is the precessional frequency. As a result, the nucleus precesses at a lower frequency. This means that it also absorbs radiofrequency electromagnetic radiation at the lower frequency to come to resonance. Consequently, each nonequivalent proton in a molecule is in a slightly different chemical environment and thus, has a slightly different amount of electronic shielding, which results in a slightly different resonance frequency.

The chemical shift (δ) of protons of methane and methyl halides are shown in Table 1. It indicates that higher is the electronegativity of the attached atoms, higher is the δ value of the protons.

Table 1: Chemical Shift of protons in Methane and Methyl Halides	
Compound	**δ value**
CH_3-H	0.23
ICH_2-H	2.16
$BrCH_2$-H	2.68
$ClCH_2$-H	3.05
FCH_2-H	4.16

Electronegative groups, such as, fluorine in CH_3F, withdraw electron density from the methyl group (inductive effect), and the effect of this electron withdrawal causes the methyl protons to experience a greater net magnetic field due to reduction of electron density around it. Hence, the protons (equivalent) in CH_3F precess with higher frequency than the protons of methane and other methyl halides. Since fluorine is most electronegative among the halogen atoms, its deshielding influence is greatest and hence, the attached protons have highest precessional frequency than that of the other methyl halides. Therefore, δ values of protons decrease from CH_3F to CH_3I.

Silicon is electropositive, and the opposite effect operates in, for example TMS; silicon pushes electrons into the methyl groups of TMS by a +I effect, and this powerful shielding effect means that the TMS protons come to resonance at low frequency (low δ value, defined as zero). The effect of charged species on chemical shift values is very marked; protons adjacent to N^+ (as in quaternary ammonium ions, R_4N^+) are very strongly deshielded (high δ values), while carbanionic centres act as powerful shielding influences on the protons (low δ values).

Correlation Chart for Proton Chemical Shift Values
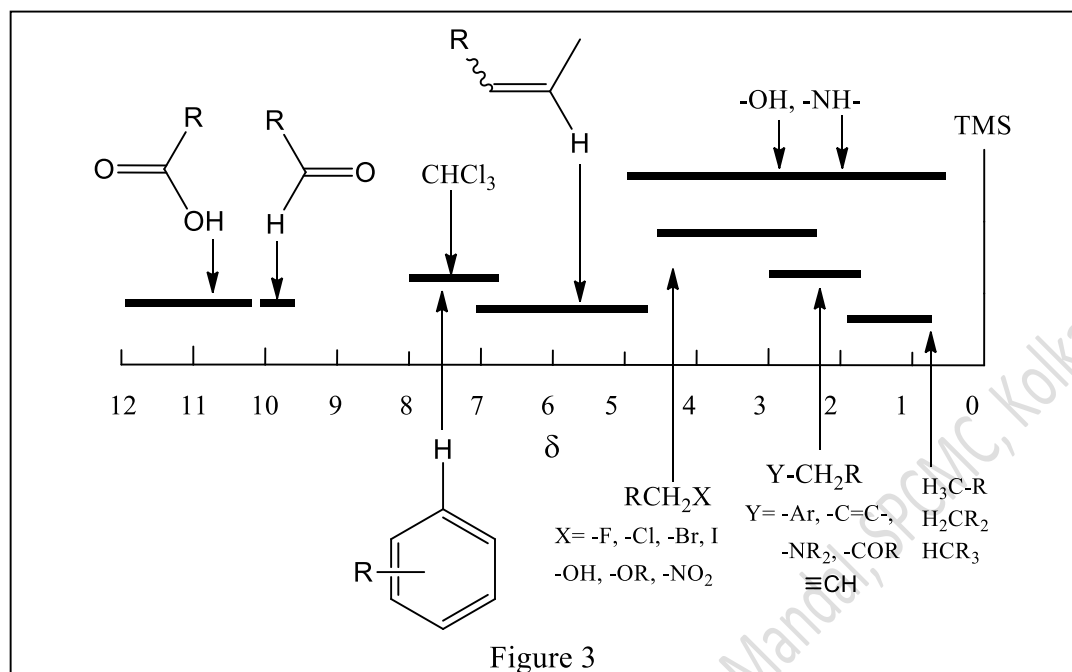
Figure 3

Magnetic Anisotropy

The correlation chart for proton chemical shifts of different compounds (Figure 3) shows that there are some types of protons with chemical shifts that are not easily explained by the local diamagnetic effect based on simple considerations of the electronegativity of the attached groups, for instance, the protons of benzene and other aromatic systems. Aryl protons generally have a chemical shift as large as that of the proton of chloroform.

Alkenes, alkynes, and aldehydes also have protons with resonance values that are not in line with the expected magnitudes of any electron-withdrawing or hybridization effects. In each of these cases, the anomalous shift is due to the presence of an unsaturated system (one with π electrons) in the vicinity of the proton in question.

Since carbon is more electronegative than hydrogen, a shift to a higher frequency in the series methane (CH_4, $\delta = 0.23$ ppm), ethane (CH_3CH_3, $\delta = 0.86$ ppm), propane ($CH_3CH_2CH_3$, $\delta = 1.33$ ppm) and isobutane [$(CH_3)_3CH$, $\delta = 1.56$ ppm] is attributed to deshielding effect of one, two and three C–C bonds, respectively.

The chemical shift positions (δ) for protons attached to C=C in alkenes is higher than can be accounted for by electronegativity effects alone.

Table 2: Chemical Shift of protons in Alkane, Alkene, and Alkyne	
Compound	**δ value**
CH_4	0.23
$H_3C\text{-}CH_3$	0.86
$H_2C=CH_2$	5.25
$HC\equiv CH$	1.88

The same is true of aldehydic protons (δ 9.5-10) and aromatic protons (δ 6-9), whereas alkyne protons appear at relatively low δ. Table 2 lists approximate δ values for these protons.

The word "anisotropic" means "non-uniform". So "magnetic anisotropy" means that there is a "non-uniform magnetic field". Electrons in π systems (e.g., aromatics, alkenes, alkynes, carbonyls etc.) interact with the applied field which induces a magnetic field that causes the anisotropy. As a result, the nearby protons will experience three fields: the applied (external) field, the induced (shielding) field of the valence electrons and the induced field due to the π system. Depending on the position of the proton in this third field, it can be either shielded (smaller δ) or deshielded (larger δ), which implies that the energy required for, and the frequency of the absorption will change. Therefore, all groups in a molecule that have π electrons generate secondary anisotropic fields.

Acetylene: The molecule is linear, and the triple bond is symmetrical about the axis. If this axis is aligned with applied magnetic field, the π electrons of the bond (the cylindrical π electron cloud) can circulate at right angles to the applied field, thus inducing their own magnetic field opposing the applied field. Since the protons lie in the magnetic axis, the magnetic lines of force induced by the circulating π electrons act to shield the protons (Figure 4).

Figure 4: Diamagnetic Anisotropic shielding of proton in Acetylene
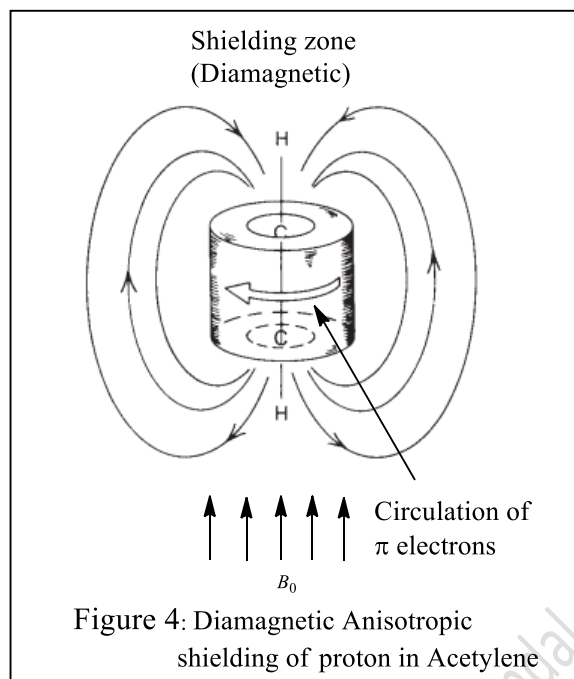
Therefore, both carbons and hydrogens in acetylene fall in the shielding zone of the induced diamagnetic anisotropic field which causes a reduction of the apparent magnetic field $[B_{eff} = (1 - \sigma) B_0]$ at the proton. Thus, the acetylenic protons appeared at upfield position (lower δ) than electronegativity of sp carbon atoms would predict.

Ethylene: when ethylene molecule is oriented perpendicular to the applied magnetic field, the external magnetic field causes a diamagnetic circulation of the π electrons (Figure 5), which, in turn, produces an induced diamagnetic field in between the double bonded atoms and a resultant paramagnetic field in the region of the olefinic protons causing a deshielding of these protons.
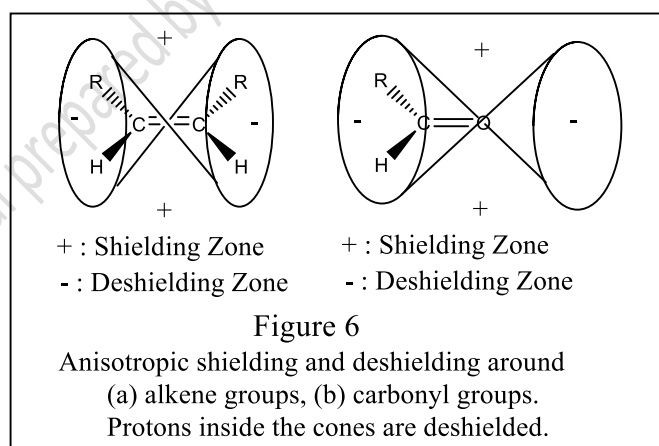

Figure 5

Diamagnetic Anisotropic shielding of proton in Ethylene
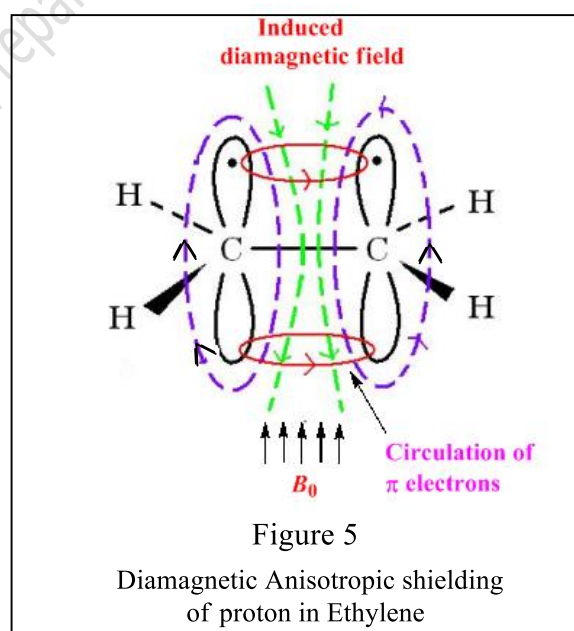
Any group held above or below the plane of the double bond will experience a *shielding effect,* since in these areas the induced field opposes B_0. In α-pinene, one of the geminal methyl groups is held in just such a shielded position, and comes to resonance at significantly lower δ (frequency) than its twin.
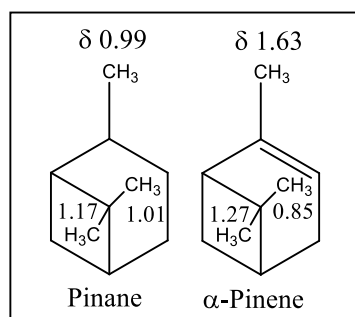
The third methyl group appears at higher δ (frequency), since it lies in the plane of the double bond and is thus deshielded. Therefore, the space around a double bond can be divided into two categories as shown in Figure 6. Deshielding occurs in the cone shaped zones, and any proton falling in this zone will have higher δ value. Shielding occurs outside the cones and protons in these zones are shielded (lower δ values).

Carbonyl Compounds: When the carbonyl group is oriented such that the plane of the trigonal carbon atom is perpendicular to the field, diamagnetic circulations in the group produce an anisotropic effect at the proton that results in deshielding (Figure 6). The effect of the applied magnetic field is greatest along the transverse axis of the C=O bond. The geometry of the molecule is such that the aldehydic proton falls in the deshielding portion of the induced magnetic field, and appears at high δ value.


Figure 6
Anisotropic shielding and deshielding around
(a) alkene groups, (b) carbonyl groups.
Protons inside the cones are deshielded.

Thus, ethylenic and aldehydic protons are deshielded by the diamagnetic anisotropic deshielding effect of the C=C and C=O groups, respectively.

Magnetic Anisotropy: Induced Ring Current

Aromatic Compounds: Aromatic nuclei contain large closed loops of π electrons. In the molecule of benzene (and aromatic compounds in general) these π electrons are delocalized cyclically over the aromatic ring. These loops of electrons are induced to circulate in the presence of the applied field, B_0, producing a substantial diamagnetic electric current, called the *ring current.*

The magnetic field associated with this electric field has the geometry and direction shown in Figure 7. The generated induced field is diamagnetic (opposing B_0) in the centre of the ring, but the returning flux outside the ring is paramagnetic (augmenting B_0).
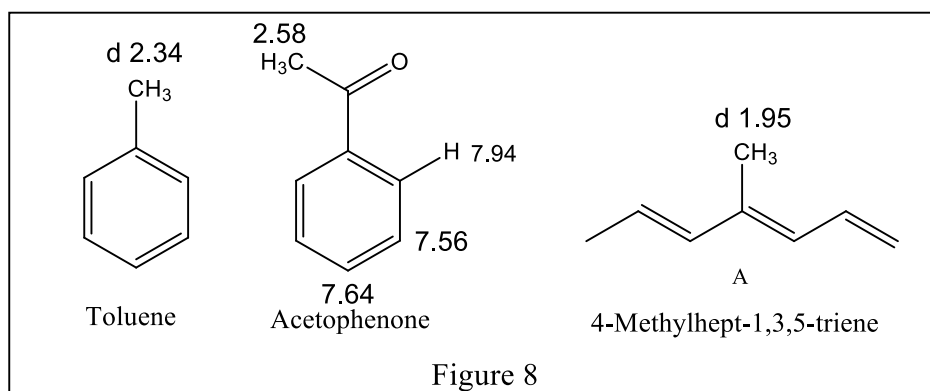

Figure 7
Anisotropic shielding and deshielding
associated with aromatic ring current
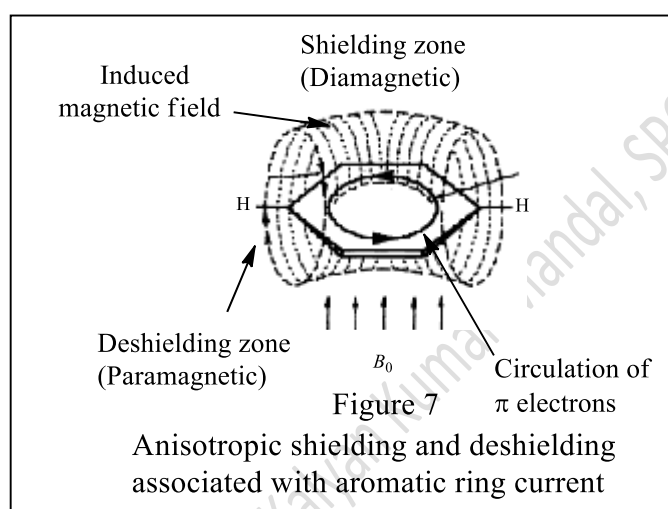
Protons around the periphery of the ring experience an augmented magnetic field [$B_{eff} = (1 + \sigma) B_0$], and consequently come to resonance at higher δ (7.26 ppm in benzene) values than would otherwise expected for being attached to an sp² hybridised carbon atom. Protons held above or below the plane of the ring resonate at low δ values because of the reduction of the apparent magnetic field [$B_{eff} = (1 - \sigma) B_0$].

Therefore, the benzene hydrogens are deshielded by the diamagnetic anisotropy of the ring. An applied magnetic field is anisotropic in the vicinity of a benzene molecule because the labile electrons in the ring interact with the applied field. This creates a non-homogeneity in the immediate vicinity of the molecule.

In toluene, the methyl protons resonate at δ 2.34, whereas a methyl group attached to an acyclic conjugated alkene, A (Figure 8) appears at δ 1.95. This is due to the greater deshielding influence of the ring current in aromatic compounds (cyclically delocalized π electrons) compared with the deshielding of conjugated alkene groups (having no cyclic delocalization).

All the ring protons of acetophenone are found downfield because of the ring current effect and electron withdrawal by the acetyl group. Moreover, the *ortho* protons are shifted slightly further downfield because of the additional deshielding effect of the carbonyl group compared to the *meta* and *para* protons. Nitrobenzene shows a similar effect.

d 2.34
CH3

Toluene

2.58
H3C
O

H 7.94

7.56

7.64
Acetophenone

d 1.95
CH3

A

4-Methylhept-1,3,5-triene

Figure 8

[18]Annulene (Figure 9) sustains a ring current, so that the twelve peripheral protons are deshielded and the six internal protons are shielded. The outer protons appear at δ 8.9, while the inner protons are at a *lower* frequency than TMS at δ -1.8. (around 20°C; molecular motion makes the spectrum change with variable temperature).

This shows that the cyclic π electron system around the periphery of the molecule sustains a substantial ring current, and therefore indicates aromatic character in a non-benzenoid ring system. Demonstration of such a ring current is therefore the best evidence for aromaticity.

[18]Annulene

δ 8.9 : 12 Outer Protons

δ -1.8 : 6 Inner Protons

Figure 9

- : Deshielding Zone
Cyclohexane
Figure 10
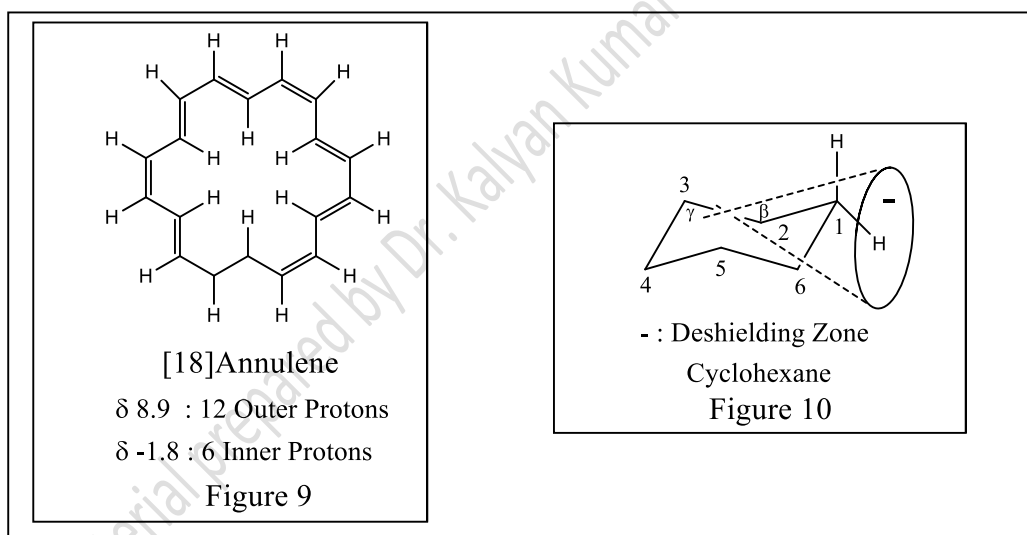
Anisotropic effects of circulating σ Electrons

In contrast with the anisotropic effects of circulating π electrons, the σ electrons of a C-C bond produce a small effect. The axis of the C-C bond is the axis of the deshielding cone (Figure 10).

The *equatorial* proton is consistently found further downfield by about 0.5 ppm than the *axial* proton on the same carbon atom in a rigid six-membered ring (e.g., in cyclohexyl system). The *axial* and *equatorial* protons on C_1 are oriented similarly with respect to C_1-C_2 and C_1-C_6, but the equatorial proton is within the deshielding cone of the C_2-C_3 bond (and C_5-C_6). Therefore, the downfield shift of equatorial proton is attributed to anisotropic deshielding by the σ electrons in the $\beta\gamma$-sigma bonds.