

NMR SPECTROSCOPY

SEM-4, CC-8
PART-4, PPT-16

Contents (Part-4)

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Nuclear Magnet Resonance (NMR) Spectroscopy (PART-4, PPT-16)

Factors Influencing Chemical Shift

There are a number of factors which influence the chemical shift at which proton resonances occur. These may be categorized as

- (a) local diamagnetic shielding effects and
- (b) the effect of neighbouring atoms or groups in the molecule

Each proton in a molecule is considered to share two bonding electrons, which are induced to circulate by the influence of the external magnetic field in a manner so as to produce local secondary fields which oppose the applied field. These local diamagnetic shielding effects are dependent on the electron density around the atom and on the extent to which the C-H bond may be polarized.

The major factors affecting chemical shifts of the protons are the following:

1. Inductive Effects
2. Hybridisation Effects
3. Diamagnetic Anisotropy
4. van der Waals Deshielding
5. Solvent Effects
6. Concentration
7. Temperature
8. Hydrogen Bonding

Inductive Effects

When a nucleus is placed in a uniform external magnetic field, the electrons surrounding it circulate in such a manner as to produce a secondary field which reduces the influence of the external magnetic field on the nucleus. This shielding influence of the surrounding electrons decreases if another electronegative atom is attached to the nucleus because the protective electronic clouds are pulled away towards the neighbouring electronegative atom, causing it to come to resonance at a lower frequency.

On the other hand, groups which donate electrons will tend to increase the electron density around the nucleus, and hence a higher frequency is required for resonance to occur since the nucleus is more shielded from the influence of the external magnetic field.

The majority of alkanes show resonances between 0.8 and 1.6 ppm. Methyl groups attached to saturated carbon atoms are the most shielded of aliphatic protons and absorb in the region

0.6-1.2 ppm. Methylene protons are less shielded and resonate around 1.3 ppm in saturated hydrocarbons while the methine protons resonate even further downfield (around 1.6 ppm).

The methylene protons of cycloalkanes absorb at similar positions to those of alkanes except in cyclopropanes in which the methylenes are significantly shielded (chemical shift: 0.1-0.5 ppm) because of the anisotropy of the cyclopropane C-C bonds. A proton will be deshielded if it is attached with an electronegative atom or group. Greater the electronegativity of the atom, greater is the deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will also be more. Therefore, the chemical shift of a proton increases as the electronegativity of the attached element increases.

When methyl groups are attached to oxygen atoms, the methyl protons resonate at about 3.3 ppm, but if methyl groups attached to nitrogen they experience a relatively higher shielding and resonate at around 2.3 ppm. Methyl groups attached to olefinic carbon atoms resonate around 1.6-1.8 ppm but if attached to aromatic rings they are deshielded and resonate around 2.4 ppm.

Multiple substituents have a stronger effect than a single substituent. The influence of the substituent drops off rapidly with distance, an electronegative element having little effect on protons that are more than three carbons distant. Table 1 and Table 2 illustrate these effects for the protons.

Table 1: Dependence of the Proton Chemical Shift (in ppm) of CH₃X on the element X

Compound CH ₃ X	CH ₃ F	CH ₃ OH	CH ₃ Cl	CH ₃ Br	CH ₃ I	CH ₄	(CH ₃) ₄ Si
δ value	4.26	3.40	3.05	2.68	2.16	0.23	0

Table 2: Substitution Effect

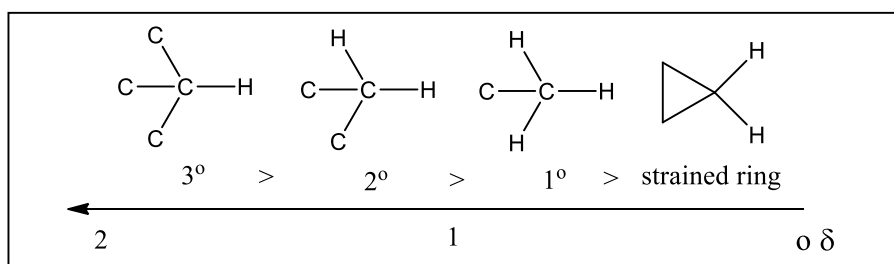
Compound	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CH ₃ CH ₂ Br	CH ₃ CH ₂ Br
δ value	3.05	5.30	7.26	3.34	1.69

Hybridisation Effects

The state of hybridisation of the carbon atom to which a proton is attached significantly influences the chemical shift of the proton. With increasing *s*-character of the carbon, the bonding electrons will be drawn closer towards the carbon and away from the hydrogen, thus decreasing the electron density around the proton. This will result in the “deshielding” of the proton and it will therefore come to resonance at higher frequency.

***sp*³ Hydrogens:** All hydrogens attached to purely *sp*³ carbon atoms (C-CH₃, C-CH₂-C, cycloalkanes) have resonance in the limited range from 0 to 1.6 ppm, provided that no electronegative elements or π -bonded groups are nearby.

Methylene hydrogens (attached to sp^3 carbons) appear at greater chemical shifts (near 1.2 to 1.4 ppm) than do methyl hydrogens. Methine hydrogens occur at higher chemical shift than methylene hydrogens. The following diagram illustrates these relationships:



Hydrogens on an sp^3 carbon that is directly attached to a heteroatom ($-O-CH_2-$, and so on) or to an unsaturated carbon ($-C=C-CH_2-$) do not fall in this region, but have greater chemical shifts.

sp^2 Hydrogens

Simple olefinic hydrogens ($-C=C-H$) have resonance in the range from 5 to 6 ppm. However, different substituents shift the olefinic proton resonances to a higher or to a lower frequency. In an $C_{sp^2}-H$ bond, the carbon atom has more s -character (33%), which effectively renders it “more electronegative” than an sp^3 carbon (25% s -character).

s -orbitals hold electrons closer to the nucleus than do the carbon p -orbitals. As the sp^2 carbon atom holds its electrons more tightly, this results in less shielding for the attached hydrogen nucleus than do an sp^3 carbon atom. Thus, vinyl hydrogens have a greater chemical shift (5 to 6 ppm) than aliphatic hydrogens on sp^3 carbons (1 to 4 ppm). Protons which are a part of a conjugated system appear downfield than when attached to a non-conjugated system. Aromatic hydrogens appear in a range further downfield (7 to 8 ppm) than to most olefinic protons.

Aldehydic protons (also attached to sp^2 carbon) appear even farther downfield (9 to 10 ppm) than aromatic protons since the inductive effect of the electronegative oxygen atom further decreases the electron density on the attached proton. The downfield positions of ethylenic, aromatic, and aldehydic proton resonances are, however, greater than one would expect based on these hybridisation differences. Another effect, called anisotropy, is responsible for the largest part of these shifts.

sp Hydrogens

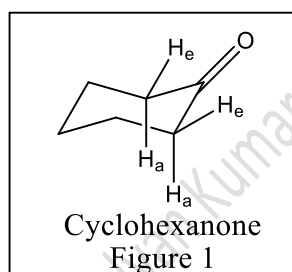
An sp carbon (50% s -character) should behave as if it were more electronegative than an sp^2 carbon. On the basis of hybridization alone, one would expect the acetylenic proton to have a chemical shift greater than that of the ethylenic proton. However, this is the opposite of what is actually observed. Acetylenic hydrogens ($C_{sp}-H$) appear anomalously at 2 to 3 ppm compared to olefinic protons which appear in the range 5-7 ppm.

This sharp difference can be explained in terms of diamagnetic anisotropic effect involving the circulation of π electrons of carbon-carbon triple bond in an applied magnetic field. This effect depends on the orientation of the molecule in an applied magnetic field.

Diamagnetic Anisotropy

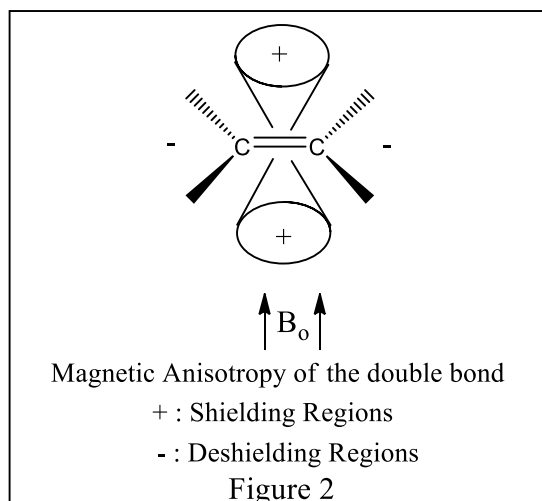
Single Bonds: The electronic clouds around protons attached to carbon atoms do not have spherical symmetry, but are asymmetrically distributed. The resulting secondary fields from protons are, therefore, “anisotropic”. A random tumbling of molecules will accordingly not result in their averaging to zero, but will reinforce or diminish the applied field, depending on the orientation of the bonds.

Thus in a rigid cyclohexane ring or in cyclohexanone (Figure 1), the axial protons are more shielded than the equatorial protons because of the anisotropy of the carbon framework, so that they appear about 0.5 ppm further upfield than their equatorial counterparts.



Double Bonds: Anisotropic effects are even more marked in the case of double bonds such as C=C, C=O, and C=N. Thus, in a double bond, the applied magnetic field causes an induced circulation of π electrons when the double bond is aligned at right angles to the applied field which tends to oppose the applied magnetic field at the centre of the double bond, but reinforces it at the ends.

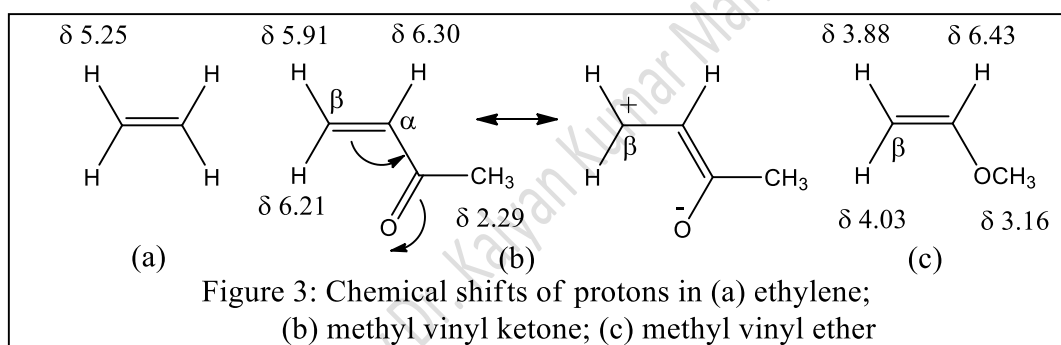
In solution, the tumbling molecules adopt any one of a large number of orientations, and the average of these various orientations would afford two shielding cones with their apexes meeting at the centre of the double bond as shown in Figure 2.



Any protons which fall in the regions of these cones (+zone) would be shielded whereas protons falling in the regions beyond the ends of the double bonds (-zone) would experience a deshielding influence. Similar situations would hold for C=O, C=S, C=N, and NO₂ groups. A striking example of such effects is provided by the aldehydic proton which lies in the deshielding zone of the carbonyl group, and is therefore shifted considerably downfield.

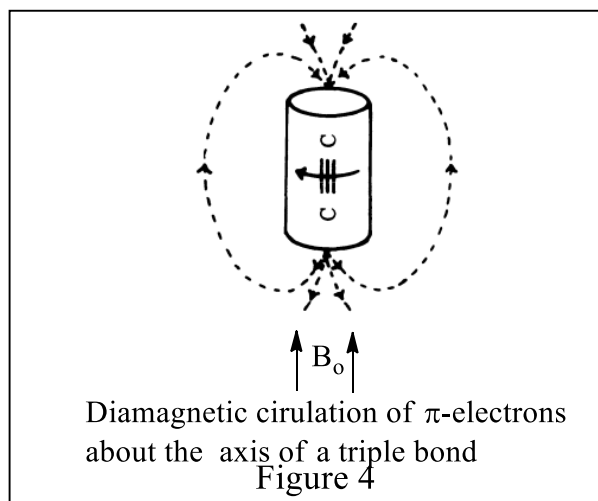
When substituents are attached to double bonds, they can significantly affect chemical shifts depending on their nature. In ethylene, the protons resonate at δ 5.25. In methyl vinyl ketone, the protons on the carbon β to the carbonyl group are deshielded because of the electron withdrawing effect of the carbonyl group, and appears at higher δ value than 5.25.

Deshielding of these β protons is due to the electropositive character of the β -carbon atom because of the contribution of the resonance structure as shown in Figure 3 (b). In methyl vinyl ether, the opposite effect is seen, the protons on the carbon β to the ethereal oxygen being strongly shielded due to its electron donating effect (of the alkoxy group). The effects of substitution of different groups on the chemical shifts of olefinic bonds are shown in Figure 3.



Triple Bonds: Triple bonds, such as those encountered in acetylenes or nitriles, have axial symmetry. The induced circulation of π electrons in acetylenes or nitriles results in the generation of a secondary magnetic field which tends to oppose the applied field at the ends but reinforces it at a certain distance along the axis.

Since acetylenic protons fall in the shielding zone of the cone they are shifted significantly upfield and resonate at a value of δ 1.88, in contrast to ethylenic protons which resonate at δ 5.25. Methyl protons in propyne (H₃C-C \equiv CH) appears somewhere outside this shielding zone, and hence resonated at δ 1.80.

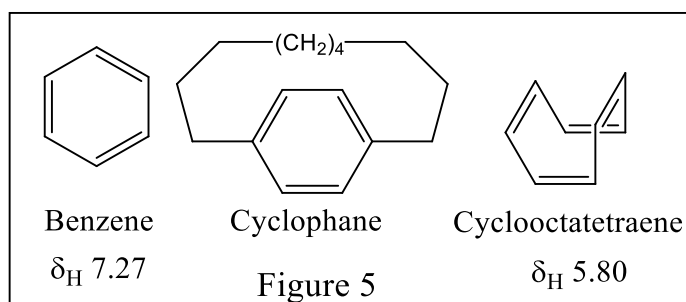


Aromatic Rings: In aromatic rings, the π electrons delocalized over the ring atoms are induced to circulate above and below the plane of the ring (in two loops on the two sides of the σ bond framework). This circulation is such as to oppose the applied magnetic field at the centre of the ring but reinforce it in the region where the aromatic protons are located. This results in a strong deshielding of the aromatic protons.

On the other hand, if a nucleus is held above the centre of the aromatic ring, it will be strongly shielded. Thus in cyclophane (Figure 5), the central methylene protons are located in the shielding region of the aromatic ring, and are therefore, shifted upfield by 0.45 ppm as compared to the methylene protons in a normal aliphatic chain.

The ring current effects are only discernible in planar conjugated cyclic molecules. In nonplanar molecules, e.g., cyclooctatetraene (Figure 5), which is tub-shaped, the delocalisation of π electrons is severely restricted, and the protons of cyclooctatetraene, therefore, resonate in the normal olefinic region (δ_{H} 5.80, cf. 5.85 in cyclohexadiene).

The effect of substituents on the chemical shifts of protons in aromatic rings is shown in Table 3. Strongly electron withdrawing groups, such as nitro or aldehyde, result in significant deshielding of the aromatic protons, the *ortho* and *para* protons being more affected than the *meta* protons on account of the greater transmission of electropositive character to the *ortho* and *para* carbons by mesomerism.



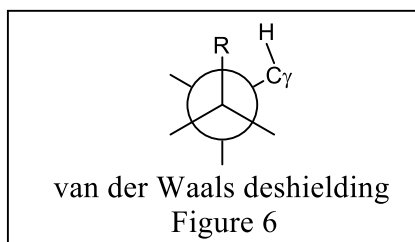
Conversely, the presence of amino groups on benzene rings causes a shielding of the *ortho* and *para* carbons because of the donation of electrons from the nitrogen lone pair to these carbon atoms, resulting in an increase in the electron density at the attached protons.

Table 3: Chemical shifts of <i>ortho</i>, <i>meta</i>, and <i>para</i> protons in monosubstituted benzenes			
δ (in ppm) from benzene (7.27)			
Substituent	<i>ortho</i>	<i>meta</i>	<i>para</i>
NO ₂	0.93	0.26	0.38
CHO	0.60	0.24	0.34
CO ₂ H	0.85	0.35	0.38
CO ₂ R	0.76	0.30	0.35
COR	0.57	0.25	0.30
CONH ₂	0.55	0.27	0.20
NHCOR	0.22	0.03	-0.17
Cl	0.02	0.00	-0.01
Br	0.20	0.00	-0.08
CH ₃	-0.15	-0.10	-0.10
OH	-0.43	-0.03	-0.34
OCH ₃	-0.39	-0.01	-0.35
NH ₂	-0.63	-0.15	-0.54
N(CH ₃) ₂	-0.50	-0.06	-0.50

van der Waals Deshielding

In a rigid molecule, it is possible for a proton to occupy a sterically hindered position, and in consequence, the electron cloud of the hindering group will tend to repel, by van der Waals electrostatic repulsion, the electron cloud surrounding the proton. The proton will be deshielded and appear at higher δ values than would be predicted in the absence of the effect.

Steric crowding involving the hydrogen atom/s (Figure 6) can result in proton-bearing carbon atoms being shielded. Steric perturbation of C-H bonds results in the electrons moving away from the hydrogen atoms and towards the carbon atoms, thus resulting in the carbon atoms (γ) being shielded (and the protons deshielded).



Solvent Effects

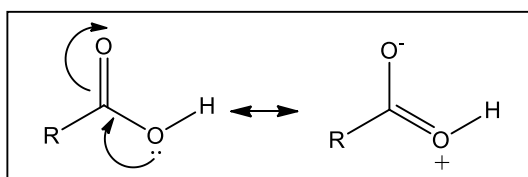
Substances dissolved in aromatic solvents generally give signals at higher fields than when dissolved in aliphatic solvents. These effects are attributed to the diamagnetic anisotropy of aromatic rings, and are more significant when intermolecular solute-solvent associations lead to complex formation.

As a result of dipole-dipole or van der Waals interactions between the solute and solvent, some orientations of the solute molecules may be more favoured than others, giving rise to shifts in the resonance frequencies of the protons of the solute molecules. NMR spectrum of a compound measured in one solvent may be slightly different from that measured in another solvent of different polarity. Hence, it is important to mention the solvent used in an NMR spectrum.

Concentration and Temperature

It is evident that the chemical shifts of exchangeable protons such as those of OH, NH, or SH groups are markedly dependent on concentration, solvent, and temperature. Protons that can form hydrogen bonding (e.g., hydroxyl or amino protons) exhibit extremely variable absorption positions over a wide range. They are usually found attached to a heteroatom.

Some of the deshielded protons are those attached to carboxylic acids. These protons have their resonances at 10 to 12 ppm. Both mesomeric and electronegativity effects of oxygen withdraw electrons from the acidic proton making it shifted enormously downfield.



Concentration and Temperature

Protons	Protons	Protons
R-OH (pure)	0.5-4.0	Can appear as a multiplet because of coupling with adjacent protons, but usually occurs as a broad singlet; position is temperature, solvent, and concentration dependent. H-bonded enols may occur from δ 11.0 to 16.0
R-OH (with a trace of acid)	4-8 (variable)	Occurs as a sharp singlet; position of line is concentration dependent
Ar-OH	4.5 (without H-bonding)	Position of signals dependent on solvent, concentration, and temperature
	9.0 (with H-bonding)	
R-CO ₂ H	10-13	Position of signals largely dependent on concentration
RNH ₂ , RNHR'	2-5	Usually sharp single line but may be broadened; position is solvent dependent

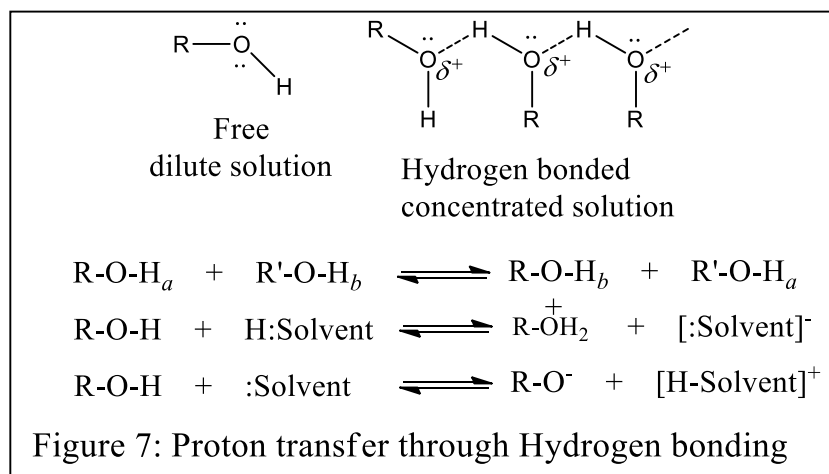
Hydrogen Bonding

Hydrogen bonding results in downfield shifts of proton resonances from their positions in the unbonded state. The higher δ values of the hydroxyl resonance of phenols or carboxylic acids are attributed to hydrogen bonding. The amount of hydrogen bonding is often a function of concentration and temperature. Increase of temperature or dilution with carbon tetrachloride can often break up hydrogen bonds and cause an upfield shift.

The more hydrogen bonding that takes place, the more deshielded a proton becomes. The more concentrated the solution, the more molecules can come into contact with each other and form hydrogen bonds. At high dilution (no H bonding), hydroxyl protons absorb near 0.5–1.0 ppm; in concentrated solution, their absorption is closer to 4–5 ppm. Protons on other heteroatoms show similar tendencies.

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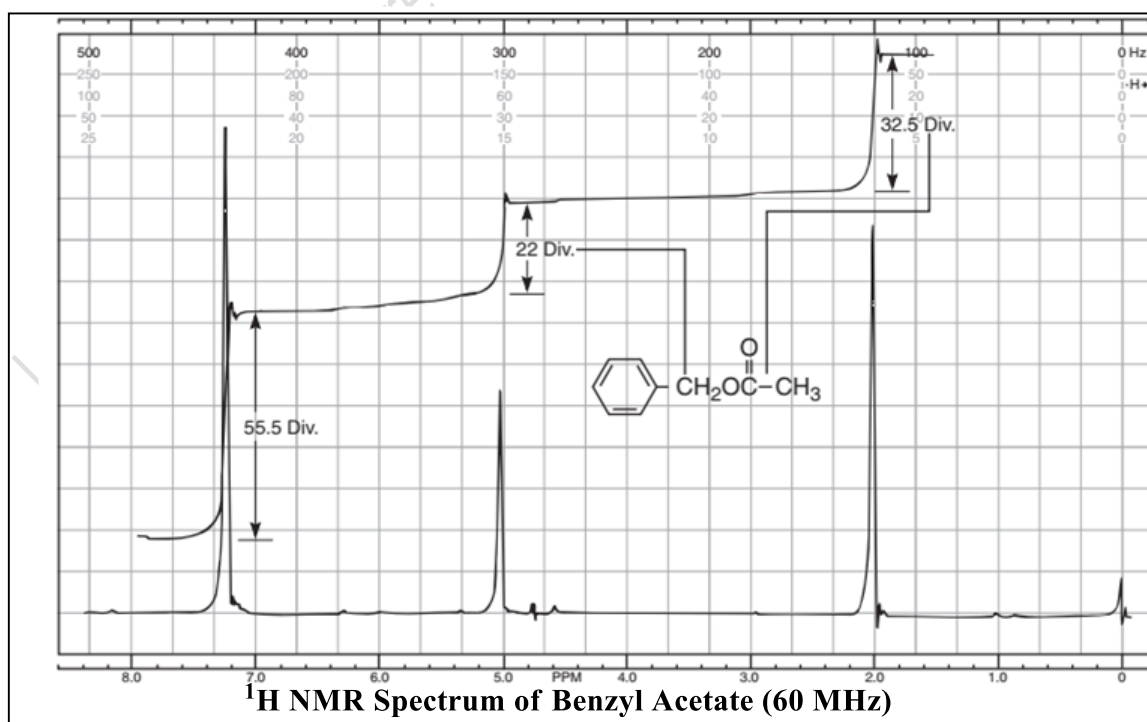
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NMR Peak Area: Integration

Integration: It is a process by which relative areas under spectral peaks are measured. These areas are proportional to the number of equivalent protons giving the signal. The NMR spectrum not only distinguishes how many different types of protons a molecule has, but also reveals how many of each type are contained within the molecule. In the NMR spectrum, the area under each peak is proportional to the number of hydrogens generating that peak.

Let us consider the ^1H NMR spectrum of benzyl acetate (Figure 8) for instance. The NMR spectrometer has the capability to electronically integrate the area under each peak. It does this by tracing over each peak a vertically rising line, called the integral, which rises in height by an amount proportional to the area under the peak. The integral values are proportional to the actual number of protons represented by the peak.



NMR Peak Area: Integration

It is noted from the spectrum that the height of the integral line does not give the absolute number of hydrogens. It gives the relative number of each type of hydrogen. For a given integral to be of any use, there must be a second integral to which it may be referred. The first integral rises for 55.5 divisions on the chart paper; the second, 22.0 divisions; and the third, 32.5 divisions. These numbers are relative. One can find ratios of the types of protons by dividing each of the larger numbers by the smallest number:

$$\frac{55.5 \text{ divisions}}{22.0 \text{ divisions}} = 2.52 \quad \frac{22.0 \text{ divisions}}{22.0 \text{ divisions}} = 1.00 \quad \frac{32.5 \text{ divisions}}{22.0 \text{ divisions}} = 1.48$$

The number ratio of the protons of all the types is 2.52:1.00:1.48. If it is assumed that the peak at 5.1 ppm is really due to two hydrogens, then one can arrive at the true ratio by multiplying each figure by 2 and rounding off to 5:2:3. The area ratio of the three peaks is 5:2:3, the same as the ratio of the numbers of the three types of hydrogens in benzyl acetate.

Clearly, the peak at 7.3 ppm, which integrates for five protons, arises from the resonance of the aromatic ring protons, whereas that at 2.0 ppm, which integrates for three protons, is due to the methyl protons. The two-proton resonance at 5.1 ppm arises from the benzyl protons. Thus, it can be said that the integrals give the simplest ratio, but not necessarily the true ratio, of numbers of protons of each type.