Organic Chemistry, *Second Edition*

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Chapter 14
Nuclear Magnetic Resonance Spectroscopy

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Nuclear Magnetic Resonance Spectroscopy

14.1 Introduction to NMR Spectroscopy

- **Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.**

- **Two common types of NMR spectroscopy are used to characterize organic structure: ^{1}H NMR is used to determine the type and number of H atoms in a molecule; ^{13}C NMR is used to determine the type of carbon atoms in the molecule.**

- **The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.**

- **When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including ^{1}H and ^{13}C.**

14.1A The Basis of NMR Spectroscopy

- When a charged particle such as a proton spins on its axis, it creates a **magnetic field**. Thus, the nucleus can be considered to be a tiny bar magnet.
- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a 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.
- The energy difference between these two states is very small (<0.1 cal).
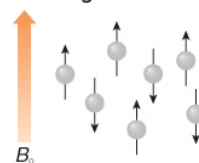

A spinning proton creates a magnetic field.

With no external magnetic field...
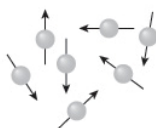
The nuclear magnets are randomly oriented.
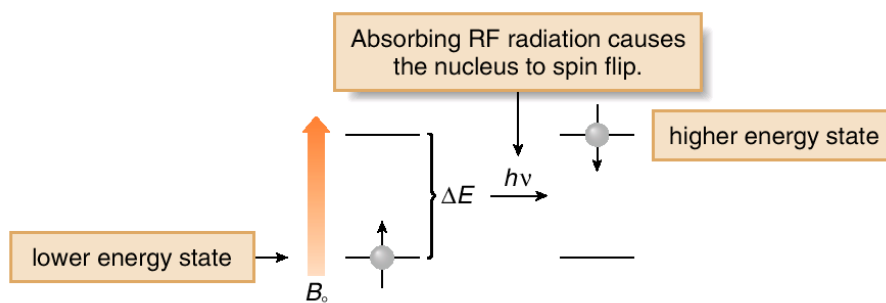
In a magnetic field...

B_0

The nuclear magnets are oriented **with or against** B_0.

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- In a magnetic field, there are now two energy states for a proton: a lower energy state with the nucleus aligned in the same direction as B_0, and a higher energy state in which the nucleus aligned against B_0.
- When an external energy source ($h\nu$) that matches the energy difference (ΔE) 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 RF region of the electromagnetic spectrum.

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- **Thus, two variables characterize NMR: an applied magnetic field B_0, the strength of which is measured in tesla (T), and the frequency ν of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz)—(1 MHz = 10^6 Hz).**

Absorbing RF radiation causes the nucleus to spin flip.

higher energy state

ΔE $h\nu$

lower energy state

$B_\circ$

- A nucleus is in *resonance* when it absorbs RF radiation and "spin flips" to a higher energy state.

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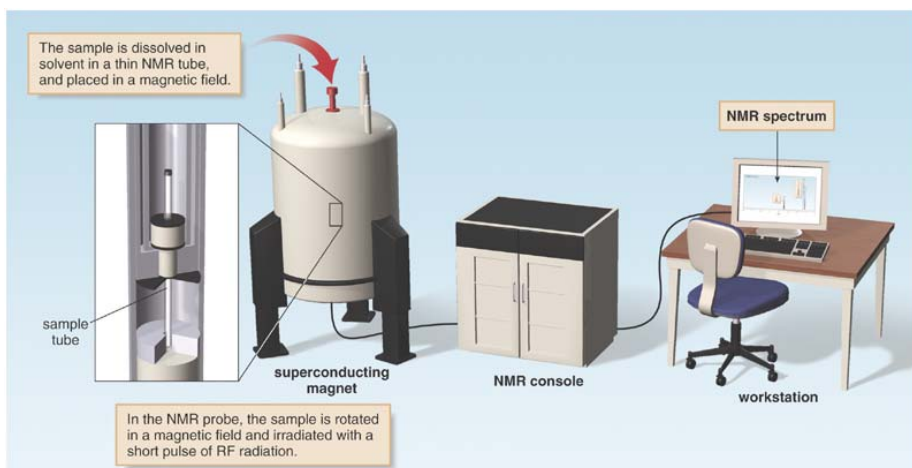- **The frequency needed for resonance and the applied magnetic field strength are proportionally related:**

$$\nu \propto B_\circ$$

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

- **NMR spectrometers are referred to as 300 MHz instruments, 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance.**
- **These spectrometers use very powerful magnets to create a small but measurable energy difference between two possible spin states.**

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The sample is dissolved in solvent in a thin NMR tube, and placed in a magnetic field.

NMR spectrum

sample tube

superconducting magnet

NMR console

workstation

In the NMR probe, the sample is rotated in a magnetic field and irradiated with a short pulse of RF radiation.

An NMR spectrometer. The sample is dissolved in a solvent, usually CDCl₃ (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.

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- **Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.**
- **The frequency at which a particular proton absorbs is determined by its electronic environment.**
- **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 ^1H, ^{13}C, ^{19}F and ^{31}P) or odd atomic numbers (such as ^2H and ^{14}N) give rise to NMR signals.**

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14.1B ^{1}H NMR—The Spectrum

- An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in parts per million (ppm).

Sample ^{1}H NMR spectrum
$CH_3OC(CH_3)_3$
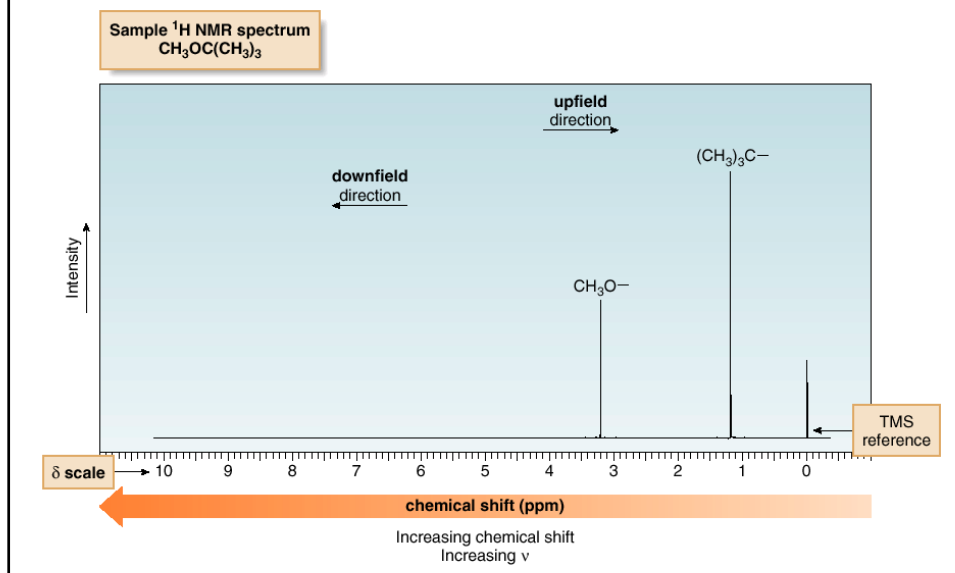
- NMR absorptions generally appear as sharp peaks.
- Increasing chemical shift is plotted from left to right.
- Most protons absorb between 0-10 ppm.
- The terms "upfield" and "downfield" describe the relative location of peaks. Upfield means to the right. Downfield means to the left.
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the δ scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.

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- The chemical shift of the *x* axis gives the position of an NMR signal, measured in ppm, according to the following equation:

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

- By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.
- Four different features of a ^{1}H NMR spectrum provide information about a compound's structure:
  a. Number of signals
  b. Position of signals
  c. Intensity of signals.
  d. Spin-spin splitting of signals.
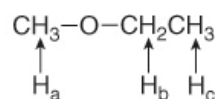
14.2 ^{1}H NMR—Number of Signals

- The number of NMR signals equals the number of different types of protons in a compound.
- Protons in different environments give different NMR signals.
- Equivalent protons give the same NMR signal.

CH_3-O-CH_3 H_a H_a
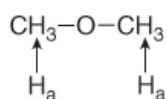
All equivalent H's
1 NMR signal

CH_3CH_2-Cl H_a H_b

2 types of H's
2 NMR signals

$CH_3-O-CH_2CH_3$ H_a H_b H_c
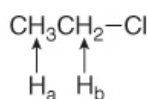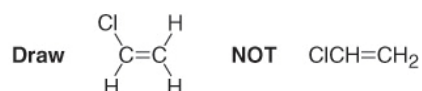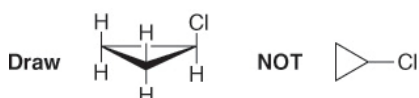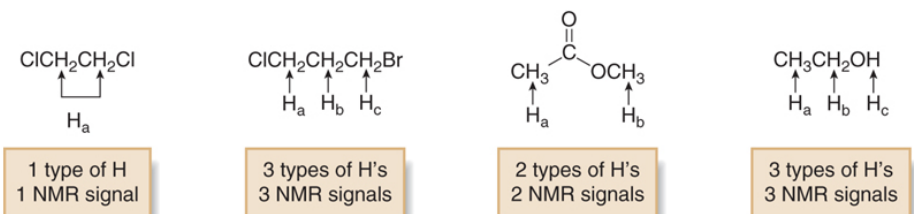
3 types of H's
3 NMR signals

- To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen.

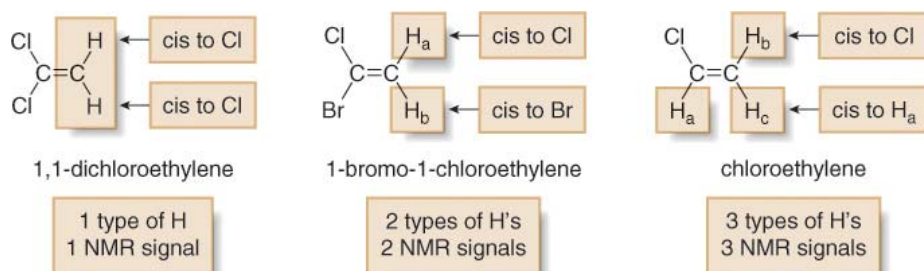Draw [cyclopropane with Cl and H's shown]   NOT [cyclopropane-Cl] | Draw [C=C with Cl, H, H, H]   NOT $ClCH=CH_2$

Figure 14.2 The number of ^{1}H NMR signals of some representative organic compounds

$ClCH_2CH_2Cl$

H_a

1 type of H
1 NMR signal

$ClCH_2CH_2CH_2Br$

H_a H_b H_c

3 types of H's
3 NMR signals

$CH_3\overset{\displaystyle O}{\underset{}{C}}OCH_3$

H_a H_b

2 types of H's
2 NMR signals

CH_3CH_2OH

H_a H_b H_c

3 types of H's
3 NMR signals

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• **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.**

1,1-dichloroethylene

Cl, H ← cis to Cl
C=C
Cl, H ← cis to Cl

1 type of H
1 NMR signal

1-bromo-1-chloroethylene

Cl, H_a ← cis to Cl
C=C
Br, H_b ← cis to Br

2 types of H's
2 NMR signals

chloroethylene

Cl, H_b ← cis to Cl
C=C
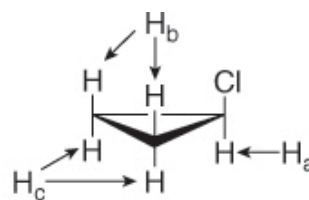H_a, H_c ← cis to H_a

3 types of H's
3 NMR signals

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- **Proton equivalency in cycloalkanes can be determined similarly.**
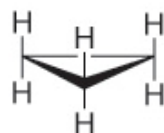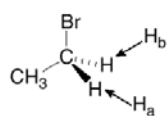

cyclopropane
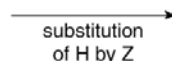
All H's are equivalent.
1 NMR signal

chlorocyclopropane

3 types of H's
3 NMR signals

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^{1}H NMR—Enantiotopic and Diastereotopic Protons.

substitution of H$_a$

substitution of H$_b$

substitution
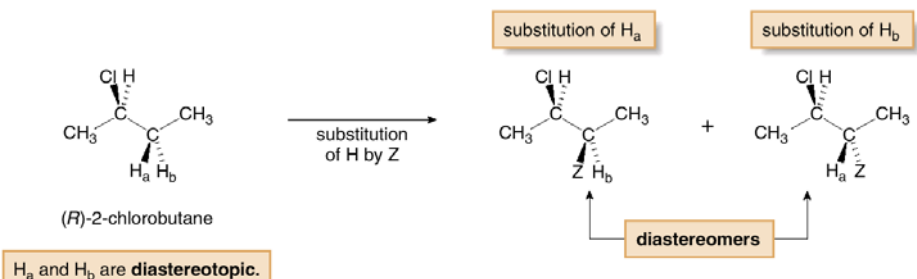of H by Z

+

enantiomers

H$_a$ and H$_b$ are **enantiotopic.**

- 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.

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¹H NMR—Enantiotopic and Diastereotopic Protons.

substitution of Hₐ

substitution of Hᵦ

(R)-2-chlorobutane
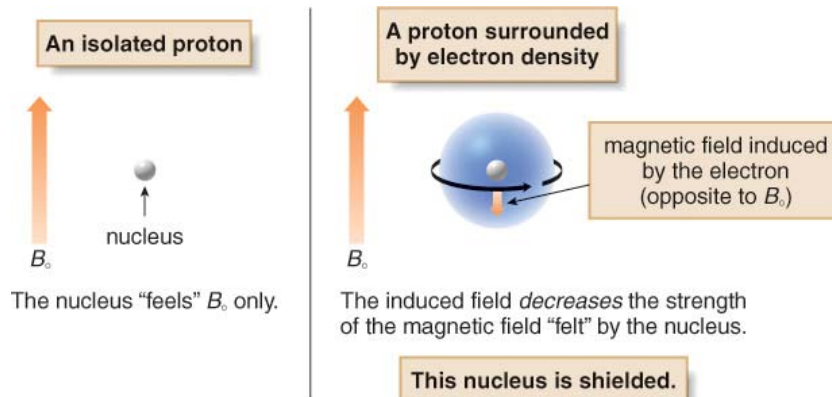
Hₐ and Hᵦ are **diastereotopic.**

diastereomers

- When substitution of two H atoms by Z forms diastereomers, the two H atoms are not equivalent, and give two NMR signals. These two H atoms are called *diastereotopic* protons.
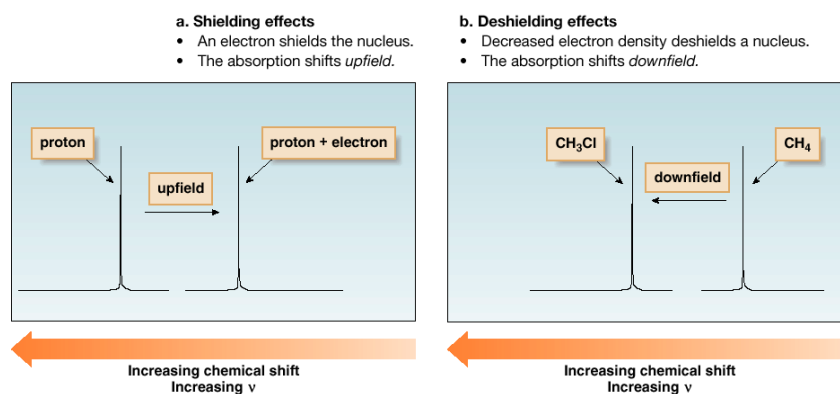
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14.3 ¹H NMR—Position of Signals

- **In the vicinity of the nucleus, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton "feels".**
- **Since the electron 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 a lower chemical shift, so shielding shifts the absorption upfield.**

An isolated proton

A proton surrounded by electron density

magnetic field induced by the electron (opposite to B_o)

nucleus

B_o

B_o

The nucleus "feels" B_o only.

The induced field *decreases* the strength of the magnetic field "felt" by the nucleus.

This nucleus is shielded.

- **The less shielded the nucleus becomes, the more of the applied magnetic field (B$_0$) it feels.**
- **This deshielded nucleus experiences a higher magnetic field strength, to 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.**
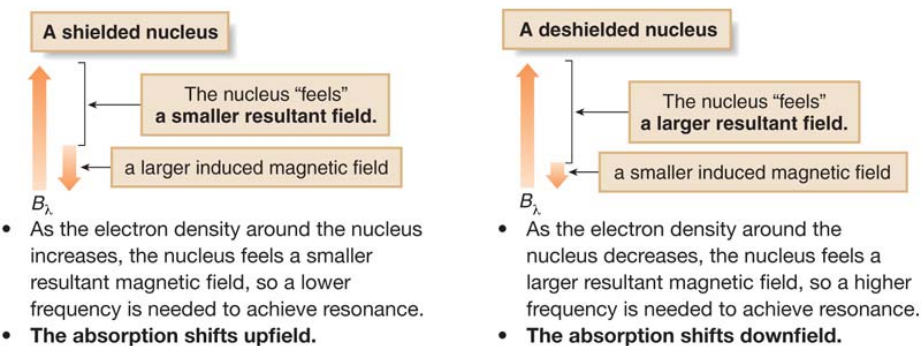- **Protons near electronegative atoms are deshielded, so they absorb downfield.**

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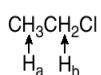Figure 14.3 How chemical shift is affected by electron density aroundna nucleus

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*.

proton

proton + electron

upfield

CH$_3$Cl

CH$_4$

downfield

Increasing chemical shift
Increasing ν

Increasing chemical shift
Increasing ν

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Figure 14.4 Shielding and deshielding effects

A shielded nucleus

The nucleus "feels" **a smaller resultant field.**

a larger induced magnetic field

B_λ

- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.
- **The absorption shifts upfield.**

A deshielded nucleus

The nucleus "feels" **a larger resultant field.**

a smaller induced magnetic field

B_λ

- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance.
- **The absorption shifts downfield.**

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CH_3CH_2Cl
H_a H_b

- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.

$BrCH_2CH_2F$
H_a H_b
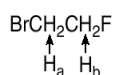
- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**

$ClCH_2CHCl_2$
H_a H_b
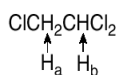
- The larger number of electronegative Cl atoms (two versus one) **deshields** H_b more than H_a, so it absorbs **downfield** from H_a.

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¹H NMR—Chemical Shift Values

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

Table 14.1	Characteristic Chemical Shifts of Common Types of Protons		
Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
sp^3 —C—H	0.9–2	sp^2 C=C—H	4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7	(benzene)—H	6.5–8
Z=C—C—H Z = C, O, N	1.5–2.5	R—C(=O)—H	9–10
—C≡C—H	~2.5	R—C(=O)—OH	10–12
sp^3 —C—H Z Z = N, O, X	2.5–4	RO—H or R—N—H	1–5

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- **The chemical shift of a C—H bond increases with increasing alkyl substitution.**

RCH_2—H R_2CH—H R_3C—H
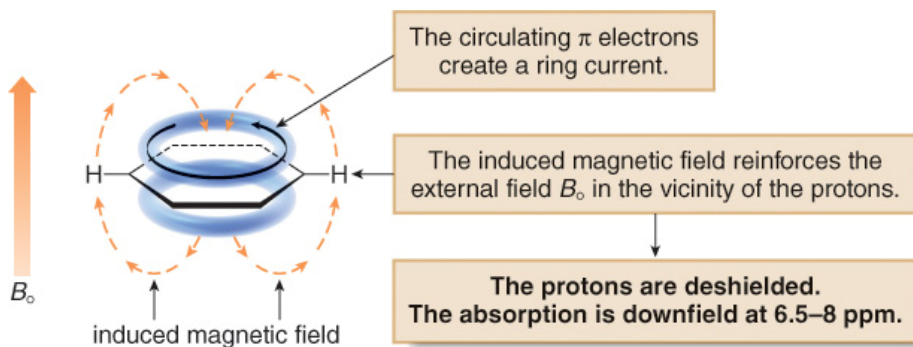~ 0.9 ppm   ~ 1.3 ppm   ~ 1.7 ppm
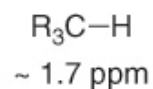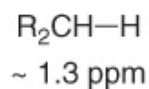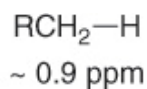
Increasing alkyl substitution
Increasing chemical shift

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14.4 ^{1}H NMR—Chemical Shift Values

- 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. Thus they are deshielded and absorb downfield.

The circulating π electrons create a ring current.

The induced magnetic field reinforces the external field B_o in the vicinity of the protons.

The protons are deshielded. The absorption is downfield at 6.5–8 ppm.

B_o

induced magnetic field

- In a magnetic field, the loosely held π electrons of the double bond create a magnetic field that reinforces the applied field in the vicinity of the protons.
- The protons now feel a stronger magnetic field, and require a higher frequency for resonance. Thus the protons are deshielded and the absorption is downfield.

The induced magnetic field reinforces the external field B_o in the vicinity of the protons.

The protons are deshielded. The absorption is downfield at 4.5–6 ppm.

B_o
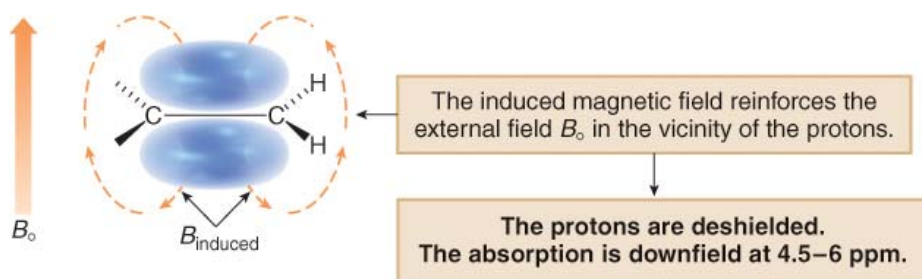
$B_{induced}$

- **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).**
- **Thus, the proton feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.**

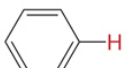The induced magnetic field opposes the external field B_o in the vicinity of the proton.

H
C
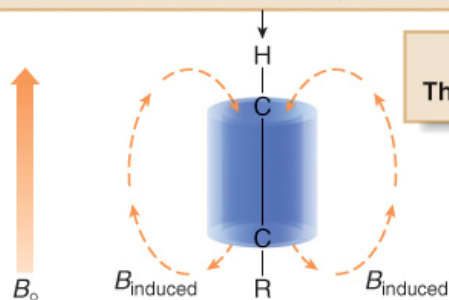
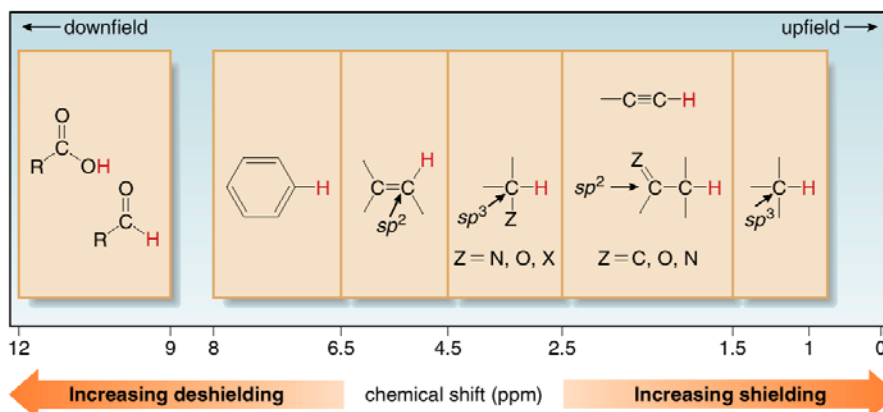The proton is shielded.
The absorption is upfield at ~2.5 ppm.

C
R

B_o $B_{induced}$ $B_{induced}$

| Table 14.2	Effect of π Electrons on Chemical Shift Values	
Proton type	**Effect**	**Chemical shift (ppm)**
(benzene ring)—H	highly deshielded	6.5–8
C=C with —H	deshielded	4.5–6
—C≡C—H	shielded	~2.5

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).

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14.5 ¹H NMR—Intensity of Signals

- **The area under an NMR signal is proportional to the number of absorbing protons.**
- **An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (integral) on the spectrum.**
- **The height of each step is proportional to the area under the peak, which in turn is proportional to the number of absorbing protons.**
- **Modern NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units.**
- **The ratio of integrals to one another gives the ratio of absorbing protons in a spectrum. Note that this gives a ratio, and not the absolute number, of absorbing protons.**

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NMR integration

$CH_3OC(CH_3)_3$

| 60 |
| 20 |

CH_3O- $(CH_3)_3C-$

chemical shift (ppm)
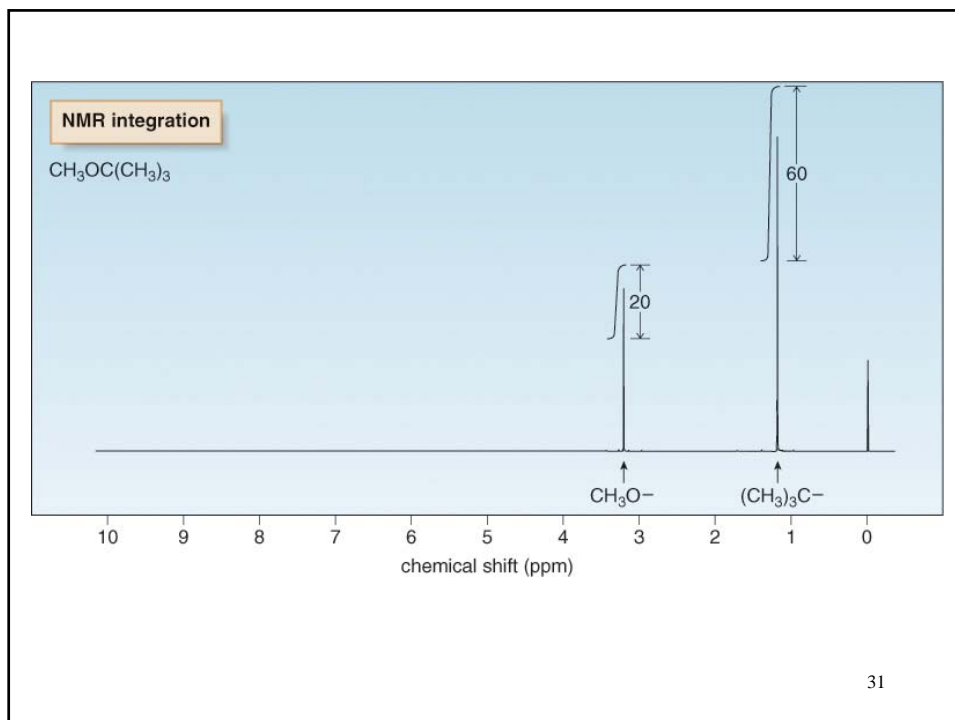
How To   Determine the Number of Protons Giving Rise to an NMR Signal

Example   A compound of molecular formula $C_9H_{10}O_2$ gives the following integrated ^{1}H NMR spectrum. How many protons give rise to each signal?

signal [A]   signal [B]   signal [C]

ppm

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.

Signal [A]:   Signal [B]:   Signal [C]:

Answer: $\frac{54}{11} = 4.9 = $ **5 H** $\frac{23}{11} = 2.1 = $ **2 H** $\frac{33}{11} = $ **3 H**

14.6 ^{1}H NMR—Spin-Spin Splitting

- **Consider the spectrum below:**

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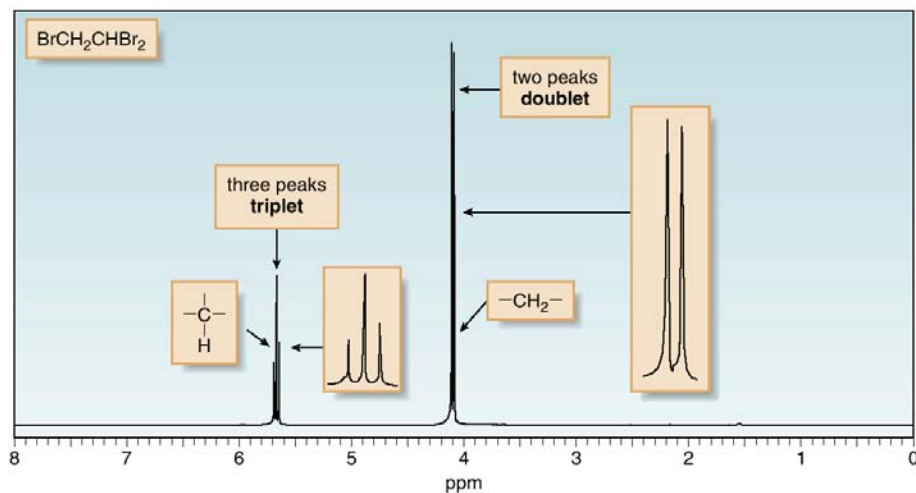
^{1}H NMR—Spin-Spin Splitting

- **Spin-spin splitting** occurs only between **nonequivalent protons** on the same carbon or adjacent carbons.

Let us consider how the **doublet** due to the CH_2 group on $BrCH_2CHBr_2$ occurs:

- **When placed in an applied electric field, (B_0), the adjacent proton ($CHBr_2$) can be aligned with ($\uparrow$) or against ($\downarrow$) B_0.**
- **Thus, the absorbing CH_2 protons feel two slightly different magnetic fields—one slightly larger than B_0, and one slightly smaller than B_0.**
- **Since 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 frequency difference, measured in Hz between two peaks of the doublet is called the coupling constant, *J*.

- One adjacent proton splits an NMR signal into a doublet.
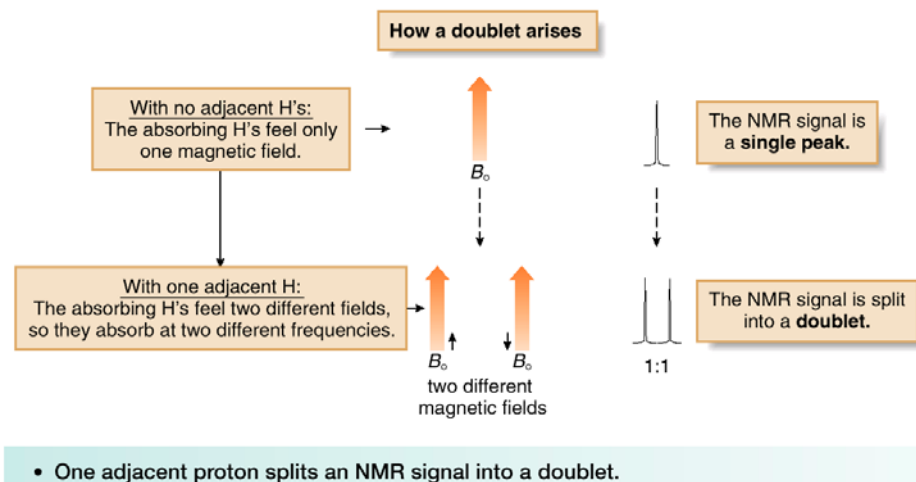
Let us now consider how a triplet arises:


- When placed in an applied magnetic field (B_0), the adjacent protons H_a and H_b can each be aligned with (↑) or against (↓) B_0.

- Thus, 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, $\uparrow_a\downarrow_b$ and $\downarrow_a\uparrow_b$—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, they are said to be coupled.**

- **The spacing between peaks in a split NMR signal, measured by the *J* value, is equal for coupled protons.**
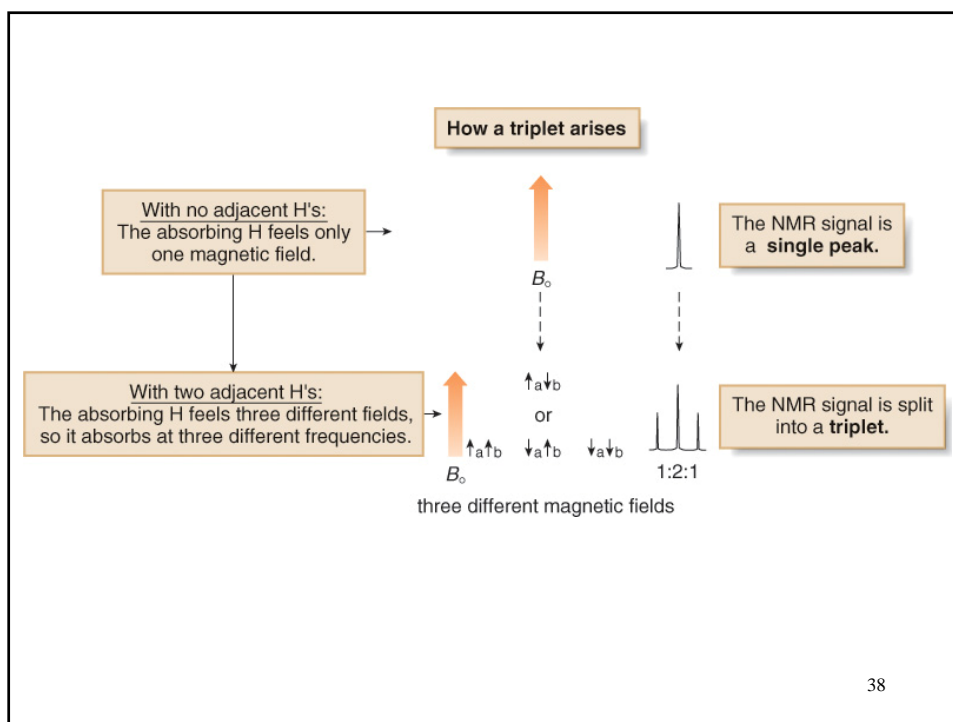
Three general rules describe the splitting patterns commonly seen in the ^{1}H NMR spectra of organic compounds.

1. Equivalent protons do not split each other's signals.

2. A set of n nonequivalent protons splits the signal of a nearby proton into n + 1 peaks.

3. Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.

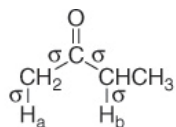**If H$_a$ and H$_b$ are not equivalent, splitting is observed when:**
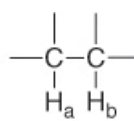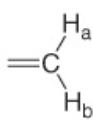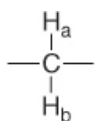
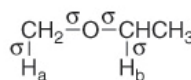| H$_a$ and H$_b$ are on the **same** carbon. | H$_a$ and H$_b$ are on **adjacent** carbons. |

Splitting is not generally observed between protons separated by more than three σ bonds.

2-butanone
H$_a$ and H$_b$ are separated by four σ bonds.

no splitting between H$_a$ and H$_b$

ethyl methyl ether
H$_a$ and H$_b$ are separated by four σ bonds.
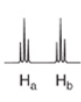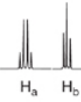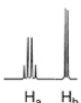
no splitting between H$_a$ and H$_b$

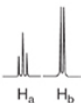| Table 14.3	Names for a Given Number of Peaks in an NMR Signal		
Number of peaks	**Name**	**Number of peaks**	**Name**
1	singlet	5	quintet
2	doublet	6	sextet
3	triplet	7	septet
4	quartet	> 7	multiplet

Table 14.4   **Common Splitting Patterns Observed in ^{1}H NMR**

Example	Pattern	Analysis (H_a and H_b are not equivalent.)			
[1] $-\overset{\mid}{\underset{H_a}{C}}-\overset{\mid}{\underset{H_b}{C}}-$		• H_a: one adjacent H_b proton ---→ • H_b: one adjacent H_a proton ---→	two peaks two peaks	---→ a **doublet** ---→ a **doublet**	
[2] $-\overset{\mid}{\underset{H_a}{C}}-\underset{H_b}{CH_2}-$		• H_a: two adjacent H_b protons ---→ • H_b: one adjacent H_a proton ---→	three peaks two peaks	---→ a **triplet** ---→ a **doublet**	
[3] $-\underset{H_a}{CH_2}\underset{H_b}{CH_2}-$		• H_a: two adjacent H_b protons ---→ • H_b: two adjacent H_a protons ---→	three peaks three peaks	---→ a **triplet** ---→ a **triplet**	
[4] $-\underset{H_a}{CH_2}\underset{H_b}{CH_3}$		• H_a: three adjacent H_b protons ---→ • H_b: two adjacent H_a protons ---→	four peaks three peaks	---→ a **quartet*** ---→ a **triplet**	
[5] $-\overset{\mid}{\underset{H_a}{C}}-\underset{H_b}{CH_3}$		• H_a: three adjacent H_b protons ---→ • H_b: one adjacent H_a proton ---→	four peaks two peaks	---→ a **quartet*** ---→ a **doublet**	

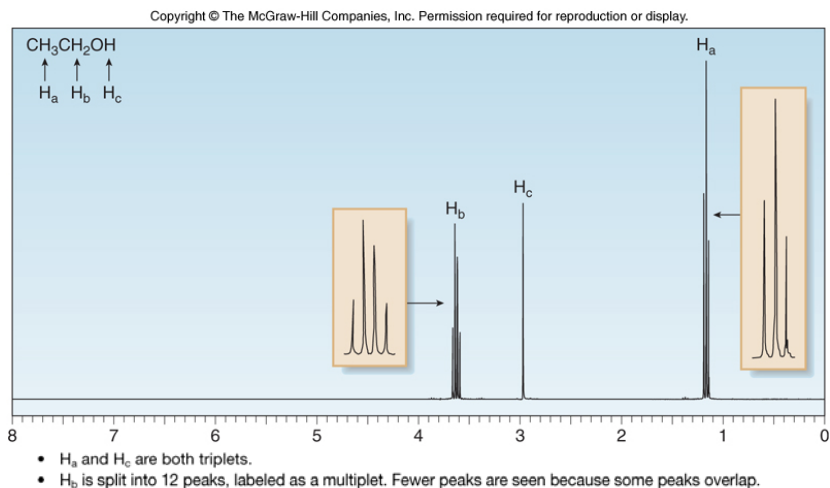*The relative area under the peaks of a quartet is 1:3:3:1.

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

Figure 14.6 The 1H NMR spectrum of 2-bromopropane, $[(CH_3)_2CHBr]$

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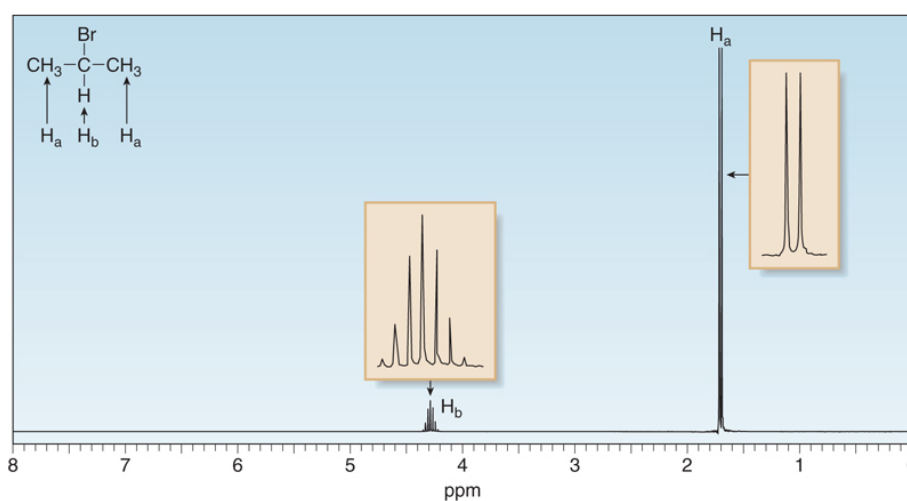
Now consider the spectrum of 1-bromopropane. Since H_a and H_c are not equivalent to each other, we cannot merely add them together and use the n + 1 rule.

Figure 14.7 The 1H NMR spectrum of 1-bromopropane, $CH_3CH_2CH_2Br$

- H_a and H_c are both triplets.
- H_b is split into 12 peaks, labeled as a multiplet. Fewer peaks are seen because some peaks overlap.

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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).

Figure 14.8 A splitting diagram for the H_b protons in 1-bromopropane
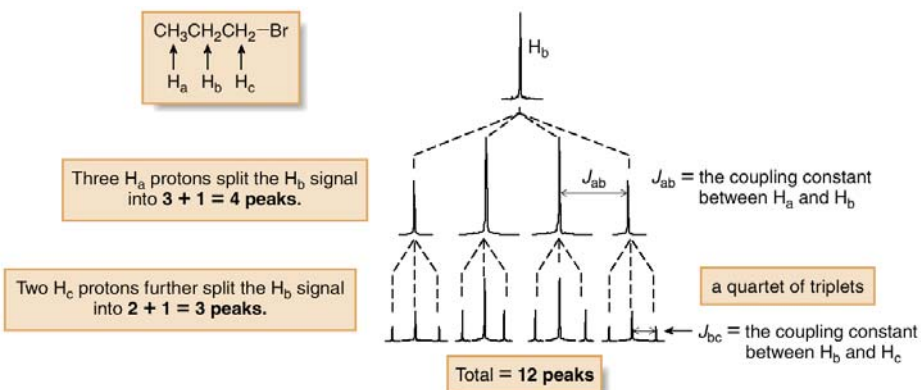
- The H_b signal is split into 12 peaks, a quartet of triplets. The number of peaks actually seen for the signal depends on the relative size of the coupling constants, J_{ab} and J_{bc}. When $J_{ab} >> J_{bc}$, as drawn in this diagram, all 12 lines of the pattern are visible. When J_{ab} and J_{bc} are similar in magnitude, peaks overlap and fewer lines are observed.

- **Protons on carbon-carbon double bonds often give characteristic splitting patterns.**
- **A disubstituted double bond can have two geminal protons, 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.**

geminal H's		cis H's		trans H's
$J_{geminal}$	$<$	J_{cis}	$<$	J_{trans}
0–3 Hz		5–10 Hz		11–18 Hz
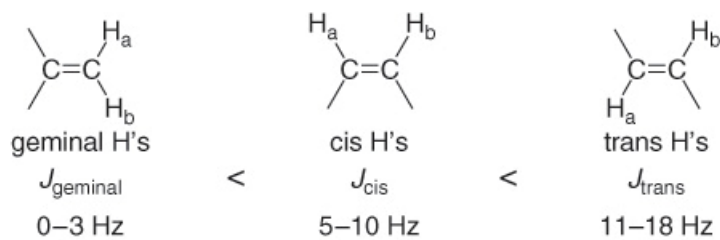
characteristic coupling constants for three types of disubstituted alkenes

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Figure 14.9 ^{1}H NMR spectra for the alkenyl protons of (*E*)- and (*Z*)-3-chloropropenoic acid

(*E*)-3-chloropropenoic acid

(*Z*)-3-chloropropenoic acid

J_{trans} = 14 Hz → ← → ← J_{trans} = 14 Hz

J_{cis} = 8 Hz → ← → ← J_{cis} = 8 Hz

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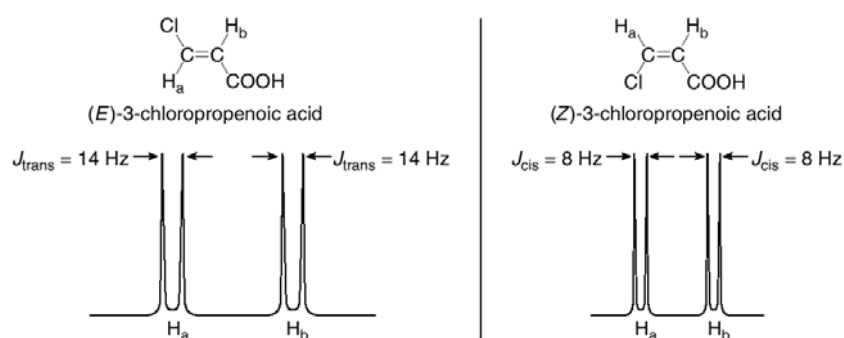
- Although both (*E*)- and (*Z*)-3-chloropropenoic acid show two doublets in their ^{1}H NMR spectra for their alkenyl protons, $J_{trans} > J_{cis}$.

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Figure 14.10 The ^{1}H NMR spectrum of vinyl acetate (CH$_2$=CHOCOCH$_3$)

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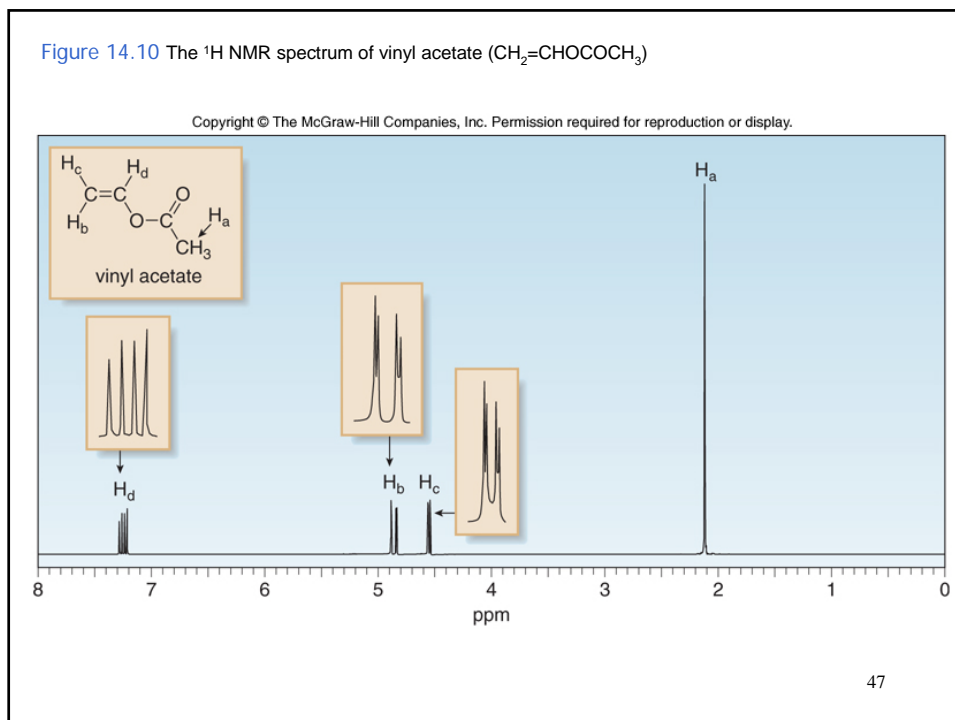
Splitting diagrams for the alkenyl protons in vinyl acetate are shown below. Note that each pattern is different in appearance because the magnitude of the coupling constants forming them is different.

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

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14.9 Other Facts About ^{1}H NMR

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.**

Figure 14.12 The ^{1}H spectrum of ethanol (CH_3CH_2OH)
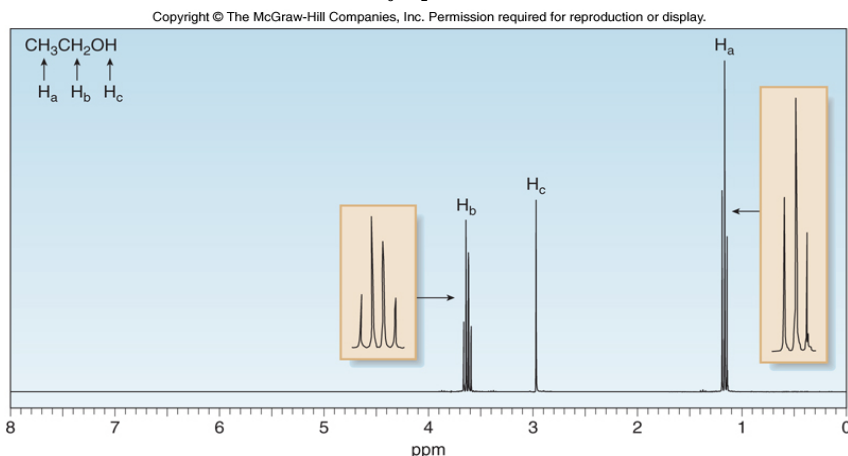
- **Ethanol (CH_3CH_2OH) has three different types of protons, so there are three signals in its NMR spectrum.**
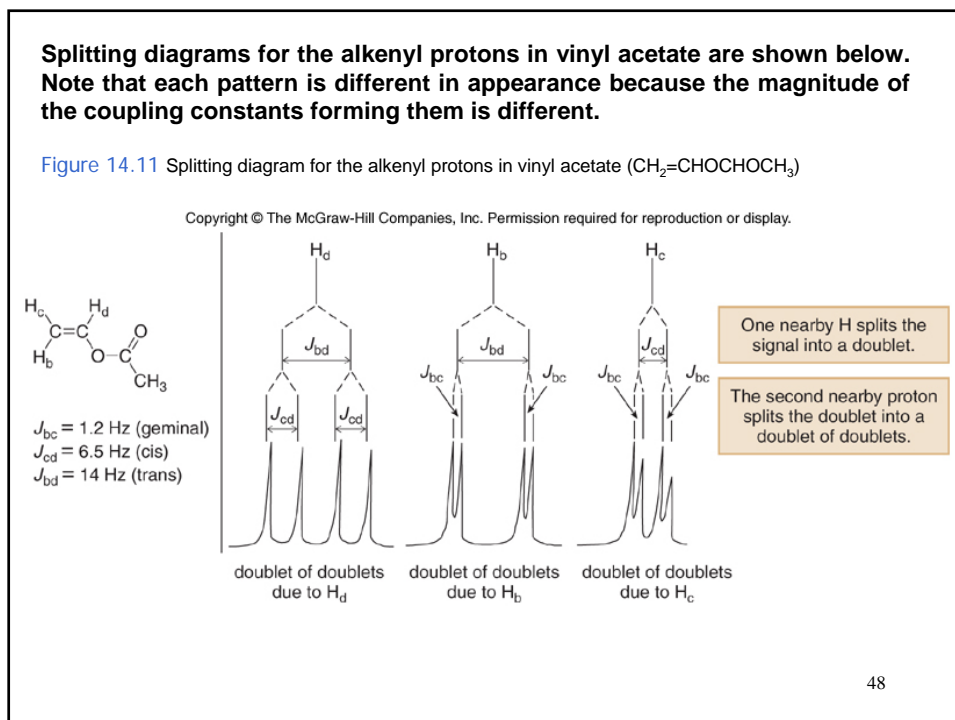
- **The H_a signal is split by the two H_b protons into three peaks (a triplet).**

- **The H_b signal is split only by 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.**

- **Protons on electronegative atoms rapidly exchange between molecules in the presence of trace amounts of acid or base. Thus, the CH_2 group of ethanol never "feels" the presence of the OH proton, because the OH proton is rapidly moving from one molecule to another.**

- **This phenomenon usually occurs with NH and OH protons.**

14.9B Cyclohexane Conformers

- Recall that cyclohexane conformers interconvert by ring flipping.
- Because the ring flipping is very rapid at room temperature, an NMR spectrum records an average of all conformers 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.
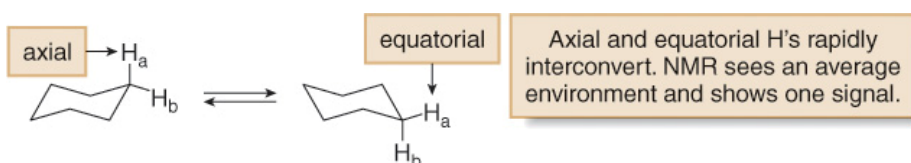
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14.9C Protons on Benzene Rings

- Benzene has six equivalent deshielded protons and exhibits a single peak in its ^1H NMR spectrum at 7.27 ppm.
- Monosubstituted benzenes contain five deshielded protons that are no longer equivalent, and the appearance of these signals is highly variable, depending on the identity of Z.

Figure 14.13 The 6.5–8 ppm region of the 1H NMR spectrum of three benzene derivatives

A benzene ring with one substituent Z

A monosubstituted benzene ring has three different types of H atoms: H_a, H_b, and H_c.
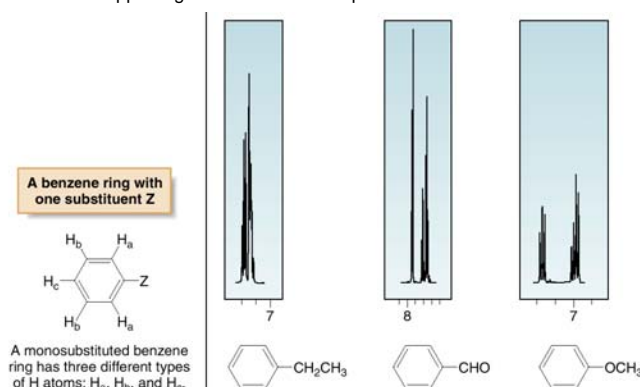
- The appearance of the signals in the 6.5–8 ppm region of the ^1H NMR spectrum depends on the identity of Z in C_6H_5Z.

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14.10 Structure Determination

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 $C_4H_8O_2$ and contains a $C=O$ absorption in its IR spectrum.

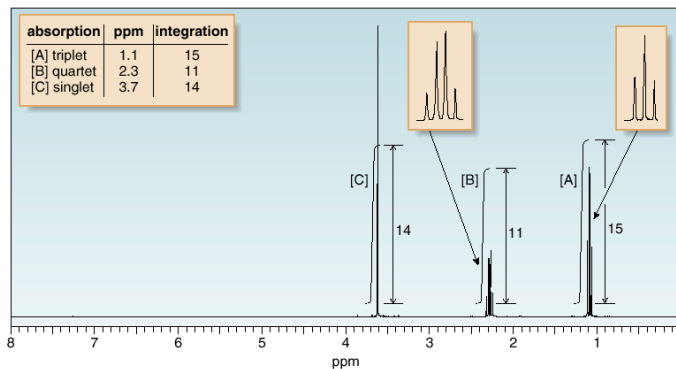| absorption	ppm	integration
[A] triplet	1.1	15
[B] quartet	2.3	11
[C] singlet	3.7	14

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).

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How To, continued . . .

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.

$$\frac{15}{5} = \boxed{3\ H_a\ \text{protons}} \qquad \frac{11}{5} = 2.2 \approx \boxed{2\ H_b\ \text{protons}} \qquad \frac{14}{5} = 2.8 \approx \boxed{3\ H_c\ \text{protons}}$$

signal [A]   signal [B]   signal [C]

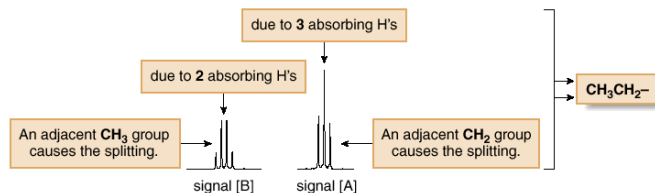| Three equivalent H's usually means a **CH_3** group.	Two equivalent H's usually means a **CH_2** group.	Three equivalent H's usually means a **CH_3** group.

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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:

$$CH_3O- \quad \text{or} \quad \underset{CH_3}{\overset{O}{\underset{\|}{C}}} \quad \text{or} \quad CH_3-\overset{|}{\underset{|}{C}}-$$
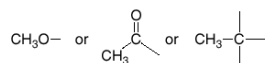
- Because signal [A] is a **triplet,** there must be **2 H's** (CH_2 group) on the adjacent carbon.
- Because signal [B] is a **quartet,** there must be **3 H's** (CH_3 group) on the adjacent carbon.
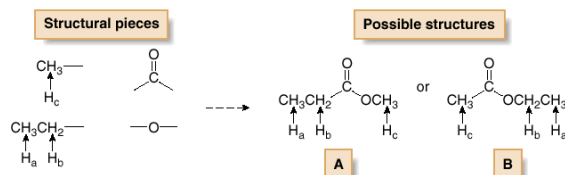- This information suggests that **X** has an **ethyl** group $---\rightarrow CH_3CH_2-$.

due to **3** absorbing H's

due to **2** absorbing H's

An adjacent **CH₃** group causes the splitting.

An adjacent **CH₂** group causes the splitting.

CH_3CH_2-

signal [B]   signal [A]

To summarize, **X** contains CH_3-, CH_3CH_2-, and $C=O$ (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 ¹H 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.

Step [4]   **Use chemical shift data to complete the structure.**

- Put the structure together in a manner that preserves the splitting data and is consistent with the reported chemical shifts.
- In this example, two isomeric structures (**A** and **B**) are possible for **X** considering the splitting data only:

Structural pieces

Possible structures

CH_3-
H_c

CH_3CH_2-
H_a H_b

$\underset{}{\overset{O}{\underset{\|}{C}}}$

$-O-$

$\underset{H_a\ H_b}{CH_3CH_2}\overset{O}{\underset{\|}{C}}\underset{H_c}{OCH_3}$ or $\underset{H_c}{CH_3}\overset{O}{\underset{\|}{C}}\underset{H_b\ H_a}{OCH_2CH_3}$

A   **B**

- Chemical shift information distinguishes the two possibilities. The electronegative O atom deshields adjacent H's, shifting them downfield between 3 and 4 ppm. If **A** is the correct structure, the singlet due to the CH_3 group (H_c) should occur downfield, whereas if **B** is the correct structure, the quartet due to the CH_2 group (H_b) should occur downfield.
- Because the NMR of **X** has a singlet (not a quartet) at 3.7, **A is the correct structure.**

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14.11 ^{13}C NMR Spectroscopy

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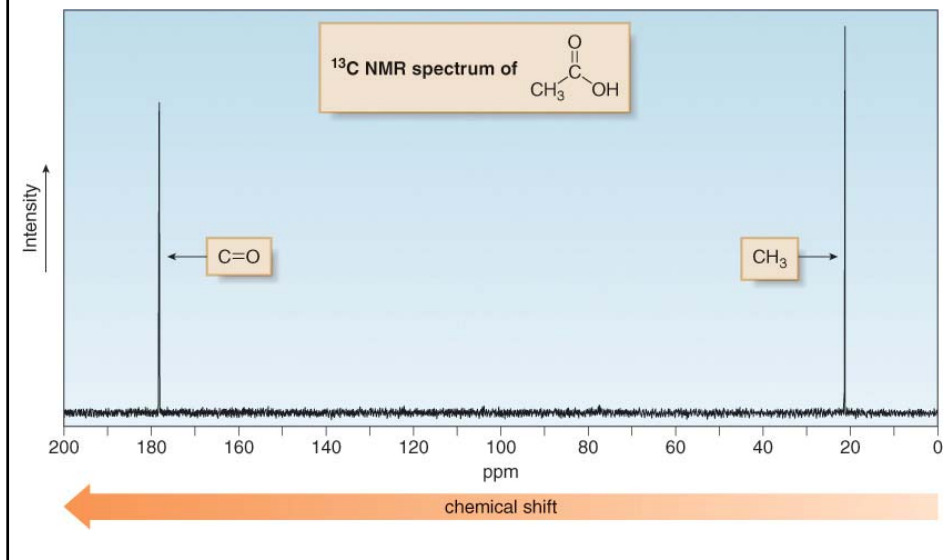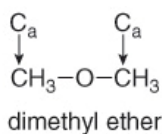

^{13}C NMR

- **The lack of splitting in a ^{13}C spectrum is a consequence of the low natural abundance of ^{13}C.**

- **Recall 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 the spectrum by using an instrumental technique that decouples the proton-carbon interactions, so that every peak in a ^{13}C NMR spectrum appears as a singlet.**

- **The two features of a ^{13}C NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.**
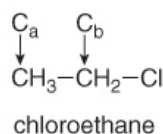
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14.11A ^{13}C NMR—Number of Signals

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

- **Because ^{13}C NMR signals are not split, the number of signals equals the number of lines in the ^{13}C spectrum.**

- **In contrast to the ^1H NMR situation, peak intensity is not proportional to the number of absorbing carbons, so ^{13}C NMR signals are not integrated.**
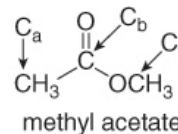

$$C_a \qquad C_a$$
$$CH_3-O-CH_3$$
dimethyl ether

1 ^{13}C NMR signal

Both C's are equivalent.

$$C_a \qquad C_b$$
$$CH_3-CH_2-Cl$$
chloroethane

2 ^{13}C NMR signals

methyl acetate

3 ^{13}C NMR signals

14.11B ^{13}C NMR—Position of Signals

- **In contrast to the small range of chemical shifts in ^1H NMR (1-10 ppm usually), ^{13}C NMR absorptions occur over a much broader range (0-220 ppm).**

- **The chemical shifts of carbon atoms in ^{13}C NMR depend on the same effects as the chemical shifts of protons in ^1H NMR.**

**Table 14.5**   Common ^{13}C Chemical Shift Values

Type of carbon	Chemical shift (ppm)	Type of carbon	Chemical shift (ppm)
$-\overset{\displaystyle\vert}{\underset{sp^3}{C}}-H$	5–45	$\overset{}{C=C}$	100–140
$-\overset{\displaystyle\vert}{\underset{sp^3}{C}}-Z$ Z = N, O, X	30–80	benzene C—	120–150
$-C\equiv C-$	65–100	$C=O$	160–210

Figure 14.14 Representative ^{13}C NMR spectra

a. 1-Propanol

$CH_3CH_2CH_2OH$
C_a C_b C_c

- The three types of C's in 1-propanol—identified as C_a, C_b, and C_c—give rise to three ^{13}C NMR signals.
- Deshielding increases with increasing proximity to the electronegative O atom, and the absorption shifts downfield; thus, in order of increasing chemical shift: $C_a < C_b < C_c$.

C_a

C_b

C_c

200 180 160 140 120 100 80 60 40 20 0
ppm

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b. Methyl acetate

CH_3 $\overset{O}{\overset{\|}{C}}$ OCH_3
C_a C_b C_c

- The three types of C's in methyl acetate—identified as C_a, C_b, and C_c—give rise to three ^{13}C NMR signals.
- The carbonyl carbon (C_b) is highly deshielded, so it absorbs farthest downfield.
- C_a, an sp^3 hybridized C that is not bonded to an O atom, is the most shielded, and so it absorbs farthest upfield.
- Thus, in order of increasing chemical shift: $C_a < C_c < C_b$.

C_c

C_a

C_b

200 180 160 140 120 100 80 60 40 20 0
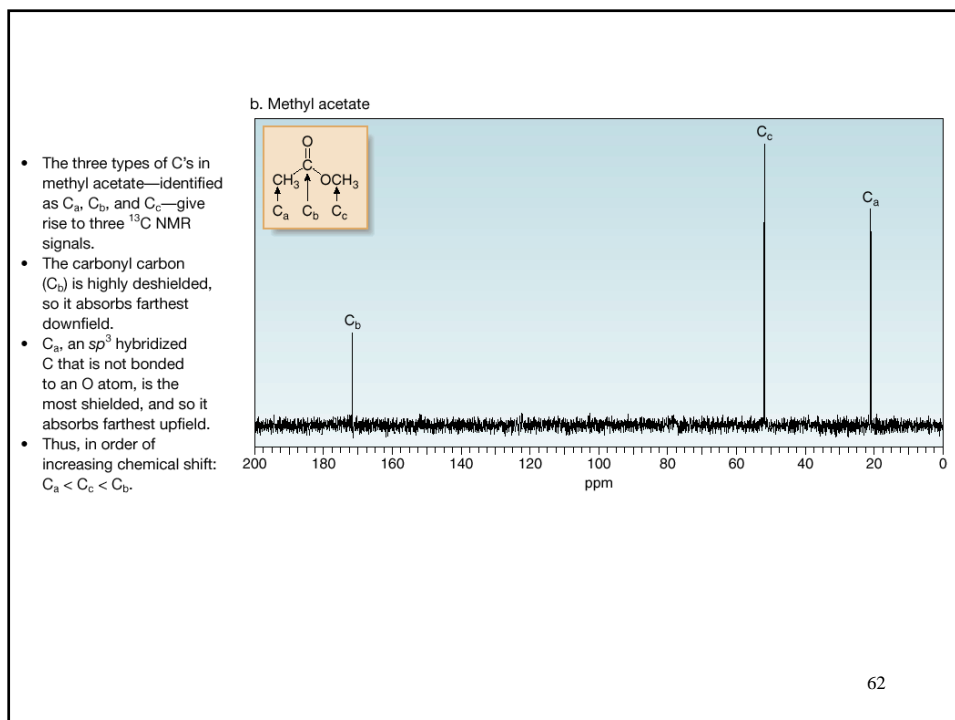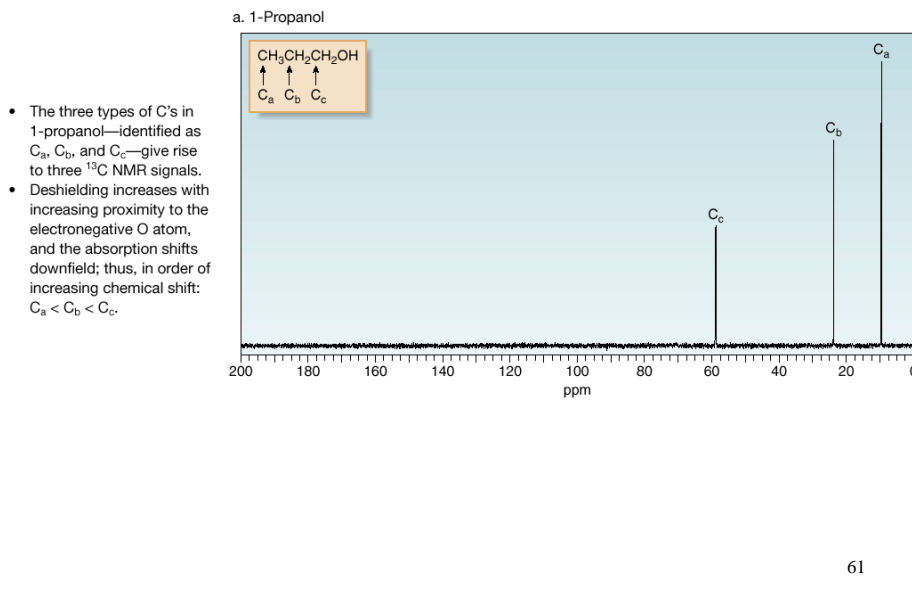ppm

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Figure 14.15 The MRI image of the lower back

An MRI instrument is especially useful for visualizing soft tissue. In 2002, 60 million MRI procedures were performed. The 2003 Nobel Prize in Physiology or Medicine was awarded to chemist Paul C. Lauterbur and physicist Sir Peter Mansfield for their contributions in developing magnetic resonance imaging.

A: Spinal cord compression from a herniated disc
B: Spinal cord (would not be visualized with conventional X-rays)

A

B

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