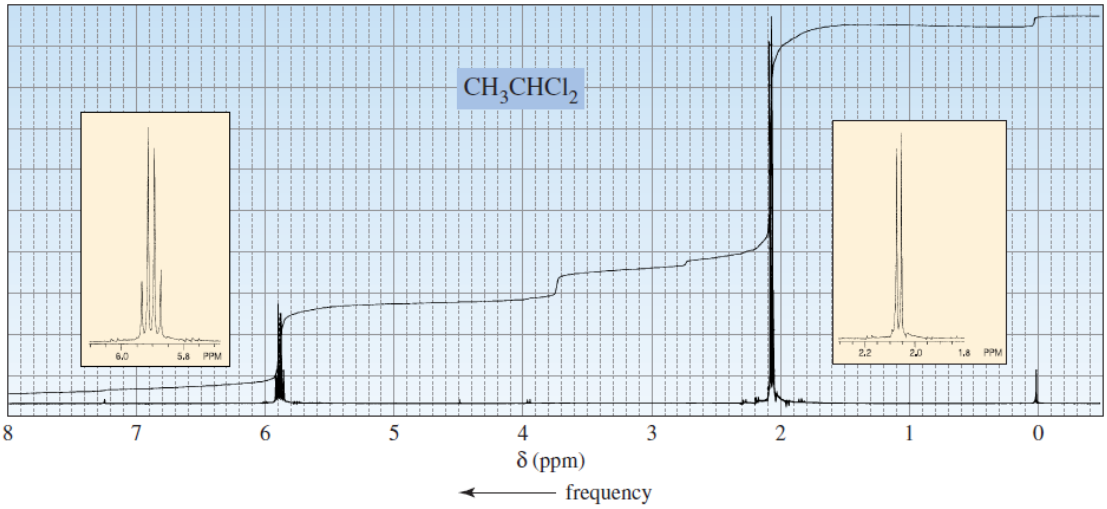
Nuclear magnetic resonance (NMR) spectroscop

Splitting of the Signals:

Notice that the **shapes** of the signals in the ^{1}H NMR spectrum of 1,1-dichloroethane (Figure 14.10) are different from the shapes of the signals in the ^{1}H NMR spectrum of 1-bromo-2,2-dimethylpropane (Figure 14.5). Both signals in Figure 14.5 are singlets (each composed of a single peak), whereas the signal for the methyl protons of 1,1 dichloroethane (the lower-frequency signal) is split into two peaks (a doublet), and the signal for the methine proton is split into four peaks (a quartet). (Magnifications of the doublet and quartet are shown as insets in Figure 14.10.) Splitting is caused by protons bonded to adjacent (i.e., directly attached) carbons. The splitting of a signal is described by the(**N + 1 rule**) **where N is the number of equivalent protons bonded to adjacent carbons**. By "equivalent protons," we mean that the protons bonded to an adjacent carbon are equivalent to each other, but not equivalent to the proton giving rise to the signal. Both signals in Figure 14.5 are singlets because neither the carbon adjacent to the methyl groups nor that adjacent to the methylene group in 1-bromo-2,2-dimethylpropane is bonded to any protons (N + 1 = 0 + 1 = 1).

In contrast, in Figure 14.10, the carbon adjacent to the methyl group in 1,1 dichloroethane is bonded to one proton, so the signal for the methyl protons is split into a doublet(N + 1 = 1 + 1 = 2) .The carbon adjacent to the carbon bonded to the methine proton is bonded to three equivalent protons, so the signal for the methine proton is split into a quartet (N + 1 = 3 + 1 = 4). The number of peaks in a signal is called the multiplicity of the signal. Splitting is always mutual: If the a protons split the b protons, then the b protons must split the a protons. The methine proton and the methyl protons are an example of coupled protons. Coupled protons split each other's signal.



▲ **Figure 14.10**
^{1}H NMR spectrum of 1,1-dichloroethane. The higher-frequency signal is an example of a quartet; the lower-frequency signal is a doublet.

More specifically, the splitting of signals occurs when different kinds of protons are close enough for their magnetic fields to influence one another—called spin–spin coupling. For example, the frequency at which the methyl protons of 1,1-dichloroethane show a signal is influenced by the magnetic field of the methine proton. If the magnetic field of the methine proton aligns **with** that of the applied magnetic field, it will add to the applied magnetic field, causing the methyl protons to show a signal at a slightly higher frequency. On the other hand, if the magnetic field of the methine proton aligns **against** the applied magnetic field, it will subtract from the applied magnetic field and the methyl protons will show a signal at a lower frequency (Figure 14.11). Therefore, the signal for the methyl protons is split into two peaks, one corresponding to the higher frequency and one corresponding to the lower frequency. Because each spin state has almost the same population, about half the methine protons are lined up with the applied magnetic field and about half are lined up against it. Therefore, the two peaks of the doublet approximately the same height and area.

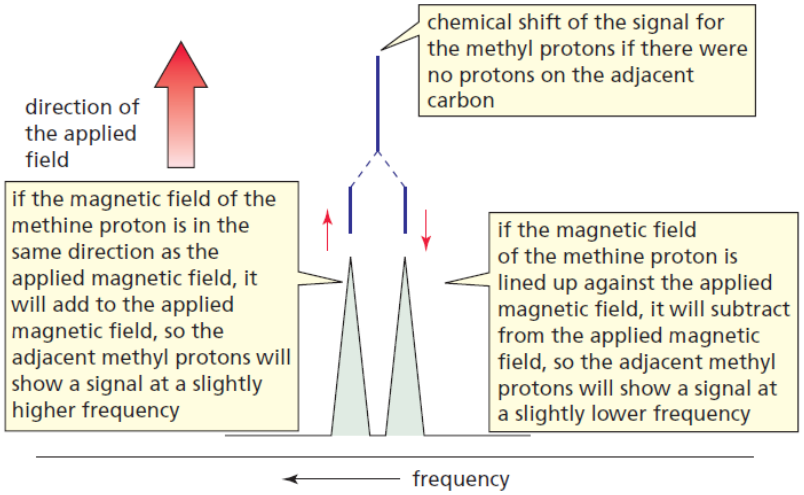


Figure 14.11
The signal for the methyl protons of 1,1-dichloroethane is split into a doublet by the methine proton.

Similarly, the frequency at which the methine proton shows a signal is influenced by the magnetic fields of the three protons bonded to the adjacent carbon. The magnetic fields of each of the three methyl protons can align with the applied magnetic field, two can align with the field and one against it, one can align with it and two against it, or all three can align against it. Because the magnetic field that the methane proton senses is affected in four different ways, its signal is a quartet (Figure 14.12).

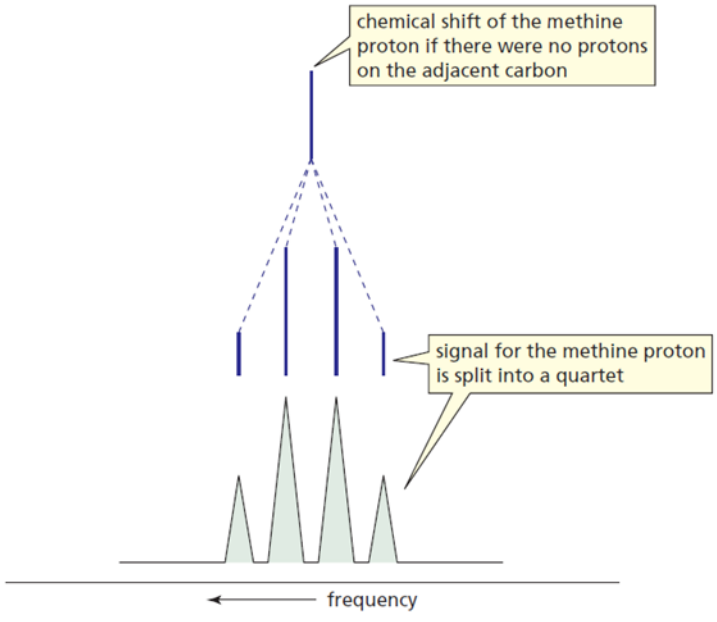
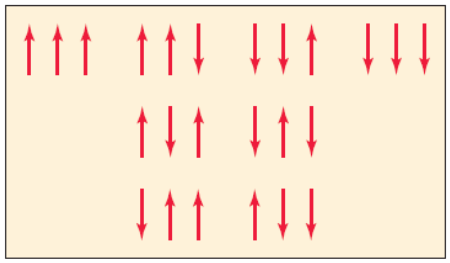


Figure 14.12
The signal for the methine proton of 1,1-dichloroethane is split into a quartet by the methyl protons.

The relative intensities of the peaks in a signal reflect the number of ways the neighboring protons can be aligned relative to the applied magnetic field. For example, a quartet has relative peak intensities of (1 : 3 : 3 : 1) because there is only one way to align the magnetic fields of three protons so that they are all with the field and only one way to align them so that they are all against the field. However, there are **three** ways to align the magnetic fields of three protons so that two are lined up with the field and one is lined up against the field (Figure 14.13). Likewise, there are three ways to align the magnetic fields of three protons so that one is lined up with the field and two are lined up against it.

Figure 14.13 ▶
The ways in which the magnetic fields of three protons can be aligned.



The relative intensities obey the mathematical mnemonic known as Pascal's triangle. According to Pascal, each number at the bottom of a triangle in the rightmost column of Table 14.2 is the sum of the two numbers to its immediate left and right in the row above it. A signal for a **proton is never split by equivalent protons**. Normally, **nonequivalent protons split each other's** signal only if they are on adjacent carbons. Splitting is a "through-bond" effect, not a "through-space" effect; it is rarely observed if the protons are separated by more than three bonds. If, however, they are separated by more than three bonds and one of the bonds is a double or triple bond, a small splitting is sometimes observed. This is called long-range coupling

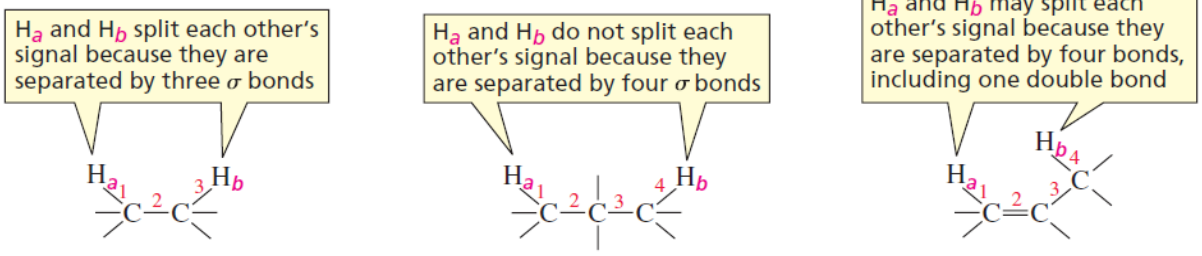


Table 14.2 Multiplicity of the Signal and Relative Intensities of the Peaks in the Signal

Number of equivalent protons causing splitting	Multiplicity of the signal	Relative peak intensities
0	singlet	1
1	doublet	1:1
2	triplet	1:2:1
3	quartet	1:3:3:1
4	quintet	1:4:6:4:1
5	sextet	1:5:10:10:5:1
6	septet	1:6:15:20:15:6:1

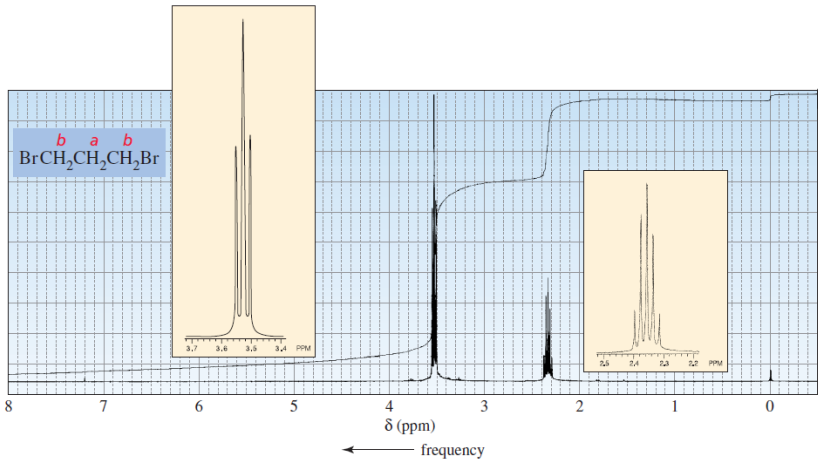


Figure 14.15 ▶ ^{1}H NMR spectrum of 1,3-dibromopropane.

There are two signals in the NMR spectrum of 1,3-dibromopropane (Figure 14.15). The signal for the Hb protons is split into a triplet by the two hydrogens on the adjacent carbon. The Ha protons have two adjacent carbons that are bonded to protons. The protons on one adjacent carbon are equivalent to the protons on the other adjacent carbon. Because the two sets of protons are equivalent, the N+1 rule is applied to both sets at the same time. In other words, *N* is equal to the sum of the equivalent protons on both carbons. So the signal for the Ha protons is split into a quintet (4 + 1 = 5) Integration

confirms that two methylene groups contribute to the Hb signal because twice as many protons give rise to the Hb signal as to the Ha signal.

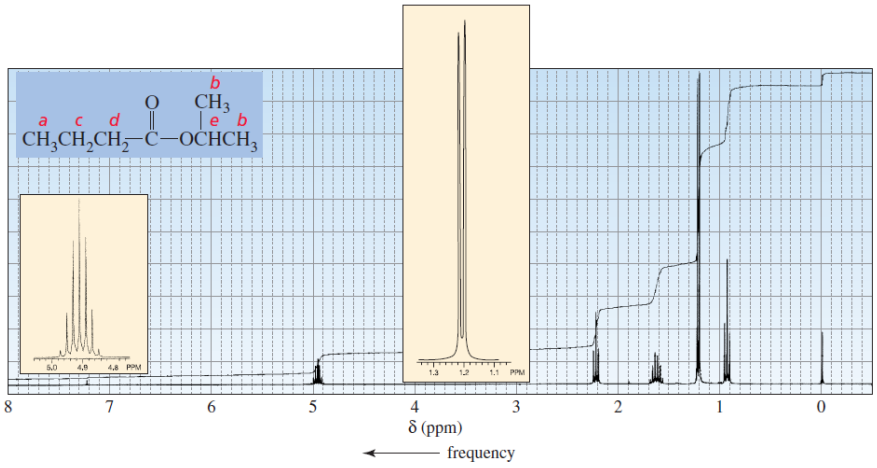


Figure 14.16 ▶
^{1}H NMR spectrum of isopropyl butanoate.

The 1H NMR spectrum of isopropyl butanoate shows five signals (Figure 14.16).The signal for the $H_{\mathbf{a}}$ protons is split into a triplet by the H_c protons. The signal for the $H_{\mathbf{b}}$ protons is split into a doublet by the $H_{\mathbf{e}}$ proton. The signal for the H_d protons is split into a triplet by the Hc protons, and the signal for the He proton is split into a septet by the Hb protons. The signal for the Hc protons is split by both the Ha and Hd protons. Because the Ha and Hd protons are not equivalent, the (N+1 rule) has to be applied separately to each set. Thus, the signal for the Hc protons will be split into a **quartet** by the Ha protons, and each of these four peaks will be split into a triplet by the Hd protons: $(N_a + 1)\ (N_d + 1) = (4)\ (3) = 12$. As a result, the signal for the protons is a **multiplet** (a signal that is more complex that a triplet, quartet, quintet, etc.). The reason we do not see 12 peaks is that some of them overlap.

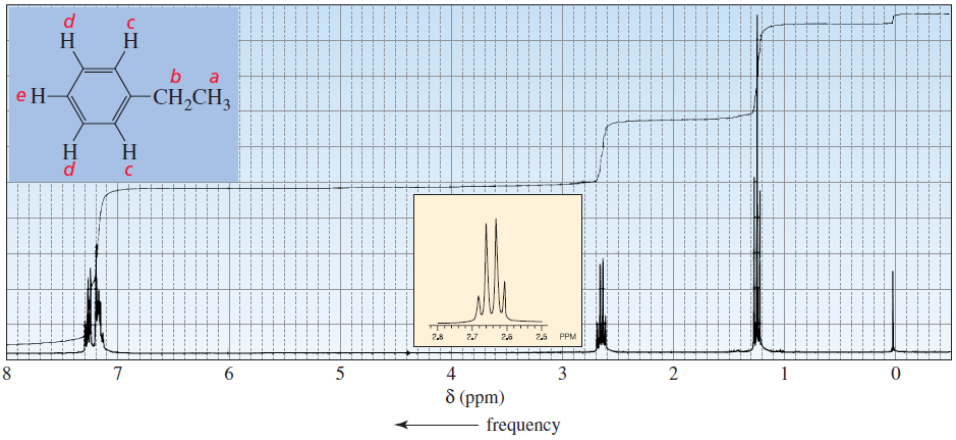
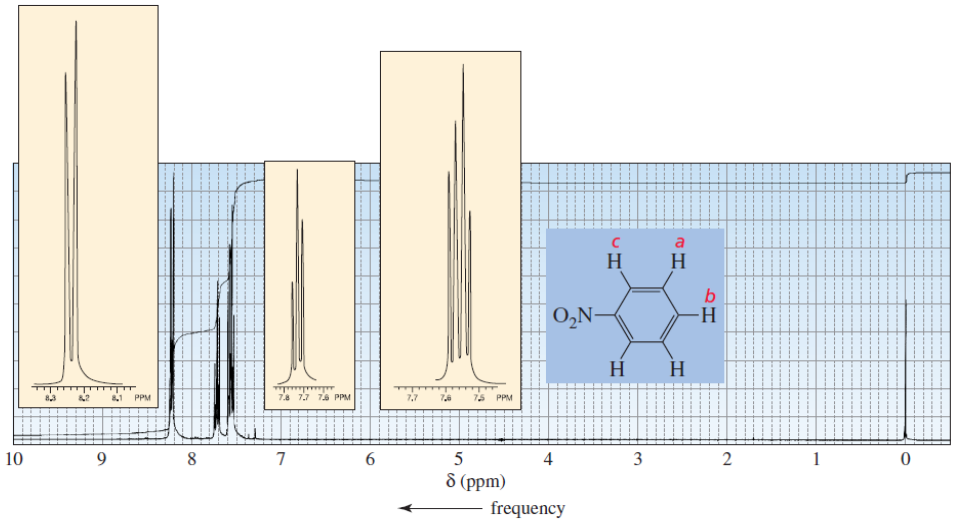


Figure 14.18 ▶ ^{1}H NMR spectrum of ethylbenzene. The signals for the H_c, H_d, and H_e protons overlap.

There are five sets of chemically equivalent protons in ethylbenzene .We see the expected triplet for the H_a protons and the quartet for the H_b protons. (This is a characteristic pattern for an ethyl group.) We expect the signal for the H_c protons to be a doublet and the signal for the H_e proton to be a triplet.

Because the H_c and H_e protons are not equivalent, they must be considered separately in determining the splitting of the signal for the H_d protons. Therefore, we expect the signal for the H_d protons to be split into a doublet by the H_c protons and each peak of the doublet to be split into another doublet by the H_e proton, forming a doublet of doublets. However, we do not see three distinct signals for the H_c, H_d and H_e protons in Figure 14.18. Instead, we see overlapping signals. Apparently, the electronic effect (i.e., the electron-donating/electronwithdrawing ability) of an ethyl substituent is not sufficiently different from that of a hydrogen to cause a difference in the environments of the H_c, H_d, and H_e protons that is large enough to allow them to appear as separate signals.

Figure 14.19 ▶
^{1}H NMR spectrum of nitrobenzene. The signals for the H_a, H_b, and H_c protons do not overlap.



The Ha, Hb and Hc protons of nitrobenzene show three distinct signals (Figure 14.19), and the multiplicity of each signal is what we predicted for the signals for the benzene ring H_c protons in is a doublet, H_b is a triplet, and Ha is a doublet of doublets The nitro group is sufficiently electron withdrawing to cause the H_a, H_b and H_c protons to be in different enough environments that their signals do not overlap.

Notice that the signals for the benzene ring protons in Figures 14.18 and 14.19 occur in the 7.0–8.5 ppm region. Other kinds of protons usually do not resonate in this region, so signals in this region of an 1H NMR spectrum indicate that the compound probably contains an aromatic ring.

a. three signals

$CH_3CH_2CH_2CH_2CH_2CH_3$

triplet | triplet

multiplet

b. three signals

$ICH_2CH_2CH_2Br$

triplet | triplet

multiplet

c. two signals

$ClCH_2CH_2CH_2Cl$

triplet

quintet

d. three signals

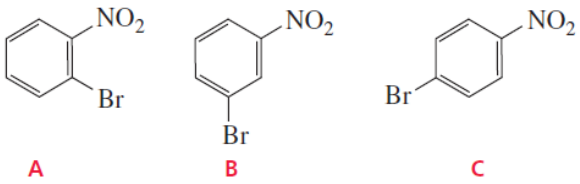
$ICH_2CH_2CHBr_2$

triplet | triplet

multiplet

PROBLEM 22

How could ^{1}H NMR spectra distinguish the following compounds?



A B C

Coupling Constants:

The distance, in hertz, between two adjacent peaks of a split NMR signal is called the **Coupling constant** (denoted by ***J***). The coupling constant for H_a being split by H_b is denoted by J_{ab}. The signals of coupled protons (protons that split each other's signal) have the same coupling constant; in other words, $J_{ab} = J_{ba}$ (Figure 14.20). Coupling constants are useful in analyzing complex NMR spectra because protons on adjacent carbons can be identified by identical coupling constants.

The magnitude of a coupling constant is independent of the operating frequency of the spectrometer—the same coupling constant is obtained from a 300-MHz instrument as from a 600-MHz instrument. The magnitude of a coupling constant is a measure of how strongly the nuclear spins of the coupled protons influence each other. It, therefore, depends on the number and type of bonds that connect the coupled protons, as well as the geometric relationship of the protons. Characteristic coupling constants are shown in Table 14.3; they range from 0 to 15 Hz. The coupling constant for two nonequivalent hydrogens on the *same* carbon is often too small to be observed (Figure 14.17), but it is large for nonequivalent hydrogens bonded to *adjacent* sp^2 carbons. Apparently, the interaction between the hydrogens is strongly affected by the intervening π electrons. We have seen that π electrons also allow long-range coupling—that is, coupling through four or more bonds.

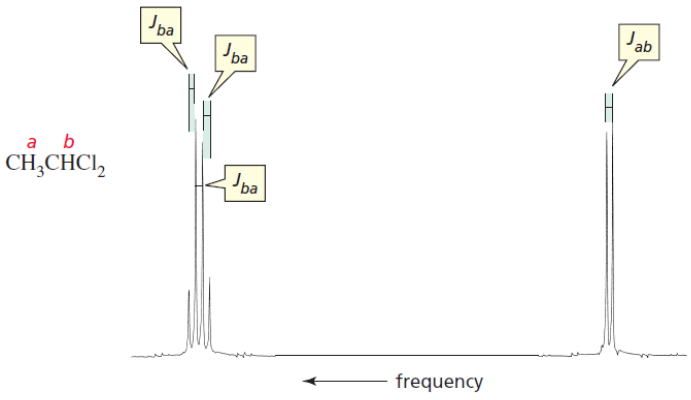
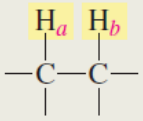
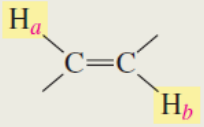
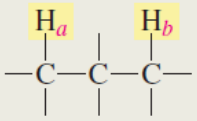
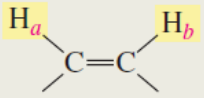
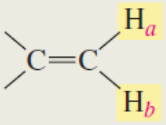
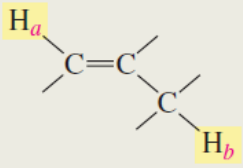


Figure 14.20
The H_a and H_b protons of 1,1-dichloroethane are coupled protons, so their signals have the same coupling constant, $J_{ab} = J_{ba}$.

Coupling constants can be used to distinguish between the ^1H NMR spectra of cis and trans alkenes. The coupling constant of *trans*-vinylic protons is significantly greater than the coupling constant of *cis*-vinylic protons (Figure 14.21), because the coupling constant depends on the dihedral angle between the two C¬H bonds in the H¬C=C¬H unit. The

coupling constant is greatest when the angle between the two C¬H bonds is 180° (trans) and smaller when it is 0° (cis). Notice the difference between J_{bd} and J_{cd} in the spectrum of 3-bromo-1-propene

Table 14.3 Approximate Values of Coupling Constants

Approximate value of J_{ab} (Hz)		Approximate value of J_{ab} (Hz)	
	7		15 (trans)
	0		10 (cis)
	2 (geminal coupling)		1 (long-range coupling)

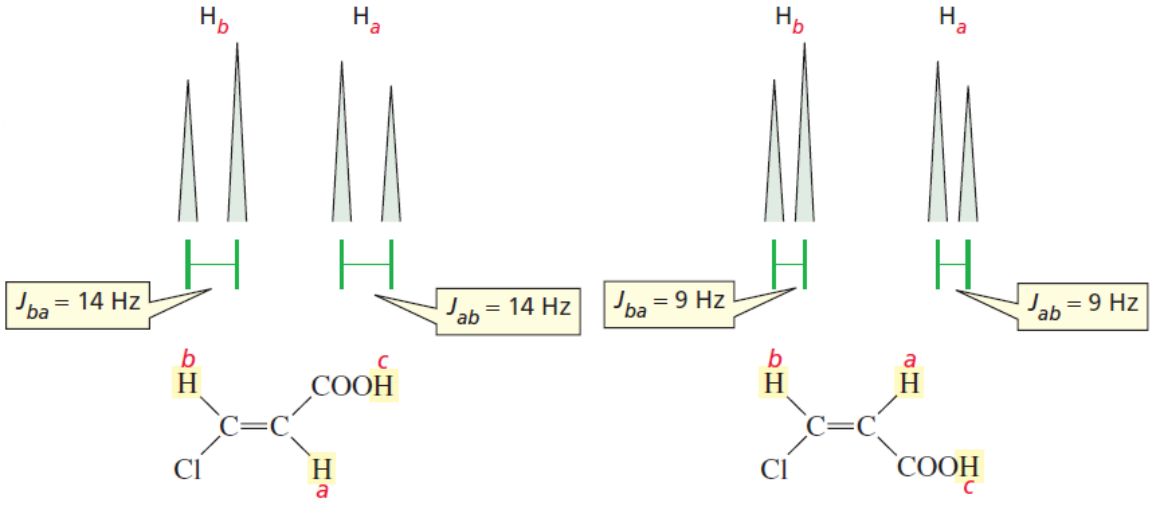
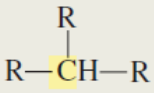
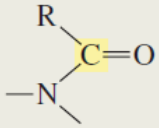
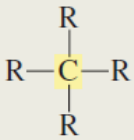
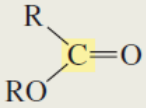
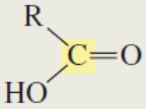
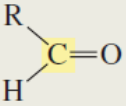
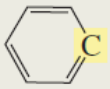
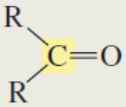
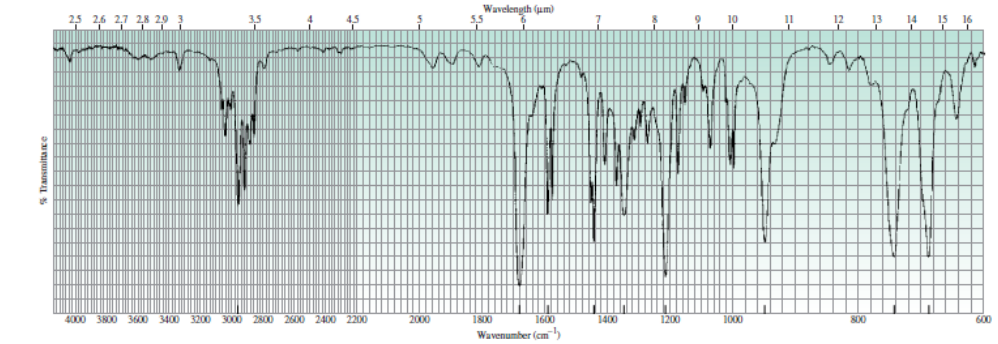


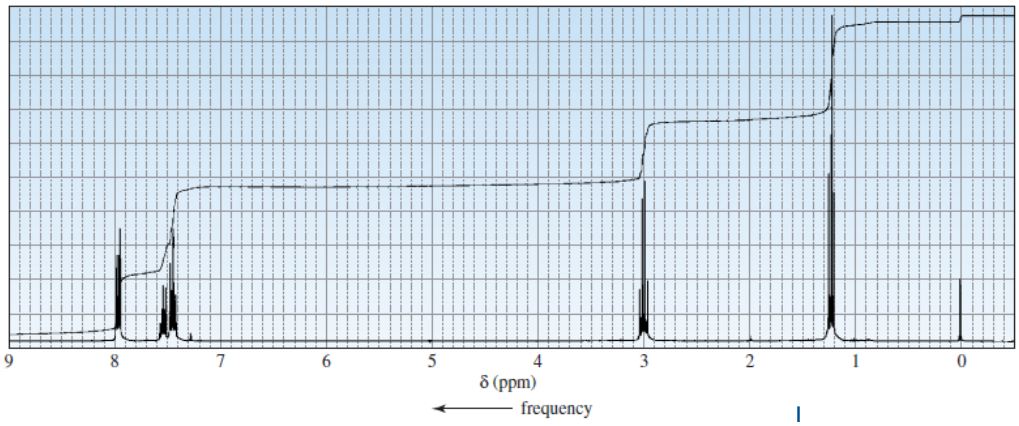
Table 14.4 Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	C—I	0–40
R—CH_3	8–35	C—Br	25–65
R—CH_2—R	15–50	C—Cl C—N C—O	35–80 40–60 50–80
	20–60		165–175
	30–40		165–175
≡C	65–85		175–185
=C	100–150		190–200
	110–170		205–220

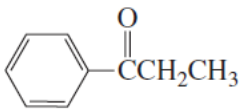
PROBLEM-SOLVING STRATEGY

Identify the compound with molecular formula $C_9H_{10}O$ that gives the IR and ^1H NMR spectra in Figure 14.22.





From the molecular formula and IR spectrum, we learn that the compound is a ketone: It has a carbonyl group at '1680 cm-1, only one oxygen, and no absorption bands at 2820 and 2720 cm-1 and that would indicate an aldehyde. That the carbonyl group absorption is at a lower frequency than normal suggests that it has partial single-bond character as a result of electron delocalization— indicating that it is attached to an *sp*2 carbon. The compound contains a benzene ring(>3000 cm-1, '1600 cm-1, and 1440 cm-1), and it has hydrogens bonded to *sp*3 carbons <3000 cm-1. In the NMR spectrum, the triplet at 1.2 ppm and the quartet at 3.0 ppm indicate the presence of an ethyl group that is attached to an electron-withdrawing group. The signals in the 7.4–8.0 ppm region confirm the presence of a benzene ring. From this information, we can conclude that the compound is the following ketone. The integration ratio (5 : 2 : 3) confirms this answer.



PROBLEM 29◆

Identify the compound with molecular formula $C_8H_{10}O$ that gives the IR and ^1H NMR spectra shown in Figure 14.23.