Melatonin, a hormone synthesized by the pineal gland, is thought to induce sleep. Because melatonin synthesis is inhibited by light, melatonin levels in the body rise as less light falls upon the eye, and drop quickly at dawn. For this reason, melatonin has become a popular dietary supplement for travelers suffering from jetlag and individuals with mild sleep disorders. Modern spectroscopic techniques have been used to characterize the structure of melatonin. In Chapter 14, we learn how nuclear magnetic resonance spectroscopy plays a key role in organic structure determination.
In Chapter 14 we continue our study of organic structure determination by learning about nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy is the most powerful tool for characterizing organic molecules, because it can be used to identify the carbon–hydrogen framework in a compound.

14.1 An Introduction to NMR Spectroscopy

Two common types of NMR spectroscopy are used to characterize organic structure:

- $^1$H NMR (proton NMR) is used to determine the number and type of hydrogen atoms in a molecule; and
- $^{13}$C NMR (carbon NMR) is used to determine the type of carbon atoms in a molecule.

Before you can learn how to use NMR spectroscopy to determine the structure of a compound, you need to understand a bit about the physics behind it. Keep in mind, though, that NMR stems from the same basic principle as all other forms of spectroscopy. Energy interacts with a molecule, and absorptions occur only when the incident energy matches the energy difference between two states.

14.1A The Basis of NMR Spectroscopy

The source of energy in NMR is radio waves. Radiation in the radiofrequency region of the electromagnetic spectrum (so-called RF radiation) has very long wavelengths, so its corresponding frequency and energy are both low. When these low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including $^1$H and $^{13}$C.

When a charged particle such as a proton spins on its axis, it creates a magnetic field. For the purpose of this discussion, therefore, a nucleus is a tiny bar magnet, symbolized by $^\uparrow$. Normally these nuclear magnets are randomly oriented in space, but in the presence of an external magnetic field, $B_0$, they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy, but the energy difference between these two states is very small (< 0.4 J/mol).

![Diagram of nuclear spins]

In a magnetic field, there are now two different energy states for a proton:

- A lower energy state with the nucleus aligned in the same direction as $B_0$
- A higher energy state with the nucleus aligned opposed to $B_0$

When an external energy source ($h\nu$) that matches the energy difference ($\Delta E$) between these two states is applied, energy is absorbed, causing the nucleus to “spin flip” from one orientation to another. The energy difference between these two nuclear spin states corresponds to the low-frequency radiation in the RF region of the electromagnetic spectrum.
A nucleus is in resonance when it absorbs RF radiation and “spin flips” to a higher energy state.

Thus, two variables characterize NMR:

- **An applied magnetic field,** $B_0$. Magnetic field strength is measured in tesla (T).
- **The frequency of radiation used for resonance,** measured in hertz (Hz) or megahertz (MHz); $(1 \text{ MHz} = 10^6 \text{ Hz})$

The frequency needed for resonance and the applied magnetic field strength are proportionally related:

$$\nu \propto B_0$$

- The stronger the magnetic field, the larger the energy difference between the two nuclear spin states, and the higher the $\nu$ needed for resonance.

Early NMR spectrometers used a magnetic field strength of ~1.4 T, which required RF radiation of 60 MHz for resonance. Modern NMR spectrometers use stronger magnets, thus requiring higher frequencies of RF radiation for resonance. For example, a magnetic field strength of 7.05 T requires a frequency of 300 MHz for a proton to be in resonance. These spectrometers use very powerful magnetic fields to create a small, but measurable energy difference between the two possible spin states. A schematic of an NMR spectrometer is shown in Figure 14.1.

If all protons absorbed at the same frequency in a given magnetic field, the spectra of all compounds would consist of a single absorption, rendering NMR useless for structure determination. Fortunately, however, this is not the case.

**Figure 14.1** Schematic of an NMR spectrometer

An NMR spectrometer. The sample is dissolved in a solvent, usually CDCl$_3$ (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded. The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.
All protons do not absorb at the same frequency. Protons in different environments absorb at slightly different frequencies, and so they are distinguishable by NMR.

The frequency at which a particular proton absorbs is determined by its electronic environment, as discussed in Section 14.3. Because electrons are moving charged particles, they create a magnetic field opposed to the applied field \( B_0 \), and the size of the magnetic field generated by the electrons around a proton determines where it absorbs. Modern NMR spectrometers use a constant magnetic field strength \( B_0 \), and then a narrow range of frequencies is applied to achieve the resonance of all protons.

Only nuclei that contain odd mass numbers (such as \(^1\)H, \(^{13}\)C, \(^{19}\)F, and \(^{31}\)P) or odd atomic numbers (such as \(^2\)H and \(^{14}\)N) give rise to NMR signals. Because both \(^1\)H and \(^{13}\)C, the less abundant isotope of carbon, are NMR active, NMR allows us to map the carbon and hydrogen framework of an organic molecule.

### 14.1B A \(^1\)H NMR Spectrum

An NMR spectrum plots the intensity of a signal against its chemical shift measured in parts per million (ppm). The common scale of chemical shifts is called the \( \delta \) (delta) scale. The proton NMR spectrum of tert-butyl methyl ether \([\text{CH}_3\text{OC(CH}_3)_3]\) illustrates several important features:

- NMR absorptions generally appear as sharp signals. The \(^1\)H NMR spectrum of \(\text{CH}_3\text{OC(CH}_3)_3\) consists of two signals: a tall peak at 1.2 ppm due to the \((\text{CH}_3)_3\text{C}^–\) group, and a smaller peak at 3.2 ppm due to the \(\text{CH}_3\text{O}^–\) group.
- Increasing chemical shift is plotted from right to left. Most protons absorb somewhere from 0–12 ppm.
- The terms upfield and downfield describe the relative location of signals. Upfield means to the right. The \((\text{CH}_3)_3\text{C}^–\) peak is upfield from the \(\text{CH}_3\text{O}^–\) peak. Downfield means to the left. The \(\text{CH}_3\text{O}^–\) peak is downfield from the \((\text{CH}_3)_3\text{C}^–\) peak.

NMR absorptions are measured relative to the position of a reference signal at 0 ppm on the \( \delta \) scale due to tetramethylsilane (TMS). TMS is a volatile and inert compound that gives a single peak upfield from other typical NMR absorptions.
The chemical shift on the \( x \) axis gives the position of an NMR signal, measured in ppm, according to the following equation:

\[
\text{chemical shift (in ppm on the } \delta \text{ scale)} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\nu \text{ of the NMR spectrometer (in MHz)}}
\]

A chemical shift gives absorptions as a fraction of the NMR operating frequency, making it independent of the spectrometer used to record a spectrum. Because the frequency of the radiation required for resonance is proportional to the strength of the applied magnetic field, \( B_0 \), reporting NMR absorptions in frequency is meaningless unless the value of \( B_0 \) is also reported. By reporting the absorption as a fraction of the NMR operating frequency, though, we get units—ppm—that are independent of the spectrometer.

**Sample Problem 14.1**

Calculate the chemical shift of an absorption that occurs at 1500 Hz downfield from TMS using a 300 MHz NMR spectrometer.

**Solution**

Use the equation that defines the chemical shift in ppm:

\[
\text{chemical shift} = \frac{1500 \text{ Hz downfield from TMS}}{300 \text{ MHz operating frequency}} = 5 \text{ ppm}
\]

**Problem 14.1**

The \(^1\text{H} \) NMR spectrum of \( \text{CH}_3\text{OH} \) recorded on a 500 MHz NMR spectrometer consists of two signals, one due to the \( \text{CH}_3 \) protons at 1715 Hz and one due to the OH proton at 1830 Hz, both measured downfield from TMS. (a) Calculate the chemical shift of each absorption. (b) Do the \( \text{CH}_3 \) protons absorb upfield or downfield from the OH proton?

**Problem 14.2**

The \(^1\text{H} \) NMR spectrum of 1,2-dimethoxyethane (\( \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 \)) recorded on a 300 MHz NMR spectrometer consists of signals at 1017 Hz and 1065 Hz downfield from TMS. (a) Calculate the chemical shift of each absorption. (b) At what frequency would each absorption occur if the spectrum were recorded on a 500 MHz NMR spectrometer?

Four different features of a \(^1\text{H} \) NMR spectrum provide information about a compound’s structure:

1. **Number of signals** (Section 14.2)
2. **Position of signals** (Sections 14.3 and 14.4)
3. **Intensity of signals** (Section 14.5)
4. **Spin–spin splitting of signals** (Sections 14.6–14.8)

### 14.2 \(^1\text{H} \) NMR: Number of Signals

**How many \(^1\text{H} \) NMR signals does a compound exhibit?** The number of NMR signals *equals* the number of different types of protons in a compound.

#### 14.2A General Principles

- Protons in different environments give different NMR signals. Equivalent protons give the same NMR signal.

In many compounds, deciding whether two protons are in identical or different environments is intuitive.
- CH₃OCH₂: Each CH₃ group is bonded to the same group (–OCH₃), making both CH₃ groups equivalent.
- CH₃CH₂Cl: The protons of the CH₃ group are different from those of the CH₂ group.
- CH₃OCH₂CH₃: The protons of the CH₂ group are different from those in each CH₃ group. The two CH₃ groups are also different from each other; one CH₃ group is bonded to –OCH₂CH₃ and the other is bonded to –CH₂OCH₃.

In some cases, it is less obvious by inspection if two protons are equivalent or different. To rigorously determine whether two protons are in identical environments (and therefore give rise to one NMR signal), replace each H atom in question by another atom Z (for example, Z = Cl). If substitution by Z yields the same compound or enantiomers, the two protons are equivalent, as shown in Sample Problem 14.2.

**Sample Problem 14.2**

How many different kinds of H atoms does CH₃CH₂CH₂CH₂CH₃ contain?

**Solution**

In comparing two H atoms, replace each H by Z (for example, Z = Cl), and examine the substitution products that result. The two CH₃ groups are identical because substitution of one H by Cl gives CH₃CH₂CH₂CH₂CH₂Cl (1-chloropentane). There are two different types of CH₂ groups, because substitution of one H by Cl gives two different products:

\[
\begin{align*}
\text{CH₃CH₂CH₂CH₂CH₃} & \quad \text{Cl} \quad \text{Cl} \\
\text{CH₃CH₂CH₂CH₂CH₃} & \quad \text{Cl} \quad \text{Cl} \\
\text{CH₃CH₂CH₂CH₂CH₃} & \quad \text{Cl} \quad \text{Cl} \\
\text{CH₃CH₂CH₂CH₂CH₃} & \quad \text{Cl} \quad \text{Cl} \\
\end{align*}
\]

Thus, CH₃CH₂CH₂CH₂CH₃ has three different types of protons and gives three NMR signals.

Figure 14.2 gives the number of NMR signals exhibited by four additional molecules. All protons—not just protons bonded to carbon atoms—give rise to NMR signals. Ethanol (CH₃CH₂OH), for example, gives three NMR signals, one of which is due to its OH proton.

**Problem 14.3**

How many ¹H NMR signals does each compound show?

a. CH₃CH₃   b. CH₃CH₂CH₃   c. CH₃CH₂CH₂CH₃   d. (CH₃)₂CHCH(CH₃)₂   e. CH₃CH₂CO₂CH₂CH₃   f. CH₃OCH₂CH(CH₃)₂   g. CH₃CH₂OCH₂CH₃   h. CH₃CH₂CH₂OH

**Problem 14.4**

How many different types of protons does CH₃CH₂CH₂CH₂CH₂CH₂CH₂Cl contain?

### 14.2B Determining Equivalent Protons in Alkenes and Cycloalkanes

To determine equivalent protons in cycloalkanes and alkenes that have restricted bond rotation, always draw in all bonds to hydrogen.
Then, in comparing two H atoms on a ring or double bond, two protons are equivalent only if they are cis (or trans) to the same groups, as illustrated with 1,1-dichloroethylene, 1-bromo-1-chloroethylene, and chloroethylene.

- **1,1-Dichloroethylene**: The two H atoms on the C=C are both cis to a Cl atom. Thus, both H atoms are equivalent.
- **1-Bromo-1-Chloroethylene**: H_a is cis to a Cl atom and H_b is cis to a Br atom. Thus, H_a and H_b are different, giving rise to two NMR signals.
- **Chloroethylene**: H_a is bonded to the carbon with the Cl atom, making it different from H_b and H_c. Of the remaining two H atoms, H_b is cis to a Cl atom and H_c is cis to a H atom, making them different. All three H atoms in this compound are different.

Proton equivalency in cycloalkanes can be determined similarly.

- **Cyclopropane**: All H atoms are equivalent, so there is only one NMR signal.
- **Chlorocyclopropane**: There are now three kinds of H atoms: H_a is bonded to a carbon bonded to a Cl; both H_b protons are cis to the Cl whereas both H_c protons are cis to another H.

**Problem 14.5** How many ¹H NMR signals does each dimethylcyclopropane show?

a. 

b. 

c. 

**14.2C Enantiotopic and Diastereotopic Protons**

Let’s look more closely at the protons of a single sp³ hybridized CH₂ group to determine whether these two protons are always equivalent to each other. Two examples illustrate different outcomes.

CH₃CH₂Br has two different types of protons—those of the CH₃ group and those of the CH₂ group—meaning that the two H atoms of the CH₂ group are equivalent to each other. To confirm this fact, we replace each H of the CH₂ group by an atom Z and examine the products of substitution. In this case, substitution of each H by Z creates a new stereogenic center, forming two products that are enantiomers.
When substitution of two H atoms by Z forms enantiomers, the two H atoms are equivalent and give a single NMR signal. These two H atoms are called enantiotopic protons.

In contrast, the two H atoms of the CH₂ group in (2R)-2-chlorobutane, which contains one stereogenic center, are not equivalent to each other. Substitution of each H by Z forms two diastereomers, and thus, these two H atoms give different NMR signals.

Sample Problem 14.3
Label the protons in each indicated CH₂ group as enantiotopic, diastereotopic, or neither.

a. The compound is achiral and has no stereogenic center. Since no new stereogenic center is formed on substitution of H by Z, the protons are neither enantiotopic nor diastereotopic. The H's within the CH₂ group are equivalent to each other and give one NMR signal.

b. The compound is achiral and has no stereogenic center. Since a new stereogenic center is formed on substitution of H by Z, the protons are enantiotopic. The H's within the CH₂ group are equivalent to each other and give one NMR signal.

c. The compound has one stereogenic center to begin with. Since a new stereogenic center is formed on substitution of H by Z, the protons are diastereotopic. The H's within the CH₂ group are different from each other and give different NMR signals.
Problem 14.6 Label the protons in each indicated CH₂ group as enantiotopic, diastereotopic, or neither.

a. CH₃CH₂CH₂CH₂CH₃  
b. CH₃CH₂CH₃CH₂CH₃  
c. CH₃CH(OH)CH₂CH₂CH₃

Problem 14.7 How many ¹H NMR signals would you expect for each compound: (a) CH₃CH(Cl)CH₂CH₃; (b) ClCH₂CH(CH₃)OCH₃; (c) CH₃CH(Br)CH₂CH₂CH₃?

14.3 ¹H NMR: Position of Signals

In the NMR spectrum of tert-butyl methyl ether in Section 14.1B, why does the CH₃O– group absorb downfield from the –C(CH₃)₃ group?

• Where a particular proton absorbs depends on its electronic environment.

14.3A Shielding and Deshielding Effects

To understand how the electronic environment around a nucleus affects its chemical shift, recall that in a magnetic field, an electron creates a small magnetic field that opposes the applied magnetic field, B₀. **Electrons are said to shield the nucleus from B₀.**

In the vicinity of the nucleus, therefore, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton “feels.” Because the proton experiences a lower magnetic field strength, it needs a lower frequency to achieve resonance. Lower frequency is to the right in an NMR spectrum, toward lower chemical shift, so shielding shifts an absorption upfield, as shown in Figure 14.3a.

**Figure 14.3** How chemical shift is affected by electron density around a nucleus

a. Shielding effects
   • An electron shields the nucleus.
   • The absorption shifts upfield.

b. Deshielding effects
   • Decreased electron density deshields a nucleus.
   • The absorption shifts downfield.
What happens if the electron density around a nucleus is decreased, instead? For example, how do the chemical shifts of the protons in CH₄ and CH₃Cl compare?

The less shielded the nucleus becomes, the more of the applied magnetic field (B₀) it feels. This deshielded nucleus experiences a higher magnetic field strength, so it needs a higher frequency to achieve resonance. Higher frequency is to the left in an NMR spectrum, toward higher chemical shift, so deshielding shifts an absorption downfield, as shown in Figure 14.3b for CH₃Cl versus CH₄. The electronegative Cl atom withdraws electron density from the carbon and hydrogen atoms in CH₃Cl, thus deshielding them relative to those in CH₄.

- Protons near electronegative atoms are deshielded, so they absorb downfield.

Figure 14.4 summarizes the effects of shielding and deshielding.

These electron density arguments explain the relative position of NMR signals in many compounds.

- The H₆ protons are deshielded because they are closer to the electronegative Cl atom, so they absorb downfield from H₅.
- Because F is more electronegative than Br, the H₆ protons are more deshielded than the H₅ protons and absorb farther downfield.
- The larger number of electronegative Cl atoms (two versus one) deshields H₆ more than H₅, so it absorbs downfield from H₅.

Sample Problem 14.4

Which of the underlined protons in each pair absorbs farther downfield: (a) CH₃CH₂CH₃ or CH₃OCH₃; (b) CH₃OCH₃ or CH₃SCH₃?

Solution

a. The CH₃ group in CH₃OCH₃ is deshielded by the electronegative O atom. Deshielding shifts the absorption downfield.

b. Because oxygen is more electronegative than sulfur, the CH₃ group in CH₃OCH₃ is more deshielded and absorbs downfield.

Problem 14.8

For each compound, which of the underlined protons absorbs farther downfield: (a) FCH₂CH₂CH₂Cl; (b) CH₂CH₂CH₂CH₂OCH₃; (c) CH₃OC(CH₃)₃?

14.3B Chemical Shift Values

Not only is the relative position of NMR absorptions predictable, but it is also possible to predict the approximate chemical shift value for a given type of proton.
Protons in a given environment absorb in a predictable region in an NMR spectrum. Table 14.1 lists the typical chemical shift values for the most common bonds encountered in organic molecules. Table 14.1 illustrates that absorptions for a given type of $C-H$ bond occur in a narrow range of chemical shift values, usually 1–2 ppm. For example, all $sp^3$ hybridized C–H bonds in alkanes and cycloalkanes absorb between 0.9 and 2.0 ppm. By contrast, absorptions due to N–H and O–H protons can occur over a broader range. For example, the OH proton of an alcohol is found anywhere in the 1–5 ppm range. The position of these absorptions is affected by the extent of hydrogen bonding, making it more variable.

The chemical shift of a particular type of C–H bond is also affected by the number of R groups bonded to the carbon atom.

Table 14.1 Characteristic Chemical Shifts of Common Types of Protons

<table>
<thead>
<tr>
<th>Type of proton</th>
<th>Chemical shift (ppm)</th>
<th>Type of proton</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp^3$ C–H</td>
<td>0.9–2</td>
<td>$sp^2$ C–H</td>
<td>4.5–6</td>
</tr>
<tr>
<td>$sp^3$ C–H</td>
<td>1.5–2.5</td>
<td>$sp^2$ C–H</td>
<td>4.5–6</td>
</tr>
<tr>
<td>$sp^3$ C–H</td>
<td>2.5–4</td>
<td>$sp^2$ C–H</td>
<td>4.5–6</td>
</tr>
<tr>
<td>RCH$_3$</td>
<td>-0.9</td>
<td>R$_2$CH–H</td>
<td>6.5–8</td>
</tr>
<tr>
<td>R$_2$CH</td>
<td>-1.3</td>
<td>R$_3$C–H</td>
<td>6.5–8</td>
</tr>
<tr>
<td>R$_3$CH</td>
<td>-1.7</td>
<td>Z = C, O, N</td>
<td>6.5–8</td>
</tr>
<tr>
<td>Z = C, O, N</td>
<td>1.5–2.5</td>
<td>Z = C, O, N</td>
<td>6.5–8</td>
</tr>
<tr>
<td>Z = C, O, N</td>
<td>2.5–4</td>
<td>Z = C, O, N</td>
<td>6.5–8</td>
</tr>
</tbody>
</table>

- Protons in a given environment absorb in a predictable region in an NMR spectrum.

A more detailed list of characteristic chemical shift values is found in Appendix F.

Problem 14.9

For each compound, first label each different type of proton and then rank the protons in order of increasing chemical shift.

a. $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Br}$

b. $\text{CH}_3\text{OCH}_2\text{OC(CH}_3_3)$

c. $\text{CH}_3\text{C}=$CH$_2\text{CH}_2\text{CH}_3$
14.4 The Chemical Shift of Protons on $sp^2$ and $sp$ Hybridized Carbons

The chemical shift of protons bonded to benzene rings, C–C double bonds, and C–C triple bonds merits additional comment.

Each of these functional groups contains π bonds with loosely held π electrons. When placed in a magnetic field, these π electrons move in a circular path, inducing a new magnetic field. How this induced magnetic field affects the chemical shift of a proton depends on the direction of the induced field in the vicinity of the absorbing proton.

Protons on Benzene Rings

In a magnetic field, the six π electrons in benzene circulate around the ring, creating a ring current. The magnetic field induced by these moving electrons reinforces the applied magnetic field in the vicinity of the protons. The protons thus feel a stronger magnetic field and a higher frequency is needed for resonance, so the protons are deshielded and the absorption is downfield.

Protons on Carbon–Carbon Double Bonds

A similar phenomenon occurs with protons on carbon–carbon double bonds. In a magnetic field, the loosely held π electrons create a magnetic field that reinforces the applied field in the vicinity of the protons. Because the protons now feel a stronger magnetic field, they require a higher frequency for resonance. The protons are deshielded and the absorption is downfield.

Protons on Carbon–Carbon Triple Bonds

In a magnetic field, the π electrons of a carbon–carbon triple bond are induced to circulate, but in this case the induced magnetic field opposes the applied magnetic field ($B_0$). The proton thus feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.
Table 14.2 summarizes the shielding and deshielding effects due to circulating π electrons.

To remember the chemical shifts of some common bond types, it is helpful to think of a ¹H NMR spectrum as being divided into six different regions (Figure 14.5).

**Table 14.2 Effect of π Electrons on Chemical Shift Values**

<table>
<thead>
<tr>
<th>Proton type</th>
<th>Effect</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenyl-CH₃</td>
<td>highly deshielded</td>
<td>6.5–8</td>
</tr>
<tr>
<td>C=CH₂-CH₂</td>
<td>deshielded</td>
<td>4.5–6</td>
</tr>
<tr>
<td>C≡CH</td>
<td>shielded</td>
<td>~2.5</td>
</tr>
</tbody>
</table>

**Figure 14.5**

Regions in the ¹H NMR spectrum

- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).
- Note: The drawn chemical shift scale is not linear.
**Sample Problem 14.5** Rank $H_a$, $H_b$, and $H_c$ in order of increasing chemical shift.

![Chemical structure](image)

**Solution**

The $H_a$ protons are bonded to an $sp^3$ hybridized carbon, so they are shielded and absorb upfield compared to $H_b$ and $H_c$. Because the $H_b$ protons are deshielded by the electronegative oxygen atom on the C to which they are bonded, they absorb downfield from $H_a$. The $H_c$ proton is deshielded by two factors. The electronegative O atom withdraws electron density from $H_c$. Moreover, because $H_c$ is bonded directly to a $C=\text{C}$, the magnetic field induced by the $\pi$ electrons causes further deshielding. Thus, in order of increasing chemical shift, $H_a < H_b < H_c$.

**Problem 14.10** Rank each group of protons in order of increasing chemical shift.

a. CH$_3$C\equivC\text{H} \\
    CH$_2$CH=\text{CH}_2 \\
    CH$_3$CH$_2$CH$_3$

b. CH$_3$C\text{OCH$_2$CH$_3$}

---

### 14.5 $^1$H NMR: Intensity of Signals

The relative intensity of $^1$H NMR signals also provides information about a compound’s structure.

- The area under an NMR signal is proportional to the number of absorbing protons.

For example, in the $^1$H NMR spectrum of CH$_3$OC(CH$_3$)$_3$, the ratio of the area under the downfield peak (due to the CH$_3$O$^-$ group) to the upfield peak [due to the $-\text{C(CH}_3)_3$ group] is 1:3. An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (an integral) on the spectrum. The height of each step is proportional to the area under the peak, which is in turn proportional to the number of absorbing protons.

![NMR integration](image)

Integrals can be manually measured, but modern NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units. If the heights of two integrals are 20 units and 60 units, the ratio of absorbing protons is 20:60, or 1:3, or 2:6, or 3:9, and so forth. This tells the ratio, not the absolute number of protons. Integration ratios are approximate, and often values must be rounded to the nearest whole number.
Problem 14.11 Which compounds give a $^1$H NMR spectrum with two signals in a ratio of 2:3?

a. CH₃CH₂Cl  

b. CH₃CH₂CH₃  

c. CH₃CH₂OCH₂CH₃  

d. CH₃OCH₂CH₂OCH₃

Knowing the molecular formula of a compound and integration values from its $^1$H NMR spectrum gives the actual number of protons responsible for a particular signal.

**HOW TO** Determine the Number of Protons Giving Rise to an NMR Signal

**Example** A compound of molecular formula C₉H₁₀O₂ gives the following integrated $^1$H NMR spectrum. How many protons give rise to each signal?

<table>
<thead>
<tr>
<th>ppm</th>
<th>signal [A]</th>
<th>signal [B]</th>
<th>signal [C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.7</td>
<td>54</td>
<td>23</td>
<td>33</td>
</tr>
</tbody>
</table>

**Step [1]** Determine the number of integration units per proton by dividing the total number of integration units by the total number of protons.

- Total number of integration units: 54 + 23 + 33 = 110 units
- Total number of protons = 10
- Divide: 110 units/10 protons = **11 units per proton**

**Step [2]** Determine the number of protons giving rise to each signal.

- To determine the number of H atoms giving rise to each signal, divide each integration value by the answer of Step [1] and round to the nearest whole number.

<table>
<thead>
<tr>
<th>Signal [A]:</th>
<th>Signal [B]:</th>
<th>Signal [C]:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Answer: 54/11 = 4.9 = 5 H</td>
<td>23/11 = 2.1 = 2 H</td>
<td>33/11 = 3 H</td>
</tr>
</tbody>
</table>

**Problem 14.12** A compound of molecular formula C₈H₁₄O₂ gives three NMR signals having the indicated integration values: signal [A] 14 units, signal [B] 12 units, and signal [C] 44 units. How many protons give rise to each signal?

**Problem 14.13** Compound A exhibits two signals in its $^1$H NMR spectrum at 2.64 and 3.69 ppm and the ratio of the absorbing signals is 2:3. Compound B exhibits two signals in its $^1$H NMR spectrum at 2.09 and 4.27 ppm and the ratio of the absorbing signals is 3:2. Which compound corresponds to CH₃O₂CCH₂CH₂CO₂CH₃ (dimethyl succinate) and which compound corresponds to CH₃CO₂CH₂CH₂O₂CCH₃ (ethylene diacetate)?

**14.6 $^1$H NMR: Spin–Spin Splitting**

The $^1$H NMR spectra you have seen up to this point have been limited to one or more single absorptions called **singlets**. In the $^1$H NMR spectrum of BrCH₂CHBr₂, however, the two signals for the two different kinds of protons are each split into more than one peak. The splitting pat-
terns, the result of spin–spin splitting, can be used to determine how many protons reside on the
carbon atoms near the absorbing proton.

To understand spin–spin splitting, we must distinguish between the absorbing protons that give rise to an
NMR signal, and the adjacent protons that cause the signal to split. The number of adjacent protons determines the observed splitting pattern.

14.6A Splitting: How a Doublet Arises

First, let’s examine how the doublet due to the CH$_2$ group in BrCH$_2$CHBr$_2$ arises. The CH$_2$ group con-
tains the absorbing protons and the CH group contains the adjacent proton that causes the splitting.

When placed in an applied magnetic field ($B_0$), the adjacent proton (CHBr$_2$) can be aligned with (↑) or
against (↓) $B_0$. As a result, the absorbing protons (CH$_2$Br) feel two slightly different magnetic fields—one slightly larger than $B_0$ and one slightly smaller than $B_0$. Because the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.

- The CH$_2$ signal appears as two peaks, called a doublet. The relative area under the peaks of a doublet is 1:1.
- The CH signal appears as three peaks, called a triplet. The relative area under the peaks of a triplet is 1:2:1.

Spin–spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons. To illustrate how spin–spin splitting arises, we’ll examine nonequivalent protons on adjacent carbons, the more common example. Spin–spin splitting arises because protons are little magnets that can be aligned with or against an applied magnetic field, and this affects the magnetic field that a nearby proton feels.

Keep in mind the difference between an NMR signal and an NMR peak. An NMR signal is the entire absorption due to a particular kind of proton. NMR peaks are contained within a signal. A doublet constitutes one signal that is split into two peaks.
• One adjacent proton splits an NMR signal into a doublet.

The two peaks of a doublet are approximately equal in area. The area under both peaks—the entire NMR signal—is due to both protons of the CH₂ group of BrCH₂CHBr₂.

The frequency difference (measured in Hz) between the two peaks of the doublet is called the coupling constant, denoted by \( J \). Coupling constants are usually in the range of 0–18 Hz, and are independent of the strength of the applied magnetic field \( B_0 \).

14.6B Splitting: How a Triplet Arises

Now let’s examine how the triplet due to the CH group in BrCH₂CHBr₂ arises. The CH group contains the absorbing proton and the CH₂ group contains the adjacent protons (Hₐ and Hₖ) that cause the splitting.

When placed in an applied magnetic field \( (B_0) \), the adjacent protons Hₐ and Hₖ can each be aligned with \( (↑) \) or against \( (↓) \) \( B_0 \). As a result, the absorbing proton feels three slightly different magnetic fields—one slightly larger than \( B_0 \), one slightly smaller than \( B_0 \), and one the same strength as \( B_0 \).

Because the absorbing proton feels three different magnetic fields, it absorbs at three different frequencies in the NMR spectrum, thus splitting a single absorption into a triplet. Because there are two different ways to align one proton with \( B_0 \) and one proton against \( B_0 \)—that is, \( ↑ \) \( a \), \( ↓ \) \( b \), and \( ↓ \) \( a \), \( ↑ \) \( b \)—the middle peak of the triplet is twice as intense as the two outer peaks, making the ratio of the areas under the three peaks 1:2:1.

• Two adjacent protons split an NMR signal into a triplet.

When two protons split each other’s NMR signals, they are said to be coupled. In BrCH₂CHBr₂, the CH proton is coupled to the CH₂ protons. The spacing between peaks in a split NMR signal, measured by the \( J \) value, is equal for coupled protons.

14.6C Splitting: The Rules and Examples

Three general rules describe the splitting patterns commonly seen in the \(^1\text{H}\) NMR spectra of organic compounds.
14.6 ¹H NMR: Spin–Spin Splitting

<table>
<thead>
<tr>
<th>Number of peaks</th>
<th>Name</th>
<th>Number of peaks</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>singlet</td>
<td>5</td>
<td>quintet</td>
</tr>
<tr>
<td>2</td>
<td>doublet</td>
<td>6</td>
<td>sextet</td>
</tr>
<tr>
<td>3</td>
<td>triplet</td>
<td>7</td>
<td>septet</td>
</tr>
<tr>
<td>4</td>
<td>quartet</td>
<td>&gt; 7</td>
<td>multiplet</td>
</tr>
</tbody>
</table>

**Rule [1]** Equivalent protons don’t split each other’s signals.

**Rule [2]** A set of \( n \) nonequivalent protons splits the signal of a nearby proton into \( n + 1 \) peaks.

- In \( \text{BrCH}_2\text{CHBr}_2 \), for example, one adjacent CH proton splits an NMR signal into two peaks (a doublet), and two adjacent CH\(_2\) protons split an NMR signal into three peaks (a triplet). Names for split NMR signals containing two to seven peaks are given in Table 14.3. An NMR signal having more than seven peaks is called a multiplet.
- The inside peaks of a split NMR signal are always most intense, with the area under the peaks decreasing from the inner to the outer peaks in a given splitting pattern.

**Rule [3]** Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.

The splitting of an NMR signal reveals the number of nearby nonequivalent protons. It tells nothing about the absorbing proton itself.

Table 14.4 illustrates common splitting patterns observed for adjacent nonequivalent protons.

Predicting splitting is always a two-step process:

- **Determine if two protons are equivalent or different.** Only nonequivalent protons split each other.
- **Determine if two nonequivalent protons are close enough to split each other’s signals.** Splitting is observed only for nonequivalent protons on the same carbon or adjacent carbons.

Several examples of spin–spin splitting in specific compounds illustrate the result of this two-step strategy.
### Table 14.4 Common Splitting Patterns Observed in $^1$H NMR

<table>
<thead>
<tr>
<th>Example</th>
<th>Pattern</th>
<th>Analysis ($H_a$ and $H_b$ are not equivalent.)</th>
</tr>
</thead>
</table>
| [1]     | ![Example 1](image1) | • $H_a$: one adjacent $H_b$ proton \(\rightarrow\) two peaks \(\rightarrow\) a doublet  
          |         | • $H_b$: one adjacent $H_a$ proton \(\rightarrow\) two peaks \(\rightarrow\) a doublet  |
| [2]     | ![Example 2](image2) | • $H_a$: two adjacent $H_b$ protons \(\rightarrow\) three peaks \(\rightarrow\) a triplet  
          |         | • $H_b$: one adjacent $H_a$ proton \(\rightarrow\) two peaks \(\rightarrow\) a doublet  |
| [3]     | ![Example 3](image3) | • $H_a$: two adjacent $H_b$ protons \(\rightarrow\) three peaks \(\rightarrow\) a triplet  
          |         | • $H_b$: two adjacent $H_a$ protons \(\rightarrow\) three peaks \(\rightarrow\) a triplet  |
| [4]     | ![Example 4](image4) | • $H_a$: three adjacent $H_b$ protons \(\rightarrow\) four peaks \(\rightarrow\) a quartet*  
          |         | • $H_b$: two adjacent $H_a$ protons \(\rightarrow\) three peaks \(\rightarrow\) a triplet  |
| [5]     | ![Example 5](image5) | • $H_a$: three adjacent $H_b$ protons \(\rightarrow\) four peaks \(\rightarrow\) a quartet*  
          |         | • $H_b$: one adjacent $H_a$ proton \(\rightarrow\) two peaks \(\rightarrow\) a doublet  |

*The relative area under the peaks of a quartet is 1:3:3:1.

---

Cl—CH$_2$CH$_2$—Cl  
- All protons are equivalent ($H_a$), so there is no splitting and the NMR signal is one singlet.

Cl—CH$_2$CH$_2$—Br  
- There are two NMR signals. $H_a$ and $H_b$ are nonequivalent protons bonded to adjacent C atoms, so they are close enough to split each other’s NMR signals. The $H_a$ signal is split into a triplet by the two $H_b$ protons. The $H_b$ signal is split into a triplet by the two $H_a$ protons.

CH$_3$C(=O)CH$_2$CH$_3$  
- There are three NMR signals. $H_a$ has no adjacent nonequivalent protons, so its signal is a singlet. The $H_b$ signal is split into a quartet by the three $H_a$ protons. The $H_c$ signal is split into a triplet by the two $H_b$ protons.

Cl=C=CH$_3$  
- There are two NMR signals. $H_a$ and $H_b$ are nonequivalent protons on the same carbon, so they are close enough to split each other’s NMR signals. The $H_a$ signal is split into a doublet by $H_b$. The $H_b$ signal is split into a doublet by $H_a$.

### Problem 14.14

Into how many peaks will each indicated proton be split?

- a. ![Example a](image6)  
- b. ![Example b](image7)  
- c. ![Example c](image8)  
- d. ![Example d](image9)  
- e. ![Example e](image10)  
- f. ![Example f](image11)
Problem 14.15 Although Cl₂CHCHCl₂ and Br₂CHCHCl₂ each have only two hydrogens, these compounds have very different ¹H NMR spectra. For each compound, give the number of ¹H NMR signals and indicate into how many peaks each signal is split.

Problem 14.16 For each compound give the number of ¹H NMR signals, and then determine how many peaks are present for each NMR signal.

a.  

b.  

c.  

d.  

Problem 14.17 Sketch the NMR spectrum of CH₃CH₂Cl, giving the approximate location of each NMR signal.

14.7 More Complex Examples of Splitting

Up to now you have studied examples of spin–spin splitting where the absorbing proton has nearby protons on one adjacent carbon only. What happens when the absorbing proton has nonequivalent protons on two adjacent carbons? Different outcomes are possible, depending on whether the adjacent nonequivalent protons are equivalent to or different from each other.

For example, 2-bromopropane [(CH₃)₂CHBr] has two types of protons—Hₐ and Hₐ—so it exhibits two NMR signals, as shown in Figure 14.6.

- The Hₐ protons have only one adjacent nonequivalent proton (Hₐ), so they are split into two peaks, a doublet.
- Hₐ has three Hₐ protons on each side. Because the six Hₐ protons are equivalent to each other, the n + 1 rule can be used to determine splitting: 6 + 1 = 7 peaks, a septet.

This is a specific example of a general rule:

- Whenever two (or three) sets of adjacent protons are equivalent to each other, use the n + 1 rule to determine the splitting pattern.

A different outcome results when an absorbing proton is flanked by adjacent protons that are not equivalent to each other. Consider the splitting pattern expected for the Hₐ protons in the...
$^1$H NMR spectrum of CH$_3$CH$_2$CH$_2$Z. H$_b$ has protons on both adjacent carbons, but since H$_a$ and H$_c$ are not equivalent to each other, we cannot merely add them together and use the $n + 1$ rule.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Z}
\]

\[
\text{H}_a \quad \text{H}_b \quad \text{H}_c
\]

Instead, to determine the splitting of H$_b$, we must consider the effect of the H$_a$ protons and the H$_c$ protons separately. The three H$_a$ protons split the H$_b$ signal into four peaks, and the two H$_c$ protons split each of these four peaks into three peaks—that is, the NMR signal due to H$_b$ consists of $4 \times 3 = 12$ peaks. Figure 14.7 shows a splitting diagram illustrating how these 12 peaks arise.

- When two sets of adjacent protons are different from each other ($n$ protons on one adjacent carbon and $m$ protons on the other), the number of peaks in an NMR signal = $(n + 1)(m + 1)$.

It is only possible to see 12 peaks in an NMR spectrum when the coupling constants between each set of nonequivalent protons—that is, $J_{ab}$ and $J_{bc}$ in this example—are different; in other words, $J_{ab} \neq J_{bc}$. Such is the case with the nonequivalent protons on carbon–carbon double bonds, which is discussed in Section 14.8. In practice, with flexible alkyl chains it is more common for $J_{ab}$ and $J_{bc}$ to be very similar or identical. In this case, peaks overlap and many fewer than 12 peaks are observed.

The $^1$H NMR spectrum of 1-bromopropane (CH$_3$CH$_2$CH$_2$Br) illustrates the result of peak overlap (Figure 14.8).

CH$_3$CH$_2$CH$_2$Br has three different types of protons—H$_a$, H$_b$, and H$_c$—so it exhibits three NMR signals. H$_b$ and H$_c$ are each triplets because they are adjacent to two H$_b$ protons. H$_b$ has protons on both adjacent carbons, and H$_a$ and H$_c$ are not equivalent to each other. The three H$_a$ protons should split the H$_b$ signal into four peaks, and the two H$_c$ protons should split each of these four peaks into three peaks—that is, the NMR signal due to H$_b$ should once again consist of $4 \times 3 = 12$ peaks. However, since $J_{ab} = J_{bc}$ in this case, peak overlap occurs and a multiplet of only six peaks is observed.

Figure 14.7
A splitting diagram for the H$_b$ protons in CH$_3$CH$_2$CH$_2$Z

- The H$_b$ signal is split into 12 peaks, a quartet of triplets. The number of peaks actually seen for the signal depends on the relative size of the coupling constants, $J_{ab}$ and $J_{bc}$. When $J_{ab} \gg J_{bc}$, as drawn in this diagram, all 12 lines of the pattern are visible. When $J_{ab}$ and $J_{bc}$ are similar in magnitude, peaks overlap and fewer lines are observed.
In CH₃CH₂CH₂Br, the \( n \) protons on one adjacent carbon and the \( m \) protons on the other adjacent carbon split the observed signal into \( n + m + 1 \) peaks. In other words, the 3 \( H_a \) protons and 2 \( H_c \) protons split the NMR signal into \( 3 + 2 + 1 = 6 \) peaks, as shown in the sextet in Figure 14.8.

**Sample Problem 14.6** How many peaks are present in the NMR signal of each indicated proton?

a. ClCH₂CH₂CH₂Cl  

\[ H_a \quad \text{Hb} \quad \text{Hc} \]

- \( H_a \) has two \( H_a \) protons on each adjacent C. Because the four \( H_a \) protons are equivalent to each other, the \( n + 1 \) rule can be used to determine splitting: \( 4 + 1 = 5 \) peaks, a quintet.

b. ClCH₂CH₂CH₂Br  

\[ H_a \quad \text{Hb} \quad \text{Hc} \]

- \( H_b \) has two \( H_a \) protons on one adjacent C and two \( H_c \) protons on the other. Because \( H_a \) and \( H_c \) are not equivalent to each other, the maximum number of peaks for \( H_b = (n + 1)(m + 1) = (2 + 1)(2 + 1) = 9 \) peaks. However, since this molecule has a flexible alkyl chain, it is likely that \( J_{ab} \) and \( J_{bc} \) are very similar, so that peak overlap occurs. In this case, the number of peaks for \( H_b = n + m + 1 = 2 + 2 + 1 = 5 \) peaks.

**Problem 14.18** How many peaks are present in the NMR signal of each indicated proton?

a. \((CH₃)₂CHCO₂CH₃\)  
b. \(CH₃CH₂CH₂CH₂CH₃\)  
c. \(C\equiv C\)  
d. \(C≡C\) (all H atoms)

**Problem 14.19** Describe the \(^{1}H\) NMR spectrum of each compound. State how many NMR signals are present, the splitting pattern for each signal, and the approximate chemical shift.

a. \(CH₃OCH₂CH₃\)  
b. \(CH₃CH₂OCH(CH₃)₂\)  
c. \(CH₃OCH₂CH₂OCH₃\)  
d. \(CH₂CH₂\)
14.8 Spin–Spin Splitting in Alkenes

Protons on carbon–carbon double bonds often give characteristic splitting patterns. A disubstituted double bond can have two geminal protons (on the same carbon atom), two cis protons, or two trans protons. When these protons are different, each proton splits the NMR signal of the other, so that each proton appears as a doublet. The magnitude of the coupling constant $J$ for these doublets depends on the arrangement of hydrogen atoms.

Thus, the $E$ and $Z$ isomers of 3-chloropropenoic acid both exhibit two doublets for the two alkenyl protons, but the coupling constant is larger when the protons are trans compared to when the protons are cis, as shown in Figure 14.9.

When a double bond is monosubstituted, there are three nonequivalent protons, and the pattern is more complicated because all three protons are coupled to each other. For example, vinyl acetate (CH$_2$=CHCOOCH$_3$) has four different types of protons, three of which are bonded to the double bond. Besides the singlet for the CH$_3$ group, each proton on the double bond is coupled to two other different protons on the double bond, giving the spectrum in Figure 14.10.

- $H_b$ has two nearby nonequivalent protons that split its signal, the geminal proton $H_c$ and the trans proton $H_d$. $H_d$ splits the $H_b$ signal into a doublet, and the $H_c$ proton splits the doublet into two doublets. This pattern of four peaks is called a **doublet of doublets**.
- $H_c$ has two nearby nonequivalent protons that split its signal, the geminal proton $H_b$ and the cis proton $H_d$. $H_d$ splits the $H_c$ signal into a doublet, and the $H_b$ proton splits the doublet into two doublets, forming another **doublet of doublets**.
- $H_d$ has two nearby nonequivalent protons that split its signal, the trans proton $H_b$ and the cis proton $H_c$. $H_b$ splits the $H_d$ signal into a doublet, and the $H_c$ proton splits the doublet into two doublets, forming another **doublet of doublets**.

Splitting diagrams for the three alkenyl protons in vinyl acetate are drawn in Figure 14.11. Note that each pattern is different in appearance because the magnitude of the coupling constants forming them is different.

**Figure 14.9**

$^1$H NMR spectra for the alkenyl protons of (E)- and (Z)-3-chloropropenoic acid

- Although both (E)- and (Z)-3-chloropropenoic acid show two doublets in their $^1$H NMR spectra for their alkenyl protons, $J_{trans} > J_{cis}$. 

\[ J_{trans} = 14 \text{ Hz} \]

\[ J_{cis} = 8 \text{ Hz} \]
Figure 14.10
The $^1$H NMR spectrum of vinyl acetate ($\text{CH}_2=\text{CHOCOCH}_3$)

Vinyl acetate is polymerized to poly(vinyl acetate) (Problem 15.30), a polymer used in paints, glues, and adhesives.

Figure 14.11
Splitting diagram for the alkenyl protons in vinyl acetate ($\text{CH}_2=\text{CHOCOCH}_3$)

Problem 14.20
Draw a splitting diagram for $H_b$ in trans-1,3-dichloropropene, given that $J_{ab} = 13.1$ Hz and $J_{bc} = 7.2$ Hz.

Problem 14.21
Identify A and B, isomers of molecular formula C$_3$H$_4$Cl$_2$, from the given $^1$H NMR data: Compound A exhibits signals at 1.75 (doublet, 3 H, $J = 6.9$ Hz) and 5.89 (quartet, 1 H, $J = 6.9$ Hz) ppm. Compound B exhibits signals at 4.16 (singlet, 2 H), 5.42 (doublet, 1 H, $J = 1.9$ Hz), and 5.59 (doublet, 1 H, $J = 1.9$ Hz) ppm.

14.9 Other Facts About $^1$H NMR Spectroscopy

14.9A OH Protons

- Under usual conditions, an OH proton does not split the NMR signal of adjacent protons.
- The signal due to an OH proton is not split by adjacent protons.
Ethanol (CH$_3$CH$_2$OH), for example, has three different types of protons, so there are three signals in its $^1$H NMR spectrum, as shown in Figure 14.12.

- The $H_a$ signal is split by the two $H_b$ protons into three peaks, a **triplet**.
- The $H_b$ signal is split by only the three $H_a$ protons into four peaks, a **quartet**. The adjacent OH proton does **not** split the signal due to $H_b$.
- $H_c$ is a **singlet** because OH protons are **not** split by adjacent protons.

Why is a proton bonded to an oxygen atom a singlet in a $^1$H NMR spectrum? Protons on electronegative elements rapidly exchange between molecules in the presence of trace amounts of acid or base. It is as if the CH$_2$ group in ethanol never “feels” the presence of the OH proton, because the OH proton is rapidly moving from one molecule to another. We therefore see a peak due to the OH proton, but it is a single peak with no splitting. This phenomenon usually occurs with NH and OH protons.

**Problem 14.22** How many signals are present in the $^1$H NMR spectrum for each molecule? What splitting is observed in each signal: (a) (CH$_3$)$_3$CCH$_2$OH; (b) CH$_3$CH$_2$CH$_2$OH; (c) (CH$_3$)$_2$CHNH$_2$?

### 14.9B Cyclohexane Conformations

How does the rotation around carbon–carbon $\sigma$ bonds and the ring flip of cyclohexane rings affect an NMR spectrum? Because these processes are rapid at room temperature, an NMR spectrum records an **average** of all conformations that interconvert.

Thus, even though each cyclohexane carbon has two different types of hydrogens—one axial and one equatorial—the two chair forms of cyclohexane rapidly interconvert them, and an NMR spectrum shows a **single signal for the average environment** that it “sees.”

**Axial and equatorial H's rapidly interconvert. NMR sees an average environment and shows one signal.**

### 14.9C Protons on Benzene Rings

Benzene has six equivalent, deshielded protons and exhibits a single peak in its $^1$H NMR spectrum at 7.27 ppm. Monosubstituted benzene derivatives—that is, benzene rings with one H atom
Using $^1$H NMR to Identify an Unknown

Once we know a compound’s molecular formula from its mass spectral data and the identity of its functional group from its IR spectrum, we can then use its $^1$H NMR spectrum to determine its structure. A suggested procedure is illustrated for compound X, whose molecular formula (C$_4$H$_8$O$_2$) and functional group (C=O) were determined in Section 13.8.
**HOW TO Use $^1$H NMR Data to Determine a Structure**

**Example** Using its $^1$H NMR spectrum, determine the structure of an unknown compound X that has molecular formula C$_4$H$_8$O$_2$ and contains a C=O absorption in its IR spectrum.

<table>
<thead>
<tr>
<th>Absorption</th>
<th>ppm</th>
<th>Integration</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A] triplet</td>
<td>1.1</td>
<td>15</td>
</tr>
<tr>
<td>[B] quartet</td>
<td>2.3</td>
<td>11</td>
</tr>
<tr>
<td>[C] singlet</td>
<td>3.7</td>
<td>14</td>
</tr>
</tbody>
</table>

**Step [1]** Determine the number of different kinds of protons.
- The number of NMR signals equals the number of different types of protons.
- This molecule has three NMR signals ([A], [B], and [C]) and therefore **three** types of protons (H$_a$, H$_b$, and H$_c$).

**Step [2]** Use the integration data to determine the number of H atoms giving rise to each signal (Section 14.5).
- Total number of integration units: 14 + 11 + 15 = 40 units
- Total number of protons = 8
- Divide: 40 units/8 protons = **5 units per proton**
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.

\[
\frac{15}{5} = 3 \text{ H}_a \text{ protons} \quad \frac{11}{5} = 2.2 \approx 2 \text{ H}_b \text{ protons} \quad \frac{14}{5} = 2.8 \approx 3 \text{ H}_c \text{ protons}
\]

- Three equivalent H's usually means a CH$_3$ group.
- Two equivalent H's usually means a CH$_2$ group.
- Three equivalent H's usually means a CH$_3$ group.

**Step [3]** Use individual splitting patterns to determine what carbon atoms are bonded to each other.
- Start with the singlets. Signal [C] is due to a CH$_3$ group with no adjacent nonequivalent H atoms. Possible structures include:

\[
\text{CH}_3\text{O}^- \text{ or } \text{CH}_3\text{O}^- \text{ or } \text{CH}_3\text{O}^{-}
\]
- Because signal [A] is a **triplet**, there must be 2 H's (CH$_2$ group) on the adjacent carbon.
- Because signal [B] is a **quartet**, there must be 3 H's (CH$_3$ group) on the adjacent carbon.
- This information suggests that X has an **ethyl** group $\text{CH}_3\text{CH}_2\text{-}$. 
To summarize, \( X \) contains \( \text{CH}_3^- \), \( \text{CH}_2\text{CH}_2^- \), and \( \text{C} = \text{O} \) (from the IR). Comparing these atoms with the molecular formula shows that one O atom is missing. Because O atoms do not absorb in a \(^1\text{H}\) NMR spectrum, their presence can only be inferred by examining the chemical shift of protons near them. O atoms are more electronegative than C, thus deshielding nearby protons, and shifting their absorption downfield.

**Problem 14.24** Propose a structure for a compound of molecular formula \( \text{C}_7\text{H}_4\text{O}_2 \) with an IR absorption at 1740 cm\(^{-1}\) and the following \(^1\text{H}\) NMR data:

<table>
<thead>
<tr>
<th>Absorption</th>
<th>ppm</th>
<th>Integration value</th>
</tr>
</thead>
<tbody>
<tr>
<td>singlet</td>
<td>1.2</td>
<td>26</td>
</tr>
<tr>
<td>triplet</td>
<td>1.3</td>
<td>10</td>
</tr>
<tr>
<td>quartet</td>
<td>4.1</td>
<td>6</td>
</tr>
</tbody>
</table>

To summarize, \( X \) contains \( \text{CH}_3^- \), \( \text{CH}_2\text{CH}_2^- \), and \( \text{C} = \text{O} \) (from the IR). Comparing these atoms with the molecular formula shows that one O atom is missing. Because O atoms do not absorb in a \(^1\text{H}\) NMR spectrum, their presence can only be inferred by examining the chemical shift of protons near them. O atoms are more electronegative than C, thus deshielding nearby protons, and shifting their absorption downfield.
Problem 14.25  Propose a structure for a compound of molecular formula C₃H₈O with an IR absorption at 3600–3200 cm⁻¹ and the following NMR spectrum:

Problem 14.26  The ¹H NMR spectrum of melatonin, the chapter-opening molecule, is more complex than other examples we have encountered, but the chemical shift and splitting patterns observed for several peaks can be explained by what we have learned about ¹H NMR thus far. (a) Which protons in melatonin give rise to signals [A]–[D]? (b) Explain the splitting pattern observed in signal [C].

Problem 14.27  Identify products A and B from the given ¹H NMR data.
   a. Treatment of CH₂=CHCOCH₃ with one equivalent of HCl forms compound A. A exhibits the following absorptions in its ¹H NMR spectrum: 2.2 (singlet, 3 H), 3.05 (triplet, 2 H), and 3.6 (triplet, 2 H) ppm. What is the structure of A?
   b. Treatment of acetone [(CH₃)₂C=O] with dilute aqueous base forms B. Compound B exhibits four singlets in its ¹H NMR spectrum at 1.3 (6 H), 2.2 (3 H), 2.5 (2 H), and 3.8 (1 H) ppm. What is the structure of B?

14.11 ¹³C NMR Spectroscopy

¹³C NMR spectroscopy is also an important tool for organic structure analysis. The physical basis for ¹³C NMR is the same as for ¹H NMR. When placed in a magnetic field, B₀, ¹³C nuclei can align themselves with or against B₀. More nuclei are aligned with B₀ because this arrange-
ment is lower in energy, but these nuclei can be made to spin flip against the applied field by applying RF radiation of the appropriate frequency.

$^{13}$C NMR spectra, like $^1$H NMR spectra, plot peak intensity versus chemical shift, using TMS as the reference signal at 0 ppm. $^{13}$C occurs in only 1.1% natural abundance, however, so $^{13}$C NMR signals are much weaker than $^1$H NMR signals. To overcome this limitation, modern spectrometers irradiate samples with many pulses of RF radiation and use mathematical tools to increase signal sensitivity and decrease background noise. The spectrum of acetic acid (CH$_3$COOH) illustrates the general features of a $^{13}$C NMR spectrum.

$^{13}$C NMR spectra are easier to analyze than $^1$H spectra because signals are not split. Each type of carbon atom appears as a single peak.

Why aren’t $^{13}$C signals split by nearby carbon atoms? Recall from Section 14.6 that splitting occurs when two NMR active nuclei—like two protons—are close to each other. Because of the low natural abundance of $^{13}$C nuclei (1.1%), the chance of two $^{13}$C nuclei being bonded to each other is very small (0.01%), and so no carbon–carbon splitting is observed.

A $^{13}$C NMR signal can also be split by nearby protons. This $^1$H–$^{13}$C splitting is usually eliminated from a spectrum, however, by using an instrumental technique that decouples the proton–carbon interactions, so that every peak in a $^{13}$C NMR spectrum is a singlet.

Two features of $^{13}$C NMR spectra provide the most structural information: the number of signals observed and the chemical shifts of those signals.

### 14.11A $^{13}$C NMR: Number of Signals

- The number of signals in a $^{13}$C spectrum gives the number of different types of carbon atoms in a molecule.

Carbon atoms in the same environment give the same NMR signal, whereas carbons in different environments give different NMR signals. The $^{13}$C NMR spectrum of CH$_3$COOH has two signals because there are two different types of carbon atoms—the C of the CH$_3$ group and the C of the carbonyl (C=O).

- Because $^{13}$C NMR signals are not split, the number of signals equals the number of lines in the $^{13}$C NMR spectrum.
Thus, the $^{13}\text{C}$ NMR spectra of dimethyl ether, chloroethane, and methyl acetate exhibit one, two, and three lines, respectively, because these compounds contain one, two, and three different types of carbon atoms.

In contrast to what occurs in proton NMR, peak intensity is not proportional to the number of absorbing carbons, so $^{13}\text{C}$ NMR signals are not integrated.

### Sample Problem 14.7

How many lines are observed in the $^{13}\text{C}$ NMR spectrum of each compound?

- a. CH$_3$CH$_2$CH$_2$CH$_3$
- b. CH$_3$CO$\text{O}$–C–CH$_3$
- c. CH$_3$=C=H

### Solution

The number of different types of carbons equals the number of lines in a $^{13}\text{C}$ NMR spectrum.

- a. 3 types of C’s → 3 $^{13}\text{C}$ NMR signals
- b. 4 types of C’s → 4 $^{13}\text{C}$ NMR signals
- c. 2 types of C’s → 2 $^{13}\text{C}$ NMR signals

### Problem 14.28

How many lines are observed in the $^{13}\text{C}$ NMR spectrum of each compound?

- a. CH$_3$CH$_2$CH$_2$CH$_3$
- b. CH$_3$CH$_2$CH$=O$–CH$_2$CH$_2$CH$_3$
- c. CH$_3$CH$_2$CH$_2$CH$_2$–O–CH$_2$CH$_2$CH$_3$

### Problem 14.29

Draw all constitutional isomers of molecular formula C$_3$H$_6$Cl$_2$.

- a. How many signals does each isomer exhibit in its $^1\text{H}$ NMR spectrum?
- b. How many lines does each isomer exhibit in its $^{13}\text{C}$ NMR spectrum?
- c. When only the number of signals in both $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy is considered, is it possible to distinguish all of these constitutional isomers?

### 14.11B $^{13}\text{C}$ NMR: Position of Signals

In contrast to the small range of chemical shifts in $^1\text{H}$ NMR (0–12 ppm usually), $^{13}\text{C}$ NMR absorptions occur over a much broader range, 0–220 ppm. The chemical shifts of carbon atoms in $^{13}\text{C}$ NMR depend on the same effects as the chemical shifts of protons in $^1\text{H}$ NMR:

- The $sp^3$ hybridized C atoms of alkyl groups are shielded and absorb upfield.
- Electronegative elements like halogen, nitrogen, and oxygen shift absorptions downfield.
- The $sp^2$ hybridized C atoms of alkenes and benzene rings absorb downfield.
- Carbonyl carbons are highly deshielded, and absorb farther downfield than other carbon types.

Table 14.5 lists common $^{13}\text{C}$ chemical shift values. The $^{13}\text{C}$ NMR spectra of 1-propanol (CH$_3$CH$_2$CH$_2$OH) and methyl acetate (CH$_3$CO$_2$CH$_3$) in Figure 14.14 illustrate these principles.
Table 14.5  Common $^{13}$C Chemical Shift Values

<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>Chemical shift (ppm)</th>
<th>Type of carbon</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp^3$ C-H</td>
<td>5–45</td>
<td>$sp^3$ C=C</td>
<td>100–140</td>
</tr>
<tr>
<td>$sp^3$ C-Z</td>
<td>30–80</td>
<td>$sp^3$ C-Z</td>
<td>120–150</td>
</tr>
<tr>
<td>$sp^3$ C=O</td>
<td>65–100</td>
<td></td>
<td>160–210</td>
</tr>
</tbody>
</table>

Z = N, O, X

Problem 14.30 Which of the indicated carbon atoms in each molecule absorbs farther downfield?

- a. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
- b. $\text{BrCH}_2\text{CHBr}_2$
- c. $\text{OCH}_3$
- d. $\text{CH}_3\text{CH}==\text{CH}_2$

Problem 14.31 Identify the carbon atoms that give rise to each NMR signal.

- a. $\text{CH}_3\text{CH(\text{OH})CH}_2\text{CH}_3$
- b. $(\text{CH}_3\text{CH}_2)_2\text{C}=\text{O}$
**Problem 14.32**

A compound of molecular formula C₄H₈O₂ shows no IR peaks at 3600–3200 or 1700 cm⁻¹. It exhibits one singlet in its ¹H NMR spectrum at 3.69 ppm, and one line in its ¹³C NMR spectrum at 67 ppm. What is the structure of this unknown?

**Problem 14.33**

Draw the structure of a compound of molecular formula C₄H₈O that has a signal in its ¹³C NMR spectrum at > 160 ppm. Then draw the structure of an isomer of molecular formula C₃H₆O that has all of its ¹³C NMR signals at < 160 ppm.
Magnetic resonance imaging (MRI)—NMR spectroscopy in medicine—is a powerful diagnostic technique (Figure 14.15a). The “sample” is the patient, who is placed in a large cavity in a magnetic field, and then irradiated with RF energy. Because RF energy has very low frequency and low energy, the method is safer than X-rays or computed tomography (CT) scans that employ high-frequency, high-energy radiation that is known to damage living cells.

Living tissue contains protons (especially the H atoms in H₂O) in different concentrations and environments. When irradiated with RF energy, these protons are excited to a higher energy spin state, and then fall back to the lower energy spin state. These data are analyzed by a computer that generates a plot that delineates tissues of different proton density (Figure 14.15b). MRIs can be recorded in any plane. Moreover, because the calcium present in bones is not NMR active, an MRI instrument can “see through” bones such as the skull and visualize the soft tissue underneath.

**KEY CONCEPTS**

**Nuclear Magnetic Resonance Spectroscopy**

**¹H NMR Spectroscopy**

1. The number of signals equals the number of different types of protons (14.2).
2. The position of a signal (its chemical shift) is determined by shielding and deshielding effects.
   - Shielding shifts an absorption upfield; deshielding shifts an absorption downfield.
   - Electronegative atoms withdraw electron density, deshield a nucleus, and shift an absorption downfield (14.3).
This proton is shielded. Its absorption is upfield, 0.9–2 ppm.  
This proton is deshielded. Its absorption is farther downfield, 2.5–4 ppm.

- Loosely held \( \pi \) electrons can either shield or deshield a nucleus. Protons on benzene rings and double bonds are deshielded and absorb downfield, whereas protons on triple bonds are shielded and absorb upfield (14.4).

[3] The area under an NMR signal is proportional to the number of absorbing protons (14.5).

  - Equivalent protons do not split each other’s signals.
  - A set of \( n \) nonequivalent protons on the same carbon or adjacent carbons splits an NMR signal into \( n + 1 \) peaks.
  - OH and NH protons do not cause splitting (14.9).
  - When an absorbing proton has two sets of nearby nonequivalent protons that are equivalent to each other, use the \( n + 1 \) rule to determine splitting.
  - When an absorbing proton has two sets of nearby nonequivalent protons that are not equivalent to each other, the number of peaks in the NMR signal = \( (n + 1)(m + 1) \). In flexible alkyl chains, peak overlap often occurs, resulting in \( n + m + 1 \) peaks in an NMR signal.

\( ^{13} \text{C} \) NMR Spectroscopy (14.11)

[1] The number of signals equals the number of different types of carbon atoms. All signals are single peaks.

[2] The relative position of \( ^{13} \text{C} \) signals is determined by shielding and deshielding effects.
  - Carbons that are \( \text{sp}^3 \) hybridized are shielded and absorb upfield.
  - Electronegative elements (N, O, and halogen) shift absorptions downfield.
  - The carbons of alkenes and benzene rings absorb downfield.
  - Carbonyl carbons are highly deshielded, and absorb farther downfield than other carbon types.

PROBLEMS

\(^1\text{H} \) NMR Spectroscopy—Determining Equivalent Protons

**14.34** How many different types of protons are present in each compound?

a. \((\text{CH}_3)_3\text{CH}\)  
b. \((\text{CH}_3)_2\text{CC(CH}_3)_3\)  
c. \(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\)  
d. \(\text{CH}_3\text{CH=CH}_2\)  
e. \(\text{CH}_3\text{CH}_2\text{CH}_{2}\text{CH}_2\text{CH}_3\)  
f. \(\text{CH}_2\text{CH}_{2}\text{C}==\text{CCH}_3\)  
g. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3\)  
h. \(\text{CH}_3\text{CH}=\text{CH}_2\)  
i. \(\text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH}_3\)  
j. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3\)

**14.35** How many \(^1\text{H} \) NMR signals does each compound give?

a. \[\text{CH}_3\]  
b. \[\text{CH}_2\text{CH}_3\]  
c. \[\text{CH}_2\text{CH}_3\]  
d. \[\text{CH}_3\]
14.36 How many $^1$H NMR signals does each natural product exhibit?

a. [Structure of caffeine]
   (from coffee beans and tea leaves)

b. [Structure of vanillin]
   (from the vanilla bean)

c. [Structure of thymol]
   (from thyme)

d. [Structure of capsaicin]
   (from hot peppers)

$^1$H NMR—Chemical Shift and Integration

14.37 Using a 300 MHz NMR instrument:
   a. How many Hz downfield from TMS is a signal at 2.5 ppm?
   b. If a signal comes at 1200 Hz downfield from TMS, at what ppm does it occur?
   c. If two peaks are separated by 2 ppm, how many Hz does this correspond to?

14.38 Acetone exhibits a singlet in its $^1$H NMR spectrum at 2.16 ppm. If CH$_2$Cl$_2$ exhibits a singlet 1570 Hz downfield from acetone on a 500 MHz NMR spectrometer, what is the chemical shift of the singlet due to CH$_2$Cl$_2$?

14.39 Which of the indicated protons in each pair absorbs farther downfield?
   a. CH$_3$CH$_2$CH$_2$CH$_3$ or CH$_3$CH$_2$CH$_2$OCH$_3$
   b. CH$_3$CH$_2$CHI or CH$_3$CH$_2$CH$_2$F
   c. CH$_3$OCH$_2$CH$_3$
   d. CH$_3$CH$_2$CHBr$_2$ or CH$_3$CH$_2$CHBr

14.40 A compound of molecular formula C$_6$H$_{10}$ gives three signals in its $^1$H NMR spectrum with the following integration units: 13, 33, 73 units. How many protons are responsible for each signal?

14.41 How could you use chemical shift and integration data in $^1$H NMR spectroscopy to distinguish between each pair of compounds? The $^1$H NMR spectrum of each compound contains only singlets.
   a. CH$_3$CO$_2$C(CH$_3$)$_3$ and CH$_3$CO$_2$CH$_3$
   b. CH$_3$OCH$_2$CH$_2$OCH$_3$ and CH$_3$OCH$_2$OCH$_3$
   c. CH$_3$CH$_2$CH$_2$CH$_3$

$^1$H NMR—Splitting

14.42 Which compounds give one singlet in the $^1$H NMR spectrum?

14.43 For the five isomeric alkanes of molecular formula C$_6$H$_{14}$, label each type of proton and indicate how many peaks each will exhibit in its $^1$H NMR signal.
14.44 Into how many peaks will the signal for each of the indicated protons be split?

a. \( \text{CH}_3\text{CH(OCH}_3)_2 \)  

b. \( \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 \)  

c. \( \text{C}_6\text{H}_5\text{CH}_3 \)  

d. \( \text{CH}_3\text{OCH}_2\text{CHCl}_2 \)  

e. \( (\text{CH}_3)_2\text{CHCO}_2\text{CH}_3 \)  

f. \( \text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH} \)  

g. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)  

h. \( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \)  

i. \( \text{CH}_3\text{CH}_2\text{H} \)  

j. \( \text{CH}_3\text{CH}_2\text{CH} = \text{C} - \text{H} \)  

k. \( \text{CH}_3\text{Br} \)  

l. \( \text{C}_6\text{H}_5\text{C} - \text{C} \)

14.45 How can you use \( ^1\text{H} \) NMR spectroscopy to distinguish between \( \text{CH}_2 = \text{C(Br)CO}_2\text{CH}_3 \) and methyl \( (2\text{E})\text{-3-bromo-2-propenoate}, \) \( \text{BrCH} = \text{CHCO}_2\text{CH}_3? \)

14.46 Label the signals due to \( \text{H}_a, \text{H}_b, \) and \( \text{H}_c \) in the \( ^1\text{H} \) NMR spectrum of acrylonitrile (\( \text{CH}_2 = \text{CHCN} \)). Draw a splitting diagram for the absorption due to the \( \text{H}_a \) proton.

\[ J_{ab} = 11.8 \text{ Hz} \]
\[ J_{bc} = 0.9 \text{ Hz} \]
\[ J_{ac} = 18 \text{ Hz} \]

13C NMR

14.47 Draw the four constitutional isomers having molecular formula \( \text{C}_4\text{H}_9\text{Br} \) and indicate how many different kinds of carbon atoms each has.

14.48 Which compounds in Problem 14.42 give one signal in their \( ^{13}\text{C} \) NMR spectra?

14.49 Explain why the carbonyl carbon of an aldehyde or ketone absorbs farther downfield than the carbonyl carbon of an ester in a \( ^{13}\text{C} \) NMR spectrum.

14.50 How many \( ^{13}\text{C} \) NMR signals does each compound exhibit?

a. \( \text{HC(CH}_3)_3 \)  

b. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \)  

c. \( \text{CH}_2\text{OCH}_3\text{(CH}_3)_2 \)  

d. \( \text{HOCH}_2\text{CH}_2\text{OH} \)  

e. \( \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_3 \)  

f. \( \text{CH}_3\text{CH}_2\text{OH} \)  

h. \( \text{CO} \)  

i. \( \text{CH}_3\text{CH}_2\text{OCH}_3 \)  

j. \( \text{CH}_3\text{CH}_2\text{CH} = \text{C} \)  

k. \( \text{CH}_3\text{Br} \)  

l. \( \text{C}_6\text{H}_5\text{C} - \text{C} \)
14.51 Rank the indicated carbon atoms in each compound in order of increasing chemical shift.

a. \( \text{CH}_3\text{CH}_2\text{OH} \)

b. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)

c. \( \text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_3 \)

d. \( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \)

14.52 Identify the carbon atoms that give rise to the signals in the \( ^{13}\text{C} \) NMR spectrum of each compound.

a. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \); \( ^{13}\text{C} \) NMR: 14, 19, 35, and 62 ppm

b. \( \text{(CH}_3)_2\text{CHO} \); \( ^{13}\text{C} \) NMR: 16, 41, and 205 ppm

c. \( \text{CH}_2=\text{C}(\text{OH})(\text{CH}_3) \); \( ^{13}\text{C} \) NMR: 23, 69, 113, and 143 ppm

14.53 a. How many signals does dimethyl fumarate \( (\text{CH}_3\text{O}_2\text{C} \equiv \text{C} \text{CH}_2\text{CH}_2\text{O}_2\text{C}) \) exhibit in its \( ^{13}\text{C} \) NMR spectrum?

b. Draw the structure of an isomer of dimethyl fumarate that has each of the following number of signals in its \( ^{13}\text{C} \) NMR spectrum: [1] three; [2] four; [5] five.

Combined Spectroscopy Problems

Additional spectroscopy problems are located at the end of Chapters 15–23 and 25.

14.54 Propose a structure consistent with each set of spectral data:

a. \( \text{C}_6\text{H}_4\text{Br}_2 \); IR peak at 3000–2850 cm\(^{-1}\); NMR (ppm):
   - 1.87 (singlet, 6 H)
   - 3.86 (singlet, 2 H)

b. \( \text{C}_6\text{H}_5\text{Br}_2 \); IR peak at 3000–2850 cm\(^{-1}\); NMR (ppm):
   - 2.4 (quintet)
   - 3.5 (triplet)

f. \( \text{C}_6\text{H}_4\text{O} \); IR peak at 3000–2850 cm\(^{-1}\); NMR (ppm):
   - 1.15 (triplet, 3 H)
   - 1.25 (triplet, 3 H)

14.55 Identify the structures of isomers A and B (molecular formula \( \text{C}_9\text{H}_9\text{O} \)).

Compound A: IR peak at 1742 cm\(^{-1}\); \(^1\text{H} \) NMR data (ppm) at 2.15 (singlet, 3 H), 3.70 (singlet, 2 H), and 7.20 (broad singlet, 5 H).

Compound B: IR peak at 1688 cm\(^{-1}\); \(^1\text{H} \) NMR data (ppm) at 1.22 (triplet, 3 H), 2.98 (quartet, 2 H), and 7.28–7.95 (multiplet, 5 H).

14.56 Compound C has a molecular ion in its mass spectrum at 146 and a prominent absorption in its IR spectrum at 1762 cm\(^{-1}\).

C shows the following \(^1\text{H} \) NMR spectral data: 1.47 (doublet, 3 H), 2.07 (singlet, 6 H), and 6.84 (quartet, 1 H) ppm. What is the structure of C?

14.57 As we will learn in Chapter 20, reaction of \( (\text{CH}_3)_2\text{CO} \) with Li\( \equiv \text{CH} \) followed by \( \text{H}_2\text{O} \) affords compound D, which has a molecular ion in its mass spectrum at 84 and prominent absorptions in its IR spectrum at 3600–3200, 3303, 2938, and 2120 cm\(^{-1}\).

D shows the following \(^1\text{H} \) NMR spectral data: 1.53 (singlet, 6 H), 2.37 (singlet, 1 H), and 2.43 (singlet, 1 H) ppm. What is the structure of D?
14.58 Identify the structures of isomers E and F (molecular formula C₄H₈O₂).

**Compound E:** IR absorption at 1743 cm⁻¹

**Compound F:** IR absorption at 1730 cm⁻¹

14.59 Identify the structures of isomers H and I (molecular formula C₈H₁₁N).

a. **Compound H:** IR absorptions at 3365, 3284, 3026, 2932, 1603, and 1497 cm⁻¹

b. **Compound I:** IR absorptions at 3367, 3286, 3027, 2962, 1604, and 1492 cm⁻¹
Propose a structure consistent with each set of data.

a. $\text{C}_9\text{H}_10\text{O}_2$: IR absorption at 1718 cm$^{-1}$

b. $\text{C}_9\text{H}_{12}$: IR absorption at 2850–3150 cm$^{-1}$

Propose a structure consistent with each set of data.

a. Compound J: molecular ion at 72; IR peak at 1710 cm$^{-1}$; $^1\text{H}$ NMR data (ppm) at 1.0 (triplet, 3 H), 2.1 (singlet, 3 H), and 2.4 (quartet, 2 H)

b. Compound K: molecular ion at 88; IR peak at 3600–3200 cm$^{-1}$; $^1\text{H}$ NMR data (ppm) at 0.9 (triplet, 3 H), 1.2 (singlet, 6 H), 1.5 (quartet, 2 H), and 1.6 (singlet, 1 H)

In the presence of a small amount of acid, a solution of acetaldehyde (CH$_3$CHO) in methanol (CH$_3$OH) was allowed to stand and a new compound L was formed. L has a molecular ion in its mass spectrum at 90 and IR absorptions at 2992 and 2941 cm$^{-1}$. L shows three signals in its $^{13}\text{C}$ NMR at 19, 52, and 101 ppm. The $^1\text{H}$ NMR spectrum of L is given below. What is the structure of L?
14.63 Treatment of \((\text{CH}_3)_2\text{CHCH(OH)CH}_2\text{CH}_3\) with TsOH affords two products (\(\text{M}\) and \(\text{N}\)) with molecular formula \(\text{C}_6\text{H}_{12}\). The \(^1\text{H NMR}\) spectra of \(\text{M}\) and \(\text{N}\) are given below. Propose structures for \(\text{M}\) and \(\text{N}\) and draw a mechanism to explain their formation.

14.64 Compound \(\text{O}\) has molecular formula \(\text{C}_{10}\text{H}_{12}\text{O}\) and shows an IR absorption at \(1687\ \text{cm}^{-1}\). The \(^1\text{H NMR}\) spectrum of \(\text{O}\) is given below. What is the structure of \(\text{O}\)?
14.65 Compound P has molecular formula C₅H₉ClO₂. Deduce the structure of P from its ¹H and ¹³C NMR spectra.

14.66 Treatment of 2-butanone (CH₃COCH₂CH₃) with strong base followed by CH₃I forms a compound Q, which gives a molecular ion in its mass spectrum at 86. The IR (> 1500 cm⁻¹ only) and ¹H NMR spectrum of Q are given below. What is the structure of Q?

14.67 Low molecular weight esters (RCO₂R) often have characteristic odors. Using its molecular formula and ¹H NMR spectral data, identify each ester.
   a. Compound R, the odor of banana: C₇H₁₄O₂; ¹H NMR: 0.93 (doublet, 6 H), 1.52 (multiplet, 2 H), 1.69 (multiplet, 1 H), 2.04 (singlet, 3 H), and 4.10 (triplet, 2 H) ppm
   b. Compound S, the odor of rum: C₇H₁₄O₂; ¹H NMR: 0.94 (doublet, 6 H), 1.15 (triplet, 3 H), 1.91 (multiplet, 1 H), 2.33 (quartet, 2 H), and 3.86 (doublet, 2 H) ppm
When 2-bromo-3,3-dimethylbutane is treated with K$^+$–OC(CH$_3$)$_3$, a single product $T$ having molecular formula C$_6$H$_{12}$ is formed. When 3,3-dimethyl-2-butanol is treated with H$_2$SO$_4$, the major product $U$ has the same molecular formula. Given the following $^1$H NMR data, what are the structures of $T$ and $U$? Explain in detail the splitting patterns observed for the three split signals in $T$.

$^1$H NMR of $T$: 1.01 (singlet, 9 H), 4.82 (doublet of doublets, 1 H, $J = 10$, 1.7 Hz), 4.93 (doublet of doublets, 1 H, $J = 18$, 1.7 Hz), and 5.83 (doublet of doublets, 1 H, $J = 18$, 10 Hz) ppm

$^1$H NMR of $U$: 1.60 (singlet) ppm

In a Baeyer–Villiger reaction, ketones (R$_2$C=O) are converted to esters (RCO$_2$R) by using peroxy acids. With an unsymmetrical ketone, two possible esters can be formed, as shown for 3,3-dimethyl-2-butanone as starting material. How could you use spectroscopic techniques—$^1$H NMR, IR, and MS—to determine which ester ($A$ or $B$) is formed?

Propose a structure consistent with each set of data.

a. A compound $X$ (molecular formula C$_6$H$_{12}$O$_2$) gives a strong peak in its IR spectrum at 1740 cm$^{-1}$. The $^1$H NMR spectrum of $X$ shows only two singlets, including one at 3.5 ppm. The $^{13}$C NMR spectrum is given below. Propose a structure for $X$.

b. A compound $Y$ (molecular formula C$_6$H$_{10}$) gives four lines in its $^{13}$C NMR spectrum (27, 30, 67, and 93 ppm), and the IR spectrum given here. Propose a structure for $Y$. 
Challenge Problems

14.71 The $^1$H NMR spectrum of $N,N$-dimethylformamide shows three singlets at 2.9, 3.0, and 8.0 ppm. Explain why the two CH$_3$ groups are not equivalent to each other, thus giving rise to two NMR signals.

\[
\begin{array}{c}
\text{H} \\
\text{-C-N(CH$_3$)$_2$} \\
\text{N,N-dimethylformamide}
\end{array}
\]

14.72 18-Annulene shows two signals in its $^1$H NMR spectrum, one at 8.9 (12 H) and one at –1.8 (6 H) ppm. Using a similar argument to that offered for the chemical shift of benzene protons, explain why both shielded and deshielded values are observed for 18-annulene.

\[
\begin{array}{c}
\text{18-annulene}
\end{array}
\]

14.73 Explain why the $^{13}$C NMR spectrum of 3-methyl-2-butanol shows five signals.

14.74 Since $^{31}$P has an odd mass number, $^{31}$P nuclei absorb in the NMR and, in many ways, these nuclei behave similarly to protons in NMR spectroscopy. With this in mind, explain why the $^1$H NMR spectrum of methyl dimethylphosphonate, CH$_3$PO(OCH$_3$)$_2$, consists of two doublets at 1.5 and 3.7 ppm.