

## CHAPTER 2

# NMR SPECTROSCOPY

*Nuclear magnetic resonance* (NMR) spectroscopy is the most useful technique for structure determination that you will encounter in your textbook. Analysis of an NMR spectrum provides information about how the individual carbon and hydrogen atoms are connected to each other in a molecule. This information enables us to determine the carbon-hydrogen framework of a compound, much the way puzzle pieces can be assembled to form a picture.

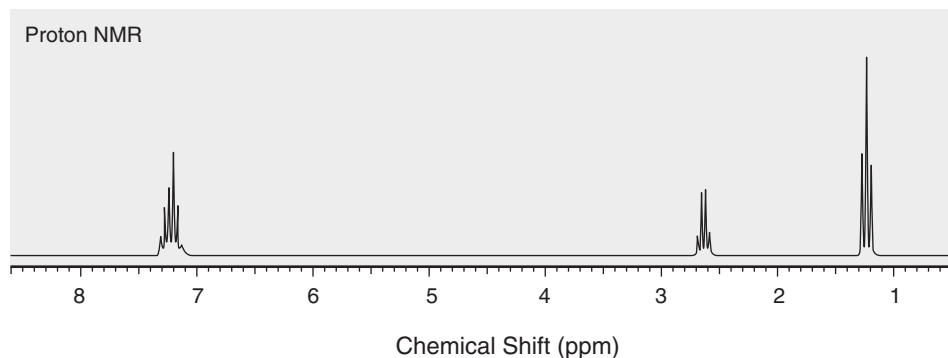
Your textbook will provide an explanation of the theoretical underpinnings of NMR spectroscopy (how it works). Here is a brief summary:

The nucleus of a hydrogen atom (which is just a proton) possesses a property called *nuclear spin*. A true understanding of this property is beyond the scope of our course, so we will think of it as a rotating sphere of charge, which generates a magnetic field, called a *magnetic moment*. When the nucleus of a hydrogen atom is subjected to an external magnetic field, the magnetic moment can align either with the field (called the  $\alpha$  spin state) or against the field (called the  $\beta$  spin state). There is a difference in energy ( $\Delta E$ ) between these two spin states. If a proton occupying the  $\alpha$  spin state is subjected to electromagnetic radiation, an absorption can take place IF the energy of the photon is equivalent to the energy gap between the spin states. The absorption causes the nucleus to *flip* to the  $\beta$  spin state, and the nucleus is said to be in *resonance* with the external magnetic field; thus the term *nuclear magnetic resonance*. NMR spectrometers employ strong magnetic fields, and the frequency of radiation typically required for nuclear resonance falls in the radio wave region of the electromagnetic spectrum (called rf radiation).

At a particular magnetic field strength, we might expect all nuclei to absorb the same frequency of rf radiation. Luckily, this is not the case, as nuclei are surrounded by electrons. In the presence of an external magnetic field, the electron density circulates, establishing a small, local magnetic field that *shields* the proton. Not all protons occupy identical electronic environments. Some protons are surrounded by more electron density and are more shielded, while other protons are surrounded by less electron density and are less shielded, or *deshielded*. As a result, protons in different electronic environments will absorb different frequencies of rf radiation. This allows us to probe the electronic environment of the hydrogen atoms in a compound.

## 2.1 CHEMICAL EQUIVALENCE

The spectrum produced by  $^1\text{H}$  NMR spectroscopy (pronounced “proton” NMR spectroscopy) is called a proton NMR spectrum. Here is an example:



The first valuable piece of information is the number of signals (the spectrum above appears to have three different signals). In addition, each signal has the following important characteristics:

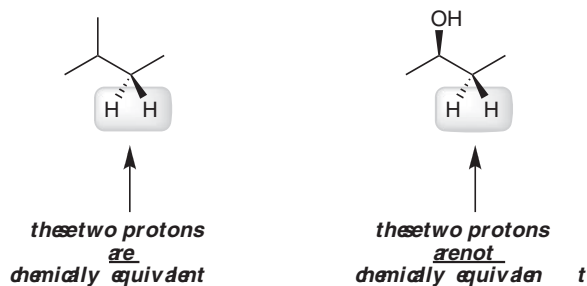
1. The *location* of each signal indicates the electronic environment of the protons giving rise to the signal.
2. The *area* under each signal indicates the number of protons giving rise to the signal.
3. The *shape* of the signal indicates the number of neighboring protons.

We will discuss these characteristics in the upcoming sections. First let's explore the information that is revealed by counting the number of signals in a spectrum.

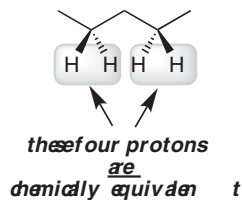
The number of signals in a proton NMR spectrum indicates the number of different kinds of protons (protons in different electronic environments). Protons that occupy identical electronic environments are called *chemically equivalent*, and they will produce only one signal.

Two protons are chemically equivalent if they can be interchanged by a symmetry operation. Your textbook will likely provide a detailed explanation, with examples. For our purposes, the following simple rules can guide you in most cases.

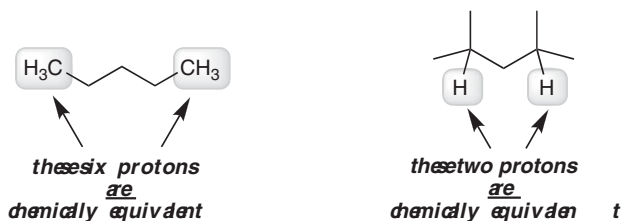
- The two protons of a CH<sub>2</sub> group will generally be chemically equivalent if the compound lacks stereocenters. But if the compound has a stereocenter, then the protons of a CH<sub>2</sub> group will generally not be chemically equivalent:



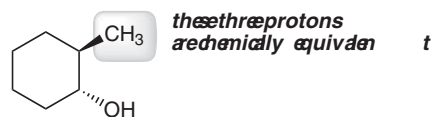
- Two CH<sub>2</sub> groups will be equivalent to each other (giving four equivalent protons) if the CH<sub>2</sub> groups can be interchanged by either rotation or reflection. Example:



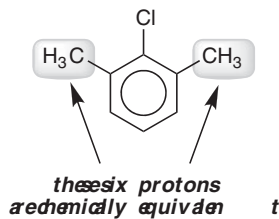
- The previous rule also applies for CH<sub>3</sub> groups or CH groups. Here are examples:



- The three protons of a CH<sub>3</sub> group are always chemically equivalent, even if there are stereocenters in the compound:



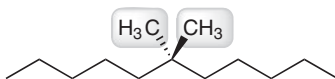
- For aromatic compounds, it will be less confusing if you draw a circle in the ring, rather than drawing alternating  $\pi$  bonds. For example, the following two methyl groups are equivalent, which can be easily seen when drawn in the following way:



**EXERCISE 2.1** Identify the number of signals expected in the <sup>1</sup>H NMR spectrum of the following compound:

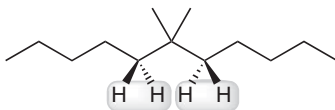


**Answer** Let's begin with the *gem*-dimethyl moiety (the two methyl groups at the center of this compound):



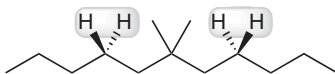
These two methyl groups are equivalent to each other, because they can be interchanged by either rotation or reflection (only one type of symmetry is necessary, but in this case we have both, reflection and rotation, so these six protons are certainly chemically equivalent). We therefore expect one signal for all six protons.

Now let's consider the following methylene ( $\text{CH}_2$ ) groups:



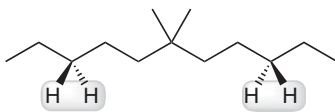
For each of these methylene groups, the two protons are chemically equivalent because there are no stereocenters. In addition, these two methylene groups will be equivalent to each other, since they can be interchanged by rotation or reflection. We therefore expect one signal for all four protons.

The same argument applies for the following two methylene groups:



These four protons are chemically equivalent. But they are different from the other methylene groups in the compound, because they cannot be interchanged with any of the other methylene groups via rotation or reflection.

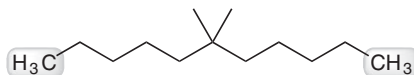
In a similar way, the following four protons are chemically equivalent:



And the following four protons are also chemically equivalent:

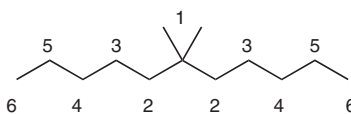


And finally, the following six protons are also chemically equivalent:



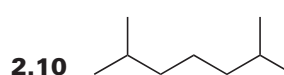
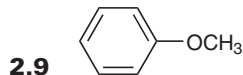
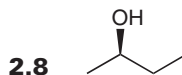
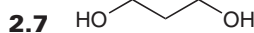
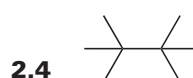
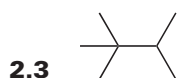
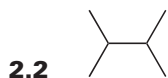
Note that these six protons are different from the six protons of the *gem*-dimethyl group in the center of the compound, because the first set of six protons cannot be interchanged with the other set of six protons via either rotation or reflection.

In total, there are six different types of protons:



So we would expect the proton NMR spectrum of this compound to have six signals.

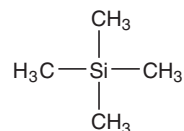
**PROBLEMS** Identify the number of signals expected in the proton NMR spectrum of each of the following compounds.



**2.11** If you look at your answers to the previous problems, you should find that one of the structures was expected to produce an NMR spectrum with only one signal. In that structure (problem 2.4), all six methyl groups were chemically equivalent. Using that example as guidance, propose two possible structures for a compound with molecular formula  $C_9H_{18}$  that exhibits an NMR spectrum with only one signal.

## 2.2 CHEMICAL SHIFT (BENCHMARK VALUES)

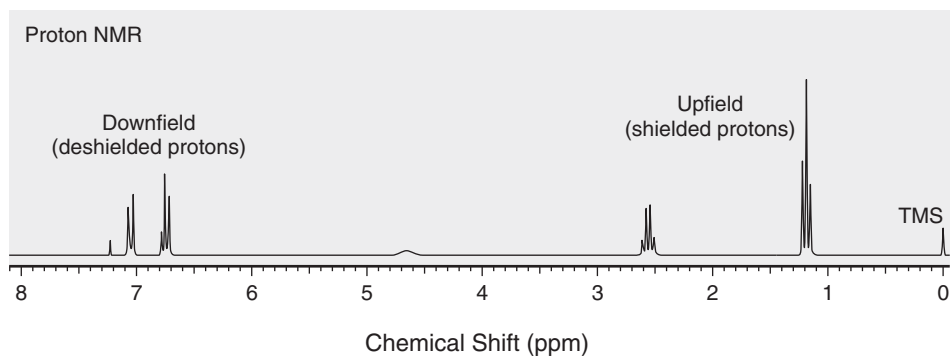
We will now begin exploring the three characteristics of every signal in an NMR spectrum. The first characteristic is the location of the signal, called its *chemical shift* ( $\delta$ ), which is defined relative to the frequency of absorption of a reference compound, tetramethylsilane (TMS):



Tetramethylsilane (TMS)

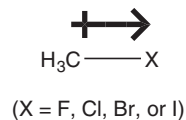
Your textbook will go into greater depth in explaining chemical shift and why it is a unitless number that is reported in parts per million (ppm). For now, we will simply point out that for most organic compounds, the signals produced will fall in a range between 0 and 10 ppm. In rare cases, it is possible to observe a signal occurring at a chemical shift below 0 ppm, which results from a proton that absorbs a lower frequency than the protons in TMS. Most protons in organic compounds absorb a higher frequency than TMS, so most chemical shifts that we encounter will be positive numbers.

The left side of an NMR spectrum is described as *downfield*, and the right side of the spectrum is described as *upfield*:



But keep in mind that these terms are used in a relative way. For example, we would say that the signal at 2.5 ppm (in the spectrum above) is downfield from the signal at 1.2 ppm. Similarly, the signal at 6.8 ppm is upfield from the signal at 7.1 ppm.

The protons of alkanes typically produce signals between 1 and 2 ppm. We will now explore some of the effects that can push a signal downfield (relative to the protons of an alkane). Recall that electronegative atoms, such as halogens, withdraw electron density from neighboring atoms:



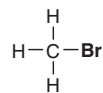
This inductive effect causes the neighboring protons to be deshielded (surrounded by less electron density), and as a result, the signal produced by these protons is shifted downfield—that is, the signal appears at a higher chemical shift than the protons of an alkane. The strength of this effect depends on the electronegativity of the halogen. Compare the chemical shifts of the protons in the following compounds:



1.0 ppm



2.2 ppm



2.7 ppm

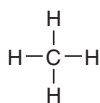


3.1 ppm

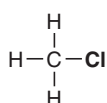


4.3 ppm

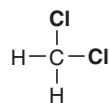
Fluorine is the most electronegative element, and therefore produces the strongest effect. When multiple halogens are present, the effect is generally additive, as can be seen when comparing the following compounds:



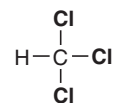
1.0 ppm



3.1 ppm

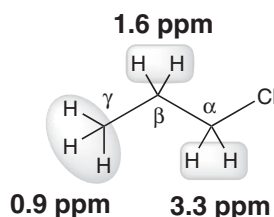


5.5 ppm



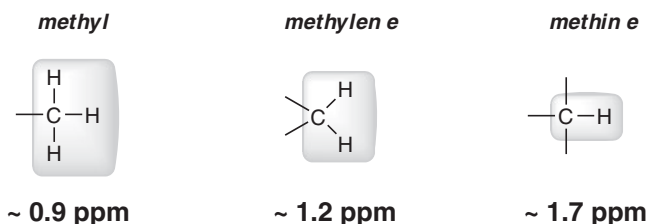
7.3 ppm

Each chlorine atom adds approximately 2 ppm to the chemical shift of the signal. An important aspect of inductive effects is the fact that they taper off drastically with distance, as can be seen by comparing the chemical shifts of the protons in the following compound:



The effect is most significant for the protons at the alpha ( $\alpha$ ) position. The protons at the beta ( $\beta$ ) position are only slightly affected, and the protons at the gamma ( $\gamma$ ) position are virtually unaffected by the presence of the chlorine atom.

By committing a few numbers to memory, you should be able to predict the chemical shifts for the protons in a wide variety of compounds, including alcohols, ethers, ketones, esters, and carboxylic acids. The following numbers can be used as benchmark values:



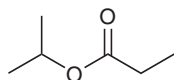
In the absence of inductive effects, a methyl group ( $\text{CH}_3$ ) will generally produce a signal near 0.9 ppm, a methylene group ( $\text{CH}_2$ ) will produce a signal near 1.2 ppm, and a methine group ( $\text{CH}$ ) will produce a signal near 1.7 ppm. These benchmark values are then modified by the presence of neighboring functional groups, in the following way:

<i>Functional group</i>	<i>Effect on <math>\alpha</math> protons</i>	<i>Example</i>
<b>Oxygen</b> of an alcohol or ether	+ 2.5	<p>methylene group (<math>\text{CH}_2</math>) = 1.2 ppm next to oxygen = +2.5 ppm <b>3.7 ppm</b></p>
<b>Oxygen</b> of an ester	+3	<p>methylene group (<math>\text{CH}_2</math>) = 1.2 ppm next to oxygen = +3.0 ppm <b>4.2 ppm</b></p>
<b>Carbonyl group</b> ( $\text{C}=\text{O}$ ) All carbonyl groups, including ketones, aldehydes, esters, etc.	+1	<p>methylene group (<math>\text{CH}_2</math>) = 1.2 ppm next to carbonyl = +1.0 ppm <b>2.2 ppm</b></p>

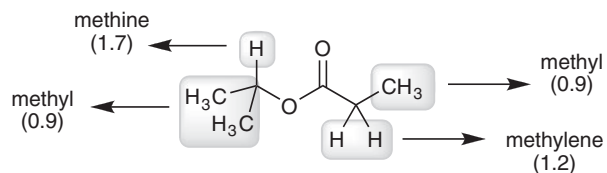
The values above represent the effect of a few functional groups on the chemical shifts of alpha protons. The effect on beta protons is generally about one-fifth of the effect on the alpha protons. For example, in an alcohol, the presence of an oxygen atom adds +2.5 ppm to the chemical shift of the alpha protons, but adds only +0.5 ppm to the beta protons. Similarly, a carbonyl group adds +1 ppm to the chemical shift of the alpha protons, but only +0.2 to the beta protons.

The values above (together with the benchmark values for methyl, methylene, and methine groups), enable us to predict the chemical shifts for the protons in a wide variety of compounds. Let's see an example.

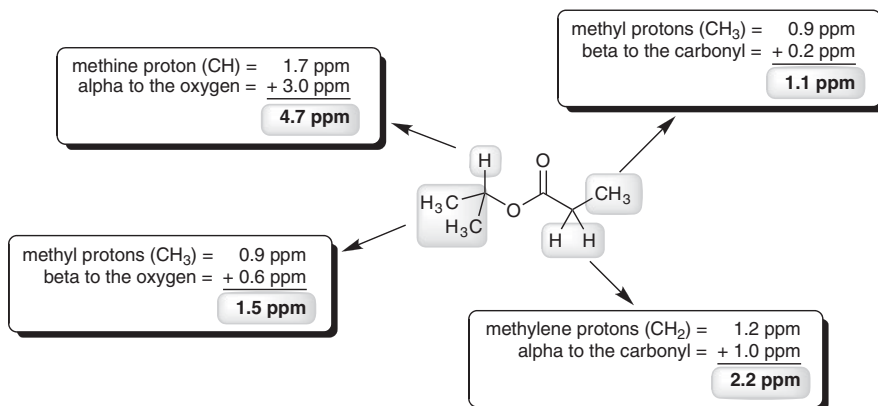
**EXERCISE 2.12** Predict the chemical shifts for the signals in the proton NMR spectrum of the following compound:



**Solution** First determine the total number of expected signals. In this compound, there are four different kinds of protons, giving rise to four distinct signals. For each type of signal, identify whether it represents methyl (0.9 ppm), methylene (1.2 ppm), or methine (1.7 ppm) groups:



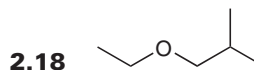
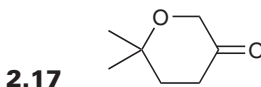
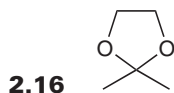
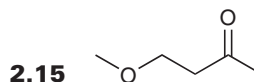
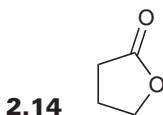
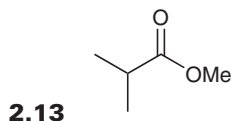
Finally, modify each of these numbers based on proximity to the oxygen and the carbonyl group:



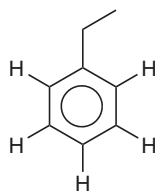


These values are only estimates, and the actual chemical shifts might differ slightly from the predicted values. Note that for the methine proton, we did not count the distant C=O bond and add +0.2, because the ester moiety is considered as one group, which has the effect of adding +3.0 to the chemical shift of the methine proton. Similarly, note that for the methylene protons, we did not add +0.5 for a distant oxygen. Once again, the ester moiety is considered as one group, which has the effect of adding +1.0 to the chemical shift of the methylene protons.

**PROBLEMS** Predict the chemical shifts for the signals in the proton NMR spectrum of each of the following compounds:



The chemical shift of a proton is also sensitive to the presence of nearby  $\pi$  electrons. This effect is particularly strong for aromatic protons (protons connected directly to an aromatic ring). In your textbook, you will find a diagram showing how (and why) the aromatic protons are affected. Here is a brief summary. The external magnetic field causes the  $\pi$  electrons to circulate, and this flow of electrons causes an induced, local magnetic field. The aromatic protons experience not only the external magnetic field, but they also experience the induced, local magnetic field. As a result, aromatic protons feel a stronger net magnetic field, which causes their signals to be shifted downfield, significantly. In fact, aromatic protons generally produce signals in the neighborhood of 7 ppm (sometimes as high as 8 ppm, sometimes as low as 6.5 ppm) in an NMR spectrum. For example, consider the structure of ethylbenzene:

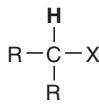



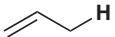
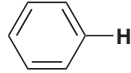

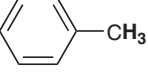
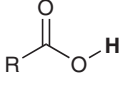


Ethylbenzene has three different kinds of aromatic protons (make sure you can identify them), producing three overlapping signals just above 7 ppm. A complex signal around 7 ppm is characteristic of compounds with aromatic protons.

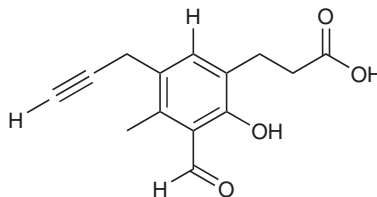
The methylene group ( $\text{CH}_2$ ) in ethylbenzene produces a signal at 2.6 ppm, rather than the expected benchmark value of 1.2 ppm. These protons have been shifted downfield because of their proximity to the aromatic ring. They are not shifted as much as the aromatic protons themselves, because the methylene protons are farther away from the ring, but there is still a noticeable effect.

All  $\pi$  electrons, whether they belong to an aromatic ring or not, have an effect on neighboring protons. For each type of  $\pi$  bond, the precise location of the nearby protons determines their chemical

shift. For example, aldehydic protons produce characteristic signals at approximately 10 ppm. Below are some important chemical shifts. It would be wise to become familiar with these numbers, as they will be required in order to interpret proton NMR spectra:

Type of proton	Chemical Shift ( $\delta$ )	Type of proton	Chemical Shift ( $\delta$ )
methyl $R-CH_3$	$\sim 0.9$	alkyl halide 	2 – 4
methylene 	$\sim 1.2$	alcohol $R-O-H$	2 – 5
methine 	$\sim 1.7$	vinyllic 	4.5 – 6.5
allylic 	$\sim 2$	aryl 	6.5 – 8
alkynyl $R-C\equiv C-H$	$\sim 2.5$	aldehyde 	$\sim 10$
aromatic methyl 	$\sim 2.5$	carboxylic acid 	$\sim 12$

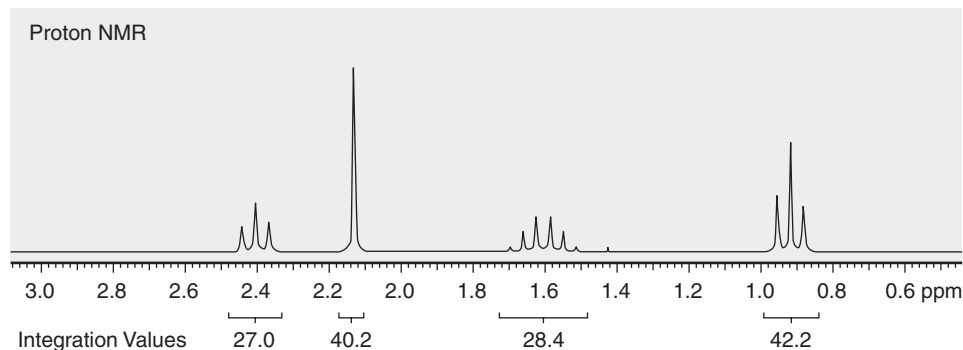
**PROBLEM 2.19** Predict the expected chemical shift for each type of proton in the following compound:



## 2.3 INTEGRATION

In the previous section, we learned about the first characteristic of every signal, chemical shift. In this section, we will explore the second characteristic, *integration*, which is the area under each signal. This value indicates the number of protons giving rise to the signal. After acquiring a spectrum,

a computer calculates the area under each signal, and then displays this area as a numerical value placed under the signal:

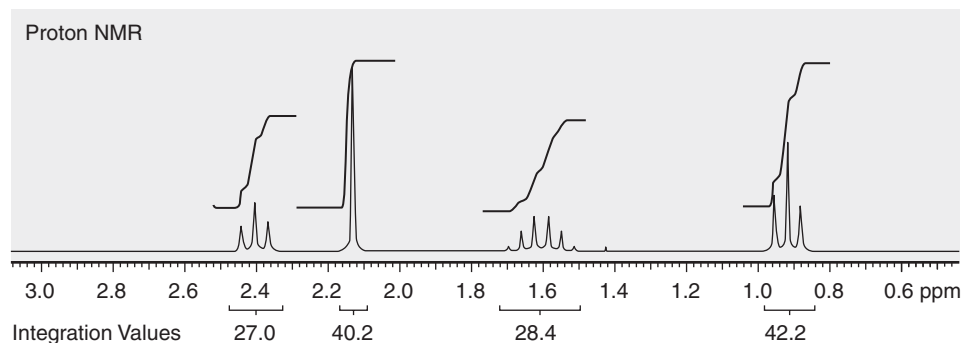


These numbers only have meaning when compared to each other. In order to convert these numbers into useful information, choose the smallest number (27.0 in this case), and then divide all integration values by this number:

$$\frac{27.0}{27.0} = 1 \quad \frac{40.2}{27.0} = 1.49 \quad \frac{28.4}{27.0} = 1.05 \quad \frac{42.2}{27.0} = 1.56$$

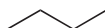
These numbers provide the *relative number*, or ratio, of protons giving rise to each signal. This means that a signal with an integration of 1.5 involves one and a half times as many protons as a signal with an integration of 1. In order to arrive at whole numbers (there is no such thing as half a proton), multiply all the numbers above by two, giving the same ratio now expressed in whole numbers, 2 : 3 : 2 : 3. In other words, the signal at 2.4 ppm represents 2 equivalent protons, and the signal at 2.1 ppm represents 3 equivalent protons.

Integration values are often represented by *step-curves*, for example:



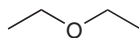
The height of each step curve represents the area under the signal. In this case, a comparison of the heights of the four step curves reveals a ratio of 2 : 3 : 2 : 3.

When interpreting integration values, don't forget that the numbers are only relative. For example, consider the structure of butane:



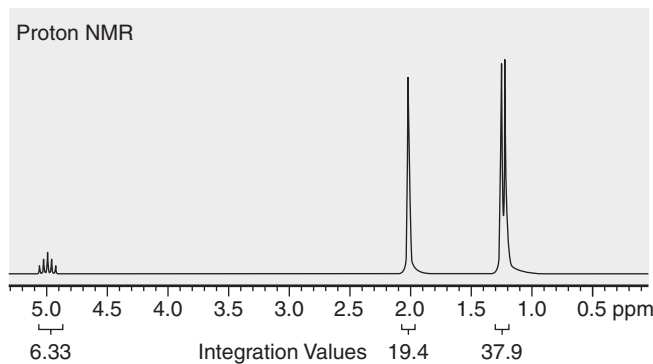
Butane has two kinds of protons, and will therefore produce two signals in its proton NMR spectrum. The methyl groups give rise to one signal and the methylene groups give another signal. A computer analyzes the area under each signal and provides numbers that allow us to calculate a ratio of 2 : 3. This ratio only indicates the relative number of protons giving rise to each signal, not the exact number of protons. In this case, the exact numbers are 4 (for the methylene groups) and 6 (for the methyl groups). When analyzing the NMR spectrum of an unknown compound, the molecular formula provides extremely useful information because it enables us to determine the exact number of protons giving rise to each signal. If we were analyzing the spectrum of butane, the molecular formula ( $C_4H_{10}$ ) would indicate that the compound has a total of 10 protons. This information then allows us to determine that the ratio of 2 : 3 must correspond with 4 protons and 6 protons, in order to give a total of 10 protons.

The previous example illustrated the important role that symmetry can play on integration values. Here is another example:



This compound has only two kinds of protons, because the two methylene groups are equivalent to each other, and the two methyl groups are equivalent to each other. The proton NMR spectrum is therefore expected to exhibit only two signals, with relative integration values of 2 : 3. But once again, the values 2 and 3 are just relative numbers. They actually represent 4 protons and 6 protons. This can be determined by inspecting the molecular formula ( $C_4H_{10}O$ ) which indicates a total of 10 protons in the compound. Since the ratio of protons is 2 : 3, this ratio must represent 4 and 6 protons, in order for the total number of protons to be 10. This analysis indicates that the molecule possesses symmetry.

**EXERCISE 2.20** A compound with molecular formula  $C_5H_{10}O_2$  has the following NMR spectrum. Determine the number of protons giving rise to each signal:

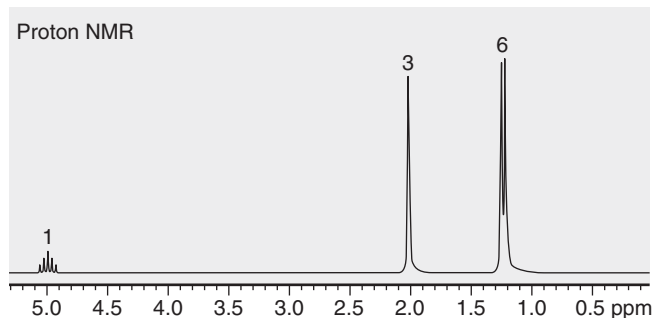


**Solution** The spectrum has three signals. Begin by comparing the relative integration values: 6.33, 19.4, and 37.9. Divide each of these three numbers by the smallest number (6.33):

$$\frac{6.33}{6.33} = 1 \quad \frac{19.4}{6.33} = 3.06 \quad \frac{37.9}{6.33} = 5.99$$

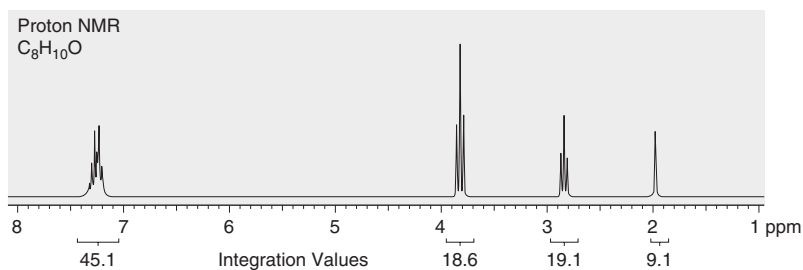
This gives a ratio of 1 : 3 : 6, but these are just relative numbers. To determine the exact number of protons giving rise to each signal, look at the molecular formula, which indicates a total of 10 protons in the compound. Therefore, the numbers 1 : 3 : 6 are not only relative values,

but they are also the exact values. Exact integration values are sometimes expressed in the following way:

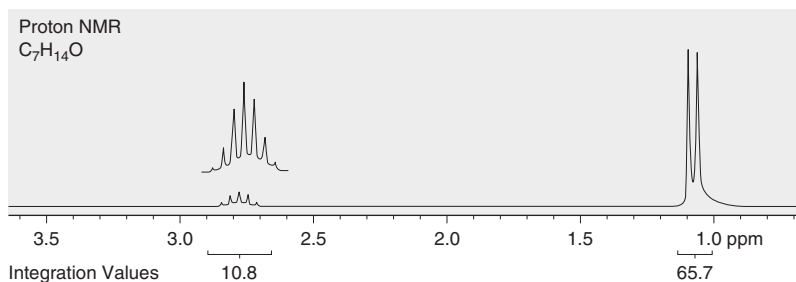


### PROBLEMS

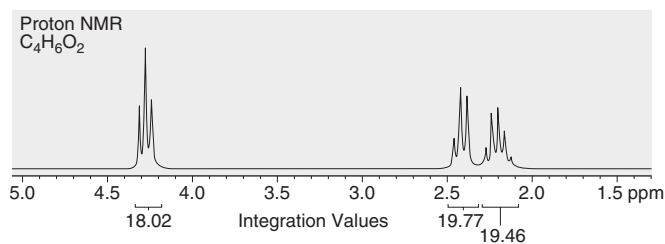
**2.21** A compound with molecular formula  $C_8H_{10}O$  has the following proton NMR spectrum. Determine the number of protons giving rise to each signal.



**2.22** A compound with molecular formula  $C_7H_{14}O$  has the following proton NMR spectrum. Determine the number of protons giving rise to each signal.

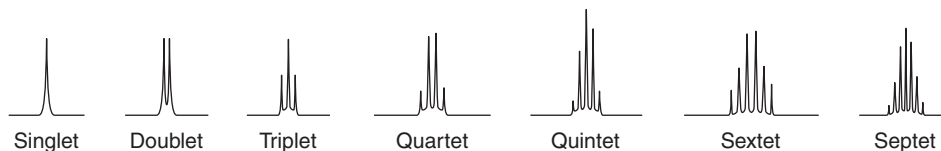


**2.23** A compound with molecular formula  $C_4H_6O_2$  has the following proton NMR spectrum. Determine the number of protons giving rise to each signal.



## 2.4 MULTIPLICITY

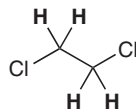
The third, and final, characteristic of each signal is its *multiplicity*, which refers to the number of peaks in the signal. A *singlet* has one peak, a *doublet* has two peaks, a *triplet* has three peaks, a *quartet* has four peaks, a *quintet* has five peaks, etc:



The multiplicity of a signal is the result of the magnetic effects of neighboring protons, and therefore indicates the number of neighboring protons. Your textbook will explain the cause for this effect in detail. The net effect can be summarized with the  $n + 1$  rule, which states the following: if  $n$  is the number of neighboring protons, then the multiplicity will be  $n + 1$ . For example, a proton with three neighbors ( $n = 3$ ) will be split into a quartet ( $n + 1 = 3 + 1 = 4$  peaks).

It is important to realize that nearby protons do not always split each other. There are two major factors that determine whether or not splitting occurs:

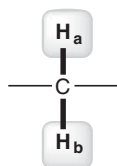
1. Equivalent protons do not split each other. Consider the two methylene groups in the following compound:



Four equivalent protons  
**no splitting**

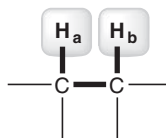
All four protons are chemically equivalent, and therefore, they do not split each other. Instead, they produce one signal that has no neighboring protons ( $n = 0$ ), so the signal is a singlet ( $n + 1$ ). In order for splitting to occur, the neighboring protons must be different than the protons producing the signal.

2. Splitting is most commonly observed when protons are separated by either two or three sigma bonds:



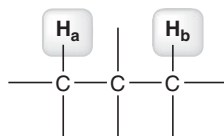
non-equivalent protons  
separated by two sigma bonds

or



non-equivalent protons  
separated by three sigma bonds

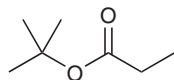
However, when two protons are separated by more than three sigma bonds, splitting is generally not observed:



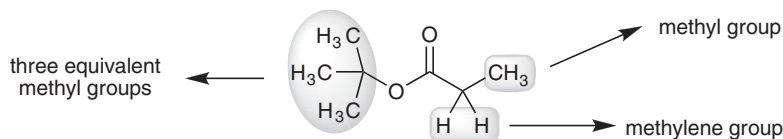
too far apart

Such long-range splitting is only observed in rigid molecules, such as bicyclic compounds, or in molecules that contain rigid structural moieties, such as allylic systems. For purposes of this introductory treatment of NMR spectroscopy, we will avoid examples that exhibit substantial long-range coupling. Make sure to look through your lecture notes to see if you covered any examples of long-range coupling.

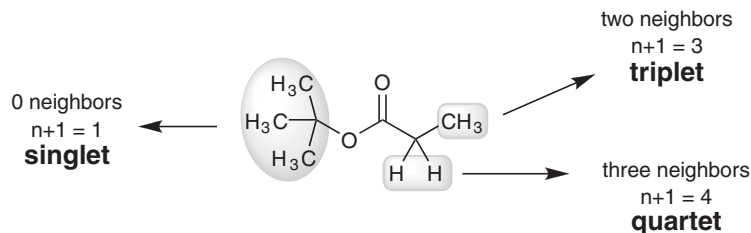
**EXERCISE 2.24** Determine the multiplicity of each signal in the expected proton NMR spectrum of the following compound:



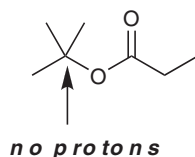
**Solution** Begin by identifying the different kinds of protons. That is, determine the number of expected signals.



This compound is expected to produce three signals in its proton NMR spectrum. Now let's analyze each signal, using the  $n + 1$  rule:

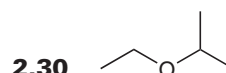
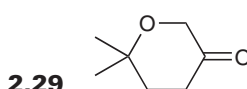
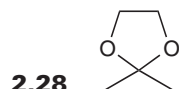
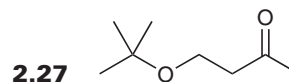
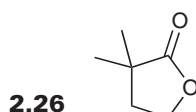
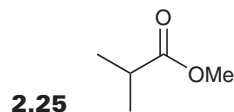


Notice that the *tert*-butyl group (on the left side of the molecule) appears as a singlet, because the following carbon atom has no protons:

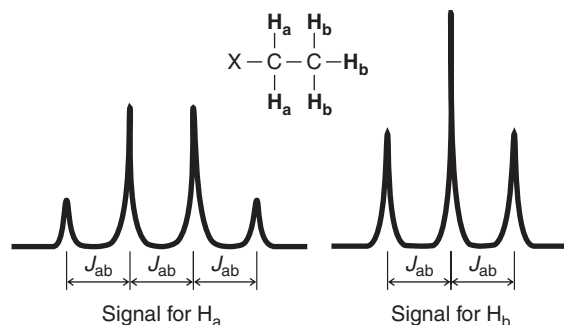


This quaternary carbon atom is directly connected to each of the three neighboring methyl groups, and as a result, each of the three methyl groups has no neighboring protons. This is characteristic of *tert*-butyl groups.

**PROBLEMS** Predict the multiplicity of each signal in the expected proton NMR spectrum of each of the following compounds:



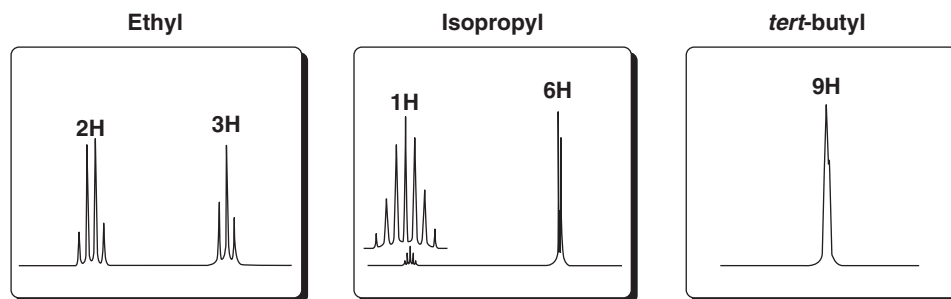
When signal splitting occurs, the distance between the individual peaks of a signal is called the *coupling constant*, or *J value*, and is measured in Hz. Neighboring protons always split each other with equivalent *J values*. For example, consider the two kinds of protons in an ethyl group:



The  $\text{H}_a$  signal is split into a quartet under the influence of its three neighbors, while the  $\text{H}_b$  signal is split into a triplet under the influence of its two neighbors.  $\text{H}_a$  and  $\text{H}_b$  are said to be coupled to each other. The coupling constant,  $J_{ab}$ , is the same in both signals. *J* values can range anywhere from 0 to 20 Hz, depending on the type of protons involved.

## 2.5 PATTERN RECOGNITION

There are a few splitting patterns that are commonly seen in proton NMR spectra, and you will save yourself time on an exam if you can recognize these patterns:



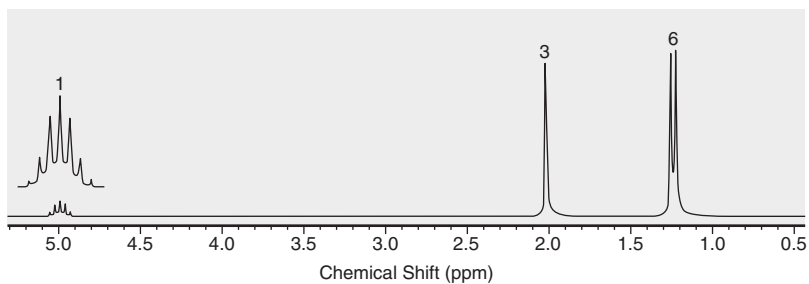


An ethyl group is characterized by a triplet with an integration of 3 and a quartet with an integration of 2. An isopropyl group is characterized by a doublet with an integration of 6 and a quartet with an integration of 1. A *tert*-butyl group is characterized by a singlet with an integration of 9.

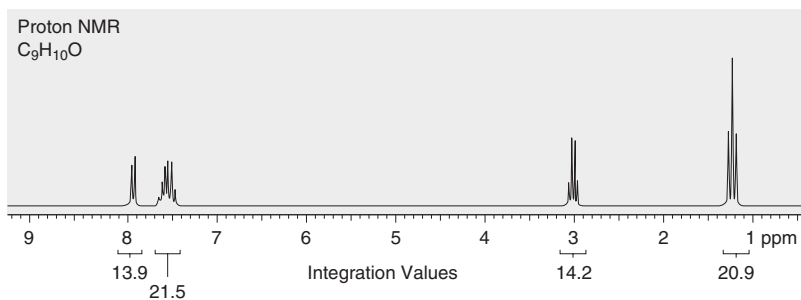
Let's get some practice recognizing these patterns.

**PROBLEMS** Below are NMR spectra of several compounds. Identify whether these compounds are likely to contain ethyl, isopropyl, and/or *tert*-butyl groups:

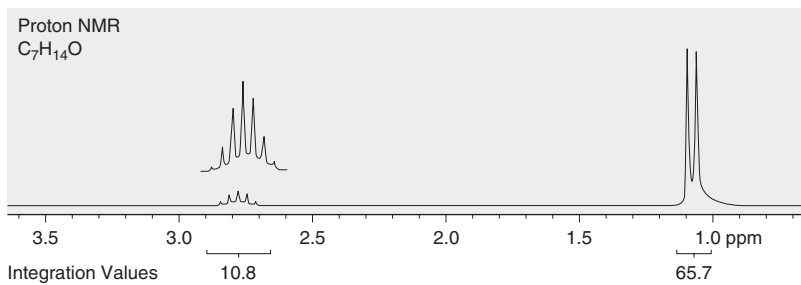
## 2.31

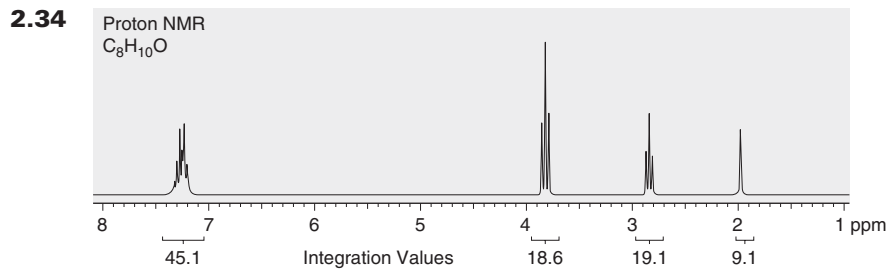


## 2.32



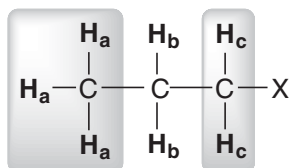
## 2.33



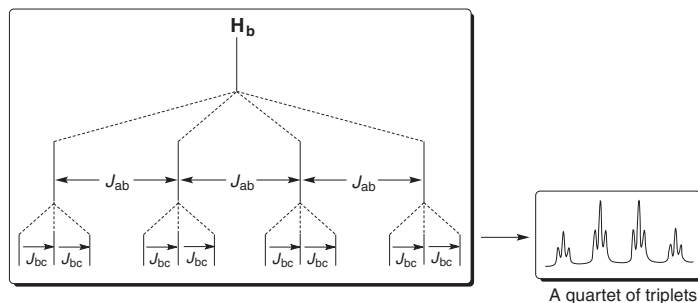


## 2.6 COMPLEX SPLITTING

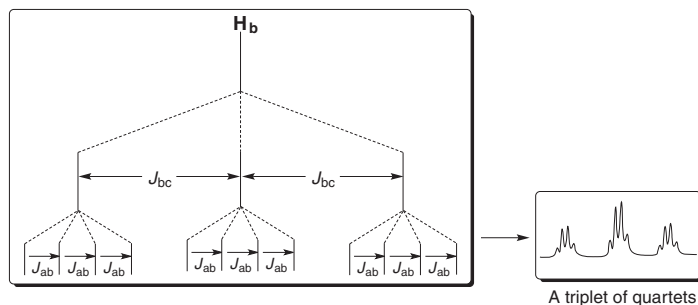
Complex splitting occurs when a proton has two different kinds of neighboring protons. For example, consider the splitting pattern that you might expect for the protons labeled H<sub>b</sub> in the following compound:



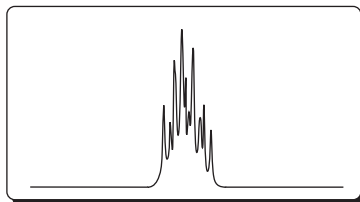
The signal for H<sub>b</sub> is being split into a quartet because of the nearby H<sub>a</sub> protons, AND it is being split into a triplet because of the nearby H<sub>c</sub> protons. The signal is therefore expected to have twelve peaks ( $4 \times 3$ ). The appearance of the signal will depend greatly on the  $J$  values. If  $J_{ab}$  is much greater than  $J_{bc}$ , then the signal will appear as a quartet of triplets, as shown in the following splitting tree:



If, however,  $J_{bc}$  is much greater than  $J_{ab}$ , then the signal will appear as a triplet of quartets:

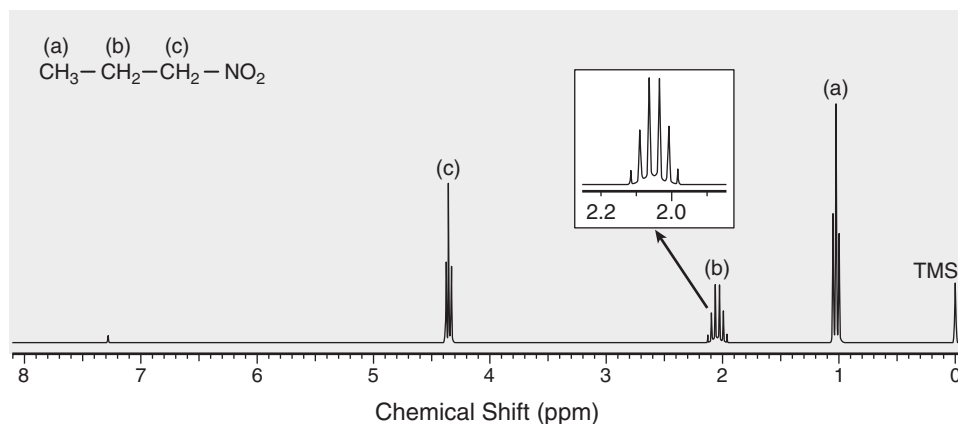


In most cases, the  $J$  values will be fairly similar, and we will observe neither a clean quartet of triplets nor a clean triplet of quartets. More often, several of the peaks will happen to overlap, producing a signal that is difficult to analyze and is often just called a *multiplet*.



A multiplet

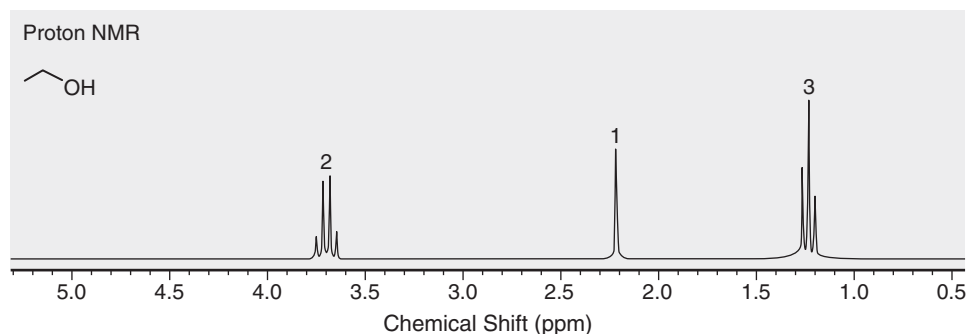
In some cases,  $J_{ab}$  and  $J_{bc}$  will be almost identical. For example, consider the proton NMR spectrum of 1-nitropropane:



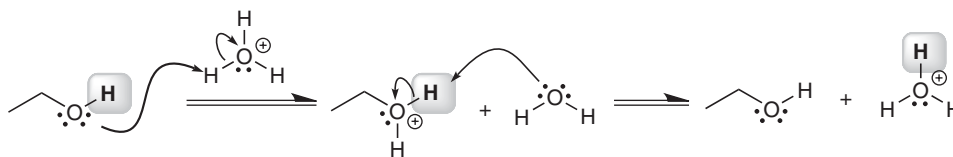
Look carefully at the splitting pattern of the  $\text{H}_b$  protons (at approximately 2 ppm). This signal looks like a sextet, because the  $J_{ab}$  and  $J_{bc}$  are so close in value. In such a case, it is “as if” there are five equivalent neighbors, even though all five protons are not equivalent.

## 2.7 NO SPLITTING

In the previous section, we saw examples of complex splitting. Now, in this section, we will explore cases where there is no splitting at all, despite the presence of neighboring protons. Consider the proton NMR spectrum of ethanol:

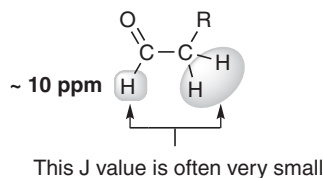


As expected, the spectrum exhibits the characteristic signals of an ethyl group (a quartet with an integration of 2 and a triplet with an integration of 3). In addition, there is another signal at 2.2 ppm, representing the hydroxyl proton (OH). Hydroxyl protons typically produce a signal between 2 and 5 ppm, and it is often difficult to predict exactly where that signal will appear. In the proton NMR spectrum above, notice that the hydroxyl proton is not split into a triplet from the neighboring methylene group. Generally, no splitting is observed across the oxygen of an alcohol, because proton exchange is a very rapid process that is catalyzed by trace amounts of acid or base:



Hydroxyl protons are said to be **labile**, because of the rapid rate at which they are exchanged. This proton transfer process occurs at a faster rate than the timescale of an NMR spectrometer, producing a blurring effect that averages out any possible splitting effect. It is possible to slow down the rate of proton transfer by scrupulously removing the trace amounts of acid and base dissolved in ethanol. Such purified ethanol does in fact exhibit splitting across the oxygen atom, and the signal at 2.2 ppm is observed to be a triplet.

There is one other common example of neighboring protons that often do not produce observable splitting. Aldehydic protons, which generally produce signals near 10 ppm, will often couple only weakly with their neighbors (i.e., a very small  $J$  value):



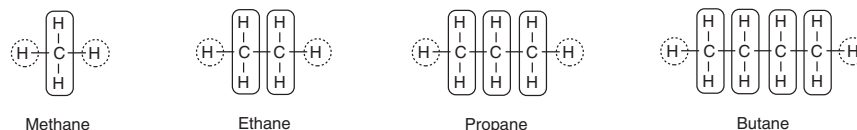
Depending on the size of the  $J$  value, splitting may or may not be noticeable. If the  $J$  value is too small, then the signal near 10 ppm will appear to be a singlet, despite the presence of neighboring protons.

## 2.8 HYDROGEN DEFICIENCY INDEX (DEGREES OF UNSATURATION)

In the previous sections of this chapter, we have learned all of the individual tools that you need for analyzing a proton NMR spectrum (considering the number of signals, analyzing chemical shifts, assessing integration values, interpreting the multiplicity of each signal, pattern recognition, etc.). Now, we are just about ready to put all of these tools together. But there is one more important tool that you will need, and we will cover that tool in this section.

Imagine that you have an unknown compound with a molecular formula of  $C_6H_{12}O$ . The molecular formula by itself does not provide enough information to draw the structure of the compound. There are many constitutional isomers of  $C_6H_{12}O$ . Nevertheless, a careful analysis of the molecular formula can often provide helpful clues about the structure of the compound. To see how this works, let's begin by analyzing the molecular formula of several alkanes.

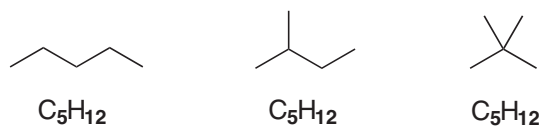
Compare the structures of the following alkanes, paying special attention to the number of hydrogen atoms attached to each carbon atom.



In each case there are two hydrogen atoms on the ends of the structures (circled), and there are two hydrogen atoms on every carbon atom. This can be summarized like this:

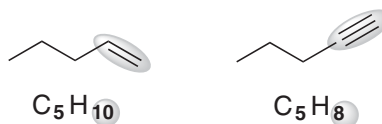


where  $n$  is the number of carbon atoms in the compound. Accordingly, the number of hydrogen atoms will be  $2n + 2$ . In other words, all of the compounds above have a molecular formula of  $C_nH_{2n+2}$ . This is true even for compounds that are branched rather than having a straight chain.

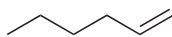


The compounds above are said to be *saturated*—that is, they possess the maximum number of hydrogen atoms possible relative to the number of carbon atoms present.

A compound with a  $\pi$  bond (a double or triple bond) will have fewer than the maximum number of hydrogen atoms. Such compounds are said to be *unsaturated*.



A compound containing a ring will also have fewer than the maximum number of hydrogen atoms, just like a compound with a double bond. For example, compare the structures of 1-hexene and cyclohexane:

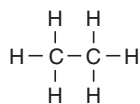


Both compounds have molecular formula (C<sub>6</sub>H<sub>12</sub>) because both are “missing” two hydrogen atoms [6 carbon atoms can accommodate  $(2 \times 6) + 2 = 14$  hydrogen atoms]. Each of these compounds is said to have one *degree of unsaturation*. The *hydrogen deficiency index (HDI)* is a measure of the number of degrees of unsaturation. A compound is said to have one degree of unsaturation for every two hydrogen atoms that are missing. For example, a compound with molecular formula C<sub>4</sub>H<sub>6</sub> is missing four hydrogen atoms (if saturated, it would be C<sub>4</sub>H<sub>10</sub>), so it has two degrees of unsaturation (HDI = 2). There are several ways for a compound to possess two degrees of unsaturation: two double bonds, or two rings, or one double bond and one ring, or one triple bond. Let’s explore all of these possibilities for C<sub>4</sub>H<sub>6</sub>:

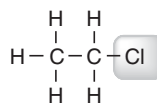
Two double bonds	One triple bond	Two rings	One ring and one double bond

These are all of the possible constitutional isomers for C<sub>4</sub>H<sub>6</sub>. With this in mind, let’s expand our skills set. Let’s explore how to calculate the HDI when other elements are present in the molecular formula.

**Halogens:** Compare the following two compounds:



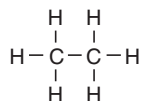
ethane



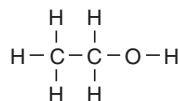
chloroethane

Notice that chlorine takes the place of a hydrogen atom. Therefore, for purposes of calculating the HDI, treat a halogen as if it were a hydrogen atom. For example, C<sub>4</sub>H<sub>9</sub>Cl should have the same HDI as C<sub>4</sub>H<sub>10</sub>.

**Oxygen:** Compare the following two compounds:



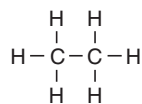
ethane



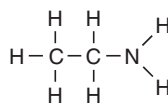
ethanol

Notice that the presence of the oxygen atom does not affect the expected number of hydrogen atoms. Therefore, whenever an oxygen atom appears in the molecular formula, it should be ignored for purposes of calculating the HDI. For example, C<sub>4</sub>H<sub>8</sub>O should have the same HDI as C<sub>4</sub>H<sub>8</sub>.

**Nitrogen:** Compare the following two compounds:



ethane



ethyl amine

Notice that the presence of a nitrogen atom changes the number of expected hydrogen atoms. It gives one more hydrogen atom than would be expected. Therefore, whenever a nitrogen atom appears in the molecular formula, one hydrogen atom must be subtracted from the molecular formula. For example,  $\text{C}_4\text{H}_9\text{N}$  should have the same HDI as  $\text{C}_4\text{H}_8$ .

In summary:

- Halogens: **Add** one H for each halogen
- Oxygen: **Ignore**
- Nitrogen: **Subtract** one H for each N

These rules will enable you to determine the HDI for most simple compounds. Alternatively, the following formula can be used:

$$\text{HDI} = (2\text{C} + 2 + \text{N} - \text{H} - \text{X})/2$$

C is the number of carbon atoms, N is the number of nitrogen atoms, H is the number of hydrogen atoms, and X is the number of halogens. This formula will work for all compounds containing C, H, N, O, and X.

Calculating the HDI is particularly helpful, because it provides clues about the structural features of the compound. For example, an HDI of zero indicates that the compound cannot have any rings or  $\pi$  bonds. That is extremely useful information when trying to determine the structure of a compound, and it is information that is easily obtained by simply analyzing the molecular formula. Similarly, an HDI of one indicates that the compound must have either one double bond *or* one ring (but not both). If the HDI is two, then there are a few possibilities: two rings, or two double bonds, or one ring and one double bond, or one triple bond. Analysis of the HDI for an unknown compound can often be a useful tool, but only when the molecular formula is known with certainty.

We will use this technique in the next section. The following exercises are designed to develop the skill of calculating and interpreting the HDI of an unknown compound whose molecular formula is known.

### EXERCISE 2.35

Calculate the HDI for a compound with molecular formula  $\text{C}_5\text{H}_8\text{Br}_2\text{O}_2$ , and identify the structural information provided by the HDI.

**Answer** Use the following calculation:

# of H's:	8
Add 1 for each Br:	+2
Ignore each O:	0
Subtract 1 for each N:	0
Total =	10

This compound will have the same HDI as a compound with molecular formula  $C_5H_{10}$ . To be fully saturated, 5 carbon atoms would require  $(5 \times 2) + 2 = 12$  H's. According to our calculation, two hydrogen atoms are missing, and, therefore, this compound has one degree of unsaturation.  $HDI = 1$ .

Alternatively, the following formula can be used:

$$HDI = (2C + 2 + N - H - X)/2 = (10 + 2 + 0 - 8 - 2)/2 = 2/2 = 1$$

With one degree of unsaturation, the compound must contain either one ring or one double bond, but not both. The compound cannot have a triple bond, as this would require two degrees of unsaturation.

**PROBLEMS** Calculate the degree of unsaturation for each of the following molecular formulas:



## 2.9 ANALYZING A PROTON NMR SPECTRUM

In this section, we will practice analyzing and interpreting NMR spectra, a process that involves four discrete steps:

1. Always begin by inspecting the molecular formula (if it is given), as it provides useful information. Specifically, calculating the hydrogen deficiency index (HDI) can provide important clues about the structure of the compound. An HDI of zero indicates that the compound does not possess any rings or  $\pi$  bonds. An HDI of 1 indicates that the compound has either one ring or one  $\pi$  bond. An HDI of four should indicate the likely presence of an aromatic ring:



four degrees of unsaturation  
( $HDI = 4$ )

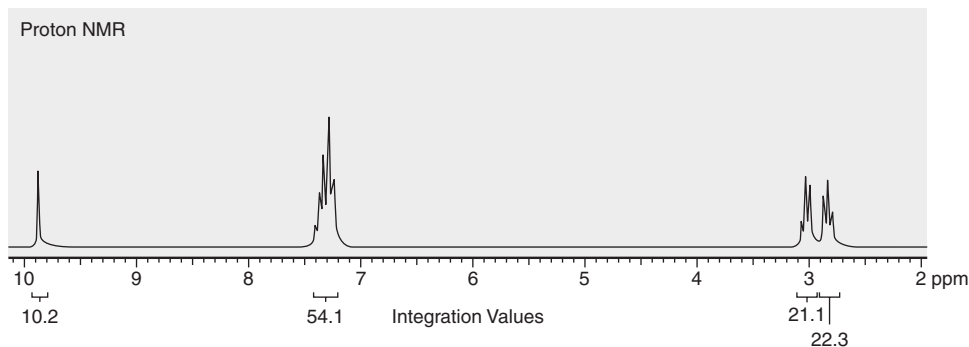
2. Consider the number of signals and integration of each signal (this gives clues about the symmetry of the compound).
3. Analyze each signal (chemical shift, integration, and multiplicity), and then draw fragments consistent with each signal. These fragments become our puzzle pieces that must be assembled to produce a molecular structure.
4. Assemble the fragments into a molecular structure.

The following exercise illustrates how this is done.



**EXERCISE 2.42**

Identify the structure of a compound with molecular formula  $C_9H_{10}O$  that exhibits the following proton NMR spectrum:

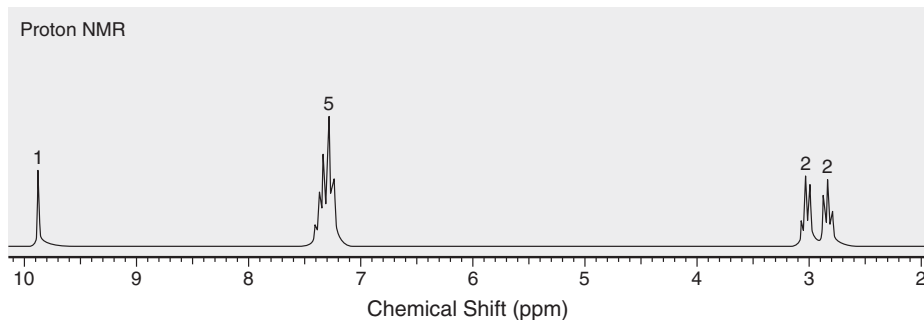


**Answer** The first step is to calculate the HDI. The molecular formula indicates 9 carbon atoms, which would require 20 hydrogen atoms in order to be fully saturated. There are only 10 hydrogen atoms, which means that 10 hydrogen atoms are missing, and therefore, the HDI is 5. This is a large number, and it would not be efficient to think about all the possible ways there are to have five degrees of unsaturation. However, anytime we encounter an HDI of 4 or more, we should be on the lookout for an aromatic ring. We must keep this in mind when analyzing the spectrum. We should expect an aromatic ring (HDI = 4) plus one other degree of unsaturation (either a ring or a double bond).

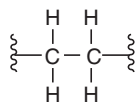
The second step is to consider the number of signals and the integration value for each signal. Any signals with large integration values would suggest the presence of symmetry elements. For example, a signal with an integration of 4 would suggest two equivalent  $CH_2$  groups. In this spectrum, we see four signals. In order to analyze the integration of each signal, we must first divide by the lowest number (10.2):

$$\frac{10.2}{10.2} = 1 \quad \frac{54.1}{10.2} = 5.30 \quad \frac{21.1}{10.2} = 2.07 \quad \frac{22.3}{10.2} = 2.19$$

The ratio is 1 : 5 : 2 : 2. Now look at the molecular formula. There are 10 protons in the compound, so the relative integration values represent the actual number of protons giving rise to each signal:

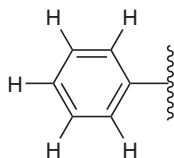


The next step is to analyze each signal. Starting upfield, there are two triplets, each with an integration of 2. This suggests that there are two adjacent methylene groups:



These signals do not appear at 1.2 where methylene groups are expected, so one or more factors is shifting these signals downfield. Our proposed structure must take that into account.

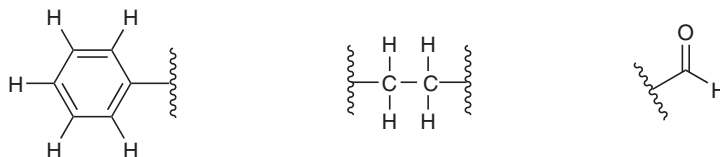
Moving downfield through the spectrum, the next signal appears just above 7 ppm, characteristic of aromatic protons (just as we suspected after analyzing the HDI). The multiplicity of aromatic protons only rarely gives useful information. More often, a messy multiplet of overlapping signals is observed. But the integration value gives important information. Specifically, there are five aromatic protons, which means that the aromatic ring is monosubstituted.



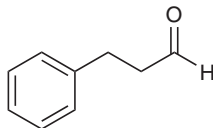
Five aromatic protons

Moving on to the last signal, we see a singlet at 10 ppm with an integration of 1. This is suggestive of an aldehydic proton.

In summary, our analysis has produced the following fragments:



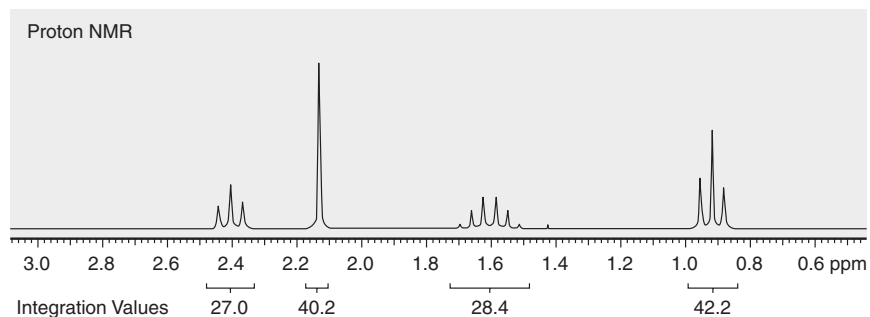
The final step is to assemble these fragments. Fortunately, there is only one way to assemble these three puzzle pieces.



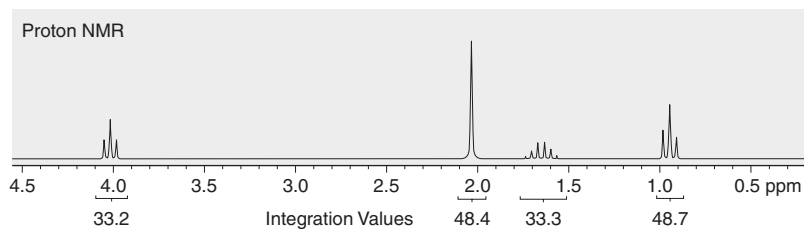
We mentioned before that each methylene group is being shifted downfield by one or more factors. Our proposed structure explains the observed chemical shifts. In particular, one methylene group is shifted significantly by the carbonyl group and slightly by the aromatic ring. The other methylene group is being shifted significantly by the aromatic ring and slightly by the carbonyl group.

## PROBLEMS

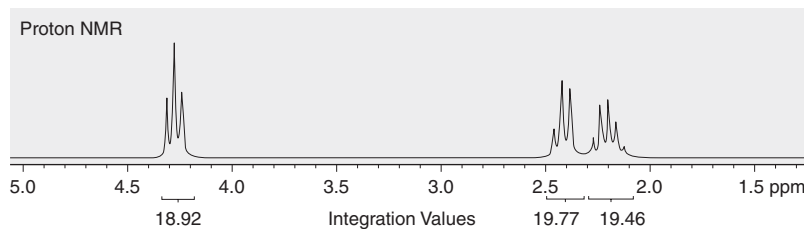
**2.43** Propose a structure for a compound with molecular formula  $C_5H_{10}O$  that is consistent with the following proton NMR spectrum.



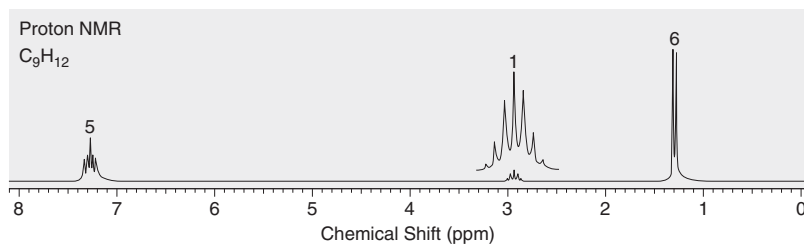
**2.44** Propose a structure for a compound with molecular formula  $C_5H_{10}O_2$  that is consistent with the following proton NMR spectrum.



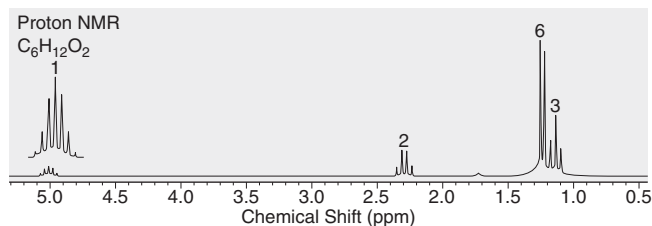
**2.45** Propose a structure for a compound with molecular formula  $C_4H_6O_2$  that is consistent with the following proton NMR spectrum.



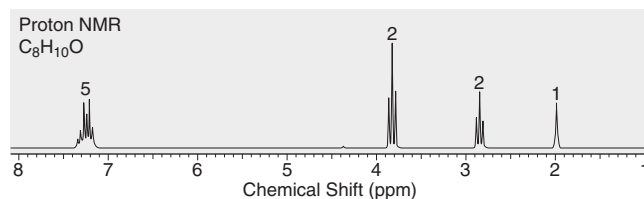
**2.46** Propose a structure for a compound with molecular formula  $C_9H_{12}$  that is consistent with the following proton NMR spectrum.



**2.47** Propose a structure for a compound with molecular formula  $\text{C}_6\text{H}_{12}\text{O}_2$  that is consistent with the following proton NMR spectrum.



**2.48** Propose a structure for a compound with molecular formula  $\text{C}_8\text{H}_{10}\text{O}$  that is consistent with the following proton NMR spectrum.

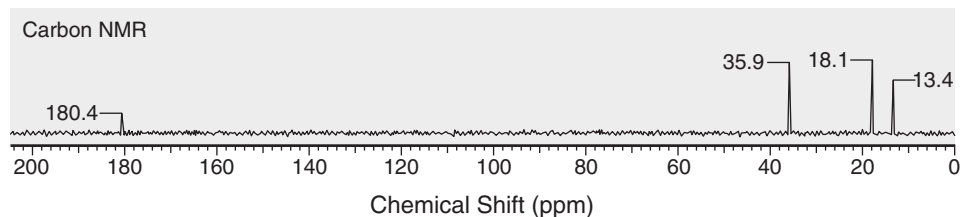


Your textbook has many more spectroscopy problems, including problems in which you are given both IR and NMR spectra. I recommend that you do ALL of those problems. The skills in this chapter were meant to prepare you for those problems.

## 2.10 $^{13}\text{C}$ NMR SPECTROSCOPY

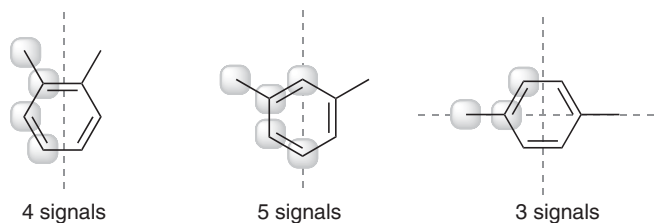
Many of the principles that apply to  $^1\text{H}$  NMR spectroscopy also apply to  $^{13}\text{C}$  NMR spectroscopy, but there are a few major differences, and we will focus on those. For example,  $^1\text{H}$  is the most abundant isotope of hydrogen, but  $^{13}\text{C}$  is only a minor isotope of carbon, representing about 1.1% of all carbon atoms found in nature. As a result, only one in every hundred carbon atoms will resonate, which demands the use of a sensitive receiver coil for  $^{13}\text{C}$  NMR.

In  $^1\text{H}$  NMR spectroscopy, we saw that each signal has three characteristics (chemical shift, integration, and multiplicity). In  $^{13}\text{C}$  NMR spectroscopy, only the chemical shift is important. The integration and multiplicity of  $^{13}\text{C}$  signals are not reported, which greatly simplifies the interpretation of  $^{13}\text{C}$  NMR spectra. Integration values are not routinely calculated in  $^{13}\text{C}$  NMR spectroscopy because the pulse technique employed by NMR spectrometers has the undesired effect of distorting the integration values, rendering them useless in most cases. Multiplicity is also not a common characteristic of  $^{13}\text{C}$  NMR signals.



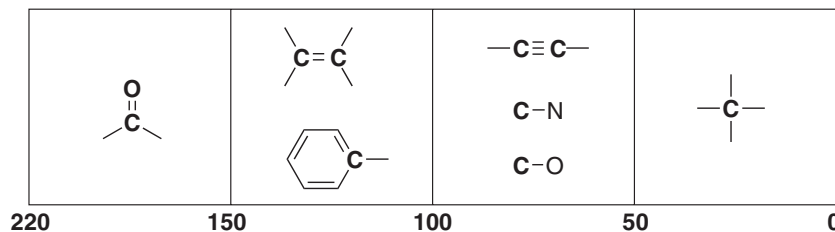
Notice that all of the signals are recorded as singlets. This is a result of a special technique, called broadband decoupling, that suppresses all  $^{13}\text{C}$ - $^1\text{H}$  splitting. If we did not use this technique, then the signal of each  $^{13}\text{C}$  atom nucleus would be split not only by the protons directly connected to it (separated by only one sigma bond), but it would also be split by the protons that are two or three sigma bonds removed. This would lead to very complex splitting patterns, and the signals would overlap to produce an unreadable spectrum. The use of broadband decoupling causes all of the  $^{13}\text{C}$  signals to collapse to singlets, which renders the spectrum more easily interpreted.

In  $^{13}\text{C}$  NMR spectroscopy, chemical shift values typically range from 0 to 220 ppm. The number of signals in a  $^{13}\text{C}$  NMR spectrum represents the number of carbon atoms in different electronic environments (not interchangeable by symmetry). Carbon atoms that are interchangeable by symmetry (either rotation or reflection) will only produce one signal. To illustrate this point, consider the compounds below. Each compound has eight carbon atoms, but does not produce eight signals. The unique carbon atoms in each compound are highlighted.



Each carbon atom that is not highlighted is equivalent to one of the highlighted carbon atoms.

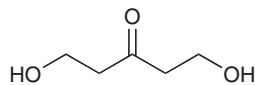
The location of each signal is dependent on shielding and deshielding effects, just as we saw in proton NMR spectroscopy. Below are chemical shifts of several important types of carbon atoms.



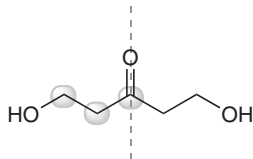
- **0–50 ppm:** This region contains signals from  $sp^3$ -hybridized carbon atoms (methyl, methylene, and methine groups).
- **50–100 ppm:** This region contains  $sp^3$ -hybridized carbon atoms that are deshielded by electronegative atoms, as well as  $sp$ -hybridized carbon atoms.
- **100–150 ppm:** This region contains  $sp^2$ -hybridized carbon atoms.
- **150–220 ppm:** This region contains the carbon atoms of carbonyl groups. These carbon atoms are highly deshielded.

Let's now use this information to solve the following exercise.

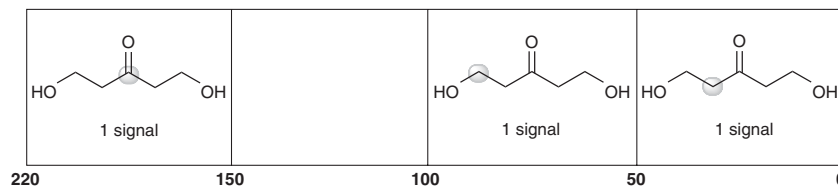
**EXERCISE 2.49** Predict the number of signals and the location of each signal in the expected  $^{13}\text{C}$  NMR spectrum of the following compound:



**Answer** Begin by determining the number of expected signals. The compound has five carbon atoms, but we must look to see if any of these carbon atoms are interchangeable by symmetry. In this case, there is symmetry, and we expect only three signals in the  $^{13}\text{C}$  NMR spectrum.

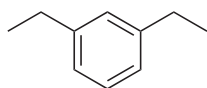


The expected chemical shifts are shown below, categorized according to the region of the spectrum in which each signal is expected to appear:

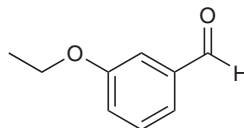


**PROBLEMS** For each compound below, predict the number of signals and the location of each signal in the expected  $^{13}\text{C}$  NMR spectrum.

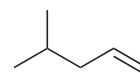
2.50



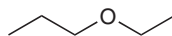
2.51



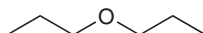
2.52



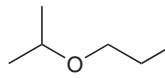
2.53



2.54



2.55



## CHAPTER 2

2.2) Two signals

2.3) Three signals

2.4) One signal

2.5) Two signals

2.6) Five signals

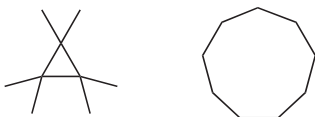
2.7) Three signals

2.8) Six signals

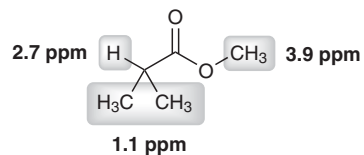
2.9) Four signals

2.10) Four signals

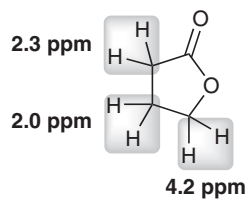
2.11)



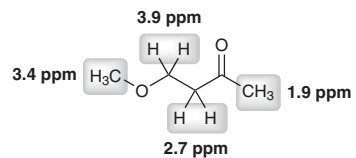
2.13)



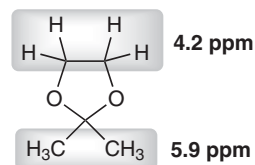
2.14)



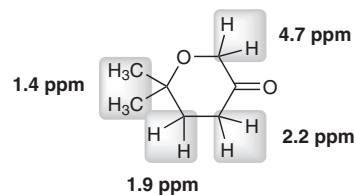
2.15)



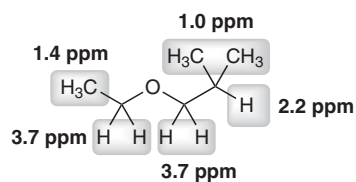
2.16)



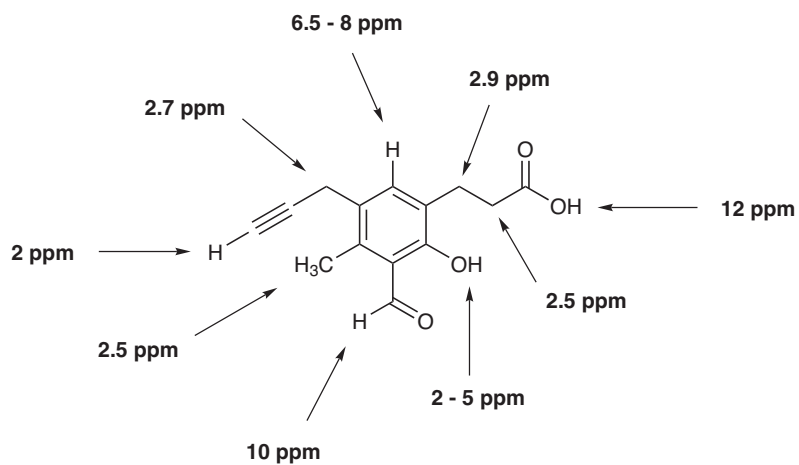
2.17)



2.18)



2.19)

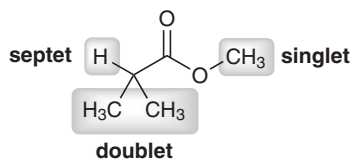


2.21) 5:2:2:1

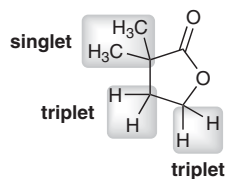
2.22) 2:12

2.23) 2:2:2

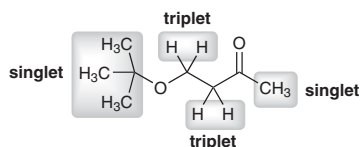
2.25)



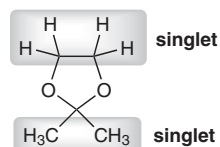
2.26)



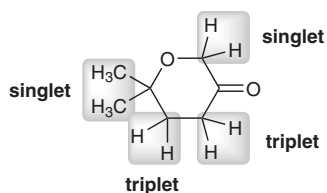
2.27)



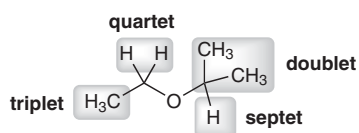
2.28)



2.29)



2.30)



2.31) Isopropyl

2.32) Ethyl

2.33) Isopropyl

2.34) Ethyl

2.36) Two degrees of unsaturation

2.37) Three degrees of unsaturation

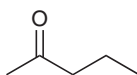
2.38) Two degrees of unsaturation

2.39) No degrees of unsaturation

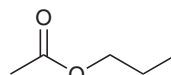
2.40) No degrees of unsaturation

2.41) Four degrees of unsaturation

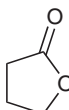
2.43)



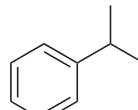
2.44)



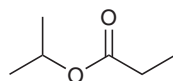
2.45)



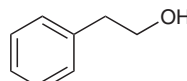
2.46)



2.47)



2.48)



2.50) Total = Six signals (two signals between 0–50 ppm, and four signals between 100–150 ppm)

2.51) Total = Nine signals (one signal between 0–50 ppm, one signal between 50–100 ppm, six signals between 100–150 ppm, and one signal between 150–220 ppm)

2.52) Total = Five signals (three signals between 0–50 ppm, and two signals between 100–150 ppm)

2.53) Total = Five signals (three signals between 0–50 ppm, and two signals between 50–100 ppm)

2.54) Total = Three signals (two signals between 0–50 ppm, and one signal between 50–100 ppm)

2.55) Total = Five signals (three signals between 0–50 ppm, and two signals between 50–100 ppm)

## CHAPTER 3

3.2)

