CHAPTER 3

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Part One: Basic Concepts

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.

3.1 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 ${}^{1}_{1}\text{H}$, ${}^{2}_{1}\text{H}$, ${}^{13}_{6}\text{C}$, ${}^{14}_{7}\text{N}$, ${}^{17}_{8}\text{O}$, and ${}^{19}_{9}\text{F}$. Notice that the nuclei of the ordinary (most abundant) isotopes of carbon and oxygen, ${}^{12}_{6}\text{C}$ and ${}^{16}_{8}\text{O}$, 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

$$+I,\ (I - 1),\ \ldots,\ (-I + 1),\ -I \qquad \textbf{Equation 3.1}$$

For instance, a proton (hydrogen nucleus) has the spin quantum number $I = \frac{1}{2}$ and has two allowed spin states $[2(\frac{1}{2}) + 1 = 2]$ 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 $[2(\frac{3}{2}) + 1 = 4]$: $-\frac{3}{2}$, $-\frac{1}{2}$, $+\frac{1}{2}$, and $+\frac{3}{2}$. Table 3.1 gives the spin quantum numbers of several nuclei.

TABLE 3.1
SPIN QUANTUM NUMBERS OF SOME COMMON NUCLEI

Element	${}^{1}_{1}\text{H}$	${}^{2}_{1}\text{H}$	${}^{12}_{6}\text{C}$	${}^{13}_{6}\text{C}$	${}^{14}_{7}\text{N}$	${}^{16}_{8}\text{O}$	${}^{17}_{8}\text{O}$	${}^{19}_{9}\text{F}$	${}^{31}_{15}\text{P}$	${}^{35}_{17}\text{Cl}$
Nuclear spin quantum number	$\frac{1}{2}$	1	0	$\frac{1}{2}$	1	0	$\frac{5}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
Number of spin states	2	3	0	2	3	0	6	2	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.

3.2 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 ($+\frac{1}{2}$) or counterclockwise ($-\frac{1}{2}$) 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 3.1 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 3.2, 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

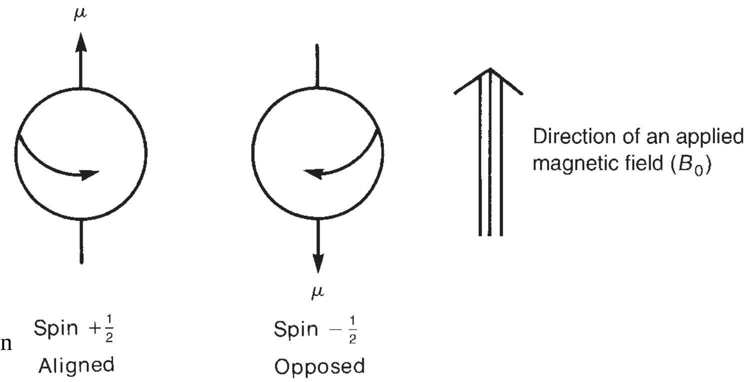


FIGURE 3.1 The two allowed spin states for a proton.

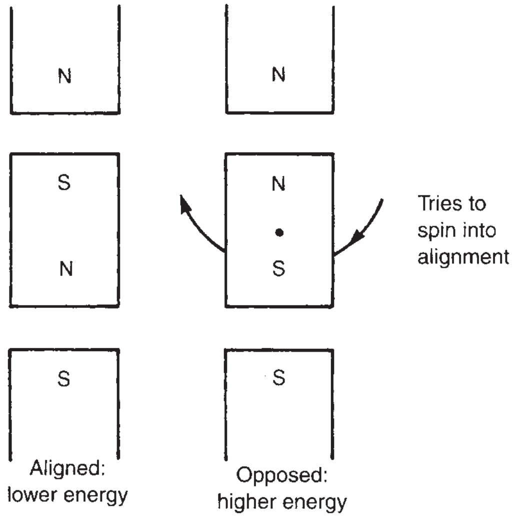


FIGURE 3.2 Aligned and opposed arrangements of bar magnets.

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 3.3.

In the case of a chlorine nucleus, there are four energy levels, as shown in Figure 3.4. 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 3.4.

3.3 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 3.5 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.

$$E_{\text{absorbed}} = (E_{-\frac{1}{2}\text{ state}} - E_{+\frac{1}{2}\text{ state}}) = h\upsilon \qquad \textbf{Equation 3.2}$$

In practice, this energy difference is a function of the strength of the applied magnetic field B_0, as illustrated in Figure 3.6.

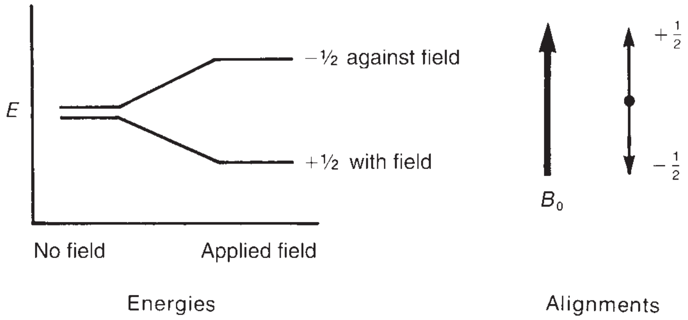


FIGURE 3.3 The spin states of a proton in the absence and in the presence of an applied magnetic field.

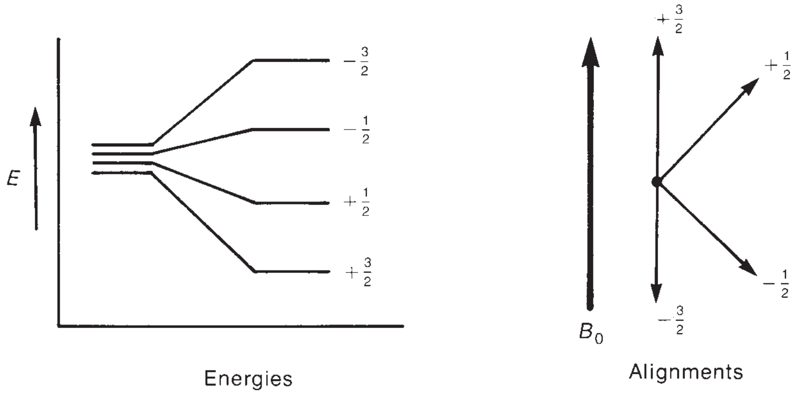


FIGURE 3.4 The spin states of a chlorine atom both in the presence and in the absence of an applied magnetic field.

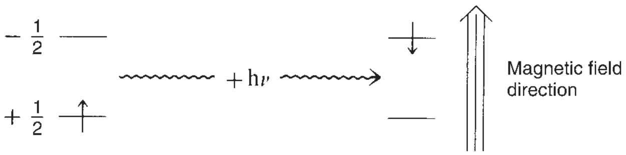


FIGURE 3.5 The NMR absorption process for a proton.

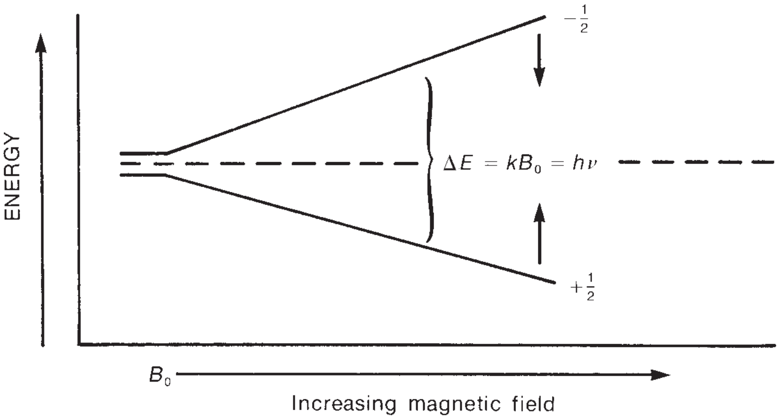


FIGURE 3.6 The spin-state energy separation as a function of the strength of the applied magnetic field B_0.

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

$$\Delta E = f(B_0) \qquad \textbf{Equation 3.3}$$

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 γ**, is a constant for each nucleus and determines the energy dependence on the magnetic field:

$$\Delta E = f(\gamma B_0) = h\nu \qquad \textbf{Equation 3.4}$$

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

$$\Delta E = \gamma\left(\frac{h}{2\pi}\right) B_0 = h\nu \qquad \textbf{Equation 3.5}$$

Solving for the frequency of the absorbed energy,

$$\nu = \left(\frac{\gamma}{2\pi}\right) B_0 \qquad \textbf{Equation 3.6}$$

If the correct value of γ 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 3.2 shows the field strengths and frequencies at which several nuclei have resonance (i.e., absorb energy and make spin transitions).

TABLE 3.2

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, γ (radians/Tesla)
^{1}H	99.98	1.00	42.6	267.53
		1.41	60.0	
		2.35	100.0	
		4.70	200.0	
		7.05	300.0	
^{2}H	0.0156	1.00	6.5	41.1
^{13}C	1.108	1.00	10.7	67.28
		1.41	15.1	
		2.35	25.0	
		4.70	50.0	
		7.05	75.0	
^{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 4 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 3.7B), 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.

3.4 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. 3.7a). A spinning nucleus behaves in a similar fashion under the influence of an applied magnetic field (Fig. 3.7b).

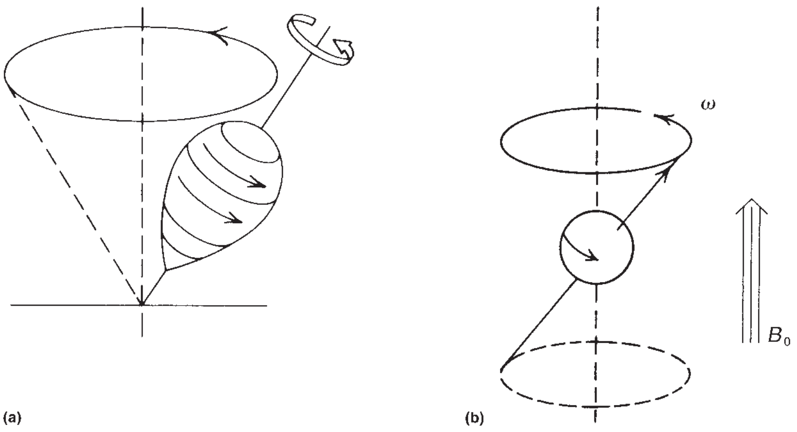


FIGURE 3.7 (a) A top precessing in the earth's gravitational field; (b) the precession of a spinning nucleus resulting from the influence of an applied magnetic field.

When the magnetic field is applied, the nucleus begins to precess about its own axis of spin with angular frequency ω, 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 3.8 schematically illustrates the resonance process.

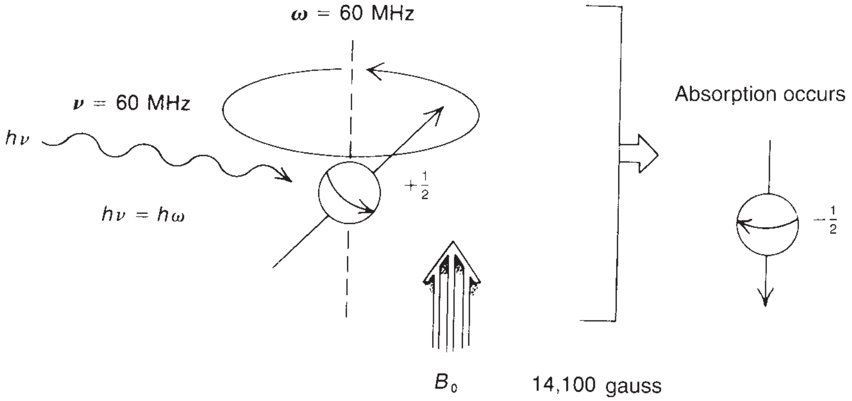


FIGURE 3.8 The nuclear magnetic resonance process; absorption occurs when $\upsilon = \omega$.

3.5 POPULATION DENSITIES OF NUCLEAR SPIN STATES

For a proton, if the applied magnetic field has a strength of approximately 1.41 Tesla, resonance occurs at about 60 MHz, and using $\Delta E = h\nu$, we can calculate that the difference in energy between the two spin states of the proton is about 2.39×10^{-5} kJ/mole. Thermal energy resulting from room temperature is sufficient to populate both of these energy levels since the energy separation between the two levels is small. There is, however, a slight excess of nuclei in the lower-energy spin state. The magnitude of this difference can be calculated using the Boltzmann distribution equations. Equation 3.7 gives the Boltzmann ratio of nuclear spins in the upper and lower levels.

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = e^{-\Delta E/kT} = e^{-h\nu/kT} \qquad \textbf{Equation 3.7}$$

$$h = 6.624 \times 10^{-34}\ \text{J}\cdot\text{sec}$$

$$k = 1.380 \times 10^{-23}\ \text{J/K} \cdot \text{molecule}$$

$$T = \text{absolute temperature (K)}$$

where ΔE is the energy difference between the upper and lower energy states, and k is the molecular (not molar) gas constant. Since $\Delta E = h\nu$, the second form of the equation is derived, where ν is the operating frequency of the instrument and h is Planck's constant.

Using Equation 3.7, one can calculate that at 298 K (25°C), for an instrument operating at 60 MHz there are 1,000,009 nuclei in the lower (favored) spin state for every 1,000,000 that occupy the upper spin state:

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = 0.999991 = \frac{1{,}000{,}000}{1{,}000{,}009}$$

In other words, in approximately 2 million nuclei, there are only 9 more nuclei in the lower spin state. Let us call this number (9) the **excess population** (Fig. 3.9).

The excess nuclei are the ones that allow us to observe resonance. When the 60-MHz radiation is applied, it not only induces transitions upward but also stimulates transitions downward. If the populations of the upper and lower states become exactly equal, we observe no net signal. This situation is called **saturation.** One must be careful to avoid saturation when performing an NMR experiment. Saturation is achieved quickly if the power of the radiofrequency signal is too high. Therefore, the very small excess of nuclei in the lower spin state is quite important to NMR spectroscopy, and we can see that very sensitive NMR instrumentation is required to detect the signal.

If we increase the operating frequency of the NMR instrument, the energy difference between the two states increases (see Fig. 3.6), which causes an increase in this excess. Table 3.3 shows how the excess increases with operating frequency. It also clearly shows why modern instrumentation has been designed with increasingly higher operating frequencies. The sensitivity of the instrument is increased, and the resonance signals are stronger, because more nuclei can undergo transition at higher frequency. Before the advent of higher-field instruments, it was very difficult to observe less-sensitive nuclei such as carbon-13, which is not very abundant (1.1%) and has a detection frequency much lower than that of hydrogen (see Table 3.2).

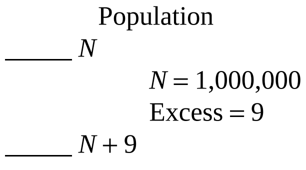


FIGURE 3.9 The excess population of nuclei in the lower spin state at 60 MHz.

TABLE 3.3
VARIATION OF ^1H EXCESS NUCLEI WITH OPERATING FREQUENCY

Frequency (MHz)	Excess Nuclei
20	3
40	6
60	9
80	12
100	16
200	32
300	48
600	96

3.6 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 3.10 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.

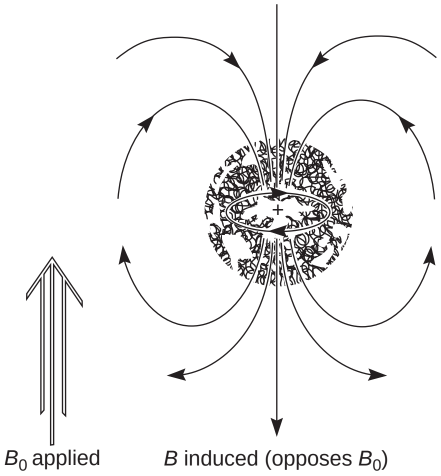


FIGURE 3.10 Diamagnetic anisotropy—the diamagnetic shielding of a nucleus caused by the circulation of valence electrons.

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

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

Equation 3.8

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 3.7). Following is a typical chemical shift scale with the sequence of δ values that would be found on a typical NMR spectrum chart.

Direction of scan ⇒

TMS

12 11 10 9 8 7 6 5 4 3 2 1 0 –1 –2 *δ* scale (ppm)

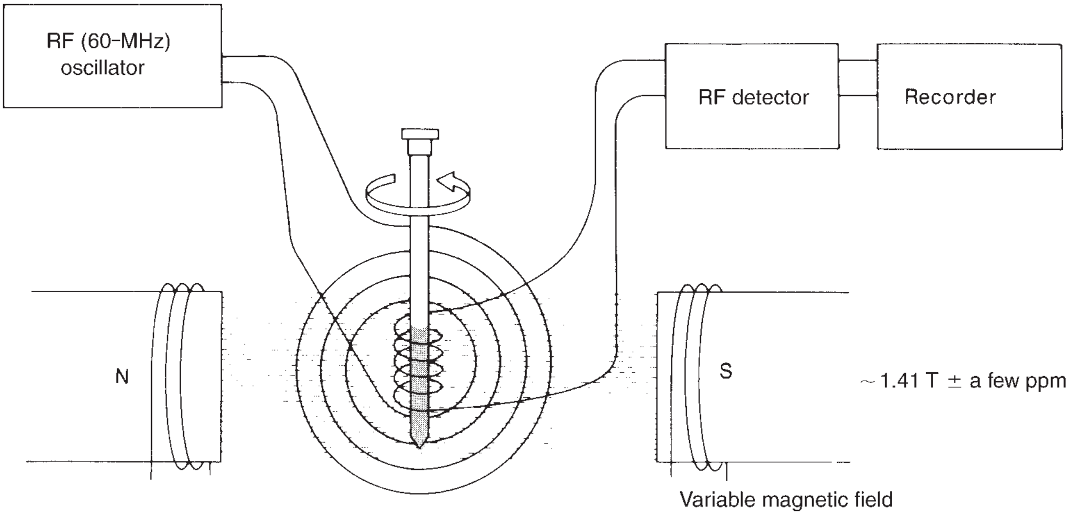
3.7 THE NUCLEAR MAGNETIC RESONANCE SPECTROMETER

A. The Continuous-Wave (CW) Instrument

Figure 3.11 schematically illustrates the basic elements of a classical 60-MHz NMR spectrometer. The sample is dissolved in a solvent containing no interfering protons (usually CCl_4 or $CDCl_3$), and a small amount of TMS is added to serve as an internal reference. The sample cell is a small cylindrical glass tube that is suspended in the gap between the faces of the pole pieces of the magnet. The sample is spun around its axis to ensure that all parts of the solution experience a relatively uniform magnetic field.

Also in the magnet gap is a coil attached to a 60-MHz radiofrequency (RF) generator. This coil supplies the electromagnetic energy used to change the spin orientations of the protons. Perpendicular to the RF oscillator coil is a detector coil. When no absorption of energy is taking place, the detector coil picks up none of the energy given off by the RF oscillator coil. When the sample absorbs energy, however, the reorientation of the nuclear spins induces a RF signal in the plane of the detector coil, and the instrument responds by recording this as a **resonance signal,** or **peak.**

At a constant field strength, the distinct types of protons in a molecule precess at slightly different frequencies. Rather than changing the frequency of the RF oscillator to allow each of the pro-



F I G U R E 3 . 1 1 The basic elements of the classical nuclear magnetic resonance spectrometer.

tons in a molecule to come into resonance, the CW NMR spectrometer uses a constant-frequency RF signal and varies the magnetic field strength. As the magnetic field strength is increased, the precessional frequencies of all the protons increase. When the precessional frequency of a given type of proton reaches 60 MHz, it has resonance. The magnet that is varied is actually a two-part device. There is a main magnet, with a strength of about 1.41 Tesla, which is capped by electromagnet pole pieces. By varying the current through the pole pieces, the worker can increase the main field strength by as much as 20 parts per million (ppm). Changing the field in this way systematically brings all of the different types of protons in the sample into resonance.

As the field strength is increased linearly, a pen travels across a recording chart. A typical spectrum is recorded as in Figure 3.12. As the pen travels from left to right, the magnetic field is increasing. As each chemically distinct type of proton comes into resonance, it is recorded as a peak on the chart. The peak at $\delta = 0$ ppm is due to the internal reference compound TMS. Since highly shielded protons precess more slowly than relatively unshielded protons, it is necessary to increase the field to induce them to precess at 60 MHz. Hence, highly **shielded** protons appear to the right of this chart, and less shielded, or **deshielded,** protons appear to the left. The region of the chart to the left is sometimes said to be **downfield** (or at **low field**), and that to the right, **upfield** (or at **high field**). Varying the magnetic field as is done in the usual spectrometer is exactly equivalent to varying the radio frequency, RF and a change of 1 ppm in the magnetic field strength (increase) has the same effect as a 1-ppm change (decrease) in the RF frequency (see Eq. 3.6). Hence, changing the field strength instead of the RF frequency is only a matter of instrumental design. Instruments that vary the magnetic field in a continuous fashion, scanning from the downfield end to the upfield end of the spectrum, are called **continuous-wave (CW) instruments.** Because the chemical shifts of

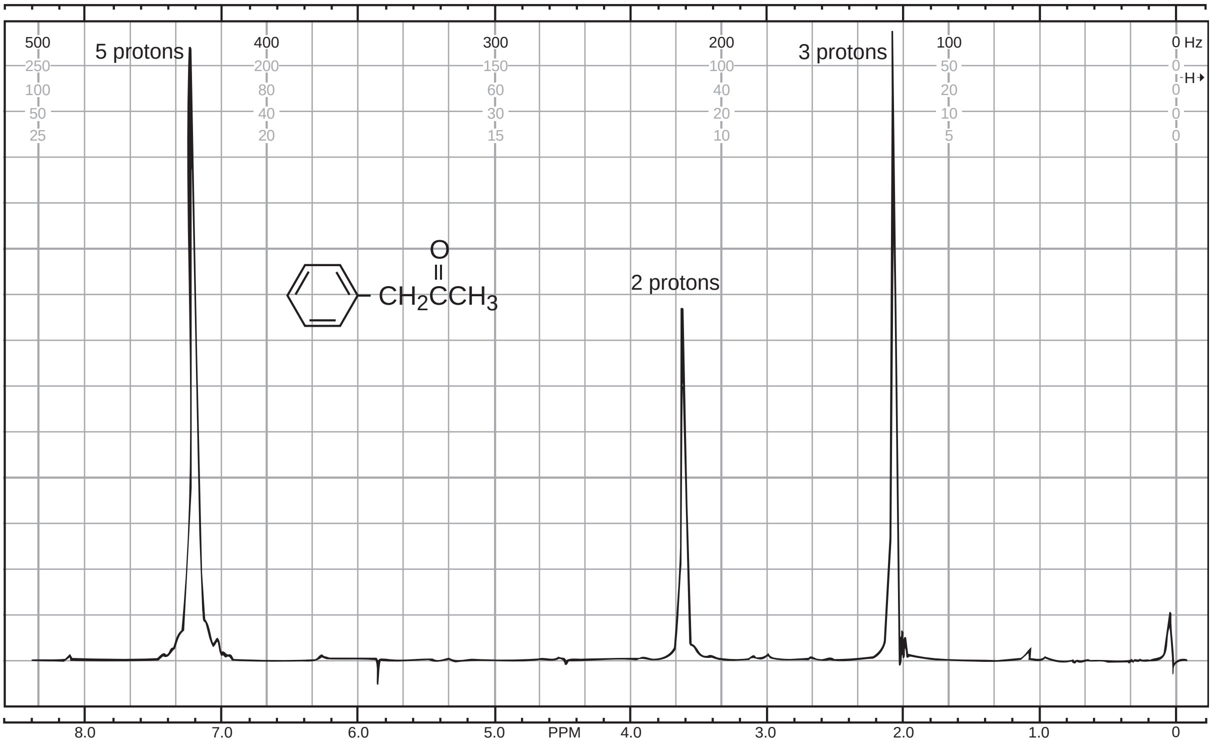


FIGURE 3.12 The 60-MHz ^{1}H nuclear magnetic resonance spectrum of phenylacetone (the absorption peak at the far right is caused by the added reference substance TMS).

the peaks in this spectrum are calculated from *frequency* differences from TMS, this type of spectrum (Fig. 3.12) is said to be a **frequency-domain spectrum.**

A distinctive characteristic enables one to recognize a CW spectrum. Peaks generated by a CW instrument have **ringing,** a decreasing series of oscillations that occurs after the instrument has scanned through the peak (Fig. 3.13). Ringing occurs because the excited nuclei do not have time to relax back to their equilibrium state before the field, and pen, of the instrument have advanced to a new position. The excited nuclei have a relaxation rate that is slower than the rate of scan. As a result, they are still emitting an oscillating, rapidly decaying signal, which is recorded as ringing. Ringing is desirable in a CW instrument and is considered to indicate that the field homogeneity is well adjusted. Ringing is most noticeable when a peak is a sharp singlet (a single, isolated peak).

B. The Pulsed Fourier Transform (FT) Instrument

The CW type of NMR spectrometer, which was described in Section 3.6A, operates by exciting the nuclei of the isotope under observation one type at a time. In the case of ^{1}H nuclei, each distinct type of proton (phenyl, vinyl, methyl, and so on) is excited individually, and its resonance peak is observed and recorded independently of all the others. As we scan, we look at first one type of hydrogen and then another, scanning until all of the types have come into resonance.

An alternative approach, common to modern, sophisticated instruments, is to use a powerful but short burst of energy, called a **pulse,** that excites all of the magnetic nuclei in the molecule simultaneously. In an organic molecule, for instance, all of the ^{1}H nuclei are induced to undergo resonance at the same time. An instrument with a 2.1-Tesla magnetic field uses a short (1- to 10-μsec) burst of 90-MHz energy to accomplish this. The source is turned on and off very quickly, generating a pulse similar to that shown in Figure 3.14a. According to a variation of the Heisenberg Uncertainty Principle, even though the frequency of the oscillator generating this pulse is set to 90 MHz, if the duration of the pulse is very short, the frequency content of the pulse is uncertain because the oscillator was not on long enough to establish a solid fundamental frequency. Therefore, the pulse actually contains a *range of frequencies* centered about the fundamental, as shown in Figure 3.14b. This range of frequencies is great enough to excite all of the distinct types of hydrogens in the molecule at once with this single burst of energy.

When the pulse is discontinued, the excited nuclei begin to lose their excitation energy and return to their original spin state, or **relax.** As each excited nucleus relaxes, it emits electromagnetic radiation.

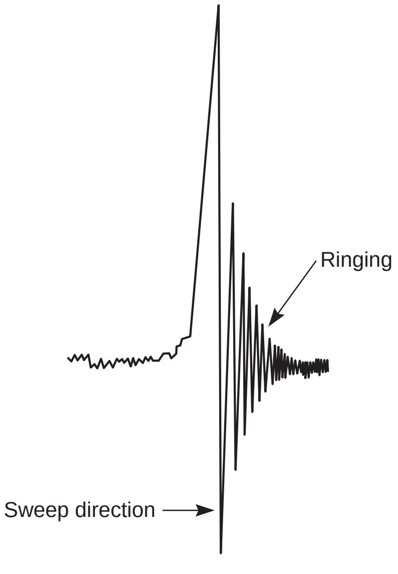


FIGURE 3.13 A CW peak that shows ringing.

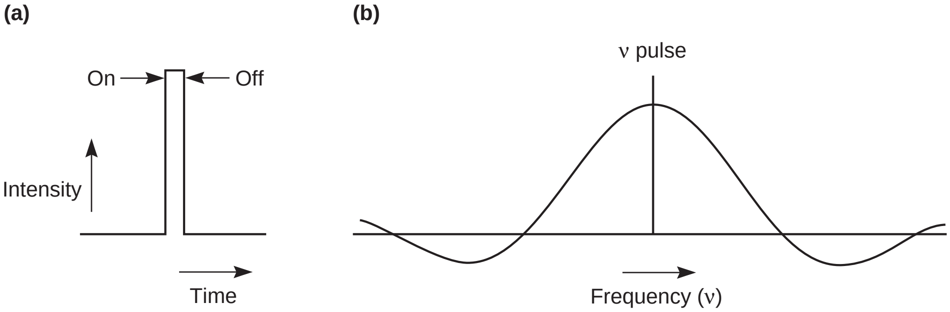


FIGURE 3.14 A short pulse. (a) The original pulse; (b) the frequency content of the same pulse.

Since the molecule contains many different nuclei, many different frequencies of electromagnetic radiation are emitted simultaneously. This emission is called a **free-induction decay (FID)** signal (Fig. 3.15). Notice that the intensity of the FID decays with time as all of the nuclei eventually lose their excitation. The FID is a superimposed combination of all the frequencies emitted and can be quite complex. We usually extract the individual frequencies due to different nuclei by using a computer and a mathematical method called a Fourier transform (FT) analysis, which is described later in this section.

If we look at a very simple molecule such as acetone, we can avoid the inherent complexities of the Fourier transform and gain a clearer understanding of the method. Figure 3.16a shows the FID for the hydrogens in acetone. This FID was determined in an instrument with a 7.05-Tesla magnet operating at 300 MHz.

Since acetone has only one type of hydrogen (all six hydrogens are equivalent), the FID curve is composed of a single sinusoidal wave. The signal decays exponentially with time as the nuclei relax and their signal diminishes. Since the horizontal axis on this signal is time, the FID is sometimes called a **time-domain signal.** If the signal did not decay in intensity, it would appear as a sine (or cosine) wave of constant intensity, as shown in Figure 3.16b. One can calculate the frequency of this wave from its measured wavelength λ (difference between the maxima).

The determined frequency is not the exact frequency emitted by the methyl hydrogens. Due to the design of the instrument, the basic frequency of the pulse is not the same as the frequency of the acetone resonance. The observed FID is actually an interference signal between the radiofrequency source (300 MHz in this case) and the frequency emitted by the excited nucleus, where the wavelength is given by

$$\lambda = \frac{1}{\nu_{\text{acetone}} - \nu_{\text{pulse}}}$$ **Equation 3.9**

In other words, this signal represents the difference in the two frequencies. Since the frequency of the pulse is known, we could readily determine the exact frequency. However, we do not need to know it since we are interested in the chemical shift of those protons, which is given by

$$\delta'_{\text{acetone}} = \frac{\nu_{\text{acetone}} - \nu_{\text{pulse}}}{\nu_{\text{pulse}}}$$ **Equation 3.10**

which can be reduced to the unit analysis

$$\text{ppm} = \frac{(\text{Hz})}{\text{MHz}}$$

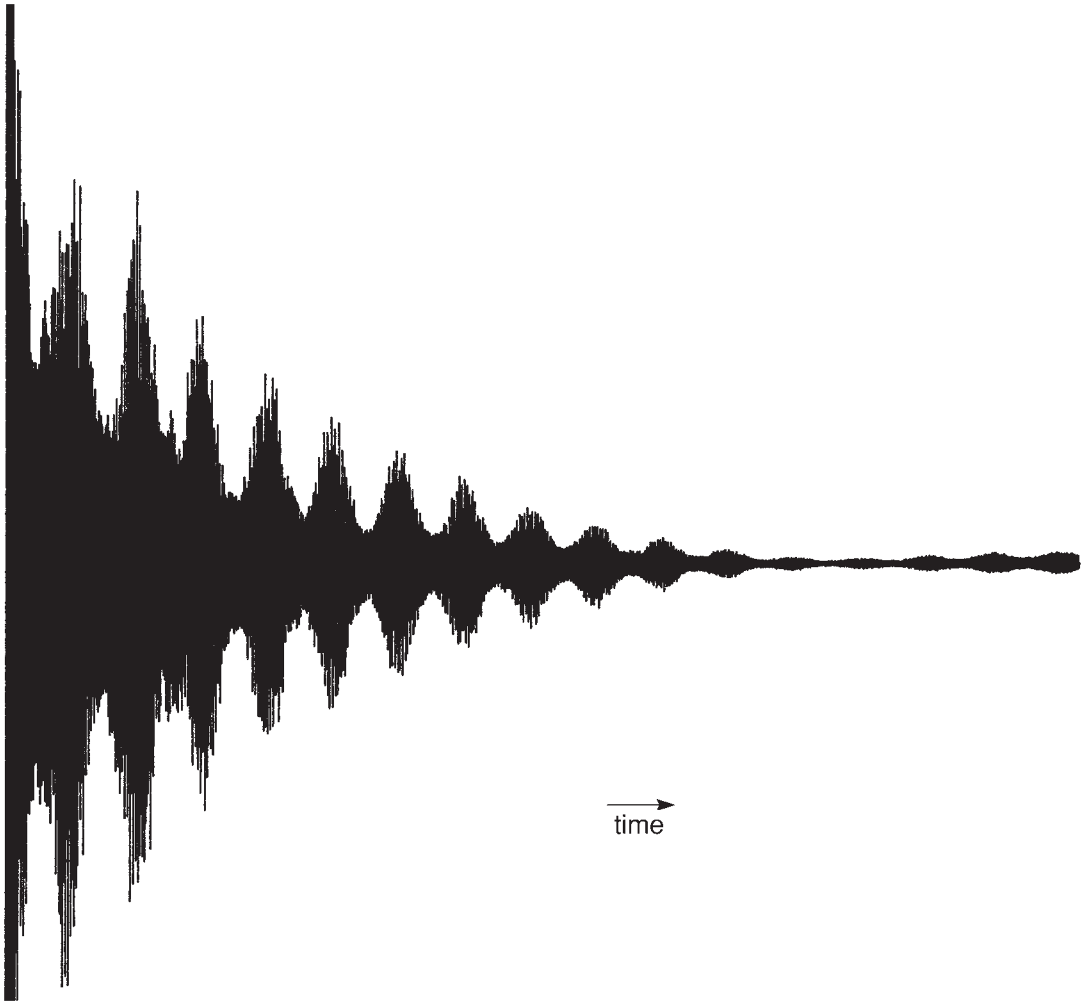


FIGURE 3.15 The ^{1}H free-induction decay (FID) signal of ethyl phenylacetate (300 MHz).

showing that δ'_{acetone} is the chemical shift of the protons of acetone from the position of the pulse, not from TMS. If we know δ'_{TMS}, the position of TMS from the pulse, the actual chemical shift of this peak can be calculated by the adjustment

$$\delta_{\text{actual}} = (\delta'_{\text{acetone}} - \delta'_{\text{TMS}}) \qquad \textbf{Equation 3.11}$$

We can now plot this peak as a chemical shift on a standard NMR spectrum chart (Fig. 3.16c).The peak for acetone appears at about 2.1 ppm. We have converted the time-domain signal to a **frequency-domain signal,** which is the standard format for a spectrum obtained by a CW instrument.

Now consider the ^{1}H FID from ethyl phenylacetate (Fig. 3.15). This complex molecule has many types of hydrogens, and the FID is the superimposition of many *different* frequencies, each of which could have a *different* decay rate! A mathematical method called a **Fourier transform,** however, will separate each of the individual components of this signal and convert them to frequencies. The Fourier transform breaks the FID into its separate sine or cosine wave components. This procedure is too complex to be carried out by eye or by hand; it requires a computer. Modern pulsed FT-NMR

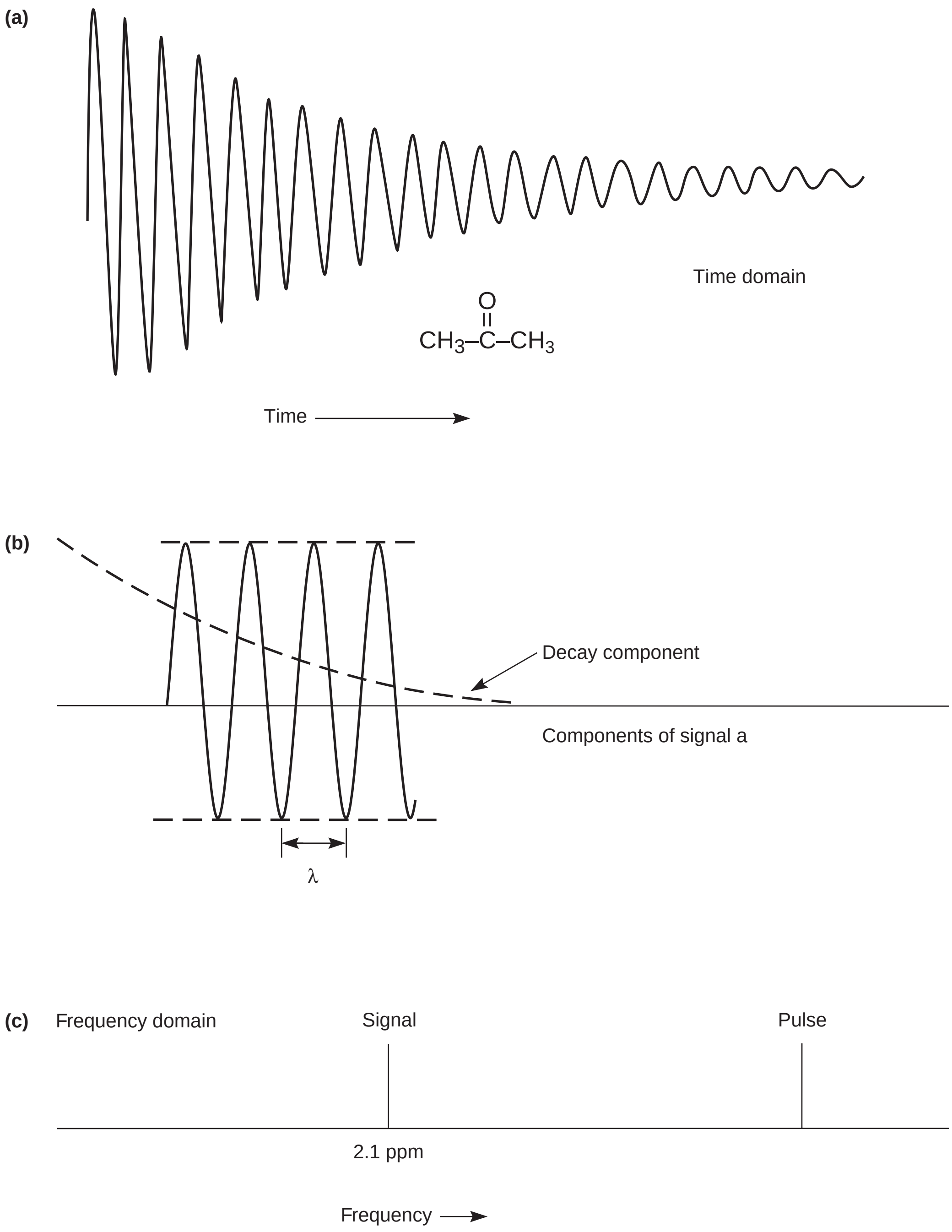


FIGURE 3.16 (a) An FID curve for the hydrogens in acetone (time domain); (b) the appearance of the FID when the decay is removed; (c) the frequency of this sine wave plotted on a frequency chart (frequency domain).

spectrometers have computers built into them that not only can work up the data by this method but also can control all of the settings of the instrument.

The pulsed FT method described here has several advantages over the CW method. It is more sensitive, and it can measure weaker signals. Five to 10 minutes are required to scan and record a

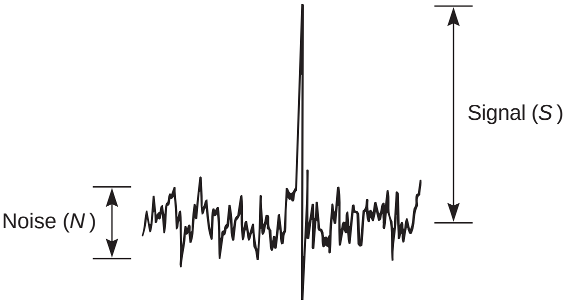


FIGURE 3.17 The signal-to-noise ratio.

CW spectrum; a pulsed experiment is much faster, and a measurement of an FID can be performed in a few seconds. With a computer and fast measurement, it is possible to repeat and average the measurement of the FID signal. This is a real advantage when the sample is small, in which case the FID is weak in intensity and has a great amount of noise associated with it. **Noise** is random electronic signals that are usually visible as fluctuations of the baseline in the signal (Fig. 3.17). Since noise is random, its intensity does not increase as many iterations of the spectrum are added together. Using this procedure, one can show that the signal-to-noise ratio improves as a function of the square root of the number of scans *n*:

$$\frac{S}{N} = f\sqrt{\mathrm{n}}$$

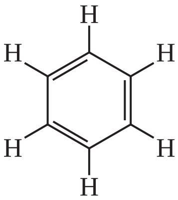
Pulsed FT-NMR is therefore especially suitable for the examination of nuclei that are not very abundant in nature, nuclei that are not strongly magnetic, or very dilute samples.

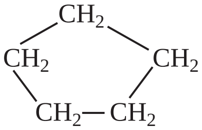
The most modern NMR spectrometers use superconducting magnets, which can have field strengths as high as 14 Tesla and operate at 600 MHz. A superconducting magnet is made of special alloys and must be cooled to liquid helium temperatures. The magnet is usually surrounded by a Dewar flask (an insulated chamber) containing liquid helium; in turn, this chamber is surrounded by another one containing liquid nitrogen. Instruments operating at frequencies above 100 MHz have superconducting magnets. NMR spectrometers with frequencies of 200 MHz, 300 MHz, and 400 MHz are now common in chemistry; instruments with frequencies of 900 MHz are used for special research projects.

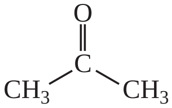
3.8 CHEMICAL EQUIVALENCE—A BRIEF OVERVIEW

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 to clarify these relationships:

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



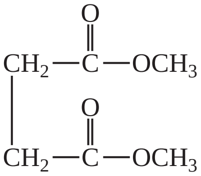


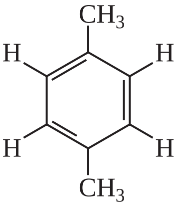


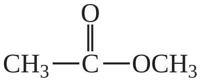
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

$(CH_3)_4Si$

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



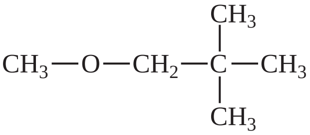




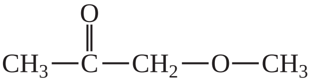
$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$

CH_3-O-CH_2Cl

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



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



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

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 5, which examines chemical and magnetic equivalence in more detail.

3.9 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. 3.12), 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 3.18 is a 60-MHz NMR spectrum of benzyl acetate, showing each of the peaks integrated in this way.

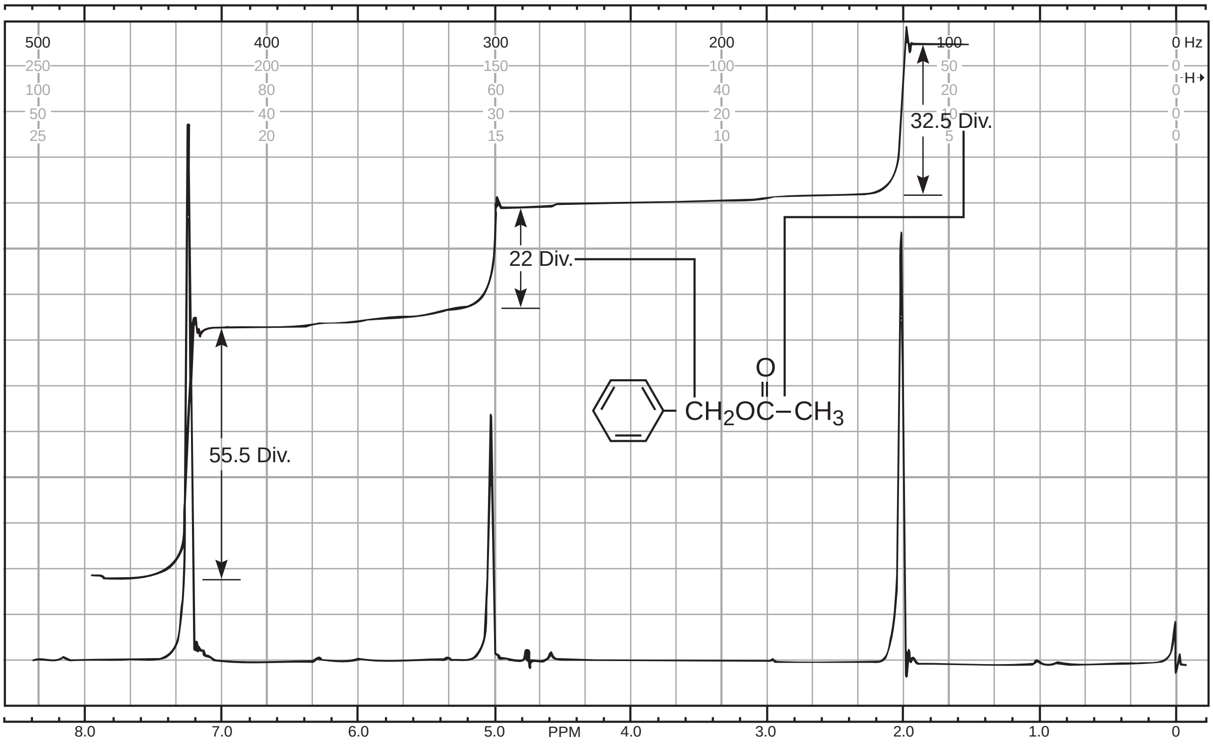


FIGURE 3.18 Determination of the integral ratios for benzyl acetate (60 MHz).

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 3.19 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 3.19 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

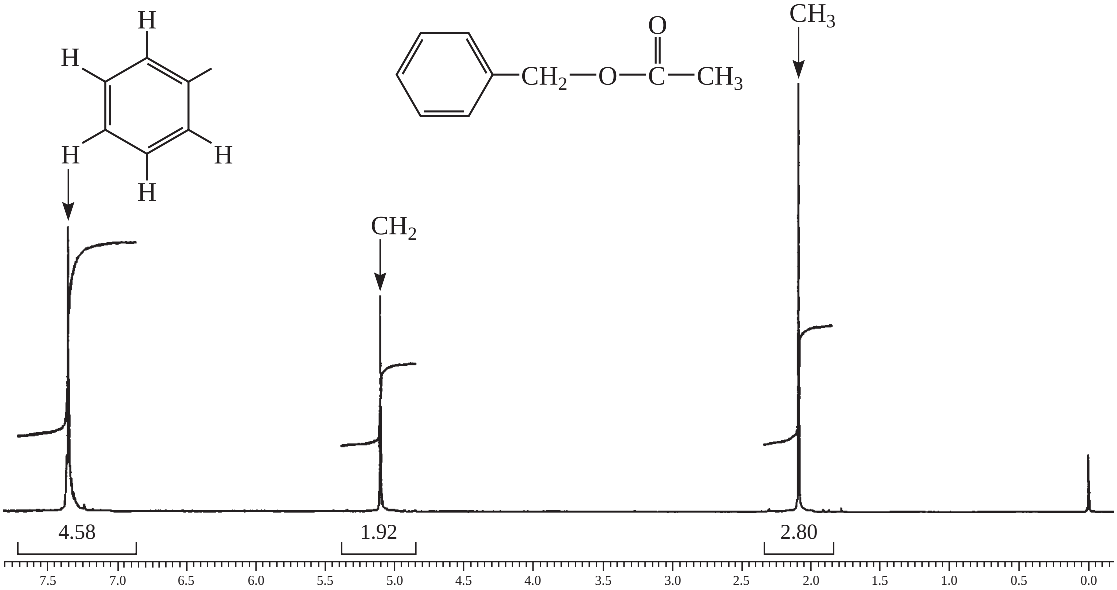


FIGURE 3.19 An integrated spectrum of benzyl acetate determined on a 300-MHz FT-NMR instrument.

that benzyl acetate has 10 total protons, so you need to massage the numbers to obtain 10 protons. 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

3.10 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. 3.12) and benzyl acetate (Fig. 3.18) 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 3.11) 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.

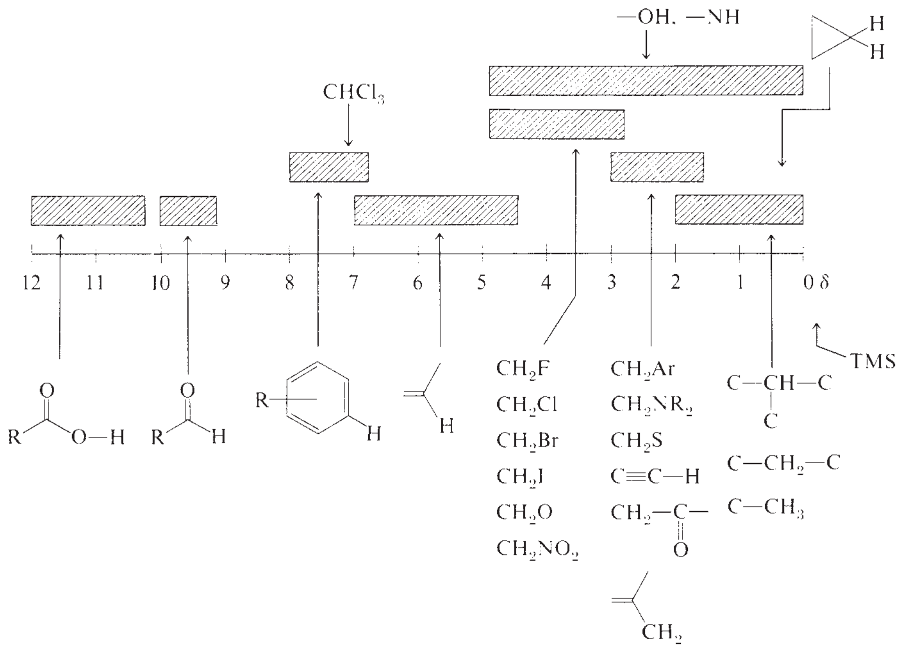


FIGURE 3.20 A simplified correlation chart for proton chemical shift values.

It is important to learn the ranges of chemical shifts over which the most common types of protons have resonance. Figure 3.20 is a correlation chart that contains the most essential and frequently encountered types of protons. Table 3.4 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 3.20 carefully. Table 3.4 and Appendix 2 give more detailed listings of chemical shifts.

3.11 LOCAL DIAMAGNETIC SHIELDING

A. Electronegativity Effects

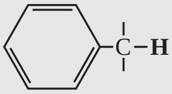
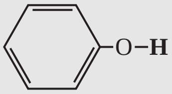
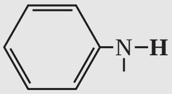
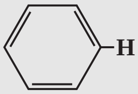
The trend of chemical shifts that is easiest to explain is that involving electronegative elements substituted on the same carbon to which the protons of interest are attached. The chemical shift simply increases as the electronegativity of the attached element increases. Table 3.5 illustrates this relationship 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 3.6 illustrates these effects for the underlined protons.

Section 3.6 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 3.10 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 3.4

APPROXIMATE CHEMICAL SHIFT RANGES (PPM) FOR SELECTED TYPES OF PROTONS[a]

$R-C\mathbf{H}_3$		0.7 – 1.3
$R-C\mathbf{H}_2-R$		1.2 – 1.4
$R_3C\mathbf{H}$		1.4 – 1.7
$R-\overset{\vert}{C}=\overset{\vert}{C}-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		1.6 – 2.6
$R-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H},\ H-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		2.1 – 2.4
$RO-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H},\ HO-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		2.1 – 2.5
$N\equiv C-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		2.1 – 3.0
		2.3 – 2.7
$R-C\equiv C-\mathbf{H}$		1.7 – 2.7
$R-S-\mathbf{H}$	var	1.0 – 4.0[b]
$R-\underset{\vert}{N}-\mathbf{H}$	var	0.5 – 4.0[b]
$R-O-\mathbf{H}$	var	0.5 – 5.0[b]
	var	4.0 – 7.0[b]
	var	3.0 – 5.0[b]
$R-\overset{O}{\overset{\Vert}{C}}-\underset{\vert}{N}-\mathbf{H}$	var	5.0 – 9.0[b]
$R-\underset{\vert}{N}-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		2.2 – 2.9
$R-S-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		2.0 – 3.0
$I-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		2.0 – 4.0
$Br-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		2.7 – 4.1
$Cl-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		3.1 – 4.1
$R-\overset{O}{\overset{\Vert}{\underset{\underset{O}{\Vert}}{S}}}-O-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		ca. 3.0
$RO-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H},\ HO-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		3.2 – 3.8
$R-\overset{O}{\overset{\Vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		3.5 – 4.8
$O_2N-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		4.1 – 4.3
$F-\overset{\vert}{\underset{\vert}{C}}-\mathbf{H}$		4.2 – 4.8
$R-\overset{\vert}{C}=\overset{\vert}{C}-\mathbf{H}$		4.5 – 6.5
		6.5 – 8.0
$R-\overset{O}{\overset{\Vert}{C}}-\mathbf{H}$		9.0 – 10.0
$R-\overset{O}{\overset{\Vert}{C}}-O\mathbf{H}$		11.0 – 12.0

[a] For those hydrogens shown as $-\overset{|}{\underset{|}{C}}-H$, 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 3.5
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

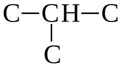
TABLE 3.6
SUBSTITUTION EFFECTS

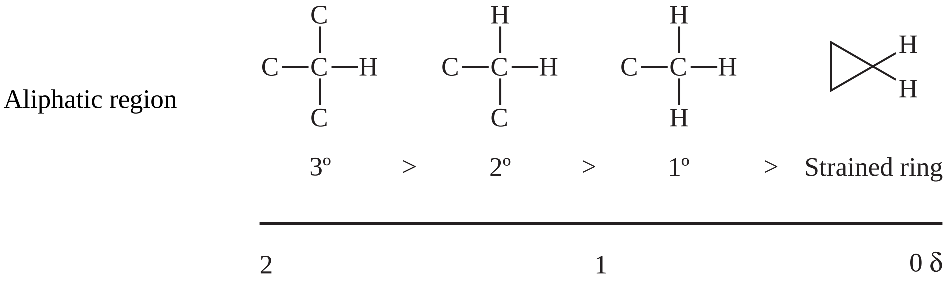
$C\underline{H}Cl_3$	$C\underline{H}_2Cl_2$	$C\underline{H}_3Cl$	$-C\underline{H}_2Br$	$-C\underline{H}_2-CH_2Br$	$-C\underline{H}_2-CH_2CH_2Br$
7.27	5.30	3.05	3.30	1.69	1.25

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

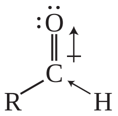
Referring to Figure 3.20 and Table 3.4, notice that all hydrogens attached to purely sp^3 carbon atoms ($C-CH_3$, $C-CH_2-C$,  $C-\underset{\underset{C}{|}}{C}H-C$, cycloalkanes) have resonance in the limited range from 0 to 2 ppm, provided that no electronegative elements or π-bonded groups are nearby. 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^2-1*s* 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 3.12). 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 3.12).



An aldehyde

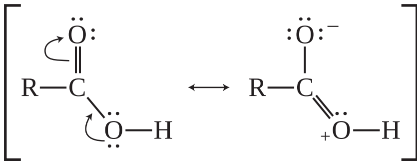
sp Hydrogens

Acetylenic hydrogens (C—H, *sp*-1*s*) appear anomalously at 2 to 3 ppm owing to anisotropy (to be discussed in Section 3.12). 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.

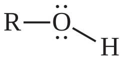
Hydrogen Bonding and Exchangeable Hydrogens

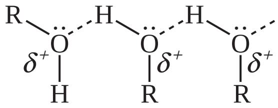
Protons that can exhibit hydrogen bonding (e.g., hydroxyl or amino protons) exhibit extremely variable absorption positions over a wide range. They are usually found attached to a heteroatom. Table 3.7 lists the ranges over which some of these types of protons are found. The more hydrogen bonding that takes place, the more deshielded a proton becomes. The amount of hydrogen bonding

TABLE 3.7
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

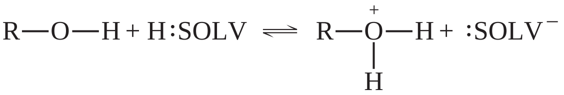
is often a function of concentration and temperature. The more concentrated the solution, the more molecules can come into contact with each other and hydrogen bond. At high dilution (no H bonding), hydroxyl protons absorb near 0.5–1.0 ppm; in concentrated solution, their absorption is closer to 4–5 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:

$$\mathrm{R{-}O{-}H_a + R'{-}O{-}H_b \rightleftharpoons R{-}O{-}H_b + R'{-}O{-}H_a}$$



$$\mathrm{R{-}O{-}H + H{:}SOLV \rightleftharpoons R{-}\underset{\displaystyle H}{\overset{+}{O}}{-}H + {:}SOLV^-}$$

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

Chapter 6 will discuss all of these situations in more detail.

3.12 MAGNETIC ANISOTROPY

Figure 3.20 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 3.21 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.

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. 3.22). Hence, acetylenic hydrogens have

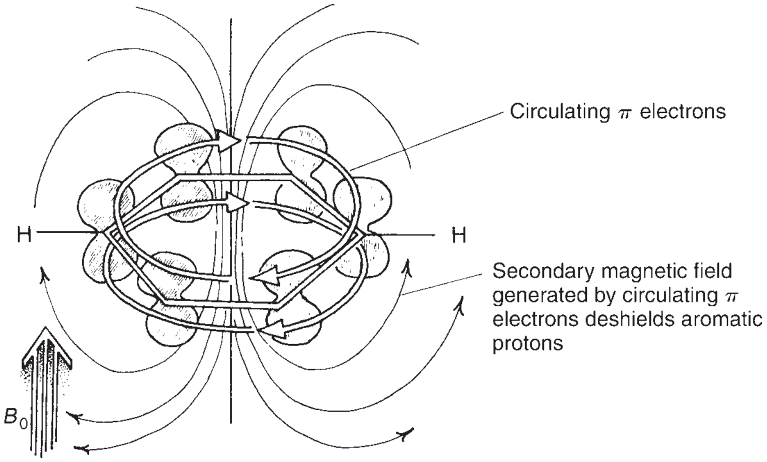


FIGURE 3.21 Diamagnetic anisotropy in benzene.

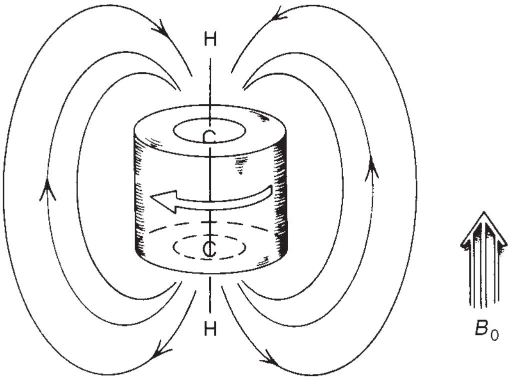


FIGURE 3.22 Diamagnetic anisotropy in acetylene.

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 3.23 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 3.24 shows the effects of anisotropy in several actual molecules.

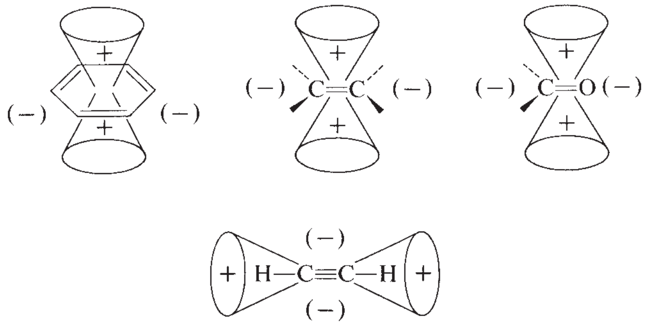


FIGURE 3.23 Anisotropy caused by the presence of π electrons in some common multiple-bond systems.

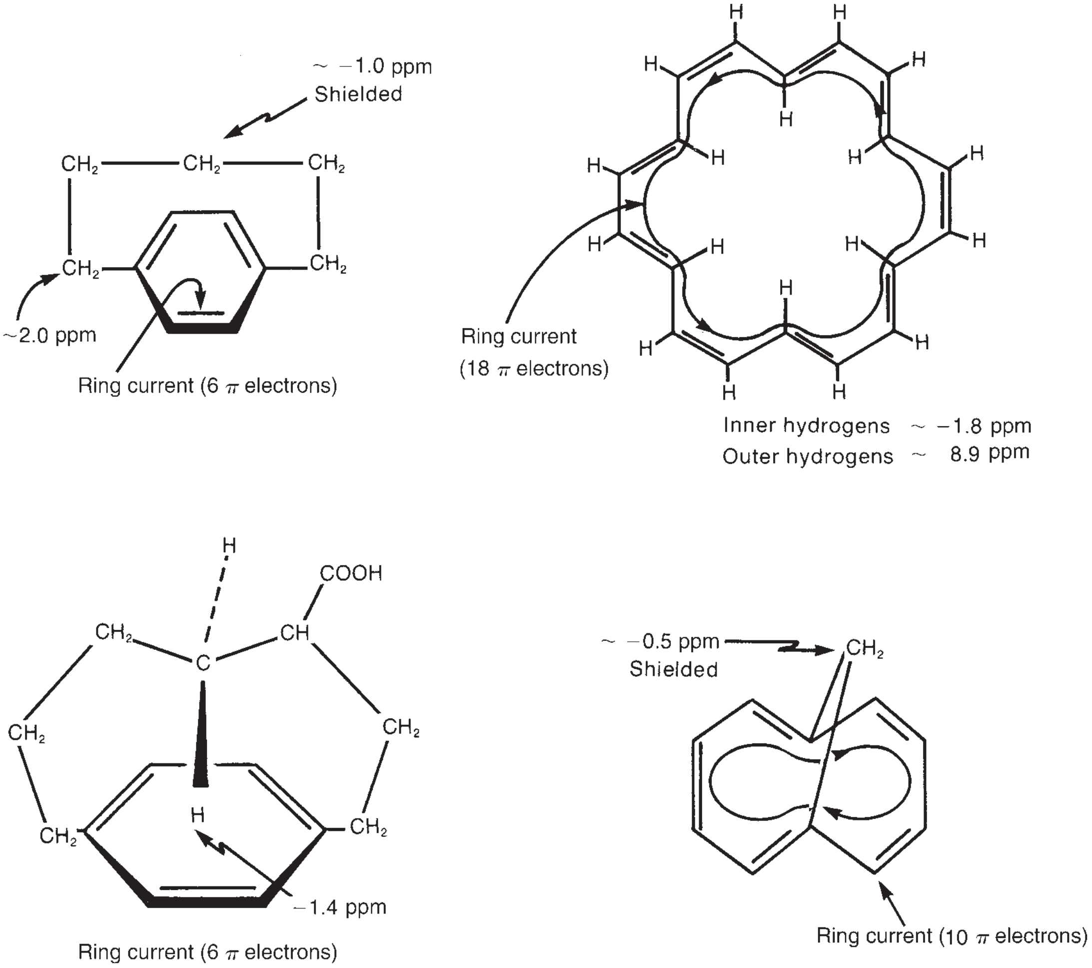
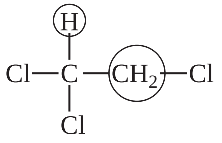


FIGURE 3.24 The effects of anisotropy in some actual molecules.

3.13 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 3.25 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.

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

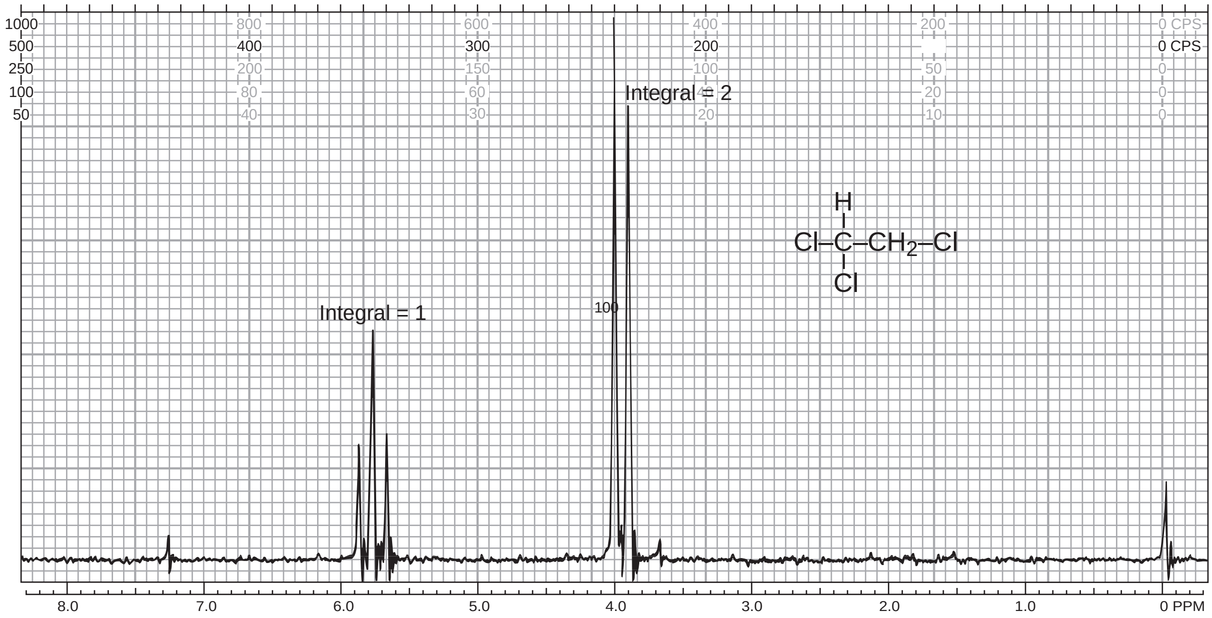
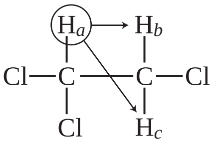
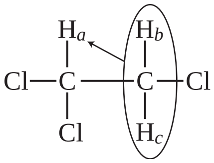


FIGURE 3.25 The ^{1}H NMR spectrum of 1,1,2-trichloroethane (60 MHz).

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).



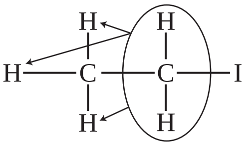
Two neighbors give a triplet
($n + 1 = 3$) (area = 1)



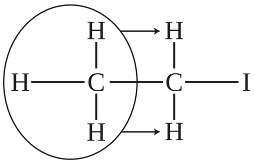
One neighbor gives a doublet
($n + 1 = 2$) (area = 2)

Equivalent protons
behave as a group

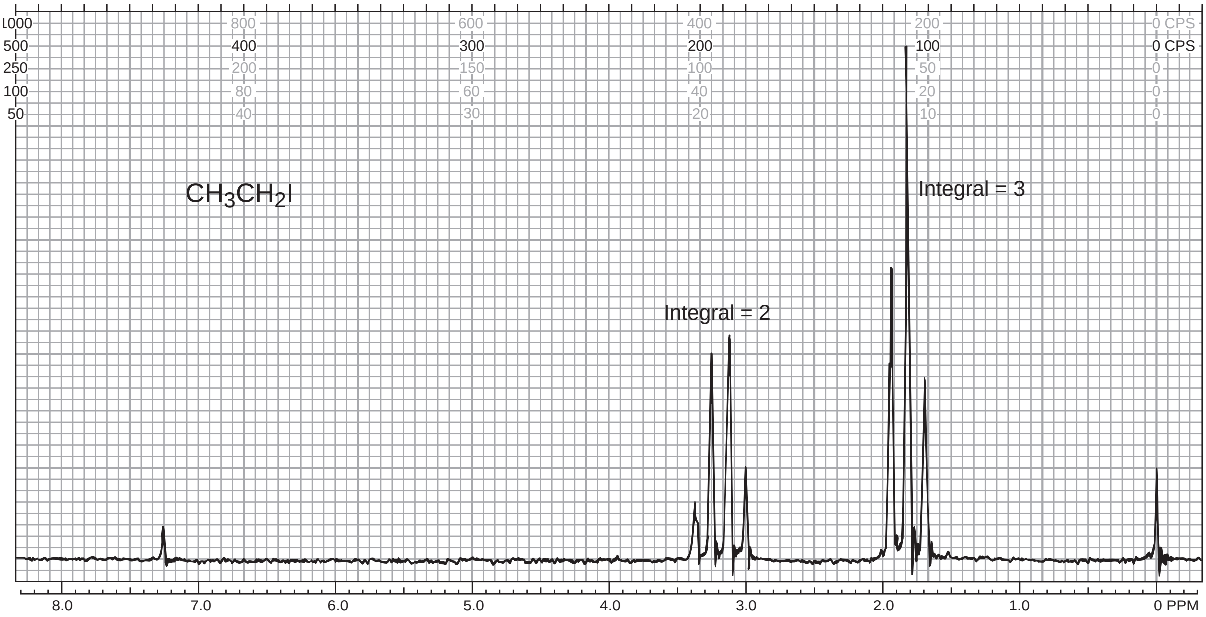
Before proceeding to explain the origin of this effect, let us examine two simpler cases predicted by the $n + 1$ Rule. Figure 3.26 is the spectrum of ethyl iodide (CH_3CH_2I). Notice that the methylene protons are split into a quartet (four peaks), and the methyl group is split into a triplet (three peaks). This is explained as follows:



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

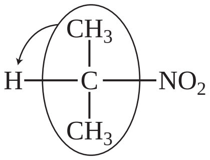


Two equivalent neighbors give a triplet
($n + 1 = 3$) (area = 3)

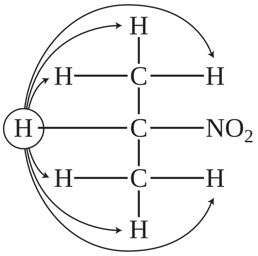


F I G U R E 3 . 2 6 The ^{1}H NMR spectrum of ethyl iodide (60 MHz).

Finally, consider 2-nitropropane, which has the spectrum given in Figure 3.27.



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 3.10 and 3.11. 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 3.8.

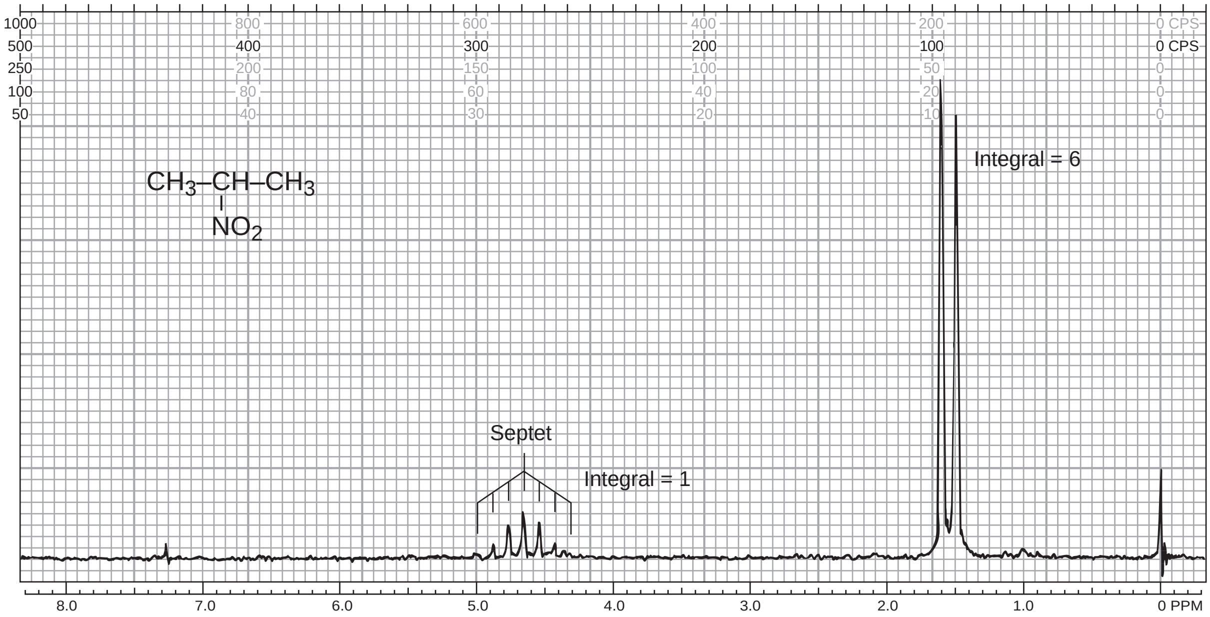
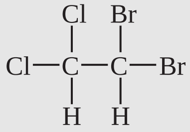
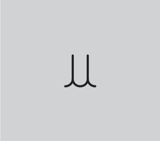
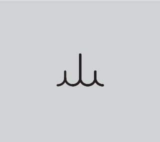
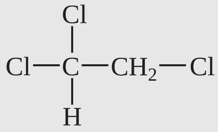
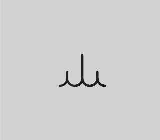
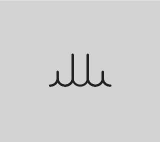
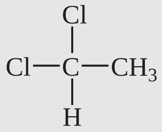
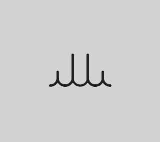
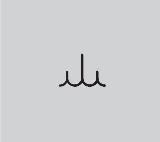
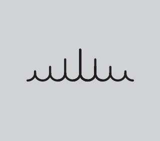
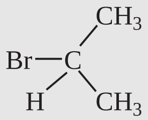
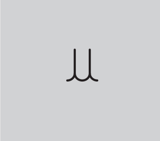


FIGURE 3.27 The ^{1}H NMR spectrum of 2-nitropropane (60 MHz).

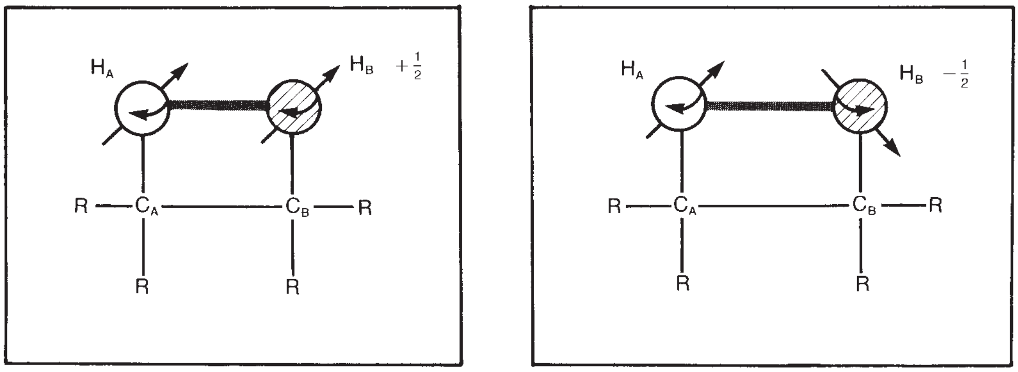
TABLE 3.8
SOME EXAMPLES OF COMMONLY OBSERVED SPLITTING PATTERNS IN COMPOUNDS

1H		 $Cl-\overset{Cl}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-Br$		1H
1H		 $Cl-\overset{Cl}{\underset{H}{C}}-CH_2-Cl$		2H
2H		$Cl-CH_2-CH_2-Br$		2H
1H		 $Cl-\overset{Cl}{\underset{H}{C}}-CH_3$		3H
2H		$Cl-CH_2-CH_3$		3H
1H		 $Br-\overset{CH_3}{\underset{H\quad CH_3}{C}}$		6H
	Downfield		Upfield	

3.14 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 3.28 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.



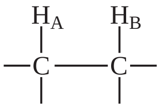
X-type molecule

Y-type molecule

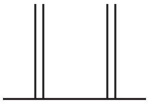
FIGURE 3.28 Two different molecules in a solution with differing spin relationships between protons H_A and H_B.

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 3.29 summarizes the spin–spin splitting situation for proton A.

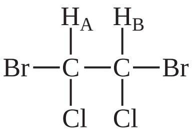
Of course, proton A also "splits" proton B since proton A can adopt two spin states as well. The final spectrum for this situation consists of two doublets:



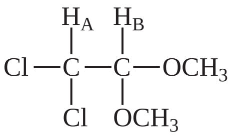
$$-\overset{H_A}{\underset{|}{\overset{|}{C}}}-\overset{H_B}{\underset{|}{\overset{|}{C}}}-$$



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:



$$\mathrm{Br}-\overset{H_A}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-\overset{H_B}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-\mathrm{Br}$$



$$\mathrm{Cl}-\overset{H_A}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-\overset{H_B}{\underset{OCH_3}{\overset{|}{\underset{|}{C}}}}-\mathrm{OCH_3}$$

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.

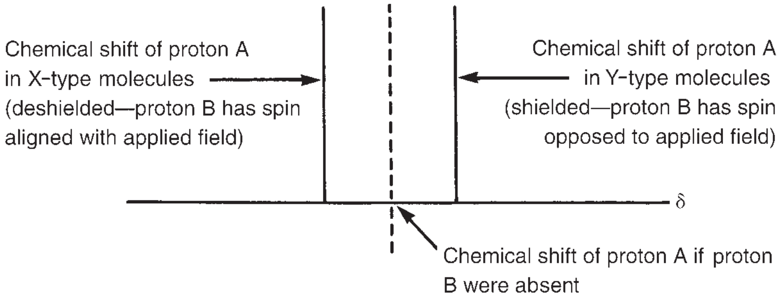


FIGURE 3.29 The origin of spin–spin splitting in proton A's NMR spectrum.

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 5 will discuss.

3.15 THE ETHYL GROUP (CH_3CH_2—)

Now consider ethyl iodide, which has the spectrum shown in Figures 3.26 and 3.30. 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 3.13. 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 3.31.

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.

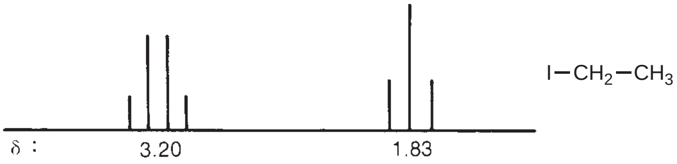


FIGURE 3.30 The ethyl splitting pattern.

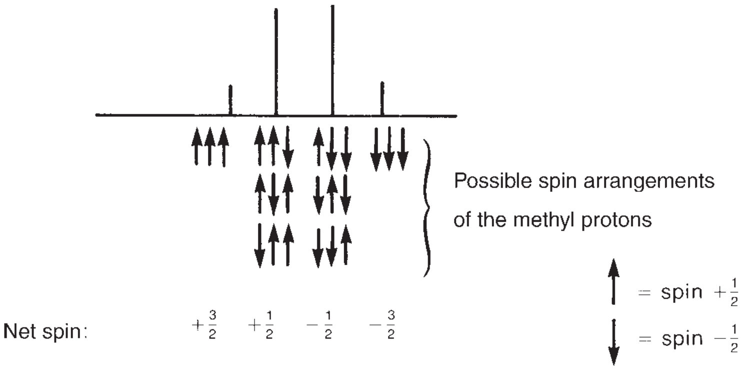


FIGURE 3.31 The splitting pattern of methylene protons due to the presence of an adjacent methyl group.

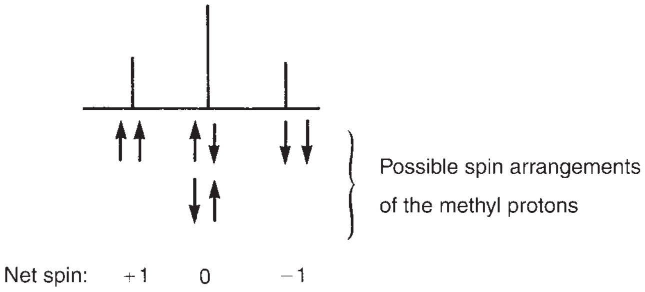


FIGURE 3.32 The splitting pattern of methyl protons due to the presence of an adjacent methylene group.

Keep in mind that there are actually 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 3.32 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.

3.16 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. 3.33). 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 3.27 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

FIGURE 3.33 Pascal's triangle.

3.17 THE COUPLING CONSTANT

Section 3.15 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 3.26 and 3.34.

The spectrum in Figure 3.26 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 δ 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. 3.35).

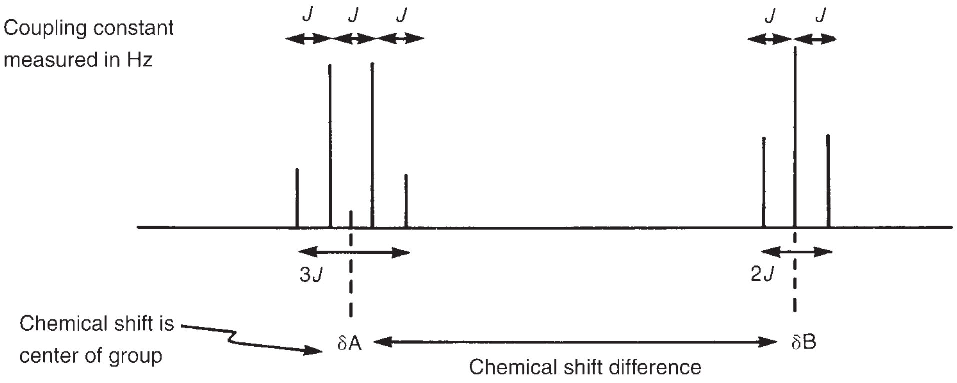


FIGURE 3.34 The definition of the coupling constants in the ethyl splitting pattern.

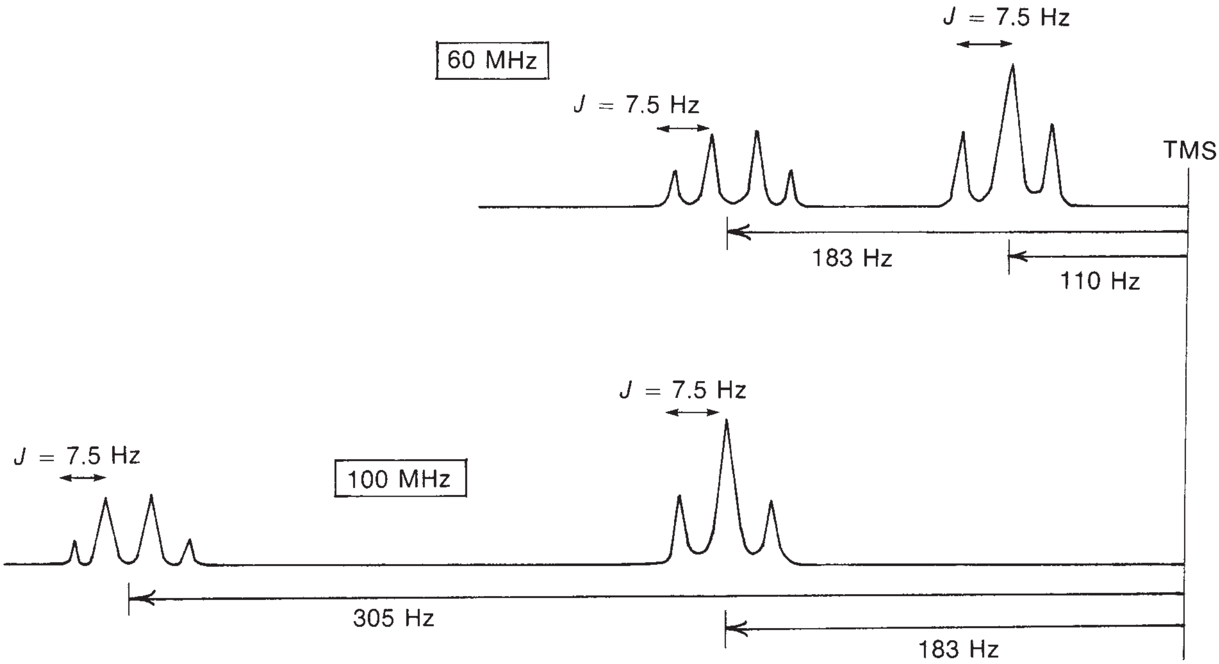
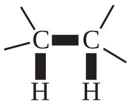
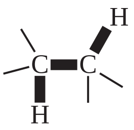


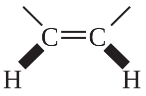
FIGURE 3.35 An illustration of the relationship between the chemical shift and the coupling constant.

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. 3.25), for which J = 6 Hz, and 2-nitropropane (Fig. 3.27), 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.

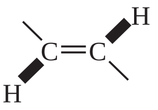




Coupling constants on modern FT-NMR spectrometers are more easily determined by printing Hertz values directly on the peaks. It is a simple matter of subtracting these values to determine the coupling constants in Hertz. See, for example, the spectra shown in Figures 3.40 and 3.46, in which peaks have been labeled in Hertz. Section 5.2 in Chapter 5 describes the various types of coupling constants associated with two-bond (^2J), three-bond (^3J), and four-bond (^4J) interactions.



^3J *cis* = 10 Hz

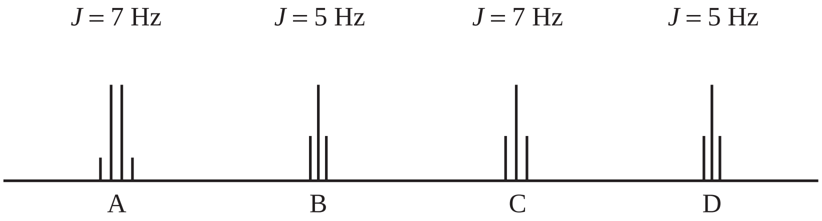


^3J *trans* = 16 Hz

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 5.8 in Chapter 5).

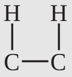
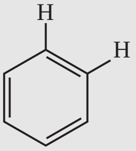
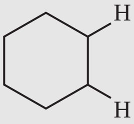
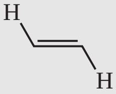
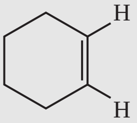
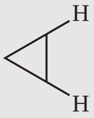
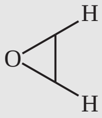
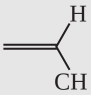
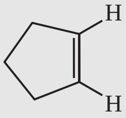
Table 3.9 gives the approximate values of some representative ^3J coupling constants. A more extensive list of coupling constants appears in Chapter 5, Section 5.2, and in Appendix 5.

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.



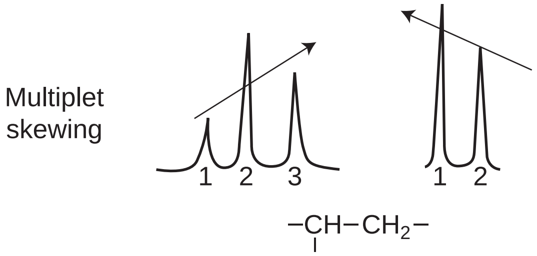
Take, for example, the preceding spectrum, which shows three triplets and one quartet. Which triplet is associated with the quartet? It is, of course, the one that has the same J values as are

TABLE 3.9
SOME REPRESENTATIVE ^3J COUPLING CONSTANTS AND THEIR APPROXIMATE VALUES (HZ)

	6 to 8		*ortho* 6 to 10		a,a 8 to 14 a,e 0 to 7 e,e 0 to 5
	11 to 18		8 to 11		*cis* 6 to 12 *trans* 4 to 8
	6 to 15				*cis* 2 to 5 *trans* 1 to 3
	4 to 10				5 to 7

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 3.25 and 3.26 for examples.



3.18 A COMPARISON OF NMR SPECTRA AT LOW– AND HIGH–FIELD STRENGTHS

Section 3.17 showed that, for a given proton, the frequency shift (in Hertz) from TMS is larger when the spectrum is determined at a higher field; however, all coupling constants remain the same as they were at low field (see Fig. 3.35). Even though the shifts in Hertz increase, the chemical shifts (in ppm) of a given proton at low field and high field are the same because we divide by a different operating frequency in each case to determine the chemical shift (Eq. 3.8). If we compare the spectra of a compound determined at both low field and high field, however, the gross appearances of the spectra will differ because, although the coupling constant has the same magnitude in Hertz regardless of operating frequency, the number of Hertz per ppm unit changes. At 60 MHz, for instance, a ppm unit equals 60 Hz, whereas at 300 MHz a ppm unit equals 300 Hz. The coupling constant does not change, but it becomes a smaller fraction of a ppm unit!

When we plot the two spectra on paper to the same parts-per-million scale (same spacing in length for each ppm), the splittings in the high-field spectrum appear compressed, as in Figure 3.36, which shows the 60-MHz and 300-MHz spectra of 1-nitropropane. The coupling has not changed in size; it has simply become a smaller fraction of a ppm unit. At higher field, it becomes necessary to use an expanded parts-per-million scale (more space per ppm) to observe the splittings. The 300-MHz multiplets are identical to those observed at 60 MHz. This can be seen in Figure 3.36b, which shows expansions of the multiplets in the 300-MHz spectrum.

With 300-MHz spectra, therefore, it is frequently necessary to show expansions if one wishes to see the details of the multiplets. In some of the examples in this chapter, we have used 60-MHz spectra—not because we are old-fashioned, but because these spectra show the multiplets more clearly without the need for expansions.

In most cases, the expanded multiplets from a high-field instrument are identical to those observed with a low-field instrument. However, there are also cases in which complex multiplets

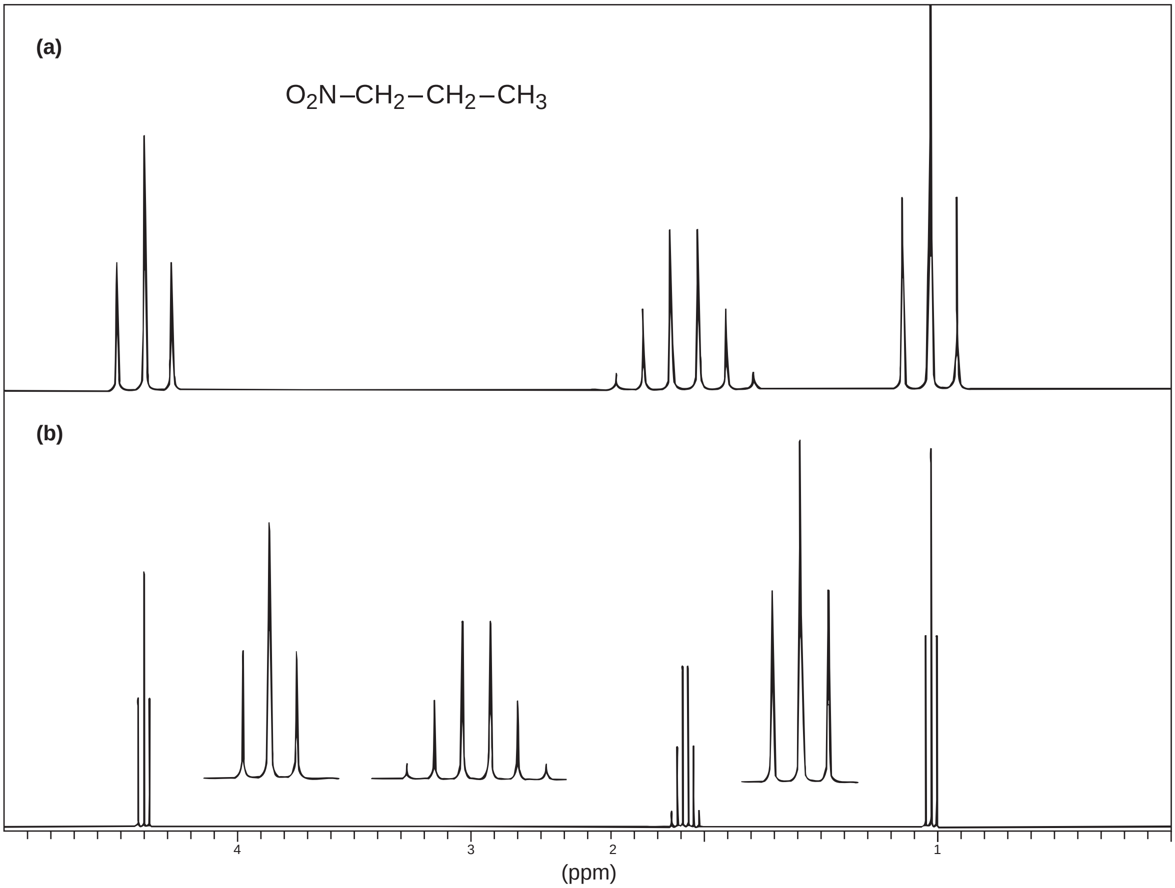


FIGURE 3.36 The NMR spectrum of 1-nitropropane. (a) Spectrum determined at 60 MHz; (b) spectrum determined at 300 MHz (with expansions).

become simplified when higher field is used to determine the spectrum. This simplification occurs because the multiplets are moved farther apart, and a type of interaction called a second-order interaction is reduced or even completely removed. Chapter 5 will discuss second-order interactions.

3.19 SURVEY OF TYPICAL ^{1}H NMR ABSORPTIONS BY TYPE OF COMPOUND

In this section, we will review the typical NMR absorptions that may be expected for compounds in each of the most common classes of organic compounds. These guidelines can be consulted whenever you are trying to establish the class of an unknown compound. Coupling behaviors commonly observed in these compounds are also included in the tables. This coupling information was not covered in this chapter, but it is discussed in Chapters 5 and 6. It is included here so that it will be useful if you wish to use this survey later.

A. Alkanes

Alkanes can have three different types of hydrogens (methyl, methylene, and methine), each of which appears in its own region of the NMR spectrum.

SPECTRAL ANALYSIS BOX—Alkanes

CHEMICAL SHIFTS

$\mathrm{R{-}C\mathbf{H}_3}$	0.7–1.3 ppm	Methyl groups are often recognizable as a tall singlet, doublet, or triplet even when overlapping other CH absorptions.
$\mathrm{R{-}C\mathbf{H}_2{-}R}$	1.2–1.4 ppm	In long chains, all of the methylene (CH_2) absorptions may be overlapped in an unresolvable group.
$\mathrm{R_3C\mathbf{H}}$	1.4–1.7 ppm	Note that methine hydrogens (CH) have a larger chemical shift than those in methylene or methyl groups.

COUPLING BEHAVIOR

$\mathrm{{-}C\mathbf{H}{-}C\mathbf{H}{-}}$	$^3J \approx 7$–8 Hz	In hydrocarbon chains, adjacent hydrogens will generally couple, with the spin–spin splitting following the *n*+1 Rule.

In alkanes (aliphatic or saturated hydrocarbons), all of the C**H** hydrogen absorptions are typically found from about 0.7 to 1.7 ppm. Hydrogens in methyl groups are the most highly shielded type of proton and are found at chemical shift values (0.7–1.3 ppm) lower than methylene (1.2–1.4 ppm) or methine hydrogens (1.4–1.7 ppm).

In long hydrocarbon chains, or in larger rings, all of the C**H** and C$\mathbf{H}_2$ absorptions may overlap in an unresolvable group. Methyl group peaks are usually separated from other types of hydrogens, being found at lower chemical shifts (higher field). However, even when methyl hydrogens are located within an unresolved cluster of peaks, the methyl peaks can often be recognized as tall singlets, doublets, or triplets clearly emerging from the absorptions of the other types of protons. Methine protons are usually separated from the other protons, being shifted further downfield.

Figure 3.37 shows the spectrum of the hydrocarbon octane. Note that the integral can be used to estimate the total number of hydrogens (the ratio of CH_3 to CH_2-type carbons) since all of the CH_2 hydrogens are in one group and the CH_3 hydrogens are in the other. The NMR spectrum shows the lowest whole-number ratios. You need to multiply by 2 to give the actual number of protons.

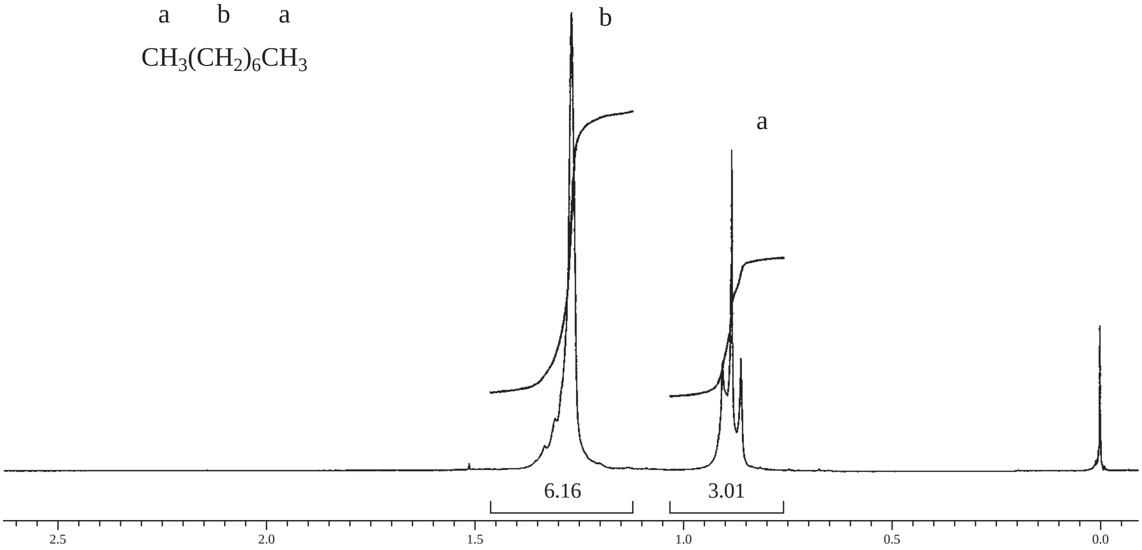


FIGURE 3.37 ^{1}H spectrum of octane.

B. Alkenes

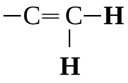
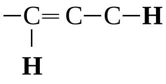
Alkenes have two types of hydrogens: vinyl (those attached directly to the double bond) and allylic hydrogens (those attached to the *α carbon*, the carbon atom attached to the double bond). Each type has a characteristic chemical shift region.

SPECTRAL ANALYSIS BOX—Alkenes

CHEMICAL SHIFTS

$C{=}C{-}\mathbf{H}$	4.5–6.5 ppm	Hydrogens attached to a double bond (vinyl hydrogens) are deshielded by the anisotropy of the adjacent double bond.
$C{=}C{-}C{-}\mathbf{H}$	1.6–2.6 ppm	Hydrogens attached to a carbon adjacent to a double bond (allyic hydrogens) are also deshielded by the anisotropy of the double bond, but because the double bond is more distant, the effect is smaller.

COUPLING BEHAVIOR

$\mathbf{H}{-}C{=}C{-}\mathbf{H}$	$^3J_{trans} \approx 11$–18 Hz $^3J_{cis} \approx 6$–15 Hz	The splitting patterns of vinyl protons may be complicated by the fact that they may not be equivalent even when located on the same carbon of the double bond (Section 5.6).
 $-C{=}\underset{\underset{\mathbf{H}}{\mid}}{C}{-}\mathbf{H}$	$^2J \approx 0$ –3 Hz	
 $-\underset{\underset{\mathbf{H}}{\mid}}{C}{=}C{-}C{-}\mathbf{H}$	$^4J \approx 0$ –3 Hz	When allylic hydrogens are present in an alkene, they may show long-range allylic coupling (Section 5.7) to hydrogens on the far double-bond carbon as well as the usual splitting due to the hydrogen on the adjacent (nearest) carbon.

Two types of NMR absorptions are typically found in alkenes: **vinyl absorptions** due to protons directly attached to the double bond (4.5–6.5 ppm) and **allylic absorptions** due to protons located on a carbon atom adjacent to the double bond (1.6–2.6 ppm). Both types of hydrogens are deshielded due to the anisotropic field of the π electrons in the double bond. The effect is smaller for the allylic hydrogens because they are more distant from the double bond. A spectrum of 2-methyl-1-pentene is shown in Figure 3.38. Note the vinyl hydrogens at 4.7 ppm and the allylic methyl group at 1.7 ppm.

The splitting patterns of both vinyl and allylic hydrogens can be quite complex due to the fact that the hydrogens attached to a double bond are rarely equivalent and to the additional complication that allylic hydrogens can couple to all of the hydrogens on a double bond, causing additional splittings. These situations are discussed in Chapter 5, Sections 5.8–5.9.

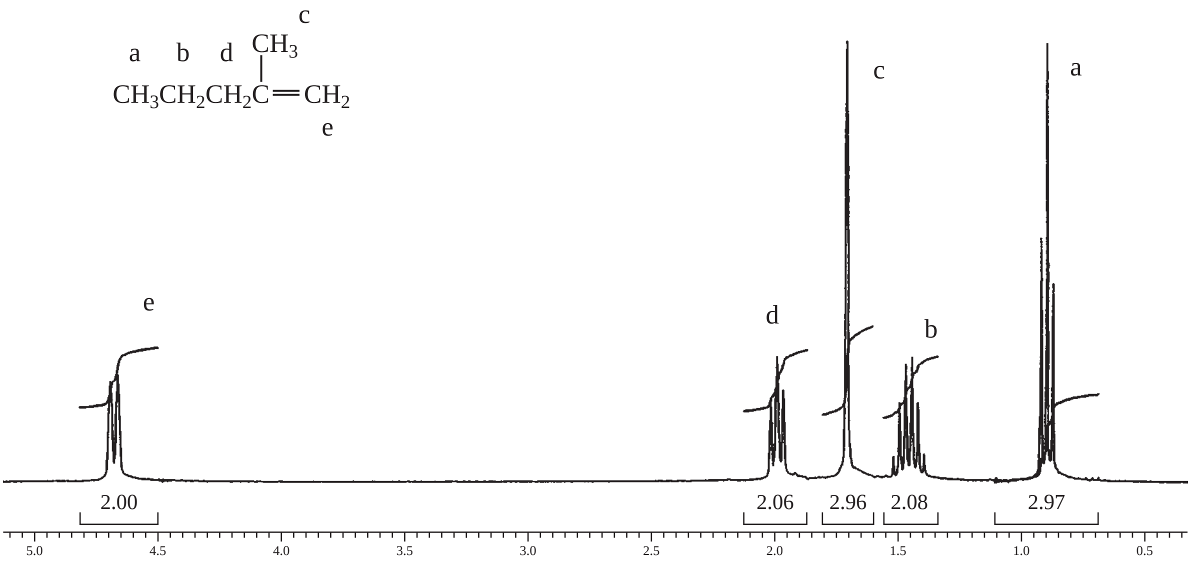


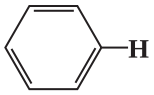
FIGURE 3.38 ^{1}H spectrum of 2-methyl-1-pentene.

C. Aromatic Compounds

Aromatic compounds have two characteristic types of hydrogens: aromatic ring hydrogens (benzene ring hydrogens) and benzylic hydrogens (those attached to an adjacent carbon atom).

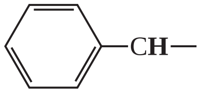
SPECTRAL ANALYSIS BOX—Aromatic Compounds

CHEMICAL SHIFTS



6.5–8.0 ppm

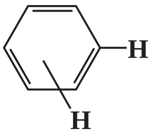
Hydrogens attached to an aromatic (benzenoid) ring have a large chemical shift, usually near 7.0 ppm. They are deshielded by the large anisotropic field generated by the electrons in the ring's π system.



2.3–2.7 ppm

Benzylic hydrogens are also deshielded by the anisotropic field of the ring, but they are more distant from the ring, and the effect is smaller.

COUPLING BEHAVIOR



$^3J_{ortho} \approx 7$–10 Hz
$^4J_{meta} \approx 2$–3 Hz
$^5J_{para} \approx 0$–1 Hz

Splitting patterns for the protons on a benzene ring are discussed in Section 5.10. It is often possible to determine the positions of the substituents on the ring from these splitting patterns and the magnitudes of the coupling constants.

The hydrogens attached to aromatic rings are easily identified. They are found in a region of their own (6.5–8.0 ppm) in which few other types of hydrogens show absorption. Occasionally, a highly deshielded vinyl hydrogen will have its absorption in this range, but this is not frequent. The hydrogens on an aromatic ring are more highly deshielded than those attached to double bonds due to the large anisotropic field that is generated by the circulation of the π electrons in the ring (ring current). See Section 3.12 for a review of this specialized behavior of aromatic rings.

The largest chemical shifts are found for ring hydrogens when electron-withdrawing groups such as $-NO_2$ are attached to the ring. These groups deshield the attached hydrogens by withdrawing electron density from the ring through resonance interaction. Conversely, electron-donating groups like methoxy ($-OCH_3$) increase the shielding of these hydrogens, causing them to move upfield.

Nonequivalent hydrogens attached to a benzene ring will interact with one another to produce spin–spin splitting patterns. The amount of interaction between hydrogens on the ring is dependent on the number of intervening bonds or the distance between them. *Ortho* hydrogens ($^3J \approx$ 7–10 Hz) couple more strongly than *meta* hydrogens ($^4J \approx$ 2–3 Hz), which in turn couple more strongly than *para* hydrogens ($^5J \approx$ 0–1 Hz). It is frequently possible to determine the substitution pattern of the ring by the observed splitting patterns of the ring hydrogens (Section 5.10). One pattern that is easily recognized is that of a *para*-disubstituted benzene ring (Fig. 5.60). The spectrum of α-chloro-*p*-xylene is shown in Figure 3.39. The highly deshielded ring hydrogens appear at 7.2 ppm and clearly show a *para*-disubstitution pattern. The chemical shift of the methyl protons at 2.3 ppm shows a smaller deshielding effect. The large shift of the methylene hydrogens is due to the electronegativity of the attached chlorine.

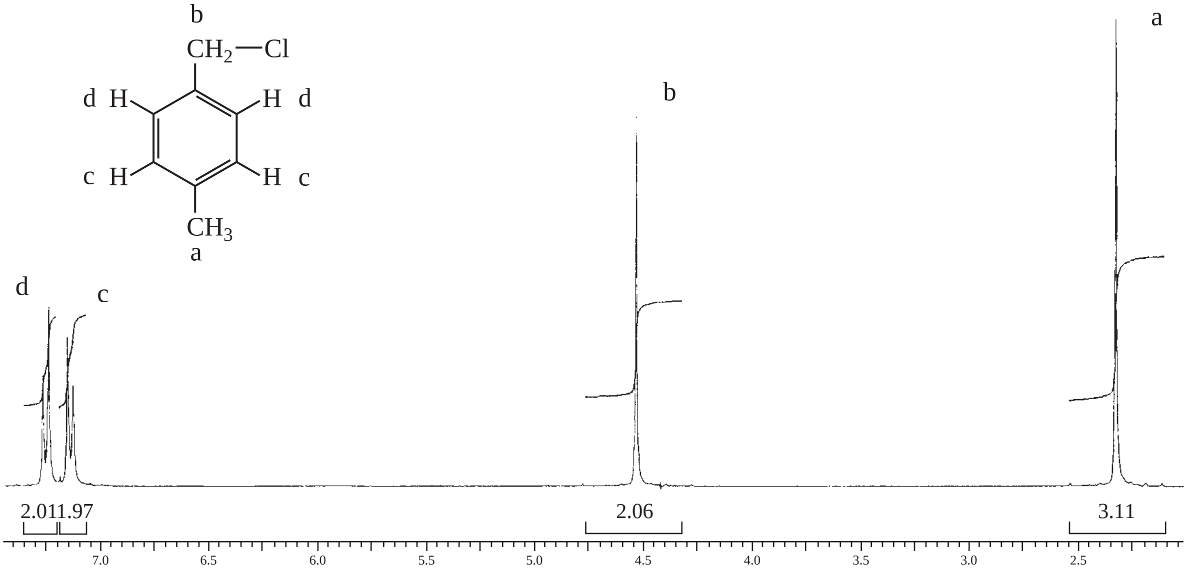


FIGURE 3.39 ^{1}H spectrum of α-chloro-p-xylene.

D. Alkynes

Terminal alkynes (those with a triple bond at the end of a chain) will show an acetylenic hydrogen, as well as the α hydrogens found on carbon atoms next to the triple bond. The acetylenic hydrogen will be absent if the triple bond is in the middle of a chain.

SPECTRAL ANALYSIS BOX—Alkynes

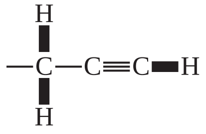
CHEMICAL SHIFTS

C≡C—**H**	1.7–2.7 ppm	The terminal or acetylenic hydrogen has a chemical shift near 1.9 ppm due to anisotropic shielding by the adjacent π bonds.
C≡C—C**H**—	1.6–2.6 ppm	Protons on a carbon next to the triple bond are also affected by the π system.

COUPLING BEHAVIOR

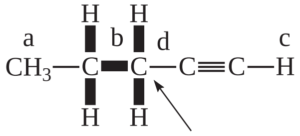
H—C≡C—C—**H**	^4J = 2–3 Hz	"Allylic coupling" is often observed in alkynes, but is relatively small.

In terminal alkynes (compounds in which the triple bond is in the 1-position), the acetylenic proton appears near 1.9 ppm. It is shifted upfield because of the shielding provided by the π electrons (Fig. 3.22). A spectrum of 1-pentyne is shown in Figure 3.40, where the insets show expansions of the 1.94 and 2.17-ppm regions of the spectrum for protons **c** and **d**, respectively. The peaks in the expansions have been labeled with Hertz (Hz) values so that coupling constants can be calculated. Note that the acetylenic proton (**c**) at 1.94 ppm appears as a triplet with a coupling constant of between 2.6 and 3.0 Hz. This coupling constant is calculated by subtraction: 585.8 – 583.2 = 2.6 Hz or 583.2 – 580.2 = 3.0 Hz, and they will vary somewhat because of experimental error. Values less than 7.0 Hz (^3J) are often attributed to a long-range coupling found in terminal alkynes, in which four bond (^4J) coupling can occur. Sections 5.2 and 5.10 in Chapter 5 provide more information about long-range coupling.



^4J = 2.6 Hz

There are two H atoms four bonds away, n = 2 + 1 = triplet



^3J = 7 Hz

There are two H atoms three bonds away, n = 2 + 1 = triplet

Proton **d** is split into a triplet by the two neighboring protons (^3J), and then the triplet is split again into doublets (see inset for proton **d** in Fig. 3.40). The type of pattern is referred to as a *triplet of doublets*. The ^3J coupling constant is calculated by subtraction, for example, counting from left to right, peak 6 from peak 4 (648.3 – 641.3 = 7.0 Hz). The ^4J coupling constant can also be calculated from the triplet of doublets, for example, peak 6 from peak 5 (643.9 – 641.3 = 2.6 Hz).

The sextet for the CH_2 group (**b**) at 1.55 ppm in Figure 3.40 results from coupling with a total of five adjacent (^3J) hydrogen atoms on carbons **d** and **a.** Finally, the triplet for the CH_3 group (**a**) at 1.0 ppm results from coupling with two adjacent (^3J) hydrogen atoms on carbon **b.**

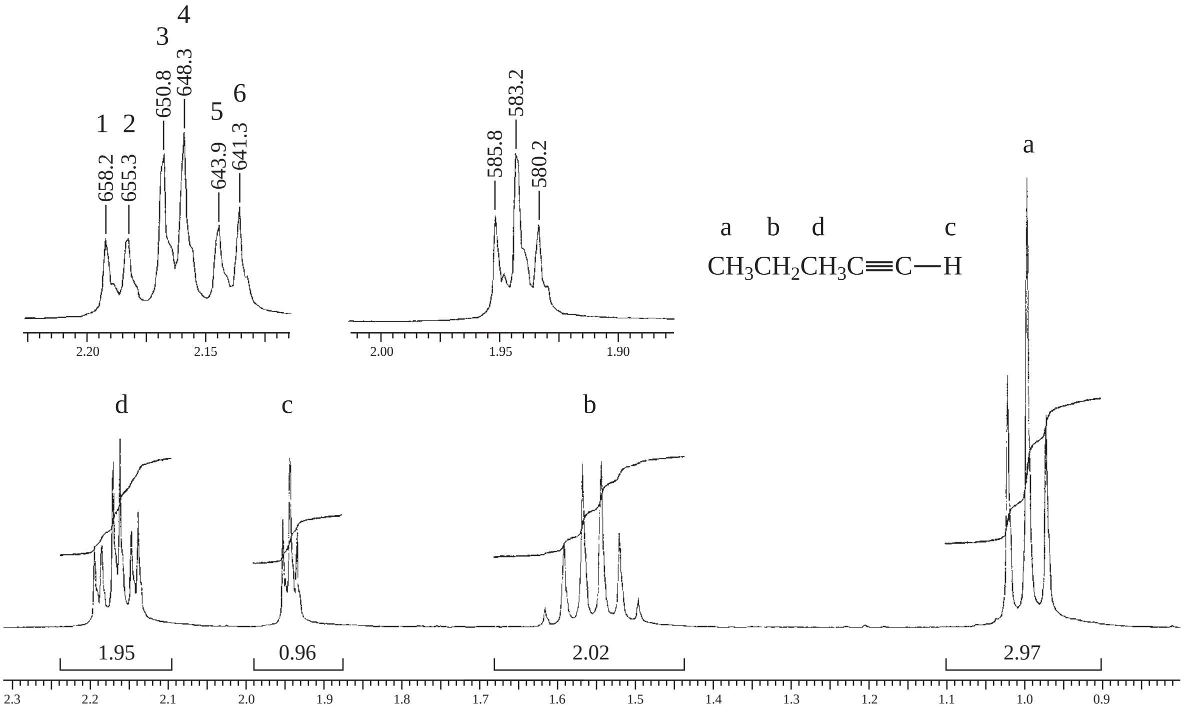


FIGURE 3.40 ^{1}H spectrum of 1-pentyne.

E. Alkyl Halides

In alkyl halides, the *α* hydrogen (the one attached to the same carbon as the halogen) will be deshielded.

SPECTRAL ANALYSIS BOX—Alkyl Halides

CHEMICAL SHIFTS

−C**H**−I	2.0– 4.0 ppm
−C**H**−Br	2.7– 4.1 ppm
−C**H**−Cl	3.1– 4.1 ppm
−C**H**−F	4.2– 4.8 ppm

The chemical shift of a hydrogen atom attached to the same carbon as a halide atom will increase (move further downfield). This deshielding effect is due to the electronegativity of the attached halogen atom. The extent of the shift is increased as the electronegativity of the attached atom increases, with the largest shift found in compounds containing fluorine.

COUPLING BEHAVIOR

−C**H**−**F**	$^2J \approx 50$ Hz
−C**H**−C**F**−	$^3J \approx 20$ Hz

Compounds containing fluorine will show spin–spin splitting due to coupling between the fluorine and the hydrogens on either the same or the adjacent carbon atom. ^{19}F has a spin of $\frac{1}{2}$. The other halogens (I, Cl, Br) do not show any coupling.

Hydrogens attached to the same carbon as a halogen are deshielded (local diamagnetic shielding) due to the electronegativity of the attached halogen (Section 3.11A). The amount of deshielding

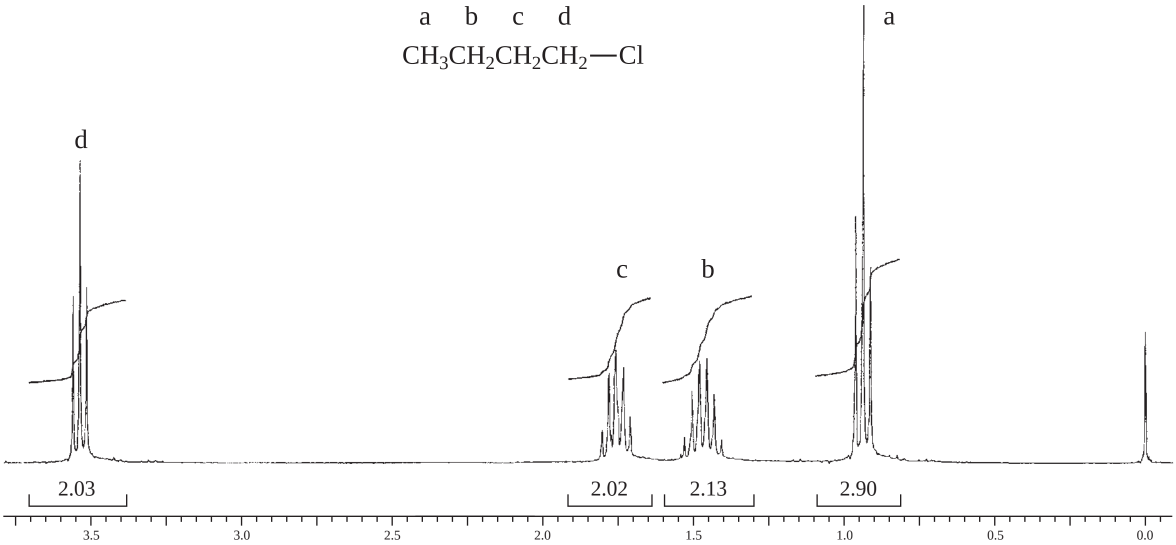


FIGURE 3.41 ^{1}H spectrum of 1-chlorobutane.

increases as the electronegativity of the halogen increases, and it is further increased when multiple halogens are present.

Compounds containing fluorine will show coupling between the fluorine and the hydrogens both on the same carbon (−C**HF**) and those hydrogens on the adjacent carbon (C**H**−C**F**−). Since the spin of fluorine (^{19}F) is $\frac{1}{2}$, the $n + 1$ Rule can be used to predict the multiplicities of the attached hydrogens. Other halogens do not cause spin–spin splitting of hydrogen peaks.

The spectrum of 1-chlorobutane is shown in Figure 3.41. Note the large downfield shift (deshielding) of the hydrogens on carbon 1 due to the attached chlorine.

F. Alcohols

In alcohols, both the hydroxyl proton and the α hydrogens (those on the same carbon as the hydroxyl group) have characteristic chemical shifts.

SPECTRAL ANALYSIS BOX—Alcohols

CHEMICAL SHIFTS

C−O**H**	0.5–5.0 ppm	The chemical shift of the −OH hydrogen is highly variable, its position depending on concentration, solvent, and temperature. The peak may be broadened at its base by the same set of factors.
C**H**−O−**H**	3.2–3.8 ppm	Protons on the α carbon are deshielded by the electronegative oxygen atom and are shifted downfield in the spectrum.

COUPLING BEHAVIOR

C**H**−O**H**	*No coupling* (*usually*), or ^3J = 5 Hz	Because of the rapid chemical exchange of the −OH proton in many solutions, coupling is not usually observed between the −OH proton and those hydrogens attached to the α carbon.

The chemical shift of the $-O\mathbf{H}$ hydrogen is variable, its position depending on concentration, solvent, temperature, and presence of water or of acidic or basic impurities. This peak can be found anywhere in the range of 0.5–5.0 ppm. The variability of this absorption is dependent on the rates of $-O\mathbf{H}$ proton exchange and the amount of hydrogen bonding in the solution (Section 6.1).

The $-O\mathbf{H}$ hydrogen is usually not split by hydrogens on the adjacent carbon ($-C\mathbf{H}-O\mathbf{H}$) because rapid exchange decouples this interaction (Section 6.1).

$$-CH-OH + \mathbf{H}A \rightleftharpoons -CH-O\mathbf{H} + HA$$ **no coupling if exchange is rapid**

Exchange is promoted by increased temperature, small amounts of acid impurities, and the presence of water in the solution. In ultrapure alcohol samples, $-C\mathbf{H}-O\mathbf{H}$ coupling is observed. A freshly purified and distilled sample, or a previously unopened commercial bottle, may show this coupling.

On occasion, one may use the rapid exchange of an alcohol as a method for identifying the $-OH$ absorption. In this method, a drop of D_2O is placed in the NMR tube containing the alcohol solution. After shaking the sample and sitting for a few minutes, the $-O\mathbf{H}$ hydrogen is replaced by deuterium, causing it to disappear from the spectrum (or to have its intensity reduced).

$$-CH-O\mathbf{H} + D_2O \rightleftharpoons -CH-OD + \mathbf{H}OD$$ **deuterium exchange**

The hydrogen on the adjacent carbon ($-C\mathbf{H}-OH$) appears in the range 3.2–3.8 ppm, being deshielded by the attached oxygen. If exchange of the O**H** is taking place, this hydrogen will not show any coupling with the $-O\mathbf{H}$ hydrogen, but will show coupling to any hydrogens on the adjacent carbon located further along the carbon chain. If exchange is not occurring, the pattern of this hydrogen may be complicated by differently sized coupling constants for the $-C\mathbf{H}-O\mathbf{H}$ and $-C\mathbf{H}-C\mathbf{H}-O-$ couplings (Section 6.1).

A spectrum of 2-methyl-1-propanol is shown in Figure 3.42. Note the large downfield shift (3.4 ppm) of the hydrogens attached to the same carbon as the oxygen of the hydroxyl group. The hydroxyl group appears at 2.4 ppm, and in this sample it shows some coupling to the hydrogens on the adjacent carbon. The methine proton at 1.75 ppm has been expanded and inset on the spectrum. There are nine

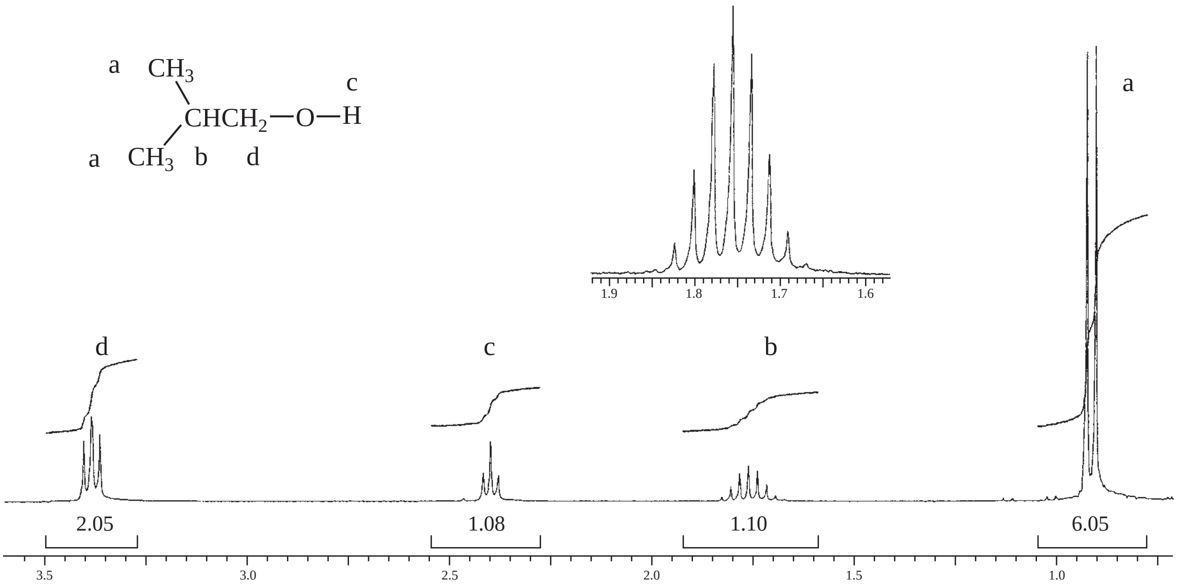


FIGURE 3.42 ^{1}H spectrum of 2-methyl-1-propanol.

peaks (nonet) in that pattern, suggesting coupling with the two methyl groups and one methylene group, $n = (3 + 3 + 2) + 1 = 9$.

G. Ethers

In ethers, the α hydrogens (those attached to the α *carbon*, which is the carbon atom attached to the oxygen) are highly deshielded.

SPECTRAL ANALYSIS BOX—Ethers

CHEMICAL SHIFTS

R—O—C**H**—	3.2–3.8 ppm	The hydrogens on the carbons attached to the oxygen are deshielded due to the electronegativity of the oxygen.

In ethers, the hydrogens on the carbon next to oxygen are deshielded due to the electronegativity of the attached oxygen, and they appear in the range 3.2–3.8 ppm. Methoxy groups are especially easy to identify as they appear as a tall singlet in this area. Ethoxy groups are also easy to identify, having both an upfield triplet and a distinct quartet in the region of 3.2–3.8 ppm. An exception is found in epoxides, in which, due to ring strain, the deshielding is not as great, and the hydrogens on the ring appear in the range 2.5–3.5 ppm.

The spectrum of butyl methyl ether is shown in Figure 3.43. The absorption of the methyl and methylene hydrogens next to the oxygen are both seen at about 3.4 ppm. The methoxy peak is

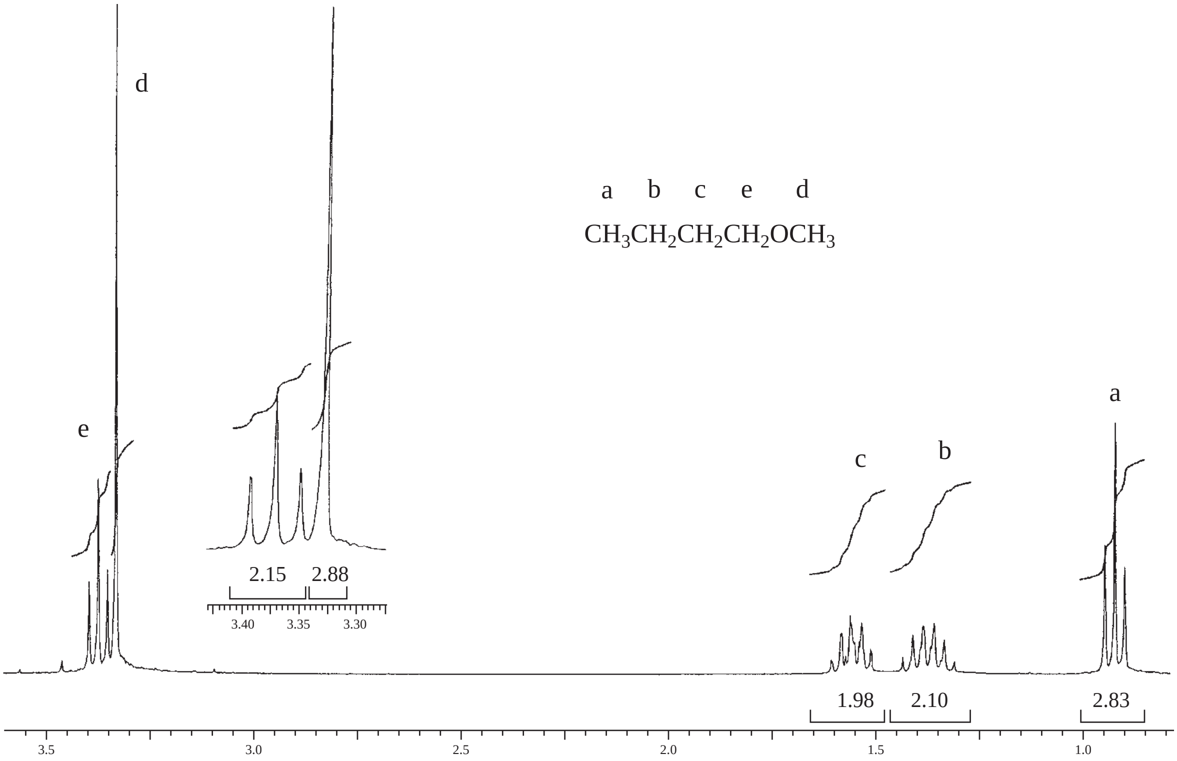


FIGURE 3.43 ^{1}H spectrum of butyl methyl ether.

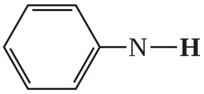
unsplit and stands out as a tall, sharp singlet. The methylene hydrogens are split into a triplet by the hydrogens on the adjacent carbon of the chain.

H. Amines

Two characteristic types of hydrogens are found in amines: those attached to nitrogen (the hydrogens of the amino group) and those attached to the α carbon (the same carbon to which the amino group is attached).

SPECTRAL ANALYSIS BOX—Amines

CHEMICAL SHIFTS

R—N—**H**	0.5–4.0 ppm	Hydrogens attached to a nitrogen have a variable chemical shift depending on the temperature, acidity, amount of hydrogen bonding, and solvent.
—C**H**—N—	2.2–2.9 ppm	The α hydrogen is slightly deshielded due to the electronegativity of the attached nitrogen.
	3.0–5.0 ppm	This hydrogen is deshielded due to the anisotropy of the ring and the resonance that removes electron density from nitrogen and changes its hybridization.

COUPLING BEHAVIOR

—**N**—**H**	$^1J \approx 50$ Hz	Direct coupling between a nitrogen and an attached hydrogen is not usually observed but is quite large when it occurs. More commonly, this coupling is obscured by quadrupole broadening by nitrogen or by proton exchange. See Sections 6.4 and 6.5.
—**N**—C**H**	$^2J \approx 0$ Hz	This coupling is usually not observed.
$\underset{\mathbf{H}}{\underset{\mid}{C}}-N-\mathbf{H}$	$^3J \approx 0$ Hz	Due to chemical exchange, this coupling is usually not observed.

Location of the —N**H** absorptions is not a reliable method for the identification of amines. These peaks are extremely variable, appearing over a wide range of 0.5–4.0 ppm, and the range is extended in aromatic amines. The position of the resonance is affected by temperature, acidity, amount of hydrogen bonding, and solvent. In addition to this variability in position, the —N**H** peaks are often very broad and weak without any distinct coupling to hydrogens on an adjacent carbon atom. This condition can be caused by chemical exchange of the —N**H** proton or by a property of nitrogen atoms called *quadrupole broadening* (see Section 6.5). The amino hydrogens will exchange with D_2O, as already described for alcohols, causing the peak to disappear.

$$-N-\mathbf{H} + D_2O \rightleftharpoons -N-D + DO\mathbf{H}$$

The —N**H** peaks are strongest in aromatic amines (anilines), in which resonance appears to strengthen the N**H** bond by changing the hybridization. Although nitrogen is a spin-active element ($I = 1$), coupling is usually not observed between either attached or adjacent hydrogen atoms, but it can appear in certain specific cases. Reliable prediction is difficult.

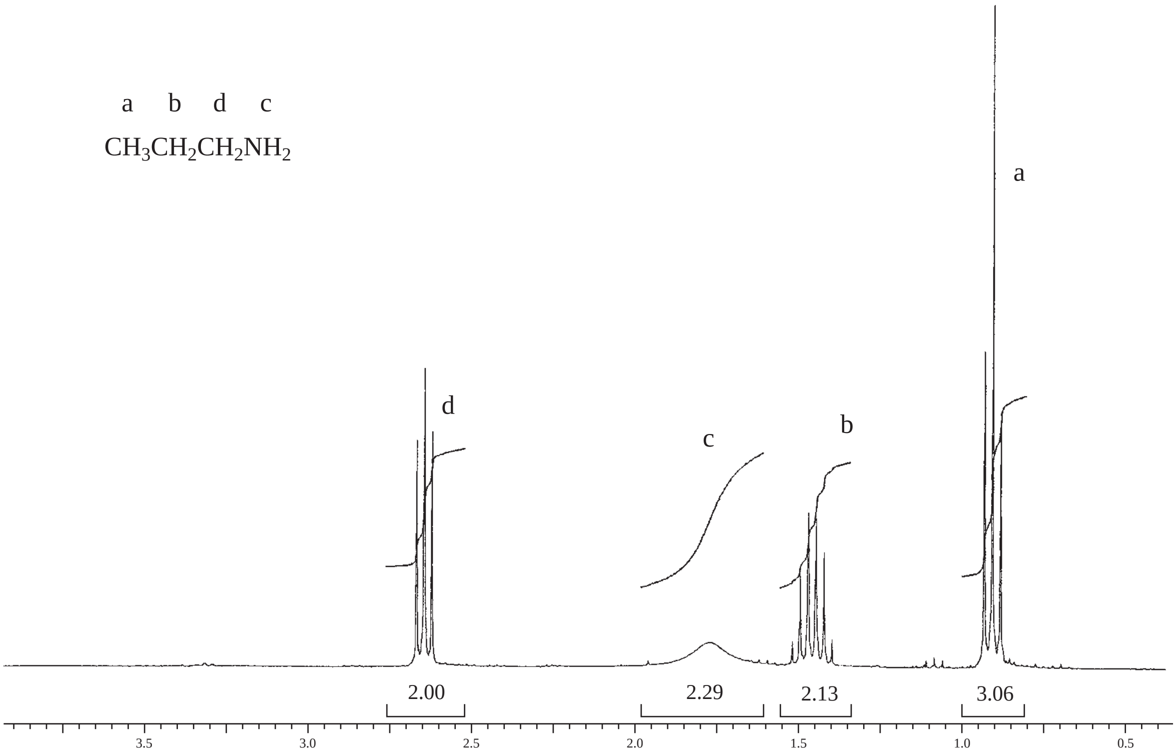


FIGURE 3.44 ^{1}H spectrum of propylamine.

The hydrogens α to the amino group are slightly deshielded by the presence of the electronegative nitrogen atom, and they appear in the range 2.2–2.9 ppm. A spectrum of propylamine is shown in Figure 3.44. Notice the weak, broad NH absorptions at 1.8 ppm and that there appears to be a lack of coupling between the hydrogens on the nitrogen and those on the adjacent carbon atom.

I. Nitriles

In nitriles, only the α hydrogens (those attached to the same carbon as the cyano group) have a characteristic chemical shift.

SPECTRAL ANALYSIS BOX—Nitriles

CHEMICAL SHIFTS

$-C\mathbf{H}-C\equiv N$	2.1–3.0 ppm	The α hydrogens are slightly deshielded by the cyano group.

Hydrogens on the adjacent carbon of a nitrile are slightly deshielded by the anisotropic field of the π-bonded electrons appearing in the range 2.1–3.0 ppm. A spectrum of valeronitrile is shown in Figure 3.45. The hydrogens next to the cyano group appear near 2.35 ppm.

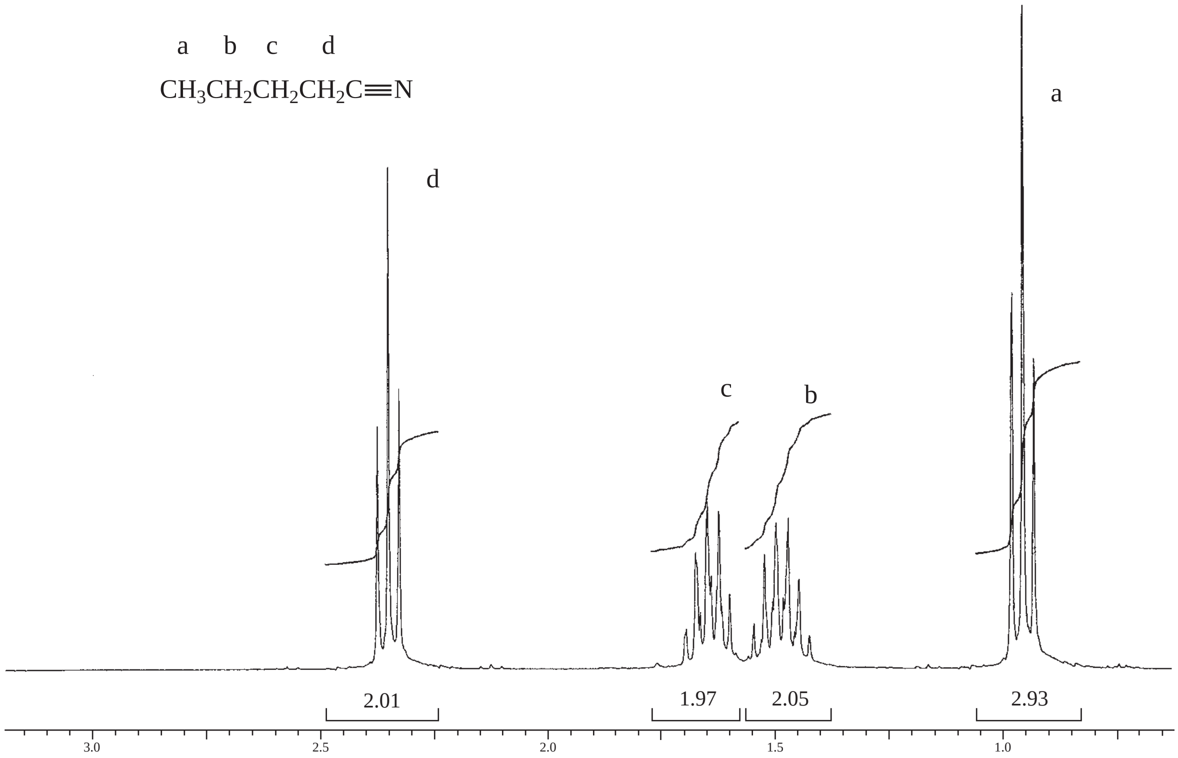


FIGURE 3.45 ^{1}H spectrum of valeronitrile.

J. Aldehydes

Two types of hydrogens are found in aldehydes: the aldehyde hydrogen and the α hydrogens (those hydrogens attached to the same carbon as the aldehyde group).

SPECTRAL ANALYSIS BOX—Aldehydes

CHEMICAL SHIFTS

R−C**H**O	9.0–10.0 ppm	The aldehyde hydrogen is shifted far downfield due to the anisotropy of the carbonyl group (C=O).
R−C**H**−CH=O	2.1–2.4 ppm	Hydrogens on the carbon adjacent to the C=O group are also deshielded due to the carbonyl group, but they are more distant, and the effect is smaller.

COUPLING BEHAVIOR

−C**H**−C**H**O	$^3J \approx$ 1–3 Hz	Coupling occurs between the aldehyde hydrogen and hydrogens on the adjacent carbon, but ^3J is small.

The chemical shift of the proton in the aldehyde group (—C**H**O) is found in the range of 9–10 ppm. Protons appearing in this region are very indicative of an aldehyde group since no other protons appear in this region. The aldehyde proton at 9.64 ppm appears as a doublet in the inset of Figure 3.46, with a ^3J = 1.5 Hz, for 2-methylpropanal (isobutyraldehyde). NMR is far more reliable than infrared spectroscopy for confirming the presence of an aldehyde group. The other regions have also been expanded and shown as insets on the spectrum and are summarized as follows:

Proton **a** 1.13 ppm (doublet, ^3J = 342.7 – 335.7 = 7.0 Hz)
Proton **b** 2.44 ppm (septet of doublets, ^3J = 738.0 – 731.0 = 7.0 Hz and ^4J = 725.5 – 724.0 = 1.5 Hz)
Proton **c** 9.64 ppm (doublet, ^3J = 2894.6 – 2893.1 = 1.5Hz)

The CH group (**b**) adjacent to the carbonyl group appears in the range of 2.1 to 2.4 ppm, which is typical for protons on the α carbon. In the present case, the pattern at 2.44 appears as a septet of doublets resulting from coupling with the adjacent two CH_3 groups (n = 6 + 1 = 7) and coupling with the aldehyde proton resulting in a septet of doublets (n = 1 + 1 = 2).

Notice that the two methyl groups (**a**) appear as a doublet, integrating for 6 H with a ^3J = 7.0 Hz. The n + 1 Rule predicts a doublet because of the presence of one adjacent proton on carbon **b**.

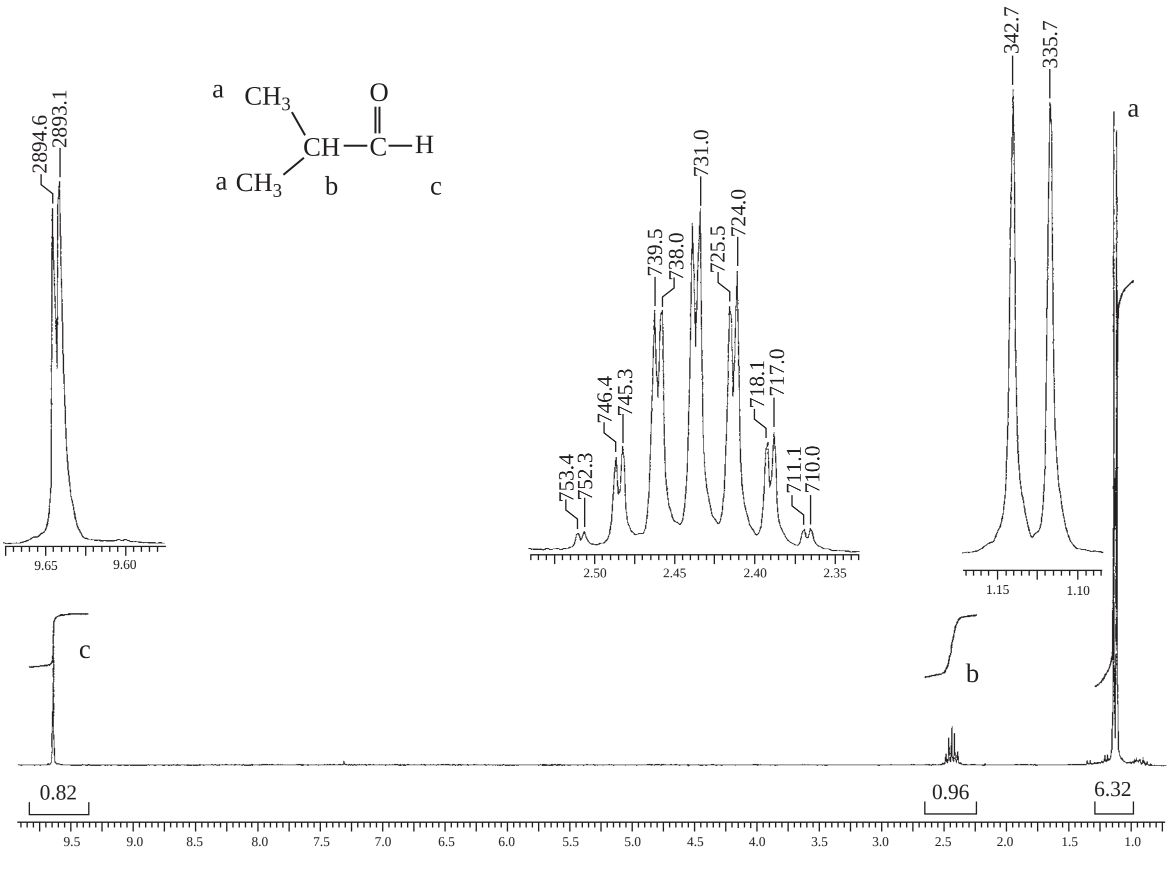


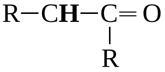
FIGURE 3.46 ^{1}H spectrum of 2-methylpropanal (isobutyraldehyde).

K. Ketones

Ketones have only one distinct type of hydrogen atom—those attached to the α carbon.

SPECTRAL ANALYSIS BOX—Ketones

CHEMICAL SHIFTS



$\mathrm{R{-}C\mathbf{H}{-}\underset{\underset{\displaystyle R}{|}}{C}{=}O}$ 2.1–2.4 ppm The α hydrogens in ketones are deshielded by the anisotropy of the adjacent C=O group.

In a ketone, the hydrogens on the carbon next to the carbonyl group appear in the range 2.1–2.4 ppm. If these hydrogens are part of a longer chain, they will be split by any hydrogens on the adjacent carbon, which is further along the chain. Methyl ketones are quite easy to distinguish since they show a sharp three-proton singlet near 2.1 ppm. Be aware that all hydrogens on a carbon next to a carbonyl group give absorptions within the range of 2.1–2.4 ppm. Therefore, ketones, aldehydes, esters, amides, and carboxylic acids would all give rise to NMR absorptions in this same area. It is necessary to look for the absence of other absorptions ($-$CHO, $-$OH, $-NH_2$, $-OCH_2R$, etc.) to confirm the compound as a ketone. Infrared spectroscopy would also be of great assistance in differentiating these types of compounds. Absence of the aldehyde, hydroxyl, amino, or ether stretching absorptions would help to confirm the compound as a ketone.

A spectrum of 5-methyl-2-hexanone is shown in Figure 3.47. Notice the tall singlet at 2.2 ppm for the methyl group (**d**) next to the carbonyl group. This is quite characteristic of a methyl ketone. Since there are no adjacent protons, one observes a singlet integrating for 3 H. Typically, carbon atoms with more attached protons are more shielded. Thus, the methyl group appears further upfield than the methylene group (**e**), which has fewer attached protons. The quartet for the methylene group **b** is clearly visible at about 1.45 ppm, but it partly overlaps the multiplet for the single proton **c**

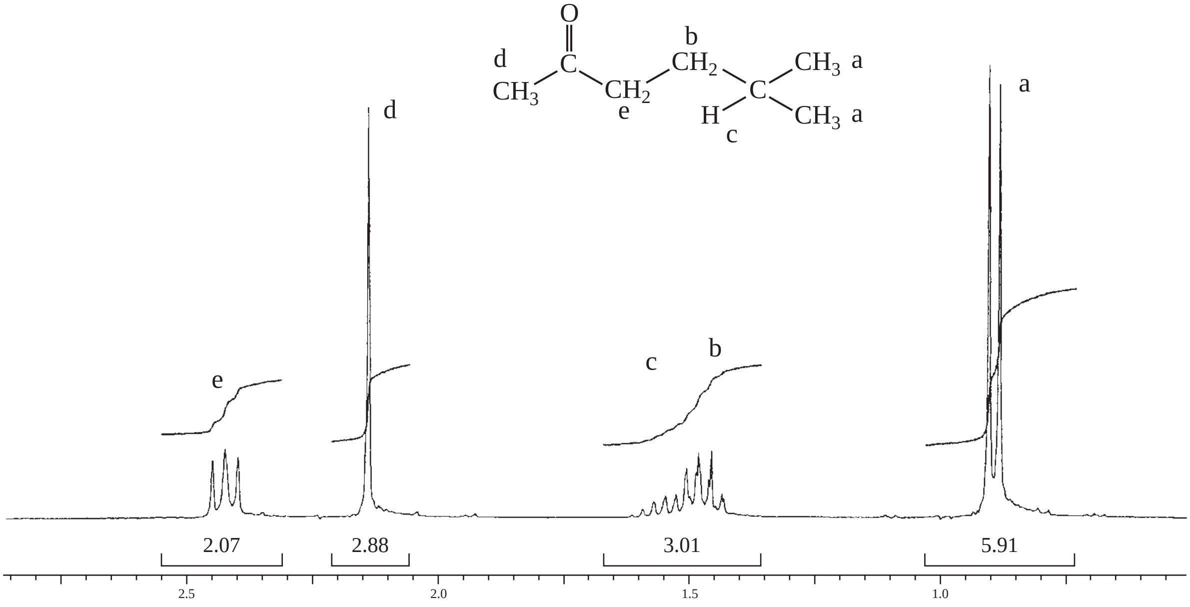


FIGURE 3.47 ^{1}H spectrum of 5-methyl-2-hexanone.

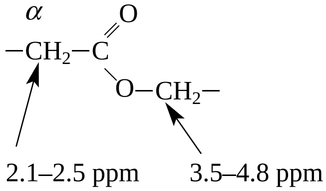
appearing at about 1.5 ppm. The doublet for the two methyl groups at about 0.9 ppm integrates for about 6 H. Remember that the doublet results from the two equivalent methyl groups seeing one adjacent proton (^3J).

L. Esters

Two distinct types of hydrogen are found in esters: those on the carbon atom attached to the oxygen atom in the *alcohol part* of the ester and those on the α carbon in the *acid part* of the ester (that is, those attached to the carbon next to the C=O group).

SPECTRAL ANALYSIS BOX—Esters

CHEMICAL SHIFTS



The α hydrogens in esters are deshielded by the anisotropy of the adjacent (C=O) group.

Hydrogens on the carbon attached to the single-bonded oxygen are deshielded due to the electronegativity of oxygen.

All hydrogens on a carbon next to a carbonyl group give absorptions in the same area (2.1–2.5 ppm). The anisotropic field of the carbonyl group deshields these hydrogens. Therefore, ketones, aldehydes, esters, amides, and carboxylic acids would all give rise to NMR absorptions in this same area. The peak in the 3.5- to 4.8-ppm region is the key to identifying an ester. The large chemical shift of these hydrogens is due to the deshielding effect of the electronegative oxygen atom, which is attached to the same carbon. Either of the two types of hydrogens mentioned may be split into multiplets if they are part of a longer chain.

A spectrum for isobutyl acetate is shown in Figure 3.48. Note that the tall singlet (**c**) at 2.1 ppm integrating for 3 H is the methyl group attached to the C=O group. If the methyl group had been attached to the singly bonded oxygen atom, it would have appeared near 3.5 to 4.0 ppm. Chemical

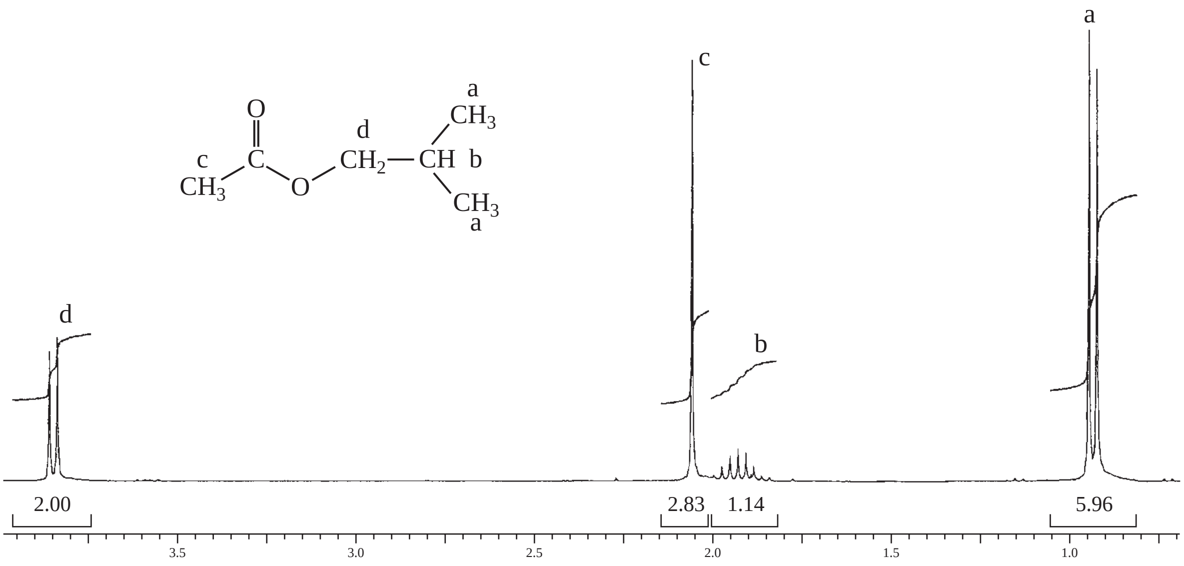


FIGURE 3.48 ^{1}H spectrum of isobutyl acetate.

shift information tells you to which side of the $-CO_2-$ group the methyl group is attached. The $-CH_2-$ group (**d**) attached to the oxygen atom is shifted downfield to about 3.85 ppm because of the electronegativity of the oxygen atom. That group integrates for 2 H and appears as a doublet because of the one neighboring proton (**b**) on the methine carbon atom. That single proton on the methine carbon appears as a multiplet that is split by the neighboring two methyl groups (**a**) and the methylene group (**d**) into a nonet (nine peaks, at 1.95 ppm). Finally, the two methyl groups appear as a doublet at 0.9 ppm, integrating for 6 H.

M. Carboxylic Acids

Carboxylic acids have the acid proton (the one attached to the $-COOH$ group) and the α hydrogens (those attached to the same carbon as the carboxyl group).

SPECTRAL ANALYSIS BOX—Carboxylic Acids

CHEMICAL SHIFTS

R−COO**H**	11.0–12.0 ppm	This hydrogen is deshielded by the attached oxygen, and it is highly acidic. This (usually broad) signal is a very characteristic peak for carboxylic acids.
−C**H**−COOH	2.1–2.5 ppm	Hydrogens adjacent to the carbonyl group are slightly deshielded.

In carboxylic acids, the hydrogen of the carboxyl group ($-COOH$) has resonance in the range 11.0–12.0 ppm. With the exception of the special case of a hydrogen in an enolic OH group that has strong internal hydrogen bonding, no other common type of hydrogen appears in this region. A peak in this region is a strong indication of a carboxylic acid. Since the carboxyl hydrogen has no neighbors, it is usually unsplit; however, hydrogen bonding and exchange many cause the peak to become *broadened* (become very wide at the base of the peak) and show very low intensity. Sometimes the acid peak is so broad that it disappears into the baseline. In that case, the acidic proton may not be observed. Infrared spectroscopy is very reliable for determining the presence of a carboxylic acid. As with alcohols, this hydrogen will exchange with water and D_2O. In D_2O, proton exchange will convert the group to $-COOD$, and the $-COO\mathbf{H}$ absorption near 12.0 ppm will disappear.

$$R-COO\mathbf{H} + D_2O \rightleftharpoons R-COOD + DO\mathbf{H} \qquad \textbf{exchange in } \mathbf{D_2O}$$

Carboxylic acids are often insoluble in $CDCl_3$, and it is common practice to determine their spectra in D_2O to which a small amount of sodium metal is added. This basic solution (NaOD, D_2O) will remove the proton, making a soluble sodium salt of the acid. However, when this is done the –COO**H** absorption will disappear from the spectrum.

$$\underset{\textbf{insoluble}}{R-COO\mathbf{H}} + NaOD \rightleftharpoons \underset{\textbf{soluble}}{R-COO^{-}Na^{+}} + DO\mathbf{H}$$

A spectrum of ethylmalonic acid is shown in Figure 3.49. The $-COOH$ absorption integrating for 2 H is shown as an inset on the spectrum. Notice that this peak is very broad due to hydrogen bonding and exchange. Also notice that proton **c** is shifted downfield to 3.1 ppm, resulting from the effect of two neighboring carbonyl groups. The normal range for a proton next to just one carbonyl group would be expected to appear in the range 2.1 to 2.5 ppm.

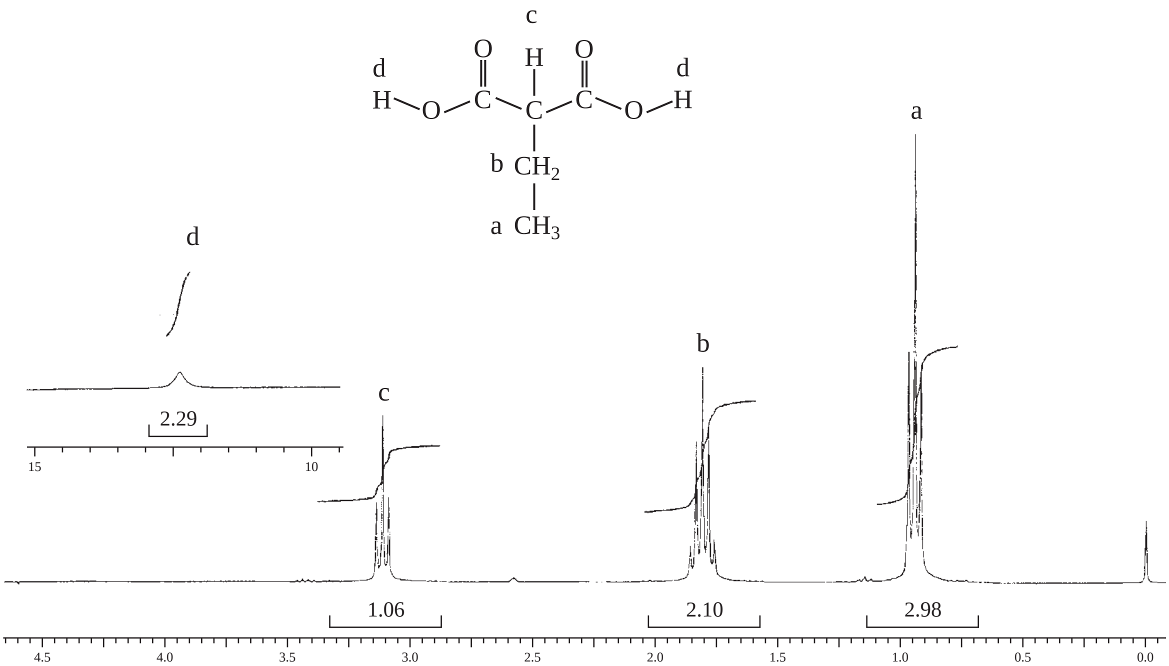


FIGURE 3.49 ^{1}H spectrum of ethylmalonic acid.

N. Amides

SPECTRAL ANALYSIS BOX—Amides

CHEMICAL SHIFTS

R(CO)−N−**H**	5.0–9.0 ppm	Hydrogens attached to an amide nitrogen are variable in chemical shift, the value being dependent on the temperature, concentration, and solvent.
−C**H**−CONH−	2.1–2.5 ppm	The α hydrogens in amides absorb in the same range as other acyl (next to C=O) hydrogens. They are slightly deshielded by the carbonyl group.
R(CO)−N−C**H**	2.2–2.9 ppm	Hydrogens on the carbon next to the nitrogen of an amide are slightly deshielded by the electronegativity of the attached nitrogen.

COUPLING BEHAVIOR

−N−H	$^1J \approx 50$ Hz	In cases in which this coupling is seen (rare), it is quite large, typically 50 Hz or more. In most cases, either the quadrupole moment of the nitrogen atom or chemical exchange decouples this interaction.
−N−C**H**−	$^2J \approx 0$ Hz	Usually not seen for the same reasons stated above.
$-\underset{\underset{\mathbf{H}}{\vert}}{\mathrm{N}}-\mathrm{C}\mathbf{H}-$	$^3J \approx 0$–7 Hz	Exchange of the amide NH is slower than in amines, and splitting of the adjacent C**H** is observed even if the N**H** is broadened.

Amides have three distinct types of hydrogens: those attached to nitrogen, α hydrogens attached to the carbon atom on the carbonyl side of the amide group, and hydrogens attached to a carbon atom that is also attached to the nitrogen atom.

The —NH absorptions of an amide group are highly variable, depending not only on their environment in the molecule, but also on temperature and the solvent used. Because of resonance between the unshared pairs on nitrogen and the carbonyl group, rotation is restricted in most amides. Without rotational freedom, the two hydrogens attached to the nitrogen in an unsubstituted amide are not equivalent, and *two different absorption peaks* will be observed, one for each hydrogen (Section 6.6). Nitrogen atoms also have a quadrupole moment (Section 6.5), its magnitude depending on the particular molecular environment. If the nitrogen atom has a large quadrupole moment, the attached hydrogens will show peak broadening (a widening of the peak at its base) and an overall reduction of its intensity.

Hydrogens adjacent to a carbonyl group (regardless of type) all absorb in the same region of the NMR spectrum: 2.1–2.5 ppm.

The spectrum of butyramide is shown in Figure 3.50. Notice the separate absorptions for the two —N**H** hydrogens (6.6 and 7.2 ppm). This occurs due to restricted rotation in this compound. The hydrogens next to the C═O group appear characteristically at 2.1 ppm.

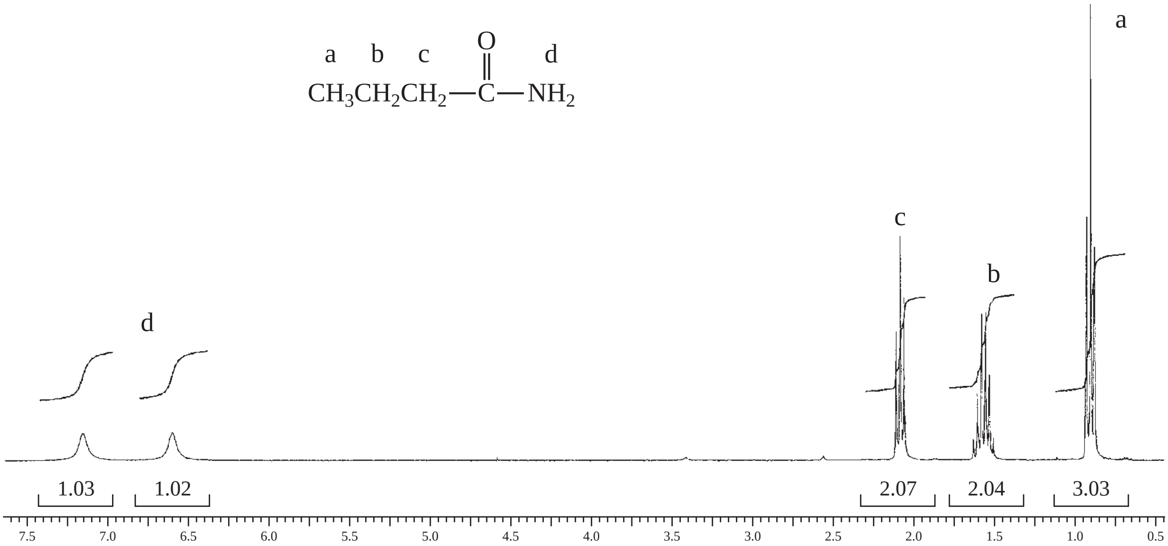


FIGURE 3.50 ^1H spectrum of butyramide.

O. Nitroalkanes

In nitroalkanes, α hydrogens, those hydrogen atoms that are attached to the same carbon atom to which the nitro group is attached, have a characteristically large chemical shift.

SPECTRAL ANALYSIS BOX—Nitroalkanes

$—C\mathbf{H}—NO_2$	4.1–4.4 ppm	Deshielded by the nitro group.

Hydrogens on a carbon next to a nitro group are highly deshielded and appear in the range 4.1–4.4 ppm. The electronegativity of the attached nitrogen and the positive formal charge assigned to that nitrogen clearly indicate the deshielding nature of this group.

A spectrum of 1-nitrobutane is shown in Figure 3.51. Note the large chemical shift (4.4 ppm) of the hydrogens on the carbon adjacent to the nitro group.

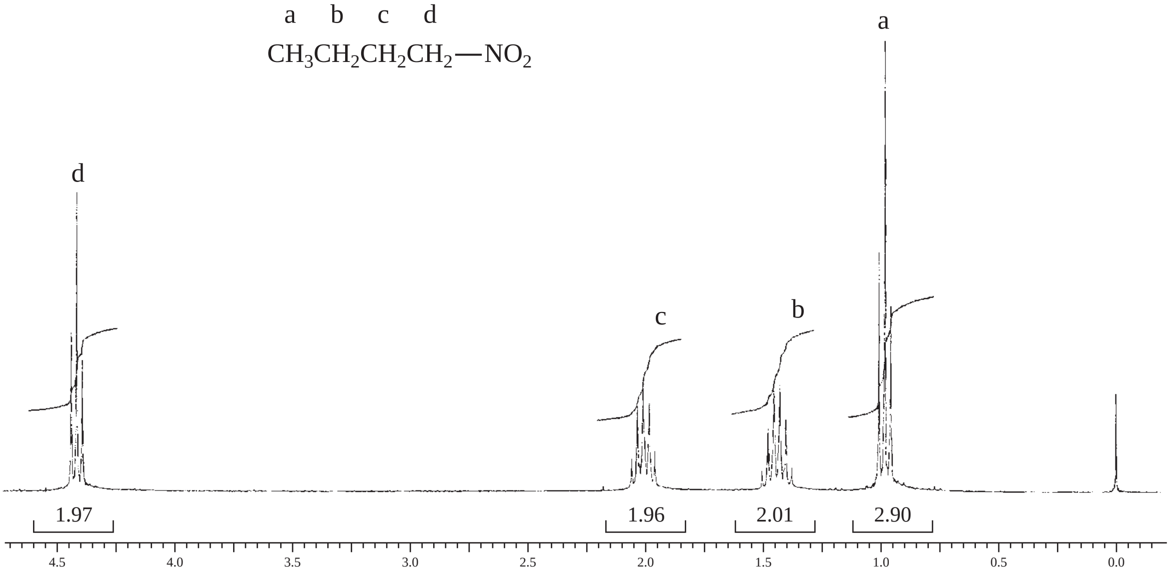


FIGURE 3.51 ^{1}H spectrum of 1-nitrobutane.

PROBLEMS

***1.** What are the allowed nuclear spin states for the following atoms?

(a) ^{14}N (b) ^{13}C (c) ^{17}O (d) ^{19}F

***2.** Calculate the chemical shift in parts per million (δ) for a proton that has resonance 128 Hz downfield from TMS on a spectrometer that operates at 60 MHz.

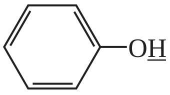
***3.** A proton has resonance 90 Hz downfield from TMS when the field strength is 1.41 Tesla (14,100 Gauss) and the oscillator frequency is 60 MHz.

(a) What will be its shift in Hertz if the field strength is increased to 2.82 Tesla and the oscillator frequency to 120 MHz?

(b) What will be its chemical shift in parts per million (δ)?

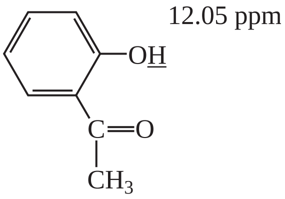
***4.** Acetonitrile (CH_3CN) has resonance at 1.97 ppm, whereas methyl chloride (CH_3Cl) has resonance at 3.05 ppm, even though the dipole moment of acetonitrile is 3.92 D and that of methyl chloride is only 1.85 D. The larger dipole moment for the cyano group suggests that the electronegativity of this group is greater than that of the chlorine atom. Explain why the methyl hydrogens on acetonitrile are actually more shielded than those in methyl chloride, in contrast with the results expected on the basis of electronegativity. (*Hint:* What kind of spatial pattern would you expect for the magnetic anisotropy of the cyano group, CN?)

***5.** The position of the OH resonance of phenol varies with concentration in solution, as the following table shows. On the other hand, the hydroxyl proton of *ortho*-hydroxyacetophenone appears at 12.05 ppm and does not show any great shift upon dilution. Explain.



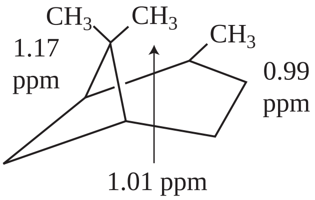
Phenol

Concentration w/v in CCl_4	δ (ppm)
100%	7.45
20%	6.75
10%	6.45
5%	5.95
2%	4.88
1%	4.37

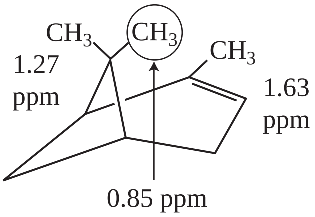


o-Hydroxyacetophenone

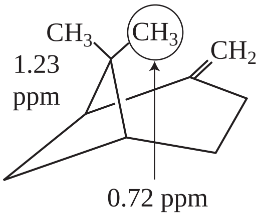
***6.** The chemical shifts of the methyl groups of three related molecules, pinane, α-pinene, and β-pinene, follow.



Pinane



α-Pinene

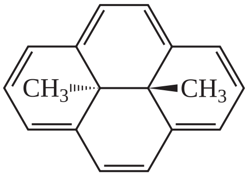


β-Pinene

Build models of these three compounds and then explain why the two circled methyl groups have such small chemical shifts.

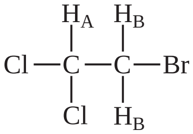
***7.** In benzaldehyde, two of the ring protons have resonance at 7.87 ppm, and the other three have resonance in the range from 7.5 to 7.6 ppm. Explain.

***8.** Make a three-dimensional drawing illustrating the magnetic anisotropy in 15,16-dihydro-15,16-dimethylpyrene, and explain why the methyl groups are observed at −4.2 ppm in the ^{1}H NMR spectrum.



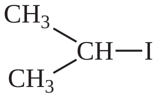
15,16-Dihydro-15,16-dimethylpyrene

***9.** Work out the spin arrangements and splitting patterns for the following spin system:

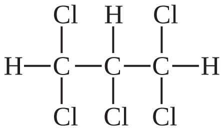


$$\begin{array}{ccccccc} & & H_A & & H_B & & \\ & & | & & | & & \\ Cl & - & C & - & C & - & Br \\ & & | & & | & & \\ & & Cl & & H_B & & \end{array}$$

***10.** Explain the patterns and intensities of the isopropyl group in isopropyl iodide.



***11.** What spectrum would you expect for the following molecule?

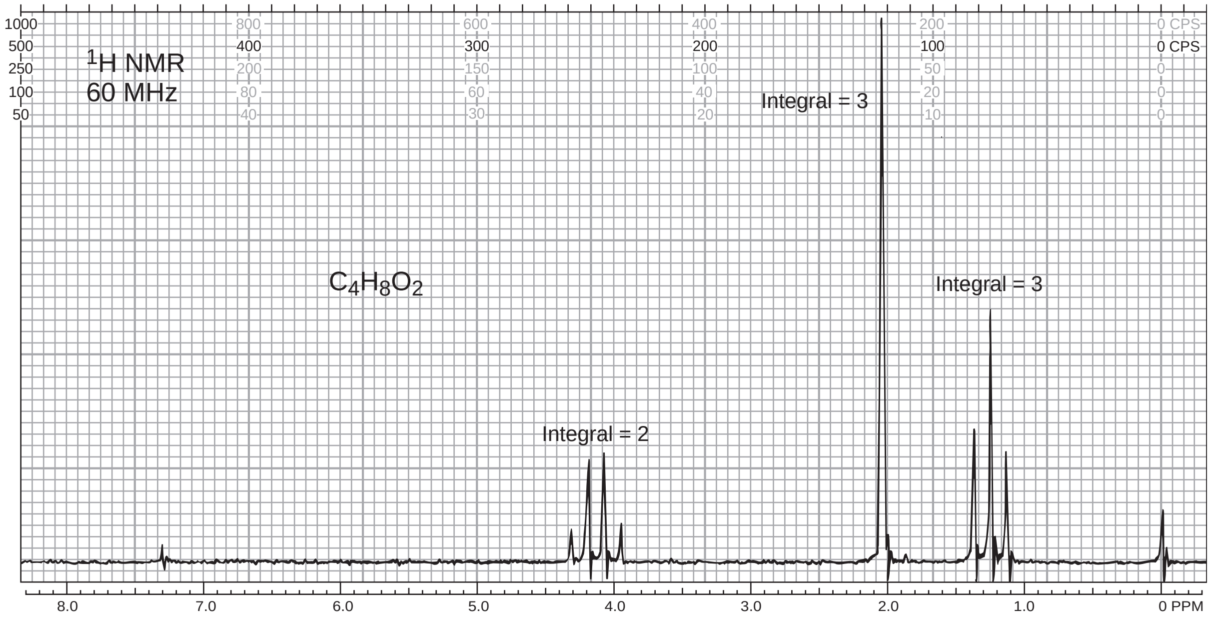


$$\begin{array}{ccccccccc} & & Cl & & H & & Cl & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & Cl & & Cl & & Cl & & \end{array}$$

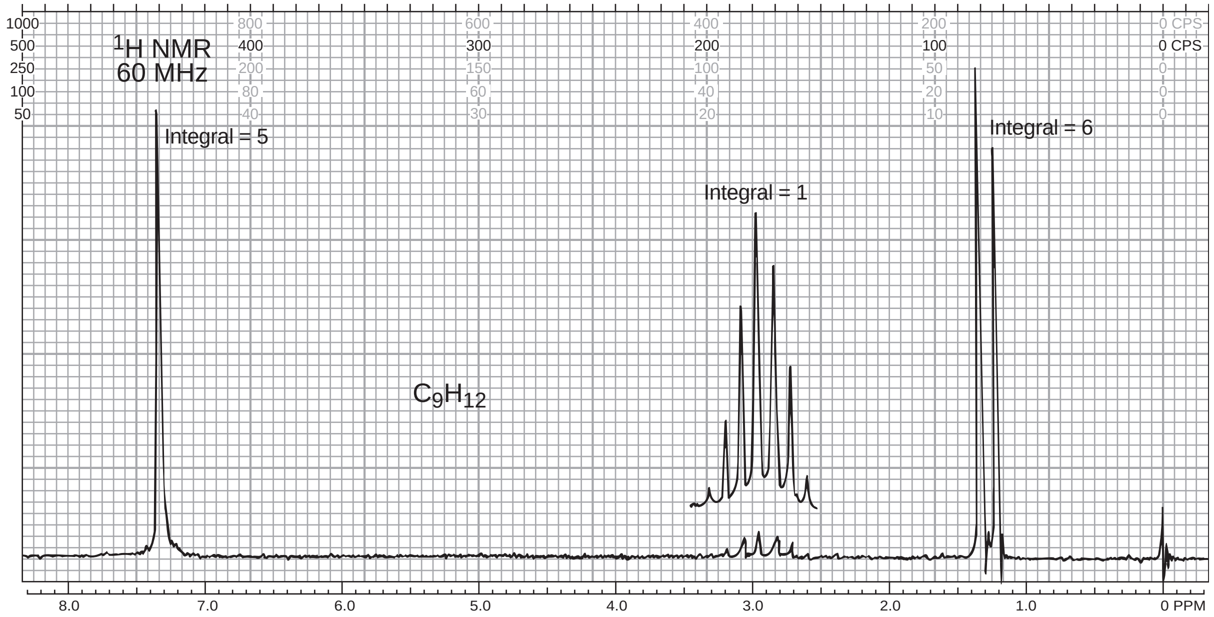
***12.** What arrangement of protons would give two triplets of equal area?

***13.** Predict the appearance of the NMR spectrum of propyl bromide.

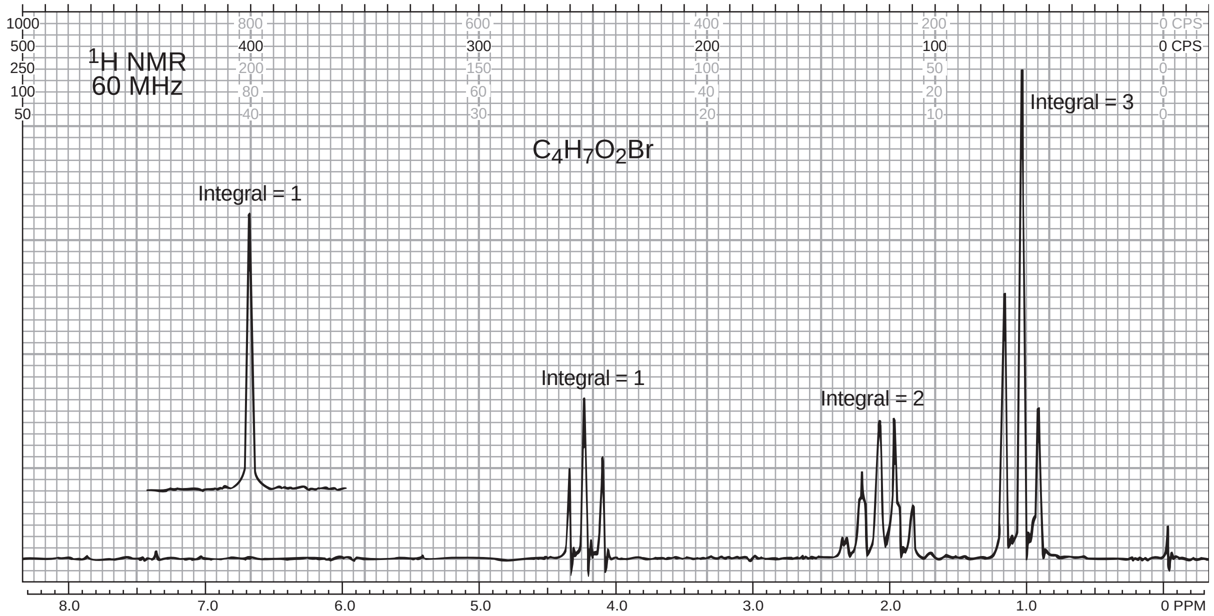
***14.** The following compound, with the formula $C_4H_8O_2$, is an ester. Give its structure and assign the chemical shift values.



***15.** The following compound is a monosubstituted aromatic hydrocarbon with the formula C_9H_{12}. Give its structure and assign the chemical shift values.



***16.** The following compound is a carboxylic acid that contains a bromine atom: $C_4H_7O_2Br$. The peak at 10.97 ppm was moved onto the chart (which runs only from 0 to 8 ppm) for clarity. What is the structure of the compound?

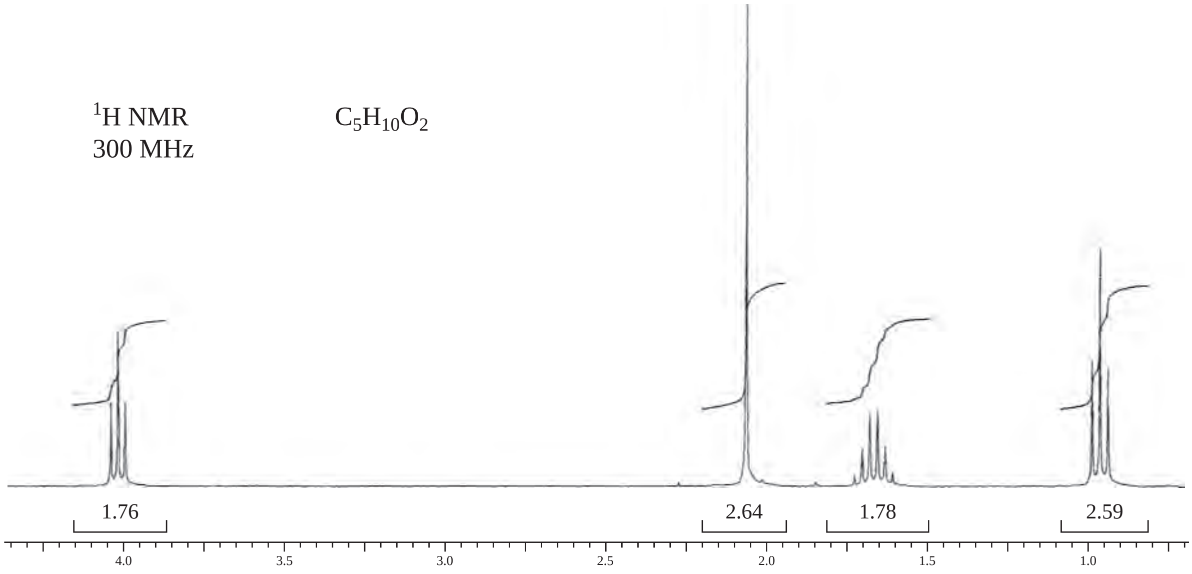


***17.** The following compounds are isomeric esters derived from acetic acid, each with formula $C_5H_{10}O_2$. Each of the spectra has been expanded so that you will be able see the splitting patterns. With the first spectrum (17a) as an example, you can use the integral curve traced on the spectrum to calculate the number of hydrogen atoms represented in each multiplet (pp. 121–123). Alternatively, you can avoid the laborious task of counting squares or using a ruler to measure the height of each integral! It is far easier to determine the integral values by using the integral numbers listed just below the peaks. These numbers are the integrated values of the area under the peaks. They are proportional to the actual number of protons, within experimental error. The process: Divide each of the integral values by the smallest integral value to get the values shown in the second column (1.76/1.76 = 1.0; 2.64/1.76 = 1.5; 1.77/1.76 = 1.01; 2.59/1.76 = 1.47). The values shown in the third column are obtained by multiplying by 2 and rounding off the resulting values. If everything works out, you should find that the total number of protons should equal the number of protons in the formula, in this case 10 protons.

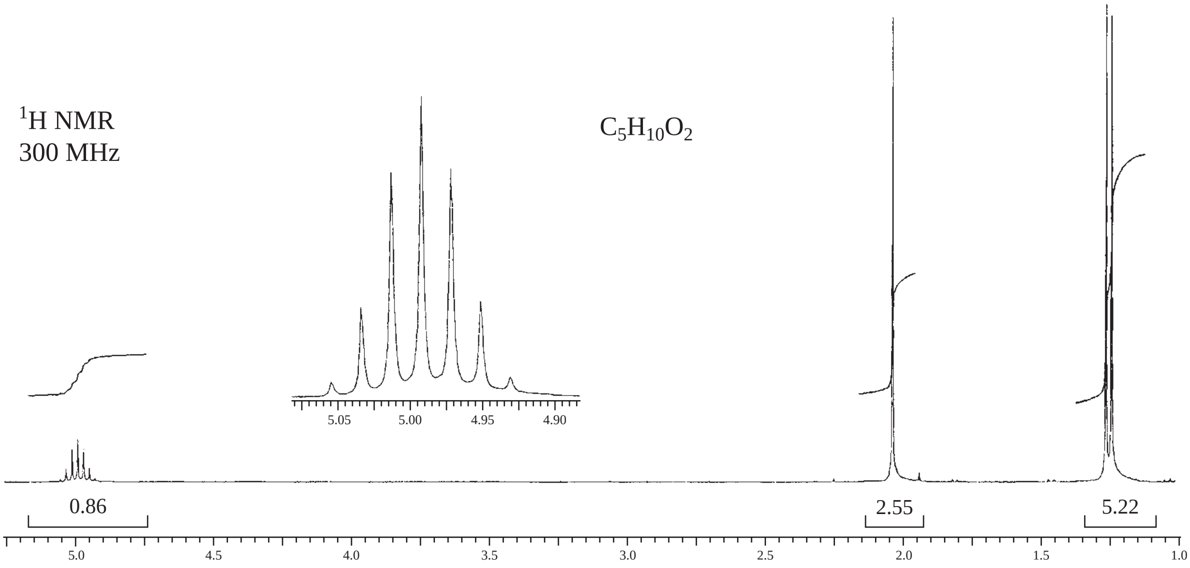
1.76	1.0	2 H
2.64	1.5	3 H
1.77	1.01	2 H
2.59	1.47	3 H
		10 protons

Often, one can inspect the spectrum and visually approximate the relative numbers of protons, thus avoiding the mathematical approach shown in the table. Using this eyeball approach, you can determine that the second spectrum (17b) yields a ratio of 1:3:6 = 10 H.

What are the structures of the two esters?

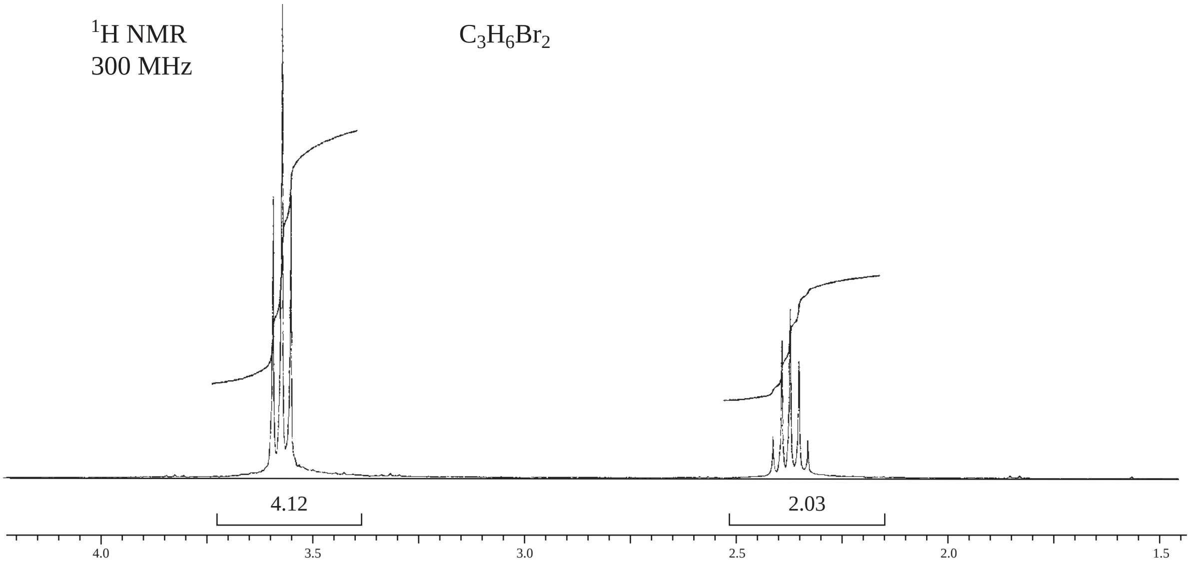


(a)

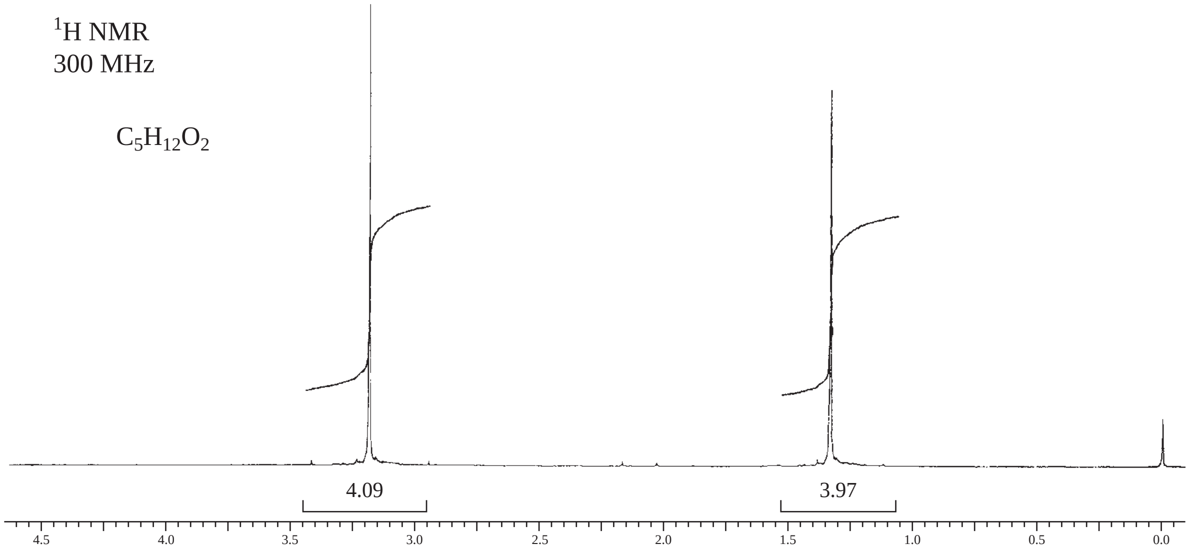


(b)

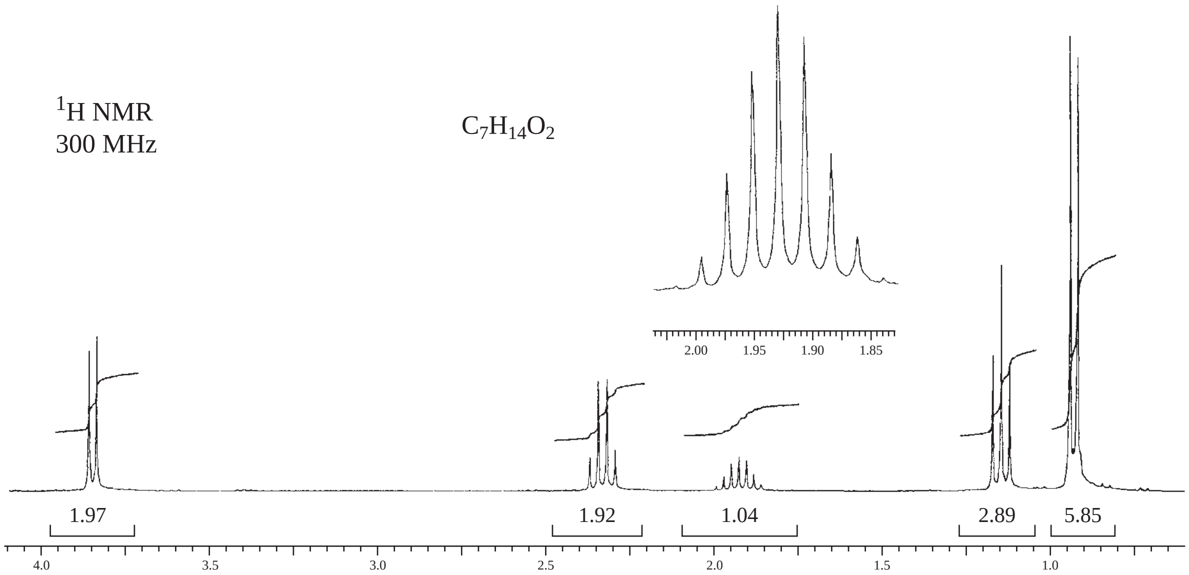
***18.** The compound that gives the following NMR spectrum has the formula $C_3H_6Br_2$. Draw the structure.



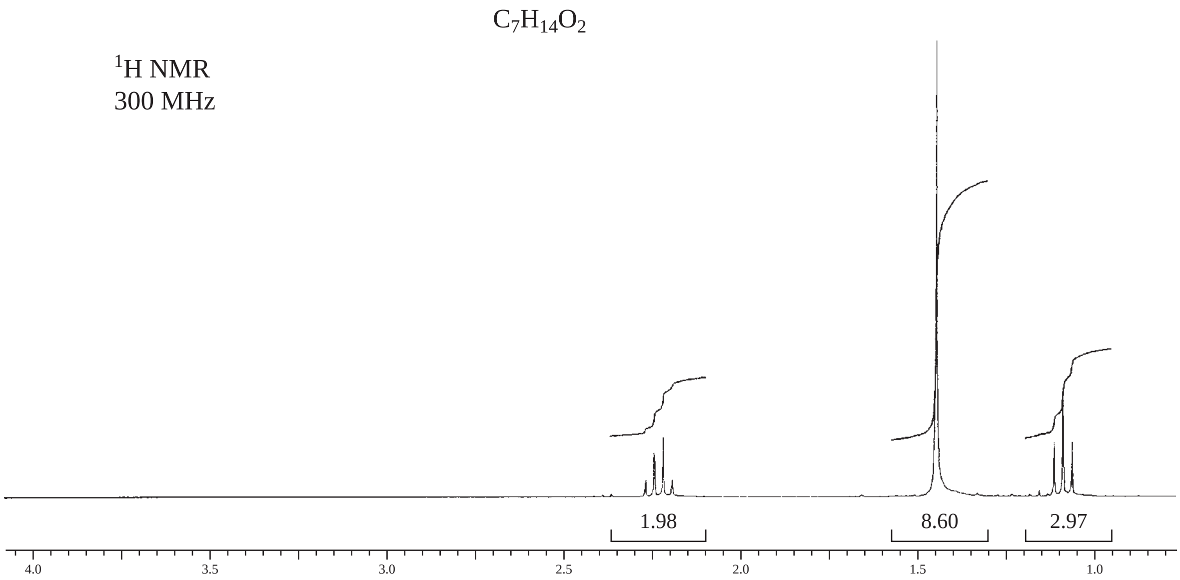
***19.** Draw the structure of an ether with formula $C_5H_{12}O_2$ that fits the following NMR spectrum:



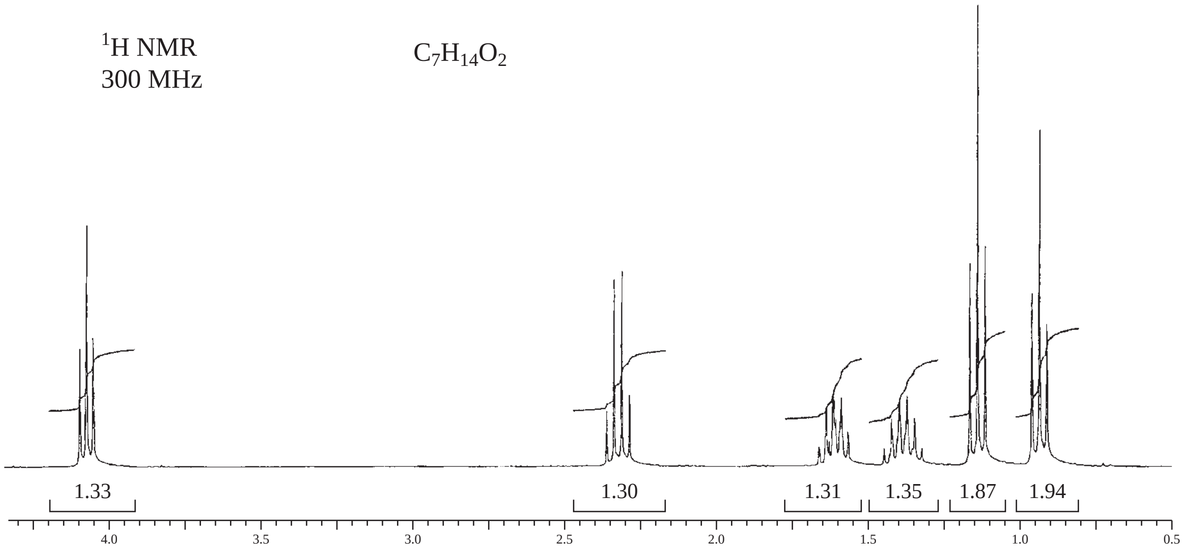
***20.** Following are the NMR spectra of three isomeric esters with the formula $C_7H_{14}O_2$, all derived from propanoic acid. Provide a structure for each.



(a)

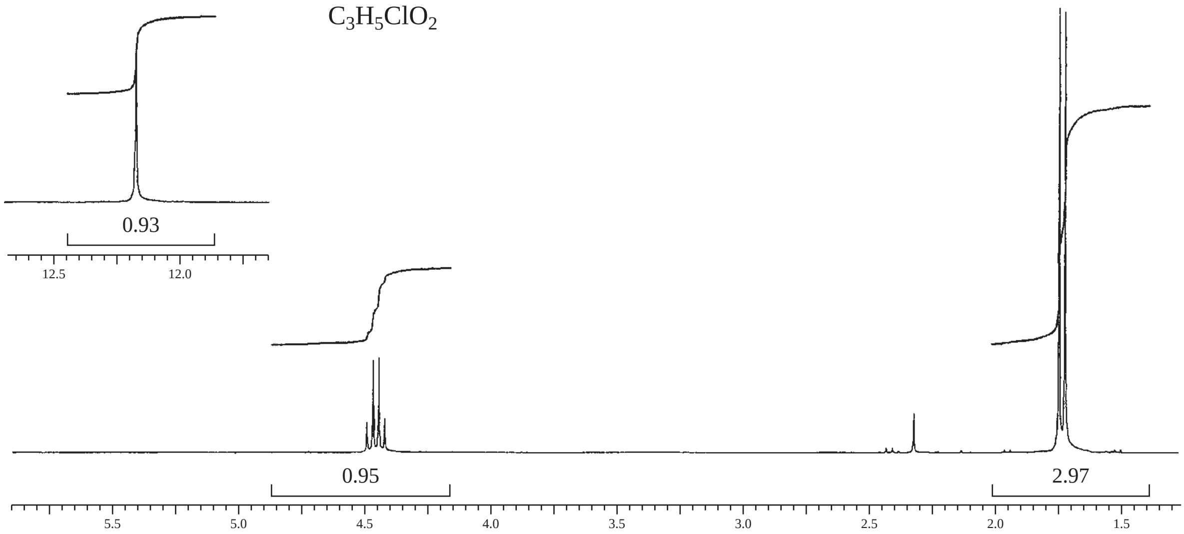

$C_7H_{14}O_2$
^1H NMR
300 MHz
1.98
8.60
2.97
4.0
3.5
3.0
2.5
2.0
1.5
1.0

(b)

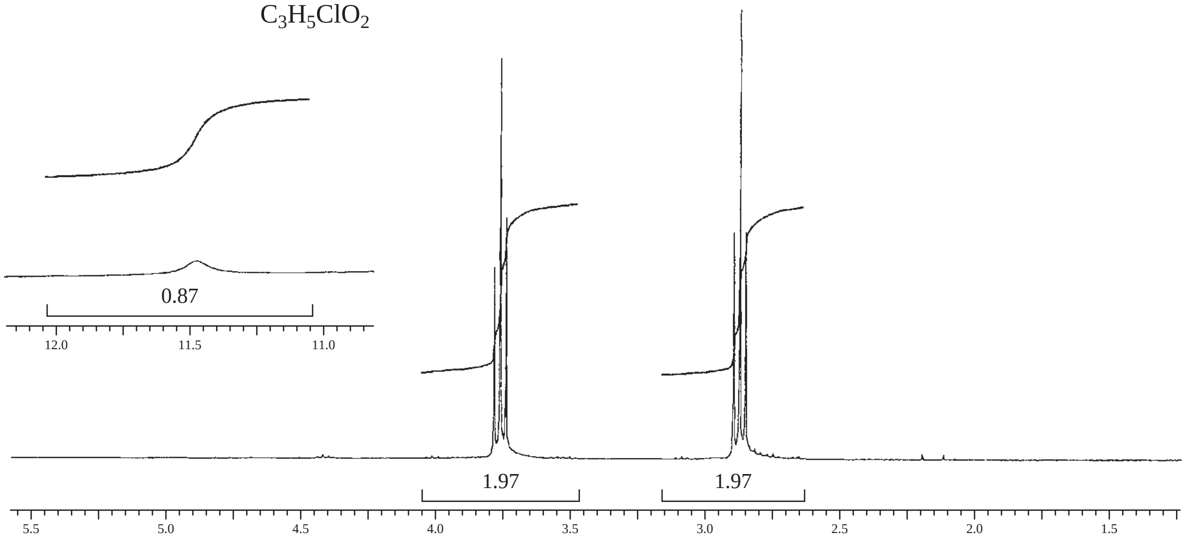

^1H NMR
300 MHz
$C_7H_{14}O_2$
1.33
1.30
1.31
1.35
1.87
1.94
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

(c)

***21.** The two isomeric compounds with the formula $C_3H_5ClO_2$ have NMR spectra shown in Problem 21a and 21b. The downfield protons appearing in the NMR spectra at about 12.1 and 11.5 ppm, respectively, are shown as insets. Draw the structures of the isomers.

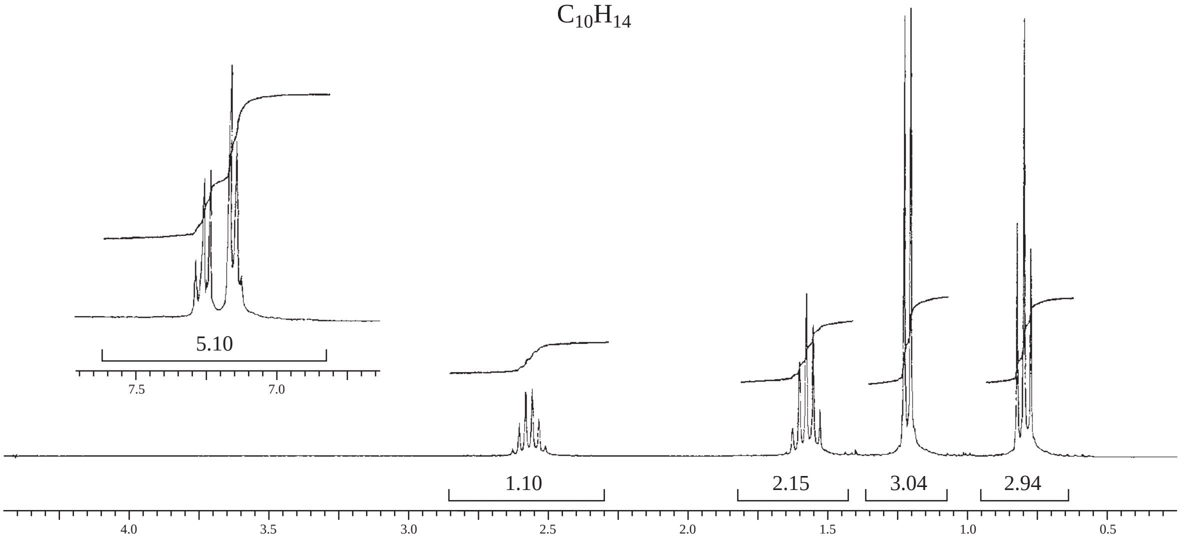


(a)

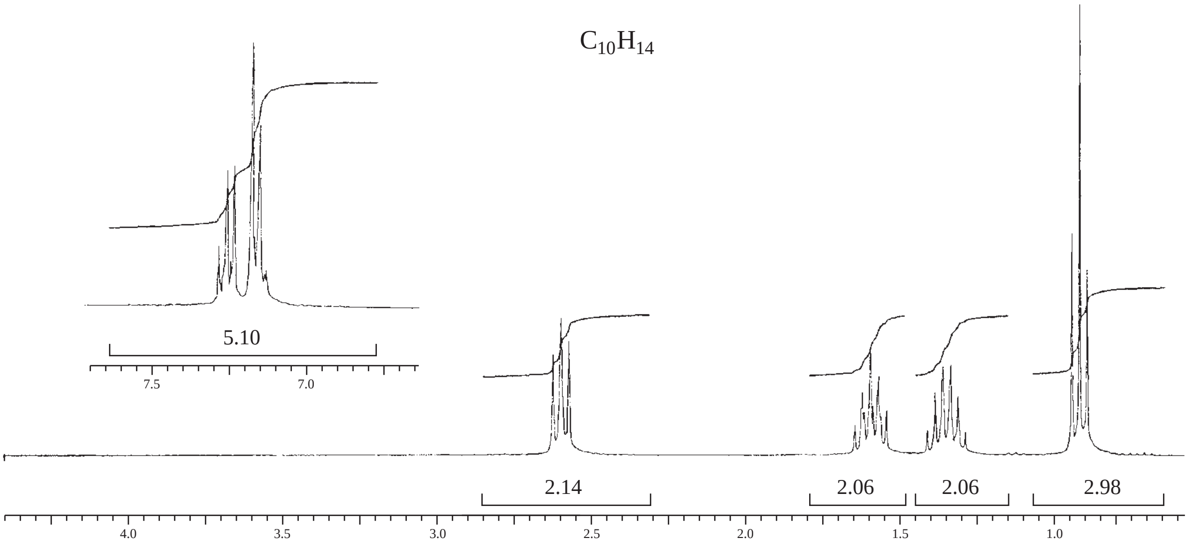


(b)

***22.** The two isomeric compounds with the formula $C_{10}H_{14}$ have NMR spectra shown in Problem 22a and 22b. Make no attempt to interpret the aromatic proton area between 7.1 and 7.3 ppm except to determine the number of protons attached to the aromatic ring. Draw the structures of the isomers.

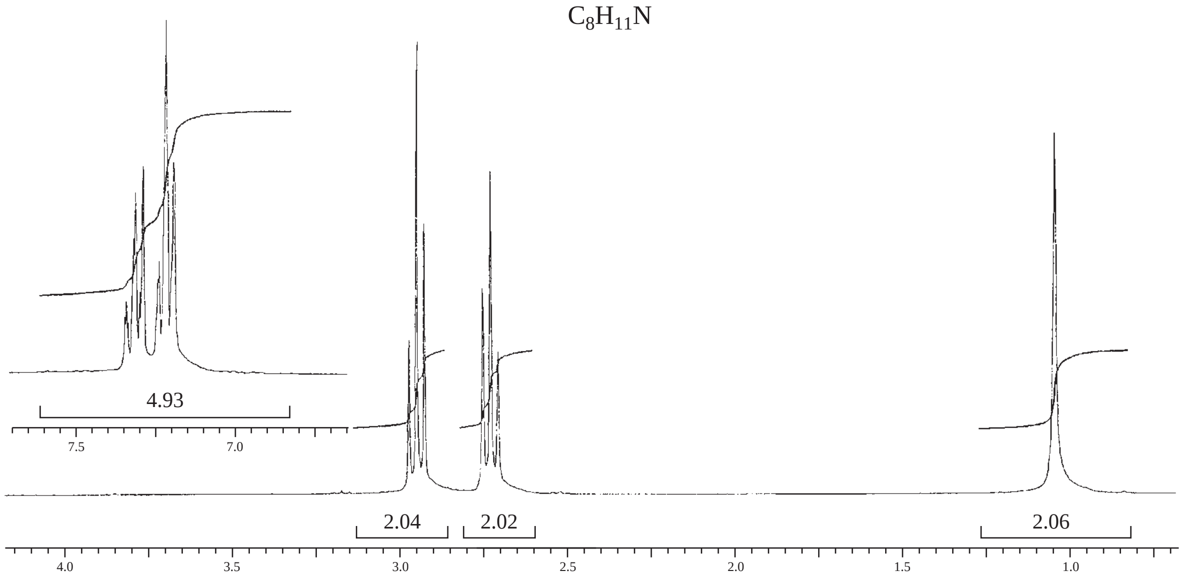


(a)

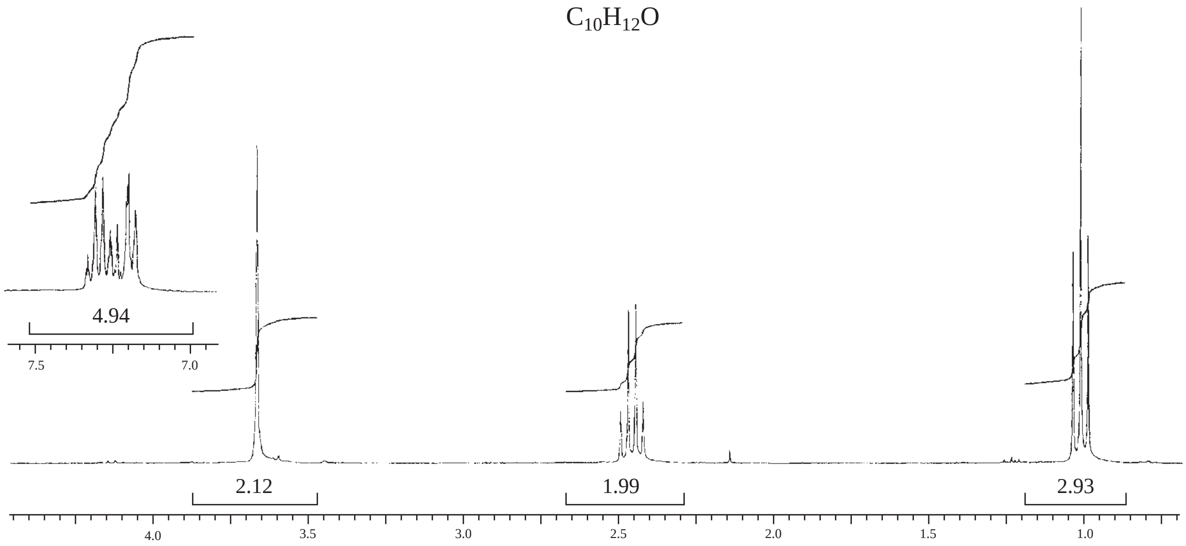


(b)

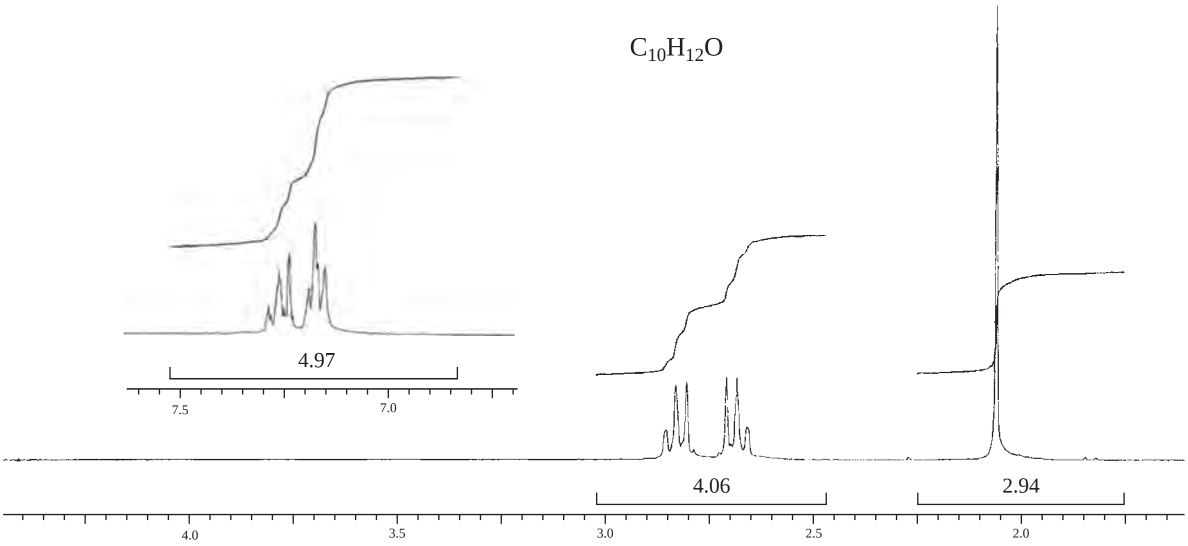
***23.** The compound with the formula $C_8H_{11}N$ has the NMR spectra shown. The infrared spectrum shows a doublet at about 3350 cm^{-1}. Make no attempt to interpret the aromatic proton area between 7.1 and 7.3 ppm except to determine the number of protons attached to the aromatic ring. Draw the structure of the compound.



24. The NMR spectra are shown for two isomeric compounds with formula $C_{10}H_{12}O$. Their infrared spectra show strong bands near 1715 cm^{-1}. Make no attempt to interpret the aromatic proton area between 7.1 and 7.4 ppm except to determine the number of protons attached to the aromatic ring. Draw the structure of the compounds.

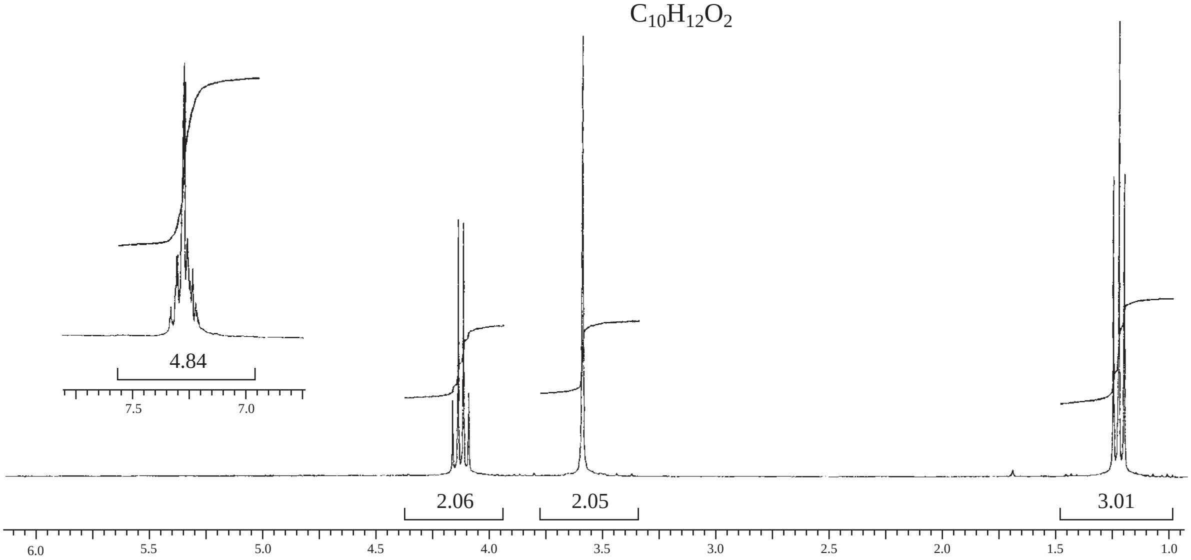


(a)

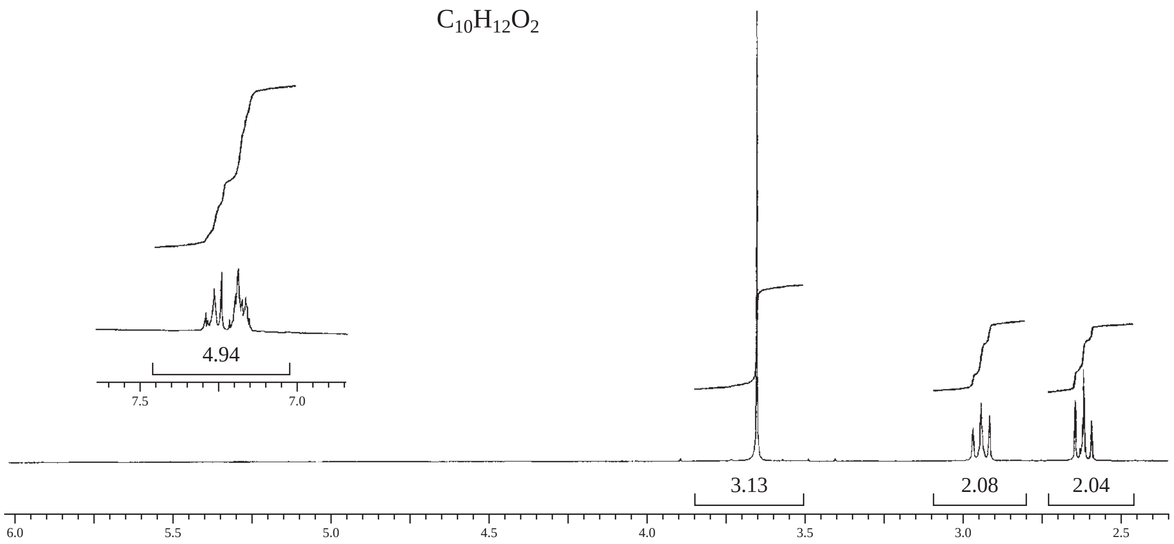


(b)

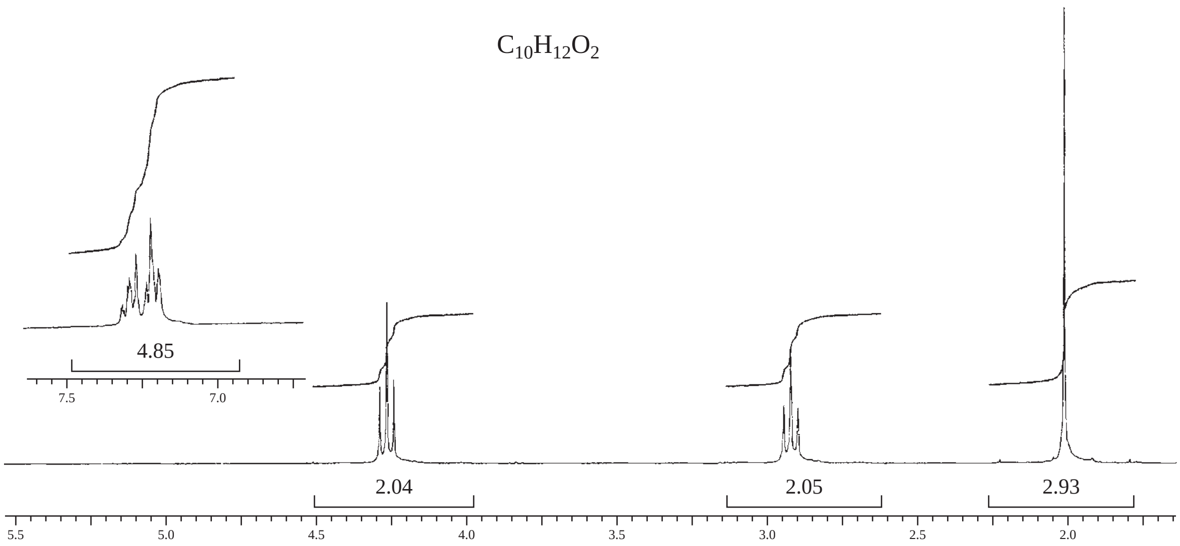
25. The NMR spectra are shown in parts a, b, c, and d for four isomeric compounds with formula $C_{10}H_{12}O_2$. Their infrared spectra show strong bands near 1735 cm^{-1}. Make no attempt to interpret the aromatic proton area between 7.0 and 7.5 ppm except to determine the number of protons attached to the aromatic ring. Draw the structures of the compounds.



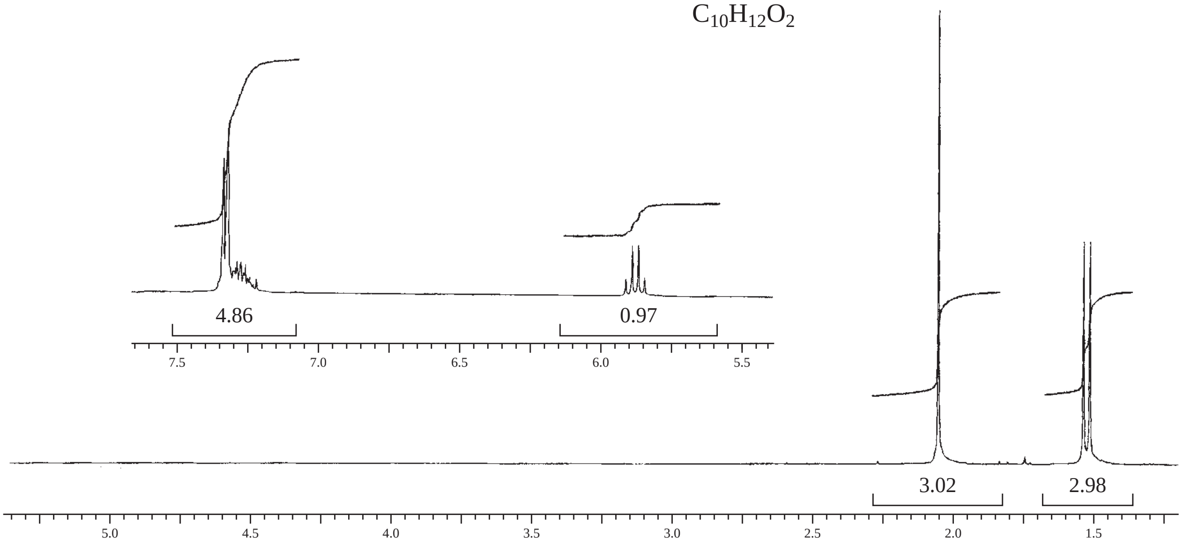
(a)


C10H12O2
4.94
7.5
7.0
3.13
2.08
2.04
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

(b)

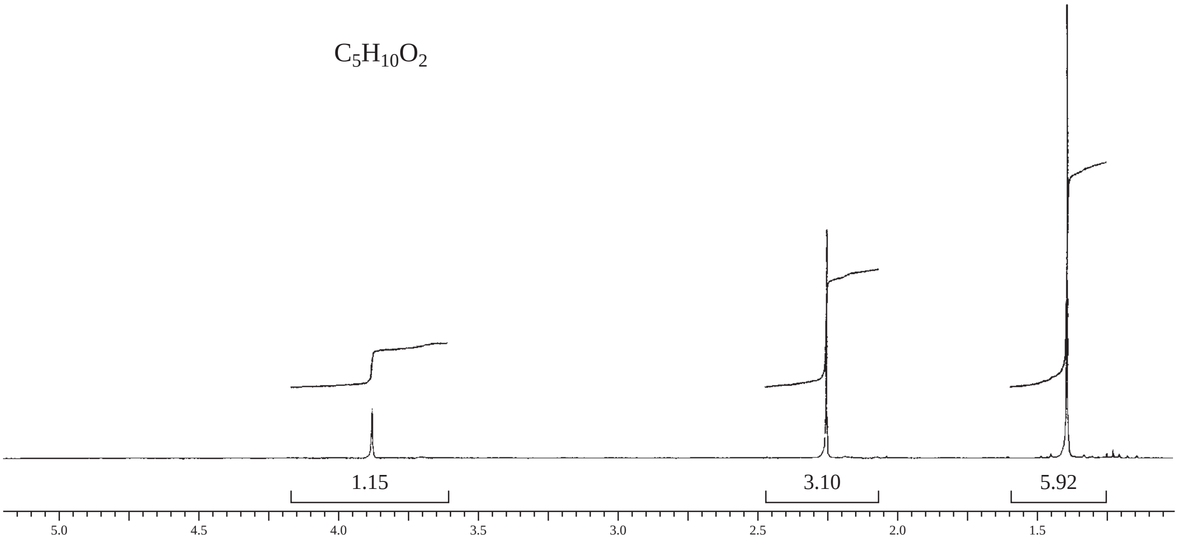

C10H12O2
4.85
7.5
7.0
2.04
2.05
2.93
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

(c)

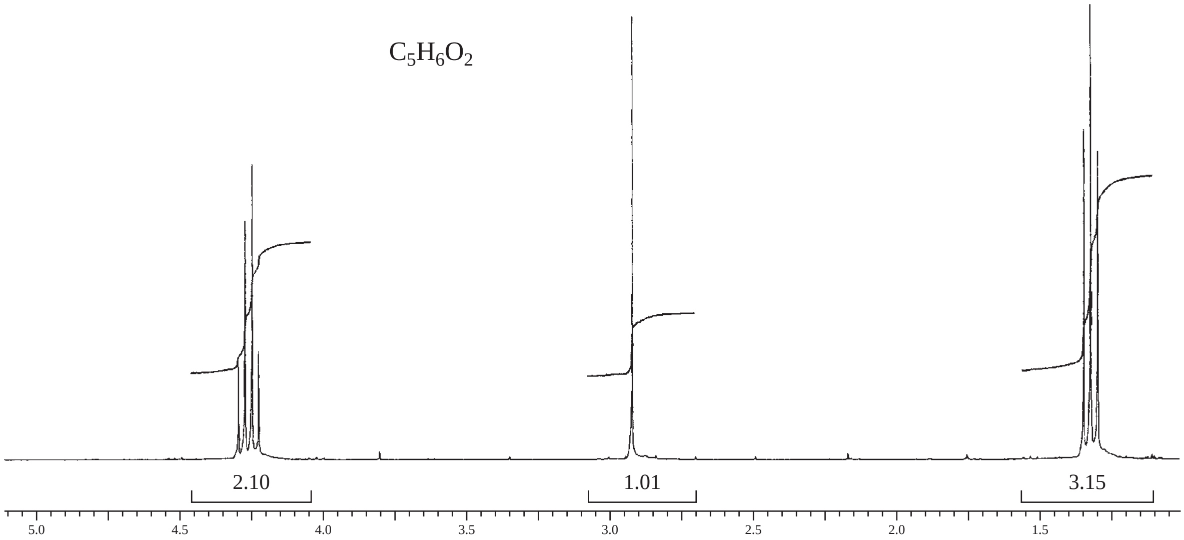


(d)

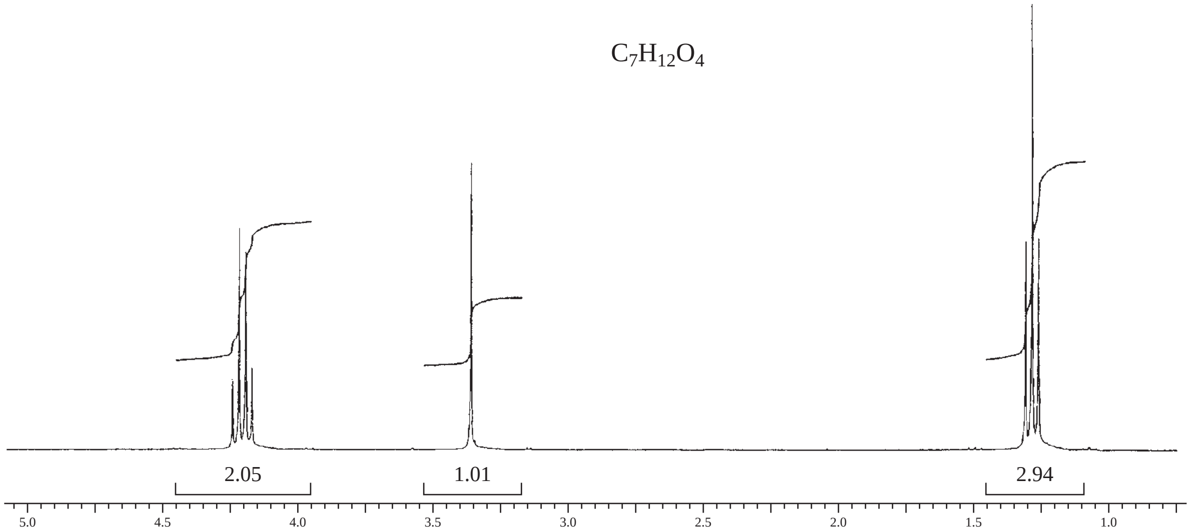
26. Along with the following NMR spectrum, this compound, with formula $C_5H_{10}O_2$, shows bands at 3450 cm^{-1} (broad) and 1713 cm^{-1} (strong) in the infrared spectrum. Draw its structure.



27. The NMR spectrum for an ester with formula $C_5H_6O_2$ is shown below. The infrared spectrum shows medium-intensity bands at 3270 and 2118 cm^{-1}. Draw the structure of the compound.



28. The NMR spectrum is shown for a compound with formula $C_7H_{12}O_4$. The infrared spectrum has strong absorption at 1740 cm^{-1} and has several strong bands in the range 1333 to 1035 cm^{-1}. Draw the structure of this compound.



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Integrated Spectral DataBase System for Organic Compounds, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan. This database includes infrared, mass spectra, and NMR data (proton and carbon-13) for a large number of compounds.

http://www.chem.ucla.edu/~webspectra/

UCLA Department of Chemistry and Biochemistry in connection with Cambridge University Isotope Laboratories, maintains a website, WebSpecta, that provides NMR and IR spectroscopy problems for students to interpret. They provide links to other sites with problems for students to solve.

http://www.nd.edu/~smithgrp/structure/workbook.html

Combined structure problems provided by the Smith group at Notre Dame University.

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