Lecture # 9

CHAPTER 5

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Part One: Basic Concepts

5.1 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 $^{1}_{1}H$, $^{2}_{1}H$, $^{13}_{6}C$, $^{14}_{7}N$, $^{17}_{8}O$, and $^{19}_{9}F$. Notice that the nuclei of the ordinary (most abundant) isotopes of carbon and oxygen, $^{12}_{6}C$ and $^{16}_{8}O$, are not included among those with the spin property. However, the nu-

TABLE 5.1
SPIN QUANTUM NUMBERS OF SOME COMMON NUCLEI

Element	$^{1}_{1}H$	$^{2}_{1}H$	$^{12}_{6}C$	$^{13}_{6}C$	$^{14}_{7}N$	$^{16}_{8}O$	$^{17}_{8}O$	$^{19}_{9}F$	$^{31}_{15}P$	$^{35}_{17}Cl$
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

5.2 NUCLEAR MAGNETIC MOMENTS

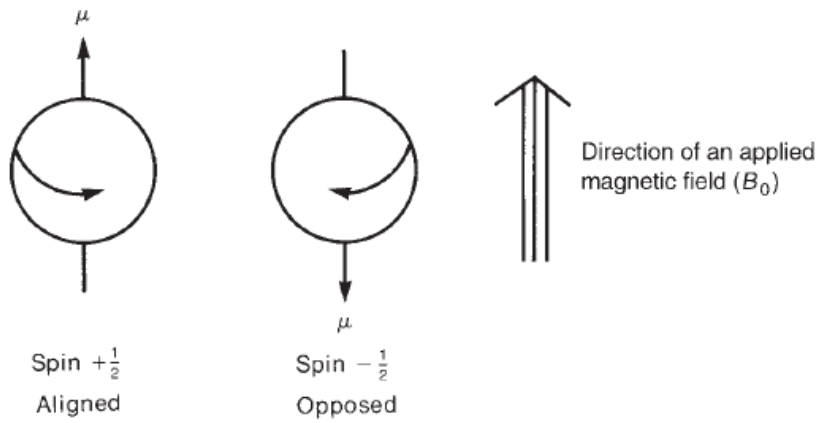


FIGURE 5.1 The two allowed spin states for a proton.

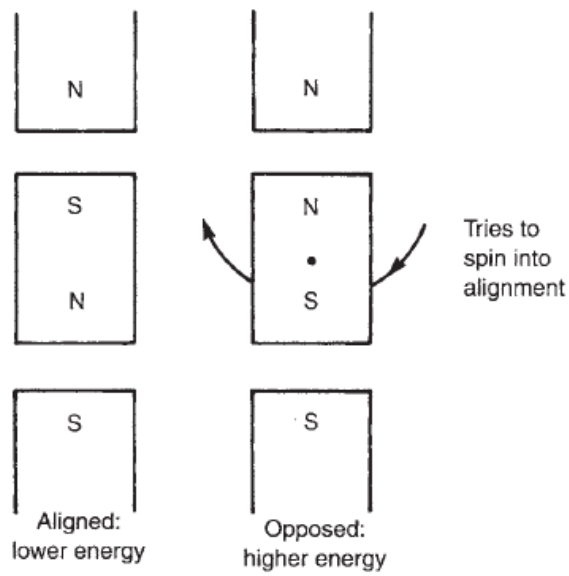


FIGURE 5.2 Aligned and opposed arrangements of bar magnets.

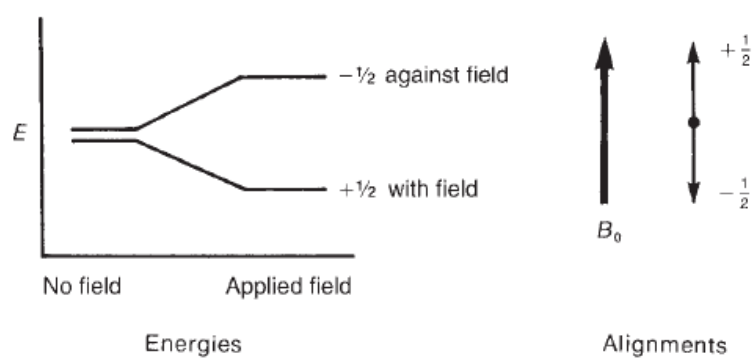


FIGURE 5.3 The spin states of a proton in the absence and in the presence of an applied magnetic field.

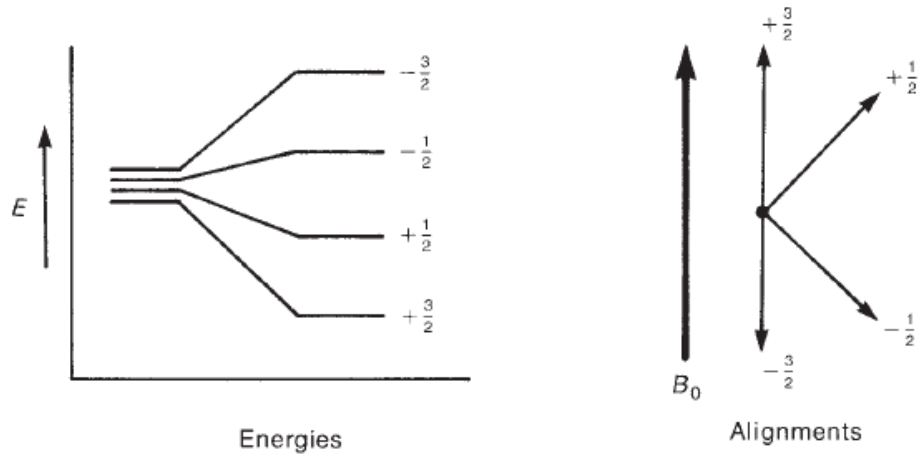


FIGURE 5.4 The spin states of a chlorine atom both in the presence and in the absence of an applied magnetic field.

5.3 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 5.5 illustrates this process for a hydrogen nucleus.

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

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

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

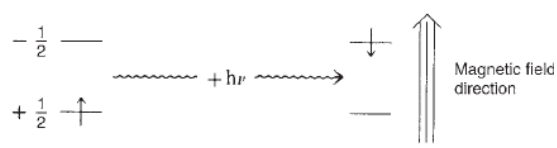


FIGURE 5.5 The NMR absorption process for a proton.

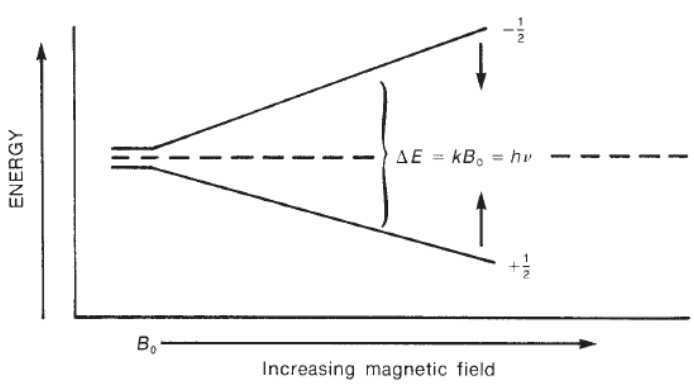


FIGURE 5.6 The spin-state energy separation as a function of the strength of the applied magnetic field B_0.

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

Solving for the frequency of the absorbed energy,

$$\upsilon = \left(\frac{\gamma}{2\pi}\right) B_0$$

TABLE 5.2
FREQUENCIES AND FIELD STRENGTHS AT WHICH SELECTED NUCLEI HAVE THEIR NUCLEAR RESONANCES

Isotope	Natural Abundance (%)	Field Strength, B_0 (Tesla[a])	Frequency, ν (MHz)	Magnetogyric Ratio, 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.

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

5.5 POPULATION DENSITIES OF NUCLEAR SPIN STATES

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = e^{-\Delta E/kT} = e^{-h\nu/kT} \qquad \textbf{Equation 5.7}$$

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

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

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

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 5.7, 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. 5.9).

TABLE 5.3
VARIATION OF ^{1}H 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

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.

5.6 THE CHEMICAL SHIFT AND SHIELDING

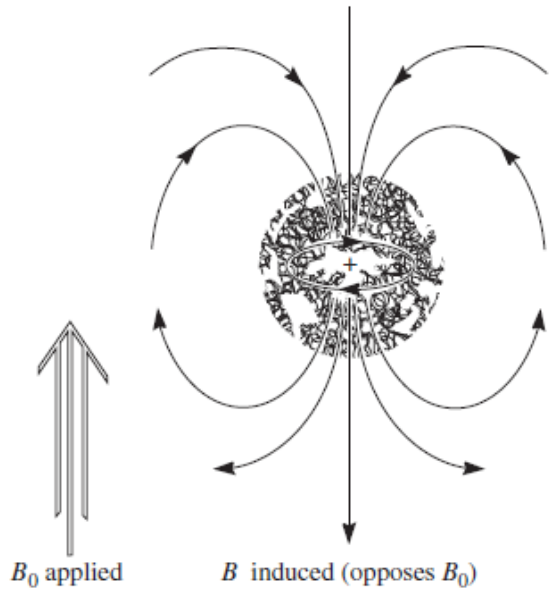


FIGURE 5.10 Diamagnetic anisotropy—the diamagnetic shielding of a nucleus caused by the circulation of valence electrons.

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**.

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

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

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

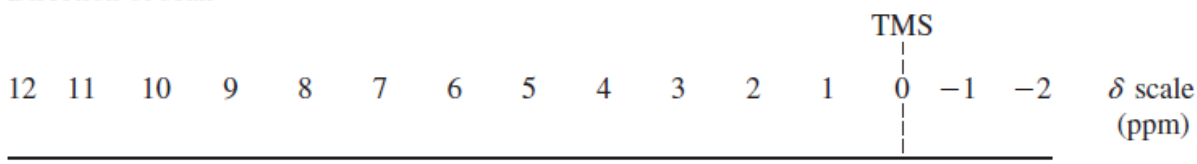
$$\delta = \frac{\text{(shift in Hz)}}{\text{(spectrometer frequency in MHz)}} \qquad \textbf{Equation 5.8}$$

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

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

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

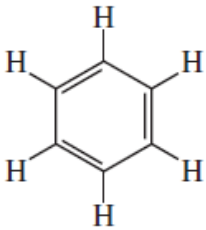
Direction of scan ⇒

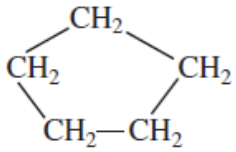


5.7 THE NUCLEAR MAGNETIC RESONANCE SPECTROMETER

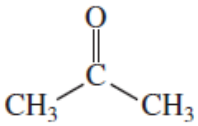
A. The Continuous-Wave (CW) Instrument

5.8 CHEMICAL EQUIVALENCE—A BRIEF OVERVIEW

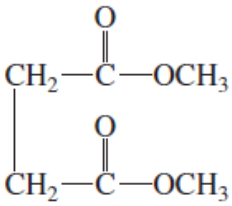


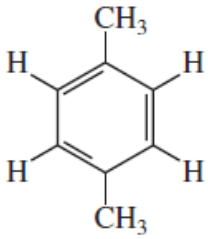


Molecules giving rise to one NMR absorption peak—all protons chemically equivalent

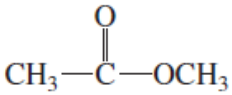


$(CH_3)_4Si$

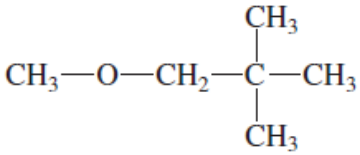


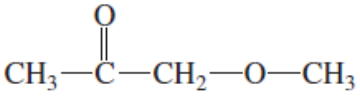


Molecules giving rise to two NMR absorption peaks—two different sets of chemically equivalent protons



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





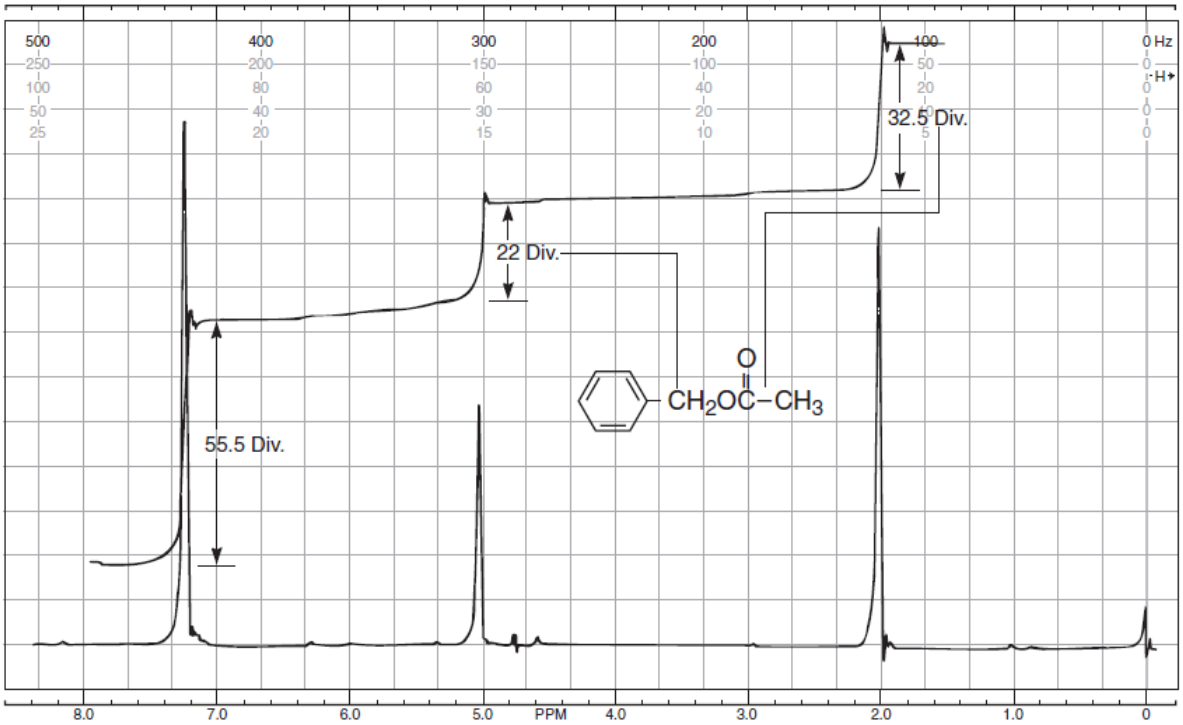


FIGURE 5.18 Determination of the integral ratios for benzyl acetate (60 MHz).

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

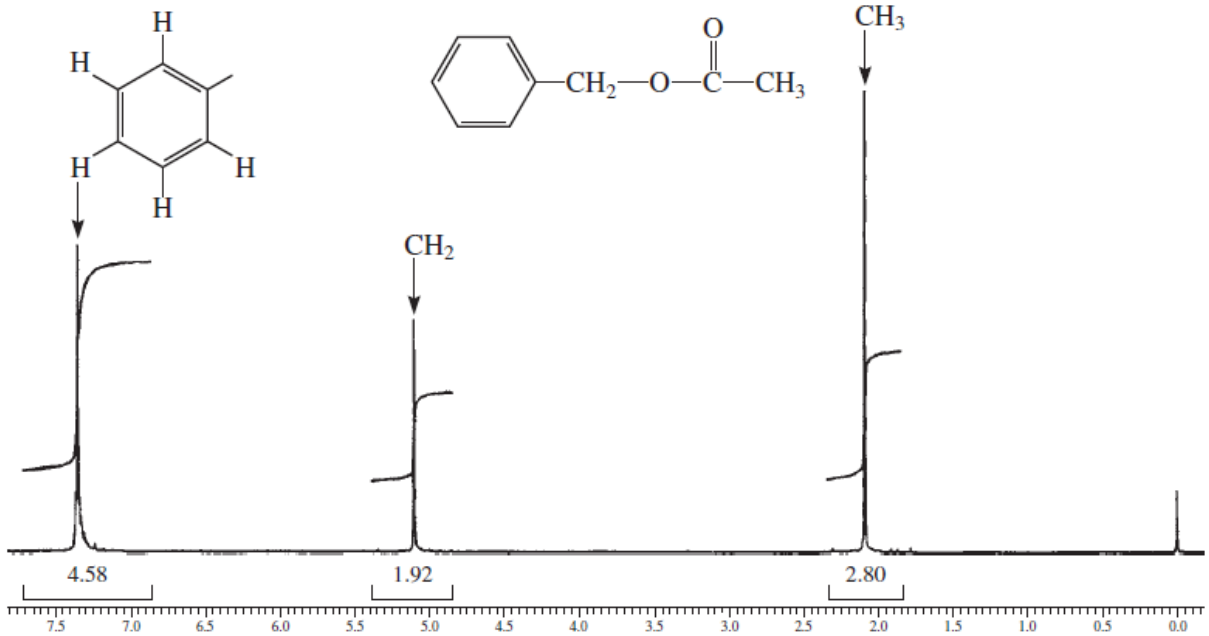


FIGURE 5.19 An integrated spectrum of benzyl acetate determined on a 300-MHz FT-NMR instrument.

5.10 CHEMICAL ENVIRONMENT AND CHEMICAL SHIFT

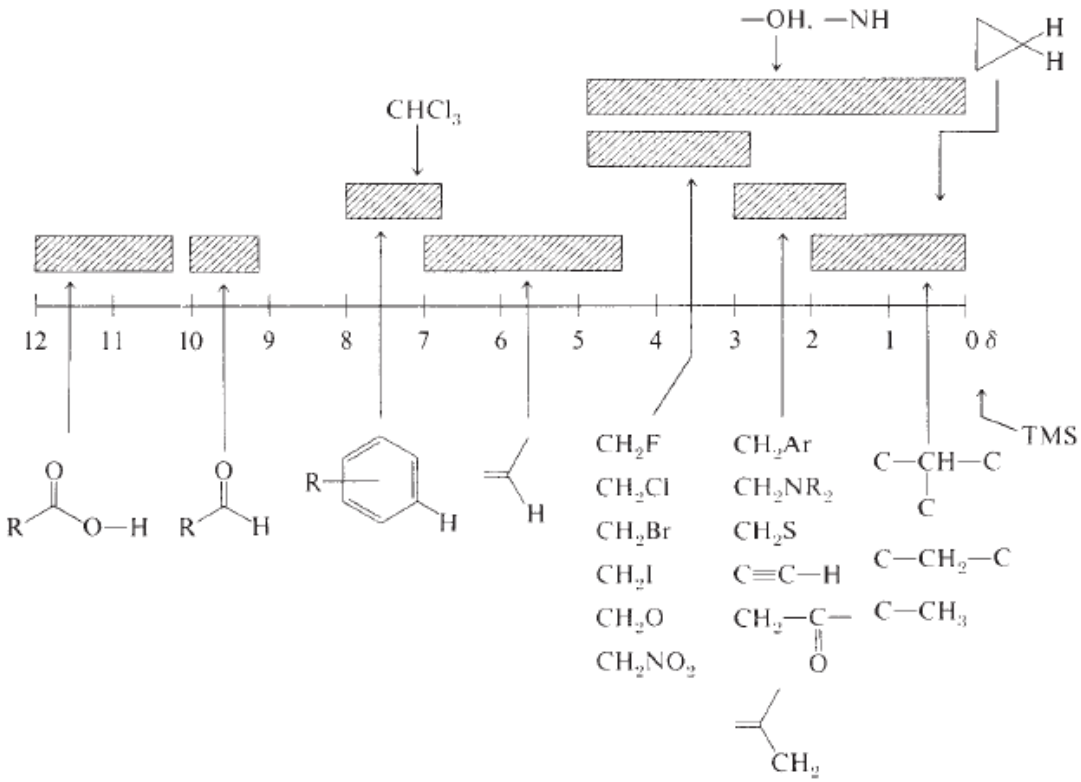


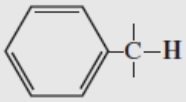
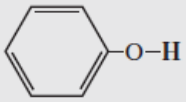
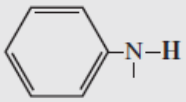
FIGURE 5.20 A simplified correlation chart for proton chemical shift values.

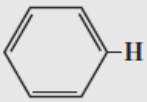
5.11 LOCAL DIAMAGNETIC SHIELDING

A. Electronegativity Effects

TABLE 5.4
APPROXIMATE CHEMICAL SHIFT RANGES (PPM) FOR SELECTED TYPES OF PROTONS[a]

$R-CH_3$	0.7 – 1.3
$R-CH_2-R$	1.2 – 1.4
R_3CH	1.4 – 1.7
$R-C=C-C-H$	1.6 – 2.6
$R-C(=O)-C-H$, $H-C(=O)-C-H$	2.1 – 2.4
$RO-C(=O)-C-H$, $HO-C(=O)-C-H$	2.1 – 2.5
$N\equiv C-C-H$	2.1 – 3.0
$R-N-C-H$	2.2 – 2.9
$R-S-C-H$	2.0 – 3.0
$I-C-H$	2.0 – 4.0
$Br-C-H$	2.7 – 4.1
$Cl-C-H$	3.1 – 4.1
$R-S(=O)_2-O-C-H$	ca. 3.0
$RO-C-H$, $HO-C-H$	3.2 – 3.8

		2.3 – 2.7
R–C≡C–H		1.7 – 2.7
R–S–H	var	1.0 – 4.0[b]
R–N(–)–H	var	0.5 – 4.0[b]
R–O–H	var	0.5 – 5.0[b]
	var	4.0 – 7.0[b]
	var	3.0 – 5.0[b]
R–C(=O)–N(–)–H	var	5.0 – 9.0[b]

R–C(=O)–O–C(–)–H	3.5 – 4.8
O_2N–C(–)–H	4.1 – 4.3
F–C(–)–H	4.2 – 4.8
R–C(–)=C(–)–H	4.5 – 6.5
	6.5 – 8.0
R–C(=O)–H	9.0 – 10.0
R–C(=O)–OH	11.0 – 12.0

[a]For those hydrogens shown as –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 (–CH(–)–), the shift is typically at the high end of the range given.

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

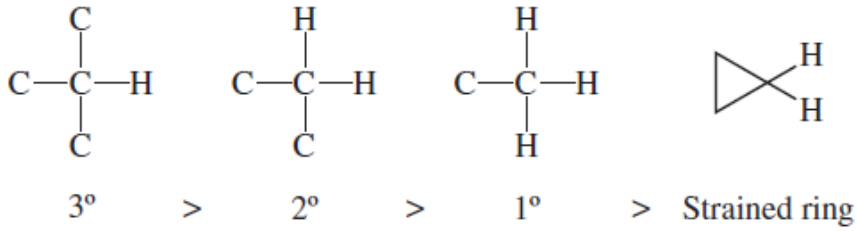
TABLE 5.5
DEPENDENCE OF THE CHEMICAL SHIFT OF CH_3X ON THE ELEMENT X

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

TABLE 5.6
SUBSTITUTION EFFECTS

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

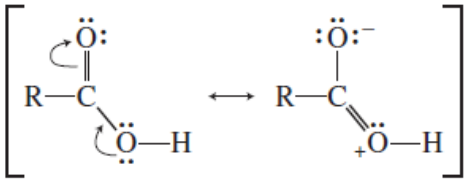
Aliphatic region



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.

TABLE 5.7
TYPICAL RANGES FOR PROTONS WITH VARIABLE CHEMICAL SHIFT

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

5.12 MAGNETIC ANISOTROPY

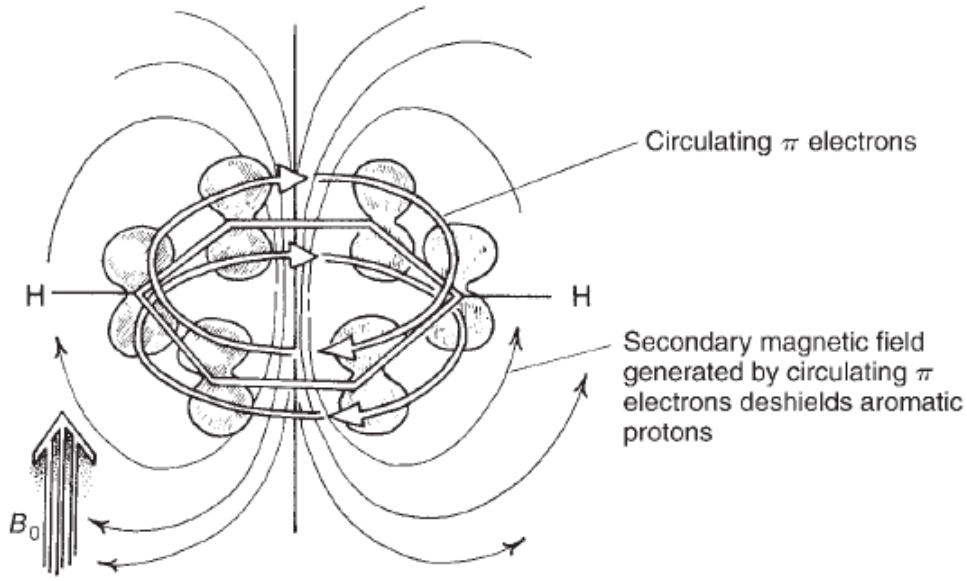


FIGURE 5.21 Diamagnetic anisotropy in benzene.

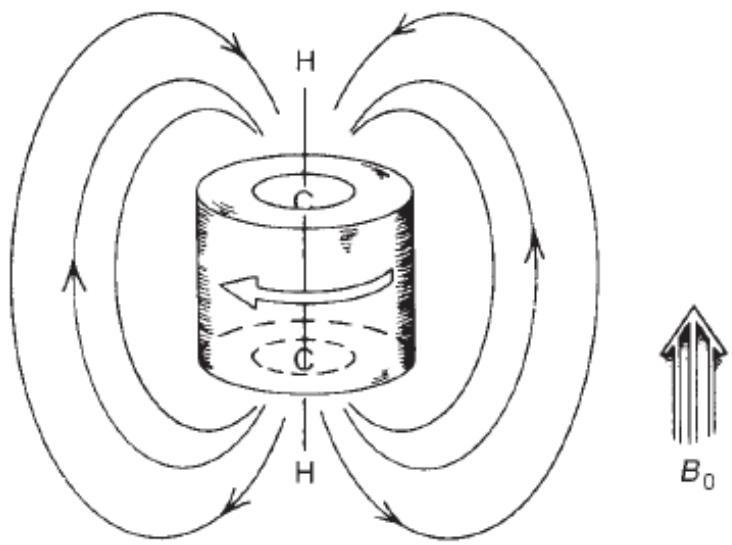


FIGURE 5.22 Diamagnetic anisotropy in acetylene.

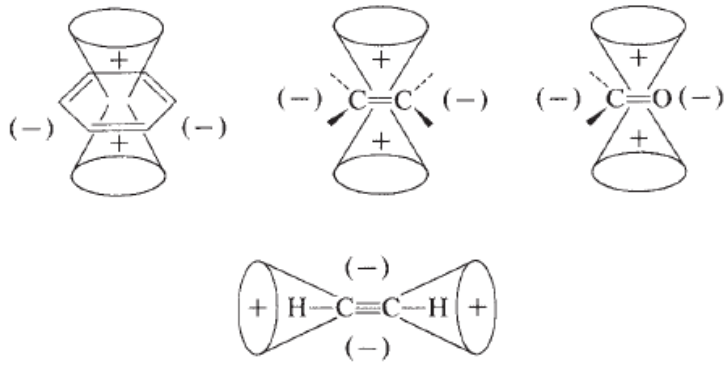


FIGURE 5.23 Anisotropy caused by the presence of π electrons in some common multiple-bond systems.

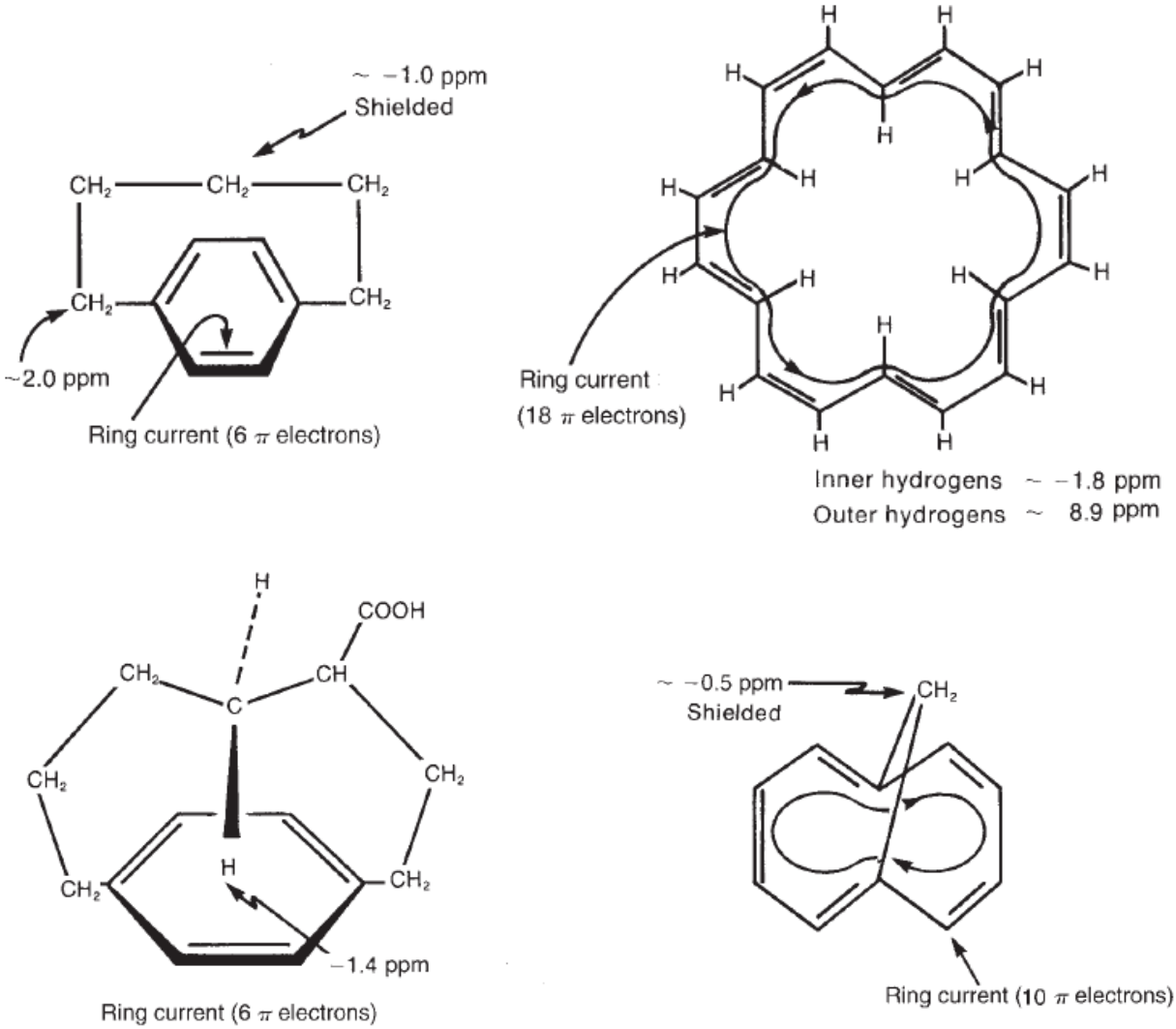
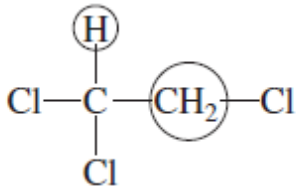


FIGURE 5.24 The effects of anisotropy in some actual molecules.

5.13 SPIN–SPIN SPLITTING (n + 1) RULE



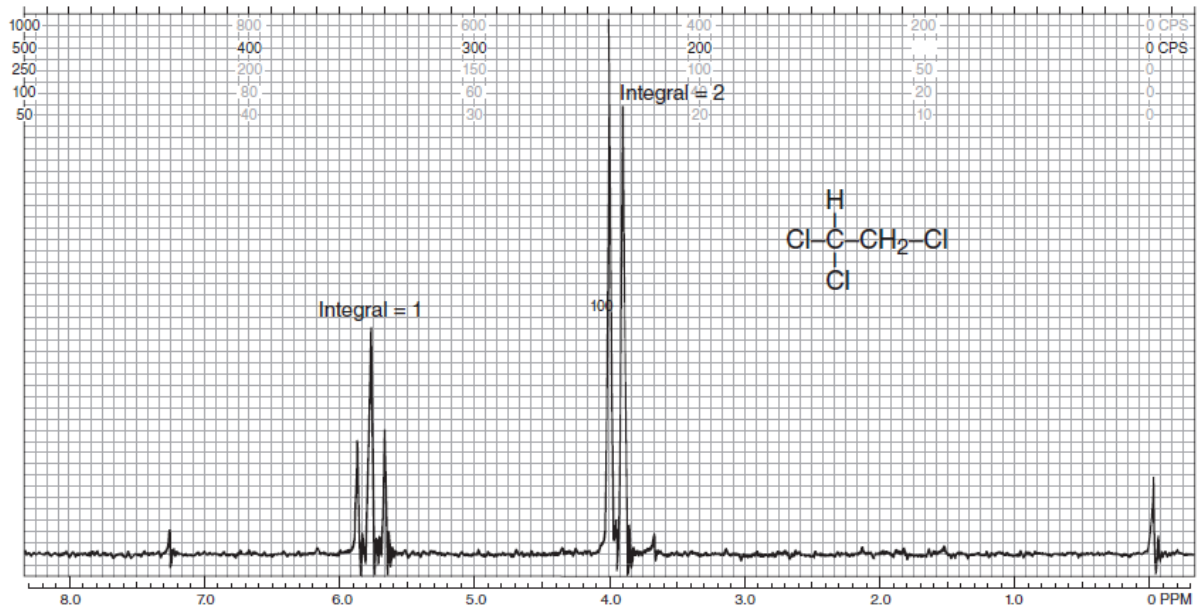


FIGURE 5.25 The ^{1}H NMR spectrum of 1,1,2-trichloroethane (60 MHz).

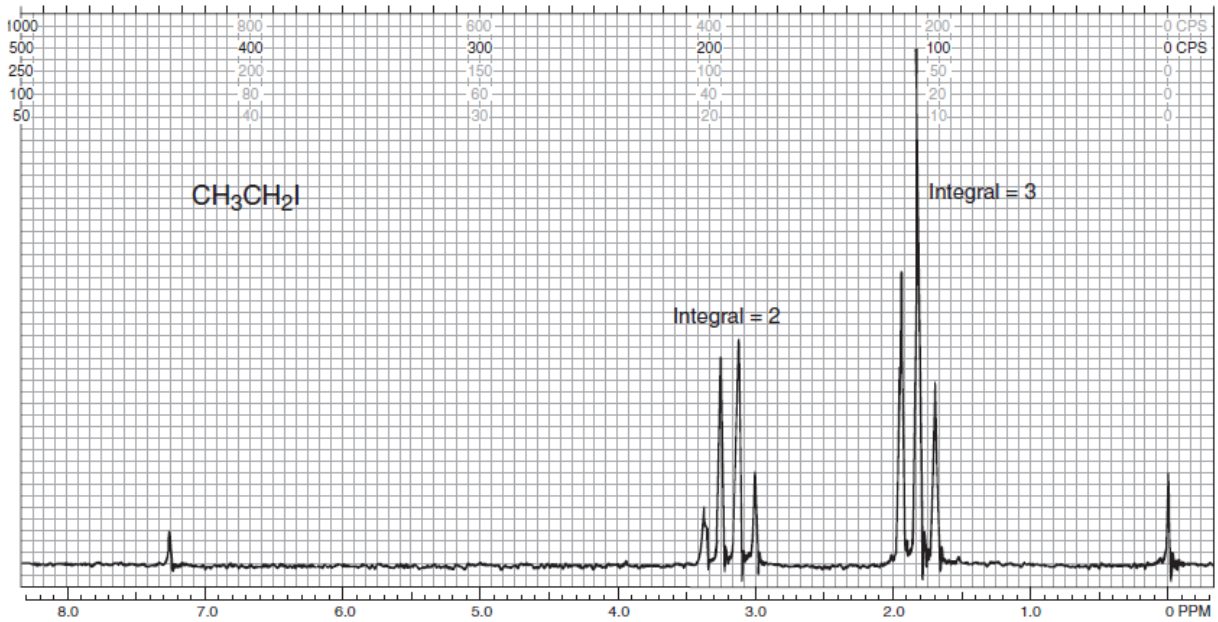


FIGURE 5.26 The ^{1}H NMR spectrum of ethyl iodide (60 MHz).

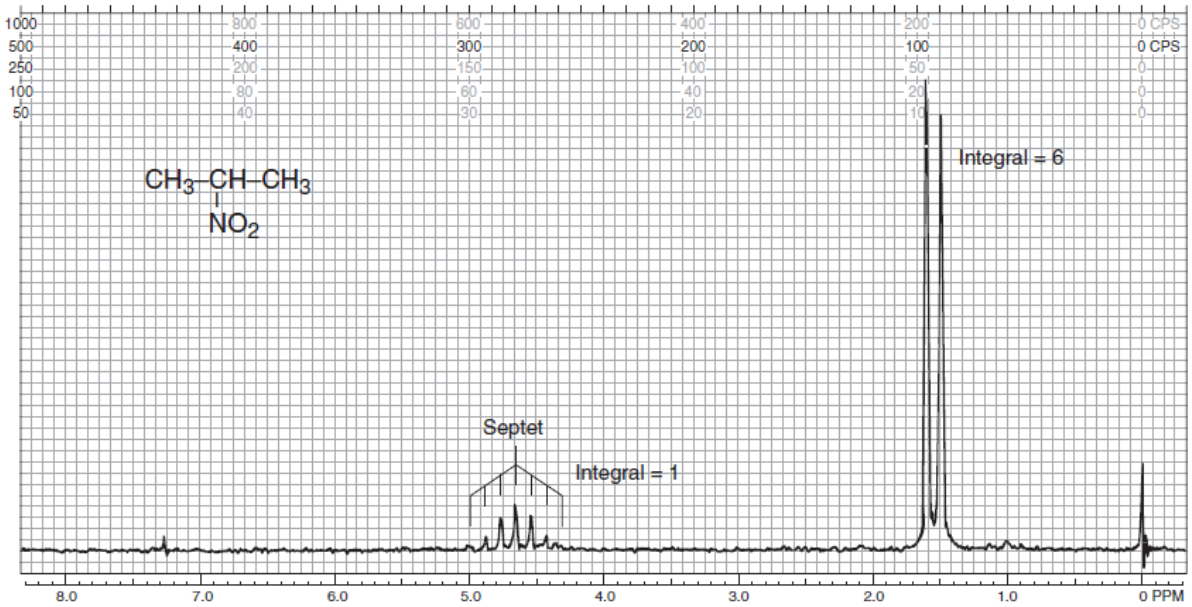


FIGURE 5.27 The ^{1}H NMR spectrum of 2-nitropropane (60 MHz).

5.16 PASCAL'S TRIANGLE

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 5.33 Pascal's triangle.

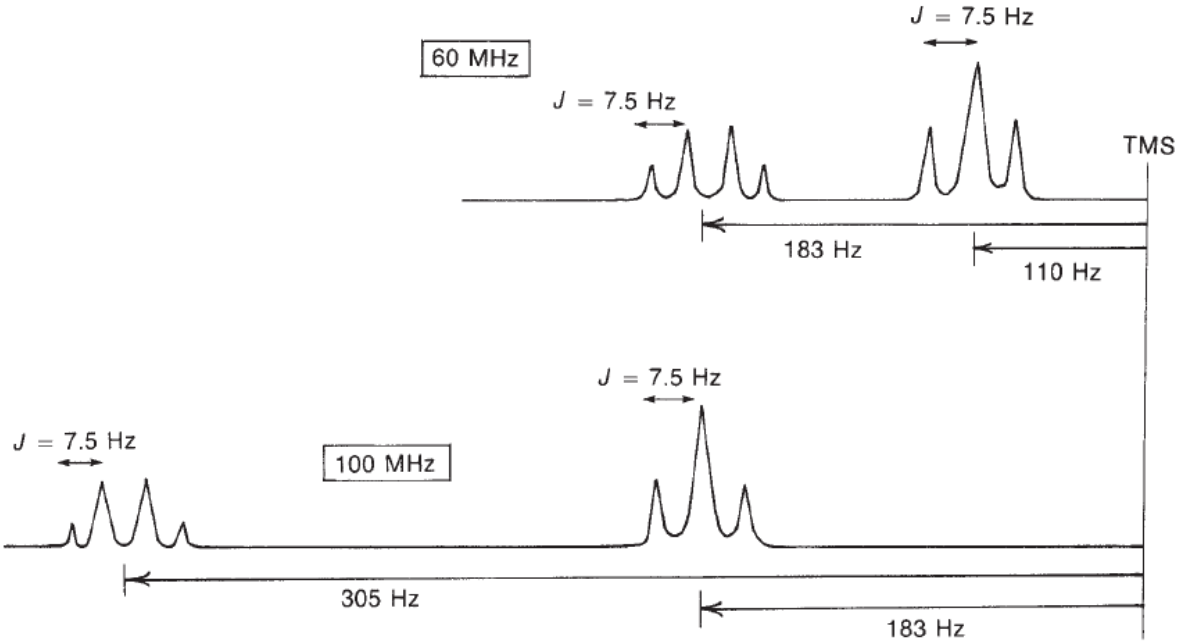
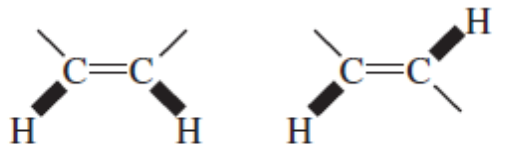
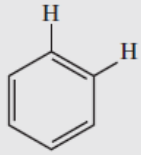
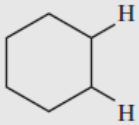
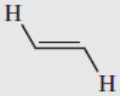
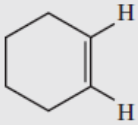
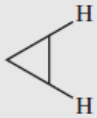
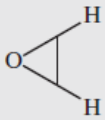
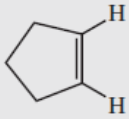


FIGURE 5.35 An illustration of the relationship between the chemical shift and the coupling constant.

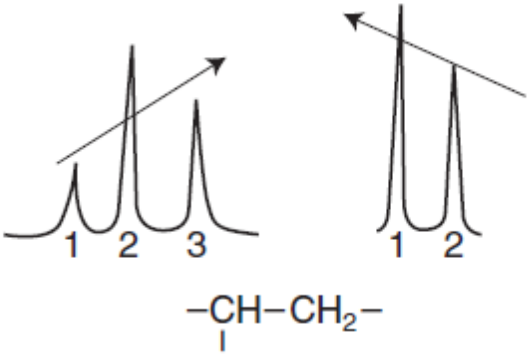


^3J *cis* = 10 Hz ^3J *trans* = 16 Hz

TABLE 5.9
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

Multiplet skewing



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

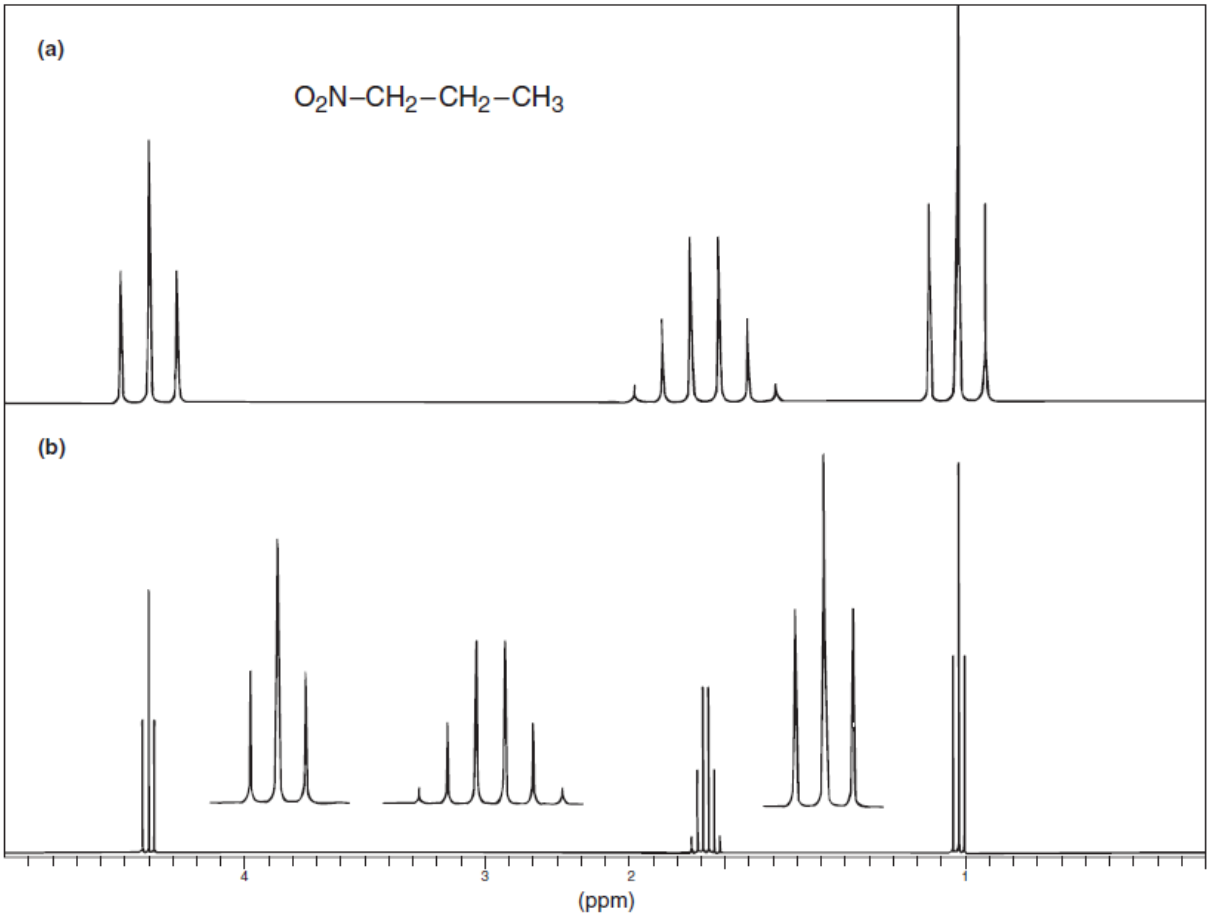


FIGURE 5.36 The NMR spectrum of 1-nitropropane. (a) Spectrum determined at 60 MHz; (b) spectrum determined at 300 MHz (with expansions).

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

A. Alkanes

SPECTRAL ANALYSIS BOX—Alkanes

CHEMICAL SHIFTS

$R-CH_3$	0.7–1.3 ppm	Methyl groups are often recognizable as a tall singlet, doublet, or triplet even when overlapping other CH absorptions.
$R-CH_2-R$	1.2–1.4 ppm	In long chains, all of the methylene (CH_2) absorptions may be overlapped in an unresolvable group.
R_3CH	1.4–1.7 ppm	Note that methine hydrogens (CH) have a larger chemical shift than those in methylene or methyl groups.

COUPLING BEHAVIOR

$-CH-CH-$	$^3J \approx 7$–8 Hz	In hydrocarbon chains, adjacent hydrogens will generally couple, with the spin–spin splitting following the n+1 Rule.

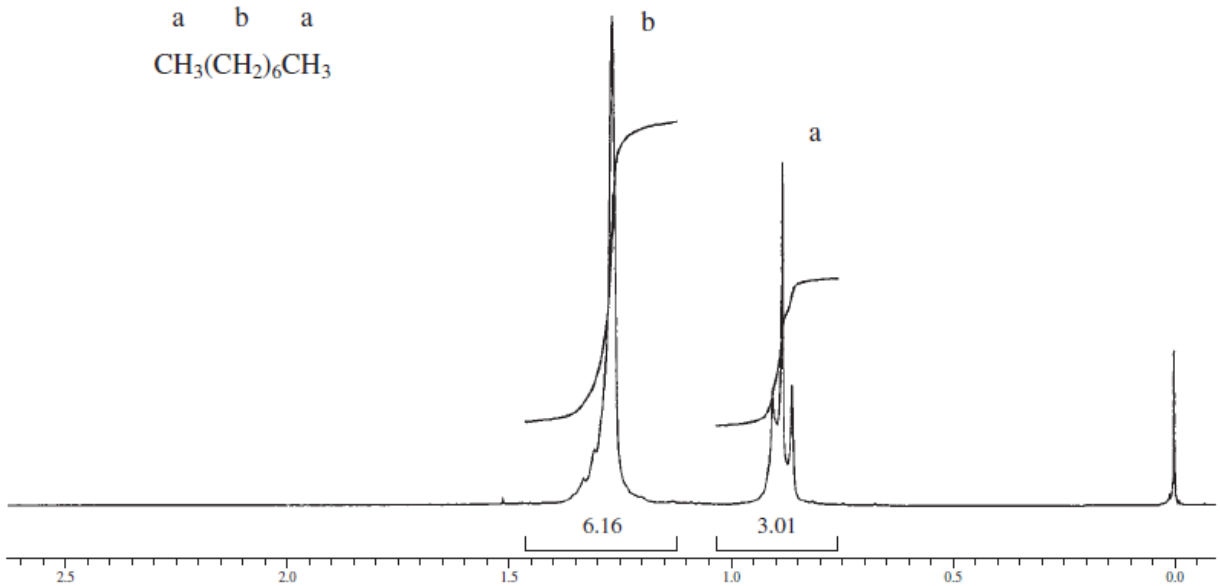


FIGURE 5.37 ^{1}H spectrum of octane (300 MHz).

B. Alkenes

SPECTRAL ANALYSIS BOX—Alkenes

CHEMICAL SHIFTS

C=C–**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–**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

H–C=C–**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 7.6).
–C=C(**H**)–**H**	$^2J \approx 0$ –3 Hz	
–C(**H**)=C–C–**H**	$^4J \approx 0$ –3 Hz	When allylic hydrogens are present in an alkene, they may show long-range allylic coupling (Section 7.7) to hydrogens on the far double-bond carbon as well as the usual splitting due to the hydrogen on the adjacent (nearest) carbon.

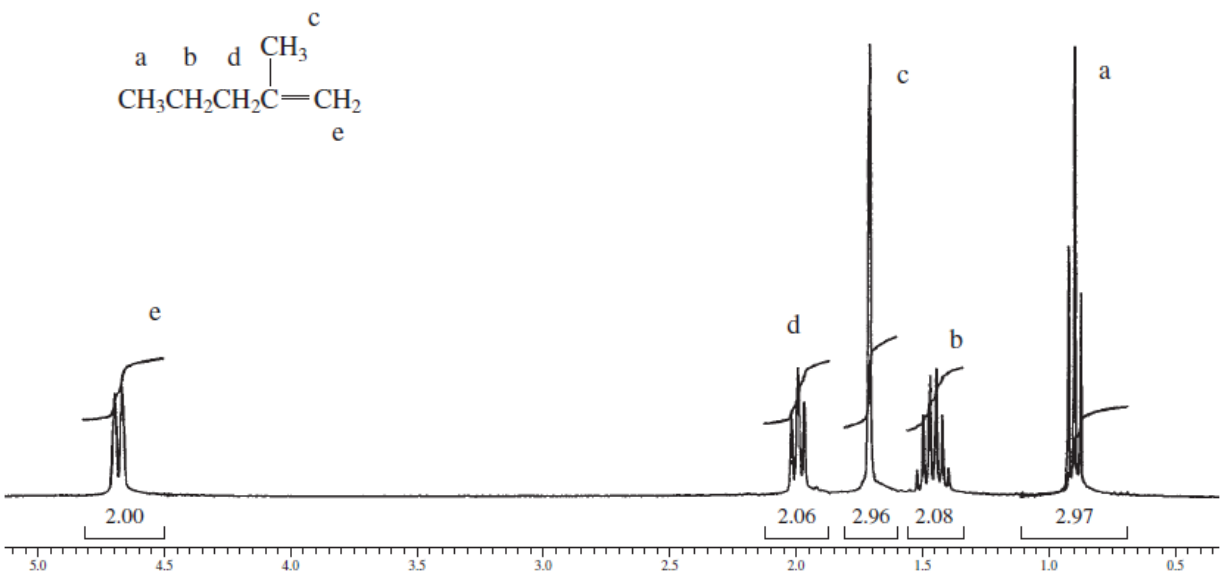
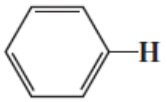


FIGURE 5.38 ^{1}H spectrum of 2-methyl-1-pentene (300 MHz).

C. Aromatic Compounds

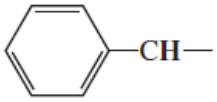
SPECTRAL ANALYSIS BOX—Aromatic Compounds

CHEMICAL SHIFTS



6.5–8.0 ppm

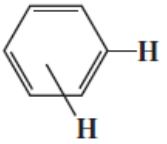
Hydrogens attached to an aromatic (benzenoid) ring have a large chemical shift, usually near 7.0 ppm. They are deshielded by the large anisotropic field generated by the electrons in the ring's π system.



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 7.10. 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.

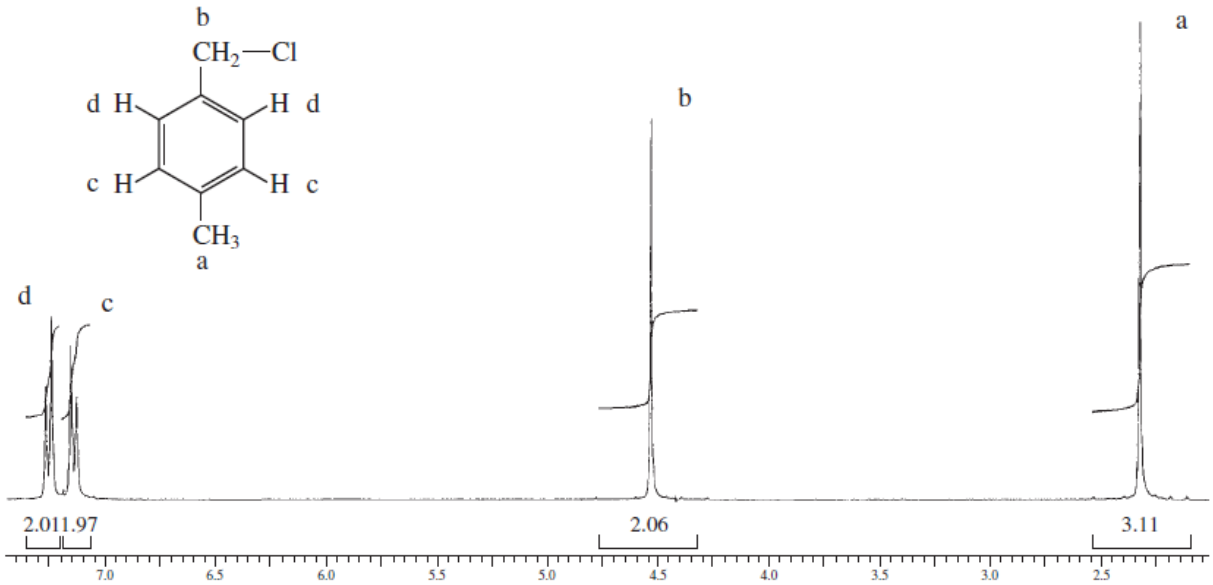


FIGURE 5.39 ^{1}H spectrum of α-chloro-*p*-xylene (300 MHz).

D. Alkynes

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—CH—	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.

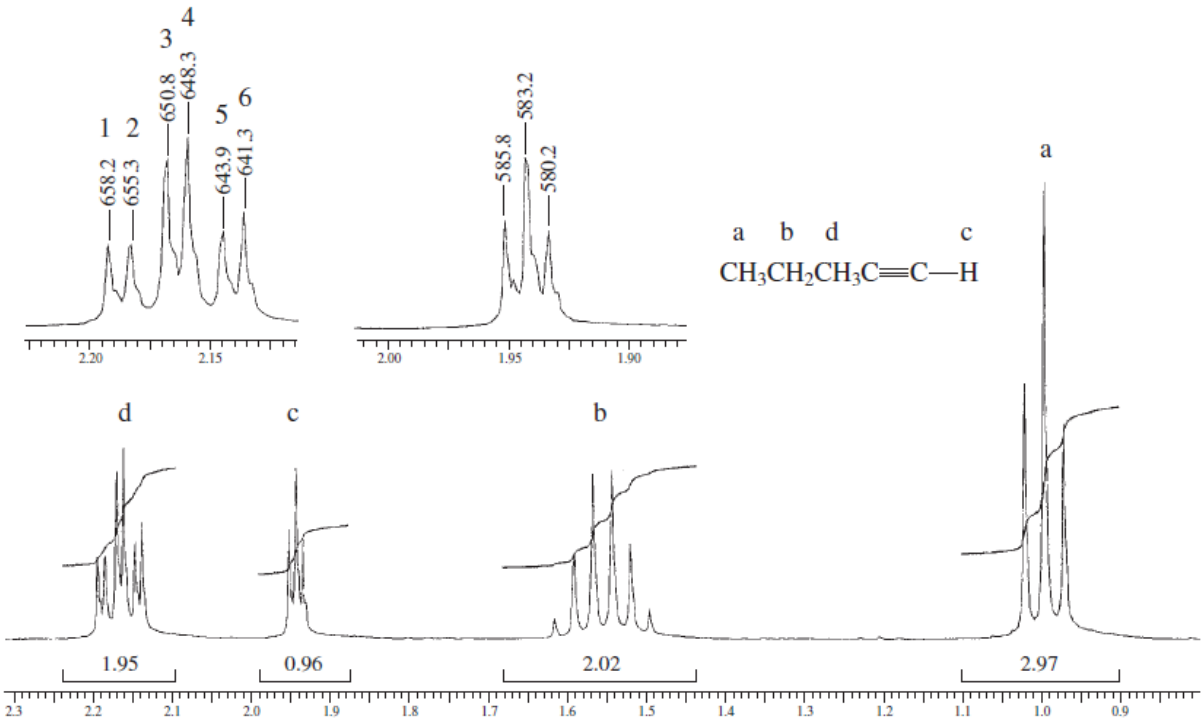


FIGURE 5.40 ^{1}H spectrum of 1-pentyne (300 MHz).

E. Alkyl Halides

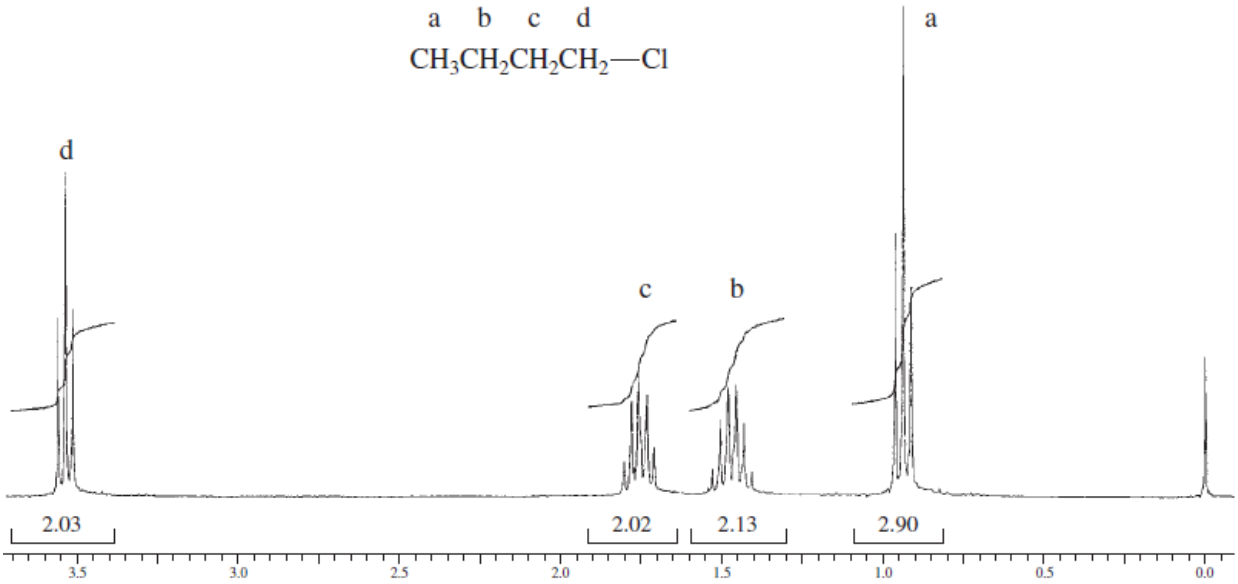
SPECTRAL ANALYSIS BOX—Alkyl Halides

CHEMICAL SHIFTS

—CH—I	2.0– 4.0 ppm	The chemical shift of a hydrogen atom attached to the same carbon as a halide atom will increase (move further downfield).
—CH—Br	2.7– 4.1 ppm	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.
—CH—Cl	3.1– 4.1 ppm	
—CH—F	4.2– 4.8 ppm	

COUPLING BEHAVIOR

—CH—F	$^2J \approx 50$ 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.
—CH—CF—	$^3J \approx 20$ Hz	



F. Alcohols

SPECTRAL ANALYSIS BOX—Alcohols

CHEMICAL SHIFTS

C—OH	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.
CH—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

CH—OH	*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.

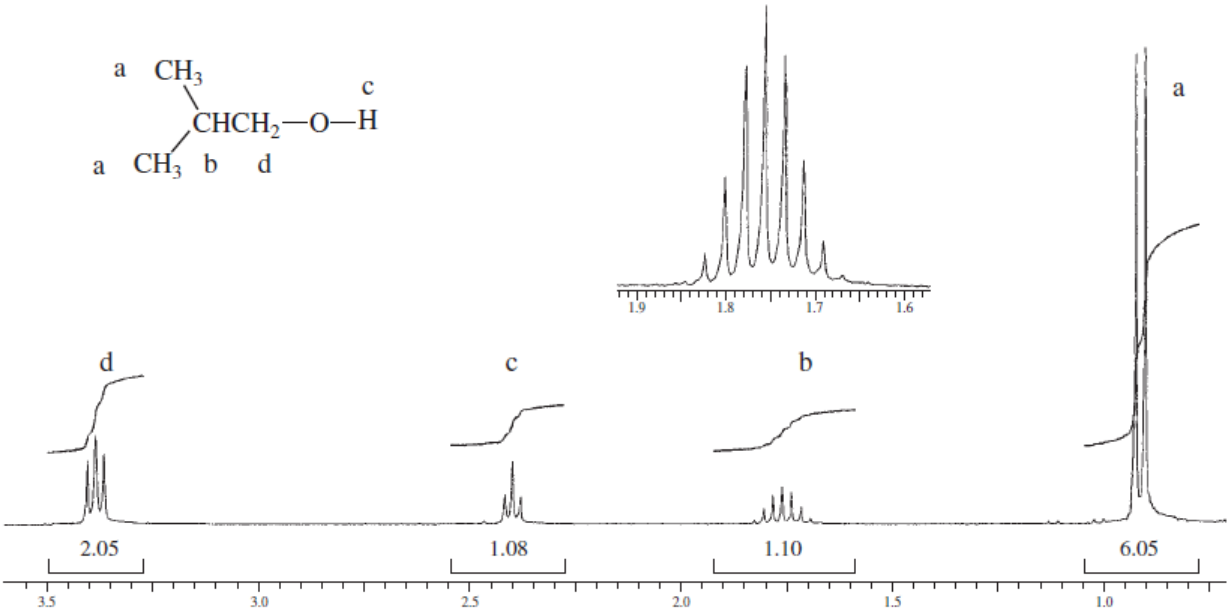


FIGURE 5.42 ^{1}H spectrum of 2-methyl-1-propanol (300 MHz).

G. Ethers

SPECTRAL ANALYSIS BOX—Ethers

CHEMICAL SHIFTS

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

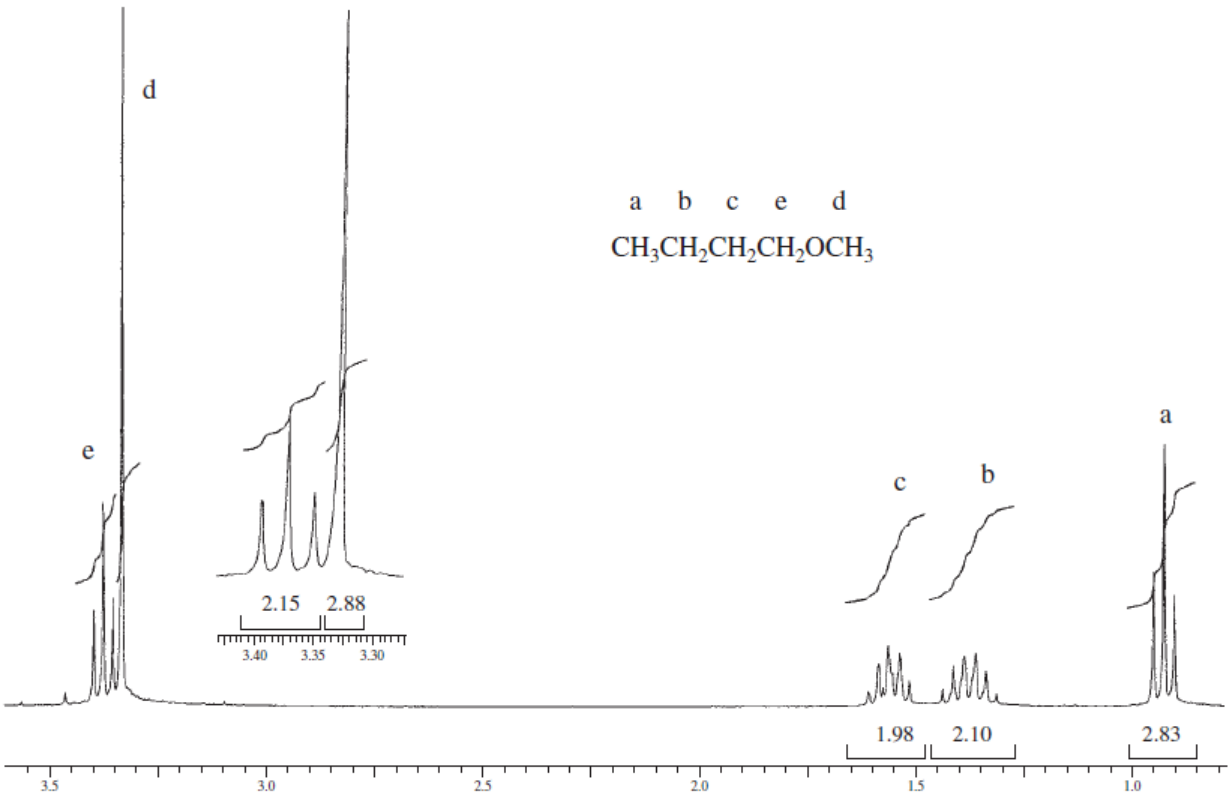
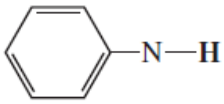


FIGURE 5.43 ^{1}H spectrum of butyl methyl ether (300 MHz).

H. Amines

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.
—**CH**—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 8.4 and 8.5.
—**N**—CH	$^2J \approx 0$ Hz	This coupling is usually not observed.
C—N—**H** | **H**	$^3J \approx 0$ Hz	Due to chemical exchange, this coupling is usually not observed.

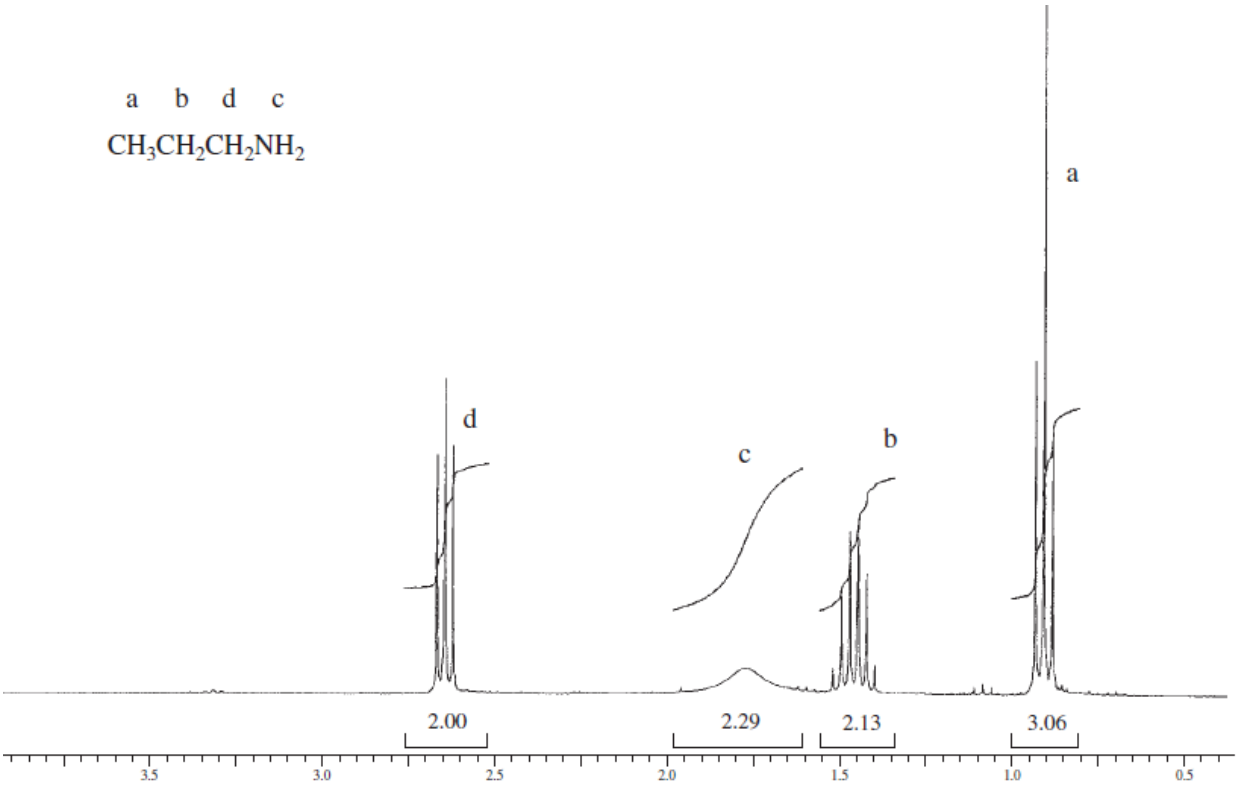


FIGURE 5.44 ^{1}H spectrum of propylamine (300 MHz).

I. Nitriles

SPECTRAL ANALYSIS BOX—Nitriles

CHEMICAL SHIFTS

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

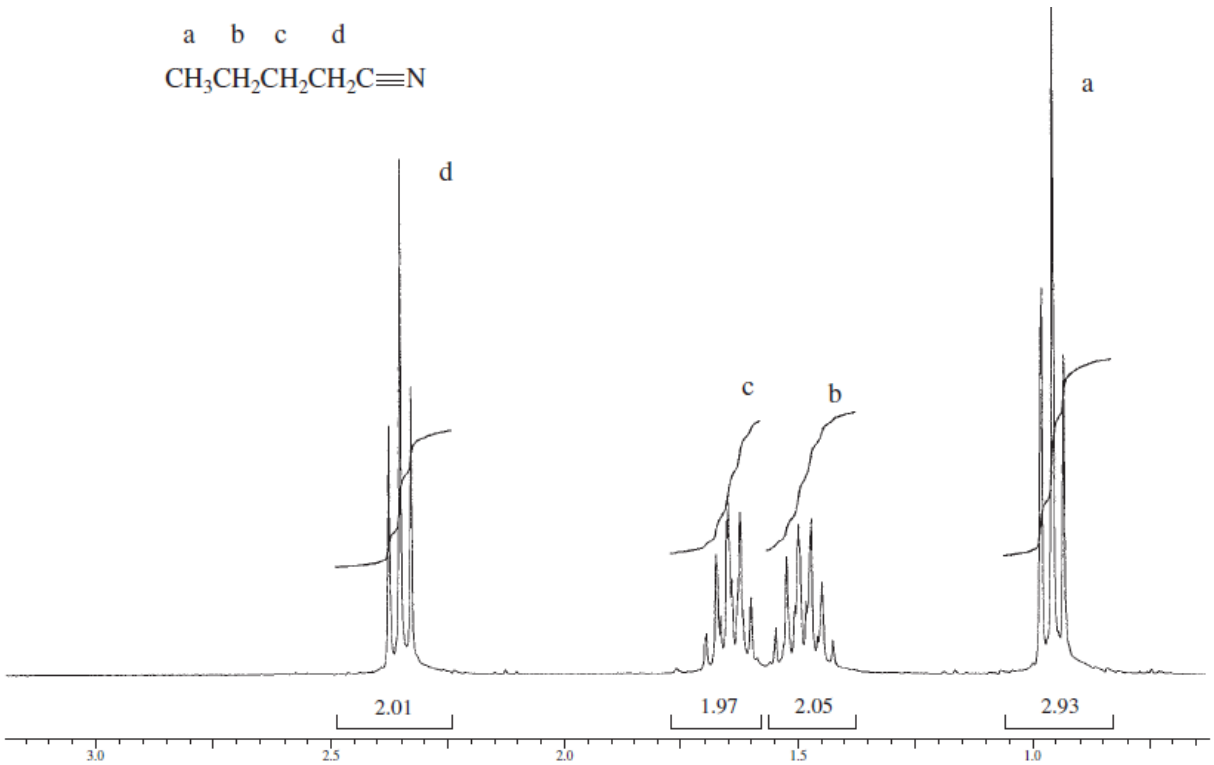


FIGURE 5.45 ^{1}H spectrum of valeronitrile (300 MHz).

J. Aldehydes

SPECTRAL ANALYSIS BOX—Aldehydes

CHEMICAL SHIFTS

R—CHO	9.0–10.0 ppm	The aldehyde hydrogen is shifted far downfield due to the anisotropy of the carbonyl group (C=O).
R—CH—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

—CH—CHO	$^3J \approx 1$–3 Hz	Coupling occurs between the aldehyde hydrogen and hydrogens on the adjacent carbon, but ^3J is small.

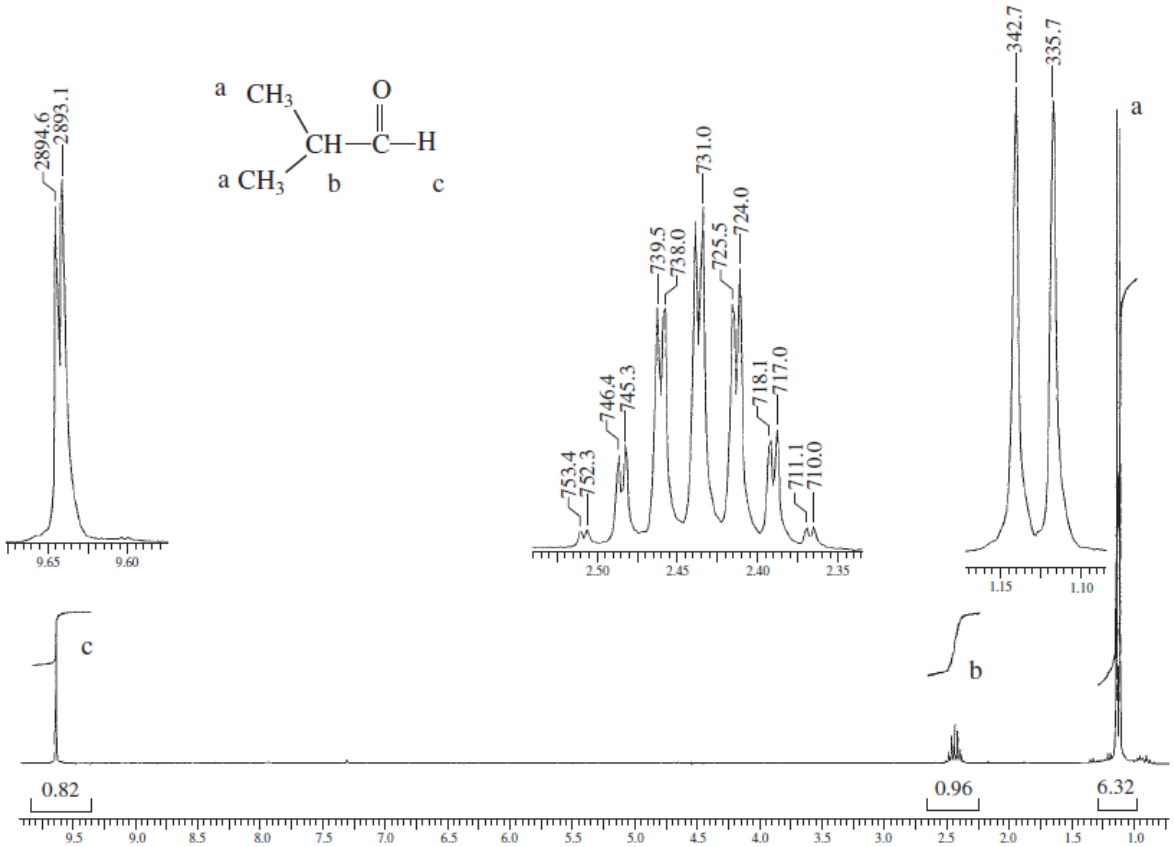


FIGURE 5.46 ^{1}H spectrum of 2-methylpropanal (isobutyraldehyde) at 300 MHz.

K. Ketones

SPECTRAL ANALYSIS BOX—Ketones

CHEMICAL SHIFTS

R—CH—C=O (R)	2.1–2.4 ppm	The α hydrogens in ketones are deshielded by the anisotropy of the adjacent C=O group.

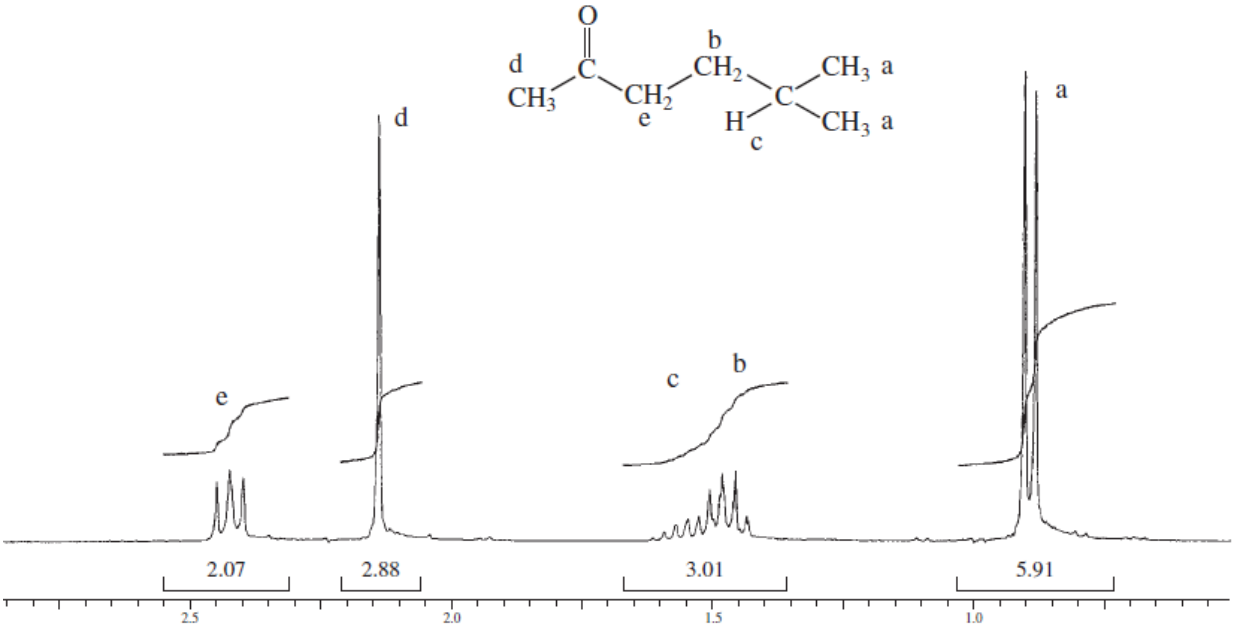
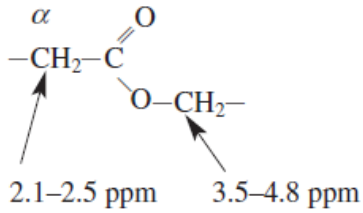


FIGURE 5.47 ^{1}H spectrum of 5-methyl-2-hexanone (300 MHz).

L. Esters

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.

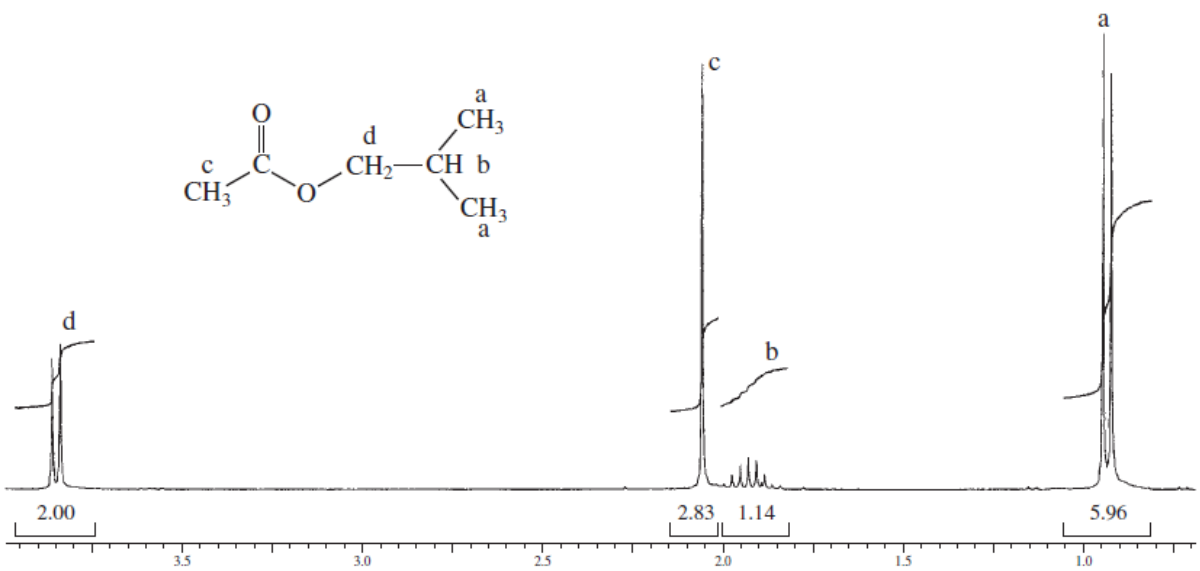


FIGURE 5.48 ^{1}H spectrum of isobutyl acetate (300 MHz).

M. Carboxylic Acids

SPECTRAL ANALYSIS BOX—Carboxylic Acids

CHEMICAL SHIFTS

R—COOH	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. Note in some cases, however, due to factors discussed below, that this peak may be so broadened as to disappear into the baseline.
—CH—COOH	2.1–2.5 ppm	Hydrogens adjacent to the carbonyl group are slightly deshielded.

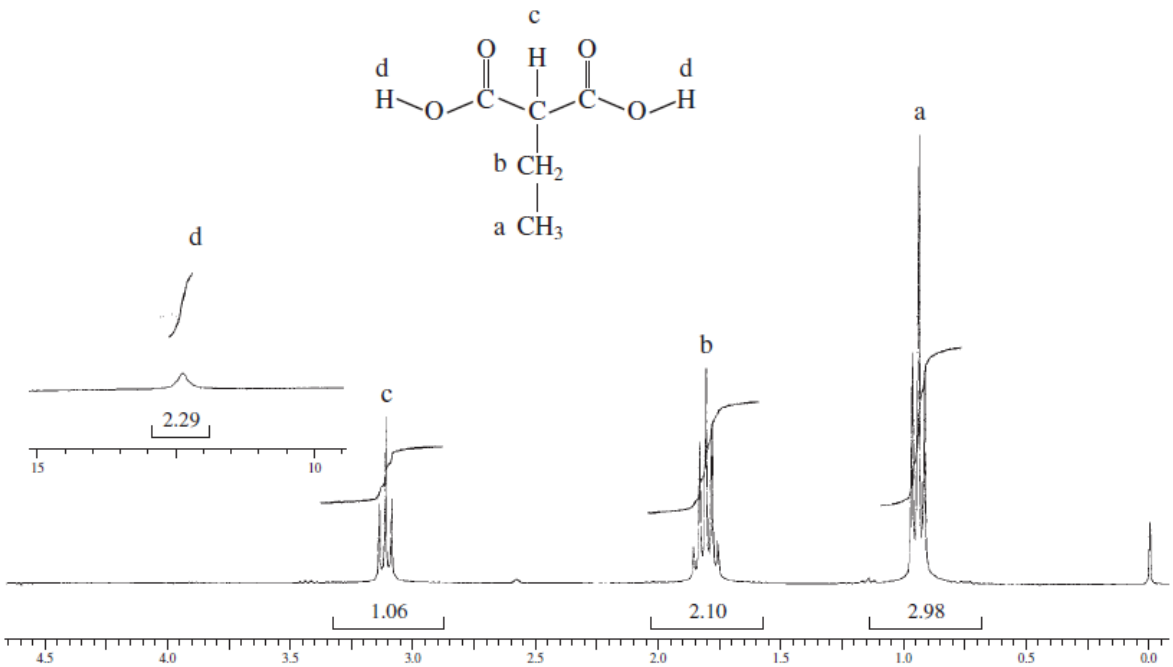


FIGURE 5.49 ^{1}H spectrum of ethylmalonic acid (300 MHz).

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.
—**CH**—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—**CH**	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**—**CH**—	$^2J \approx 0$ Hz	Usually not seen for the same reasons stated above.
—N(H)—**CH**—	$^3J \approx 0$–7 Hz	Exchange of the amide NH is slower than in amines, and splitting of the adjacent **CH** is observed even if the **NH** is broadened.

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		
$-CH-NO_2$	4.1–4.4 ppm	Deshielded by the nitro group.

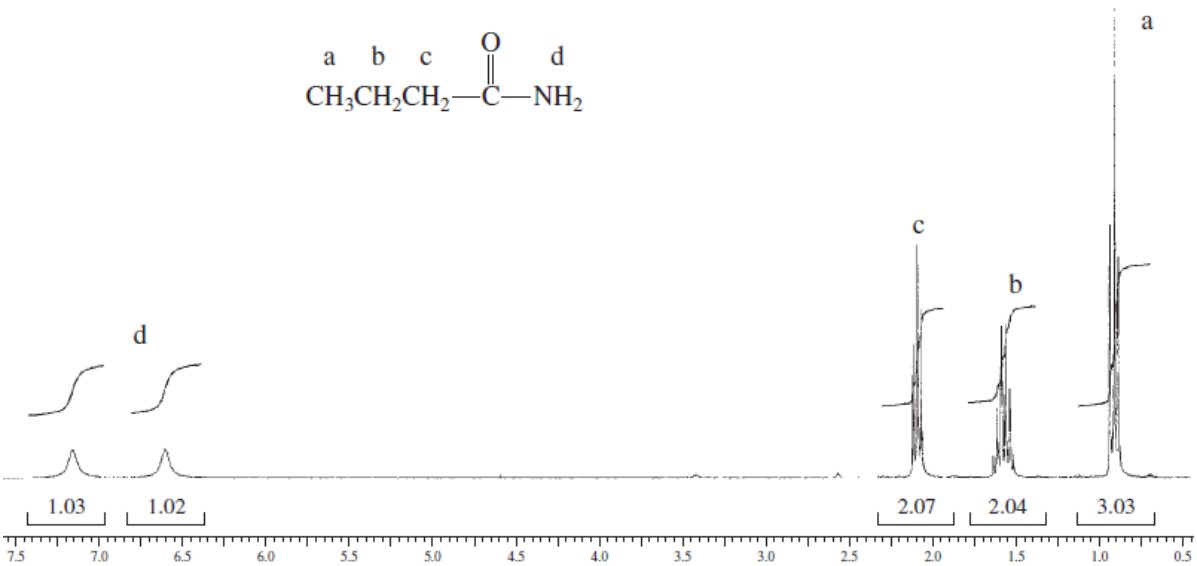


FIGURE 5.50 ^{1}H spectrum of butyramide (300 MHz).

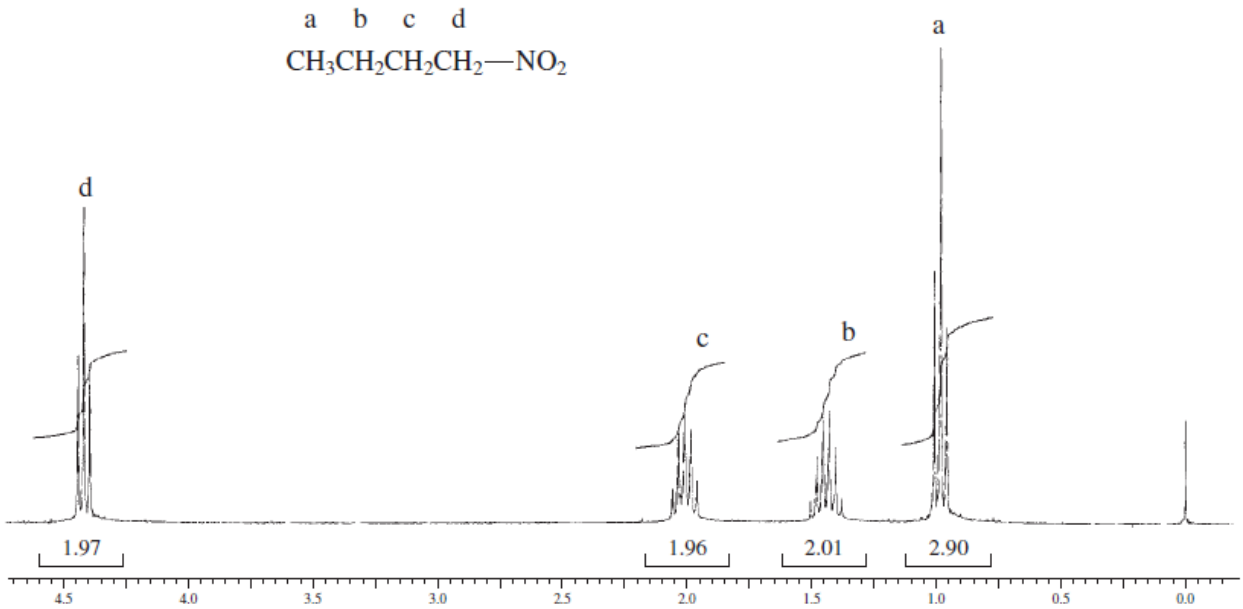
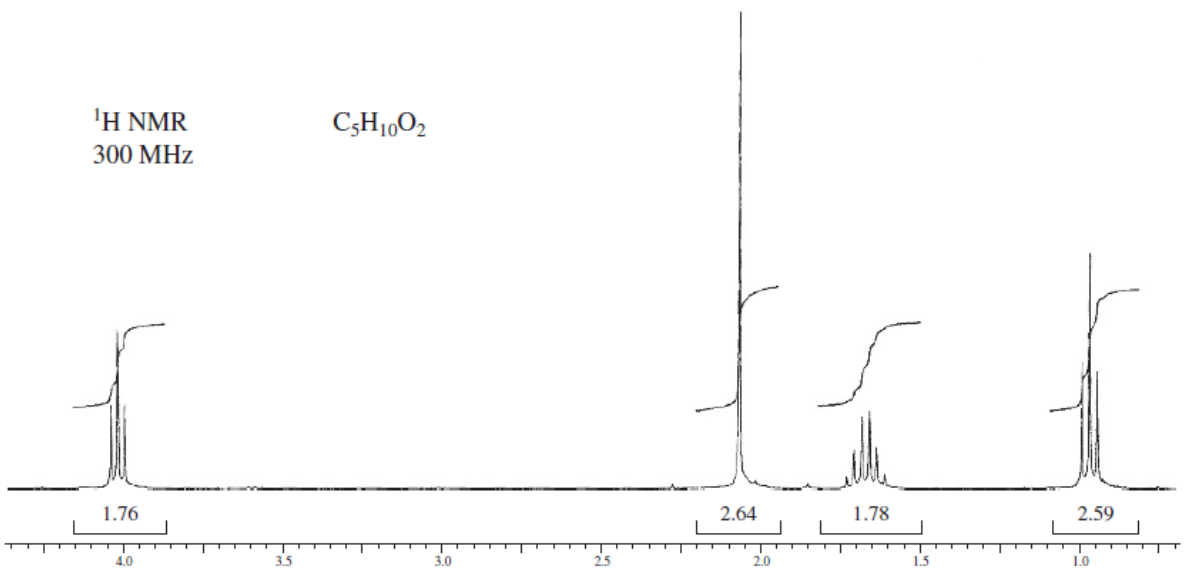


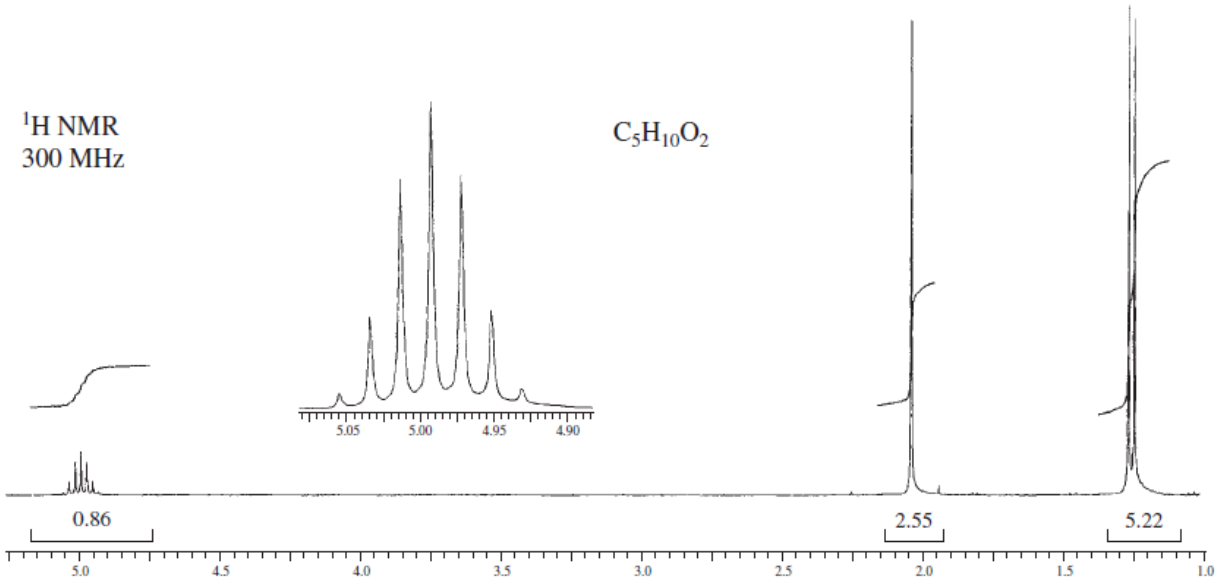
FIGURE 5.51 ^1H spectrum of 1-nitrobutane (300 MHz).

■ EXAMPLE 1

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.



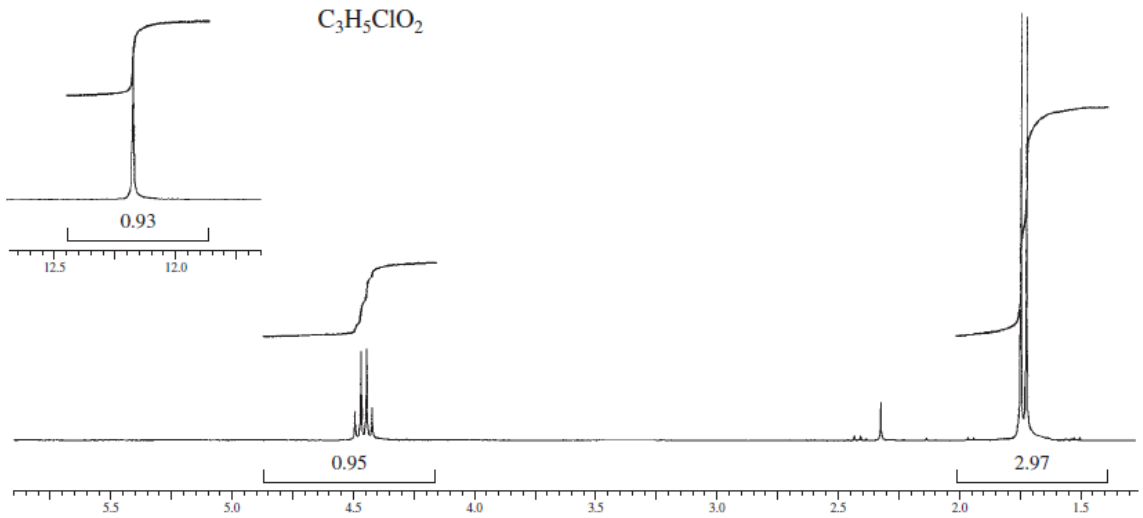
(a)



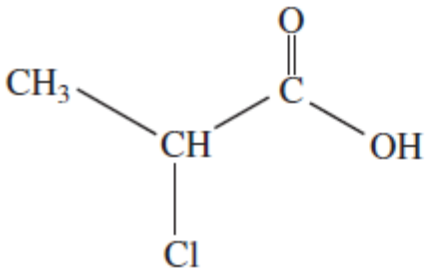
(b)

■ EXAMPLE 2

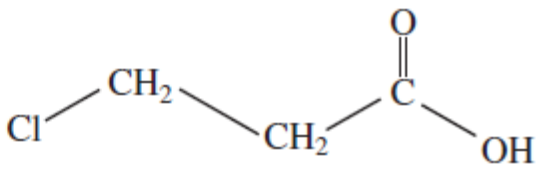
The two isomeric compounds with the formula $C_3H_5ClO_2$ have NMR spectra shown in Example 2a and 2b. The downfield protons appearing in the NMR spectra at about 12.1 and 11.5 ppm, respectively, are shown as insets.



(a)



2-chloroproanoic acid



3-chloropropanoic acid