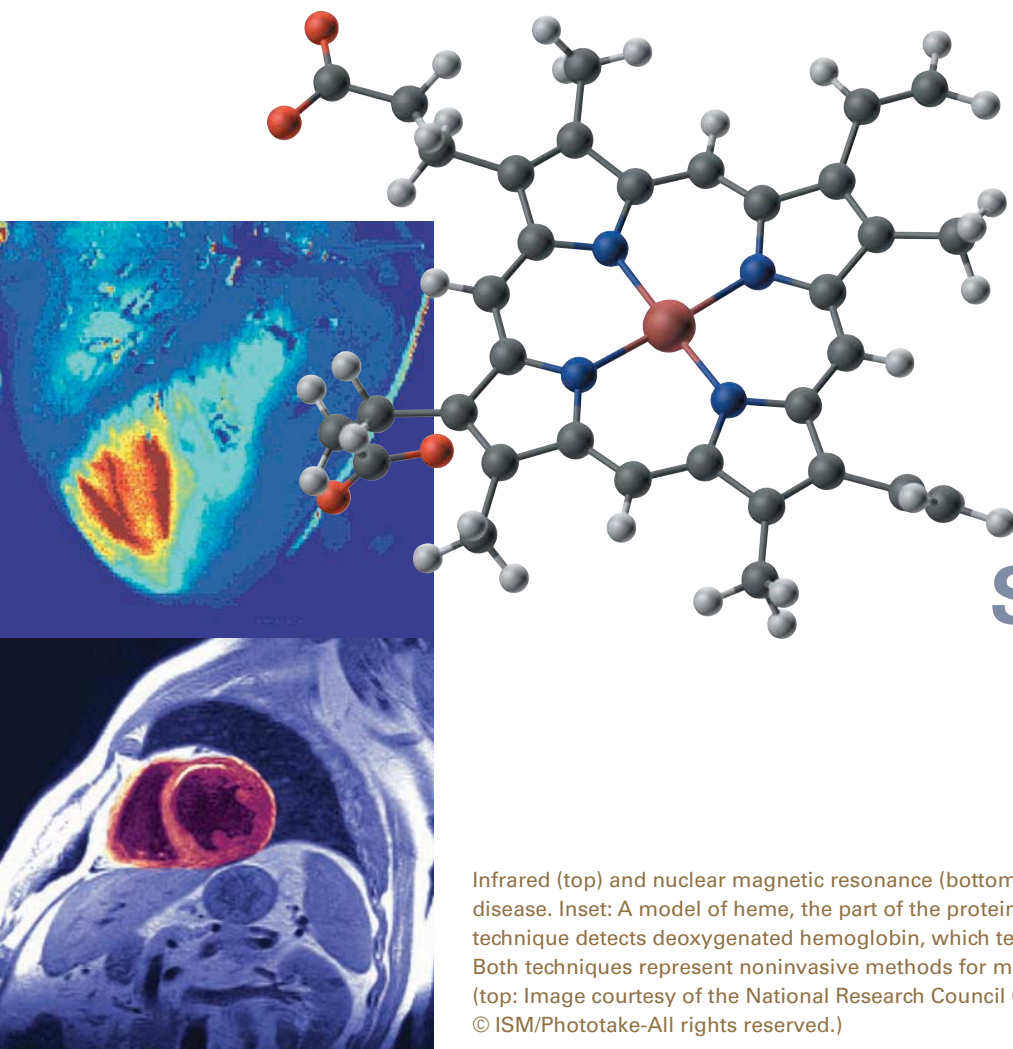


11



Spectroscopy

Infrared (top) and nuclear magnetic resonance (bottom) image of heart with CAD, coronary artery disease. Inset: A model of heme, the part of the protein hemoglobin that binds oxygen. The infrared technique detects deoxygenated hemoglobin, which tends to occur in high levels in blocked arteries. Both techniques represent noninvasive methods for medical imaging of the body. (top: Image courtesy of the National Research Council Canada; bottom: © Sovereign, © ISM/Phototake-All rights reserved.)

KEY QUESTIONS

- 11.1 What Is Electromagnetic Radiation?
- 11.2 What Is Molecular Spectroscopy?
- 11.3 What Is Infrared Spectroscopy?
- 11.4 How Do We Interpret Infrared Spectra?
- 11.5 What Is Nuclear Magnetic Resonance?
- 11.6 What Is Shielding?
- 11.7 What Is an NMR Spectrum?
- 11.8 How Many Resonance Signals Will a Compound Yield in Its NMR Spectrum?
- 11.9 What Is Signal Integration?
- 11.10 What Is Chemical Shift?
- 11.11 What Is Signal Splitting?

- 11.12 What Is ^{13}C -NMR Spectroscopy, and How Does It Differ from ^1H -NMR Spectroscopy?
- 11.13 How Do We Solve an NMR Problem?

HOW TO

- 11.1 How to Approach Infrared Spectroscopy Structure Determination Problems
- 11.2 How to Determine Whether an Atomic Nucleus Has a Spin (Behaves as If It Were a Tiny Bar Magnet)

CHEMICAL CONNECTIONS

- 11A Infrared Spectroscopy: A Window on Brain Activity
- 11B Magnetic Resonance Imaging

DETERMINING THE MOLECULAR structure of a compound is a central theme in science. In medicine, for example, the structure of any drug must be known before the drug can be approved for use in patients. In the biotechnology and pharmaceutical industries, knowledge of a compound's structure can provide new leads to promising therapeutics. In organic chemistry,

knowledge of the structure of a compound is essential to its use as a reagent or a precursor to other molecules.

Chemists rely almost exclusively on instrumental methods of analysis for structure determination. We begin this chapter with a treatment of infrared (IR) spectroscopy, followed by a treatment of nuclear magnetic resonance (NMR) spectroscopy. These two commonly used techniques involve the interaction of molecules with electromagnetic radiation. Thus, in order to understand the fundamentals of spectroscopy, we must first review some of the fundamentals of electromagnetic radiation.

11.1 What Is Electromagnetic Radiation?

Electromagnetic radiation

Light and other forms of radiant energy.

Wavelength (λ) The distance between two consecutive identical points on a wave.

Frequency (ν) A number of full cycles of a wave that pass a point in a second.

Hertz (Hz) The unit in which wave frequency is reported; s^{-1} (read *per second*).

Gamma rays, X rays, ultraviolet light, visible light, infrared radiation, microwaves, and radio waves are all part of the electromagnetic spectrum. Because **electromagnetic radiation** behaves as a wave traveling at the speed of light, it is described in terms of its wavelength and frequency. Table 11.1 summarizes the wavelengths, frequencies, and energies of some regions of the electromagnetic spectrum.

Wavelength is the distance between any two consecutive identical points on the wave. Wavelength is given the symbol λ (Greek lowercase lambda) and is usually expressed in the SI base unit of meters. Other derived units commonly used to express wavelength are given in Table 11.2.

The **frequency** of a wave is the number of full cycles of the wave that pass a given point in a second. Frequency is given the symbol ν (Greek nu) and is reported in **hertz** (Hz), which has the unit of reciprocal seconds (s^{-1}). Wavelength and frequency are inversely proportional, and we can calculate one from the other from the relationship

$$\nu\lambda = c$$

TABLE 11.1 Wavelength, Frequency, and Energy Relationships of Some Regions of the Electromagnetic Spectrum

	4×10^{-7}		5×10^{-7}		6×10^{-7}		7×10^{-7}							
	Visible light			Radio waves										
	γ-rays			X rays		UV	Infrared		Microwaves	FM	AM	Long radio waves		
Wavelength (m)	3×10^{-16}	3×10^{-14}	3×10^{-12}	3×10^{-10}	3×10^{-8}	3×10^{-6}	3×10^{-4}	3×10^{-2}	3	3×10^2	3×10^4	3×10^6	3×10^8	
Frequency (Hz)	10^{24}	10^{22}	10^{20}	10^{18}	10^{16}	10^{14}	10^{12}	10^{10}	10^8	10^6	10^4	10^2	10	
Energy (kJ/mol)	4×10^{11}	4×10^9	4×10^7	4×10^5	4×10^3	4×10^1	4×10^{-1}	4×10^{-3}	4×10^{-5}	4×10^{-7}	4×10^{-9}	4×10^{-11}	4×10^{-13}	

TABLE 11.2 Common Units Used to Express Wavelength (λ)

Unit	Relation to Meter	
meter (m)	—	
millimeter (mm)	1 mm = 10^{-3} m	
micrometer (μm)	1 μm = 10^{-6} m	
nanometer (nm)	1 nm = 10^{-9} m	
Angstrom (\AA)	1 \AA = 10^{-10} m	

where ν is frequency in hertz, c is the velocity of light (3.00×10^8 m/s), and λ is the wavelength in meters. For example, consider infrared radiation—or heat radiation, as it is also called—with wavelength 1.5×10^{-5} m. The frequency of this radiation is

$$\nu = \frac{3.0 \times 10^8 \text{ m/s}}{1.5 \times 10^{-5} \text{ m}} = 2.0 \times 10^{13} \text{ Hz}$$

An alternative way to describe electromagnetic radiation is in terms of its properties as a stream of particles. We call these particles **photons**. The energy in a mole of photons and the frequency of radiation are related by the equation

$$E = h\nu = h\frac{c}{\lambda}$$

where E is the energy in kJ/mol and h is Planck's constant, 3.99×10^{-13} kJ \cdot s \cdot mol $^{-1}$ (9.54×10^{-14} kcal \cdot s \cdot mol $^{-1}$). This equation tells us that high-energy radiation corresponds to short wavelengths, and vice versa. Thus, ultraviolet light (higher energy) has a shorter wavelength (approximately 10^{-7} m) than infrared radiation (lower energy), which has a wavelength of approximately 10^{-5} m.

EXAMPLE 11.1

Calculate the energy, in kilojoules per mole of radiation, of a wave with wavelength $2.50 \mu\text{m}$. What type of radiant energy is this? (Refer to Table 11.1.)

STRATEGY

Use the relationship $E = hc/\lambda$. Make certain that the dimensions for distance are consistent: If the dimension of wavelength is meters, then express the velocity of light in meters per second.

SOLUTION

First convert $2.50 \mu\text{m}$ to meters, using the relationship $1 \mu\text{m} = 10^{-6}$ m (Table 11.2):

$$2.50 \mu\text{m} \times \frac{10^{-6} \text{ m}}{1 \mu\text{m}} = 2.50 \times 10^{-6} \text{ m}$$

Now substitute this value into the equation $E = hc/\lambda$:

$$\begin{aligned} E &= \frac{hc}{\lambda} = 3.99 \times 10^{-13} \frac{\text{kJ}\cdot\text{s}}{\text{mol}} \times 3.00 \times 10^8 \frac{\text{m}}{\text{s}} \times \frac{1}{2.50 \times 10^{-6} \text{ m}} \\ &= 47.7 \text{ kJ/mol (11.4 kcal/mol)} \end{aligned}$$

Electromagnetic radiation with energy of 47.7 kJ/mol is radiation in the infrared region.

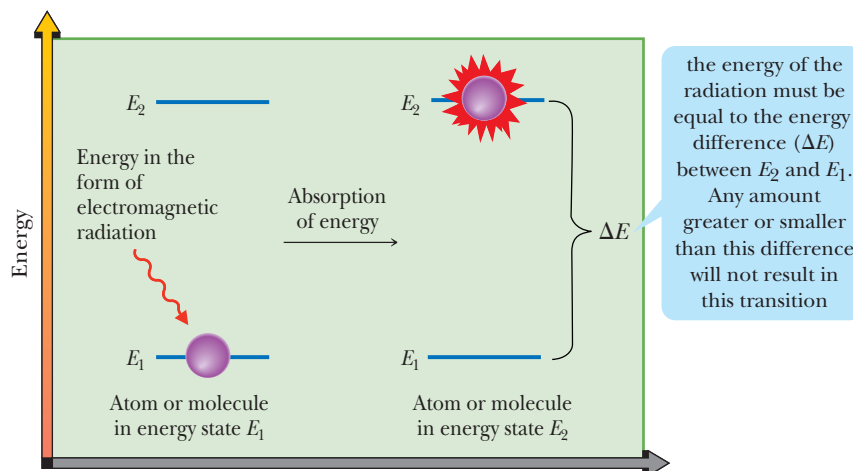
See problems 11.18–11.20

PROBLEM 11.1

Calculate the energy of red light (680 nm) in kilocalories per mole. Which form of radiation carries more energy, infrared radiation with wavelength $2.50 \mu\text{m}$ or red light with wavelength 680 nm?

FIGURE 11.1

Absorption of energy in the form of electromagnetic radiation excites an atom or a molecule in energy state E_1 to a higher energy state E_2 .



11.2 What Is Molecular Spectroscopy?

Organic molecules are flexible structures. They rotate in solution, their bonds stretch, bend, and rotate, and they contain electrons that can move from one electronic energy level to another. We know from experimental observations and from theories of molecular structure that all energy changes within a molecule are quantized; that is, they are subdivided into small, but well-defined, increments. For example, vibrations of bonds within molecules can undergo transitions only between allowed vibrational energy levels.

We can cause an atom or molecule to undergo a transition from energy state E_1 to a higher energy state E_2 by irradiating it with electromagnetic radiation corresponding to the energy difference between states E_1 and E_2 , as illustrated schematically in Figure 11.1. When the atom or molecule returns to the ground state E_1 , an equivalent amount of energy is emitted.

Molecular spectroscopy is the experimental process of measuring which frequencies of radiation a substance absorbs or emits and then correlating those frequencies with specific types of molecular structures. In **nuclear magnetic resonance (NMR) spectroscopy**, we irradiate a compound under the influence of a strong magnetic field with radio-frequency radiation, the absorption of which causes nuclei to be in a higher energy spin state. We will have more to say about NMR spectroscopy in Section 11.5. In **infrared (IR) spectroscopy**, we irradiate a compound with infrared radiation, the absorption of which causes covalent bonds to change from a lower vibrational energy level to a higher one. Because different functional groups have different bond strengths, the energy required to bring about these transitions will vary from one functional group to another. Thus, in infrared spectroscopy, we detect functional groups by the vibrations of their bonds.

11.3 What Is Infrared Spectroscopy?

A. The Vibrational Infrared Spectrum

In organic chemistry, we use a portion of the electromagnetic spectrum called the **vibrational infrared region**. This region extends from 2.5×10^{-6} to 25×10^{-6} m and corresponds to energies from 48–4.8 kJ/mol (11–1.2 kcal/mol). We commonly refer to radiation in the vibrational infrared region by its **wavenumber** ($\bar{\nu}$), the number of waves per centimeter:

$$\bar{\nu} = \frac{1}{\lambda \text{ (cm)}} = \frac{10^{-2} \text{ (m} \cdot \text{cm}^{-1}\text{)}}{\lambda \text{ (m)}}$$

Molecular spectroscopy

The study of the frequencies of electromagnetic radiation that are absorbed or emitted by substances and the correlation between these frequencies and specific types of molecular structure.

Vibrational infrared The portion of the infrared region that extends from 4000 to 400 cm^{-1} .

Wavenumber ($\bar{\nu}$) A characteristic of electromagnetic radiation equal to the number of waves per centimeter.

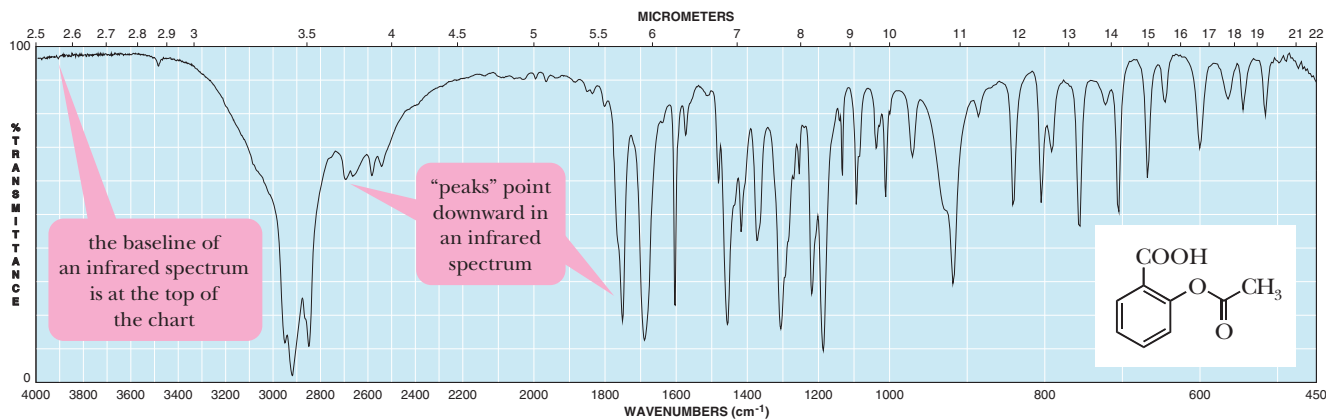


FIGURE 11.2
Infrared spectrum of aspirin.

Expressed in wavenumbers, the vibrational region of the infrared spectrum extends from 4000 to 400 cm^{-1} (the unit cm^{-1} is read “reciprocal centimeter”):

$$\bar{\nu} = \frac{10^{-2} \text{ m} \cdot \text{cm}^{-1}}{2.5 \times 10^{-6} \text{ m}} = 4000 \text{ cm}^{-1} \quad \bar{\nu} = \frac{10^{-2} \text{ m} \cdot \text{cm}^{-1}}{25 \times 10^{-6} \text{ m}} = 400 \text{ cm}^{-1}$$

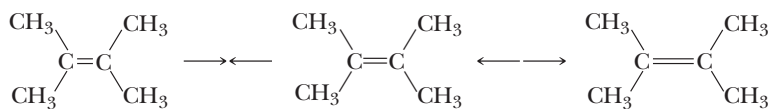
An advantage of using wavenumbers is that they are directly proportional to energy; the higher the wavenumber, the higher is the energy of radiation.

Figure 11.2 shows an infrared spectrum of aspirin. The horizontal axis at the bottom of the chart is calibrated in wavenumbers (cm^{-1}); that at the top is calibrated in wavelength (micrometers, μm). The wavenumber scale is often divided into two or more linear regions. For all spectra reproduced in this text, it is divided into three linear regions: 4000–2200 cm^{-1} , 2200–1000 cm^{-1} , and 1000–450 cm^{-1} . The vertical axis measures transmittance, with 100% transmittance at the top and 0% transmittance at the bottom. Thus, the baseline for an infrared spectrum (100% transmittance of radiation through the sample = 0% absorption) is at the top of the chart, and the absorption of radiation corresponds to a trough or valley. Strange as it may seem, we commonly refer to infrared absorptions as peaks, even though they are actually troughs.

B. Molecular Vibrations

For a molecule to absorb infrared radiation, the bond undergoing vibration must be polar, and its vibration must cause a periodic change in the bond dipole; the greater the polarity of the bond, the more intense is the absorption. Any vibration that meets this criterion is said to be **infrared active**. Covalent bonds in homonuclear diatomic molecules, such as H_2 and Br_2 , and some carbon–carbon double bonds in symmetrical alkenes and alkynes do not absorb infrared radiation because they are not polar bonds. The multiple bonds in the following two molecules, for example, do not have a dipole moment and, therefore, are not infrared active:

Neither of the unsaturated bonds in these molecules is infrared active because the vibrational motions shown do not result in a change in bond dipole (due to the symmetry about these bonds).



2,3-Dimethyl-2-butene



2-Butyne

EXAMPLE 11.2

Determine the functional group that is most likely present if IR absorption appears at

(a) 1705 cm^{-1} (b) 2200 cm^{-1}

STRATEGY

Refer to correlation Table 11.3. Eventually, through the continual practice of problems in this chapter, many of these vibrational stretching frequencies and intensities will become familiar to you.

SOLUTION

(a) A C=O group (b) a C—C triple bond

See problems 11.29–11.31

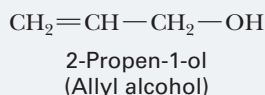
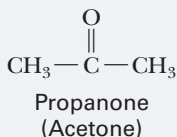
PROBLEM 11.2

A compound shows strong, very broad IR absorption in the region from 3200 to 3500 cm^{-1} and strong absorption

at 1715 cm^{-1} . What functional group accounts for both of these absorptions?

EXAMPLE 11.3

Propanone and 2-propen-1-ol are constitutional isomers. Show how to distinguish between these two isomers by IR spectroscopy.

**STRATEGY**

Because IR spectroscopy distinguishes between characteristic vibrational frequencies of differing *functional groups*, identify

the *different* functional groups in the pair of molecules and predict (using correlation tables) the vibrational frequencies that these functional groups would exhibit in an IR spectrum.

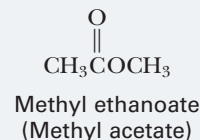
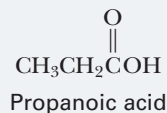
SOLUTION

Only propanone shows strong absorption in the C=O stretching region, 1630 – 1800 cm^{-1} . Alternatively, only 2-propen-1-ol shows strong absorption in the O—H stretching region, 3200 – 3500 cm^{-1} .

See problems 11.29–11.31

PROBLEM 11.3

Propanoic acid and methyl ethanoate are constitutional isomers. Show how to distinguish between these two compounds by IR spectroscopy.

**11.4 How Do We Interpret Infrared Spectra?**

Interpreting spectroscopic data is a skill that is easy to acquire through practice and exposure to examples. An IR spectrum will reveal not only the functional groups that are present in a sample, but also those that can be excluded from consideration. Often, we can determine the structure of a compound solely from the data in the spectrum of the compound and from information found in Table 11.3. Other times, we may need additional information, such as the molecular formula of the compound, or knowledge of the reactions used to synthesize the molecule. In this section, we will see specific examples of IR spectra for characteristic functional groups. Familiarizing yourself with them will help you to master the technique of spectral interpretation.

Chemical

Connections 11A

INFRARED SPECTROSCOPY: A WINDOW ON BRAIN ACTIVITY

Some of the great advantages of infrared spectroscopy are the relatively low cost, sensitivity, and speed of its instrumentation. The medical and scientific community recognized these benefits, along with the fact that some frequencies of infrared light can harmlessly penetrate human tissue and bone, in creating a technique called functional Near Infrared Spectroscopy (fNIRS). In fNIRS, a patient is fitted with headgear containing many fiber optic cables that allow infrared light in the 700–1000 nm range to be shone through the skull and into the brain. Separate fiber optic cables in the headgear collect the light that reemerges from the brain and direct it to

a spectrophotometer, which quantifies the intensity of the light. The instrument measures changes in the concentration of oxygenated and deoxygenated hemoglobin, which absorbs light in the 700–1000 nm range. Because an assortment of tasks that the brain may be asked to carry out results in varying blood flow and oxygenation levels in different parts of the brain, fNIRS can be used to determine how certain thoughts or actions affect brain activity.

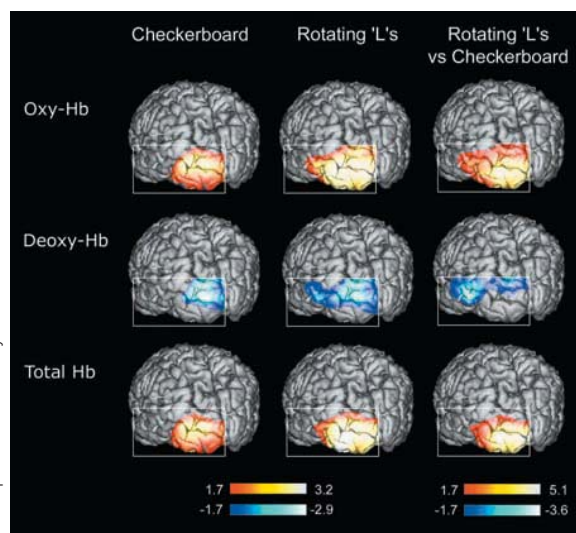
Questions

Could fNIRS be used to detect free oxygen (O_2) levels in the lungs? Why or why not?



AFP/Getty Images, Inc.

From Matthias L. Schroeter, *NeuroImage* 21: 284, Figure 2 (2004).
Photo provided courtesy of M. Schroeter.



A research subject is asked to perform several mental tasks (left) while fNIRS analysis reveals varying levels of oxy- and deoxyhemoglobin in the blood flowing through the subject's brain.

A. Alkanes, Alkenes, and Alkynes

Figure 11.4 shows an infrared spectrum of decane. The strong peak with multiple splittings between 2850 and 3000 cm^{-1} is characteristic of alkane C—H stretching. The C—H peak is strong in this spectrum because there are so many C—H bonds and no other functional groups. Because alkane CH, CH_2 , and CH_3 groups are present in many organic compounds, this peak is among the most commonly encountered in infrared spectroscopy.

Figure 11.5 shows the infrared spectrum of cyclopentene, which shows the easily recognized alkene stretching band slightly to the left of (at a greater wavenumber than) 3000 cm^{-1} . Also characteristic of alkenes is stretching at 1600 cm^{-1} . Notice that because cyclopentene has alkyl CH_2 groups, the characteristic alkane C—H stretching peak is also observed just below 3000 cm^{-1} .

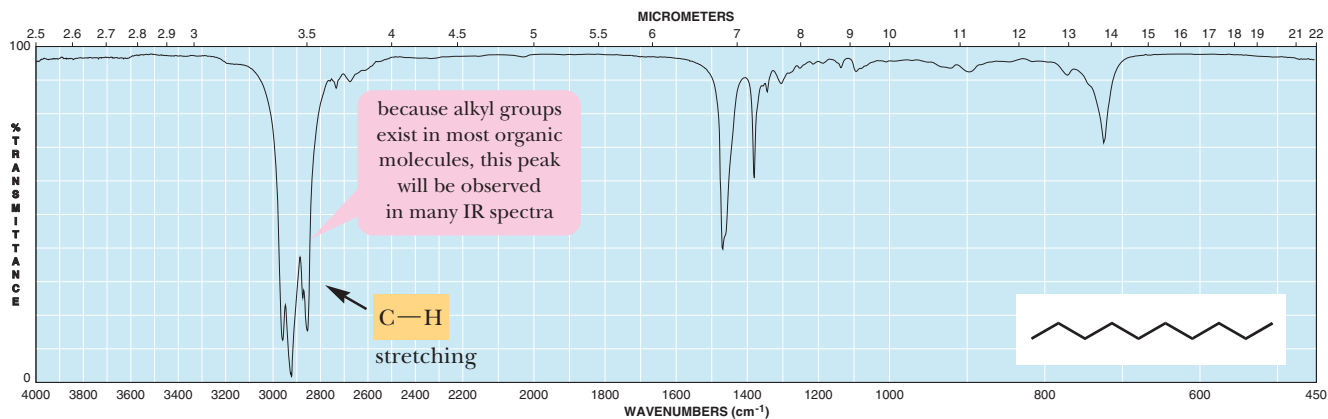


FIGURE 11.4
Infrared spectrum of decane.

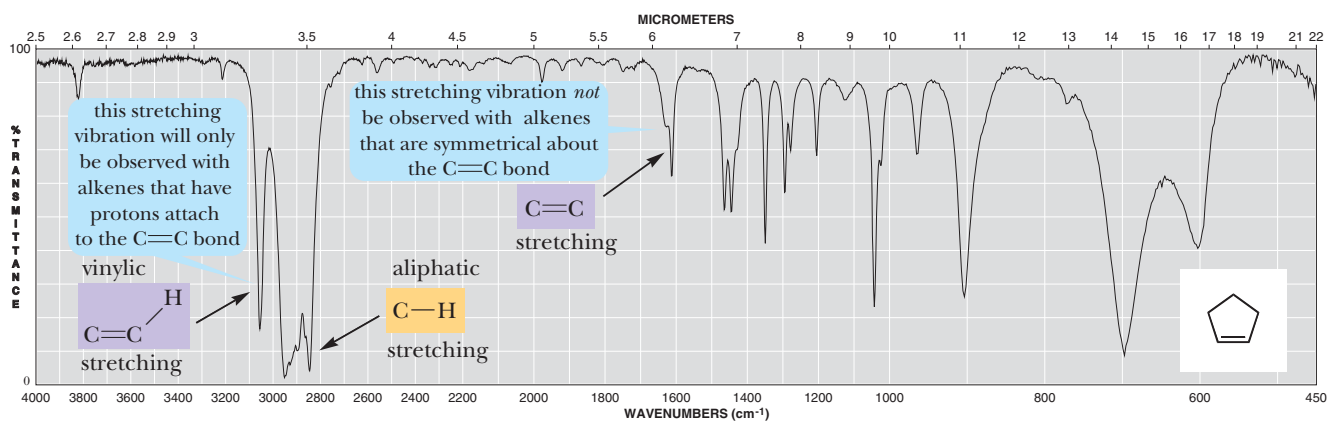


FIGURE 11.5
Infrared spectrum of cyclopentene.

Terminal alkynes exhibit $\text{C}\equiv\text{C}-\text{H}$ stretching at 3300 cm^{-1} . This absorption band is absent in internal alkynes, because the triple bond is not bonded to a proton. All alkynes absorb weakly between 2100 and 2260 cm^{-1} , due to $\text{C}\equiv\text{C}$ stretching. This stretching shows clearly in the spectrum of 1-octyne (Figure 11.6).

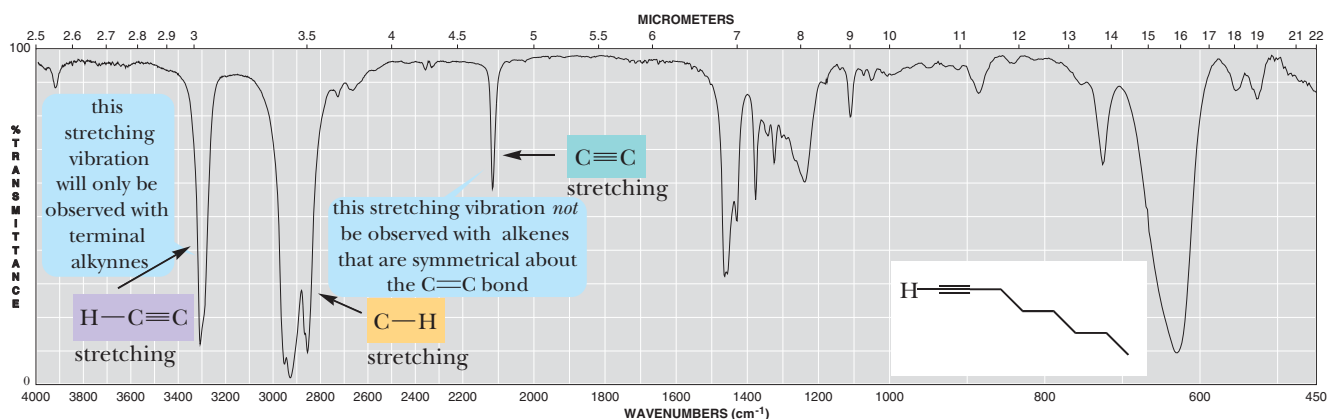


FIGURE 11.6
Infrared spectrum of 1-octyne.

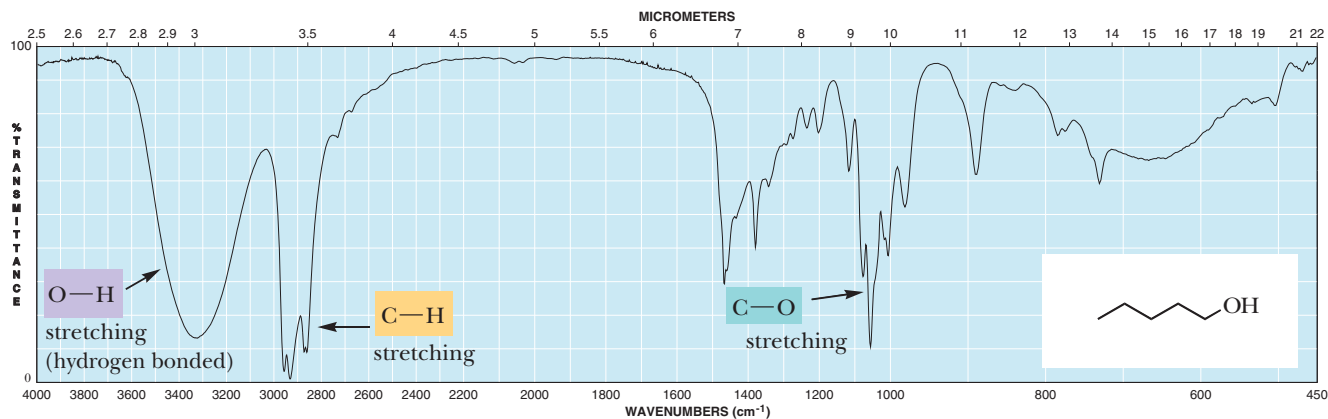


FIGURE 11.7
Infrared spectrum of 1-pentanol.

B. Alcohols

Alcohols such as 1-pentanol are easily recognized by their characteristic O—H stretching absorption (Figure 11.7). Both the position of this absorption and its intensity depend on the extent of hydrogen bonding (Section 8.1C). Under normal conditions, where there is extensive hydrogen bonding between alcohol molecules, O—H stretching occurs as a broad peak at 3200–3500 cm⁻¹. The C—O stretching vibration of alcohols appears in the range 1050–1250 cm⁻¹.

C. Ethers

The C—O stretching frequencies of ethers are similar to those observed in alcohols and esters (1070 and 1150 cm⁻¹). The presence or absence of O—H stretching at 3200–3500 cm⁻¹ for a hydrogen-bonded O—H can be used to distinguish between an ether and an alcohol. The C—O stretching vibration is also present in esters. In this case, we can use the presence or absence of C=O stretching to distinguish between an ether and an ester. Figure 11.8 shows an infrared spectrum of diethyl ether. Notice the absence of O—H stretching.

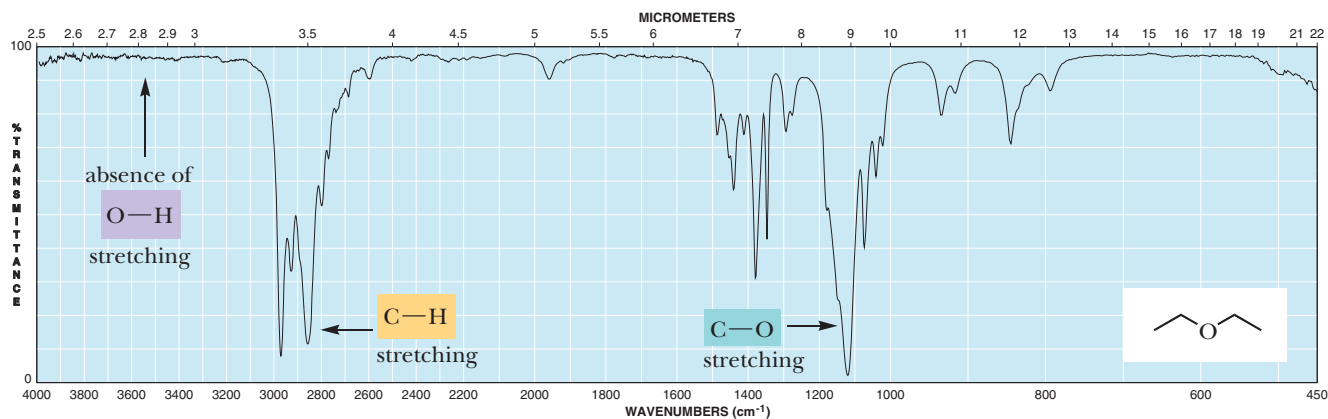


FIGURE 11.8
Infrared spectrum of diethyl ether.

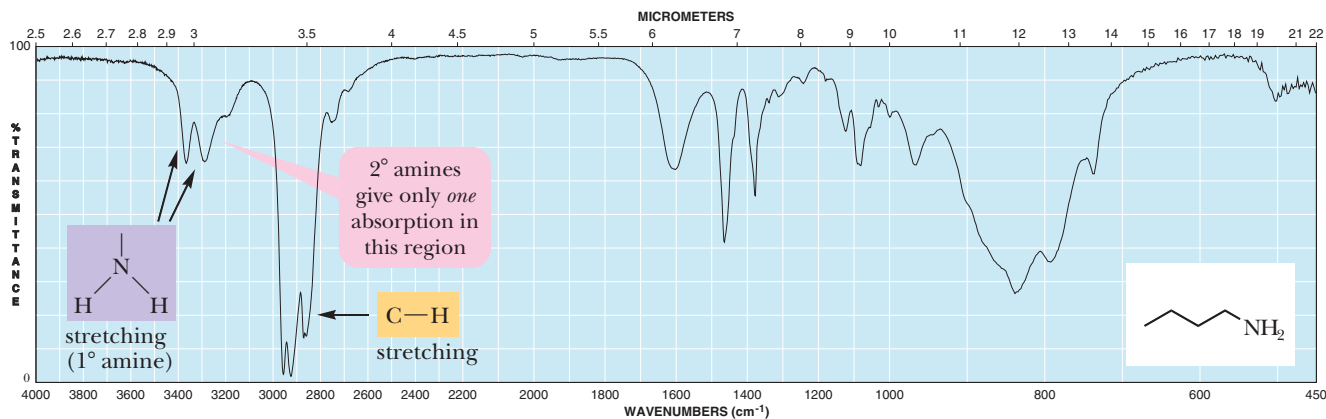


FIGURE 11.9
Infrared spectrum of butanamine, a primary amine.

D. Amines

The most important and readily observed infrared absorptions of primary and secondary amines are due to N—H stretching vibrations and appear in the region from 3100 to 3500 cm⁻¹. Primary amines have two peaks in this region, one caused by a symmetric stretching vibration and the other by asymmetric stretching. The two N—H stretching absorptions characteristic of a primary amine can be seen in the IR spectrum of butanamine (Figure 11.9). Secondary amines give only one absorption in this region. Tertiary amines have no N—H and therefore are transparent in this region of the infrared spectrum.

E. Aldehydes and Ketones

Aldehydes and ketones (Section 1.7C) show characteristic strong infrared absorption between 1705 and 1780 cm⁻¹ associated with the stretching vibration of the carbon–oxygen double bond. The stretching vibration for the carbonyl group of menthone occurs at 1705 cm⁻¹ (Figure 11.10).

Because several different functional groups contain a carbonyl group, it is often not possible to tell from absorption in this region alone whether the carbonyl-containing compound is an aldehyde, a ketone, a carboxylic acid, or an ester.

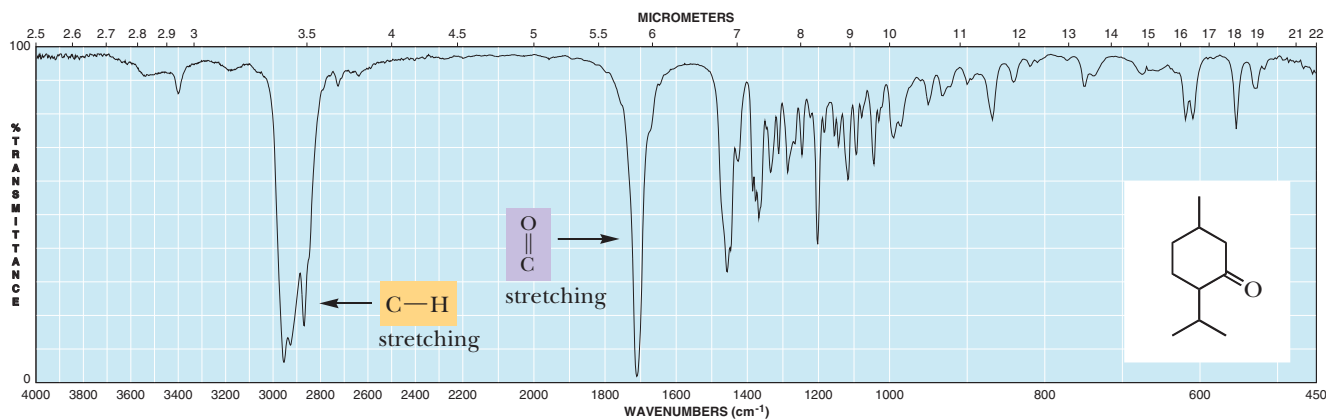


FIGURE 11.10
Infrared spectrum of menthone.

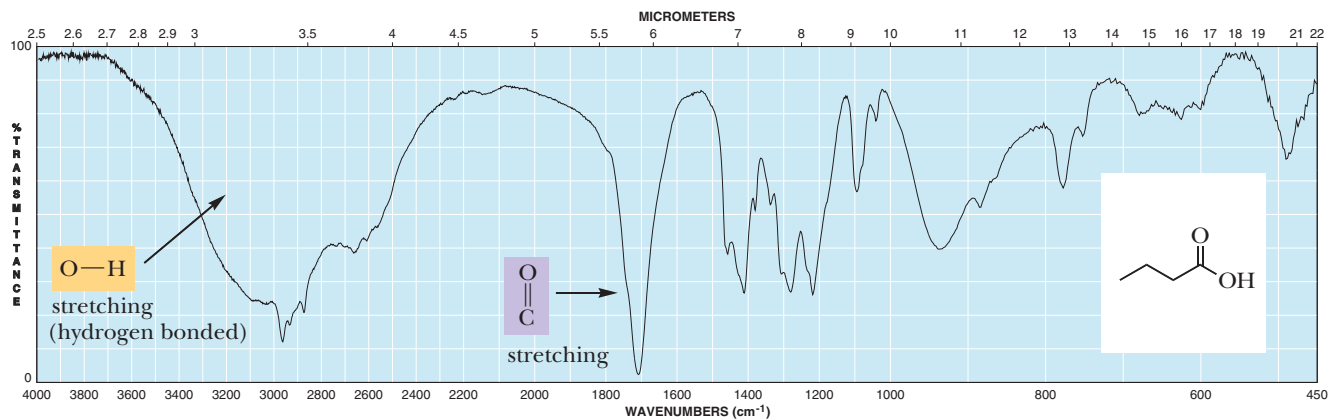


FIGURE 11.11
Infrared spectrum of butanoic acid.

F Carboxylic Acids and Their Derivatives

The carboxyl group of a carboxylic acid gives rise to two characteristic absorptions in the infrared spectrum. One of these occurs in the region from 1700 to 1725 cm^{-1} and is associated with the stretching vibration of the carbonyl group. This region is essentially the same as that for the absorption of the carbonyl groups of aldehydes and ketones. The other infrared absorption characteristic of a carboxyl group is a peak between 2400 and 3400 cm^{-1} due to the stretching vibration of the O—H group. This peak, which often overlaps the C—H stretching absorptions, is generally very broad due to hydrogen bonding between molecules of the carboxylic acid. Both C=O and O—H stretchings can be seen in the infrared spectrum of butanoic acid, shown in Figure 11.11.

Esters display strong C=O stretching absorption in the region between 1735 and 1800 cm^{-1} . In addition, they display strong C—O stretching absorption in the region from 1000 to 1250 cm^{-1} (Figure 11.12).

The carbonyl stretching of amides occurs at 1630 – 1680 cm^{-1} , a lower series of wavenumbers than for other carbonyl compounds. Primary and secondary amides show N—H stretching in the region from 3200 to 3400 cm^{-1} ; primary amides (RCONH_2) show two N—H absorptions, whereas secondary amides (RCONHR) show only a single N—H absorption. Tertiary amides, of course, do not show N—H stretching absorptions. See the three spectra in Figure 11.13.

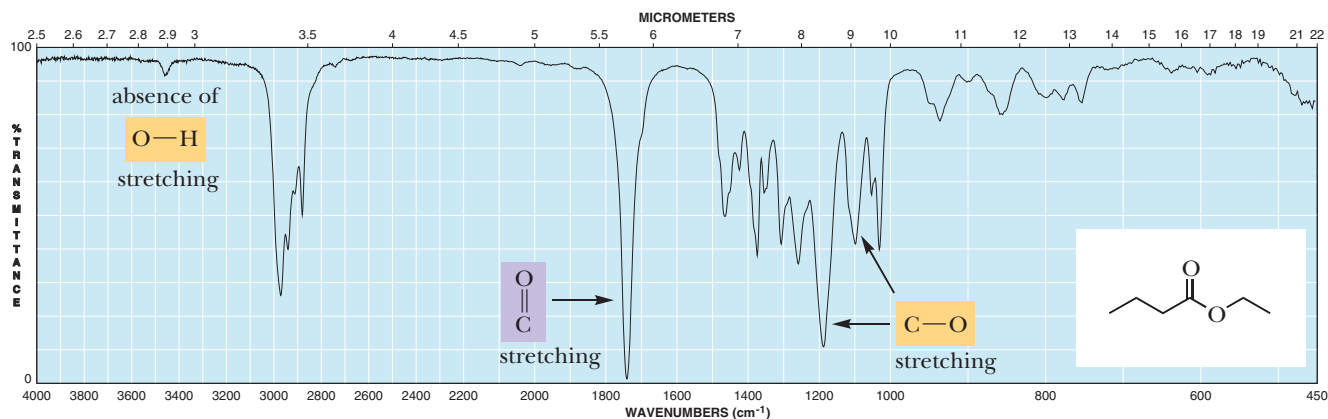
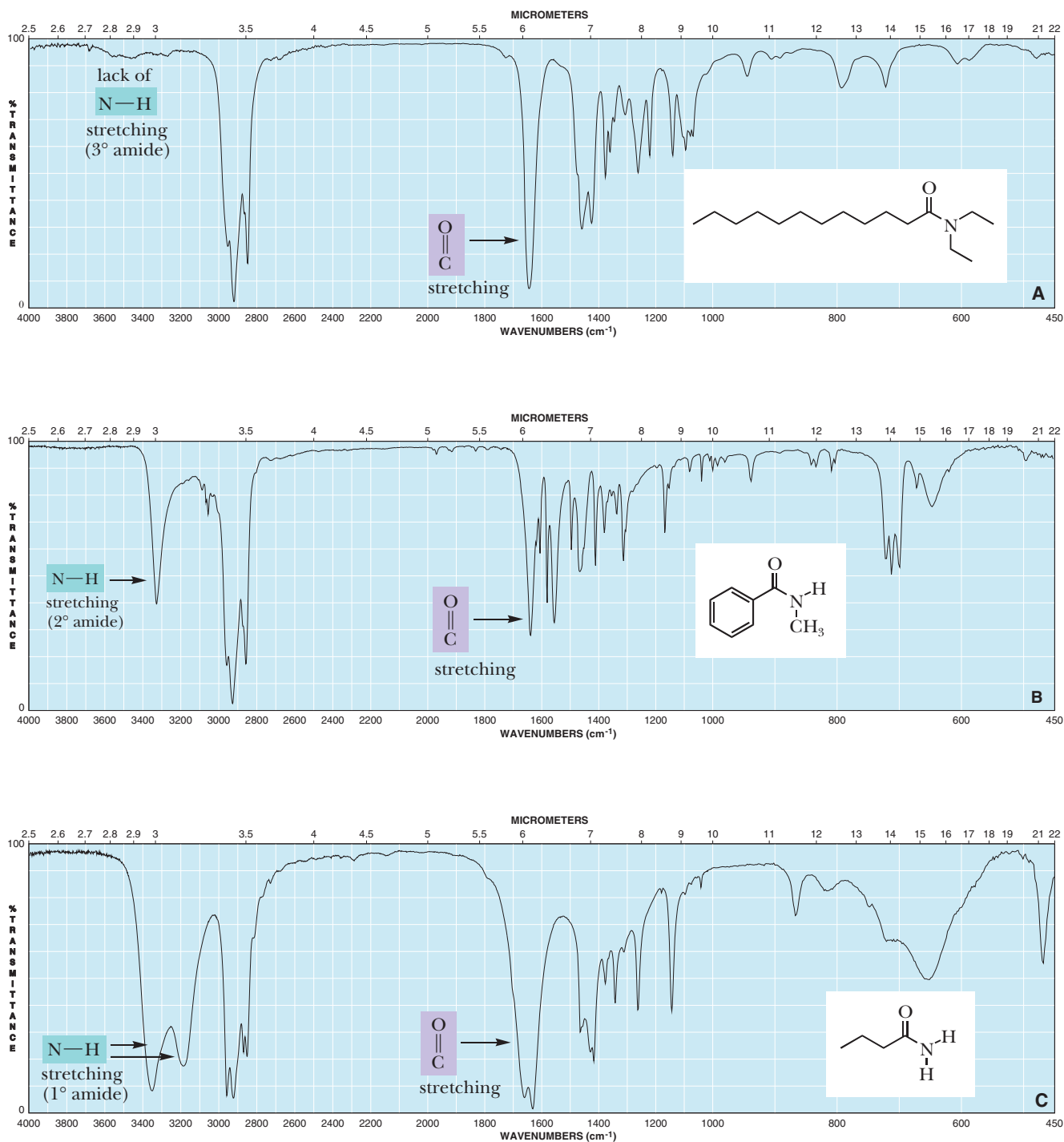


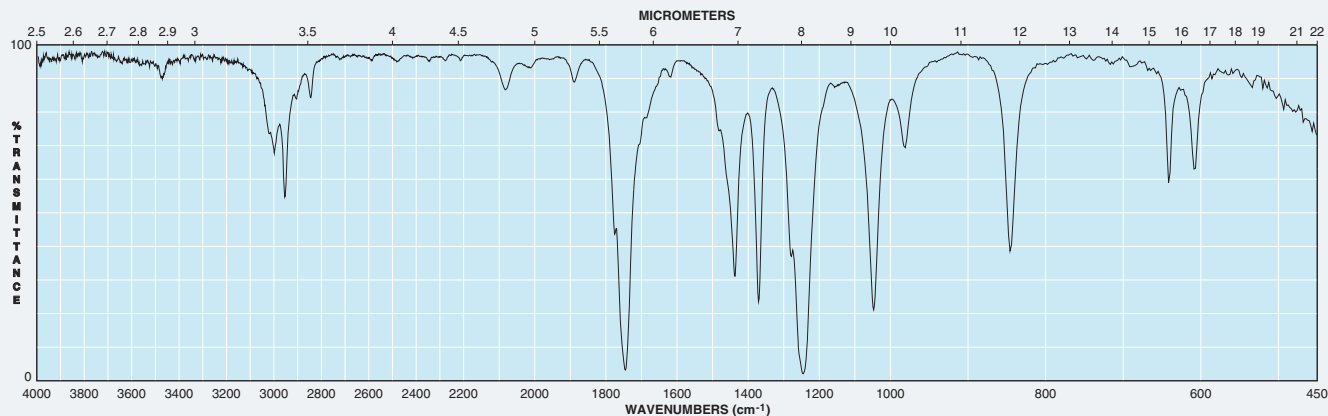
FIGURE 11.12
Infrared spectrum of ethyl butanoate.

**FIGURE 11.13**

Infrared spectra of *N,N*-diethyldodecanamide (A, a tertiary amide), *N*-methylbenzamide (B, a secondary amide), butanamide (C, a primary amide).

EXAMPLE 11.4

An unknown compound with the molecular formula $C_3H_6O_2$ yields the following IR spectrum. Draw possible structures for the unknown.

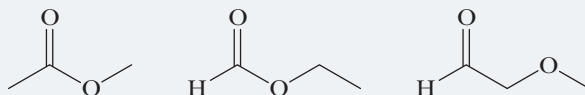


STRATEGY

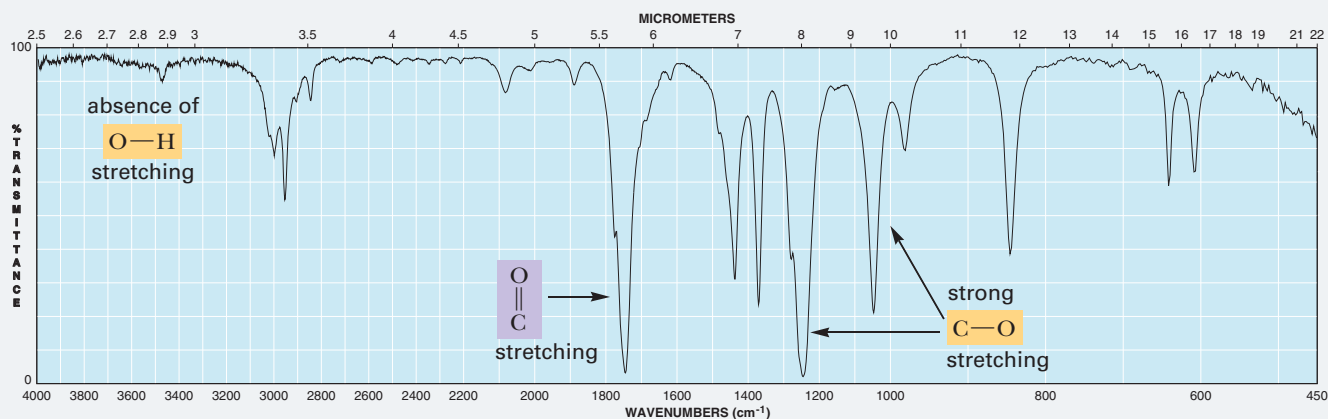
Start at 4000 cm^{-1} and move down the wavenumber scale. Make note of characteristic peaks, especially those that are unique to certain functional groups. Observe that the absence of peaks also provides clues for the types of functional groups that cannot be present. Once all the possible functional groups have been identified, propose chemical structures using these functional groups and the elements provided by the molecular formula. In Section 11.4G, we learn the concept of index of hydrogen deficiency, which can also be used in these types of problems to determine the structure of an unknown compound.

SOLUTION

The IR spectrum shows a strong absorption at approximately 1750 cm^{-1} , which is indicative of a $C=O$ group. The spectrum also shows strong $C-O$ absorption peaks at 1250 and 1050 cm^{-1} . Furthermore, there are no peaks above 3100 cm^{-1} , which eliminates the possibility of an $O-H$ group. On the basis of these data, three structures are possible for the given molecular formula:



The spectrum can now be annotated as follows:



See problems 11.22–11.28

PROBLEM 11.4

What does the value of the wavenumber of the stretching frequency for a particular functional group indicate about the relative strength of the bond in that functional group?

G. Index of Hydrogen Deficiency

We can obtain valuable information about the structural formula of an unknown compound by inspecting its molecular formula. In addition to learning the number of atoms of carbon, hydrogen, oxygen, nitrogen, and so forth in a molecule of the compound, we can determine what is called its **index of hydrogen deficiency**, which is the sum of the number of rings and pi bonds in a molecule. We determine this quantity by comparing the number of hydrogens in the molecular formula of a compound of unknown structure with the number of hydrogens in a **reference compound** with the same number of carbon atoms and with no rings or pi bonds. The molecular formula of a reference hydrocarbon is C_nH_{2n+2} (Section 3.1).

Index of hydrogen deficiency The sum of the number of rings and pi bonds in a molecule.

$$\text{Index of hydrogen deficiency} = \frac{(H_{\text{reference}} - H_{\text{molecule}})}{2}$$

EXAMPLE 11.5

Calculate the index of hydrogen deficiency for 1-hexene, with the molecular formula C_6H_{12} , and account for this deficiency by reference to the structural formula of the compound.

STRATEGY

Determine the number of hydrogens in the reference compound; then use the formula

$$\text{Index of hydrogen deficiency} = \frac{(H_{\text{reference}} - H_{\text{molecule}})}{2}$$

SOLUTION

The molecular formula of the reference hydrocarbon with six carbon atoms is C_6H_{14} . The index of hydrogen deficiency of 1-hexene is $(14 - 12)/2 = 1$ and is accounted for by the one pi bond in 1-hexene.

See problems 11.21–11.28

PROBLEM 11.5

Calculate the index of hydrogen deficiency of cyclohexene, C_6H_{10} , and account for this deficiency by reference to the structural formula of the compound.

To determine the molecular formula of a reference compound containing elements besides carbon and hydrogen, write the formula of the reference hydrocarbon, add to it other elements contained in the unknown compound, and make the following adjustments to the number of hydrogen atoms:

1. For each atom of a monovalent Group 7 element (F, Cl, Br, I) added to the reference hydrocarbon, subtract one hydrogen; halogen substitutes for hydrogen and reduces the number of hydrogens by one per halogen. The general formula of an acyclic monochloroalkane, for example, is $C_nH_{2n+1}Cl$.
2. No correction is necessary for the addition of atoms of Group 6 elements (O, S, Se) to the reference hydrocarbon. Inserting a divalent Group 6 element into a reference hydrocarbon does not change the number of hydrogens.
3. For each atom of a trivalent Group 5 element (N and P) added to the formula of the reference hydrocarbon, add one hydrogen. Inserting a trivalent Group 5 element adds one hydrogen to the molecular formula of the reference compound. The general molecular formula for an acyclic alkylamine, for example, is $C_nH_{2n+3}N$.

EXAMPLE 11.6

Isopentyl acetate, a compound with a bananalike odor, is a component of the alarm pheromone of honeybees. The molecular formula of isopentyl acetate is $C_7H_{14}O_2$. Calculate the index of hydrogen deficiency of this compound.

STRATEGY

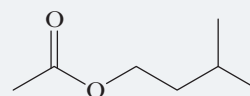
Determine the number of hydrogens in the reference compound and then use the formula

$$\text{Index of hydrogen deficiency} = \frac{(H_{\text{reference}} - H_{\text{molecule}})}{2}$$

SOLUTION

The molecular formula of the reference hydrocarbon is C_7H_{16} . Adding oxygens to this formula does not require any

correction in the number of hydrogens. The molecular formula of the reference compound is $C_7H_{16}O_2$, and the index of hydrogen deficiency is $(16 - 14)/2 = 1$, indicating either one ring or one pi bond. Following is the structural formula of isopentyl acetate, which contains one pi bond, in this case in the carbon–oxygen double bond:

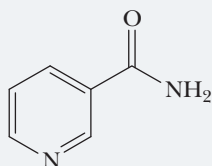


Isopentyl acetate

See problems 11.21–11.28

PROBLEM 11.6

The index of hydrogen deficiency of niacin is 5. Account for this value by reference to the structural formula of niacin.

Nicotinamide
(Niacin)**Approach Infrared Spectroscopy Structure Determination Problems****HOW TO 11.1**

It is useful to develop a systematic approach to problems that ask you to determine a structure given a molecular formula and an infrared spectrum. Following are some guidelines for tackling such problems.

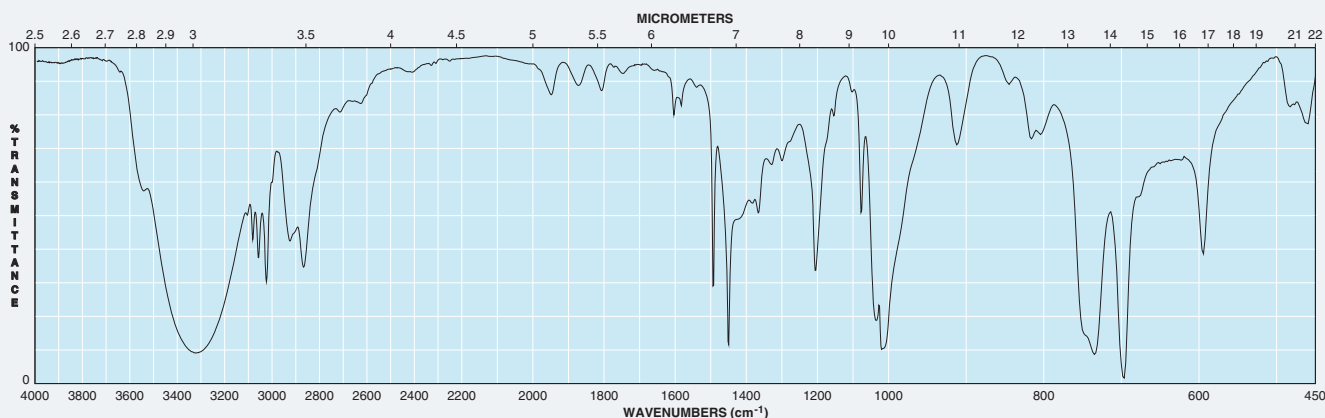
- Determine the index of hydrogen deficiency (IHD).** Knowing the potential number of rings, double bonds, or triple bonds in an unknown compound is of great assistance in solving the structure. For example, if $IHD = 1$, you know that the unknown can have either a ring or a double bond, but not both. It also cannot have a triple bond because that would require an $IHD = 2$.
- Move from left to right to identify functional groups in the IR spectrum.** Because the types of transitions in an IR spectrum become less specific as absorptions approach and go lower than 1000 cm^{-1} , it is most useful to start on the left

side of an IR spectrum. The shorter the bond, the higher in wavenumber its absorption. This is why $O-H$, $N-H$, and $C-H$ bond vibrations occur above 3900 cm^{-1} . Proceeding to the right, we then encounter $C-C$ triple bond stretching vibrations. $C=O$ bonds are shorter than $C=C$ bonds and therefore occur at higher wavenumbers ($1800\text{--}1650\text{ cm}^{-1}$) than $C=C$ bonds ($1680\text{--}1600\text{ cm}^{-1}$).

- Draw possible structures and verify your structures with the data.** Do not try to think of the answer entirely in your mind. Rather, jot down some structures on paper. Once you have one or more possible structures, verify that these possibilities work with the IHD value and the functional groups indicated by the IR spectrum. Usually, incorrect structures will obviously conflict with one or more of these data items.

EXAMPLE 11.7

Determine possible structures for a compound that yields the following IR spectrum and has a molecular formula of C_7H_8O :

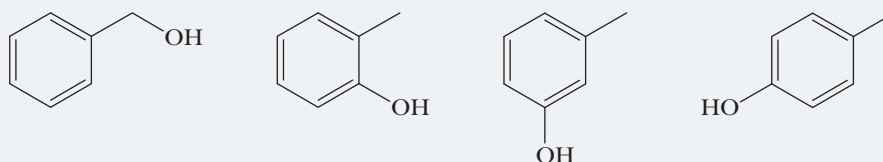


STRATEGY

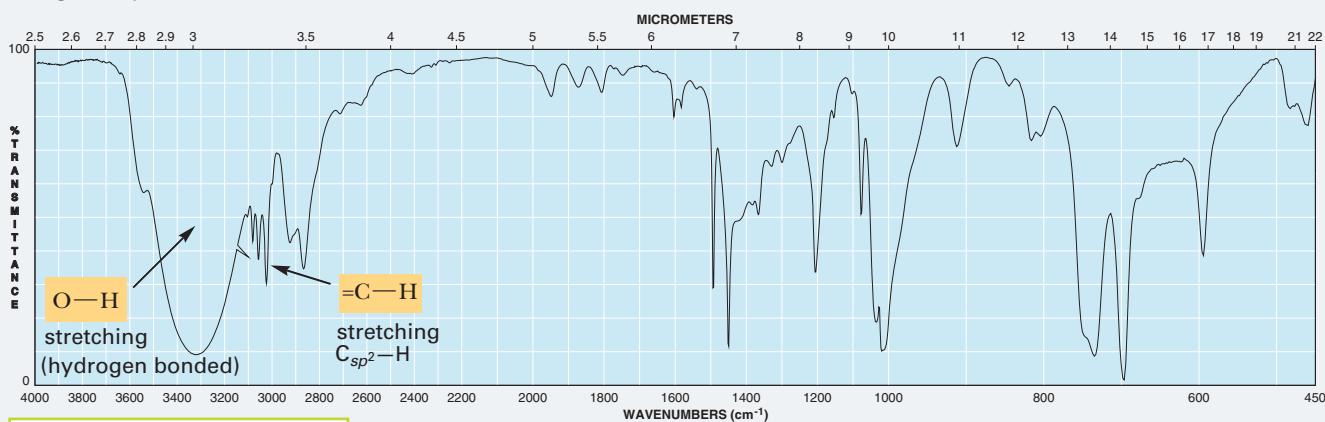
Determine the index of hydrogen deficiency and use this value as a guide to the combination of rings, double bonds, or triple bonds possible in the unknown. Analyze the IR spectrum, starting at 4000 cm^{-1} and moving down the wavenumber scale. Make note of characteristic peaks, especially those that are unique to certain functional groups. Note that the absence of peaks also provides clues for the types of functional groups that cannot be present. Once all the possible functional groups have been identified, propose chemical structures using these functional groups and the elements provided by the molecular formula.

SOLUTION

The index of hydrogen deficiency for C_7H_8O is 4, based on the reference formula C_7H_{16} . We can exclude $C-C$ triple bonds because of the absence of a peak from the triple bond $C-C$ stretch ($2100\text{--}2260\text{ cm}^{-1}$) and the absence of a terminal alkyne $C-H$ stretch (3300 cm^{-1}). We see $C-H$ stretching peaks just above 3000 cm^{-1} . However, we don't see $C=C$ double bond stretching between 1600 and 1680 cm^{-1} . Recall that aromatic hydrocarbons do not exhibit the same chemical properties as alkenes, so an arene ring remains a possibility. Benzene, with 3 double bonds and a ring, would have an index of hydrogen deficiency of 4 (this is a common functional group to keep in mind whenever we encounter an IHD of 4 or more). By considering a benzene ring as a possibility, the remaining structural possibilities are limited. Because there is no strong absorption between 1630 and 1800 cm^{-1} , a carbonyl group ($C=O$) can be excluded. The last piece of evidence is the strong, broad $O-H$ stretching peak at approximately 3310 cm^{-1} . Because we must have an OH group, we cannot propose any structures with an OCH_3 (ether) group. Based on this interpretation of the spectrum, the following four structures are possible:



The given spectrum can now be annotated as follows:



See problems 11.22–11.28

PROBLEM 11.7

Determine possible structures for the same spectrum (above) for a compound with molecular formula $C_8H_{10}O$. What does example 11.7 and this problem tell you about the effectiveness of IR spectroscopy for determining the structure of an unknown compound?

The preceding example illustrates the power and limitations of IR spectroscopy. The power lies in its ability to provide us with information regarding the functional groups in a molecule. IR spectroscopy does not, however, provide us with information on how those functional groups are connected. Fortunately, another type of spectroscopy—nuclear magnetic resonance (NMR) spectroscopy—does provide us with connectivity information.

11.5 What Is Nuclear Magnetic Resonance?

The phenomenon of nuclear magnetic resonance was first detected in 1946 by U.S. scientists Felix Bloch and Edward Purcell, who shared the 1952 Nobel Prize for Physics for their discoveries. The particular value of nuclear magnetic resonance (NMR) spectroscopy is that it gives us information about the number and types of atoms in a molecule, for example, about the number and types of hydrogens using $^1\text{H-NMR}$ spectroscopy, and about the number and types of carbons using $^{13}\text{C-NMR}$ spectroscopy.

From your study of general chemistry, you may already be familiar with the concept that an electron has a **spin** and that a spinning charge creates an associated magnetic field. In effect, an electron behaves as if it is a tiny bar magnet. An atomic nucleus that has an odd mass or an odd atomic number also has a spin and behaves as if it is a tiny bar magnet. Recall that when designating isotopes, a superscript represents the mass of the element.

Determine Whether an Atomic Nucleus Has a Spin (Behaves as If It Were a Tiny Bar Magnet)**HOW TO 11.2**

Determine the mass and atomic number of the atom. If *either* is an odd number, the atom will have a spin and behave as a tiny bar magnet.

atomic mass (may vary for isotopes of the same element)

m
Atom
n

atomic number (always the same for all isotopes of any element)

EXAMPLE 11.8

Which of the following nuclei are capable of behaving like tiny bar magnets?

- (a) $^{14}_6\text{C}$ (b) $^{14}_7\text{N}$

STRATEGY

Any nucleus that has a spin (those that have either an odd mass or an odd atomic number) will act as a tiny bar magnet.

SOLUTION

- (a) $^{14}_6\text{C}$, a radioactive isotope of carbon, has neither an odd mass number nor an odd atomic number and therefore cannot behave as if it were a tiny bar magnet.
- (b) $^{14}_7\text{N}$, the most common naturally occurring isotope of nitrogen (99.63% of all nitrogen atoms), has an odd atomic number and therefore behaves as if it were a tiny bar magnet.

PROBLEM 11.8

Which of the following nuclei are capable of behaving like tiny bar magnets?

- (a) $^{31}_{15}\text{P}$ (b) $^{195}_{78}\text{Pt}$

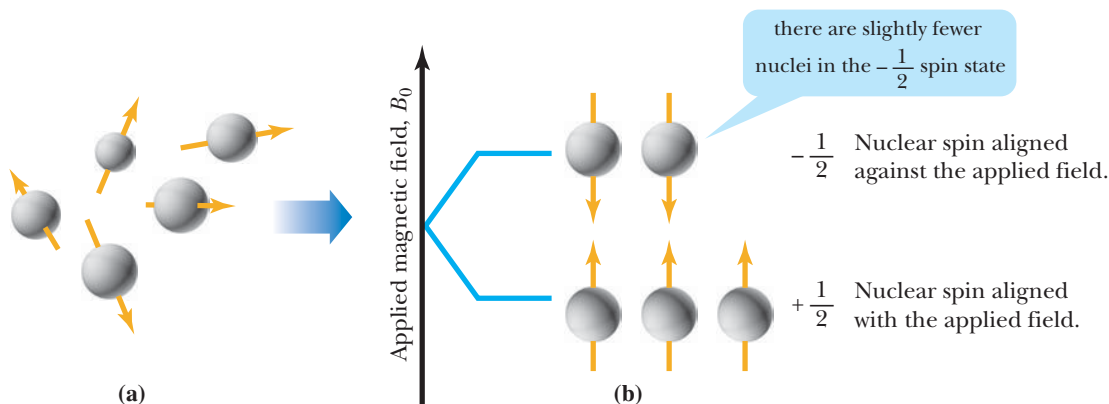


FIGURE 11.14

^1H and ^{13}C nuclei (a) in the absence of an applied magnetic field and (b) in the presence of an applied field. ^1H and ^{13}C nuclei with spin $+\frac{1}{2}$ are aligned with the applied magnetic field and are in the lower spin energy state; those with spin $-\frac{1}{2}$ are aligned against the applied magnetic field and are in the higher spin energy state.

Within a collection of ^1H and ^{13}C atoms, the spins of their tiny nuclear bar magnets are completely random in orientation. When we place them between the poles of a powerful magnet, however, interactions between their nuclear spins and the **applied magnetic field** are quantized, and only two orientations are allowed (Figure 11.14).

The difference in energy between these nuclear spin states for ^1H is 0.120 J/mol (0.0286 cal/mol), which corresponds to electromagnetic radiation of approximately 300 MHz (300,000,000 Hz). The difference in energy for the two spin states of ^{13}C is 0.035 J/mol (0.0072 cal/mol). Both of these values fall within the radio-frequency range of the electromagnetic spectrum, and irradiation of the nuclei in the lower energy spin state with radio-frequency radiation of the appropriate energy causes them to absorb energy and results in their nuclear spins flipping from the lower energy state to the higher energy state, as illustrated in Figure 11.15. In this context, **resonance** is defined as the absorption of electromagnetic radiation by a spinning nucleus and the resulting flip of its nuclear spin state. The instrument we use to detect this absorption and resulting flip of nuclear spin state records it as a **resonance signal**.

Resonance The absorption of electromagnetic radiation by a spinning nucleus and the resulting “flip” of its spin from a lower energy state to a higher energy state.

Resonance signal A recording of nuclear magnetic resonance in an NMR spectrum.

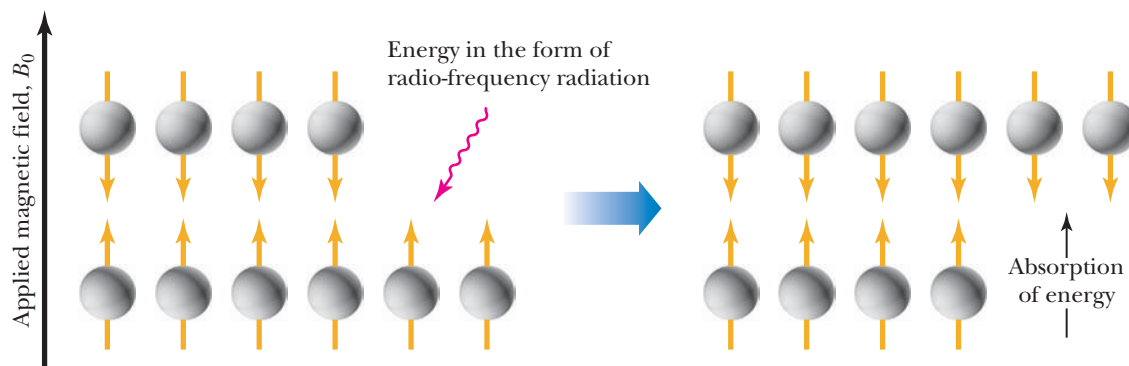


FIGURE 11.15

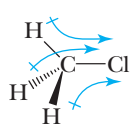
An example of resonance for nuclei of spin $\frac{1}{2}$.

11.6 What Is Shielding?

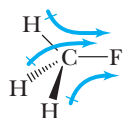
If all ^1H nuclei absorbed the same frequency of electromagnetic radiation (i.e., if they all resonated at the same frequency), all hydrogens in a compound would give rise to one and only one NMR signal, and NMR spectroscopy would be an ineffective technique for determining the structure of a molecule. Fortunately, hydrogens in most organic molecules are surrounded by electrons and by other atoms. The electrons that surround a nucleus also have spin and thereby create **local magnetic fields** that oppose the applied field. Although these local magnetic fields created by electrons are orders of magnitude weaker than the applied magnetic fields used in NMR spectroscopy, they act to shield hydrogens from the applied field. The greater the **shielding** of a particular hydrogen by local magnetic fields, the greater is the strength of the applied field necessary to bring that hydrogen into resonance.

Shielding In NMR spectroscopy, electrons around a nucleus create their own local magnetic fields and thereby shield the nucleus from the applied magnetic field.

As we learned in previous chapters, the electron density around a nucleus can be influenced by the atoms that surround the nucleus. For example, the electron density around the hydrogen atoms in fluoromethane is less than that around the hydrogen atoms in chloromethane, due to the greater electronegativity of fluorine relative to chlorine. Thus, we can say that the hydrogen atoms in chloromethane are *more shielded* than the hydrogen atoms in fluoromethane:



Chlorine is less electronegative than fluorine, resulting in a smaller inductive effect and thereby a greater electron density around each hydrogen. We say that the hydrogens in chloromethane are more **shielded** (by their local environment) than those in fluoromethane.



Fluorine's greater electronegativity produces a larger inductive effect and thereby reduces the electron density around each hydrogen. We say that these hydrogens are **deshielded**.

The differences in resonance frequencies among the various ^1H nuclei within a molecule caused by shielding are generally very small. The difference between the resonance frequencies of hydrogens in chloromethane compared with those in fluoromethane, for example, is only 360 Hz under an applied field of 7.05 tesla. Considering that the radio-frequency radiation used at this applied field is approximately 300 MHz (300×10^6 Hz), the difference in resonance frequencies between these two sets of hydrogens is only slightly greater than 1 **part per million** (1 ppm) compared with the irradiating frequency.

$$\frac{360 \text{ Hz}}{300 \times 10^6 \text{ Hz}} = \frac{1.2}{10^6} = 1.2 \text{ ppm}$$

NMR spectrometers are able to detect these small differences in resonance frequencies. The importance of shielding for elucidating the structure of a molecule will be discussed in Section 11.10.

11.7 What Is an NMR Spectrum?

Resonance of nuclei is achieved in an NMR spectrometer (Figure 11.16), which consists of a powerful magnet, a radio-frequency generator, a radio-frequency detector, and a sample chamber. Analysis of a sample produces a ^1H -NMR spectrum (Figure 11.17), which consists of a horizontal axis representing the **delta (δ) scale**, with values from 0 on the right to 10 on the left, and a vertical axis representing the intensity of the resonance signal.

It is customary to measure the resonance frequencies of individual nuclei relative to the resonance frequency of the same nuclei in a reference compound. The

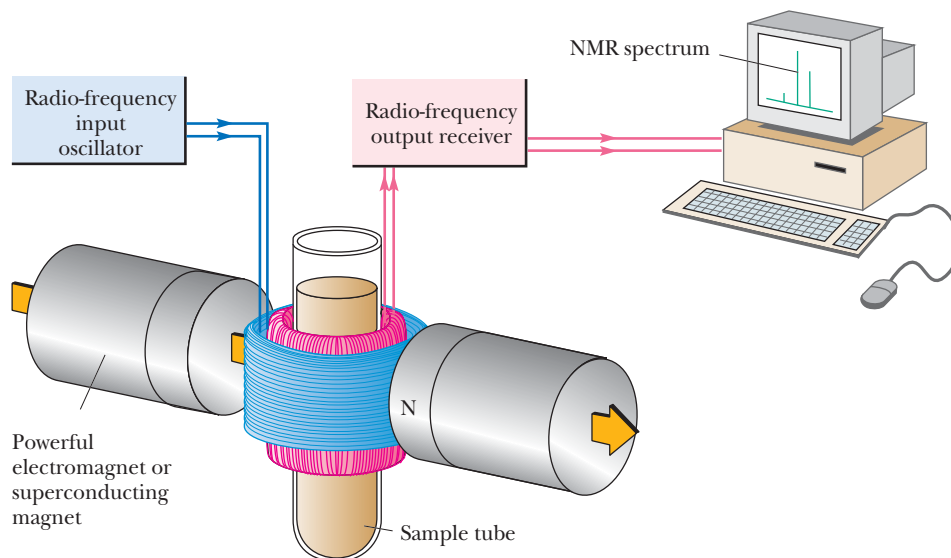
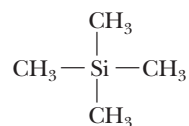


FIGURE 11.16
Schematic diagram of a nuclear magnetic resonance spectrometer.

reference compound now universally accepted for ^1H -NMR and ^{13}C -NMR spectroscopy is **tetramethylsilane (TMS)** because it is relatively unreactive and its hydrogen and carbon atoms are highly shielded due to the less electronegative silicon atom. The latter fact ensures that most other resonance signals will be less shielded than the signal for TMS.



Tetramethylsilane (TMS)

When we determine a ^1H -NMR spectrum of a compound, we report how far the resonance signals of its hydrogens are shifted from the resonance signal of the hydrogens in TMS. When we determine a ^{13}C -NMR spectrum, we report how far the resonance signals of its carbons are shifted from the resonance signal of the four carbons in TMS.

To standardize reporting of NMR data, workers have adopted a quantity called the **chemical shift** (δ). Chemical shift is calculated by dividing the shift in frequency of a signal (relative to that of TMS) by the operating frequency of the spectrometer. Because NMR spectrometers operate at MHz frequencies (i.e., millions of Hz), we express the chemical shift in parts per million. A sample calculation is provided for the signal at 2.05 ppm in the

Chemical shift, δ The position of a signal on an NMR spectrum relative to the signal of tetramethylsilane (TMS); expressed in delta (δ) units, where 1 δ equals 1 ppm.

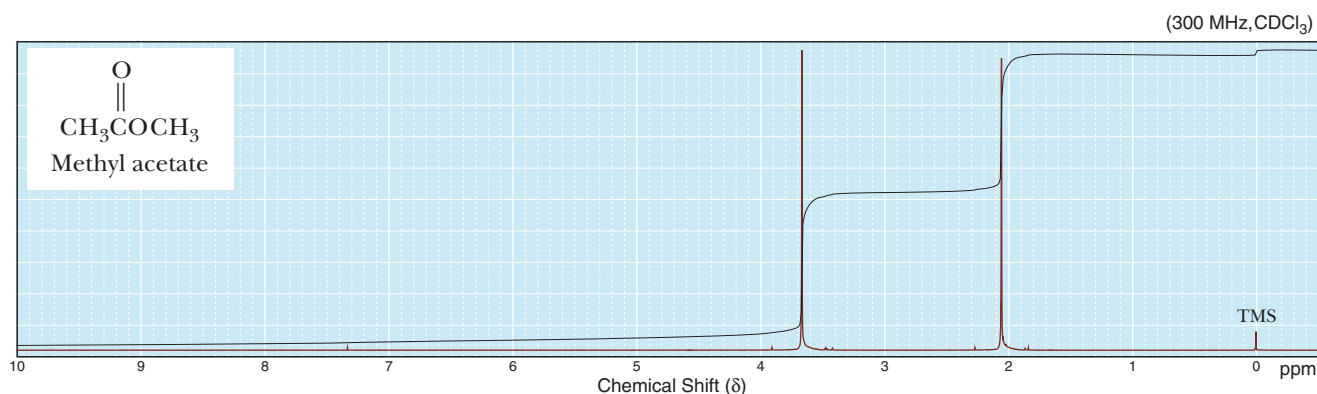


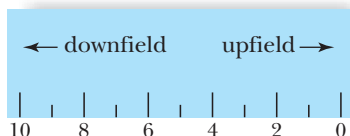
FIGURE 11.17
 ^1H -NMR spectrum of methyl acetate.

^1H -NMR spectrum for methyl acetate (Figure 11.17), a compound used in the manufacture of artificial leather.

$$\delta = \frac{\text{Shift in frequency of a signal from TMS (Hz)}}{\text{Operating frequency of the spectrometer (Hz)}}$$

the hydrogens on this methyl group cause a signal to occur 615 Hz from the TMS signal in a 300 MHz NMR spectrometer

e.g., $\text{CH}_3\text{C}(=\text{O})\text{OCH}_3$ $\frac{615 \text{ Hz}}{300 \times 10^6 \text{ Hz}} = \frac{2.05 \text{ Hz}}{\text{million Hz}} = 2.05 \text{ parts per million (ppm)}$



Downfield A term used to refer to the relative position of a signal on an NMR spectrum. Downfield indicates a peak to the left of the spectrum (a weaker applied field).

Upfield A term used to refer to the relative position of a signal on an NMR spectrum. Upfield indicates a peak to the right of the spectrum (a stronger applied field).

Equivalent hydrogens Hydrogens that have the same chemical environment.

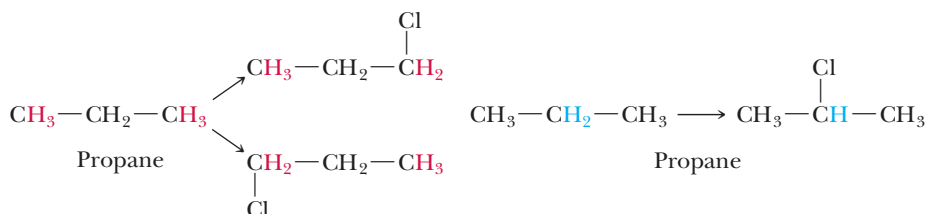
The small signal at $\delta 0$ in this spectrum represents the hydrogens of the reference compound, TMS. The remainder of the spectrum consists of two signals: one for the hydrogens of the $-\text{OCH}_3$ group and one for the hydrogens of the methyl bonded to the carbonyl group. It is not our purpose at the moment to determine why each set of hydrogens gives rise to its respective signal, but only to recognize the form in which we record an NMR spectrum and to understand the meaning of the calibration marks.

A note on terminology. If a signal is shifted toward the left on the chart paper, we say that it is shifted **downfield**, meaning that nuclei giving rise to that signal are less shielded and come into resonance at a weaker applied field. Conversely, if a signal is shifted toward the right of the spectrum, we say that it is shifted **upfield**, meaning that nuclei giving rise to that signal are more shielded and come into resonance at a stronger applied field.

11.8 How Many Resonance Signals Will a Compound Yield in Its NMR Spectrum?

Given the structural formula of a compound, how do we know how many signals to expect? The answer is that **equivalent hydrogens** give the same ^1H -NMR signal; conversely, non-equivalent hydrogens give different ^1H -NMR signals. A direct way to determine which hydrogens in a molecule are equivalent is to replace each in turn by a test atom, such as a halogen atom. Two hydrogens treated in this way are equivalent if their “substituted” versions are the same compound or if they are enantiomers of each other. If replacement gives compounds that are different and not enantiomers, the two hydrogens are nonequivalent.

Using this substitution test, we can show that propane contains two sets of equivalent hydrogens: a set of six equivalent 1° hydrogens and a set of two equivalent 2° hydrogens. Thus we would expect to see two signals, one for the six equivalent $-\text{CH}_3$ hydrogens and one for the two equivalent $-\text{CH}_2-$ hydrogens:

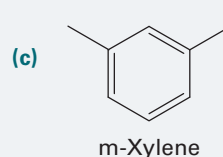
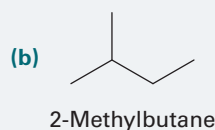
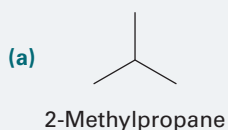


Replacement of any of the **red** hydrogens by chlorine gives 1-chloropropane; thus, all the **red** hydrogens are **equivalent**.

Replacement of either of the **blue** hydrogens by chlorine gives 2-chloropropane; thus, both of the **blue** hydrogens are **equivalent**.

EXAMPLE 11.9

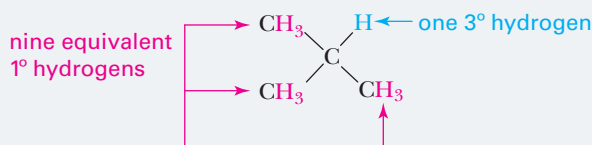
State the number of sets of equivalent hydrogens in each compound and the number of hydrogens in each set:

**STRATEGY**

A reliable way to determine whether hydrogens are equivalent is to replace each with a halogen and name the resulting compound. Hydrogens are equivalent if the two molecules containing their replacements are the same compound or are enantiomers.

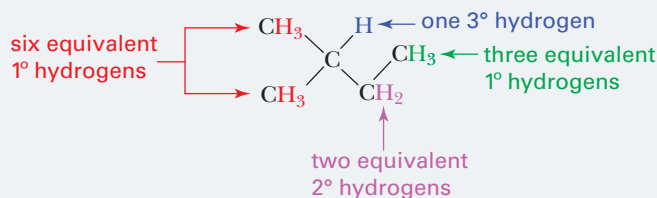
SOLUTION

(a) 2-Methylpropane contains two sets of equivalent hydrogens—a set of nine equivalent 1° hydrogens and one 3° hydrogen:



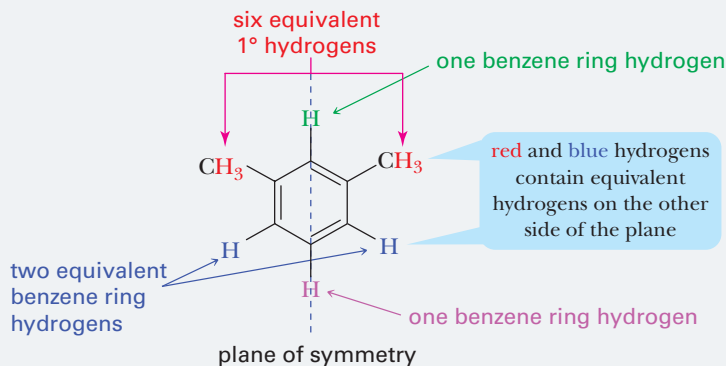
Replacing any one of the red hydrogens with a chlorine yields 1-chloro-2-methylpropane. Replacing the blue hydrogen with a chlorine yields 2-chloro-2-methylpropane.

(b) 2-Methylbutane contains four sets of equivalent hydrogens—two different sets of 1° hydrogens, one set of 2° hydrogens, and one 3° hydrogen:



Replacing any one of the red hydrogens with a chlorine yields 1-chloro-2-methylbutane. Replacing the blue hydrogen with a chlorine yields 2-chloro-2-methylbutane. Replacing a purple hydrogen with a chlorine yields 2-chloro-3-methylbutane. Replacing a green hydrogen with chlorine yields 1-chloro-3-methylbutane.

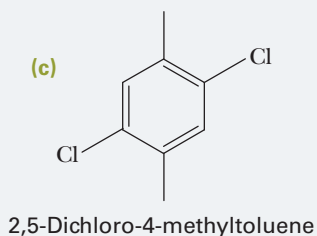
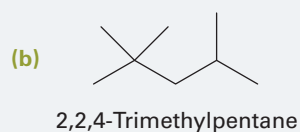
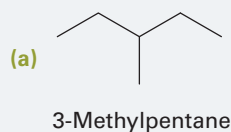
(c) *m*-Xylene contains four sets of equivalent hydrogens—one set of methyl group hydrogens, one set of hydrogens on the benzene ring *ortho* to one methyl group, one hydrogen on the benzene ring *ortho* to both methyl groups, and one hydrogen on the benzene ring *meta* to both methyl groups. In this solution, symmetry is used to illustrate equivalency.



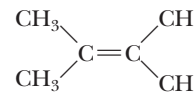
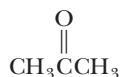
See problem 11.32

PROBLEM 11.9

State the number of sets of equivalent hydrogens in each compound and the number of hydrogens in each set:



Symmetrical compounds tend to contain a higher amount of equivalent hydrogens, and thus fewer resonance signals in their NMR spectra. Here are four symmetrical organic compounds, each of which has one set of equivalent hydrogens and gives one signal in its $^1\text{H-NMR}$ spectrum:



Propanone (Acetone)

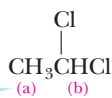
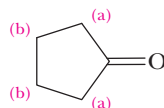
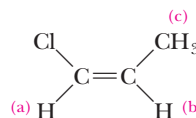
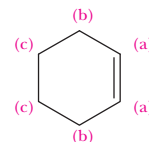
1,2-Dichloroethane

Cyclopentane

2,3-Dimethyl-2-butene

Molecules with two or more sets of equivalent hydrogens give rise to a different resonance signal for each set. 1,1-Dichloroethane, for example, has three equivalent 1° hydrogens (a) and one 2° hydrogen (b); there are two resonance signals in its $^1\text{H-NMR}$ spectrum.

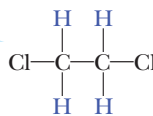
each letter represents a signal in the NMR spectrum

1,1-Dichloroethane
(2 signals)Cyclopentanone
(2 signals)(Z)-1-Chloropropene
(3 signals)Cyclohexene
(3 signals)

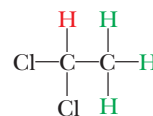
Notice how, by simply counting signals, you can distinguish between the constitutional isomers of 1,2-dichloroethane and 1,1-dichloroethane.

Isomers of $\text{C}_2\text{H}_4\text{Cl}_2$

an NMR spectrum of this isomer would show only one signal



1,2-Dichloroethane

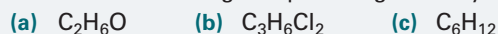


1,1-Dichloroethane

an NMR spectrum of this isomer would show two signals

EXAMPLE 11.10

Each of the following compounds gives only one signal in its $^1\text{H-NMR}$ spectrum. Propose a structural formula for each.

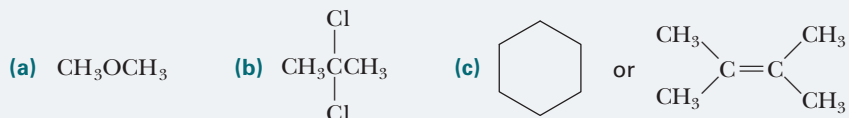


STRATEGY

Use index of hydrogen deficiency and the number of signals in an NMR spectrum to guide your choice of structure. A compound that yields fewer signals than it has hydrogen atoms indicates symmetry in the molecule.

SOLUTION

Following are structural formulas for each of the given compounds. Notice that, for each structure, the replacement of any hydrogen with a chlorine will yield the same compound regardless of the hydrogen being replaced.

**PROBLEM 11.10**

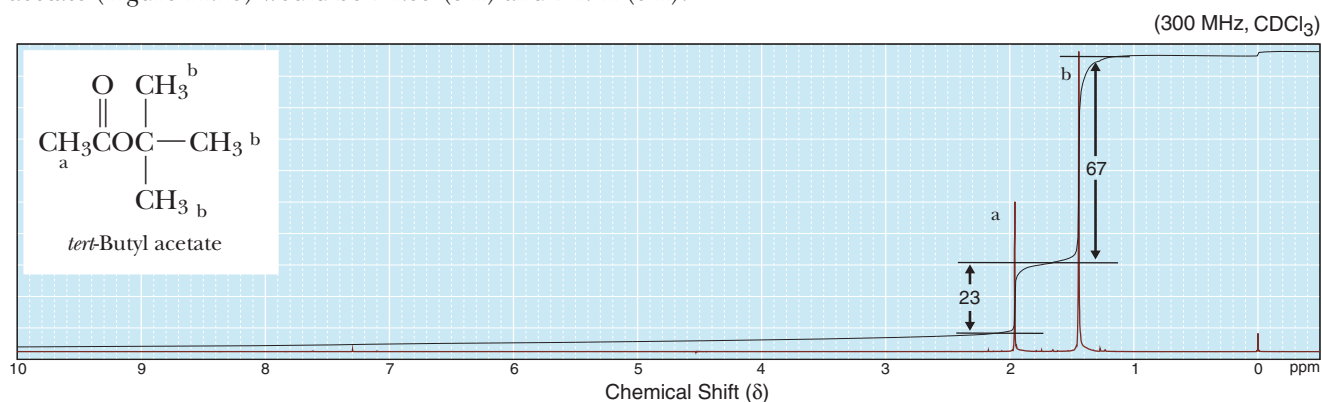
Each of the following compounds gives only one signal in its $^1\text{H-NMR}$ spectrum. Propose a structural formula for each compound.

- (a) $\text{C}_3\text{H}_6\text{O}$ (b) C_5H_{10} (c) C_5H_{12} (d) $\text{C}_4\text{H}_6\text{Cl}_4$

11.9 What Is Signal Integration?

We have just seen that the number of signals in a $^1\text{H-NMR}$ spectrum gives us information about the number of sets of equivalent hydrogens. Signal areas in a $^1\text{H-NMR}$ spectrum can be measured by a mathematical technique called *integration*. In the spectra shown in this text, this information is displayed in the form of a **line of integration** superposed on the original spectrum. The vertical rise of the line of integration over each signal is proportional to the area under that signal, which, in turn, is proportional to the number of hydrogens giving rise to the signal.

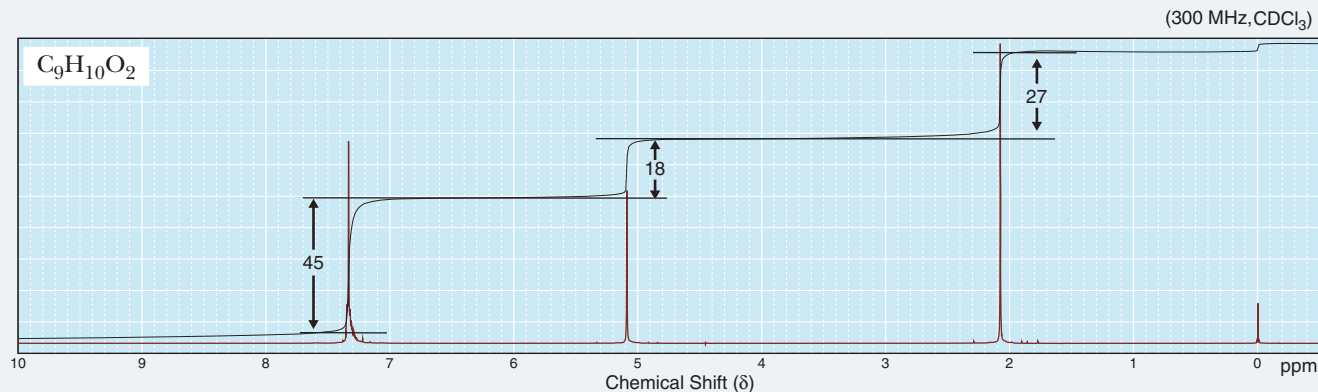
Figure 11.18 shows an integrated $^1\text{H-NMR}$ spectrum of the gasoline additive *tert*-butyl acetate ($\text{C}_6\text{H}_{12}\text{O}_2$). The spectrum shows signals at δ 1.44 and 1.95. The integrated height of the upfield (to the right) signal is nearly three times as tall as the height of the downfield (to the left) signal (the heights can be accurately determined by assuming that the distance between horizontal grid lines is 10 units). This relationship corresponds to an **integration ratio** of 3:1. We know from the molecular formula that there is a total of 12 hydrogens in the molecule. The ratios obtained from the integration lines are consistent with the presence of one set of 9 equivalent hydrogens and one set of 3 equivalent hydrogens. We will often make use of shorthand notation in referring to an NMR spectrum of a molecule. The notation lists the chemical shift of each signal, beginning with the most deshielded signal and followed by the number of hydrogens that give rise to each signal (based on the integration). The shorthand notation describing the spectrum of *tert*-butyl acetate (Figure 11.18) would be δ 1.95 (3H) and δ 1.44 (9H).

**FIGURE 11.18**

$^1\text{H-NMR}$ spectrum of *tert*-butyl acetate, $\text{C}_6\text{H}_{12}\text{O}_2$, showing a line of integration. The ratio of signal heights for the two peaks is 3:1, which, for a molecule possessing 12 hydrogens, corresponds to 9 equivalent hydrogens of one set and 3 equivalent hydrogens of another set.

EXAMPLE 11.11

Following is a $^1\text{H-NMR}$ spectrum for a compound with the molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$. From an analysis of the integration line, calculate the number of hydrogens giving rise to each signal.



STRATEGY

Once the lengths of the integration lines are determined, divide all the numbers by the lowest value to obtain a minimized ratio. For example, if the lengths of the integration lines are 4 : 12 : 8, the minimized ratio becomes $(4 : 12 : 8)/4 = 1 : 3 : 2$. The minimized ratio values can be treated as the true number of hydrogens if the sum of these numbers is equal to the number of hydrogens from the molecular formula. If the molecular formula contains a greater number of hydrogens than the sum of the ratio values, the ratio values need to be multiplied by some factor to bring their sum to that of the total number of hydrogens. For example, if the minimized ratio is 1 : 3 : 2 and the total number of hydrogens is 12, the ratio must be adjusted by a factor of 2 to be 2 : 6 : 4.

SOLUTION

The ratio of the relative signal heights (obtained from the number of horizontal chart divisions) is 5 : 2 : 3 (from downfield to upfield). The molecular formula indicates that there are 10 hydrogens. Thus, the signal at δ 7.34 represents 5 hydrogens, the signal at δ 5.08 represents 2 hydrogens, and the signal at δ 2.06 represents 3 hydrogens. Consequently, the signals and the number of hydrogens each signal represents are δ 7.34 (5H), δ 5.08 (2H), and δ 2.06 (3H).

PROBLEM 11.11

The line of integration of the two signals in the $^1\text{H-NMR}$ spectrum of a ketone with the molecular formula $\text{C}_7\text{H}_{14}\text{O}$ shows a vertical rise of 62 and 10 chart divisions. Calculate the number of hydrogens giving rise to each signal, and propose a structural formula for this ketone.

11.10 What Is Chemical Shift?

The position of a signal along the x -axis of an NMR spectrum is known as the **chemical shift** of that signal (Section 11.7). The chemical shift of a signal in a $^1\text{H-NMR}$ spectrum can give us valuable information about the type of hydrogens giving rise to that absorption. Hydrogens on methyl groups bonded to sp^3 hybridized carbons, for example, give a signal near δ 0.8–1.0 (compare Figure 11.18). Hydrogens on methyl groups bonded to a carbonyl carbon give signals near δ 2.1–2.3 (compare Figures 11.17 and 11.18), and hydrogens on methyl groups bonded to oxygen give signals near δ 3.7–3.9 (compare Figure 11.17). Table 11.4 lists the average chemical shift for most of the types of hydrogens we deal with in this text.

TABLE 11.4 Average Values of Chemical Shifts of Representative Types of Hydrogens

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
(CH ₃) ₄ Si	0 (by definition)	$\begin{array}{c} \text{O} \\ \\ \text{R} \end{array} \text{COCH}_3$	3.7–3.9
RCH ₃	0.8–1.0	$\begin{array}{c} \text{O} \\ \\ \text{R} \end{array} \text{COCH}_2\text{R}$	4.1–4.7
RCH ₂ R	1.2–1.4	RCH ₂ I	3.1–3.3
R ₃ CH	1.4–1.7	RCH ₂ Br	3.4–3.6
R ₂ C=CRCHR ₂	1.6–2.6	RCH ₂ Cl	3.6–3.8
RC≡CH	2.0–3.0	RCH ₂ F	4.4–4.5
ArCH ₃	2.2–2.5	ArOH	4.5–4.7
ArCH ₂ R	2.3–2.8	R ₂ C=CH ₂	4.6–5.0
ROH	0.5–6.0	R ₂ C=CHR	5.0–5.7
RCH ₂ OH	3.4–4.0	ArH	6.5–8.5
RCH ₂ OR	3.3–4.0	$\begin{array}{c} \text{O} \\ \\ \text{R} \end{array} \text{CH}$	9.5–10.1
R ₂ NH	0.5–5.0	$\begin{array}{c} \text{O} \\ \\ \text{R} \end{array} \text{COH}$	10–13
$\begin{array}{c} \text{O} \\ \\ \text{R} \end{array} \text{CCH}_3$	2.1–2.3		
$\begin{array}{c} \text{O} \\ \\ \text{R} \end{array} \text{CCH}_2\text{R}$	2.2–2.6		

*Values are approximate. Other atoms within the molecule may cause the signal to appear outside these ranges.

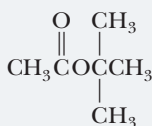
Notice that most of the values shown fall within a rather narrow range from 0 to 13 δ units (ppm). In fact, although the table shows a variety of functional groups and hydrogens bonded to them, we can use the following rules of thumb to remember the chemical shifts of most types of hydrogen:

Chemical Shift (δ)	Type of Hydrogen
0–2	H bonded to an sp^3 carbon.
2–2.8	H bonded to an sp^3 carbon that is at an allylic or benzylic position (i.e., adjacent to a C–C double bond or a benzene ring).
2–4.5	H bonded to an sp^3 carbon that is close to an electronegative element such as N, O, or X. The more electronegative the element, the higher is the chemical shift. Also, the closer the electronegative atom, the higher is the chemical shift.
4.6–5.7	H bonded to an sp^2 carbon in an alkene.
6.5–8.5	H bonded to an sp^2 carbon in an aromatic compound.
9.5–10.1	H bonded to a C=O (an aldehyde hydrogen).
10–13	H of a carboxyl (COOH) group.

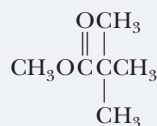
follow these rules of thumb for most ¹H-NMR spectra problems

EXAMPLE 11.12

Following are two constitutional isomers with the molecular formula C₆H₁₂O₂:



(1)



(2)

- Predict the number of signals in the ¹H-NMR spectrum of each isomer.
- Predict the ratio of areas of the signals in each spectrum.
- Show how to distinguish between these isomers on the basis of chemical shift.

STRATEGY

This example poses a series of steps that you will repeat often when asked to predict the $^1\text{H-NMR}$ spectrum of a compound. First, determine the number of signals by determining the number of equivalent hydrogens (Section 11.8). Then predict the ratio of areas of the signals by counting the number of hydrogens in each equivalent set (if the set of ratios can be reduced further, divide each number by a value that produces whole number ratios). Finally, predict the chemical shift of each set of equivalent hydrogens. If the rules of thumb for predicting chemical shift do not apply, refer to Table 11.4.

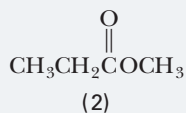
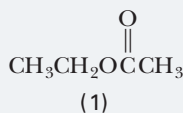
SOLUTION

- (a) Each compound contains a set of nine equivalent methyl hydrogens and a set of three equivalent methyl hydrogens.
- (b) The $^1\text{H-NMR}$ spectrum of each consists of two signals in the ratio 9:3, or 3:1.

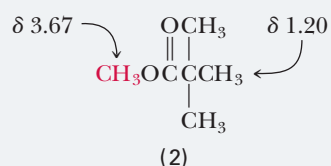
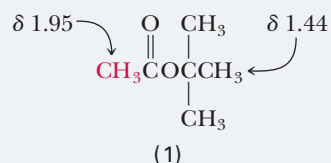
See problems 11.38, 11.42

PROBLEM 11.12

Following are two constitutional isomers with the molecular formula $\text{C}_4\text{H}_8\text{O}_2$:



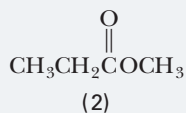
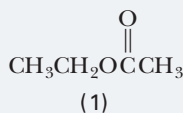
- (c) The two constitutional isomers can be distinguished by the chemical shift of the single $-\text{CH}_3$ group, or in other words, the signal that integrates to 3 (shown in red for each compound). Using our rules of thumb, we find that the hydrogens of CH_3O are less shielded (appear farther downfield) than the hydrogens of $\text{CH}_3\text{C}=\text{O}$. Table 11.4 gives approximate values for each chemical shift. Experimental values are as follows:



See problems 11.38, 11.42

PROBLEM 11.12

Following are two constitutional isomers with the molecular formula $\text{C}_4\text{H}_8\text{O}_2$:



- (a) Predict the number of signals in the $^1\text{H-NMR}$ spectrum of each isomer.
- (b) Predict the ratio of areas of the signals in each spectrum.
- (c) Show how to distinguish between these isomers on the basis of chemical shift.

11.11 What Is Signal Splitting?

We have now seen three kinds of information that can be derived from an examination of a $^1\text{H-NMR}$ spectrum:

1. From the number of signals, we can determine the number of sets of equivalent hydrogens.
2. By integrating over signal areas, we can determine the relative numbers of hydrogens giving rise to each signal.
3. From the chemical shift of each signal, we can derive information about the types of hydrogens in each set.

We can derive a fourth kind of information from the splitting pattern of each signal. Consider, for example, the $^1\text{H-NMR}$ spectrum of 1,1,2-trichloroethane (Figure 11.19), a solvent for waxes and natural resins. This molecule contains two 2° hydrogens and one 3° hydrogen, and, according to what we have learned so far, we predict two signals with relative areas 2:1, corresponding to the two hydrogens of the $-\text{CH}_2-$ group and the one hydrogen of the $-\text{CHCl}_2$ group. You see from the spectrum, however, that there are in fact five **peaks**. How can this be, when we predict only two signals? The answer is that a hydrogen's resonance frequency can be affected by the tiny magnetic fields of other hydrogens close by. Those fields cause the signal to be **split** into numerous peaks.

Peak (NMR) The units into which an NMR signal is split—two peaks in a doublet, three peaks in a triplet, and so on.

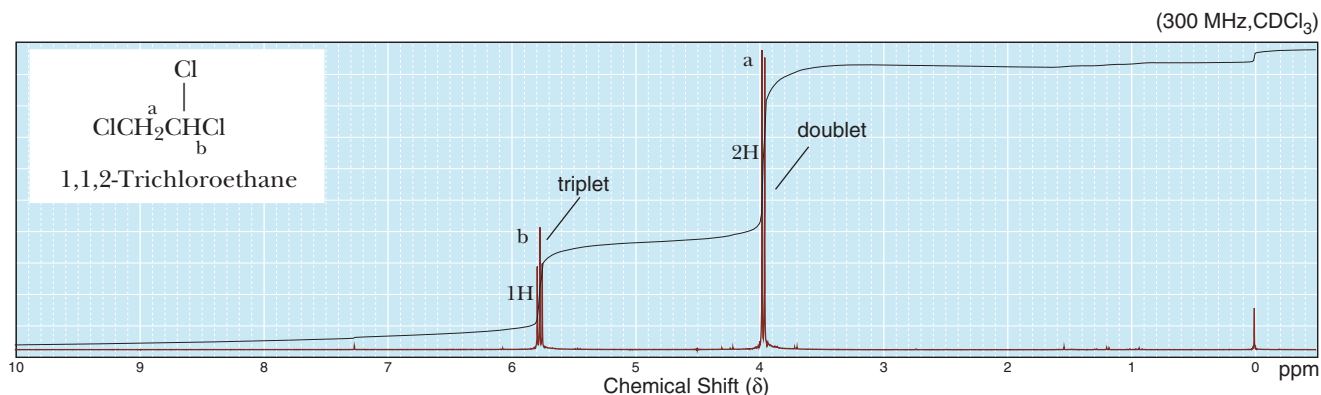


FIGURE 11.19
 $^1\text{H-NMR}$ spectrum of 1,1,2-trichloroethane.

Hydrogens split each other if they are separated by no more than three bonds—for example, $\text{H}-\text{C}-\text{C}-\text{H}$ or $\text{H}-\text{C}=\text{C}-\text{H}$. (There are three bonds in each case.) If there are more than three bonds, as in $\text{H}-\text{C}-\text{C}-\text{C}-\text{H}$, then there is normally no splitting. A signal with just one peak is called a **singlet**. A signal that is split into two peaks is called a **doublet**. Signals that are split into three and four peaks are called **triplets** and **quartets**, respectively.

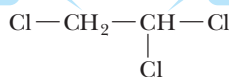
The grouping of two peaks at δ 3.96 in the $^1\text{H-NMR}$ spectrum of 1,1,2-trichloroethane is the signal for the hydrogens of the $-\text{CH}_2-$ group, and the grouping of three peaks at δ 5.77 is the signal for the single hydrogen of the $-\text{CHCl}_2$ group. We say that the CH_2 signal at δ 3.96 is split into a doublet and that the CH signal at δ 5.77 is split into a triplet. In this phenomenon, called **signal splitting**, the $^1\text{H-NMR}$ signal from one set of hydrogens is split by the influence of neighboring nonequivalent hydrogens.

The degree of signal splitting can be predicted on the basis of the **($n + 1$) rule**, according to which, if a hydrogen has n hydrogens nonequivalent to it, but equivalent among themselves, on the same or adjacent atom(s), then the $^1\text{H-NMR}$ signal of the hydrogen is split into $(n + 1)$ peaks.

Let us apply the $(n + 1)$ rule to the analysis of the spectrum of 1,1,2-trichloroethane. The two hydrogens of the $-\text{CH}_2-$ group have one nonequivalent neighboring hydrogen ($n = 1$); their signal is split into a doublet ($1 + 1 = 2$). The single hydrogen of the $-\text{CHCl}_2$ group has a set of two nonequivalent neighboring hydrogens ($n = 2$); its signal is split into a triplet ($2 + 1 = 3$).

For these hydrogens, $n = 1$;
 their signal is split into $(1 + 1)$
 or 2 peaks—a **doublet**

For this hydrogen, $n = 2$;
 its signal is split into $(2 + 1)$
 or 3 peaks—a **triplet**



It is important to remember that the $(n + 1)$ rule of signal splitting applies only to hydrogens with *equivalent* neighboring hydrogens. When more than one set of neighboring hydrogens exists, the $(n + 1)$ rule no longer applies. An example of where the $(n + 1)$ rule no longer applies is illustrated in the $^1\text{H-NMR}$ spectrum of 1-chloropropane. The two hydrogens on carbon 2 (a CH_2 group) of 1-chloropropane are flanked on

Singlet A signal that consists of one peak; the hydrogens that give rise to the signal have no neighboring nonequivalent hydrogens.

Doublet A signal that is split into two peaks; the hydrogens that give rise to the signal have one neighboring nonequivalent hydrogen.

Triplet A signal that is split into three peaks; the hydrogens that give rise to the signal have two neighboring nonequivalent hydrogens that are equivalent to each other.

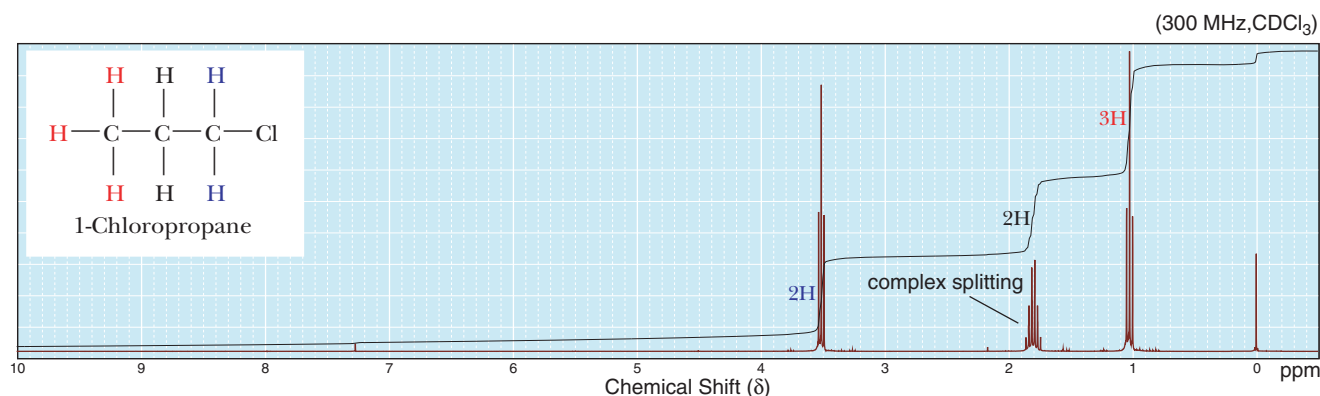
Quartet A signal that is split into four peaks; the hydrogens that give rise to the signal have three neighboring nonequivalent hydrogens that are equivalent to each other.

Signal splitting Splitting of an NMR signal into a set of peaks by the influence of neighboring nuclei.

($n + 1$) rule The $^1\text{H-NMR}$ signal of a hydrogen or set of equivalent hydrogens with n other hydrogens on neighboring carbons is split into $(n + 1)$ peaks.

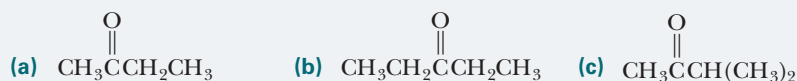
Multiplet A signal that is split into multiple peaks, often of an irregular pattern, due to the presence of more than one type of neighboring hydrogens.

one side by a set of 2H on carbon 1, and on the other side by a set of 3H on carbon 3. Because the sets of hydrogen on carbons 1 and 3 are nonequivalent to each other and also nonequivalent to the hydrogens on carbon 2, they cause the signal for the CH₂ group on carbon 2 to be split into a complex pattern, which we will refer to simply as a **multiplet**.



EXAMPLE 11.13

Predict the number of signals and the splitting pattern of each signal in the ¹H-NMR spectrum of each compound.

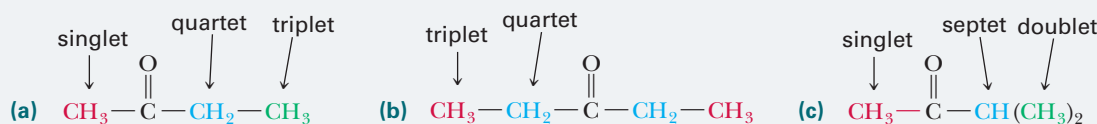


STRATEGY

Determine the number of signals by determining the number of equivalent hydrogens (Section 11.8). For each set of equivalent hydrogens, determine the number of equivalent neighbors (*n*) and apply the (*n* + 1) rule to determine the splitting pattern.

SOLUTION

The sets of equivalent hydrogens in each molecule are color coded. In molecule (a), the signal for the red methyl group is unsplit (a singlet) because the group is too far (>3 bonds) from any other hydrogens. The blue—CH₂— group has three neighboring hydrogens (*n* = 3) and thus shows a signal split into a quartet (3 + 1 = 4). The green methyl group has two neighboring hydrogens (*n* = 2), and its signal is split into a triplet. The integration ratios for these signals would be 3:2:3. Parts (b) and (c) can be analyzed in the same way. Thus, molecule (b) shows a triplet and a quartet in the ratio 3:2. Molecule (c) shows a singlet, a septet (6 + 1 = 7), and a doublet in the ratio 3:1:6.



See problem 11.32

PROBLEM 11.13

Following are pairs of constitutional isomers. Predict the number of signals and the splitting pattern of each signal in the ¹H-NMR spectrum of each isomer.



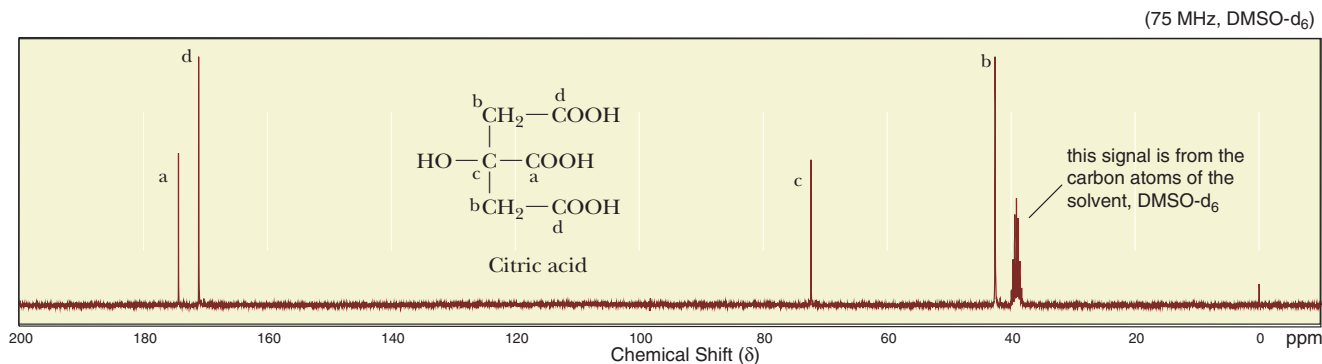


FIGURE 11.20
Hydrogen-decoupled ^{13}C -NMR spectrum of citric acid.

11.12 What Is ^{13}C -NMR Spectroscopy, and How Does It Differ from ^1H -NMR Spectroscopy?

Nuclei of carbon-12, the most abundant (98.89%) natural isotope of carbon, do not have nuclear spin and are not detected by NMR spectroscopy. Nuclei of carbon-13 (natural abundance 1.11%), however, do have nuclear spin and are detected by NMR spectroscopy in the same manner as hydrogens are detected. Thus, NMR can be used to obtain information about 1.11% of all the carbon atoms in a sample. Just as in ^1H -NMR spectroscopy, ^{13}C -NMR spectroscopy yields a signal for each set of equivalent carbons in a molecule.

Because both ^{13}C and ^1H have spinning nuclei and generate magnetic fields, ^{13}C couples with each ^1H bonded to it and gives a signal split according to the $(n + 1)$ rule. In the most common mode for recording a ^{13}C spectrum, this coupling is eliminated by instrumental techniques, so as to simplify the spectrum. In these **hydrogen-decoupled spectra**, all ^{13}C signals appear as singlets. The hydrogen-decoupled ^{13}C -NMR spectrum of citric acid (Figure 11.20), a compound used to increase the solubility of many pharmaceutical drugs in water, consists of four singlets. Again, notice that, as in ^1H -NMR, equivalent carbons generate only one signal.

Chemical

Connections 11B

MAGNETIC RESONANCE IMAGING

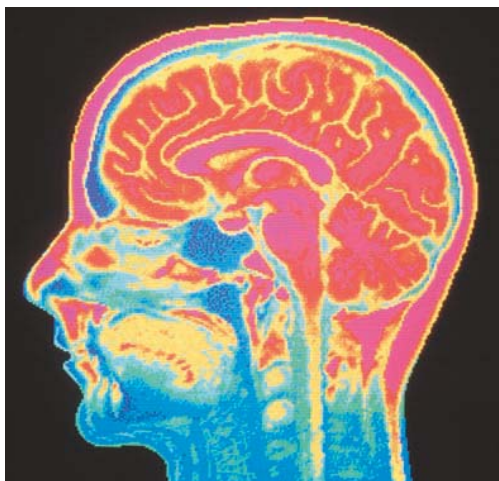
Nuclear magnetic resonance was discovered and explained by physicists in the 1950s, and, by the 1960s, it had become an invaluable analytical tool for chemists. By the early 1970s, it was realized that the imaging of parts of the body via NMR could be a valuable addition to diagnostic medicine. Because the term *nuclear magnetic resonance* sounds to many people as if the technique might involve radioactive material, health care personnel call the technique *magnetic resonance imaging* (MRI).

The body contains several nuclei that, in principle, could be used for MRI. Of these, hydrogens, most of which come from water, triglycerides (fats), and membrane phospholipids, give the most useful

signals. Phosphorus MRI is also used in diagnostic medicine.

Recall that, in NMR spectroscopy, energy in the form of radio-frequency radiation is absorbed by nuclei in the sample. The relaxation time is the characteristic time at which excited nuclei give up this energy and relax to their ground state.

In 1971, Raymond Damadian discovered that the relaxation of water in certain cancerous tumors takes much longer than the relaxation of water in normal cells. Thus, it was reasoned that if a relaxation image of the body could be obtained, it might be possible to identify tumors at an early stage. Subsequent work demonstrated that many tumors can be identified in this way.



Mehau Kulyk/Photo Researchers, Inc

Computer-enhanced MRI scan of a normal human brain with pituitary gland highlighted

Another important application of MRI is in the examination of the brain and spinal cord. White and gray matter, the two different layers of the brain, are easily distinguished by MRI, which is useful in the study of such diseases as multiple sclerosis. Magnetic

resonance imaging and X-ray imaging are in many cases complementary: The hard, outer layer of bone is essentially invisible to MRI, but shows up extremely well in X-ray images, whereas soft tissue is nearly transparent to X rays, but shows up in MRI.

The key to any medical imaging technique is knowing which part of the body gives rise to which signal. In MRI, the patient is placed in a magnetic field gradient that can be varied from place to place. Nuclei in the weaker magnetic field gradient absorb radiation at a lower frequency. Nuclei elsewhere, in the stronger magnetic field, absorb radiation at a higher frequency. Because a magnetic field gradient along a single axis images a plane, MRI techniques can create views of any part of the body in slicelike sections. In 2003, Paul Lauterbur and Sir Peter Mansfield were awarded the Nobel Prize in Physiology or Medicine for their discoveries that led to the development of these imaging techniques.

Question

In ^1H -NMR spectroscopy, the chemical sample is set spinning on its long axis to ensure that all parts of the sample experience a homogeneous applied field. Homogeneity is also required in MRI. Keeping in mind that the “sample” in MRI is a human being, how do you suppose this is achieved?

Table 11.5 shows approximate chemical shifts in ^{13}C -NMR spectroscopy. As with ^1H -NMR, we can use the following rules of thumb to remember the chemical shifts of various types of carbons:

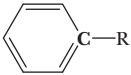
follow these rules of thumb for most ^{13}C -NMR spectra problems

Chemical Shift (δ)	Type of Carbon
0–50	sp^3 carbon ($3^\circ > 2^\circ > 1^\circ$).
50–80	sp^3 carbon bonded to an electronegative element such as N, O, or X. The more electronegative the element, the larger is the chemical shift.
100–160	sp^2 carbon of an alkene or an aromatic compound.
160–180	carbonyl carbon of a carboxylic acid or carboxylic acid derivative (Chapters 13 and 14).
180–210	carbonyl carbon of a ketone or an aldehyde (Chapter 12).

Notice how much broader the range of chemical shifts is for ^{13}C -NMR spectroscopy (0–210 ppm) than for ^1H -NMR spectroscopy (0–12 ppm). Because of this expanded scale, it is very unusual to find any two nonequivalent carbons in the same molecule with identical chemical shifts. Most commonly, each different type of carbon within a molecule has a distinct signal that is clearly resolved (i.e., separated) from all other signals. Notice further that the chemical shift of carbonyl carbons is quite distinct from the chemical shifts of sp^3 hybridized carbons and other types of sp^2 hybridized carbons. The presence or absence of a carbonyl carbon is quite easy to recognize in a ^{13}C -NMR spectrum.

A great advantage of ^{13}C -NMR spectroscopy is that it is generally possible to count the number of different types of carbon atoms in a molecule. There is one caution here, however: Because of the particular manner in which spin-flipped ^{13}C nuclei return to their lower energy states, integrating signal areas is often unreliable, and it is generally not possible to determine the number of carbons of each type on the basis of the signal areas.

TABLE 11.5 ^{13}C -NMR Chemical Shifts

Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
RCH_3	0–40		110–160
RCH_2R	15–55	RCOR	160–180
R_3CH	20–60	RCNR_2	165–180
RCH_2I	0–40	RCOH	175–185
RCH_2Br	25–65	$\text{RCH}_2\text{C}(\text{O})\text{R}$	180–210
RCH_2Cl	35–80		
R_3COH	40–80		
R_3COR	40–80		
$\text{RC}\equiv\text{CR}$	65–85		
$\text{R}_2\text{C}=\text{CR}_2$	100–150		

EXAMPLE 11.14

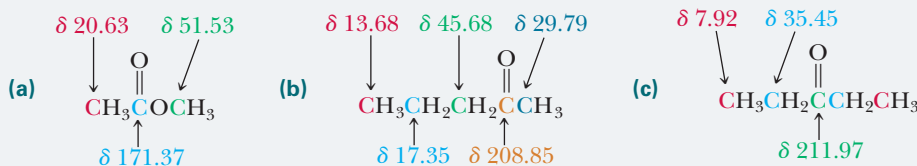
Predict the number of signals in a proton-decoupled ^{13}C -NMR spectrum of each compound:

**STRATEGY**

Because we cannot replace each carbon atom with a halogen (as we did to determine equivalency in ^1H -NMR), inasmuch as a halogen only has a valence of 1, we will need to use symmetry to determine equivalency.

SOLUTION

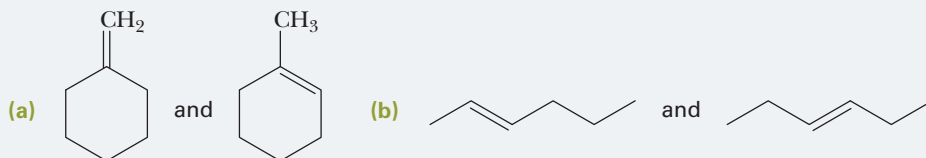
Here is the number of signals in each spectrum, along with the chemical shift of each, color coded to the carbon responsible for that signal. The chemical shifts of the carbonyl carbons are quite distinctive (Table 11.5) and occur at δ 171.37, 208.85, and 211.97 in these examples.



See problem 11.33

PROBLEM 11.14

Explain how to distinguish between the members of each pair of constitutional isomers, on the basis of the number of signals in the ^{13}C -NMR spectrum of each isomer:



11.13 How Do We Solve an NMR Problem?

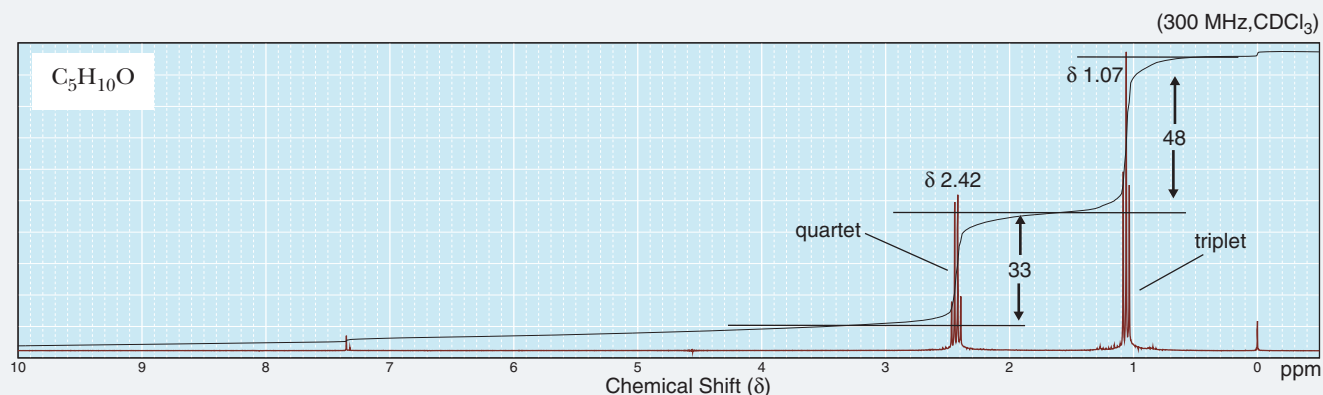
One of the first steps in determining the molecular structure of a compound is to establish the compound's molecular formula. In the past, this was most commonly done by elemental analysis, combustion to determine the percent composition, and so forth. More commonly today, we determine molecular weight and molecular formula by a technique known as *mass spectrometry* (an explanation of the technique is beyond the scope of this book). In the examples that follow, we assume that the molecular formula of any unknown compound has already been determined, and we proceed from there, using spectral analysis to determine a structural formula.

The following steps may prove helpful as a systematic approach to solving $^1\text{H-NMR}$ spectral problems:

- Step 1: Molecular formula and index of hydrogen deficiency.** Examine the molecular formula, calculate the index of hydrogen deficiency (Section 11.4G), and deduce what information you can about the presence or absence of rings or pi bonds.
- Step 2: Number of signals.** Count the number of signals to determine the minimum number of sets of equivalent hydrogens in the compound.
- Step 3: Integration.** Use signal integration and the molecular formula to determine the number of hydrogens in each set.
- Step 4: Pattern of chemical shifts.** Examine the NMR spectrum for signals characteristic of the most common types of equivalent hydrogens. (See the general rules of thumb for $^1\text{H-NMR}$ chemical shifts in Section 11.10.) Keep in mind that the ranges are broad and that hydrogens of each type may be shifted either farther upfield or farther downfield, depending on details of the molecular structure in question.
- Step 5: Splitting patterns.** Examine splitting patterns for information about the number of nonequivalent hydrogen neighbors.
- Step 6: Structural formula.** Write a structural formula consistent with the information learned in Steps 1–5.

EXAMPLE 11.15

Following is a $^1\text{H-NMR}$ spectrum for a compound that is a colorless liquid with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$. Propose a structural formula for the compound.



STRATEGY

$^1\text{H-NMR}$ spectra can be approached by (1) calculating the index of hydrogen deficiency and deducing what information you can about the presence or absence of rings or pi bonds, (2) counting the number of signals to determine the

minimum number of sets of equivalent hydrogens in the compound, (3) using signal integration and the molecular formula to determine the number of hydrogens in each set, (4) examining the NMR spectrum for signals characteristic of the most common types of equivalent hydrogens, (5) examining splitting patterns for information about the number of nonequivalent hydrogen neighbors, and (6) writing a structural formula consistent with the information learned in Steps 1–5.

SOLUTION

STEP 1: Molecular formula and index of hydrogen deficiency. The reference compound is $C_5H_{12}O$; therefore, the index of hydrogen deficiency is 1. The molecule thus contains either one ring or one pi bond.

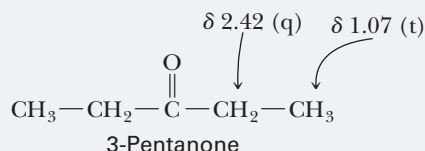
STEP 2: Number of signals. There are two signals (a triplet and a quartet) and therefore two sets of equivalent hydrogens.

STEP 3: Integration. By signal integration, we calculate that the number of hydrogens giving rise to each signal is in the ratio 3:2. Because there are 10 hydrogens, we conclude that the signal assignments are δ 1.07 (6H) and δ 2.42 (4H).

STEP 4: Pattern of chemical shifts. The signal at δ 1.07 is in the alkyl region and, based on its chemical shift, most probably represents a methyl group. No signal occurs at δ 4.6 to 5.7; thus, there are no vinylic hydrogens. (If a carbon–carbon double bond is in the molecule, no hydrogens are on it; that is, it is tetrasubstituted.)

STEP 5: Splitting pattern. The methyl signal at δ 1.07 is split into a triplet (t); hence, it must have two neighboring hydrogens, indicating $-CH_2CH_3$. The signal at δ 2.42 is split into a quartet (q); thus, it must have three neighboring hydrogens, which is also consistent with $-CH_2CH_3$. Consequently, an ethyl group accounts for these two signals. No other signals occur in the spectrum; therefore, there are no other types of hydrogens in the molecule.

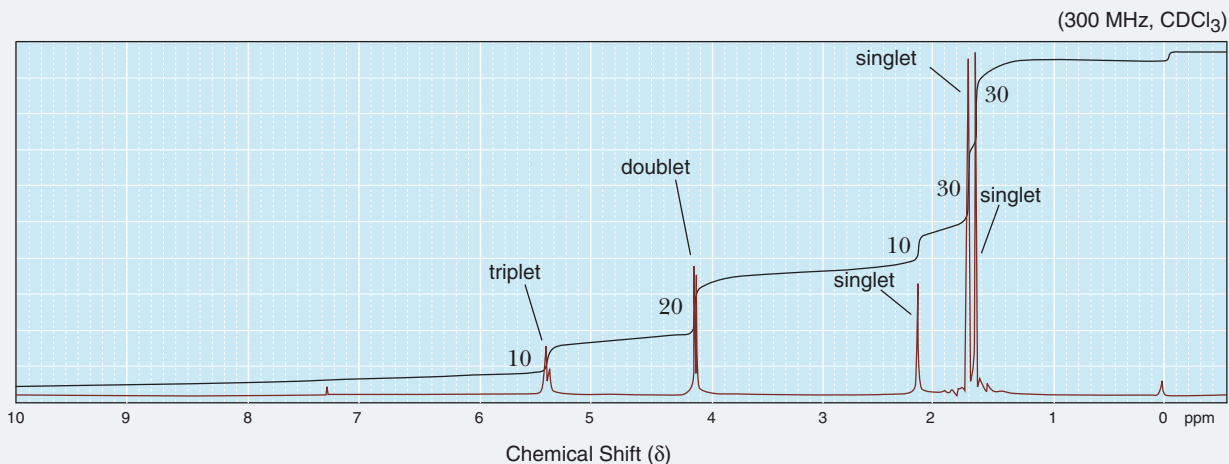
STEP 6: Structural formula. Put the information learned in the previous steps together to arrive at the following structural formula. Note that the chemical shift of the methylene group ($-CH_2-$) at δ 2.42 is consistent with an alkyl group adjacent to a carbonyl group.



See problems 11.35–11.37, 11.39–11.41, 11.43–11.62

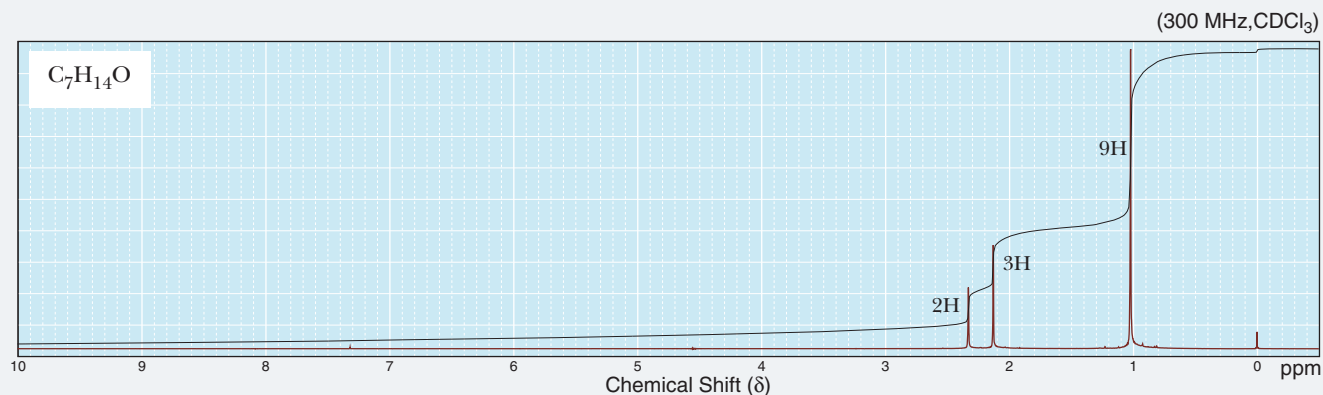
PROBLEM 11.15

Following is a $^1\text{H-NMR}$ spectrum for prenilol, a compound that possesses a fruity odor and that is commonly used in perfumes. Prenilol has the molecular formula $C_5H_{10}O$. Propose a structural formula for prenilol.



EXAMPLE 11.16

Following is a $^1\text{H-NMR}$ spectrum for a compound that is a colorless liquid with the molecular formula $\text{C}_7\text{H}_{14}\text{O}$. Propose a structural formula for the compound.



STRATEGY

$^1\text{H-NMR}$ spectra can be approached by (1) calculating the index of hydrogen deficiency and deducing what information you can about the presence or absence of rings or pi bonds, (2) counting the number of signals to determine the minimum number of sets of equivalent hydrogens in the compound, (3) using signal integration and the molecular formula to determine the number of hydrogens in each set, (4) examining the NMR spectrum for signals characteristic of the most common types of equivalent hydrogens, (5) examining splitting patterns for information about the number of nonequivalent hydrogen neighbors, and (6) writing a structural formula consistent with the information learned in Steps 1–5.

SOLUTION

STEP 1: Molecular formula and index of hydrogen deficiency. The index of hydrogen deficiency is 1; thus, the compound contains one ring or one pi bond.

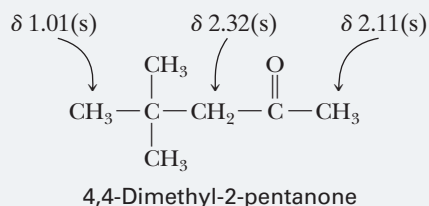
STEP 2: Number of signals. There are three signals and therefore three sets of equivalent hydrogens.

STEP 3: Integration. By signal integration, we calculate that the number of hydrogens giving rise to each signal is in the ratio 2:3:9, reading from left to right.

STEP 4: Pattern of chemical shifts. The singlet at δ 1.01 is characteristic of a methyl group adjacent to an sp^3 hybridized carbon. The singlets at δ 2.11 and 2.32 are characteristic of alkyl groups adjacent to a carbonyl group.

STEP 5: Splitting pattern. All signals are singlets (s), which means that none of the hydrogens are within three bonds of each other.

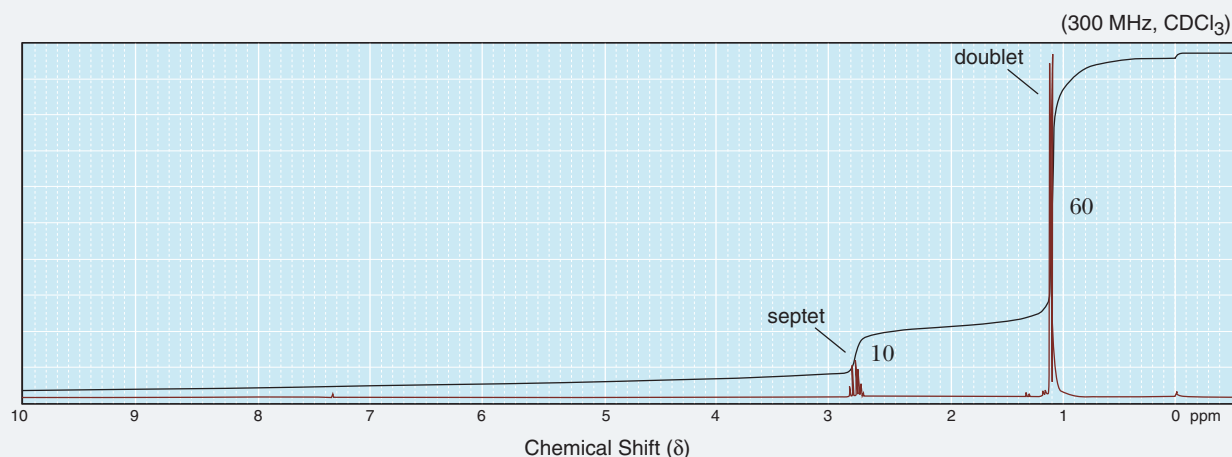
STEP 6: Structural formula. The compound is 4,4-dimethyl-2-pentanone:



See problems 11.35–11.37, 11.39–11.41, 11.43–11.62

PROBLEM 11.16

Following is a $^1\text{H-NMR}$ spectrum for a compound that is a colorless liquid with the molecular formula $\text{C}_7\text{H}_{14}\text{O}$. Propose a structural formula for the compound.

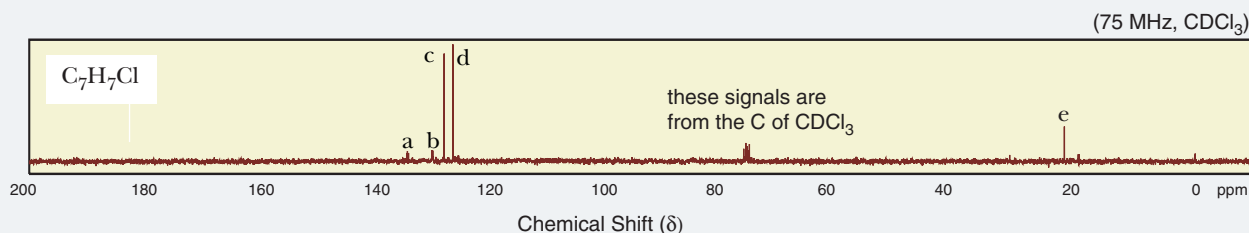


The following steps may prove helpful as a systematic approach to solving ¹³C-NMR spectral problems:

- Step 1: Molecular formula and index of hydrogen deficiency.** Examine the molecular formula, calculate the index of hydrogen deficiency (Section 11.4G), and deduce what information you can about the presence or absence of rings or pi bonds.
- Step 2: Number of signals.** Count the number of signals to determine the minimum number of sets of equivalent carbons in the compound.
- Step 3: Pattern of chemical shifts.** Examine the NMR spectrum for signals characteristic of the most common types of equivalent carbons (see the general rules of thumb for ¹³C-NMR chemical shifts in Section 11.12). Keep in mind that these ranges are broad and that carbons of each type may be shifted either farther upfield or farther downfield, depending on details of the molecular structure in question.
- Step 4: Structural formula.** Write a structural formula consistent with the information learned in Steps 1–3. *Note:* Because ¹³C-NMR does not provide information about neighboring hydrogens, it may be more difficult to elucidate the structure of a compound based solely on ¹³C-NMR data.

EXAMPLE 11.17

Following is a ¹³C-NMR spectrum for a compound that is a colorless liquid with the molecular formula C₇H₇Cl. Propose a structural formula for the compound.



STRATEGY

¹³C-NMR spectra can be approached by (1) calculating the index of hydrogen deficiency and deducing what information you can about the presence or absence of rings or pi bonds, (2) counting the number of signals to determine the minimum number of sets of equivalent carbons in the compound, (3) examining the NMR spectrum for signals characteristic of the most common types of equivalent carbons, and (4) writing a structural formula consistent with the information learned in Steps 1–3.

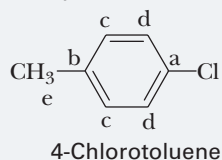
SOLUTION

STEP 1: Molecular formula and index of hydrogen deficiency. The index of hydrogen deficiency is 4; thus, the compound can contain a myriad combination of rings or pi bonds.

STEP 2: Number of signals. There are five signals and therefore five sets of equivalent carbons. Because there are seven carbons total, there must be symmetry in the molecule.

STEP 3: Pattern of chemical shifts. The signal (e) at δ 23 is characteristic of an sp^3 hybridized carbon. The four signals (a–d) between δ 120 and 140 are characteristic of sp^2 hybridized carbons. Because it would be unlikely for a molecule with only seven carbon atoms to have 4 pi bonds (due to IHD = 4), it is likely that these signals represent the carbons of a benzene ring.

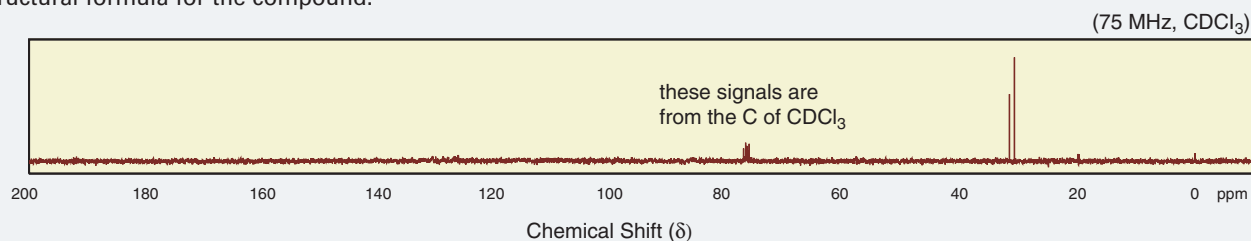
STEP 4: Structural formula. Because there must be symmetry in the molecule, the most likely structure of the compound is:



See problems 11.34, 11.38, 11.39, 11.43, 11.44, 11.50–11.54

PROBLEM 11.17

Following is a ^{13}C -NMR spectrum for a compound that is a colorless liquid with the molecular formula $\text{C}_4\text{H}_8\text{Br}_2$. Propose a structural formula for the compound.



SUMMARY OF KEY QUESTIONS

11.1 What Is Electromagnetic Radiation?

• **Electromagnetic radiation** is a wave traveling at the speed of light that can be described in terms of its **wavelength** (λ) and its **frequency** (ν).

• Frequency is reported in **hertz (Hz)**.

• An alternative way to describe electromagnetic radiation is in terms of its energy where $E = h\nu$.

11.2 What Is Molecular Spectroscopy?

• **Molecular spectroscopy** is the experimental process of measuring which frequencies of radiation are absorbed or

emitted by a substance and correlating these patterns with details of molecular structure.

11.3 What Is Infrared Spectroscopy?

• **Infrared spectroscopy** is molecular spectroscopy applied to frequencies of infrared radiation.

• To be **infrared active**, a bond must be polar; the more polar it is, the stronger is its absorption of IR radiation.

• Interactions of molecules with **infrared radiation** excite covalent bonds to higher vibrational energy levels.

• The simplest vibrations that give rise to the absorption of infrared radiation are **stretching** and **bending** vibrations.

• The **vibrational infrared** spectrum extends from 4000 to 400 cm^{-1} . Radiation in this region is referred to by its wavenumber ($\bar{\nu}$) in reciprocal centimeters (cm^{-1}).

• Stretching may be symmetrical or asymmetrical.

- A **correlation table** is a list of the absorption patterns of functional groups. The intensity of a peak is referred to as **strong (s)**, **medium (m)**, or **weak (w)**. Stretching vibrations for most functional groups appear in the region from 3400 to 1000 cm^{-1} .
- The region from 1000 to 400 cm^{-1} is referred to as the **fingerprint region**, so called because absorption bands in this region are unique to each compound.

11.4 How Do We Interpret Infrared Spectra?

- The **index of hydrogen deficiency** is the sum of the number of rings and pi bonds in a molecule. It can be determined by comparing the number of hydrogens in the molecular formula of a compound of unknown structure with the number of hydrogens in a reference compound with the same number of carbon atoms and with no rings or pi bonds.
- Using the index of hydrogen deficiency along with knowledge of characteristic IR absorptions for various functional groups, one can determine the possible structures for an unknown whose molecular formula is known.

11.5 What Is Nuclear Magnetic Resonance?

- An atomic nucleus that has an odd mass or an odd atomic number also has a **spin** and behaves as if it were a tiny bar magnet.
- When a collection of ^1H and ^{13}C atoms is placed between the poles of a powerful magnet, interactions between their nuclear spins and the applied magnetic field are quantized, and only two orientations are allowed.
- When placed between the poles of a powerful magnet, the nuclear spins of these elements become aligned either with the applied field or against it.
- Nuclear spins aligned with the applied field are in the lower energy state; those aligned against the applied field are in the higher energy state.
- **Resonance** is the absorption of electromagnetic radiation by a nucleus and the resulting “flip” of its nuclear spin from a lower energy spin state to a higher energy spin state.

11.6 What Is Shielding?

- The experimental conditions required to cause nuclei to resonate are affected by the local chemical and magnetic environment.
- Electrons around a hydrogen also have spin and create a local magnetic field that **shields** the hydrogen from the applied field.

11.7 What Is an NMR Spectrum?

- An **NMR spectrometer** records resonance as a signal, and the collection of all resonance signals for a sample is its **NMR spectrum**.

11.8 How Many Resonance Signals Will a Compound Yield in Its NMR Spectrum?

- **Equivalent hydrogens** within a molecule have identical chemical shifts.

11.9 What Is Signal Integration?

- The area of a ^1H -NMR signal is proportional to the number of equivalent hydrogens giving rise to that **signal**. Determination of these areas is termed **integration**.

11.10 What Is Chemical Shift?

- In a ^1H -NMR spectrum, a resonance signal is reported by how far it is shifted from the resonance signal of the 12 equivalent hydrogens in **tetramethylsilane (TMS)**.
- A resonance signal in a ^{13}C -NMR spectrum is reported by how far it is shifted from the resonance signal of the four equivalent carbons in TMS.
- A **chemical shift** (δ) is the frequency shift from TMS, divided by the operating frequency of the spectrometer.

11.11 What Is Signal Splitting?

- In **signal splitting**, the ^1H -NMR signal from one hydrogen or set of equivalent hydrogens is split by the influence of nonequivalent hydrogens on the same or adjacent carbon atoms.
- According to the **($n + 1$) rule**, if a hydrogen has n hydrogens that are nonequivalent to it, but are equivalent

among themselves, on the same or adjacent carbon atom(s), its ^1H -NMR signal is split into $(n + 1)$ peaks.

- **Complex splitting** occurs when a hydrogen is flanked by two or more sets of hydrogens and those sets are nonequivalent.
- Splitting patterns are commonly referred to as **singlets, doublets, triplets, quartets, quintets, and multiplets**.

11.12 What Is ^{13}C -NMR Spectroscopy, and How Does It Differ from ^1H -NMR Spectroscopy?

- A ^{13}C -NMR spectrum normally spans the range δ 0–210 (versus δ 0–13 for ^1H -NMR).
- ^{13}C -NMR spectra are commonly recorded in a **hydrogen-**

decoupled instrumental mode. In this mode, all ^{13}C signals appear as singlets.

- Integration is not normally performed in ^{13}C -NMR.

11.13 How Do We Solve an NMR Problem?

- ^1H -NMR spectra can be approached by (1) calculating the index of hydrogen deficiency and deducing what information you can about the presence or absence of rings or pi bonds, (2) counting the number of signals to determine the minimum number of sets of equivalent hydrogens in the compound, (3) using signal integration and the molecular formula to determine the number of hydrogens in each set, (4) examining the NMR spectrum for signals characteristic of the most common types of equivalent hydrogens, (5) examining splitting patterns for information about the number of nonequivalent hydrogen neigh-

bors, and (6) writing a structural formula consistent with the information learned in Steps 1–5.

- ^{13}C -NMR spectra can be approached by (1) calculating the index of hydrogen deficiency and deducing what information you can about the presence or absence of rings or pi bonds, (2) counting the number of signals to determine the minimum number of sets of equivalent carbons in the compound, (3) examining the NMR spectrum for signals characteristic of the most common types of equivalent carbons, and (4) writing a structural formula consistent with the information learned in Steps 1–3.

QUICK QUIZ

Answer true or false to the following questions to assess your general knowledge of the concepts in this chapter. If you have difficulty with any of them, you should review the appropriate section in the chapter (shown in parentheses) before attempting the more challenging end-of-chapter problems.

1. A weak absorption band in an infrared spectrum can be attributed to, among other things, absorption of infrared light by a low polarity bond. (11.3)
2. Integration reveals the number of neighboring hydrogens in a ^1H -NMR spectrum. (11.11)
3. Wavelength and frequency are directly proportional. That is, as wavelength increases, frequency increases. (11.1)
4. An alkene (vinylic) hydrogen can be distinguished from a benzene ring hydrogen via ^1H -NMR spectroscopy. (11.10)
5. IR spectroscopy can be used to distinguish between a terminal alkyne and an internal alkyne. (11.4)
6. The NMR signal of a shielded nucleus appears more upfield than the signal for a deshielded nucleus. (11.7)
7. A transition between two energy states, E_1 and E_2 , can be made to occur using light equal to or greater than the energy difference between E_1 and E_2 . (11.2)
8. The chemical shift of a nucleus depends on its resonance frequency. (11.7)
9. A compound with the molecular formula $\text{C}_5\text{H}_{10}\text{O}$ could contain a C—C triple bond, two C=O bonds, or two rings. (11.4)
10. A ketone can be distinguished from an aldehyde via ^{13}C -NMR spectroscopy. (11.12)
11. A compound with the molecular formula $\text{C}_7\text{H}_{12}\text{O}$ has an index of hydrogen deficiency of 2. (11.4)
12. A ^1H -NMR spectrum with an integration ratio of 3:1:2 could represent a compound with the molecular formula $\text{C}_5\text{H}_9\text{O}$. (11.9)
13. Electromagnetic radiation can be described as a wave, as a particle, and in terms of energy. (11.1)
14. A set of hydrogens are equivalent if replacing each of them with a halogen results in compounds of the same name. (11.8)
15. The collection of absorption peaks in the 1000–400 cm^{-1} region of an IR spectrum is unique to a particular compound (i.e., no two compounds will yield the same spectrum in this region). (11.3)
16. The area under each peak in a ^1H -NMR spectrum can be determined using a technique known as integration. (11.9)
17. All atomic nuclei have a spin, which allows them to be analyzed by NMR spectroscopy. (11.5)
18. C—H stretching vibrations occur at higher wavenumbers than C—C stretching vibrations. (11.4)
19. The resonance frequency of a nucleus depends on its amount of shielding. (11.6)

20. It is not possible to use IR spectroscopy to distinguish between a ketone and a carboxylic acid. (11.4)
21. A carboxylic acid can be distinguished from an aldehyde via $^1\text{H-NMR}$ spectroscopy. (11.10)
22. A wavenumber, $\bar{\nu}$, is directly proportional to frequency. (11.3)
23. Resonance is the excitation of a magnetic nucleus in one spin state to a higher spin state. (11.5)
24. IR spectroscopy cannot be used to distinguish between an alcohol and an ether. (11.4)
25. A compound with an index of hydrogen deficiency of 1 can contain either one ring, one double bond, or one triple bond. (11.4)
26. Infrared spectroscopy measures transitions between electronic energy levels. (11.2)
27. A set of hydrogens represented by a doublet indicates that there are two neighboring equivalent hydrogens. (11.11)
28. The index of hydrogen deficiency can reveal the possible number of rings, double bonds, or triple bonds in a compound based solely on its molecular formula. (11.4)
29. TMS, tetramethylsilane, is a type of solvent used in NMR spectroscopy. (11.7)
30. Light of wavelength 400 nm is higher in energy than light of wavelength 600 nm. (11.1)
31. The methyl carbon of 1-chlorobutane will yield a $^1\text{H-NMR}$ signal that appears as a triplet. (11.11)
32. A compound with the molecular formula $\text{C}_6\text{H}_{14}\text{FN}$ has an index of hydrogen deficiency of 1. (11.4)
33. IR spectroscopy can be used to distinguish between 1°, 2°, and 3° amines. (11.4)

Answers: (1) T (2) F (3) F (4) T (5) T (6) T (7) F (8) T (9) F (10) F (11) T (12) F (13) T (14) T (15) T (16) T (17) F (18) T (19) T (20) F (21) T (22) T (23) T (24) F (25) F (26) F (27) F (28) T (29) F (30) T (31) T (32) F (33) T

Detailed explanations for many of these answers can be found in the accompanying Solutions Manual.

PROBLEMS

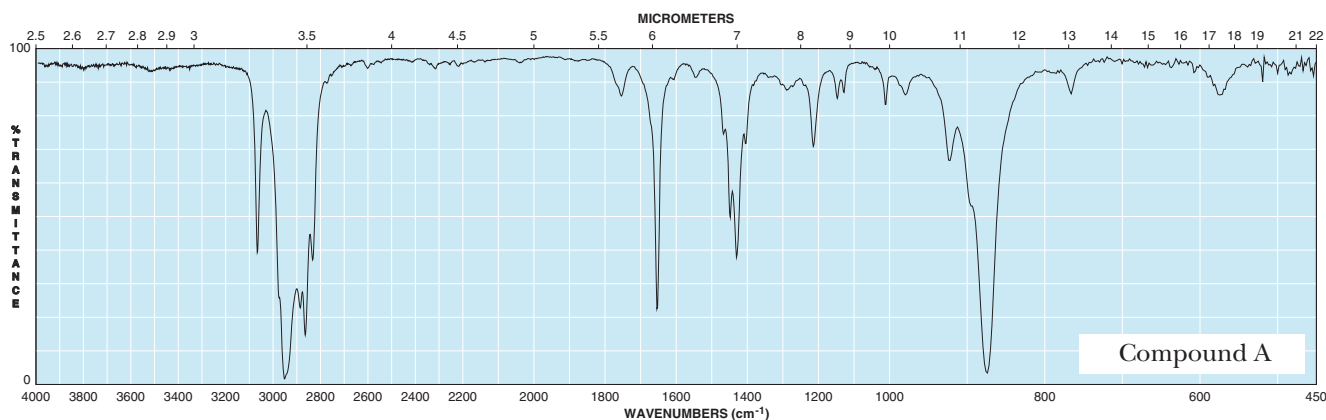
A problem marked with an asterisk indicates an applied “real-world” problem. Answers to problems whose numbers are printed in blue are given in Appendix D.

Section 11.1 Electromagnetic Radiation

- 11.18 Which puts out light of higher energy, a green laser pointer or a red laser pointer? (See Example 11.1)
- 11.19 Calculate the energy, in kilocalories per mole of radiation, of a wave with wavelength 2 m. What type of radiant energy is this? (See Example 11.1)
- 11.20 A molecule possesses molecular orbitals that differ in energy by 82 kcal/mol. What wavelength of light would be required to cause a transition between these two energy levels? What region of the electromagnetic spectrum does this energy correspond to? (See Example 11.1)

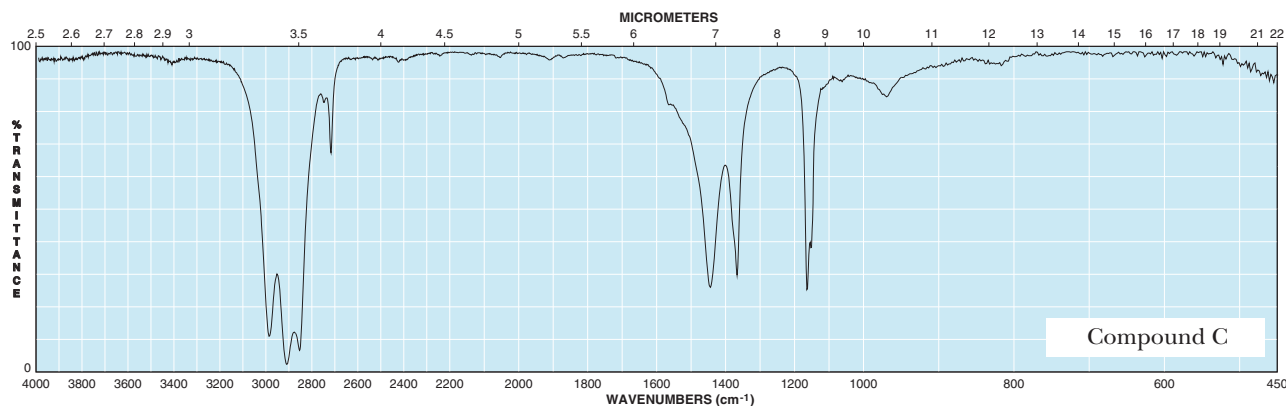
Section 11.4 Interpreting Infrared Spectra

- *11.21 Calculate the index of hydrogen deficiency of each compound: (See Examples 11.5, 11.6)
- Aspirin, $\text{C}_9\text{H}_8\text{O}_4$
 - Ascorbic acid (vitamin C), $\text{C}_6\text{H}_8\text{O}_6$
 - Pyridine, $\text{C}_5\text{H}_5\text{N}$
 - Urea, $\text{CH}_4\text{N}_2\text{O}$
 - Cholesterol, $\text{C}_{27}\text{H}_{46}\text{O}$
 - Trichloroacetic acid, $\text{C}_2\text{HCl}_3\text{O}_2$
- 11.22 Compound A, with the molecular formula C_6H_{10} , reacts with H_2/Ni to give compound B, with the molecular formula C_6H_{12} . The IR spectrum of compound A is provided. From this information about compound A tell (See Examples 11.4–11.7)
- Its index of hydrogen deficiency.
 - The number of rings or pi bonds (or both) in compound A.
 - What structural feature(s) would account for compound A's index of hydrogen deficiency.



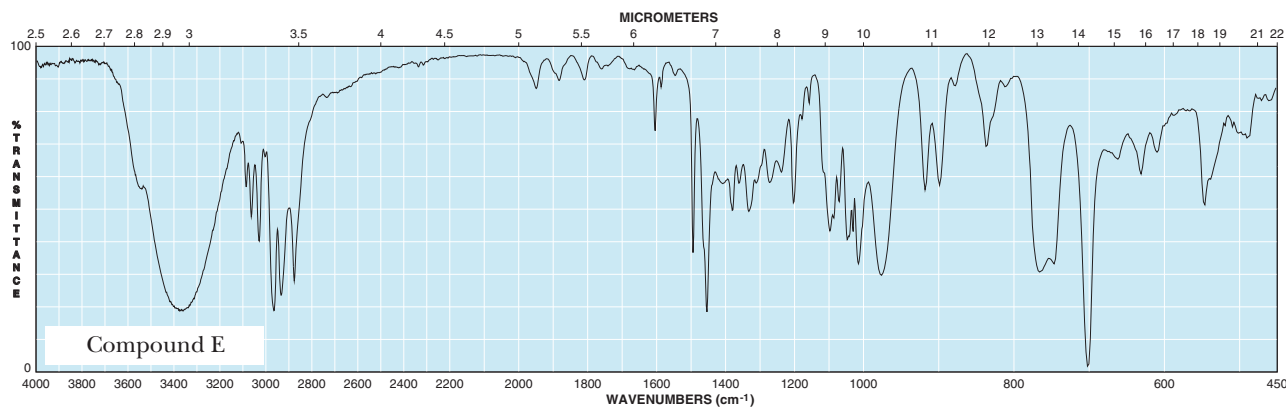
11.23 Compound C, with the molecular formula C_6H_{12} , reacts with H_2/Ni to give compound D, with the molecular formula C_6H_{14} . The IR spectrum of compound C is provided. From this information about compound C, tell (See Examples 11.4–11.7)

- Its index of hydrogen deficiency.
- The number of rings or pi bonds (or both) in compound C.
- What structural feature(s) would account for compound C's index of hydrogen deficiency.



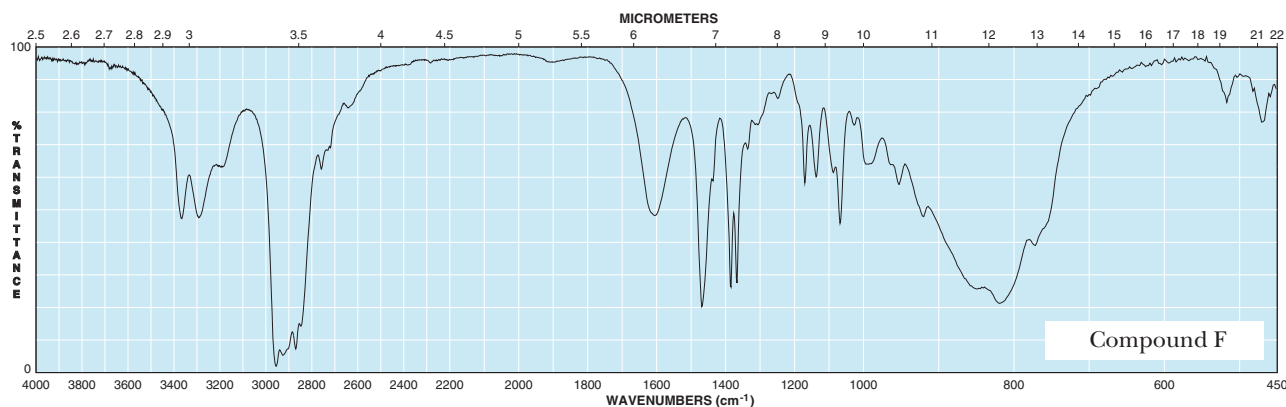
11.24 Examine the following IR spectrum and the molecular formula of compound E, $C_9H_{12}O$: Tell (See Examples 11.4–11.7)

- Its index of hydrogen deficiency.
- The number of rings or pi bonds (or both) in compound E.
- What one structural feature would account for this index of hydrogen deficiency.
- What oxygen-containing functional group compound E contains.



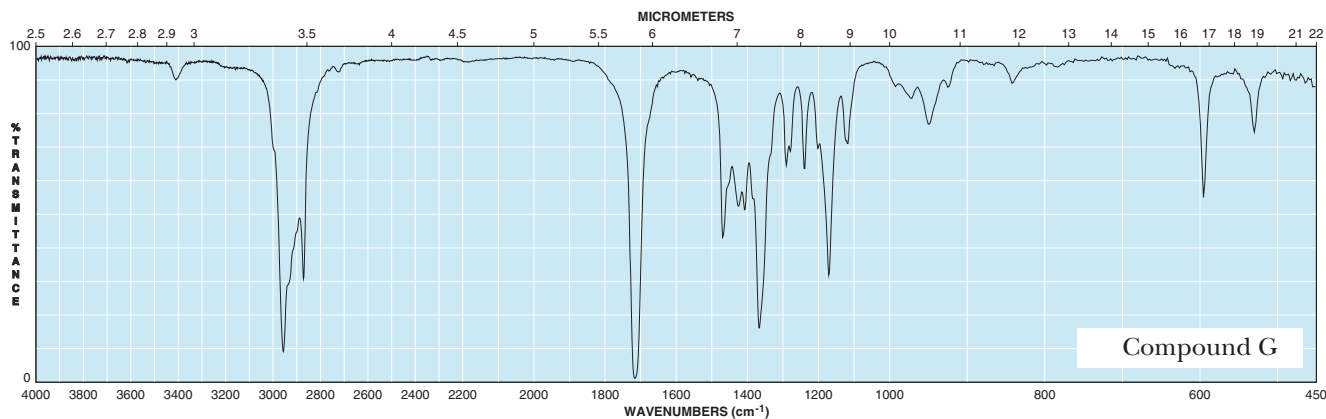
11.25 Examine the following IR spectrum and the molecular formula of compound F, $C_5H_{13}N$: Tell (See Examples 11.4–11.7)

- Its index of hydrogen deficiency.
- The number of rings or pi bonds (or both) in compound F.
- The nitrogen-containing functional group(s) compound F might contain.



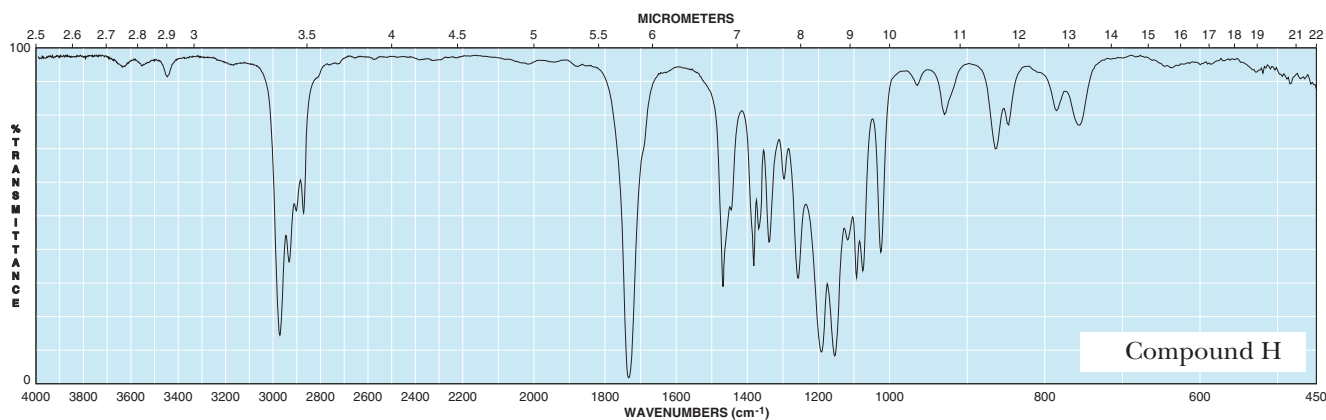
11.26 Examine the following IR spectrum and the molecular formula of compound G, $C_6H_{12}O$: Tell (See Examples 11.4–11.7)

- Its index of hydrogen deficiency.
- The number of rings or pi bonds (or both) in compound G.
- What structural features would account for this index of hydrogen deficiency.



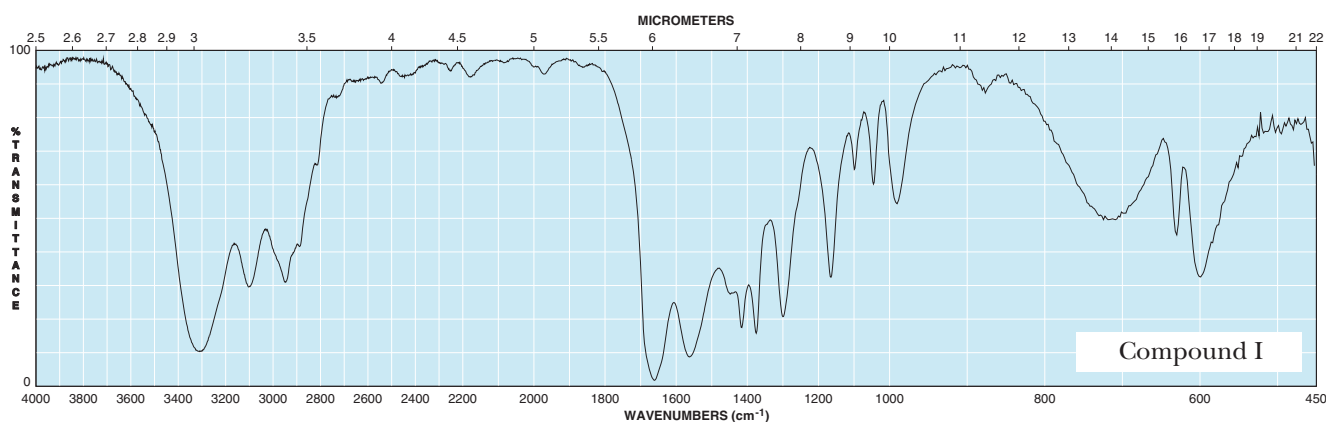
11.27 Examine the following IR spectrum and the molecular formula of compound H, $C_6H_{12}O_2$: Tell (See Examples 11.4–11.7)

- Its index of hydrogen deficiency.
- The number of rings or pi bonds (or both) in compound H.
- The oxygen-containing functional group(s) compound H might contain.



11.28 Examine the following IR spectrum and the molecular formula of compound I, C_3H_7NO : Tell (See Examples 11.4–11.7)

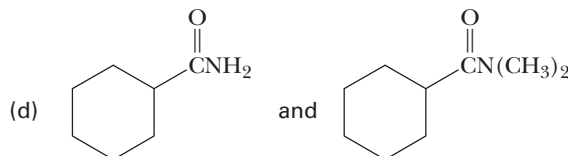
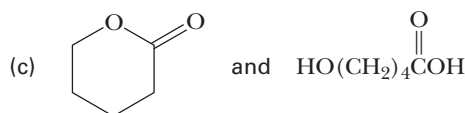
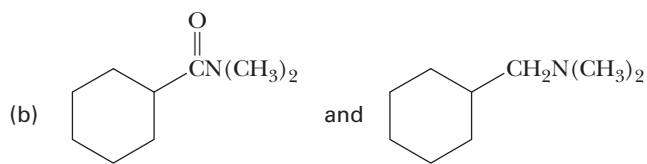
- Its index of hydrogen deficiency.
- The number of rings or pi bonds (or both) in compound I.
- The oxygen- and nitrogen-containing functional group(s) in compound I.



11.29 Show how IR spectroscopy can be used to distinguish between the compounds in each of the following pairs: (See Examples 11.2, 11.3)

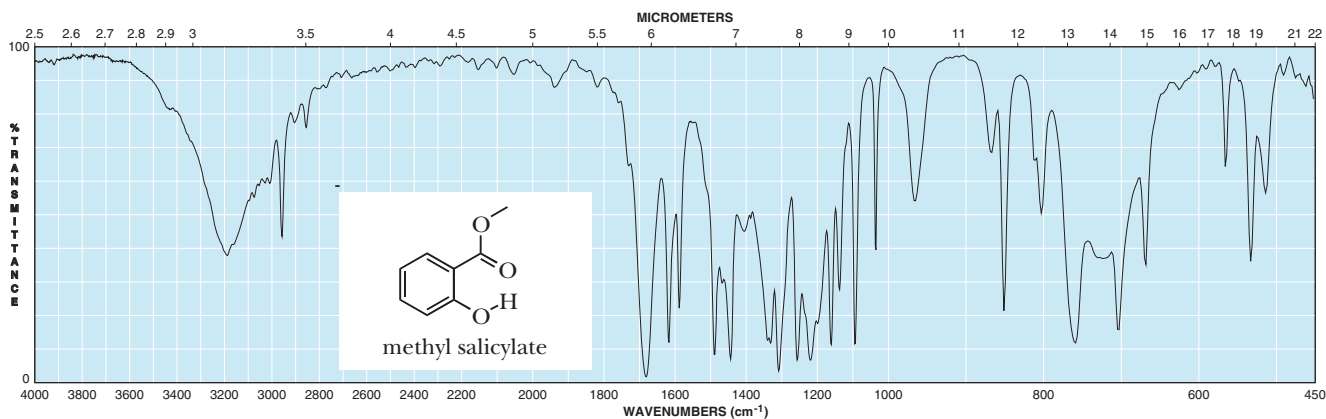
- 1-Butanol and diethyl ether
- Butanoic acid and 1-butanol
- Butanoic acid and 2-butanone
- Butanal and 1-butene
- 2-Butanone and 2-butanol
- Butane and 2-butene

11.30 For each pair of compounds that follows, list one major feature that appears in the IR spectrum of one compound, but not the other. In your answer, state what type of bond vibration is responsible for the spectral feature you list, and give its approximate position in the IR spectrum. (See Examples 11.2, 11.3)



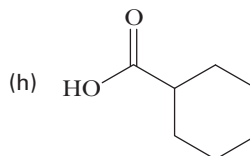
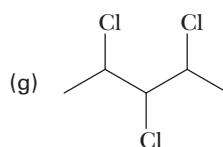
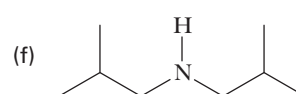
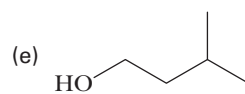
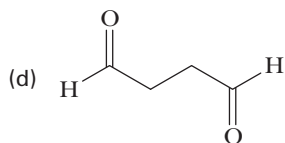
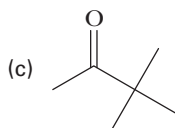
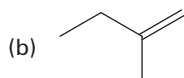
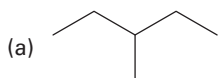
***11.31** Following are an infrared spectrum and a structural formula for methyl salicylate, the fragrant component of oil of wintergreen. On this spectrum, locate the absorption peak(s) due to (See Examples 11.2, 11.3)

- O—H stretching of the hydrogen-bonded —OH group (very broad and of medium intensity).
- C—H stretching of the aromatic ring (sharp and of weak intensity).
- C=O stretching of the ester group (sharp and of strong intensity).
- C=C stretching of the aromatic ring (sharp and of medium intensity).



Section 11.8 Equivalency of Hydrogens and Carbons

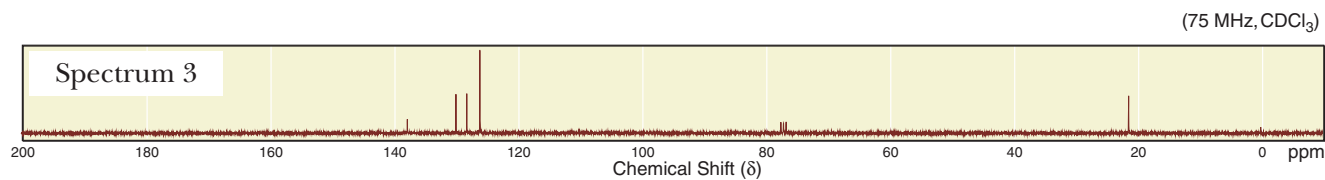
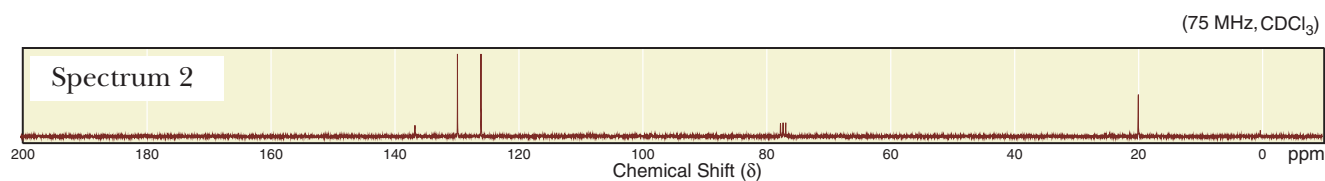
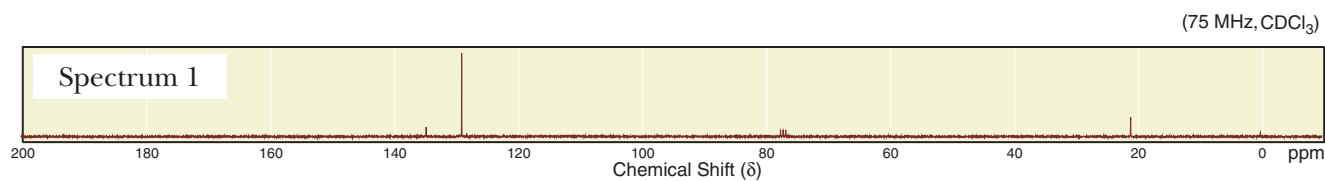
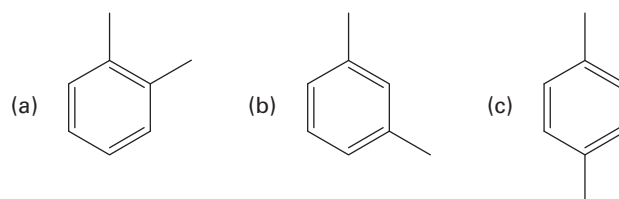
11.32 Determine the number of signals you would expect to see in the $^1\text{H-NMR}$ spectrum of each of the following compounds. (See Example 11.9)



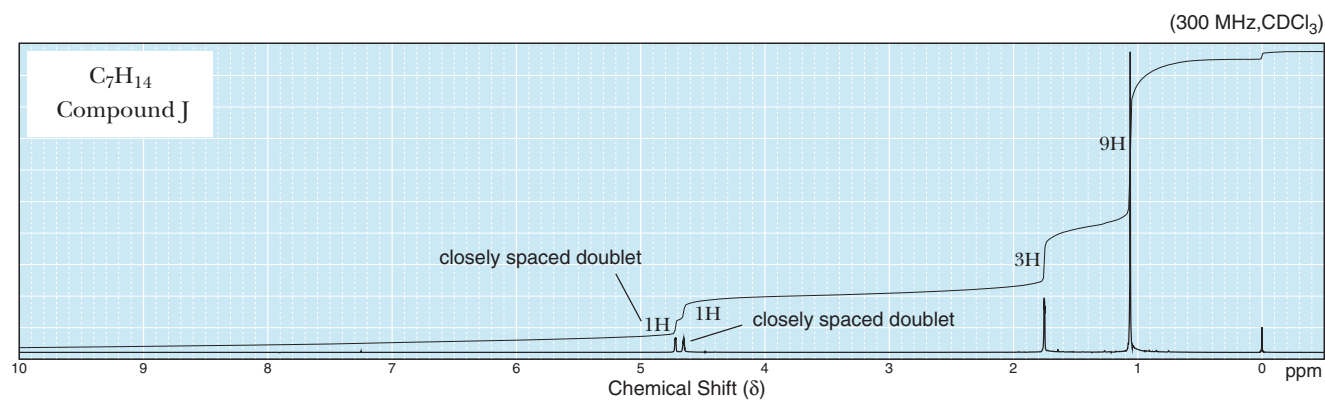
11.33 Determine the number of signals you would expect to see in the $^{13}\text{C-NMR}$ spectrum of each of the compounds in Problem 11.31. (See Example 11.14)

Section 11.13 Interpreting $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ Spectra

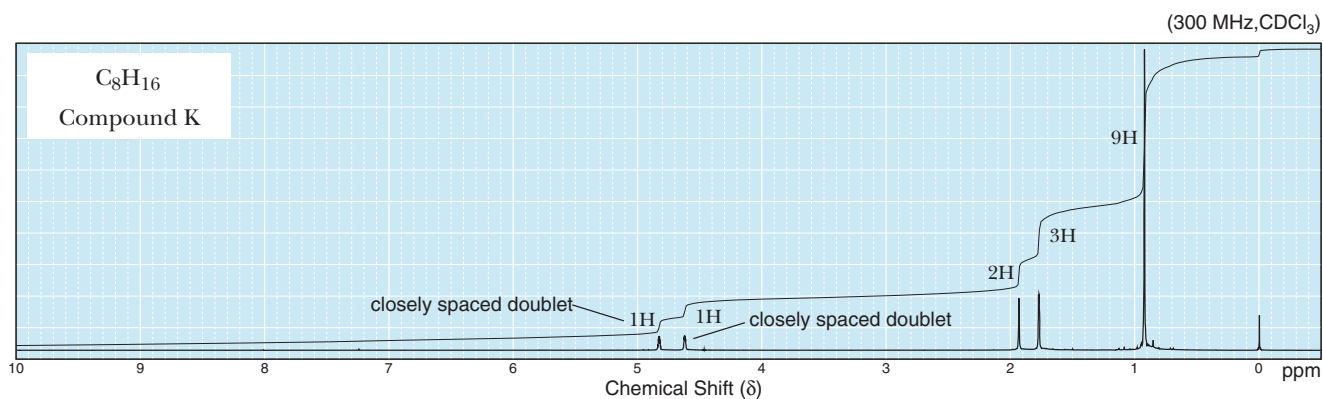
11.34 Following are structural formulas for the constitutional isomers of xylene and three sets of $^{13}\text{C-NMR}$ spectra. Assign each constitutional isomer its correct spectrum. (See Example 11.17)



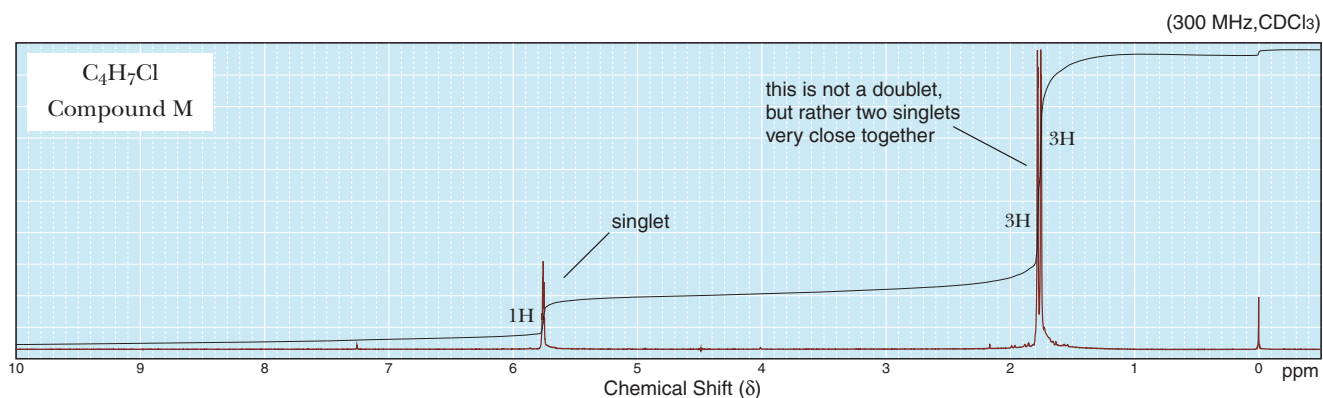
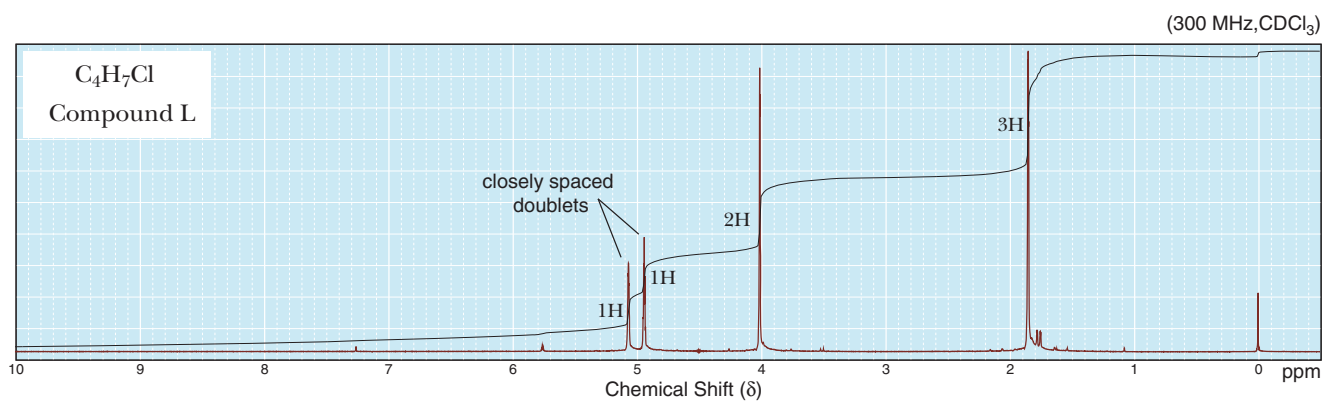
11.35 Following is a $^1\text{H-NMR}$ spectrum for compound J, with the molecular formula C_7H_{14} . Compound J decolorizes a solution of bromine in carbon tetrachloride. Propose a structural formula for compound J. (See Examples 11.15, 11.16)



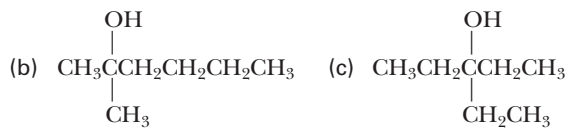
- 11.36 Following is a $^1\text{H-NMR}$ spectrum for compound K, with the molecular formula C_8H_{16} . Compound K decolorizes a solution of Br_2 in CCl_4 . Propose a structural formula for compound K. (See Examples 11.15, 11.16)



- 11.37 Following are the $^1\text{H-NMR}$ spectra of compounds L and M, each with the molecular formula $\text{C}_4\text{H}_7\text{Cl}$. Each compound decolorizes a solution of Br_2 in CCl_4 . Propose structural formulas for compounds L and M. (See Examples 11.15, 11.16)



- 11.38 Following are the structural formulas of three alcohols with the molecular formula $\text{C}_7\text{H}_{16}\text{O}$ and three sets of $^{13}\text{C-NMR}$ spectral data. Assign each constitutional isomer to its correct spectral data. (See Example 11.17)



Spectrum 1	Spectrum 2	Spectrum 3
74.66	70.97	62.93
30.54	43.74	32.79
7.73	29.21	31.86
	26.60	29.14
	23.27	25.75
	14.09	22.63
		14.08

11.39 Alcohol N, with the molecular formula $C_6H_{14}O$, undergoes acid-catalyzed dehydration when it is warmed with phosphoric acid, giving compound O, with the molecular formula C_6H_{12} , as the major product. A 1H -NMR spectrum of compound N shows peaks at δ 0.89 (t, 6H), 1.12 (s, 3H), 1.38 (s, 1H), and 1.48 (q, 4H). The ^{13}C -NMR spectrum of compound N shows peaks

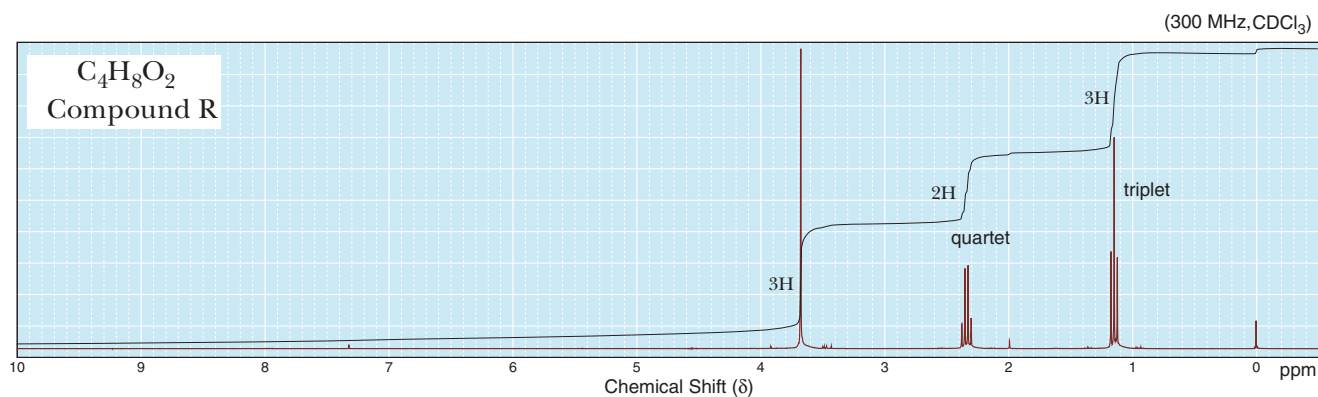
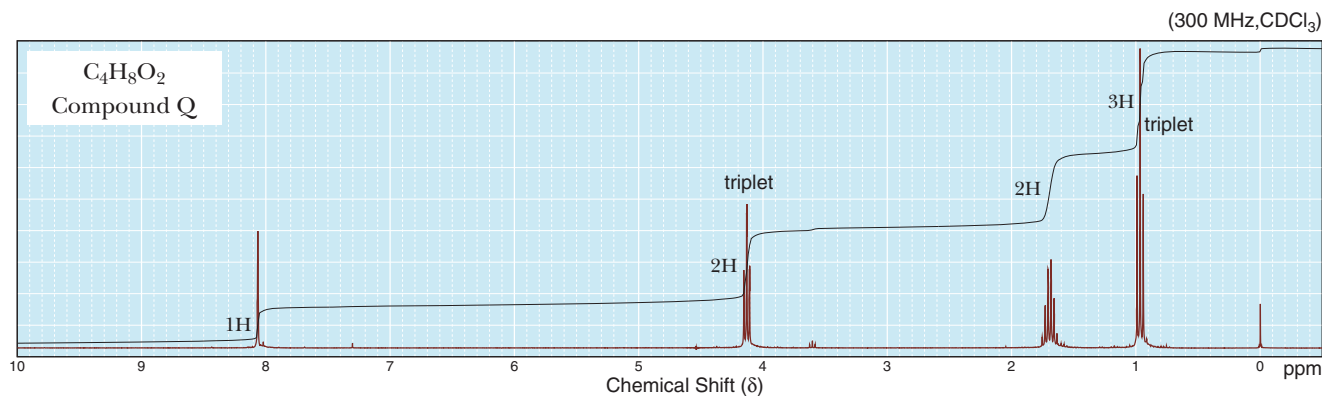
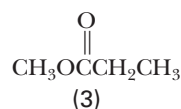
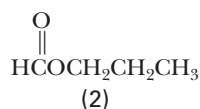
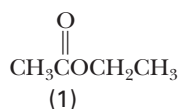
at δ 72.98, 33.72, 25.85, and 8.16. Propose structural formulas for compounds N and O. (See Examples 11.15–11.17)

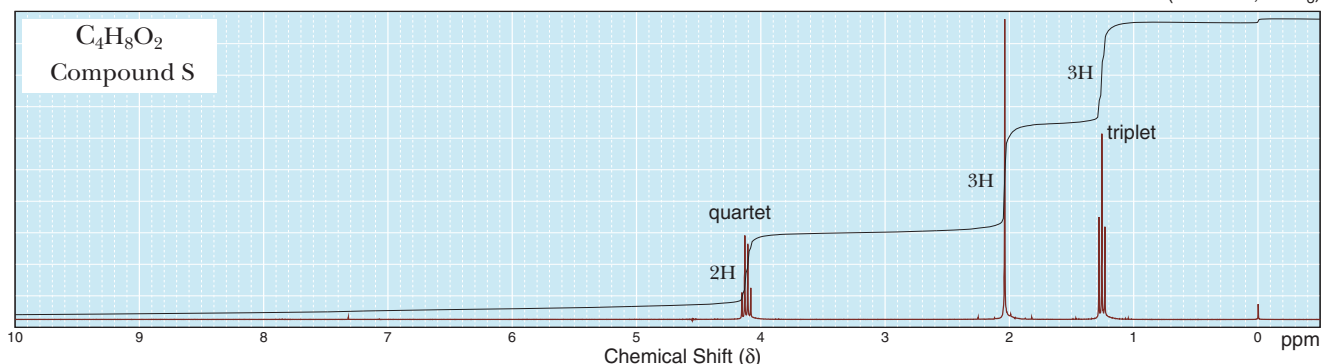
11.40 Compound P, $C_6H_{14}O$, does not react with sodium metal and does not discharge the color of Br_2 in CCl_4 . The 1H -NMR spectrum of compound P consists of only two signals: a 12H doublet at δ 1.1 and a 2H septet at δ 3.6. Propose a structural formula for compound P. (See Examples 11.15, 11.16)

11.41 Propose a structural formula for each haloalkane: (See Examples 11.15, 11.16)

- (a) $C_2H_4Br_2$ δ 2.5 (d, 3H) and 5.9 (q, 1H)
- (b) $C_4H_8Cl_2$ δ 1.67 (d, 6H) and 2.15 (q, 2H)
- (c) $C_5H_8Br_4$ δ 3.6 (s, 8H)
- (d) C_4H_9Br δ 1.1 (d, 6H), 1.9 (m, 1H), and 3.4 (d, 2H)
- (e) $C_5H_{11}Br$ δ 1.1 (s, 9H) and 3.2 (s, 2H)
- (f) $C_7H_{15}Cl$ δ 1.1 (s, 9H) and 1.6 (s, 6H)

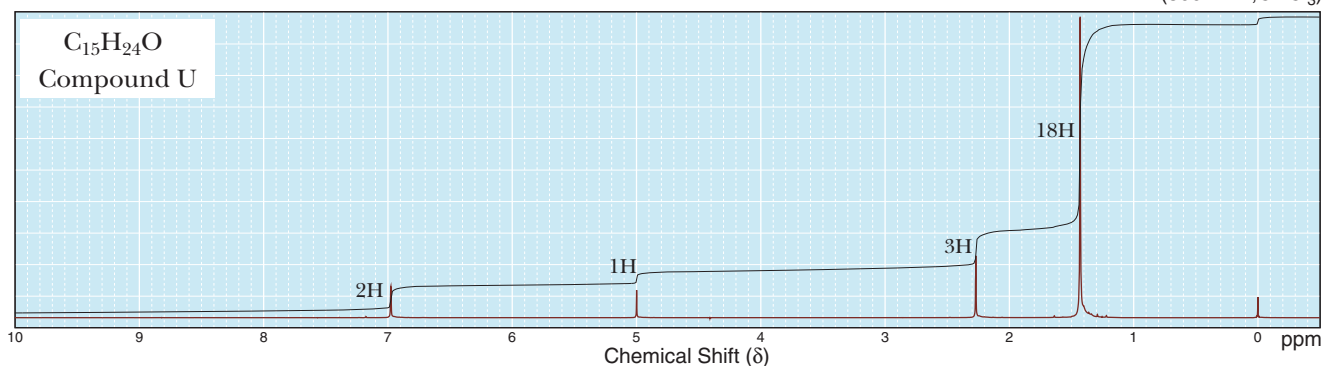
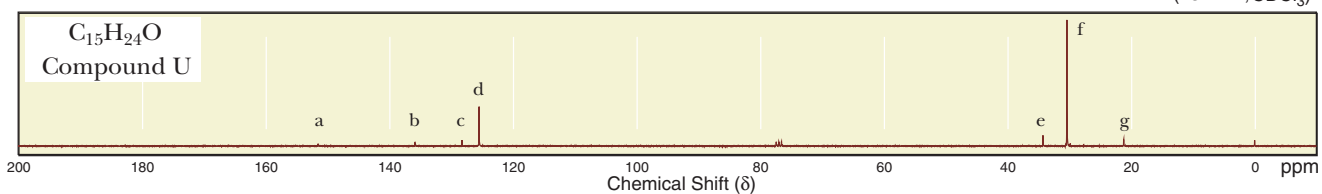
11.42 Following are structural formulas for esters (1), (2), and (3) and three 1H -NMR spectra. Assign each compound its correct spectrum (Q, R, or S) and assign all signals to their corresponding hydrogens. (See Examples 11.15, 11.16)



(300 MHz, CDCl₃)

11.43 Compound T, C₁₀H₁₀O₂, is insoluble in water, 10% NaOH, and 10% HCl. A ¹H-NMR spectrum of compound T shows signals at δ 2.55 (s, 6H) and 7.97 (s, 4H). A ¹³C-NMR spectrum of compound T shows four signals. From this information, propose a structural formula for T. (See Examples 11.15–11.17)

11.44 Compound U, C₁₅H₂₄O, is used as an antioxidant in many commercial food products, synthetic rubbers, and petroleum products. Propose a structural formula for compound U based on its ¹H-NMR and ¹³C-NMR spectra. (See Example 11.15–11.17)

(300 MHz, CDCl₃)(75 MHz, CDCl₃)

11.45 Propose a structural formula for these compounds, each of which contains an aromatic ring: (See Examples 11.15, 11.16)

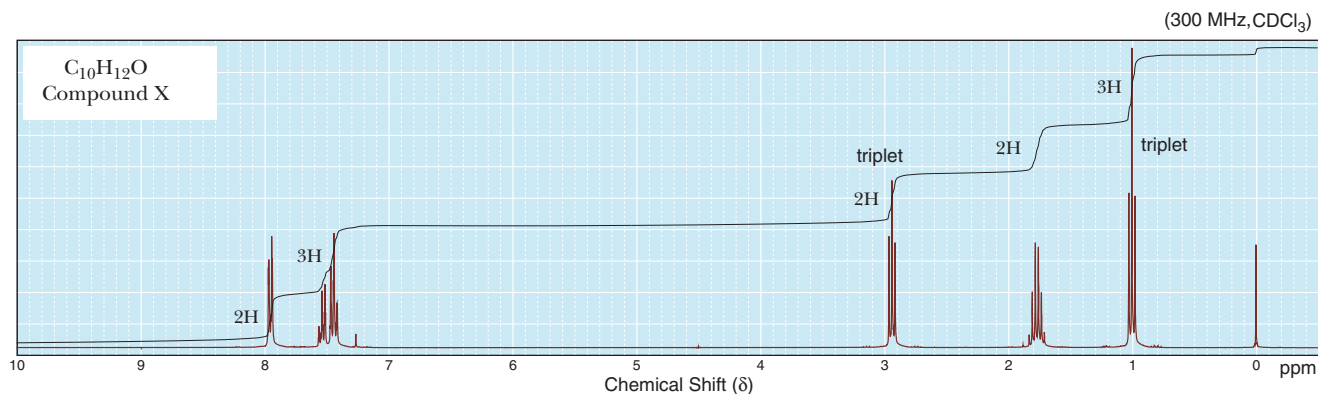
- C₉H₁₀O δ 1.2 (t, 3H), 3.0 (q, 2H), and 7.4–8.0 (m, 5H)
- C₁₀H₁₂O₂ δ 2.2 (s, 3H), 2.9 (t, 2H), 4.3 (t, 2H), and 7.3 (s, 5H)
- C₁₀H₁₄ δ 1.2 (d, 6H), 2.3 (s, 3H), 2.9 (septet, 1H), and 7.0 (s, 4H)
- C₈H₉Br δ 1.8 (d, 3H), 5.0 (q, 1H), and 7.3 (s, 5H)

11.46 Compound V, with the molecular formula C₉H₁₂O, readily undergoes acid-catalyzed dehydration to give compound W, with the molecular formula C₉H₁₀. A ¹H-NMR spectrum of compound V shows signals at δ 0.91 (t, 3H), 1.78 (m, 2H), 2.26 (s, 1H), 4.55 (t, 1H), and 7.31 (m, 5H). From this information, propose structural formulas for compounds V and W. (See Examples 11.15, 11.16)

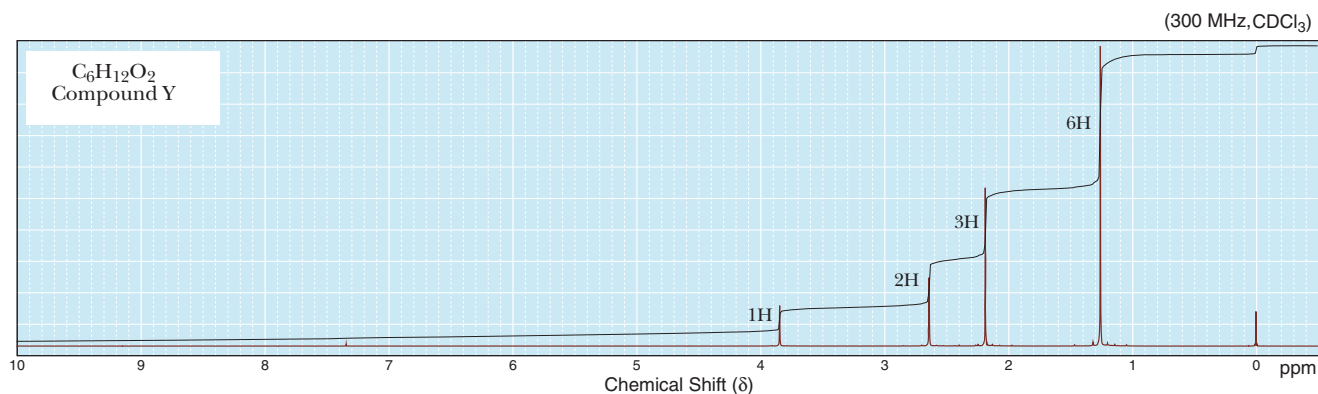
11.47 Propose a structural formula for each ketone: (See Examples 11.15, 11.16)

- C₄H₈O δ 1.0 (t, 3H), 2.1 (s, 3H), and 2.4 (q, 2H)
- C₇H₁₄O δ 0.9 (t, 6H), 1.6 (sextet, 4H), and 2.4 (t, 4H)

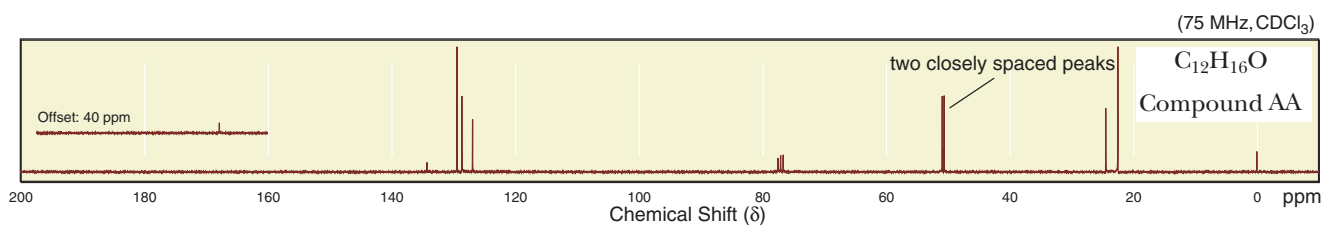
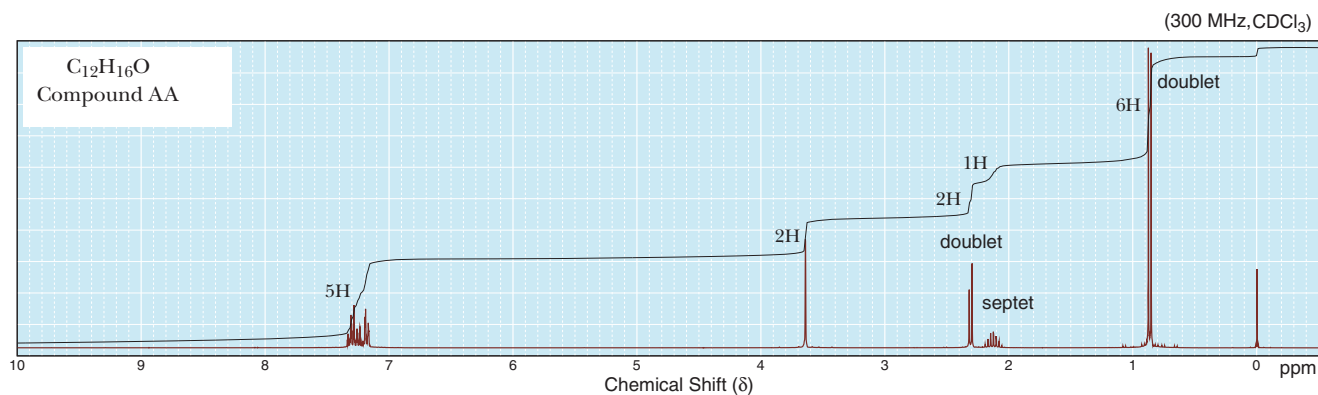
11.48 Propose a structural formula for compound X, a ketone with the molecular formula $C_{10}H_{12}O$: (See Examples 11.15, 11.16)



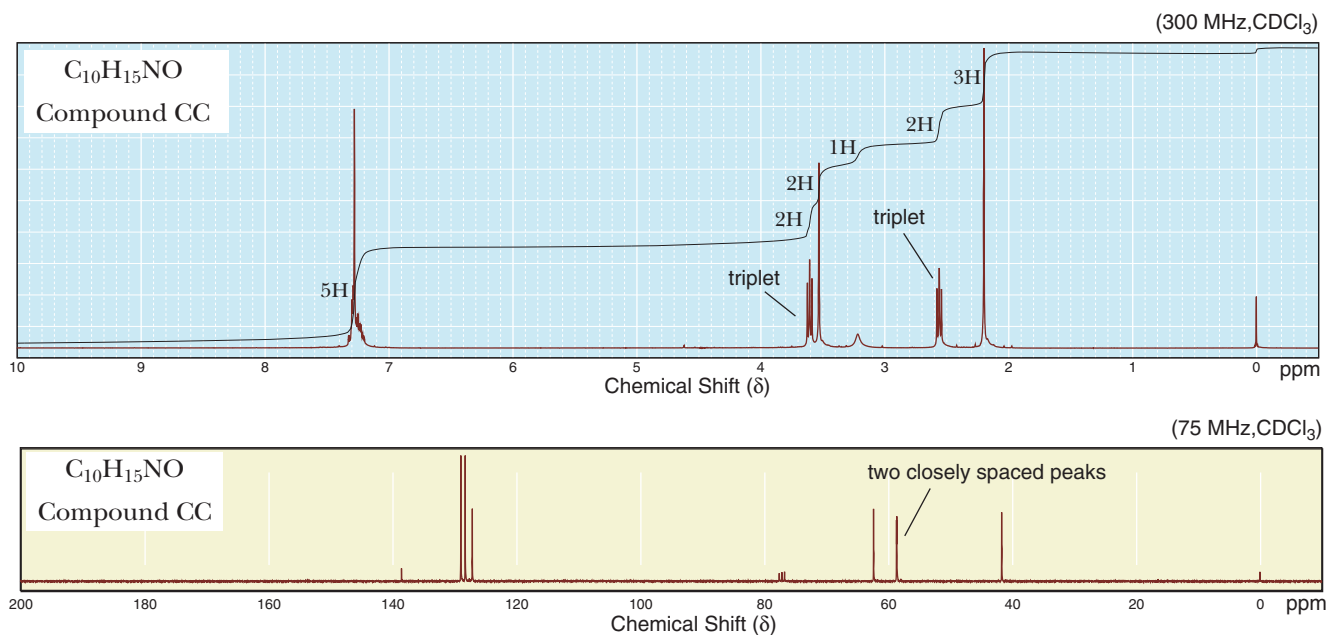
11.49 Following is a 1H -NMR spectrum for compound Y, with the molecular formula $C_6H_{12}O_2$. Compound Y undergoes acid-catalyzed dehydration to give compound Z, $C_6H_{10}O$. Propose structural formulas for compounds Y and Z. (See Examples 11.15, 11.16)



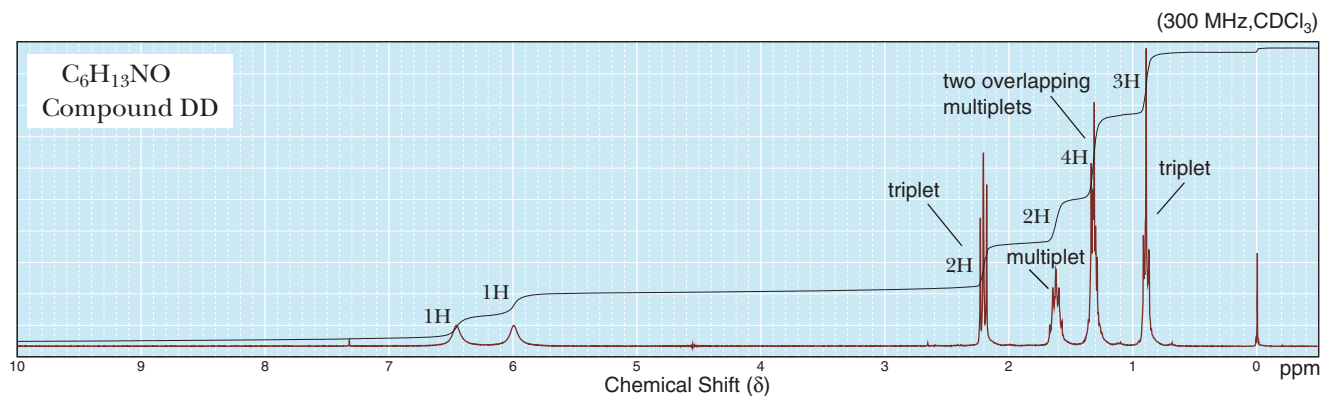
11.50 Propose a structural formula for compound AA, with the molecular formula $C_{12}H_{16}O$. Following are its 1H -NMR and ^{13}C -NMR spectra: (See Examples 11.15–11.17)



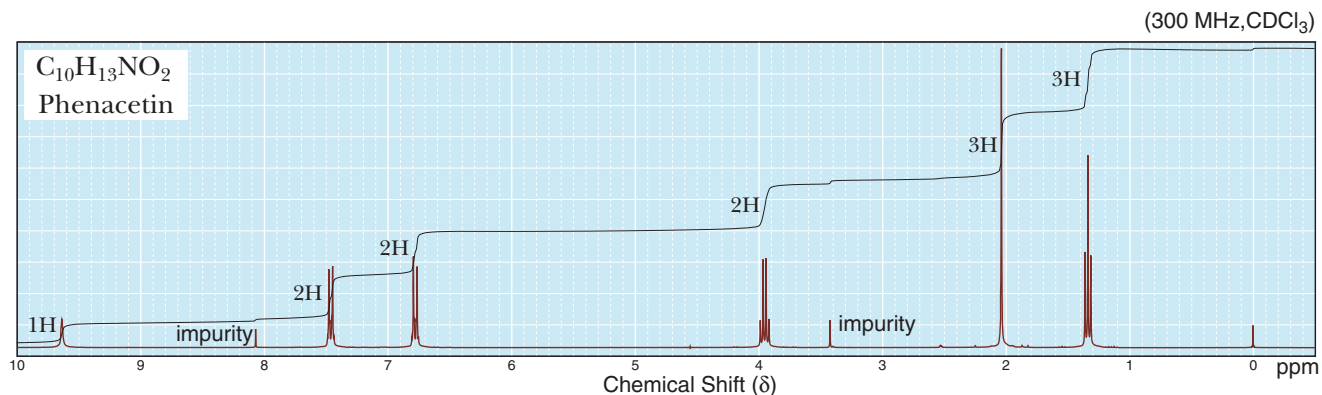
11.54 Following are $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of compound CC, with the molecular formula $\text{C}_{10}\text{H}_{15}\text{NO}$. Propose a structural formula for this compound. (See Examples 11.15–11.17)



11.55 Propose a structural formula for amide DD, with the molecular formula $\text{C}_6\text{H}_{13}\text{NO}$: (See Examples 11.15, 11.16)

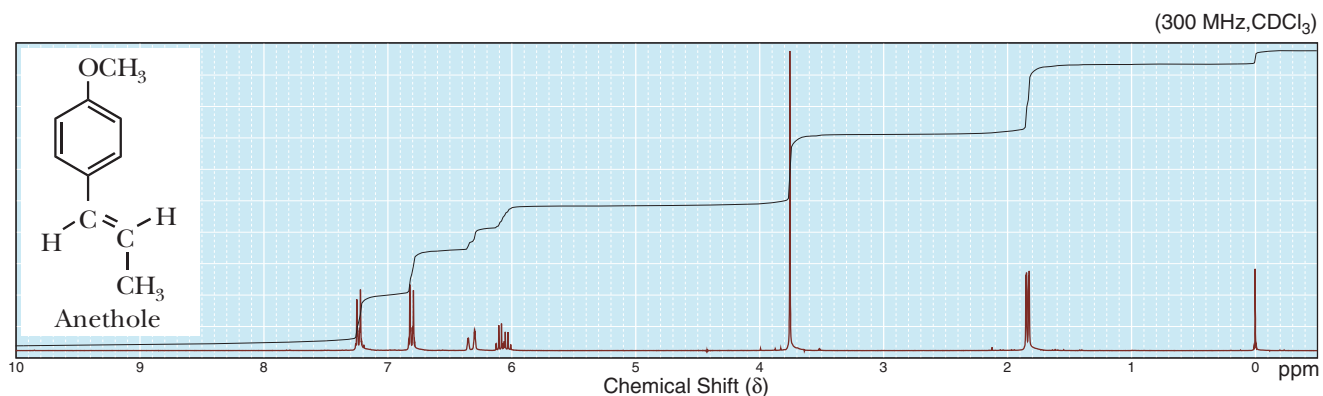


11.56 Propose a structural formula for the analgesic phenacetin, with molecular formula $\text{C}_{10}\text{H}_{13}\text{NO}_2$, based on its $^1\text{H-NMR}$ spectrum: (See Examples 11.15, 11.16)

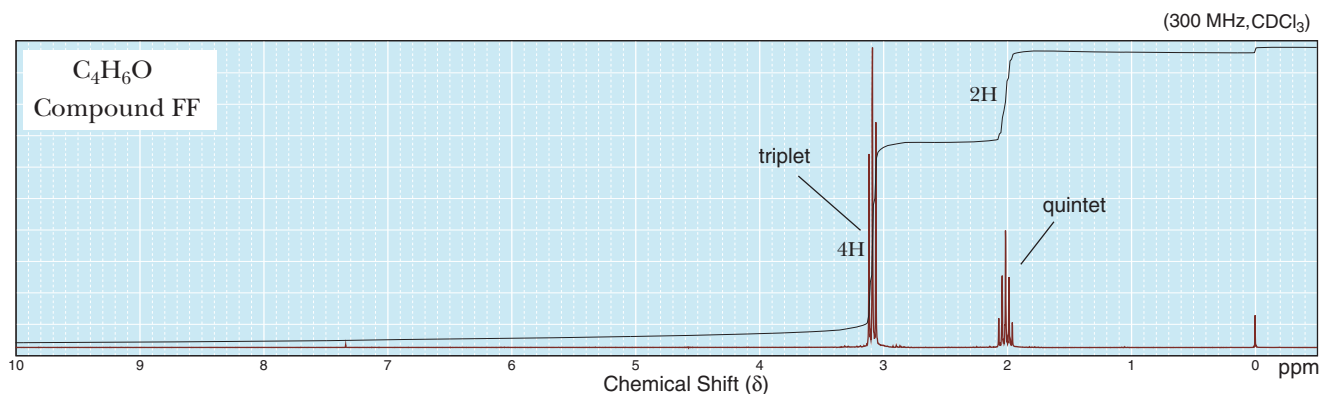
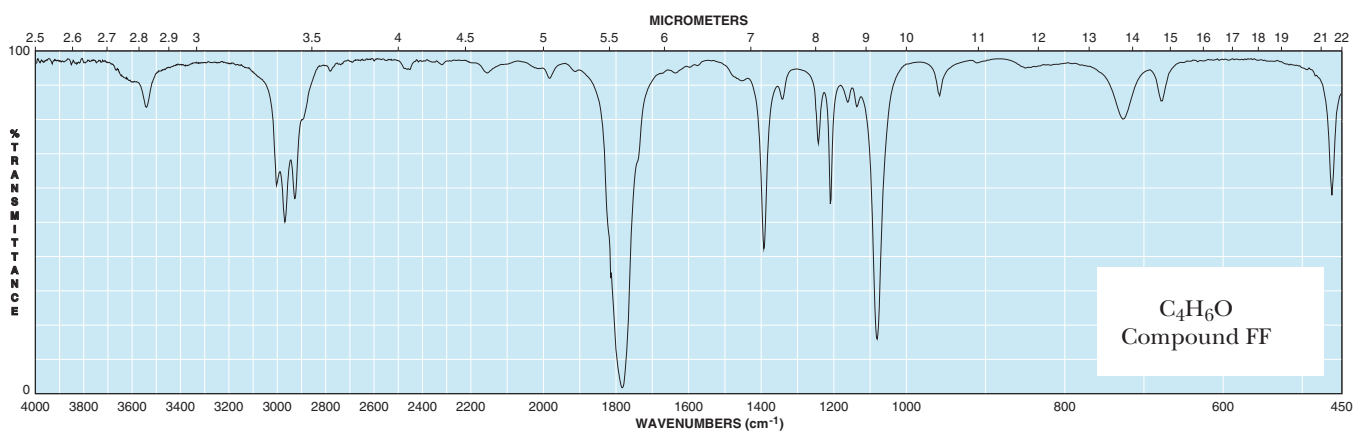


11.57 Propose a structural formula for compound EE, an oily liquid with the molecular formula $C_8H_9NO_2$. Compound EE is insoluble in water and aqueous NaOH, but dissolves in 10% HCl. When its solution in HCl is neutralized with NaOH, compound EE is recovered unchanged. A 1H -NMR spectrum of compound EE shows signals at δ 3.84 (s, 3H), 4.18 (s, 2H), 7.60 (d, 2H), and 8.70 (d, 2H). (See Examples 11.15, 11.16)

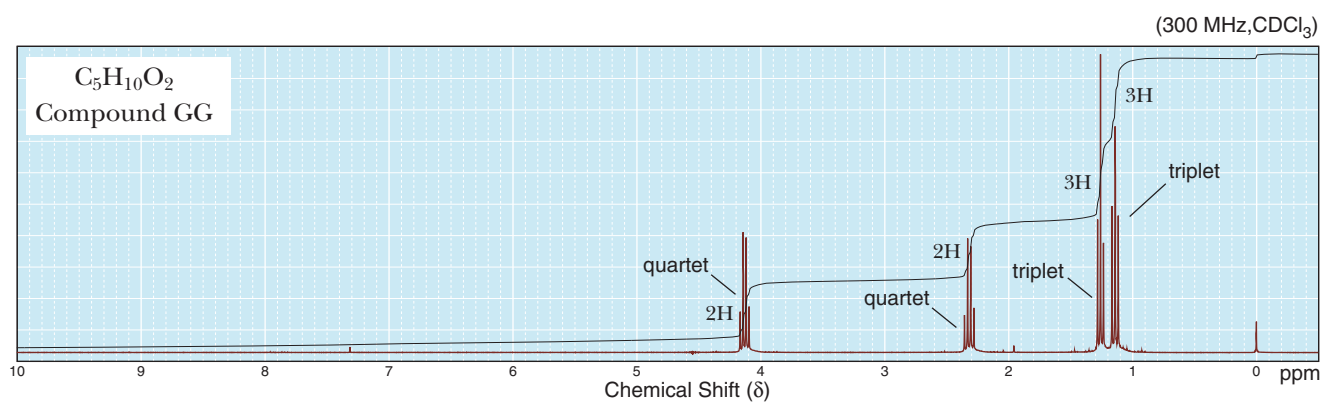
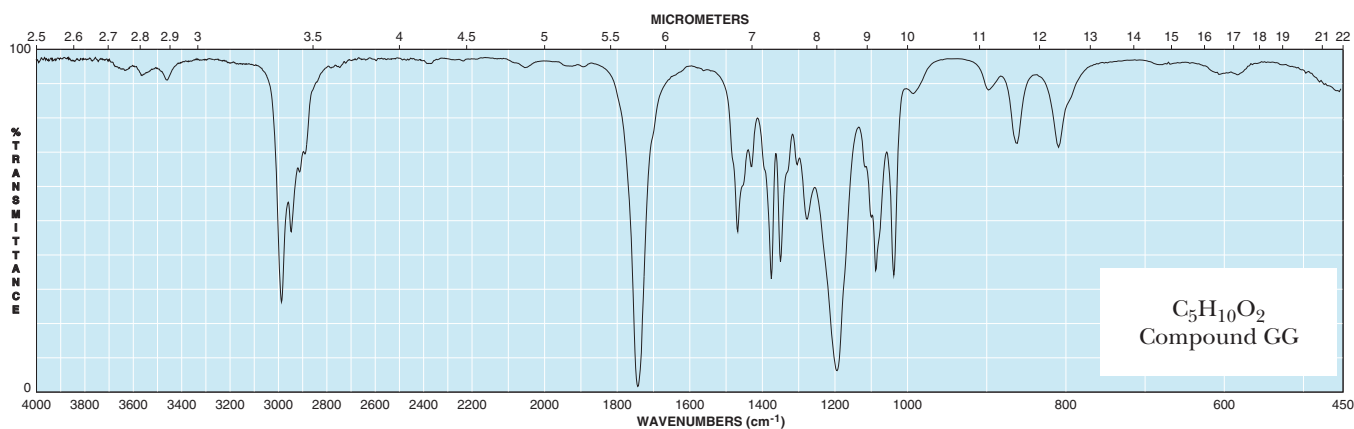
11.58 Following is a 1H -NMR spectrum and a structural formula for anethole, $C_{10}H_{12}O$, a fragrant natural product obtained from anise. Using the line of integration, determine the number of protons giving rise to each signal. Show that this spectrum is consistent with the structure of anethole. (See Examples 11.15, 11.16)



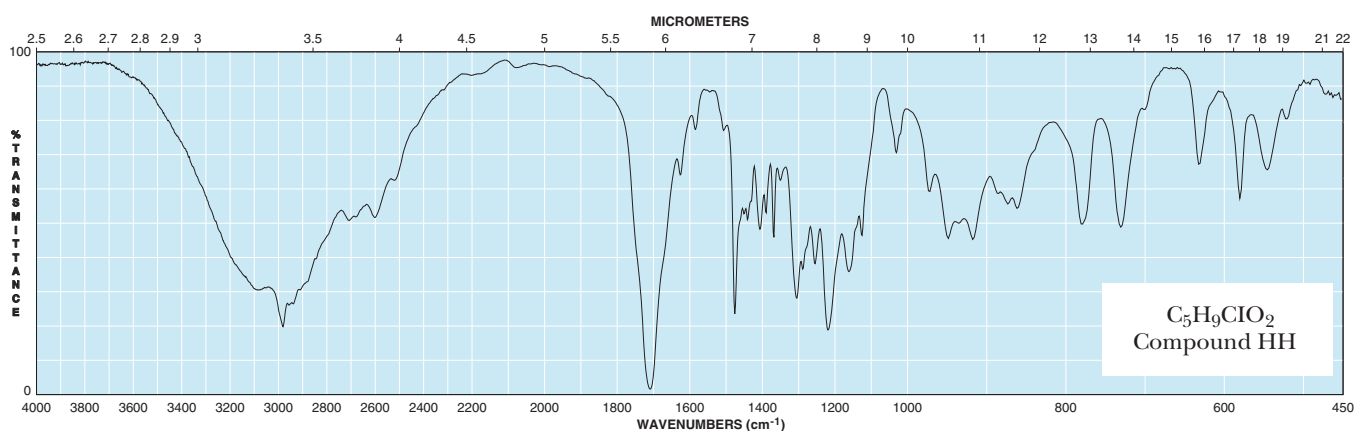
11.59 Propose a structural formula for compound FF, with the molecular formula C_4H_6O , based on the following IR and 1H -NMR spectra: (See Examples 11.15, 11.16)

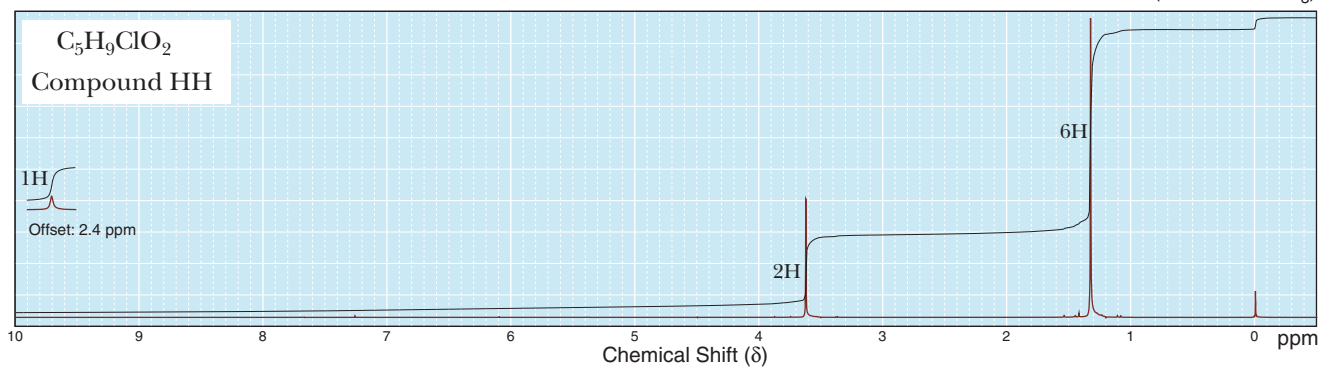


11.60 Propose a structural formula for compound GG, with the molecular formula $C_5H_{10}O_2$, based on the following IR and 1H -NMR spectra: (See Examples 11.15, 11.16)

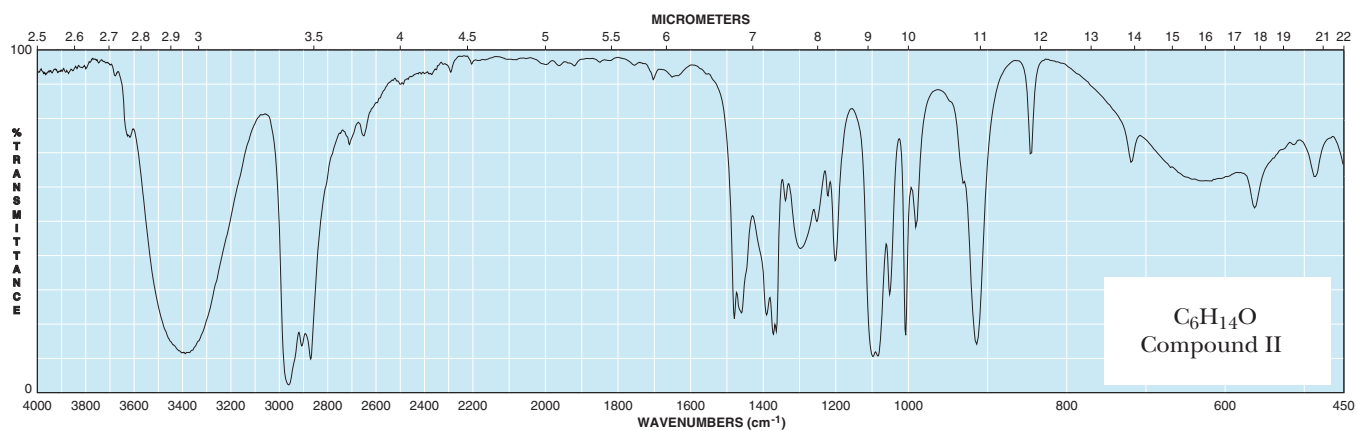
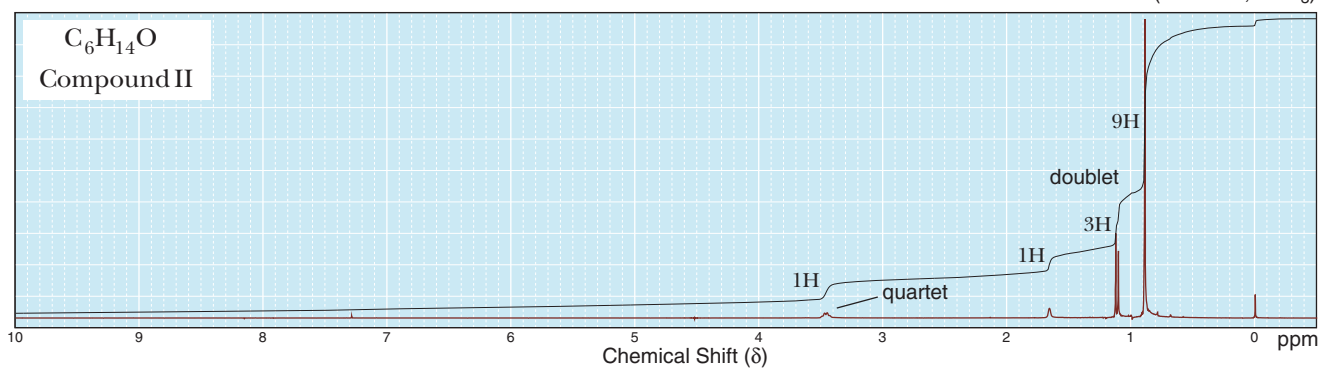


11.61 Propose a structural formula for compound HH, with the molecular formula $C_5H_9ClO_2$, based on the following IR and 1H -NMR spectra: (See Examples 11.15, 11.16)



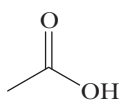
(300 MHz, CDCl₃)

11.62 Propose a structural formula for compound II, with the molecular formula C₆H₁₄O, based on the following IR and ¹H-NMR spectra: (See Examples 11.15, 11.16)

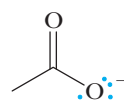
(300 MHz, CDCl₃)

LOOKING AHEAD

11.63 Predict the position of the C=O stretching absorption in acetate ion relative to that in acetic acid:

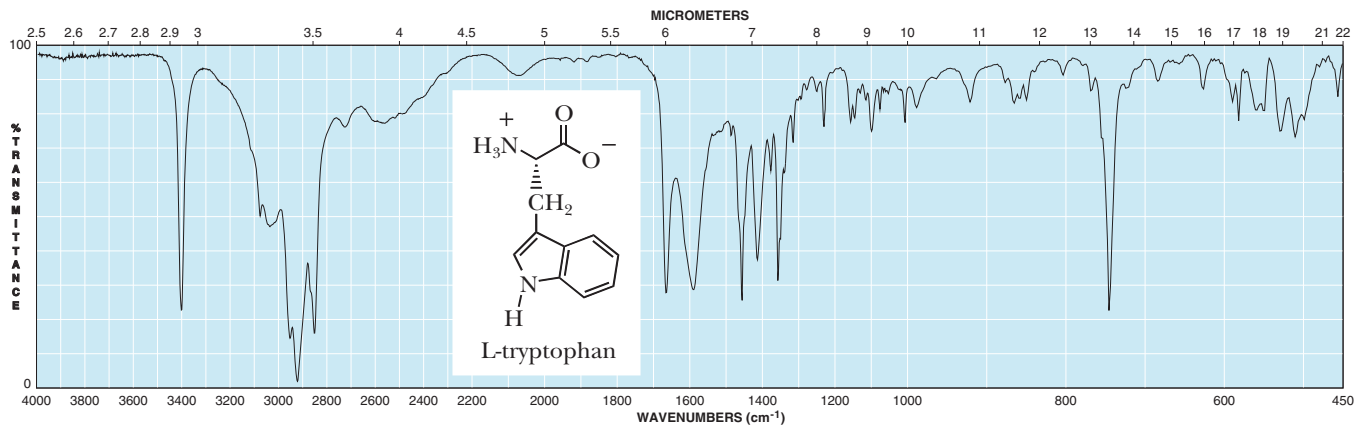


Acetic acid



Acetate ion

***11.64** Following is the IR spectrum of L-tryptophan, a naturally occurring amino acid that is abundant in foods such as turkey:

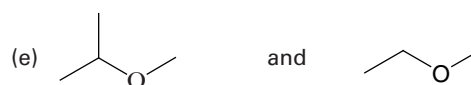
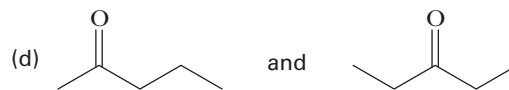
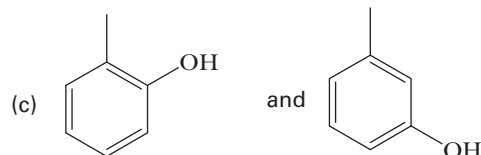
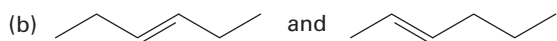
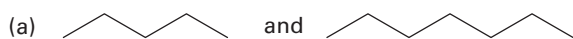


For many years, the L-tryptophan in turkey was believed to make people drowsy after Thanksgiving dinner. Scientists now know that consuming L-tryptophan makes one drowsy only if the compound is taken on an empty stomach. Therefore, it is unlikely that one's

Thanksgiving Day turkey is the cause of drowsiness. Notice that L-tryptophan contains one stereocenter. Its enantiomer, D-tryptophan, does not occur in nature but can be synthesized in the laboratory. What would the IR spectrum of D-tryptophan look like?

GROUP LEARNING ACTIVITIES

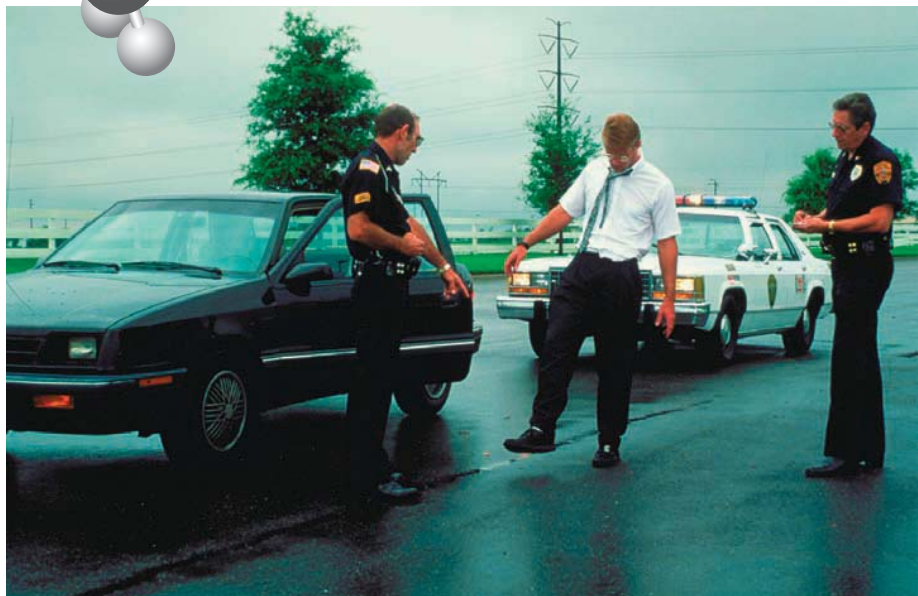
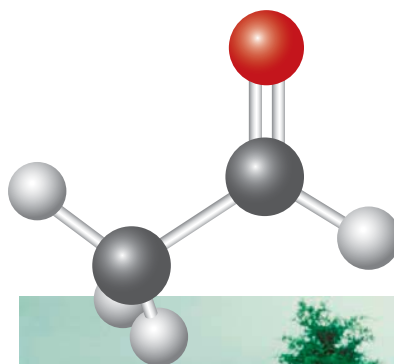
11.65 Discuss whether IR or NMR spectroscopy could be used to distinguish between the following pairs of molecules. Be very specific in describing the spectral data that would allow you to identify each compound. Assume that you do not have the reference spectra of either molecule.



12

Aldehydes and Ketones

Ethanol from alcoholic beverages is first metabolized to acetaldehyde before being broken down further in the body. The reactivity of the carbonyl group of acetaldehyde allows it to bind to proteins in the body, the products of which lead to tissue damage and organ disease. Inset: A model of acetaldehyde. (Novastock/Stock Connection/Glow Images)



KEY QUESTIONS

- 12.1 What Are Aldehydes and Ketones?
- 12.2 How Are Aldehydes and Ketones Named?
- 12.3 What Are the Physical Properties of Aldehydes and Ketones?
- 12.4 What Is the Most Common Reaction Theme of Aldehydes and Ketones?
- 12.5 What Are Grignard Reagents, and How Do They React with Aldehydes and Ketones?
- 12.6 What Are Hemiacetals and Acetals?
- 12.7 How Do Aldehydes and Ketones React with Ammonia and Amines?

- 12.8 What Is Keto–Enol Tautomerism?
- 12.9 How Are Aldehydes and Ketones Oxidized?
- 12.10 How Are Aldehydes and Ketones Reduced?

HOW TO

- 12.1 How to Predict the Product of a Grignard Reaction
- 12.2 How to Determine the Reactants Used to Synthesize a Hemiacetal or Acetal

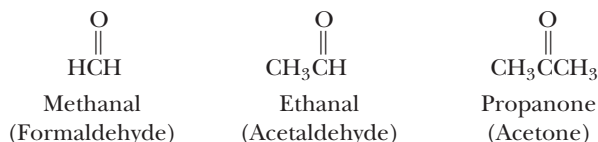
CHEMICAL CONNECTIONS

- 12A A Green Synthesis of Adipic Acid

IN THIS AND several of the following chapters, we study the physical and chemical properties of compounds containing the carbonyl group, $C=O$. Because this group is the functional group of aldehydes, ketones, and carboxylic acids and their derivatives, it is one of the most important functional groups in organic chemistry and in the chemistry of biological systems. The chemical properties of the carbonyl group are straightforward, and an understanding of its characteristic reaction themes leads very quickly to an understanding of a wide variety of organic reactions.

12.1 What Are Aldehydes and Ketones?

The functional group of an **aldehyde** is a carbonyl group bonded to a hydrogen atom (Section 1.7C). In methanal (common name: formaldehyde), the simplest aldehyde, the carbonyl group is bonded to two hydrogen atoms. In other aldehydes, it is bonded to one hydrogen atom and one carbon atom. The functional group of a **ketone** is a carbonyl group bonded to two carbon atoms (Section 1.7C). Following are Lewis structures for the aldehydes methanal and ethanal, and a Lewis structure for propanone, the simplest ketone. Under each in parentheses is its common name:



Aldehyde A compound containing a carbonyl group bonded to hydrogen (a CHO group).

Ketone A compound containing a carbonyl group bonded to two carbons.

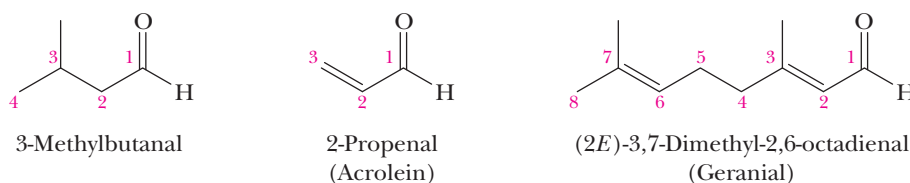
A carbon–oxygen double bond consists of one sigma bond formed by the overlap of sp^2 hybrid orbitals of carbon and oxygen and one pi bond formed by the overlap of parallel $2p$ orbitals. The two nonbonding pairs of electrons on oxygen lie in the two remaining sp^2 hybrid orbitals (Figure 1.20).

12.2 How Are Aldehydes and Ketones Named?

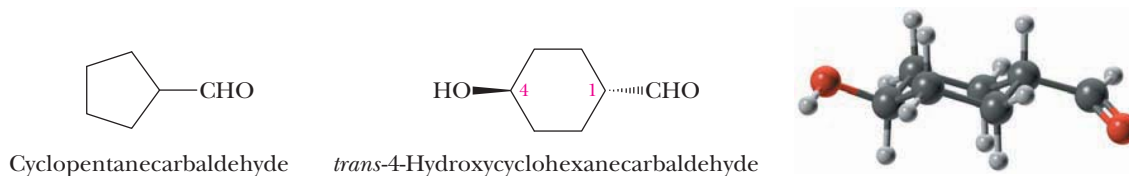
A. IUPAC Nomenclature

The IUPAC system of nomenclature for aldehydes and ketones follows the familiar pattern of selecting the longest chain of carbon atoms that contains the functional group as the parent alkane. We show the aldehyde group by changing the suffix *-e* of the parent alkane to *-al*, as in methanal (Section 3.5). Because the carbonyl group of an aldehyde can appear only at the end of a parent chain and numbering must start with that group as carbon-1, its position is unambiguous; there is no need to use a number to locate it.

For **unsaturated aldehydes**, the presence of a carbon–carbon double bond is indicated by the infix *-en-*. As with other molecules with both an infix and a suffix, the location of the suffix determines the numbering pattern.



For cyclic molecules in which —CHO is bonded directly to the ring, we name the molecule by adding the suffix *-carbaldehyde* to the name of the ring. We number the atom of the ring bearing the aldehyde group as number 1:



Among the aldehydes for which the IUPAC system retains common names are benzaldehyde and cinnamaldehyde. Note here the alternative ways of writing the phenyl group.