UNIT - NMR SPECTROSCOPY

Nuclear magnetic resonance (NMR) is a spectroscopic method that is even more important to the organic chemist than infrared spectroscopy. Many nuclei may be studied by NMR techniques, but hydrogen and carbon are most commonly available. Whereas infrared (IR) spectroscopy reveals the types of functional groups present in a molecule, NMR gives information about the number of magnetically distinct atoms of the type being studied. When hydrogen nuclei (protons) are studied, for instance, one can determine the number of each of the distinct types of hydrogen nuclei as well as obtain information regarding the nature of the immediate environment of each type. Similar information can be determined for the carbon nuclei. The combination of IR and NMR data is often sufficient to determine completely the structure of an unknown molecule.

NUCLEAR SPIN STATES

Many atomic nuclei have a property called **spin:** the nuclei behave as if they were spinning. In fact, any atomic nucleus that possesses either *odd* mass, *odd* atomic number, or both has a quantized **spin angular momentum** and a magnetic moment. The more common nuclei that possess spin include ${}^{1}_{1}H$, ${}^{2}_{1}H$, ${}^{13}_{6}C$, ${}^{14}_{7}N$, ${}^{17}_{8}O$, and ${}^{19}_{9}F$. Notice that the nuclei of the ordinary (most abundant) isotopes of carbon and oxygen, ${}^{12}_{6}C$ and ${}^{16}_{8}O$, are not included among those with the spin property. However, the nucleus of the ordinary hydrogen atom, the proton, does have spin. For each nucleus with spin, the number of allowed spin states it may adopt is quantized and is determined by its nuclear spin quantum number *I*. For each nucleus, the number *I* is a physical constant, and there are $2I + 1$ allowed spin states with integral differences ranging from $+I$ to $-I$. The individual spin states fit into the sequence

$$+I, (I - 1), \ldots, (-I + 1), -I \qquad \textbf{Equation 5.1}$$

For instance, a proton (hydrogen nucleus) has the spin quantum number $I=\frac{1}{2}$ and has two allowed spin states $\left[2\left(\frac{1}{2}\right)+1=2\right]$ for its nucleus: $-\frac{1}{2}$ and $+\frac{1}{2}$. For the chlorine nucleus, $I=\frac{3}{2}$ and there are four allowed spin states $\left[2\left(\frac{3}{2}\right)+1=4\right]$: $-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}$, and $+\frac{3}{2}$. Table 5.1 gives the spin quantum numbers of several nuclei.

Table 5.1: Spin quantum numbers of some common nuclei

Element	Nuclear spin quantum number	Number of spin states
${}^{1}_{1}H$	$\frac{1}{2}$	2
${}^{2}_{1}H$	1	3
${}^{12}_{6}C$	0	0
${}^{13}_{6}C$	$\frac{1}{2}$	2
${}^{14}_{7}N$	1	3
${}^{16}_{8}O$	0	0
${}^{17}_{8}O$	$\frac{5}{2}$	6

$^{19}_{9}F$	$\frac{1}{2}$	2
$^{31}_{15}P$	$\frac{1}{2}$	2
$^{35}_{17}Cl$	$\frac{3}{2}$	4

In the absence of an applied magnetic field, all the spin states of a given nucleus are of equivalent energy (degenerate), and in a collection of atoms, all of the spin states should be almost equally populated, with the same number of atoms having each of the allowed spins.

NUCLEAR MAGNETIC MOMENTS

Spin states are not of equivalent energy in an applied magnetic field because the nucleus is a charged particle, and any moving charge generates a magnetic field of its own. Thus, the nucleus has a magnetic moment μ generated by its charge and spin. A hydrogen nucleus may have a clockwise $\left(+\frac{1}{2}\right)$ or counterclockwise $\left(-\frac{1}{2}\right)$ spin, and the nuclear magnetic moments (μ) in the two cases are pointed in opposite directions. In an applied magnetic field, all protons have their magnetic moments either aligned with the field or opposed to it. Figure 5.1 illustrates these two situations.

Hydrogen nuclei can adopt only one or the other of these orientations with respect to the applied field. The spin state $+\frac{1}{2}$ is of lower energy since it is aligned with the field, while the spin state $-\frac{1}{2}$ is of higher energy since it is opposed to the applied field. This should be intuitively obvious to anyone who thinks a little about the two situations depicted in Figure 5.2, involving magnets. The aligned configuration of magnets is stable (low energy). However, where the magnets are opposed (not aligned), the center magnet is repelled out of its current (high-energy) orientation. If the central magnet were placed on a pivot, it would spontaneously spin around the pivot into alignment (low energy). Hence, as an external magnetic field is applied, the degenerate spin states split into two states of unequal energy, as shown in Figure 5.3.

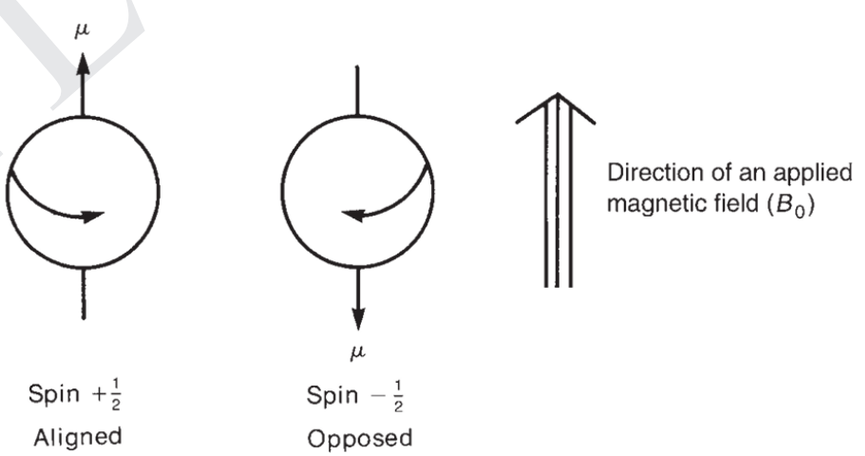


Fig. 5.1: The two allowed spin states for a proton.

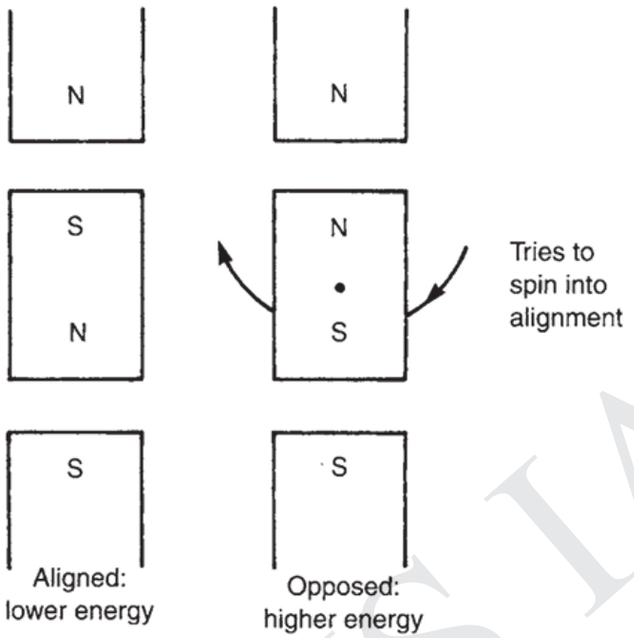


Fig. 5.2: Aligned and opposed arrangements of bar magnets.

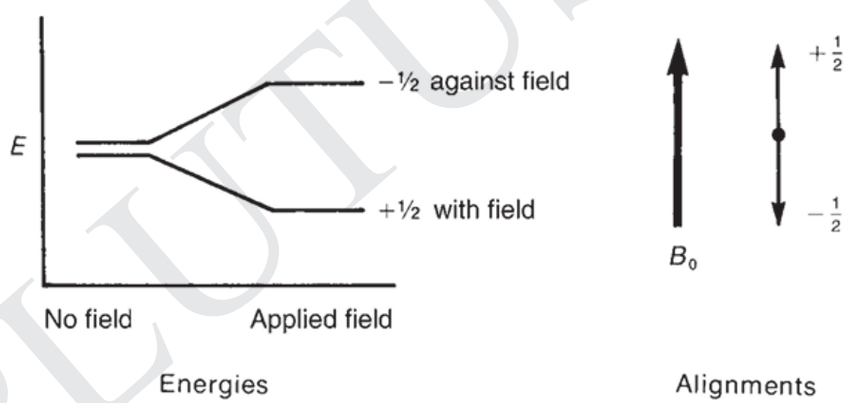


Fig. 5.3: The spin states of a proton in the absence and in the presence of an applied magnetic field.

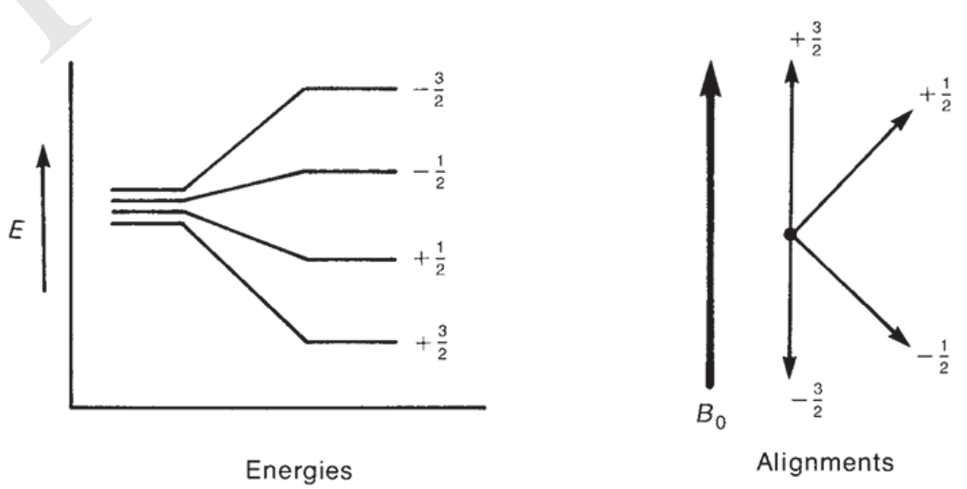


Fig. 5.4: The spin states of a chlorine atom both in the presence and in the absence of an applied magnetic field.

In the case of a chlorine nucleus, there are four energy levels, as shown in Figure 5.4. The $+\frac{3}{2}$ and $-\frac{3}{2}$ spin states are aligned with the applied field and opposed to the applied field, respectively. The $+\frac{1}{2}$ and $-\frac{1}{2}$ spin states have intermediate orientations, as indicated by the vector diagram on the right in Figure 5.4.

ABSORPTION OF ENERGY

The nuclear magnetic resonance phenomenon occurs when nuclei aligned with an applied field are induced to absorb energy and change their spin orientation with respect to the applied field. Figure 5.5 illustrates this process for a hydrogen nucleus.

The energy absorption is a quantized process, and the energy absorbed must equal the energy difference between the two states involved.

$$E_{absorbed} = \left(E_{-\frac{1}{2}\text{state}} - E_{+\frac{1}{2}\text{state}}\right) = h\nu \qquad \textbf{Equation 5.2}$$

In practice, this energy difference is a function of the strength of the applied magnetic field B_0, as illustrated in Figure 5.6.

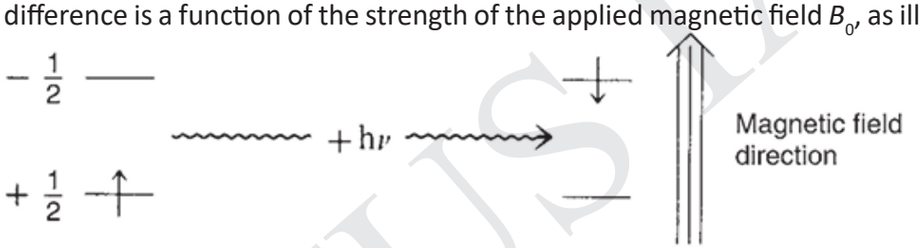


Fig. 5.5: The NMR absorption process for a proton.

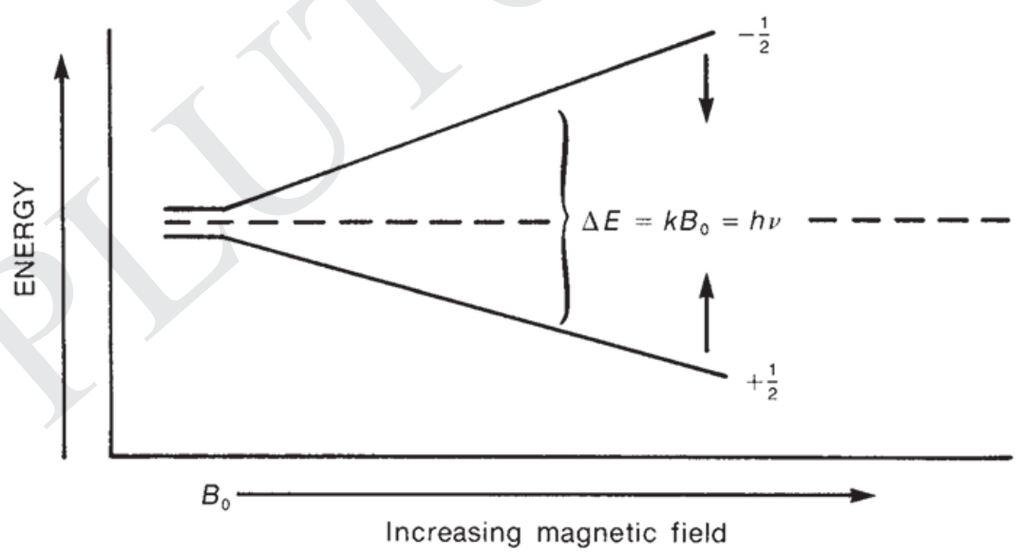


Fig. 5.6: The spin-state energy separation as a function of the strength of the applied magnetic field B_0.

The stronger the applied magnetic field, the greater the energy difference between the possible spin states:

$$\Delta E = f(B_0) \qquad \textbf{Equation 5.3}$$

The magnitude of the energy-level separation also depends on the particular nucleus involved. Each nucleus (hydrogen, chlorine, and so on) has a different ratio of magnetic moment to angular momentum since each has different charge and mass. This ratio, called the **magnetogyric ratio ϒ,** is a constant for each nucleus and determines the energy dependence on the magnetic field:

$$\Delta E = f(\Upsilon B_0) = h\nu \qquad \textbf{Equation 5.4}$$

Since the angular momentum of the nucleus is quantized in units of $h/2\pi$, the final equation takes the form

$$\Delta E = \gamma\left(\frac{h}{2\pi}\right)B_0 = h\nu \qquad \textbf{Equation 5.5}$$

Solving for the frequency of the absorbed energy,

$$\nu = \left(\frac{\gamma}{2\pi}\right)B_0 \qquad \textbf{Equation 5.6}$$

If the correct value of ϒ for the proton is substituted, one finds that an unshielded proton should absorb radiation of frequency 42.6 MHz in a field of strength 1 Tesla (10,000 Gauss) or radiation of frequency 60.0 MHz in a field of strength 1.41 Tesla (14,100 Gauss). Table 5.2 shows the field strengths and frequencies at which several nuclei have resonance (i.e., absorb energy and make spin transitions).

Table 5.2: Frequencies and field strengths at which selected nuclei have their nuclear resonances

Isotope	Natural Abundance (%)	Field Strength, B_0 (Tesla[a])	Frequency, ν (MHz)	Magnetogyric Ratio, ϒ (radians/Tesla)
^{1}H	99.98	1.00 1.41 2.35 4.70 7.05	42.6 60.0 100.0 200.0 300.0	267.53
^{2}H	0.0156	1.00	6.5	41.1
^{13}C	1.108	1.00 1.41 2.35 4.70 7.05	10.7 15.1 25.0 50.0 75.0	67.28
^{19}F	100.0	1.00	40.0	251.7
^{31}P	100.0	1.00	17.2	108.3

[a] 1 Tesla = 10,000 Gauss.

Although many nuclei are capable of exhibiting magnetic resonance, the organic chemist is mainly interested in hydrogen and carbon resonances. This chapter emphasizes hydrogen. Chapter 6 will discuss nuclei other than hydrogen—for example, carbon-13, fluorine-19, phosphorus-31, and deuterium (hydrogen-2).

For a proton (the nucleus of a hydrogen atom), if the applied magnetic field has a strength of approximately 1.41 Tesla, the difference in energy between the two spin states of the proton is about 2.39×10^{-5} kJ/mole. Radiation with a frequency of about 60 MHz (60,000,000 Hz), which lies in the radiofrequency (RF) region of the electromagnetic spectrum, corresponds to this energy difference. Other nuclei have both larger and smaller energy differences between spin states than do hydrogen nuclei. The earliest nuclear magnetic resonance spectrometers applied a variable magnetic field with a range of strengths near 1.41 Tesla and supplied a constant radiofrequency radiation of 60 MHz. They effectively induced transitions only among proton (hydrogen) spin states in a molecule and were not useful for other nuclei. Separate instruments were required to observe transitions in the nuclei of other elements, such as carbon and phosphorus. Fourier transform instruments (Section 5.7B), which are in common use today, are equipped to observe the nuclei of several different elements in a single instrument. Instruments operating at frequencies of 300 and 400 MHz are now quite common, and instruments with frequencies above 600 MHz are found in the larger research universities.

THE MECHANISM OF ABSORPTION (RESONANCE)

To understand the nature of a nuclear spin transition, the analogy of a child's spinning top is useful. Protons absorb energy because they begin to precess in an applied magnetic field. The phenomenon of precession is similar to that of a spinning top. Owing to the influence of the earth's gravitational field, the top begins to "wobble," or precess, about its axis (Fig. 5.7a). A spinning nucleus behaves in a similar fashion under the influence of an applied magnetic field (Fig. 5.7b).

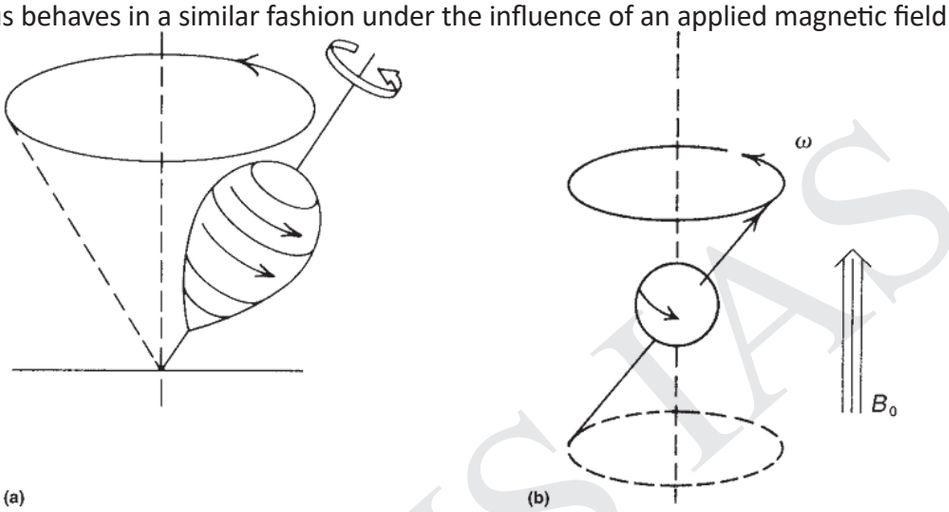


Fig. 5.7: (a) A top precessing in the earth's gravitational field; (b) the precession of a spinning nucleus resulting from the influence of an applied magnetic field.

When the magnetic field is applied, the nucleus begins to precess about its own axis of spin with angular frequency , which is sometimes called its **Larmor frequency**. The frequency at which a proton precesses is directly proportional to the strength of the applied magnetic field; the stronger the applied field, the higher the rate (angular frequency ω) of precession. For a proton, if the applied field is 1.41 Tesla (14,100 Gauss), the frequency of precession is approximately 60 MHz.

Since the nucleus has a charge, the precession generates an oscillating electric field of the same frequency. If radiofrequency waves of this frequency are supplied to the precessing proton, the energy can be absorbed. That is, when the frequency of the oscillating electric field component of the incoming radiation just matches the frequency of the electric field generated by the precessing nucleus, the two fields can couple, and energy can be transferred from the incoming radiation to the nucleus, thus causing a spin change. This condition is called **resonance**, and the nucleus is said to have resonance with the incoming electromagnetic wave. Figure 5.8 schematically illustrates the resonance process.

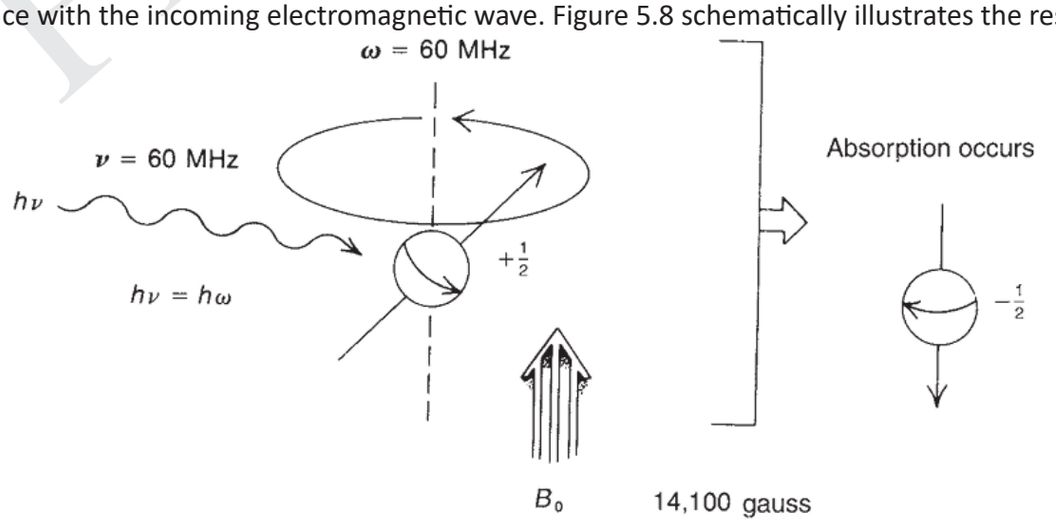


Fig. 5.8: The nuclear magnetic resonance process; absorption occurs when ν = ω.

THE CHEMICAL SHIFT AND SHIELDING

Nuclear magnetic resonance has great utility because not all protons in a molecule 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 valence-shell electron densities vary from one proton to another. The protons are **shielded** by the electrons that surround them. In an applied magnetic field, the valence electrons of the protons are caused to circulate. This circulation, called a local diamagnetic current, generates a counter magnetic field that opposes the applied magnetic field. Figure 5.10 illustrates this effect, which is called **diamagnetic shielding** or **diamagnetic anisotropy**.

Circulation of electrons around a nucleus can be viewed as being similar to the flow of an electric current in an electric wire. From physics, we know that the flow of a current through a wire induces a magnetic field. In an atom, the local diamagnetic current generates a secondary, induced magnetic field that has a direction opposite that of the applied magnetic field.

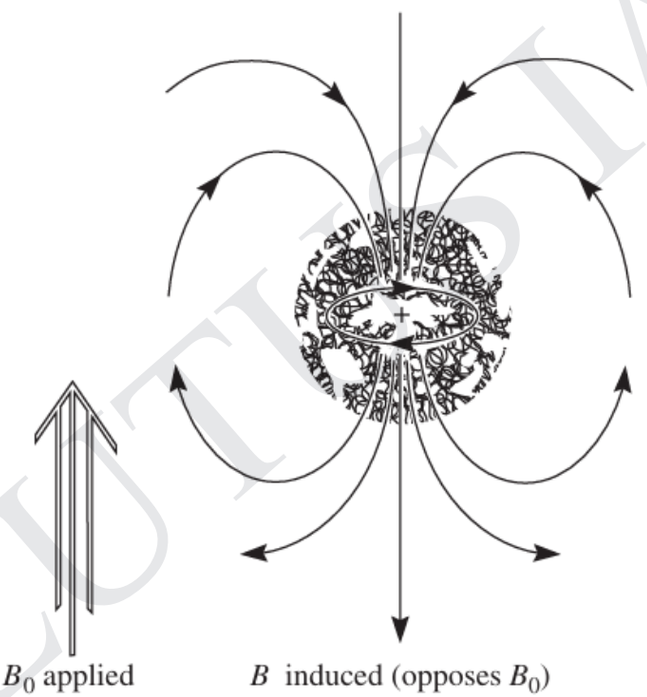


Fig. 5.10: Diamagnetic anisotropy—the diamagnetic shielding of a nucleus caused by the circulation of valence electrons.

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 the electron density around a nucleus, the greater the induced counter field that opposes the applied field. The counter field that shields a nucleus diminishes the net applied magnetic field that the nucleus experiences. As a result,the nucleus precesses at a lower frequency. This means that it also absorbs radiofrequency radiation at this lower frequency. Each proton in a molecule is in a slightly different chemical environment and consequently has a slightly different amount of electronic shielding,which results in a slightly different resonance frequency.

These differences in resonance frequency are very small. For instance, the difference between the resonance frequencies of the protons in chloromethane and those in fluoromethane is only 72 Hz when the applied field is 1.41 Tesla. Since the radiation used to induce proton spin transitions at that magnetic field strength is of a frequency near 60 MHz, the difference between chloromethane and fluoromethane represents a change in frequency of only slightly more than one part per million! It is very difficult to measure exact frequencies to that precision; hence,no attempt is made to measure the exact resonance frequency of any proton. Instead,a reference compound is placed in the solution of the substance to be measured,and the resonance frequency of each proton in the sample is measured relative to the resonance frequency of the protons of the reference substance. In other words, the frequency *difference* is measured directly. The standard

reference substance that is used universally is **tetramethylsilane, $(CH_3)_4Si$,** also called **TMS**. This compound was chosen initially because the protons of its methyl groups are more shielded than those of most other known compounds. At that time,no compounds that had better-shielded hydrogens than TMS were known, and it was assumed that TMS would be a good reference substance since it would mark one end of the range. Thus,when another compound is measured, the resonances of its protons are reported in terms of how far (in Hertz) they are shifted from those of TMS.

The shift from TMS for a given proton depends on the strength of the applied magnetic field. In an applied field of 1.41 Tesla the resonance of a proton is approximately 60 MHz, whereas in an applied field of 2.35 Tesla (23,500 Gauss) the resonance appears at approximately 100 MHz. The ratio of the resonance frequencies is the same as the ratio of the two field strengths:

$$\frac{100\text{ MHz}}{60\text{ MHz}} = \frac{2.35\text{ Tesla}}{1.41\text{ Tesla}} = \frac{23{,}500\text{ Gauss}}{14{,}100\text{ Gauss}} = \frac{5}{3}$$

Hence, for a given proton, the shift (in Hertz) from TMS is $\frac{5}{3}$ larger in the 100-MHz range (B_0 = 2.35 Tesla) than in the 60-MHz range (B_0 = 1.41 Tesla). This can be confusing for workers trying to compare data if they have spectrometers that differ in the strength of the applied magnetic field. The confusion is easily overcome if one defines a new parameter that is independent of field strength—for instance, by dividing the shift in Hertz of a given proton by the frequency in megahertz of the spectrometer with which the shift value was obtained. In this manner, a field-independent measure called the **chemical shift** (δ) is obtained

$$\delta = \frac{(\text{shift in Hz})}{(\text{spectrometer frequency in MHz})} \qquad \textbf{Equation 5.8}$$

The chemical shift in δ units expresses the amount by which a proton resonance is shifted from TMS, in parts per million (ppm), of the spectrometer's basic operating frequency. Values of δ for a given proton are always the same irrespective of whether the measurement was made at 60 MHz (B_0 = 1.41 Tesla) or at 100 MHz (B_0 = 2.35 Tesla). For instance, at 60 MHz the shift of the protons in CH_3Br is 162 Hz from TMS, while at 100 MHz the shift is 270 Hz. However, both of these correspond to the same value of δ(2.70 ppm):

$$\delta = \frac{162\text{ Hz}}{60\text{ MHz}} = \frac{270\text{ Hz}}{100\text{ MHz}} = 2.70\text{ ppm}$$

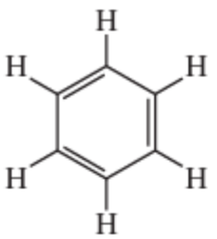
By agreement, most workers report chemical shifts in **delta (δ) units,** or **parts per million (ppm),** of the main spectrometer frequency. On this scale, the resonance of the protons in TMS comes at exactly 0.00 ppm (by definition).

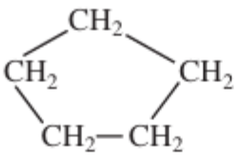
The NMR spectrometer actually scans from high δ values to low ones (as will be discussed in Section 5.7). Following is a typical chemical shift scale with the sequence of δ values that would be found on a typical NMR spectrum chart.

CHEMICAL EQUIVALENCE—A BRIEF OVERVIEW

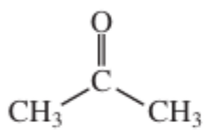
All of the protons found in chemically identical environments within a molecule are **chemically equivalent,** and they often exhibit the same chemical shift. Thus, all the protons in tetramethylsilane (TMS) or all the protons in benzene, cyclopentane, or acetone—which are molecules that have protons that are equivalent by symmetry considerations—have resonance at a single value of δ (but a different value from that of each of the other molecules in the same group). Each such compound gives rise to a single absorption peak in its NMR spectrum. The protons are said to be chemically equivalent. On the other hand, a molecule that has sets of protons that are chemically distinct from one another may give rise to a different absorption peak from each set, in which case the sets of protons are chemically nonequivalent.

The following examples should help clarify these relationships:

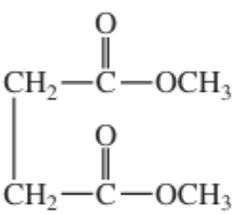


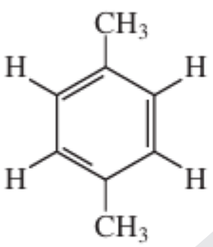


Molecules giving rise to one NMR absorption peak—all protons chemically equivalent

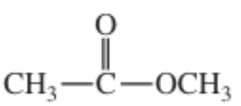


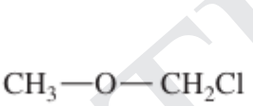
$(CH_3)_4Si$

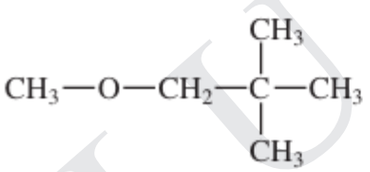




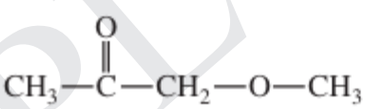
Molecules giving rise to two NMR absorption peaks—two different sets of chemically equivalent protons







Molecules giving rise to three NMR absorption peaks—three different sets of chemically equivalent protons



You can see that an NMR spectrum furnishes a valuable type of information on the basis of the number of different peaks observed; that is, the number of peaks corresponds to the number of chemically distinct types of protons in the molecule. Often,protons that are chemically equivalent are also **magnetically equivalent**. Note, however, that *in some instances, protons that are chemically equivalent are not magnetically equivalent.* We will explore this circumstance in Chapter 7, which examines chemical and magnetic equivalence in more detail.

INTEGRALS AND INTEGRATION

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. Hence, in phenylacetone (see Fig. 5.12), 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. 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. Figure 5.18 is a 60-MHz NMR spectrum of benzyl acetate, showing each of the peaks integrated in this way.

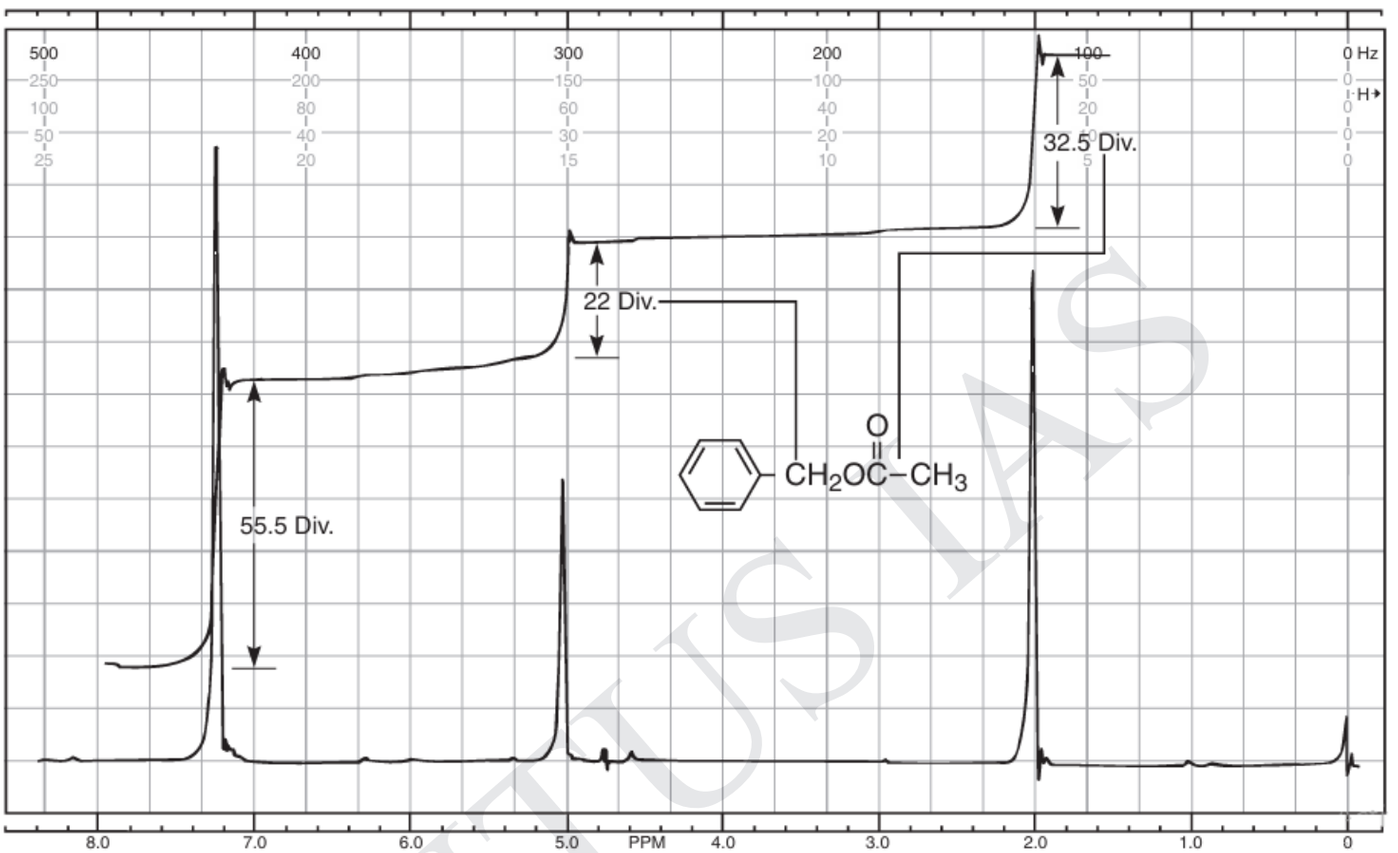


Fig. 5.18: Determination of the integral ratios for benzyl acetate (60 MHz).

Note 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. Benzyl acetate provides a good example of this. 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:

$$\frac{55.5 \text{ div}}{22.0 \text{ div}} = 2.52 \qquad \frac{22.0 \text{ div}}{22.0 \text{ div}} = 1.00 \qquad \frac{32.5 \text{ div}}{22.0 \text{ div}} = 1.48$$

Thus, the number ratio of the protons of all the types is 2.52:1.00:1.48. If we assume that the peak at 5.1 ppm is really due to two hydrogens, and if we assume that the integrals are slightly (as much as 10%) in error, then we arrive at the true ratio by multiplying each figure by 2 and rounding off to 5:2:3. 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. Notice that the integrals give the simplest ratio, but not necessarily the true ratio, of numbers of protons of each type.

The spectrum of benzyl acetate shown in Figure 5.19 was obtained on a modern FT-NMR instrument operating at 300 MHz. The spectrum is similar to that obtained at 60 MHz. Integral lines are shown as before,but in addition,you will observe that digitized integral values for the integrals are printed below the peaks. The areas under the curve are relative and not absolute. The integral values are proportional to the actual number of protons represented by the peak. You will need to "massage" the numbers shown in Figure 5.19 to obtain the actual number of protons represented by a particular peak. You will find that it is much easier to do the math when digitized values are provided rather than by measuring the change in heights of the integral line. Notice that benzyl acetate has 10 total protons, so you need to massage the numbers to obtain 10 protons.

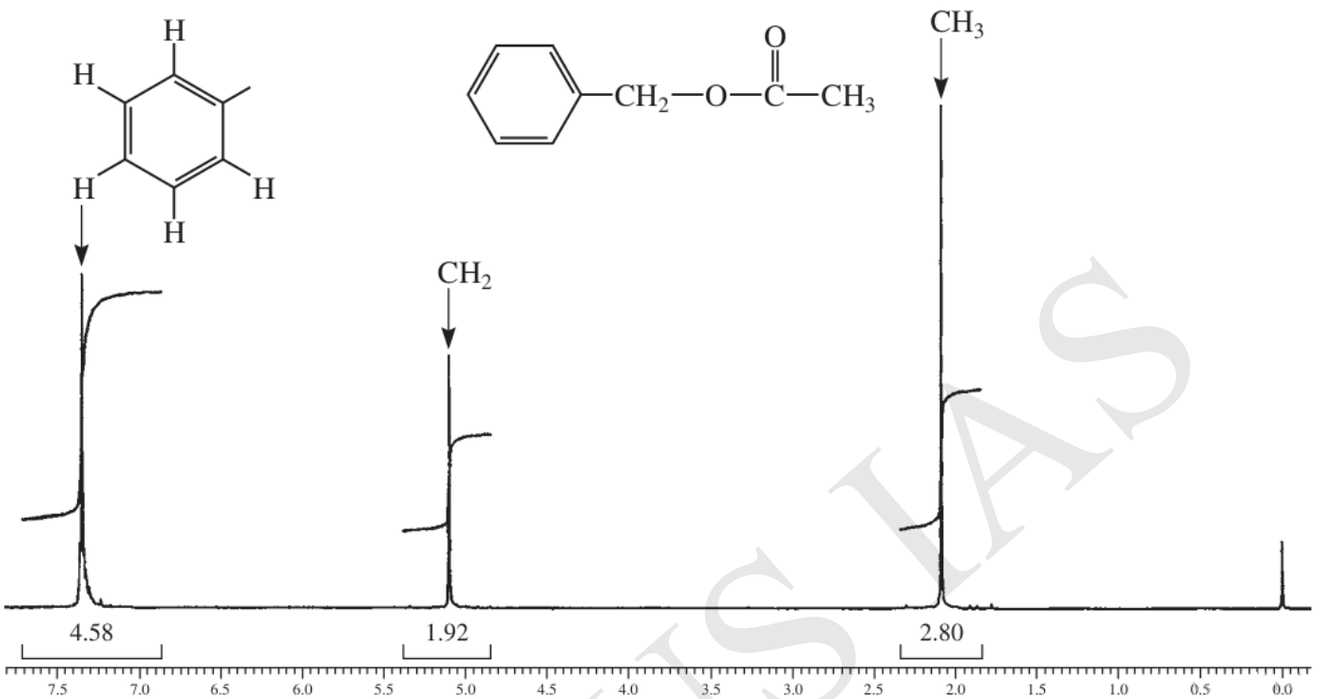


Fig. 5.19: An integrated spectrum of benzyl acetate determined on a 300-MHz FT-NMR instrument.

Proceed as follows:

Divide by the Smallest Integral Value	Multiply by 2	Round Off
4.58/1.92 = 2.39	(2.39)(2) = 4.78	5H
1.92/1.92 = 1.0	(1.0)(2) = 2.0	2H
2.80/1.92 = 1.46	(1.46)(2) = 2.92	3H
		10H

CHEMICAL ENVIRONMENT AND CHEMICAL SHIFT

If the resonance frequencies of all protons in a molecule were the same, NMR would be of little use to the organic chemist. Not only do different types of protons have different chemical shifts, but each also has a characteristic value of chemical shift. Every type of proton has only a limited range of δ values over which it gives resonance. Hence, the numerical value (in δ units or ppm) of the chemical shift for a proton gives a clue regarding the type of proton originating the signal, just as an infrared frequency gives a clue regarding the type of bond or functional group.

For instance, notice that the aromatic protons of both phenylacetone (Fig. 5.12) and benzyl acetate (Fig. 5.18) have resonance near 7.3 ppm, and that both of the methyl groups attached directly to a carbonyl have resonance at about 2.1 ppm. Aromatic protons characteristically have resonance near 7 to 8 ppm, whereas acetyl groups (methyl groups of this type) have their resonance near 2 ppm. These values of chemical shift are diagnostic. Notice also how the resonance of the benzyl (—CH_2—) protons comes at a higher value of chemical shift (5.1 ppm) in benzyl acetate than in phenylacetone (3.6 ppm). Being attached to the electronegative element oxygen,these protons are more deshielded (see Section 5.11) than those in phenylacetone. A trained chemist would readily recognize the probable presence of the oxygen from the value of chemical shift shown by these protons.

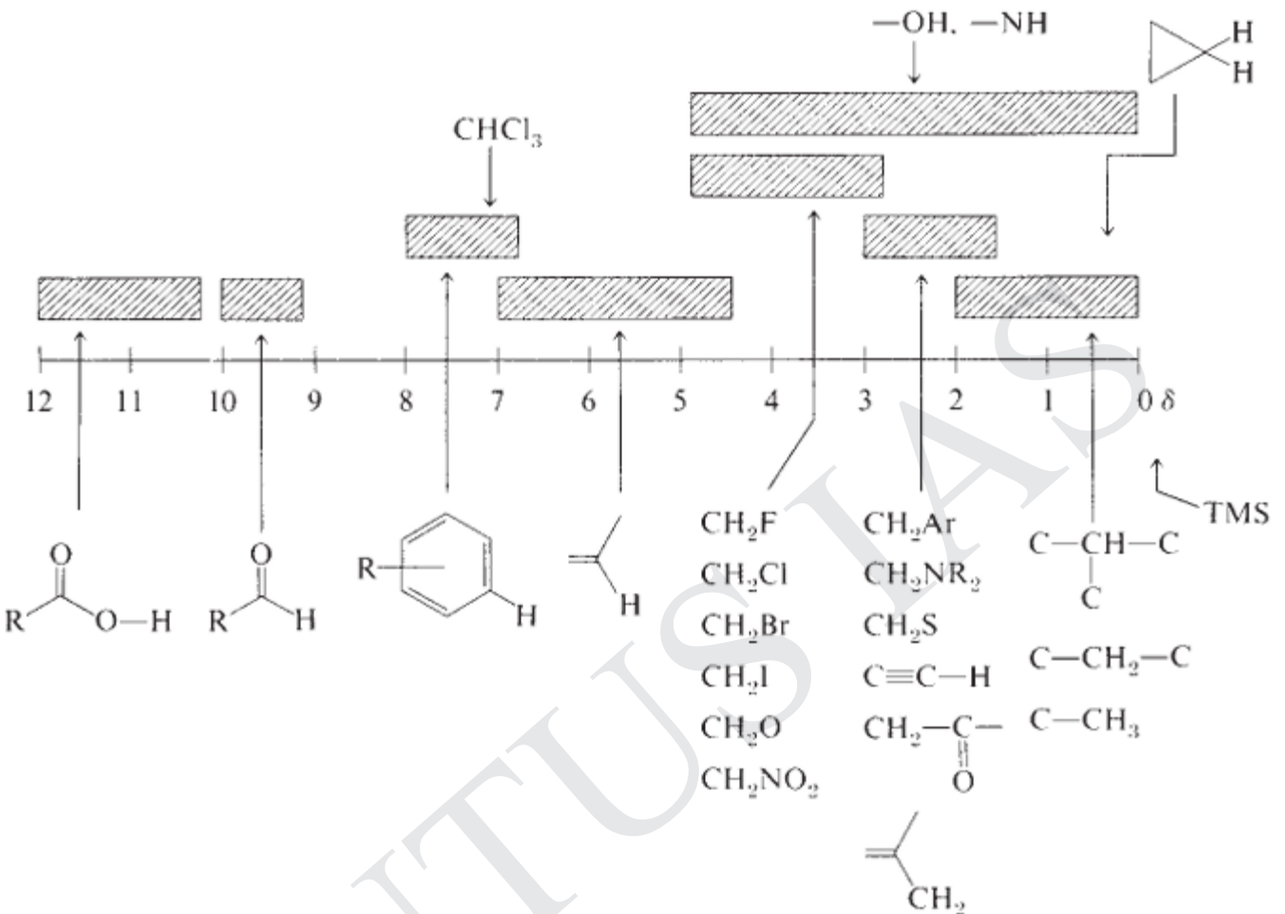


Fig. 5.20: A simplified correlation chart for proton chemical shift values.

It is important to learn the ranges of chemical shifts over which the most common types of protons have resonance. Figure 5.20 is a correlation chart that contains the most essential and frequently encountered types of protons. Table 5.4 lists the chemical shift ranges for selected types of protons. For the beginner, it is often difficult to memorize a large body of numbers relating to chemical shifts and proton types. One actually need do this only crudely. It is more important to "get a feel" for the regions and the types of protons than to know a string of actual numbers. To do this, study Figure 5.20 carefully. Table 5.4 and Appendices 2 and 3 give more detailed listings of chemical shifts.

LOCAL DIAMAGNETIC SHIELDING

A. Electronegativity Effects

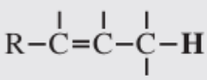
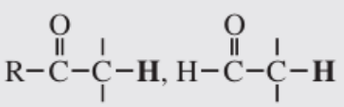
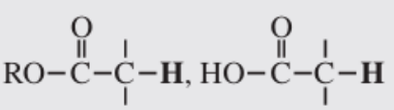
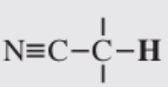
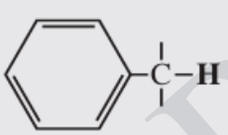
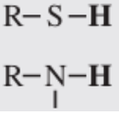
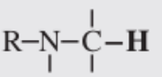
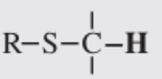
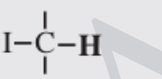
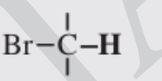
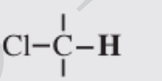
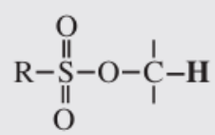
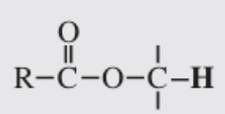
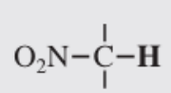
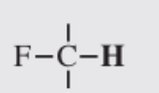
The trend of chemical shifts that is easiest to explain is that involving electronegative elements substituted on the same carbon to which the protons of interest are attached. The chemical shift simply increases as the electronegativity of the attached element increases. Table 5.5 illustrates this relationship for several compounds of the type CH_3X.

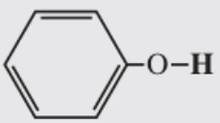
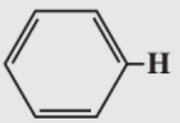
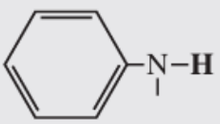
Multiple substituents have a stronger effect than a single substituent. The influence of the substituent drops off rapidly with distance, an electronegative element having little effect on protons that are more than three carbons distant. Table 5.6 illustrates these effects for the underlined protons.

Section 5.6 briefly discussed the origin of the electronegativity effect. Electronegative substituents attached to a carbon atom, because of their electron-withdrawing effects, reduce the valence electron density around the protons attached to that carbon. These electrons, it will be recalled, shield the proton from the applied magnetic field. Figure 5.10 illustrates this effect, called *local diamagnetic shielding*. Electronegative substituents on carbon reduce the local diamagnetic shielding in the vicinity of the attached protons because they reduce the electron density around those

protons. Substituents that have this type of effect are said to deshield the proton. The greater the electronegativity of the substituent, the more it deshields protons and hence the greater is the chemical shift of those protons.

Table 5.4: Approximate chemical shift ranges (ppm) for selected types of protons[a]

$R-CH_3$		0.7 – 1.3
$R-CH_2-R$		1.2 – 1.4
R_3CH		1.4 – 1.7
		1.6 – 2.6
		2.1 – 2.4
		2.1 – 2.5
		2.1 – 3.0
		2.3 – 2.7
$R-C\equiv C-H$		1.7 – 2.7
$R-S-H$	var	1.0 – 4.0[b]
	var	0.5 – 4.0[b]
		2.2 – 2.9
		2.0 – 3.0
		2.0 – 4.0
		2.7 – 4.1
		3.1 – 4.1
		ca. 3.0
		3.2 – 3.8
		3.5 – 4.8
		4.1 – 4.3
		4.2 – 4.8

R–O–**H**	var	0.5 – 5.0[b]	R–C=C–**H**	4.5 – 6.5
	var	4.0 – 7.0[b]		6.5 – 8.0
	var	3.0 – 5.0[b]	R–C(=O)–**H**	9.0 – 10.0
R–C(=O)–N–**H**	var	5.0 – 9.0[b]	R–C(=O)–O**H**	11.0 – 12.0

[a]For those hydrogens shown as $-\underset{|}{C}-H$, if that hydrogen is part of a methyl group (CH_3) the shift is generally at the low end of the range given, if the hydrogen is in a methylene group ($-CH_2-$) the shift is intermediate, and if the hydrogen is in a methine group ($-\underset{|}{C}H-$), the shift is typically at the high end of the range given.

[b]The chemical shift of these groups is variable, depending not only on the chemical environment in the molecule, but also on concentration, temperature, and solvent.

Table 5.5: Dependence of the Chemical Shift of CH_3X on the Element X

Compound CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ	4.26	3.40	3.05	2.68	2.16	0.23	0

Table 5.6: Substitution Effects

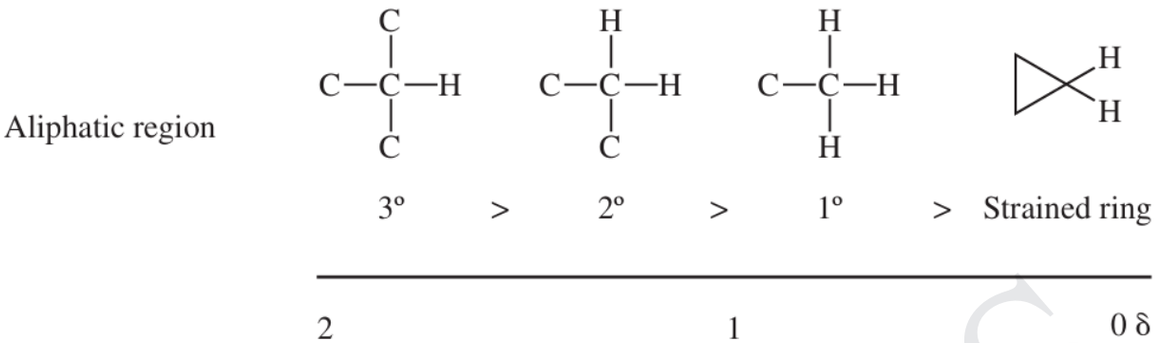
$C\underline{H}Cl_3$	$C\underline{H}_2Cl_2$	$C\underline{H}_3Cl$	$-C\underline{H}_2Br$	$-C\underline{H}_2-CH_2Br$	$-C\underline{H}_2-CH_2CH_2Br$
7.27	5.30	3.05	3.30	1.69	1.25

B. Hybridization Effects

The second important set of trends is that due to differences in the hybridization of the atom to which hydrogen is attached.

***sp*³ Hydrogens**

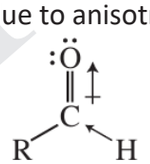
Referring to Figure 5.20 and Table 5.4, notice that all hydrogens attached to purely *sp*³ carbon atoms (C—CH_3, C—CH_2—C, $C-\underset{|}{C}H-C$, cycloalkanes) have resonance in the limited range from 0 to 2 ppm, provided that no electronegative elements or π-bonded groups are nearby. At the extreme right of this range are TMS (0 ppm) and hydrogens attached to carbons in highly strained rings (0–1 ppm)—as occurs, for example, with cyclopropyl hydrogens. Most methyl groups occur near 1 ppm if they are attached to other *sp*³ carbons. Methylene-group hydrogens (attached to *sp*³ carbons) appear at greater chemical shifts (near 1.2 to 1.4 ppm) than do methyl-group hydrogens. Tertiary methine hydrogens occur at higher chemical shift than secondary hydrogens, which in turn have a greater chemical shift than do primary or methyl hydrogens. The following diagram illustrates these relationships:



Of course, hydrogens on an sp^3 carbon that is 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 vinyl hydrogens (—C=C—H) have resonance in the range from 4.5 to 7 ppm. In an sp^2-1s C—H bond, the carbon atom has more *s* character (33% *s*), which effectively renders it "more electronegative" than an sp^3 carbon (25% *s*). Remember that *s* orbitals hold electrons closer to the nucleus than do the carbon *p* orbitals. If the sp^2 carbon atom holds its electrons more tightly, this results in less shielding for the H nucleus than in an sp^3-1*s* bond. Thus, vinyl hydrogens have a greater chemical shift (5 to 6 ppm) than aliphatic hydrogens on sp^3 carbons (1 to 4 ppm). Aromatic hydrogens appear in a range farther downfield (7 to 8 ppm). The downfield positions of vinyl and aromatic resonances are, however, greater than one would expect based on these hybridization differences. Another effect, called anisotropy, is responsible for the largest part of these shifts (and will be discussed in Section 5.12). Aldehyde 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. Aldehyde protons, like aromatic and alkene protons, exhibit an anomalously large chemical shift due to anisotropy (Section 5.12).



An aldehyde

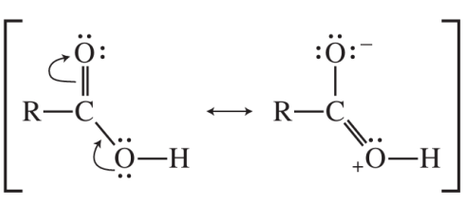
sp Hydrogens

Acetylenic hydrogens (C—H, *sp*-1*s*) appear anomalously at 2 to 3 ppm owing to anisotropy (to be discussed in Section 5.12). On the basis of hybridization alone, as already discussed, one would expect the acetylenic proton to have a chemical shift greater than that of the vinyl proton. An *sp* carbon should behave as if it were more electronegative than an sp^2 carbon. This is the opposite of what is actually observed.

C. Acidic and Exchangeable Protons; Hydrogen Bonding

Acidic Hydrogens

Some of the least-shielded protons are those attached to carboxylic acids. These protons have their resonances at 10 to 12 ppm.



Both resonance and the electronegativity effect of oxygen withdraw electrons from the acid proton.

Hydrogen Bonding and Exchangeable Hydrogens

Protons that can exhibit 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. Table 5.7 lists the ranges over which some of these types of protons are found. The more hydrogen bonding that takes place, the more deshielded a proton becomes. The amount of hydrogen bonding

Table 5.7: Typical Ranges for Protons with Variable Chemical Shift

Acids	RCOOH	10.5–12.0 ppm
Phenols	ArOH	4.0–7.0
Alcohols	ROH	0.5–5.0
Amines	RNH_2	0.5–5.0
Amides	$RCONH_2$	5.0–8.0
Enols	CH=CH—OH	>15

is often a function of concentration and temperature. The more concentrated the solution, the more molecules can come into contact with each other and hydrogen bond. 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.

Free (dilute solution) Hydrogen bonded (concentrated solution)

Hydrogens that can exchange either with the solvent medium or with one another also tend to be variable in their absorption positions. The following equations illustrate possible situations:

$$R—O—H_a + R'—O—H_b \rightleftharpoons R—O—H_b + R'—O—H_a$$

$$R—O—H + H{:}SOLV \rightleftharpoons R—\overset{+}{O}(H)—H + {:}SOLV^-$$

$$R—O—H + {:}SOLV \rightleftharpoons H{:}SOLV^+ + R—O{:}^-$$

Chapter 8 will discuss all of these situations in more detail.

MAGNETIC ANISOTROPY

Figure 5.20 clearly shows that there are some types of protons with chemical shifts that are not easily explained by simple considerations of the electronegativity of the attached groups. For instance, consider 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.

Take benzene, for example. When it is placed in a magnetic field, the π electrons in the aromatic ring system are induced to circulate around the ring. This circulation is called a **ring current**. The moving electrons generate a magnetic field much like that generated in a loop of wire through which a current is induced to flow. The magnetic field covers a spatial volume large enough that it influences the shielding of the benzene hydrogens. Figure 5.21 illustrates this phenomenon. The benzene hydrogens are said to be deshielded by the diamagnetic anisotropy of the ring. In electromagnetic terminology, an isotropic field is one of either uniform density or spherically symmetric distribution; an anisotropic field

is not isotropic; that is, it is nonuniform. 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 nonhomogeneity in the immediate vicinity of the molecule. Thus, a proton attached to a benzene ring is influenced by three magnetic fields: the strong magnetic field applied by the electromagnets of the NMR spectrometer and two weaker fields, one due to the usual shielding by the valence electrons around the proton, and the other due to the anisotropy generated by the ring-system π electrons. It is the anisotropic effect that gives the benzene protons a chemical shift that is greater than expected. These protons just happen to lie in a deshielding region of the anisotropic field. If a proton were placed in the center of the ring rather than on its periphery, it would be found to be shielded since the field lines there would have the opposite direction from those at the periphery.

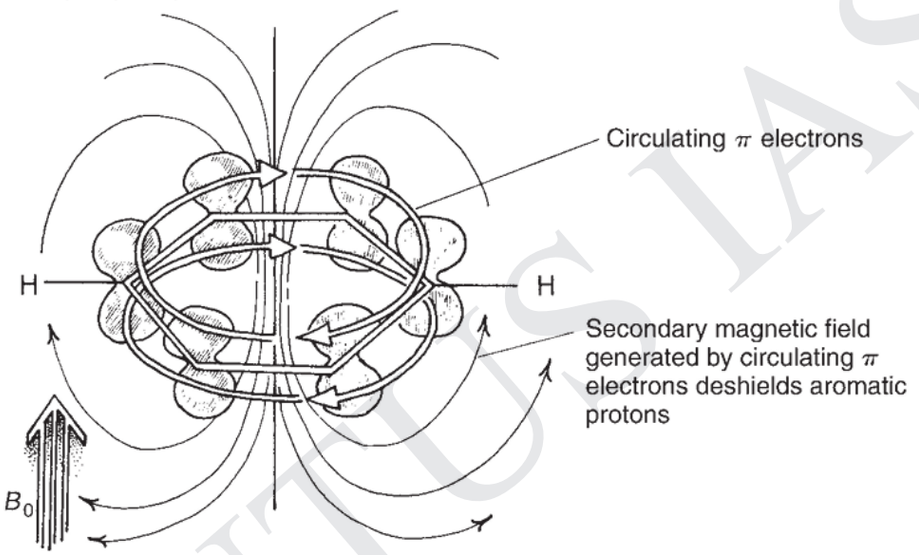


Fig. 5.21: Diamagnetic anisotropy in benzene.

All groups in a molecule that have π electrons generate secondary anisotropic fields. In acetylene, the magnetic field generated by induced circulation of the π electrons has a geometry such that the acetylenic hydrogens are shielded (Fig. 5.22). Hence, acetylenic hydrogens have resonance at higher field than expected. The shielding and deshielding regions due to the various π electron functional groups have characteristic shapes and directions, and Figure 5.23 illustrates these for a number of groups. Protons falling within the conical areas are shielded, and those falling outside the conical areas are deshielded. The magnitude of the anisotropic field diminishes with distance, and beyond a certain distance there is essentially no anisotropic effect. Figure 5.24 shows the effects of anisotropy in several actual molecules.

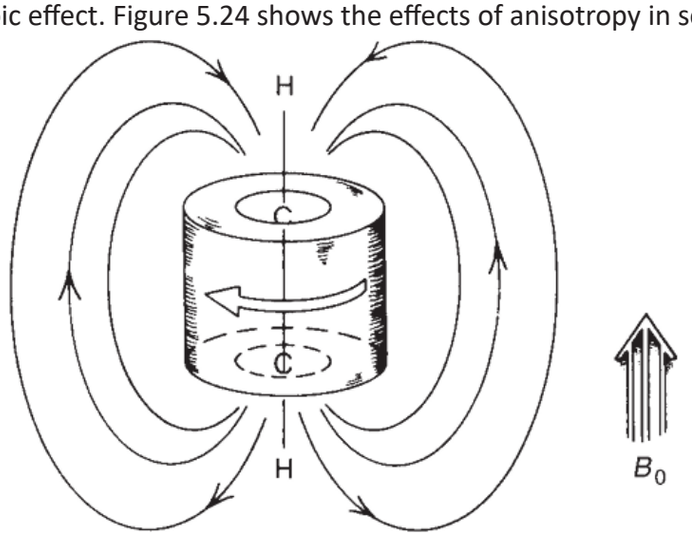


Fig. 5.22: Diamagnetic anisotropy in acetylene.

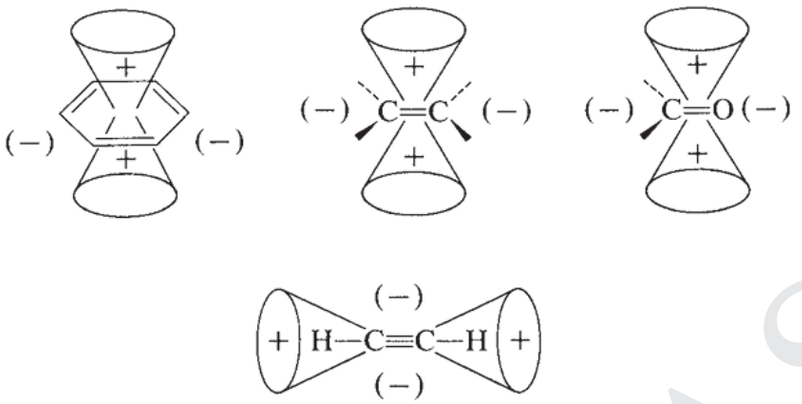


Fig. 5.23: Anisotropy caused by the presence of π electrons in some common multiple-bond systems.

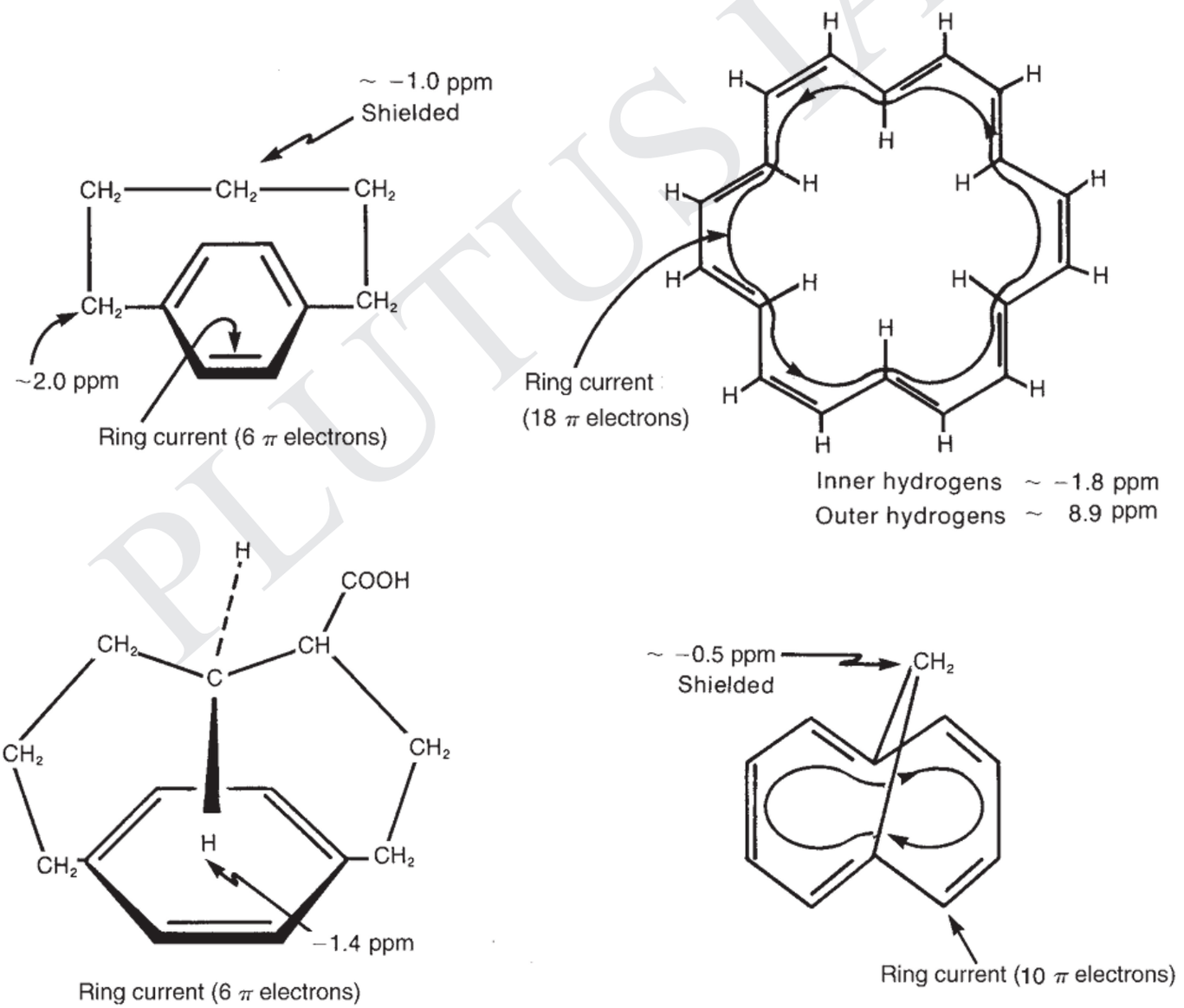
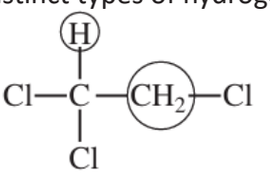


Fig. 5.24: The effects of anisotropy in some actual molecules.

SPIN–SPIN SPLITTING (*n* + 1) RULE

We have discussed the manner in which the chemical shift and the integral (peak area) can give information about the number and types of hydrogens contained in a molecule. A third type of information to be found in the NMR spectrum is that derived from the spin–spin splitting phenomenon.

Even in simple molecules, one finds that each type of proton rarely gives a single resonance peak. For instance, in 1,1,2-trichloroethane there are two chemically distinct types of hydrogens:



On the basis of the information given thus far, one would predict two resonance peaks in the NMR spectrum of 1,1,2-trichloroethane, with an area ratio (integral ratio) of 2:1. In reality, the high-resolution NMR spectrum of this compound has five peaks: a group of three peaks (called a **triplet**) at 5.77 ppm and a group of two peaks (called a **doublet**) at 3.95 ppm. Figure 5.25 shows this spectrum. The methine (CH) resonance (5.77 ppm) is said to be split into a triplet, and the methylene resonance (3.95 ppm) is split into a doublet. The area under the three triplet peaks is 1, relative to an area of 2 under the two doublet peaks.

This phenomenon, called **spin–spin splitting,** can be explained empirically by the so-called ***n* + 1 Rule**. Each type of proton "senses" the number of equivalent protons (*n*) on the carbon atom(s) next to the one to which it is bonded, and its resonance peak is split into (*n* + 1) components.

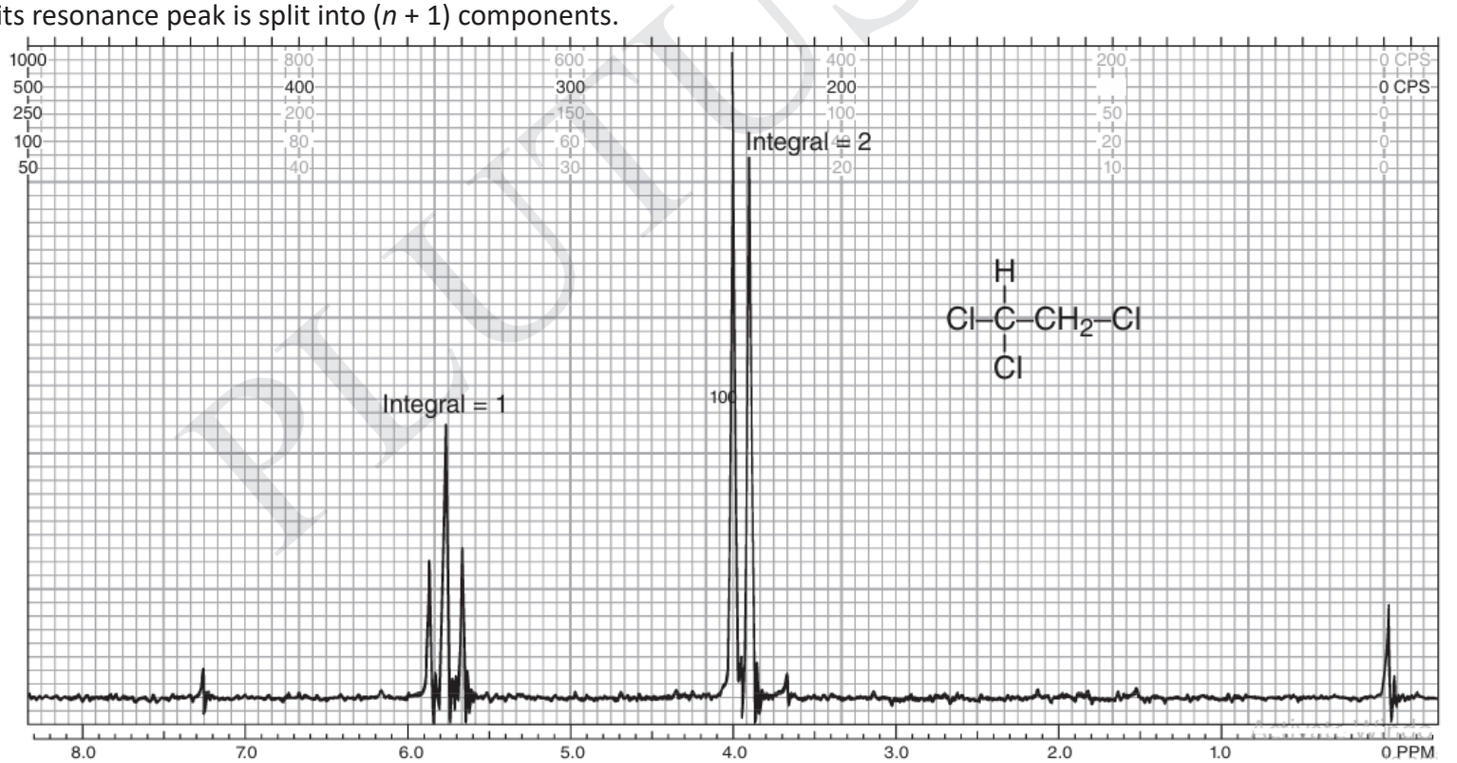
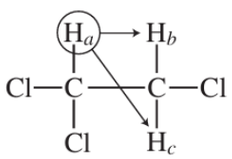
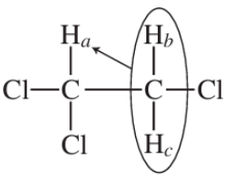


Fig. 5.25: The ^{1}H NMR spectrum of 1,1,2-trichloroethane (60 MHz).

Examine the case at hand, 1,1,2-trichloroethane, utilizing the *n* + 1 Rule. First, the lone methine hydrogen is situated next to a carbon bearing two methylene protons. According to the rule, it has two equivalent neighbors (*n* = 2) and is split into *n* + 1 = 3 peaks (a triplet). The methylene protons are situated next to a carbon bearing only one methine hydrogen. According to the rule, these protons have one neighbor (*n* = 1) and are split into *n* + 1 = 2 peaks (a doublet).



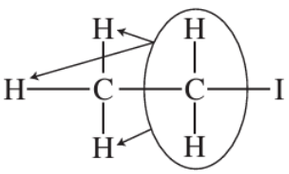
Two neighbors give a triplet
($n + 1 = 3$) (area = 1)



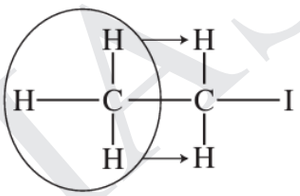
One neighbor gives a doublet
($n + 1 = 2$) (area = 2)

Equivalent protons
behave as a group

Before proceeding to explain the origin of this effect, let us examine two simpler cases predicted by the $n + 1$ Rule. Figure 5.26 is the spectrum of ethyl iodide (CH_3CH_2I). Notice that the methylene protons are split into a quartet (four peaks), and the methyl group is split into a triplet (three peaks). This is explained as follows:



Three equivalent neighbors give a quartet
($n + 1 = 4$) (area = 2)



Two equivalent neighbors give a triplet
($n + 1 = 3$) (area = 3)

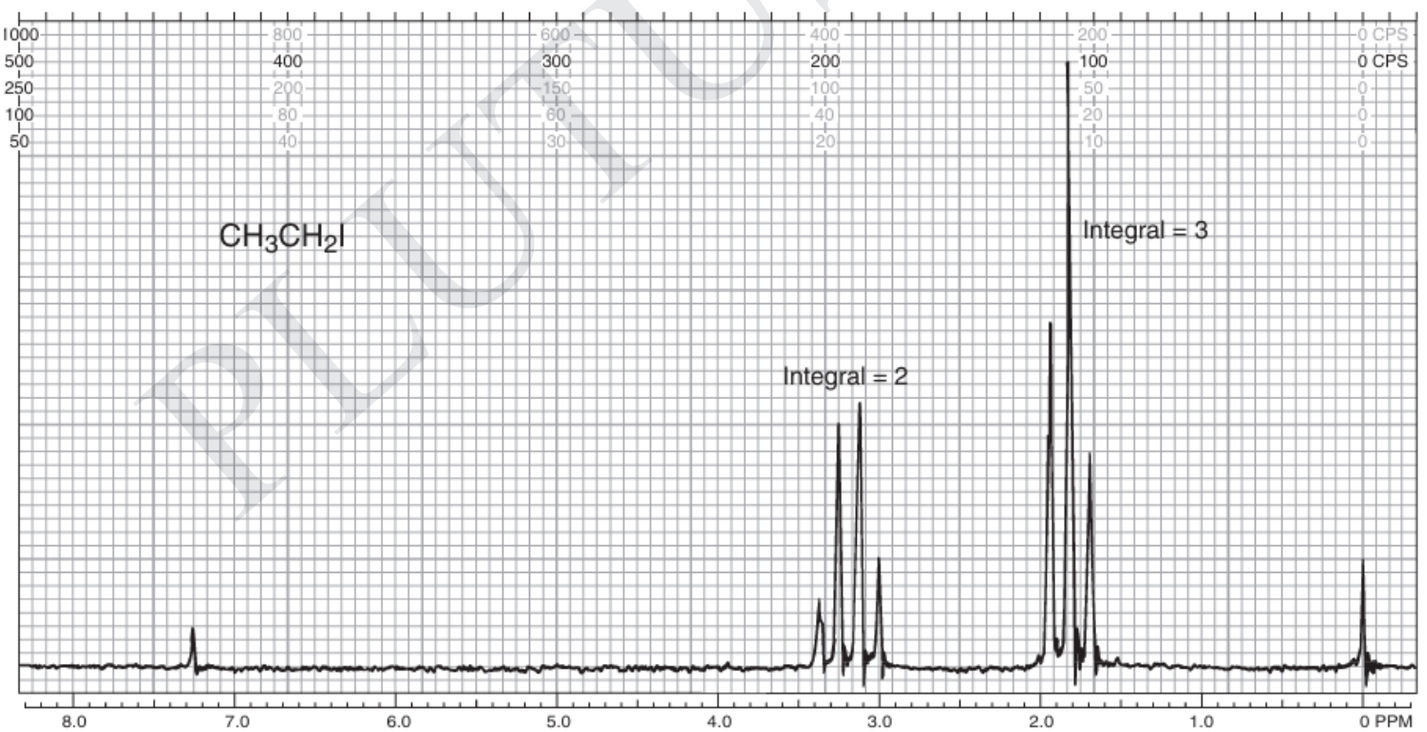
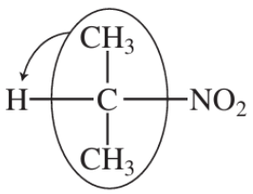
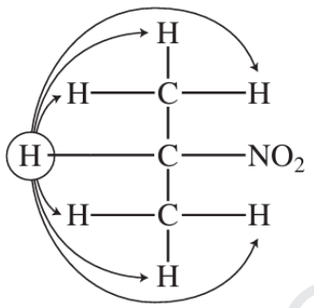


Fig. 5.26: The ^1H NMR spectrum of ethyl iodide (60 MHz).

Finally, consider 2-nitropropane, which has the spectrum given in Figure 5.27.



One neighbor gives a doublet
$(n + 1 = 2)$ (area = 6)



Six equivalent neighbors give a septet
$(n + 1 = 7)$ (area = 1)

Notice that in the case of 2-nitropropane there are two adjacent carbons that bear hydrogens (two carbons, each with three hydrogens), and that all six hydrogens as a group split the methine hydrogen into a **septet**.

Also notice that the chemical shifts of the various groups of protons make sense according to the discussions in Sections 5.10 and 5.11. Thus, in 1,1,2-trichloroethane, the methine hydrogen (on a carbon bearing two Cl atoms) has a larger chemical shift than the methylene protons (on a carbon bearing only one Cl atom). In ethyl iodide, the hydrogens on the carbon-bearing iodine have a larger chemical shift than those of the methyl group. In 2-nitropropane, the methine proton (on the carbon bearing the nitro group) has a larger chemical shift than the hydrogens of the two methyl groups. Finally, note that the spin–spin splitting gives a new type of structural information. It reveals how many hydrogens are adjacent to each type of hydrogen that is giving an absorption peak or, as in these cases, an absorption multiplet. For reference, some commonly encountered spin–spin splitting patterns are collected in Table 5.8.

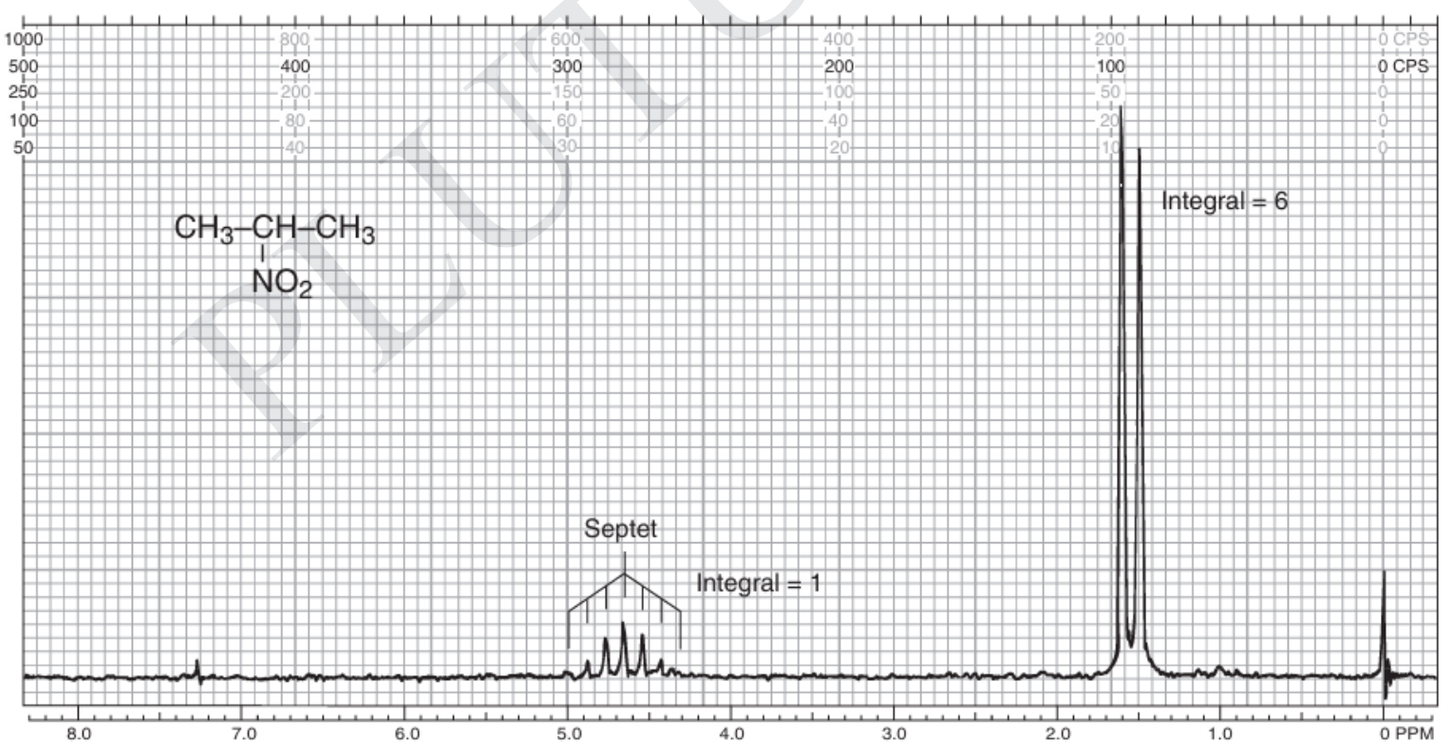
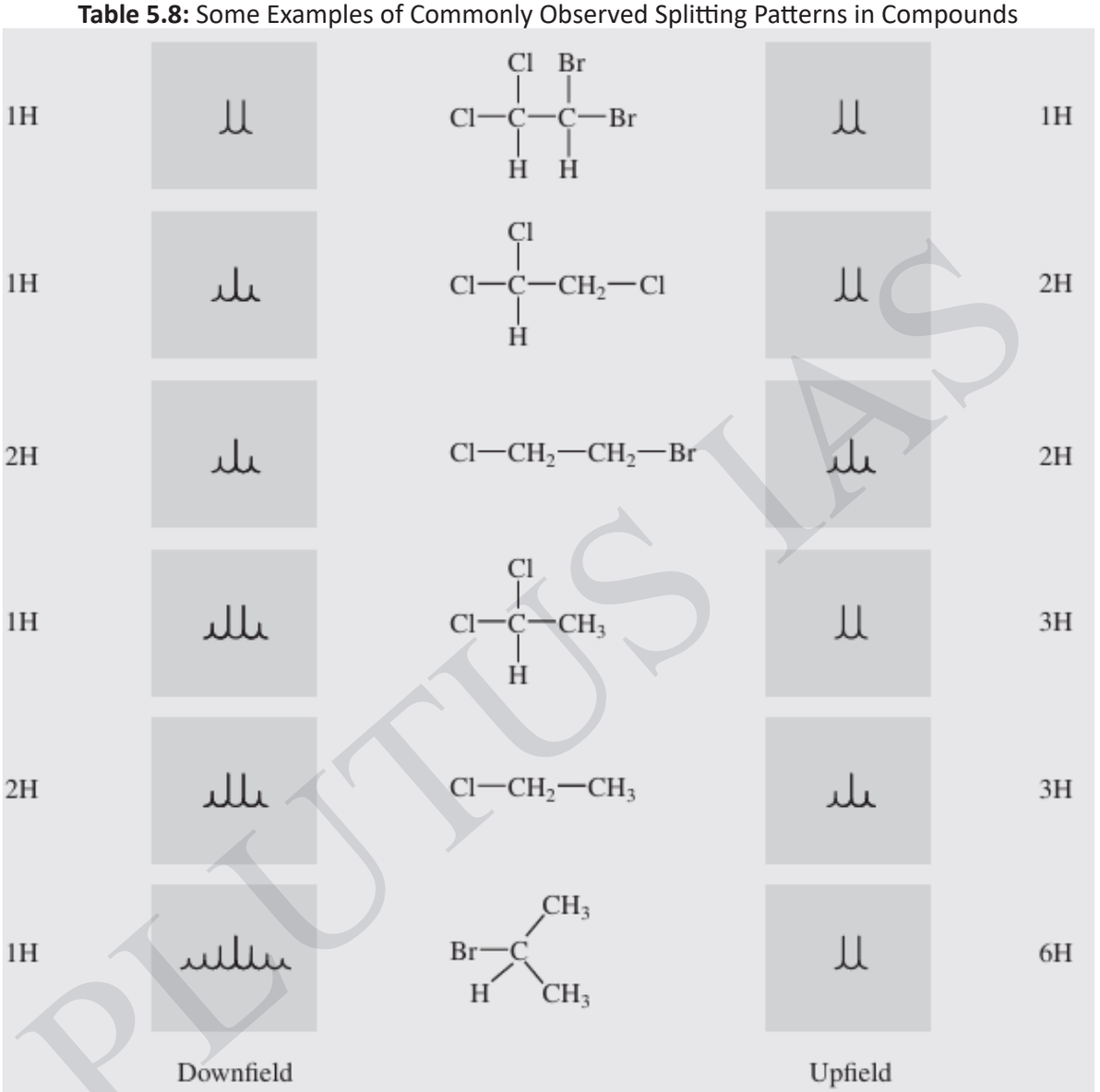


Fig. 5.27: The ^{1}H NMR spectrum of 2-nitropropane (60 MHz).

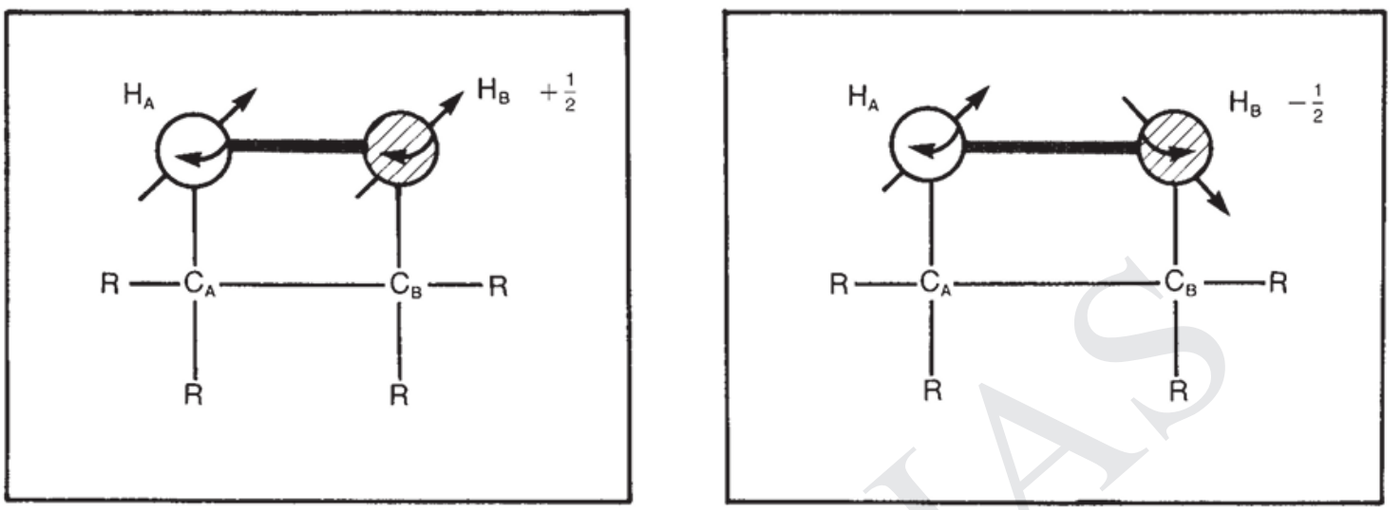
Table 5.8: Some Examples of Commonly Observed Splitting Patterns in Compounds



THE ORIGIN OF SPIN–SPIN SPLITTING

Spin–spin splitting arises because hydrogens on adjacent carbon atoms can "sense" one another. The hydrogen on carbon A can sense the spin direction of the hydrogen on carbon B. In some molecules of the solution, the hydrogen on carbon B has spin $+\frac{1}{2}$ (X-type molecules); in other molecules of the solution, the hydrogen on carbon B has spin $-\frac{1}{2}$ (Y-type molecules). Figure 5.28 illustrates these two types of molecules.

The chemical shift of proton A is influenced by the direction of the spin in proton B. Proton A is said to be **coupled** to proton B. Its magnetic environment is affected by whether proton B has a $+\frac{1}{2}$ or a $-\frac{1}{2}$ spin state. Thus, proton A absorbs at a slightly different chemical shift value in type X molecules than in type Y molecules. In fact,in X-type molecules,proton A is slightly deshielded because the field of proton B is aligned with the applied field,and its magnetic moment adds to the applied field. In Y-type molecules, proton A is slightly shielded with respect to what its chemical shift would be in the absence of coupling. In this latter case,the field of proton B diminishes the effect of the applied field on proton A.



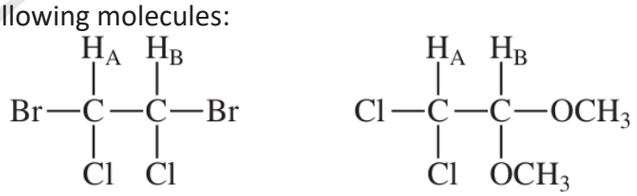
X-type molecule Y-type molecule

Fig. 5.28: Two different molecules in a solution with differing spin relationships between protons H_A and H_B.

Since in a given solution there are approximately equal numbers of X- and Y-type molecules at any given time, two absorptions of nearly equal intensity are observed for proton A. The resonance of proton A is said to have been split by proton B, and the general phenomenon is called **spin–spin splitting**. Figure 5.29 summarizes the spin–spin splitting situation for proton A.

Of course, proton A also "splits" proton B since proton A can adopt two spin states as well. The final spectrum for this situation consists of two doublets:

Two doublets will be observed in any situation of this type except one in which protons A and B are identical by symmetry, as in the case of the first of the following molecules:



The first molecule would give only a single NMR peak since protons A and B have the same chemical shift value and are, in fact, identical. The second molecule would probably exhibit the two-doublet spectrum since protons A and B are not identical and would surely have different chemical shifts.

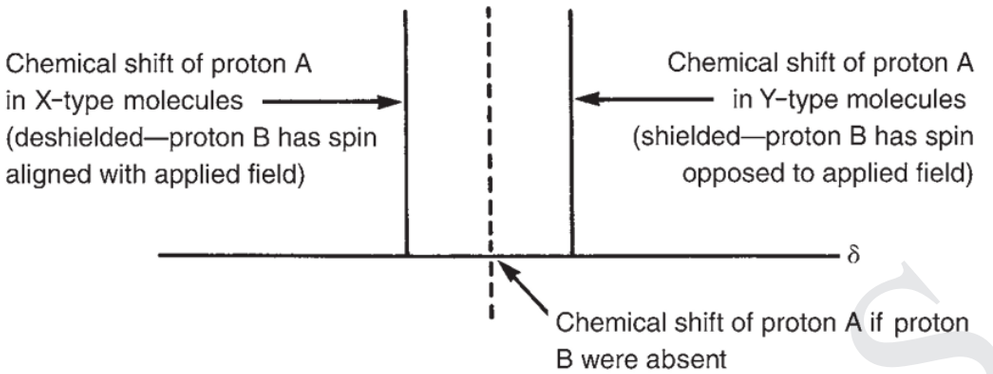


Fig. 5.29: The origin of spin–spin splitting in proton A's NMR spectrum.

Note that except in unusual cases, coupling (spin–spin splitting) occurs only between hydrogens on adjacent carbons. Hydrogens on nonadjacent carbon atoms generally do not couple strongly enough to produce observable splitting, although there are some important exceptions to this generalization, which Chapter 7 will discuss.

THE ETHYL GROUP (CH_3CH_2—)

Now consider ethyl iodide, which has the spectrum shown in Figures 5.26 and 5.30. The methyl protons give rise to a triplet centered at 1.83 ppm, and the methylene protons give a quartet centered at 3.20 ppm. This pattern and the relative intensities of the component peaks can be explained with the use of the model for the two-proton case outlined in Section 5.13. First, look at the methylene protons and their pattern, which is a quartet. The methylene protons are split by the methyl protons, and to understand the splitting pattern, you must examine the various possible spin arrangements of the protons for the methyl group, which are shown in Figure 5.31.

Some of the eight possible spin arrangements are identical to each other since one methyl proton is indistinguishable from another and since there is free rotation in a methyl group. Taking this into consideration, there are only four different types of arrangements. There are, however, three possible ways to obtain the arrangements with net spins of $+\frac{1}{2}$ and $-\frac{1}{2}$. Hence, these arrangements are three times more probable statistically than are the $+\frac{3}{2}$ and $-\frac{3}{2}$ spin arrangements. Thus, one notes in the splitting pattern of the methylene protons that the center two peaks are more intense than the outer ones. In fact, the intensity ratios are 1:3:3:1. Each of these different spin arrangements of the methyl protons (except the sets of degenerate ones, which are effectively identical) gives the methylene protons in that molecule a different chemical shift value. Each of the spins in the $+\frac{3}{2}$ arrangement tends to deshield the methylene proton with respect to its position in the absence of coupling. The $+\frac{1}{2}$ arrangement also deshields the methylene proton, but only slightly, since the two opposite spins cancel each other's effects. The $-\frac{1}{2}$ arrangement shields the methylene proton slightly, whereas the $-\frac{3}{2}$ arrangement shields the methylene proton more strongly.

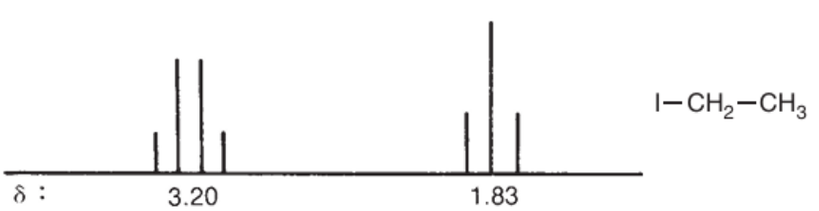


Fig. 5.30: The ethyl splitting pattern.

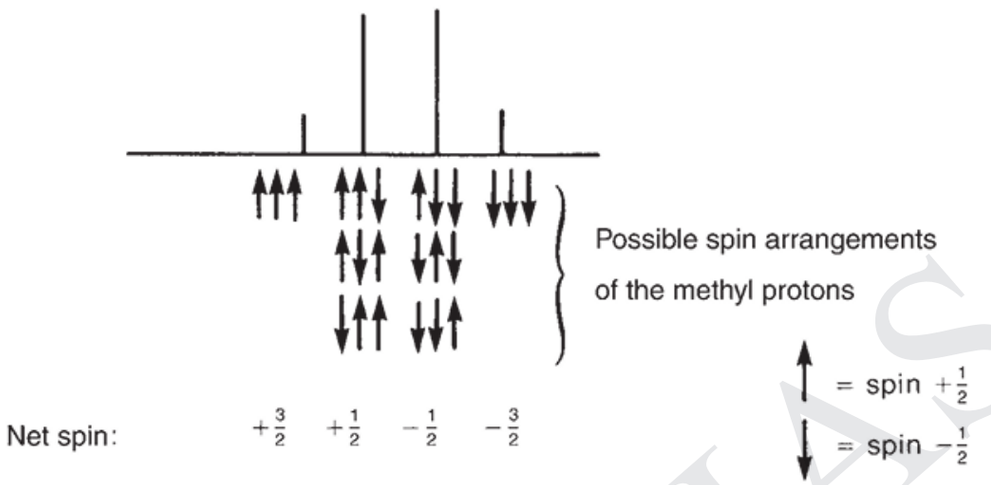


Fig. 5.31: The splitting pattern of methylene protons due to the presence of an adjacent methyl group.

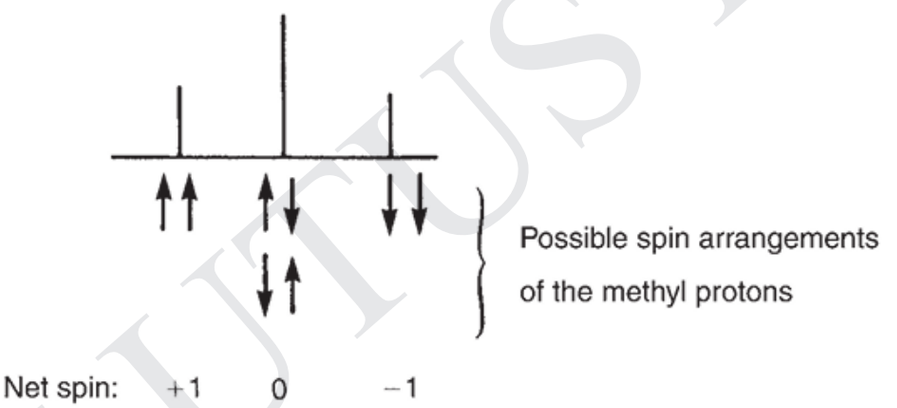


Fig. 5.32: The splitting pattern of methyl protons due to the presence of an adjacent methylene group.

Keep in mind that there are, in fact, four different "types" of molecules in the solution, each type having a different methyl spin arrangement. Each spin arrangement causes the methylene protons in that molecule to have a chemical shift different from those in a molecule with another methyl spin arrangement (except, of course, when the spin arrangements are indistinguishable, or degenerate). Molecules having the $+\frac{1}{2}$ and $-\frac{1}{2}$ spin arrangements are three times more numerous in solution than those with the $+\frac{3}{2}$ and $-\frac{3}{2}$ spin arrangements.

Figure 5.32 provides a similar analysis of the methyl splitting pattern, showing the four possible spin arrangements of the methylene protons. Examination of this figure makes it easy to explain the origin of the triplet for the methyl group and the intensity ratios of 1:2:1.

Now one can see the origin of the ethyl pattern and the explanation of its intensity ratios. The occurrence of spin–spin splitting is very important for the organic chemist as it gives additional structural information about molecules. Namely, it reveals the number of nearest proton neighbors each type of proton has. From the chemical shift one can determine what type of proton is being split, and from the integral (the area under the peaks) one can determine the relative numbers of the types of hydrogen. This is a great amount of structural information, and it is invaluable to the chemist attempting to identify a particular compound.

PASCAL'S TRIANGLE

We can easily verify that the intensity ratios of multiplets derived from the $n + 1$ Rule follow the entries in the mathematical mnemonic device called **Pascal's triangle** (Fig. 5.33). Each entry in the triangle is the sum of the two entries above it and to its immediate left and right. Notice that the intensities of the outer peaks of a multiplet such as a septet are so small compared to the inner peaks that they are often obscured in the baseline of the spectrum. Figure 5.27 is an example of this phenomenon.

Singlet				1			
Doublet				1	1		
Triplet			1	2	1		
Quartet		1	3	3	1		
Quintet	1	4	6	4	1		
Sextet	1	5	10	10	5	1	
Septet	1	6	15	20	15	6	1

Fig. 5.33: Pascal's triangle.

THE COUPLING CONSTANT

Section 5.15 discussed the splitting pattern of the ethyl group and the intensity ratios of the multiplet components but did not address the quantitative amount by which the peaks were split. The distance between the peaks in a simple multiplet is called the **coupling constant** *J*. The coupling constant is a measure of how strongly a nucleus is affected by the spin states of its neighbor. The spacing between the multiplet peaks is measured on the same scale as the chemical shift, and the coupling constant is always expressed in Hertz (Hz). In ethyl iodide, for instance, the coupling constant *J* is 7.5 Hz. To see how this value was determined, consult Figures 5.26 and 5.34.

The spectrum in Figure 5.26 was determined at 60 MHz; thus, each ppm of chemical shift (δ unit) represents 60 Hz. Inasmuch as there are 12 grid lines per ppm, each grid line represents (60 Hz)/12 = 5 Hz. Notice the top of the spectrum. It is calibrated in cycles per second (cps), which are the same as Hertz, and since there are 20 chart divisions per 100 cps, one division equals (100 cps)/20 = 5 cps = 5 Hz. Now examine the multiplets. The spacing between the component peaks is approximately 1.5 chart divisions, so

$$J = 1.5 \text{ div} \times \frac{5 \text{ Hz}}{1 \text{ div}} = 7.5 \text{ Hz}$$

That is, the coupling constant between the methyl and methylene protons is 7.5 Hz. When the protons interact, the magnitude (in ethyl iodide) is always of this same value, 7.5 Hz. The amount of coupling is constant, and hence *J* can be called a coupling constant.

The invariant nature of the coupling constant can be observed when the NMR spectrum of ethyl iodide is determined at both 60 MHz and 100 MHz. A comparison of the two spectra indicates that the 100-MHz spectrum is greatly expanded over the 60-MHz spectrum. The chemical shift in Hertz for the CH_3 and CH_2 protons is much larger in the 100-MHz spectrum, although the chemical shifts in units (ppm) for these protons remain identical to those in the 60-MHz spectrum. Despite the expansion of the spectrum determined at the higher spectrometer frequency, careful examination of the spectra indicates that the coupling constant between the CH_3 and CH_2 protons is 7.5 Hz in both spectra! The spacings of the lines of the triplet and the lines of the quartet do not expand when the spectrum of ethyl iodide is determined at 100 MHz. The extent of coupling between these two sets of protons remains constant irrespective of the spectrometer frequency at which the spectrum was determined (Fig. 5.35).

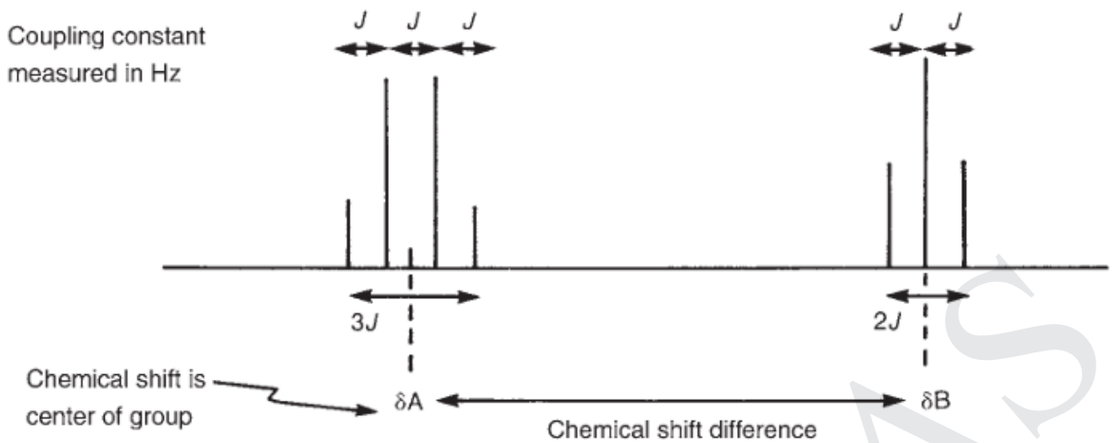


Fig. 5.34: The definition of the coupling constants in the ethyl splitting pattern.

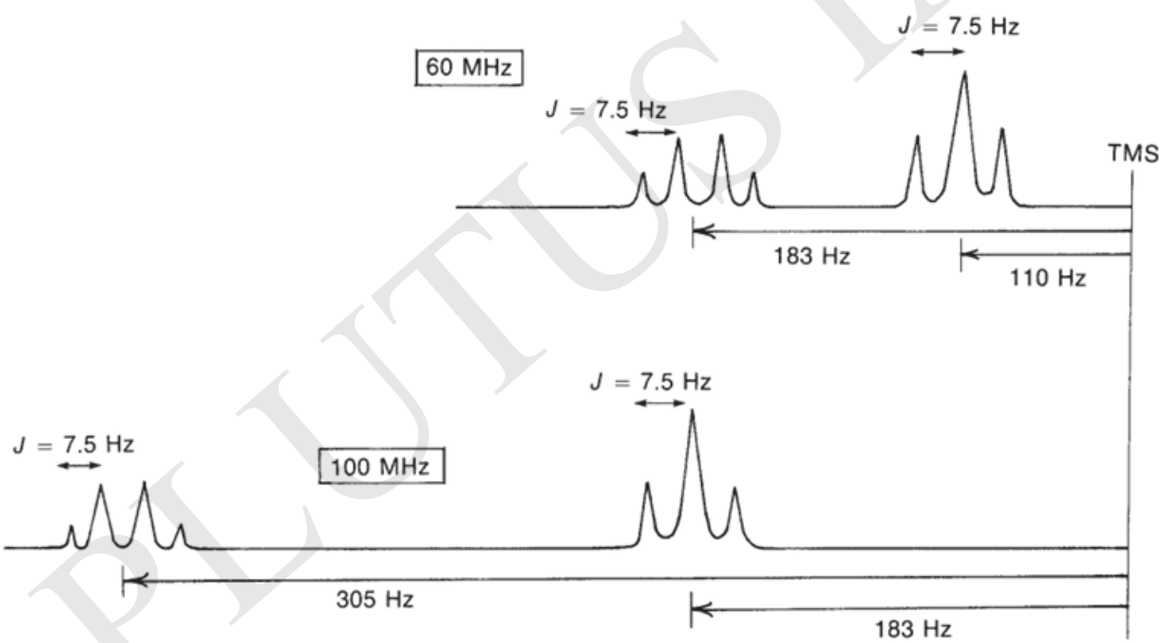
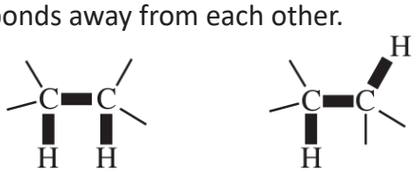


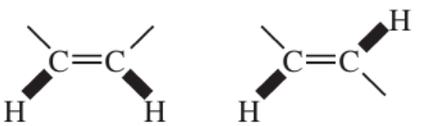
Fig. 5.35: An illustration of the relationship between the chemical shift and the coupling constant.

For the interaction of most aliphatic protons in acyclic systems, the magnitudes of coupling constants are always near 7.5 Hz. Compare, for example, 1,1,2-trichloroethane (Fig. 5.25), for which J = 6 Hz, and 2-nitropropane (Fig. 5.27), for which J = 7 Hz. These coupling constants are typical for the interaction of two hydrogens on adjacent sp^3-hybridized carbon atoms. Two hydrogen atoms on adjacent carbon atoms can be described as a three-bond interaction and abbreviated as ^3J. Typical values for this most commonly observed coupling is approximately 6 to 8 Hz. The bold lines in the diagram show how the hydrogen atoms are three bonds away from each other.



Coupling constants on modern FT-NMR spectrometers are more easily determined by printing Hertz values directly on the peaks. It is a simple matter of subtracting these values to determine the coupling constants in Hertz. See, for example, the spectra shown in Figures 5.40 and 5.46, in which peaks have been labeled in Hertz. Section 7.2 in Chapter

7 describes the various types of coupling constants associated with two-bond (^2J), three-bond (^3J), and four-bond (^4J) interactions.



^3J *cis* = 10 Hz ^3J *trans* = 16 Hz

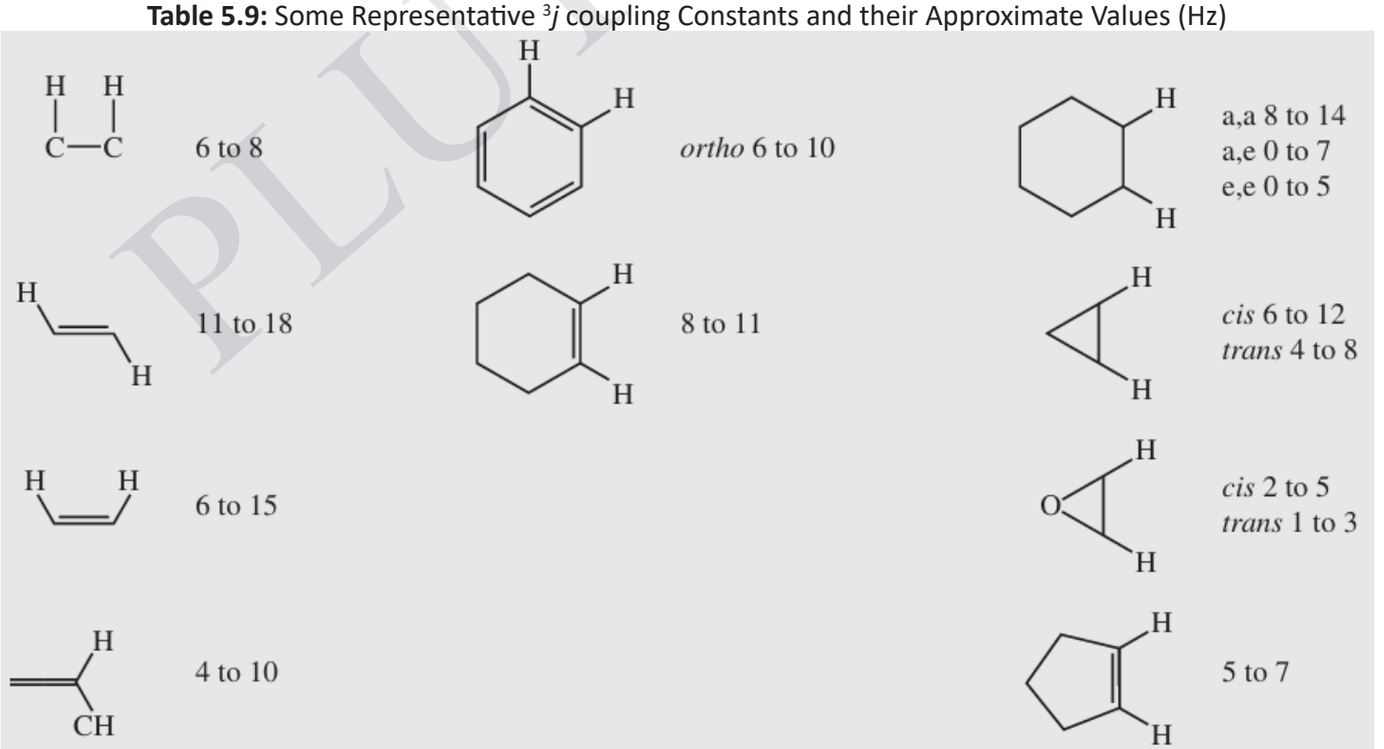
In alkenes, the ^3J coupling constants for hydrogen atoms that are *cis* to each other have values near 10 Hz,while the ^3J coupling constants for hydrogen atoms that are trans are larger, 16 Hz. A study of the magnitude of the coupling constant can give important structural information (see Section 7.8 in Chapter 7).

Table 5.9 gives the approximate values of some representative ^3J coupling constants. A more extensive list of coupling constants appears in Chapter 7, Section 7.2, and in Appendix 5.

Before closing this section,we should take note of an axiom: *the coupling constants of the groups of protons that split one another must be identical* within experimental error. This axiom is extremely useful in interpreting a spectrum that may have several multiplets,each with a different coupling constant.

$J = 7$ Hz $J = 5$ Hz $J = 7$ Hz $J = 5$ Hz

Table 5.9: Some Representative ^3j coupling Constants and their Approximate Values (Hz)



Take, for example, the preceding spectrum, which shows three triplets an done quartet. Which triplet is associated with the quartet? It is, of course, the one that has the same *J* values as are found in the quartet. The protons in each group

interact to the same extent. In this example, with the *J* values given, clearly quartet A (*J* = 7 Hz) is associated with triplet C (*J* = 7 Hz) and not with triplet B or D (*J* = 5 Hz). It is also clear that triplets B and D are related to each other in the interaction scheme.

Multiplet skewing ("leaning") is another effect that can sometimes be used to link interacting multiplets. There is a tendency for the outermost lines of a multiplet to have nonequivalent heights. For instance, in a triplet, line 3 may be slightly taller than line 1, causing the multiplet to "lean." When this happens, the taller peak is usually in the direction of the proton or group of protons causing the splitting. This second group of protons leans toward the first one in the same fashion. If arrows are drawn on both multiplets in the directions of their respective skewing, these arrows will point at each other. See Figures 5.25 and 5.26 for examples.