

# Organic Chemistry, *Fourth Edition*

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## Chapter 14 Lecture Outline

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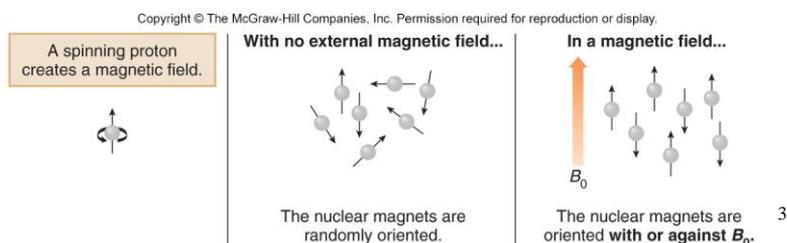
### Nuclear Magnetic Resonance Spectroscopy

- 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:
  - $^1\text{H}$  NMR is used to determine the type and number of H atoms in a molecule; and
  - $^{13}\text{C}$  NMR is used to determine the type of carbon atoms in a molecule.
- The source of energy in NMR is radio waves (so-called RF radiation) 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  $^1\text{H}$  and  $^{13}\text{C}$ .

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## Magnetic Fields in NMR

- When a charged particle such as a proton spins on its axis, it creates a magnetic field, causing the nucleus to act like 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).

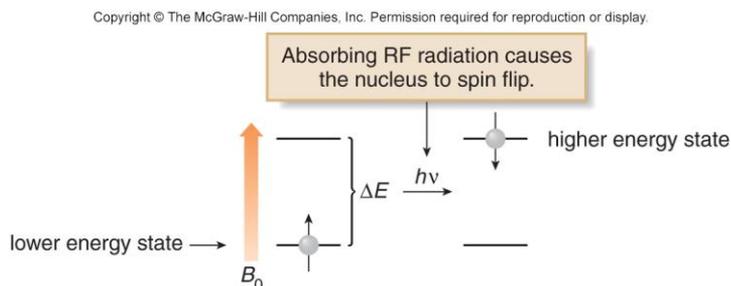


## Energy and Nuclear Spin

- 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 is aligned against  $B_0$ .
- 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 RF region of the electromagnetic spectrum.

## Resonance Energy

- Two variables characterize NMR:
  - An applied magnetic field  $B_0$ , the strength of which is measured in tesla (T)
  - The frequency  $\nu$  of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz)
- A nucleus is in resonance when it absorbs RF radiation and “spin flips” to a higher energy state.



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## Resonance Frequency

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

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$$\nu \propto B_0$$

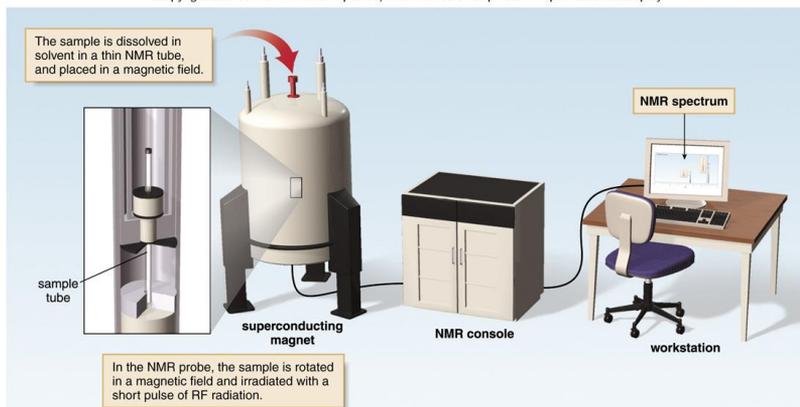
- The stronger the magnetic field, the larger the energy difference between the two nuclear spin states, and the higher the  $\nu$  needed for resonance.
- NMR spectrometers are referred to as 300 MHz instruments, 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used 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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# NMR Schematic

Figure 14.1

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**An NMR spectrometer.** The sample is dissolved in a solvent, usually  $\text{CDCl}_3$  (deuteriochloroform), 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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## Electron Environment

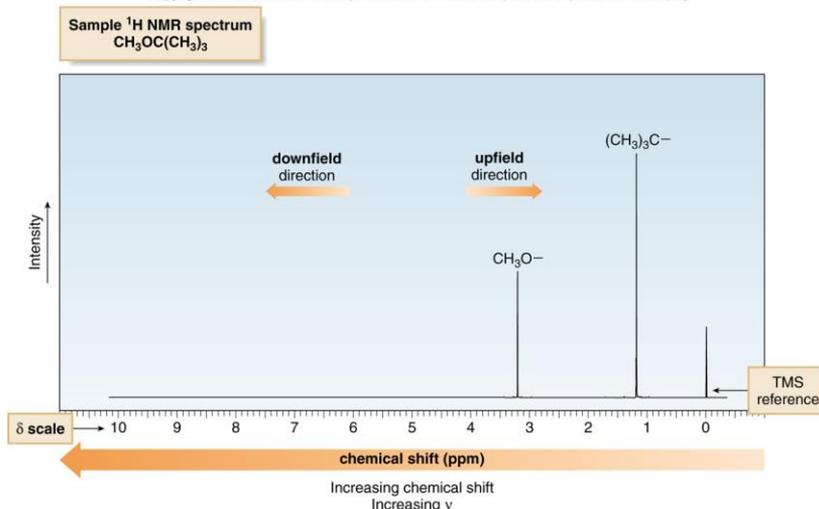
- The frequency at which a particular proton absorbs is determined by its electronic environment.
- Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The size of the magnetic field generated by the electrons around a proton determines where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

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# $^1\text{H}$ NMR Spectra

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

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## Interpreting $^1\text{H}$ NMR Spectra

- NMR absorptions generally appear as sharp peaks.
- Most protons absorb between 0-10 ppm.
- The terms “upfield” and “downfield” describe the relative location of peaks.
  - **Upfield** means to the right (higher magnetic field).
  - **Downfield** means to the left (lower magnetic field).
- An external standard,  $(\text{CH}_3)_4\text{Si}$  (tetramethylsilane) is added to the sample tube prior to the NMR measurement.
  - NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the  $\delta$  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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## Chemical Shift

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

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

- By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.

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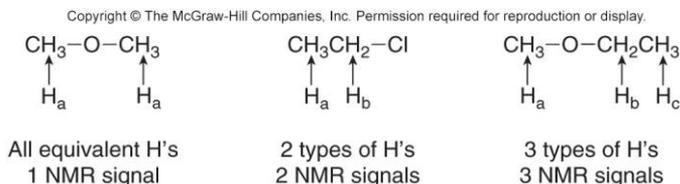
## Structural Information from Features of a $^1\text{H}$ NMR Spectrum

- **Number of signals:** indicates the number of different types of hydrogen in a molecule.
- **Position of signals:** indicates what types of hydrogen the molecule contains.
- **Intensity of signals:** indicates the relative amounts (how many) of each kind of hydrogen in the molecule.
- **Spin-spin splitting of signals:** gives further information of the neighboring environment for the various hydrogens in the molecule.

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## Number of Signals in $^1\text{H}$ NMR

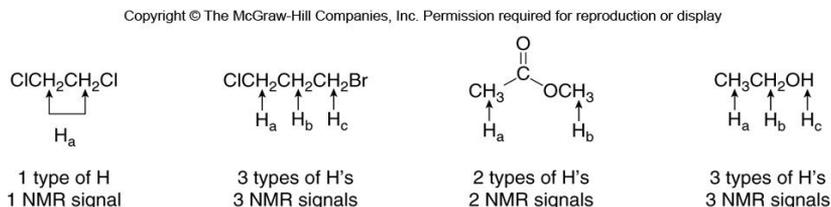
- The number of NMR signals equals the number of different types of protons in a compound.
- Protons in different environments give different NMR signals.
- Equivalent protons give the same NMR signal.



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## Number of $^1\text{H}$ NMR Signals—Examples

Figure 14.2

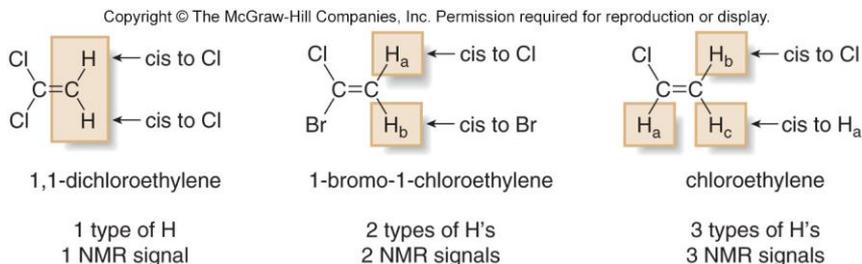


- To rigorously determine if two hydrogens in a molecule are the same:
  - replace each hydrogen by a different atom, Z (e.g., Cl) and
  - determine if the resulting compound is the same or different.
  - For example, replacement of each methyl hydrogen at  $\text{C}_1$  and  $\text{C}_5$  in pentane produces 1-chloropentane, replacement of each methylene hydrogen at  $\text{C}_2$  and  $\text{C}_4$  leads to 2-chloropentane and at  $\text{C}_3$  forms 3-chloropentane.

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## Number of $^1\text{H}$ NMR Signals—Alkenes

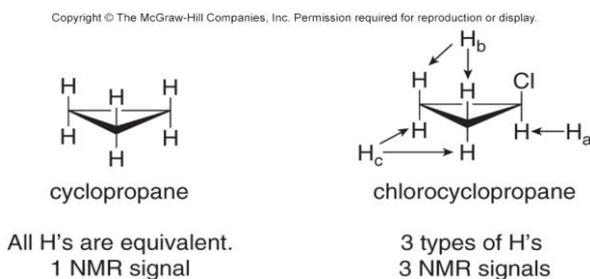
- In comparing two H atoms on a ring or double bond, two protons are equivalent only if they are cis (or trans) to the same groups.



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## Number of $^1\text{H}$ NMR Signals—Cycloalkanes

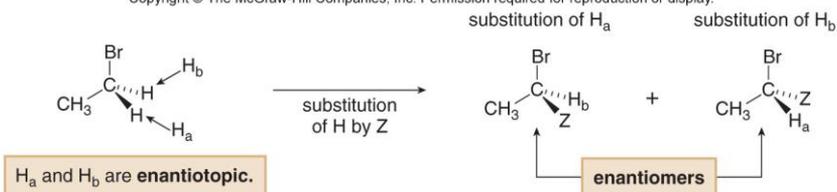
- To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen and determine whether or not they are cis (or trans) to the same groups.



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# Enantiotopic Protons

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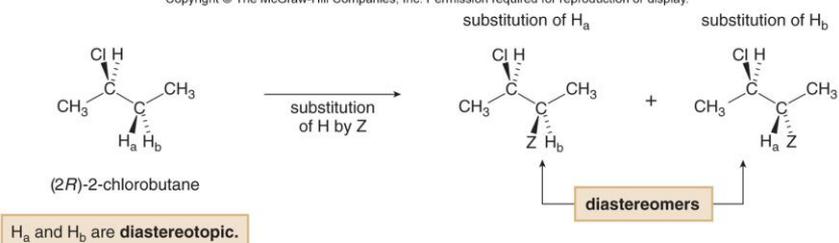
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- When substitution of two H atoms by Z forms enantiomers, the two H atoms are equivalent and give a single NMR signal. These two H atoms are called *enantiotopic* protons.

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# Diastereotopic Protons

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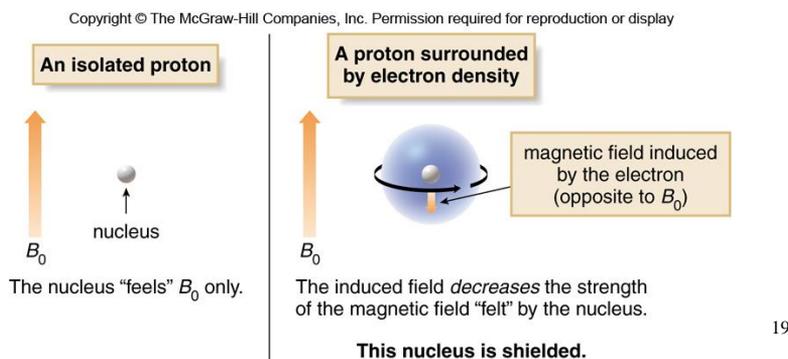


- When substitution of two H atoms by Z forms diastereomers, the two H atoms are not equivalent, and give two NMR signals. These two H atoms are called *diastereotopic* protons.

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## Shielding of Nuclei

- In the vicinity of the nucleus, the magnetic field generated by the circulating electron opposes the applied field and 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.



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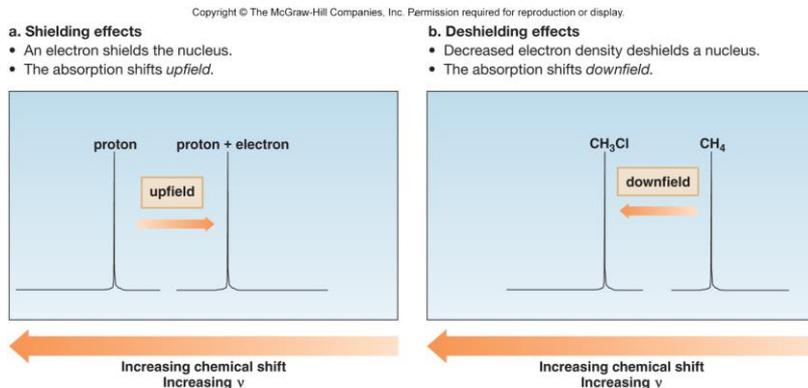
## Shielding and Resonant Frequency

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

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# Shielding and Chemical Shift

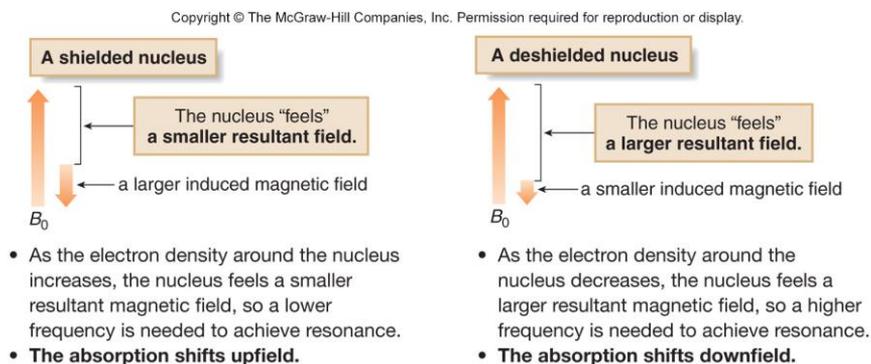
Figure 14.3



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## Summary of Shielding

Figure 14.4



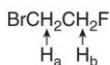
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## Shielding and Signal Position

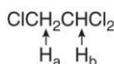
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- The H<sub>b</sub> protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H<sub>a</sub>.



- Because F is more electronegative than Br, the H<sub>b</sub> protons are more **deshielded** than the H<sub>a</sub> protons and absorb farther **downfield**.



- The larger number of electronegative Cl atoms (two versus one) **deshields** H<sub>b</sub> more than H<sub>a</sub>, so it absorbs **downfield** from H<sub>a</sub>.

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## Characteristic Chemical Shifts

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

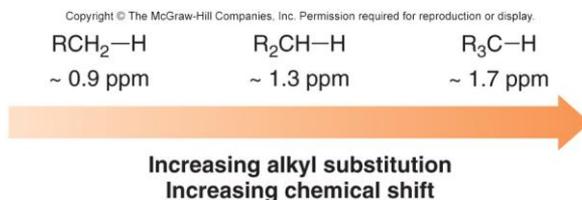
Table 14.1 Characteristic Chemical Shifts of Common Types of Protons

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
$\begin{array}{c}   \\ \text{---C---H} \\   \\ \text{sp}^3 \end{array}$ <ul style="list-style-type: none"> <li>RCH<sub>3</sub>      ~0.9</li> <li>R<sub>2</sub>CH<sub>2</sub>    ~1.3</li> <li>R<sub>3</sub>CH      ~1.7</li> </ul>	0.9–2	$\begin{array}{c} \text{H} \\   \\ \text{C=C} \\   \\ \text{sp}^2 \end{array}$	4.5–6
			6.5–8
$\begin{array}{c} \text{Z} \\   \\ \text{C=C---H} \\   \\ \text{Z} \end{array}$ <p>Z = C, O, N</p>	1.5–2.5		9–10
—C≡C—H	~2.5		10–12
$\begin{array}{c}   \\ \text{---C---H} \\   \\ \text{sp}^3 \\ \text{Z} \end{array}$ <p>Z = N, O, X</p>	2.5–4	RO—H or R—N—H	1–5

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## Substitution and Chemical Shift

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

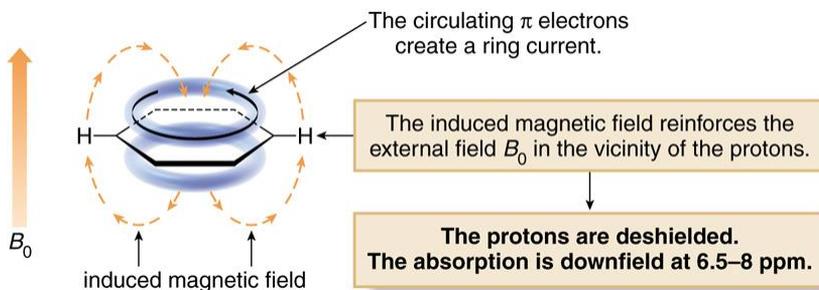


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## Aromatic Deshielding

- In a magnetic field, the six  $\pi$  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 meaning they are deshielded and absorb downfield.

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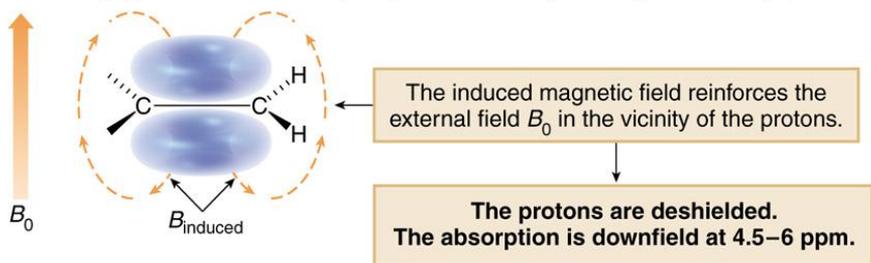


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## Alkene Chemical Shifts

- In a magnetic field, the loosely held  $\pi$  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 meaning the protons are deshielded and absorb downfield.

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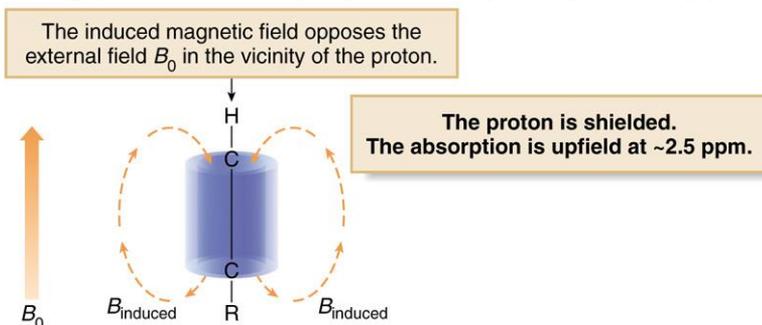


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## Alkyne Chemical Shifts

- In a magnetic field, the  $\pi$  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.

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# Summary of $\pi$ Electron and Chemical Shift

**Table 14.2** Effect of  $\pi$  Electrons on Chemical Shift Values

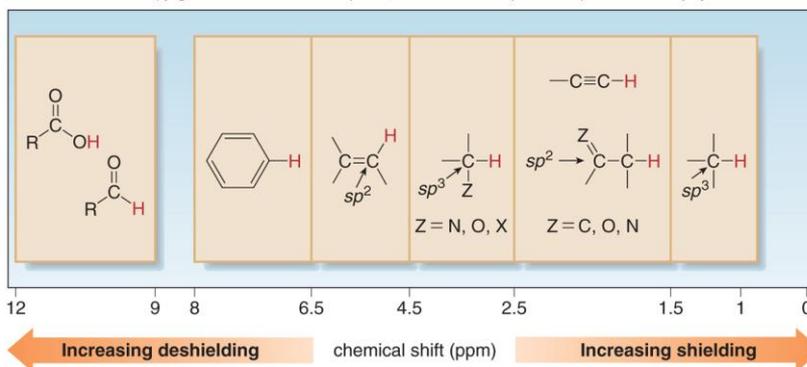
Proton type	Effect	Chemical shift (ppm)
	highly deshielded	6.5–8
	deshielded	4.5–6
$\text{—C}\equiv\text{C—H}$	shielded	–2.5

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## Regions in the $^1\text{H}$ NMR Spectrum

Figure 14.5

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- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).

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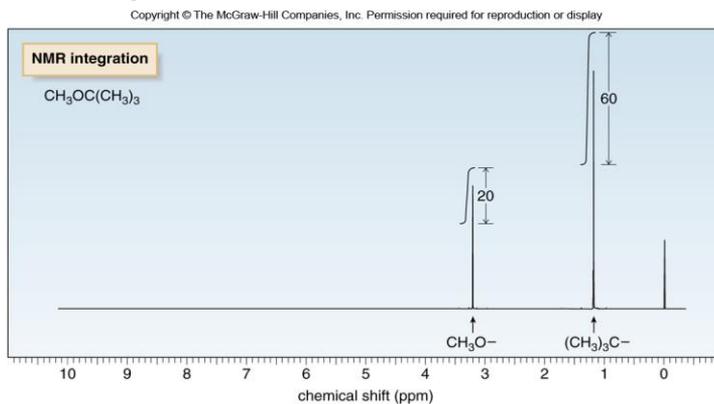
## Intensity of $^1\text{H}$ NMR Signals

- The area under an NMR signal is proportional to the number of absorbing protons.
- An NMR spectrometer can **integrate** the area under the peaks, and print 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.

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## $^1\text{H}$ NMR Integration

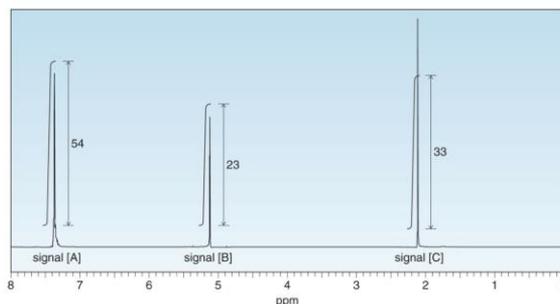
- Modern NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units.
- The ratio of integrals to one another gives the ratio of absorbing protons in a spectrum.
- Note that this gives a ratio, and not the absolute number, of absorbing protons.



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**How To** Determine the Number of Protons Giving Rise to an NMR Signal

**Example** A compound of molecular formula  $C_2H_{10}O_2$  gives the following integrated  $^1H$  NMR spectrum. How many protons give rise to each signal?



**How To, continued . . .**

**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:  $110 \text{ units}/10 \text{ protons} = 11 \text{ units per proton}$

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

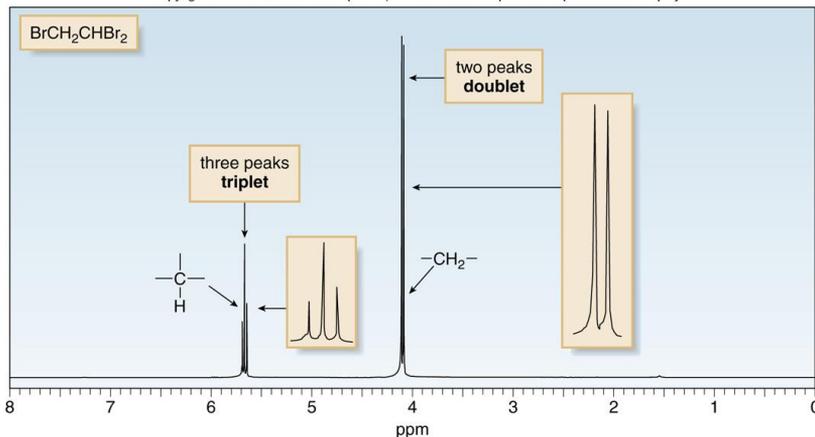
- To determine the number of H atoms giving rise to each signal, divide each integration value by the answer of Step [1] and round to the nearest whole number.

$$\text{Answer: } \frac{54}{11} = 4.9 \approx 5 \text{ H} \quad \left| \quad \frac{23}{11} = 2.1 \approx 2 \text{ H} \quad \left| \quad \frac{33}{11} = 3 \text{ H}$$

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## $^1H$ NMR—Spin-Spin Splitting

- The spectra up to this point have been limited to single absorptions called singlets.
- Often signals for different protons are split into more than one peak.



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# $^1\text{H}$ NMR—Spin-Spin Splitting

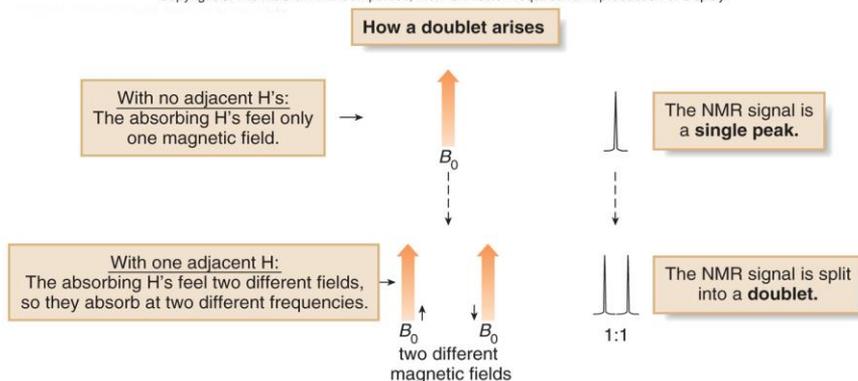
- **Spin-spin splitting** occurs only between nonequivalent protons on the same carbon or adjacent carbons.
- How does the doublet due to the  $\text{CH}_2$  group on  $\text{BrCH}_2\text{CHBr}_2$  occur?
  - When placed in an applied electric field, ( $B_0$ ), the adjacent proton ( $\text{CHBr}_2$ ) can be aligned with ( $\uparrow$ ) or against ( $\downarrow$ )  $B_0$ .
  - Thus, the absorbing  $\text{CH}_2$  protons feel two slightly different magnetic fields—one slightly larger than  $B_0$ , and one slightly smaller than  $B_0$ .
  - They absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.

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## Coupling Constants

The frequency difference, measured in Hz between two peaks of the doublet is called the **coupling constant,  $J$** .

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- One adjacent proton splits an NMR signal into a doublet.

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## How Triplets Arise

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- When placed in an applied magnetic field ( $B_0$ ), the adjacent protons  $H_a$  and  $H_b$  can each be aligned with ( $\uparrow$ ) or against ( $\downarrow$ )  $B_0$ .
- Thus, the absorbing proton feels three slightly different magnetic fields:
  - one slightly larger than  $B_0$ .
  - one slightly smaller than  $B_0$ .
  - 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, splitting a single absorption into a triplet.

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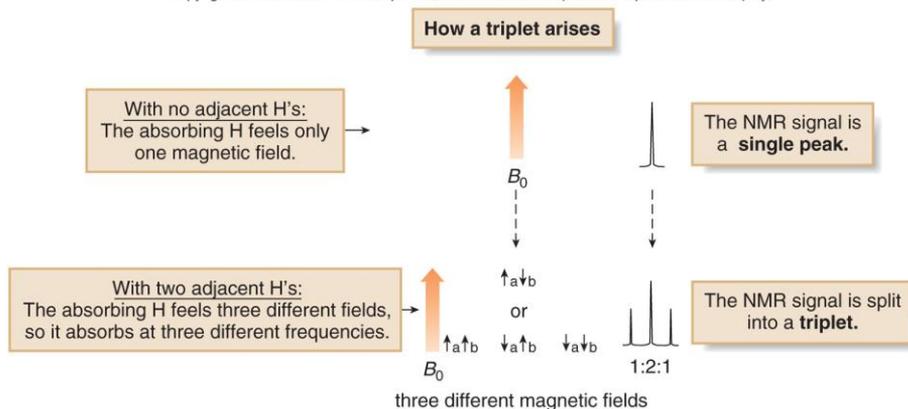
## Triplets

- Because there are two different ways to align one proton with  $B_0$ , and one proton against  $B_0$ :
  - $\uparrow_a \downarrow_b$  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.
- 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.

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# Formation of Triplets

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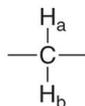


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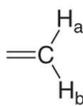
## Splitting Patterns

- **Three general rules describe the splitting patterns commonly seen in the  $^1\text{H}$  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.**

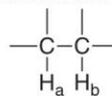
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$\text{H}_a$  and  $\text{H}_b$  are on the **same** carbon.



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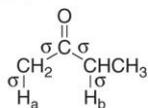
$\text{H}_a$  and  $\text{H}_b$  are on **adjacent** carbons.

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# Proximity and Splitting

**Splitting is not generally observed between protons separated by more than three  $\sigma$  bonds.**

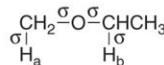
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2-butanone

$H_a$  and  $H_b$  are separated by four  $\sigma$  bonds.

**no splitting** between  $H_a$  and  $H_b$



ethyl methyl ether

$H_a$  and  $H_b$  are separated by four  $\sigma$  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

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

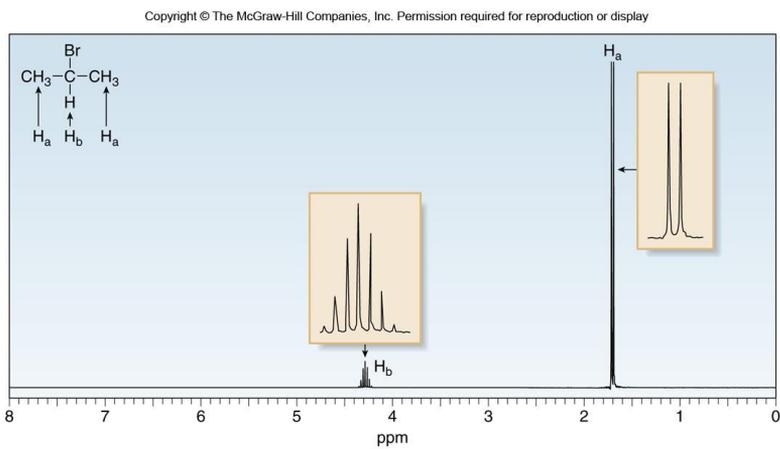
Example	Pattern	Analysis ( $H_a$ and $H_b$ are not equivalent.)
[1]		<ul style="list-style-type: none"> <li><math>H_a</math>: one adjacent <math>H_b</math> proton <math>\dashrightarrow</math> two peaks <math>\dashrightarrow</math> a <b>doublet</b></li> <li><math>H_b</math>: one adjacent <math>H_a</math> proton <math>\dashrightarrow</math> two peaks <math>\dashrightarrow</math> a <b>doublet</b></li> </ul>
[2]		<ul style="list-style-type: none"> <li><math>H_a</math>: two adjacent <math>H_b</math> protons <math>\dashrightarrow</math> three peaks <math>\dashrightarrow</math> a <b>triplet</b></li> <li><math>H_b</math>: one adjacent <math>H_a</math> proton <math>\dashrightarrow</math> two peaks <math>\dashrightarrow</math> a <b>doublet</b></li> </ul>
[3]		<ul style="list-style-type: none"> <li><math>H_a</math>: two adjacent <math>H_b</math> protons <math>\dashrightarrow</math> three peaks <math>\dashrightarrow</math> a <b>triplet</b></li> <li><math>H_b</math>: two adjacent <math>H_a</math> protons <math>\dashrightarrow</math> three peaks <math>\dashrightarrow</math> a <b>triplet</b></li> </ul>
[4]		<ul style="list-style-type: none"> <li><math>H_a</math>: three adjacent <math>H_b</math> protons <math>\dashrightarrow</math> four peaks <math>\dashrightarrow</math> a <b>quartet*</b></li> <li><math>H_b</math>: two adjacent <math>H_a</math> protons <math>\dashrightarrow</math> three peaks <math>\dashrightarrow</math> a <b>triplet</b></li> </ul>
[5]		<ul style="list-style-type: none"> <li><math>H_a</math>: three adjacent <math>H_b</math> protons <math>\dashrightarrow</math> four peaks <math>\dashrightarrow</math> a <b>quartet*</b></li> <li><math>H_b</math>: one adjacent <math>H_a</math> proton <math>\dashrightarrow</math> two peaks <math>\dashrightarrow</math> a <b>doublet</b></li> </ul>

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

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# <sup>1</sup>H NMR of 2-Bromopropane

Figure 14.6



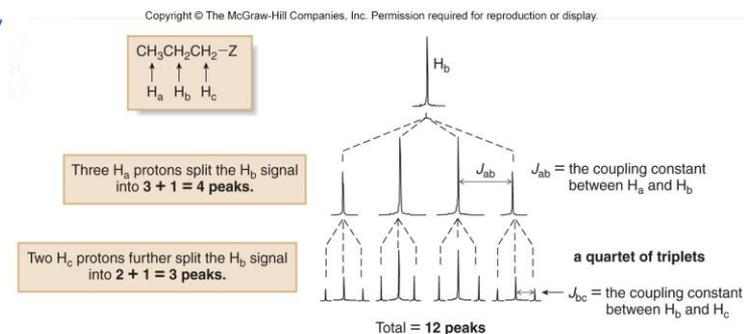
- The 6  $H_a$  protons are split by the one  $H_b$  proton to give a doublet.
- The  $H_b$  proton is split by 6 equivalent  $H_a$  protons to yield a septet.

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## More Complex Splitting Patterns

- 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 14.7



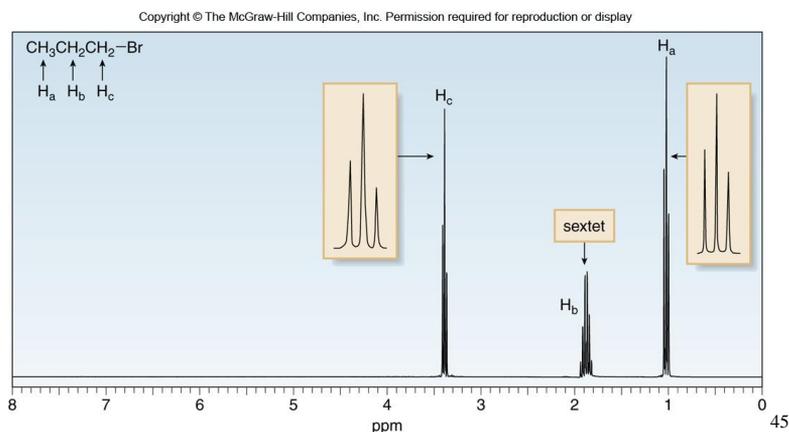
- The  $H_b$  signal is split into 12 peaks, a quartet of triplets. The number of peaks actually seen for the signal depends on the relative size of the coupling constants,  $J_{ab}$  and  $J_{bc}$ . When  $J_{ab} \gg J_{bc}$ , as drawn in this diagram, all 12 lines of the pattern are visible. When 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

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## $^1\text{H}$ NMR of 1-Bromopropane

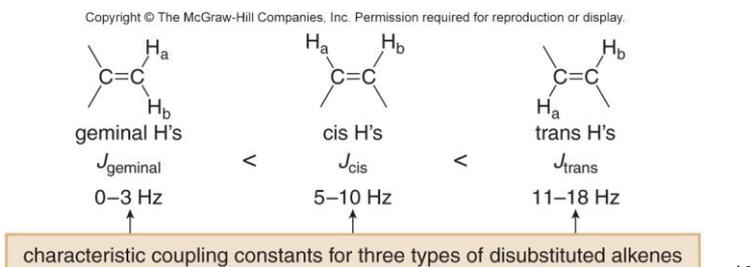
- Since  $\text{H}_a$  and  $\text{H}_c$  are not equivalent to each other, we cannot always add them together and use the  $n + 1$  rule.
- However, since the coupling constants,  $J_{ab}$  and  $J_{bc}$ , are very similar, the signal for  $\text{H}_b$  is a sextet (follows the  $n + 1$  rule).

Figure 14.8



## Coupling Constants for Alkenes

- 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.

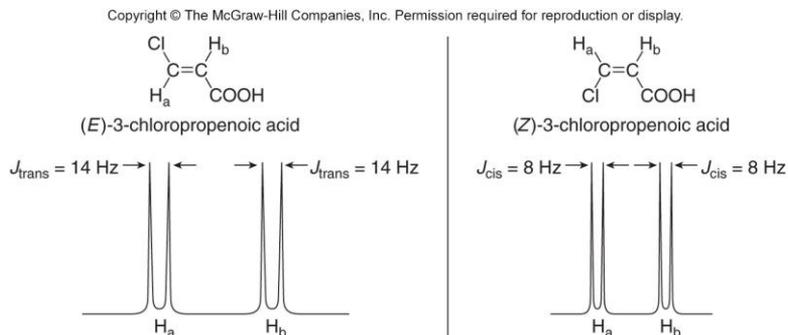


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# Splitting Patterns for Alkenes

Figure 14.9

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

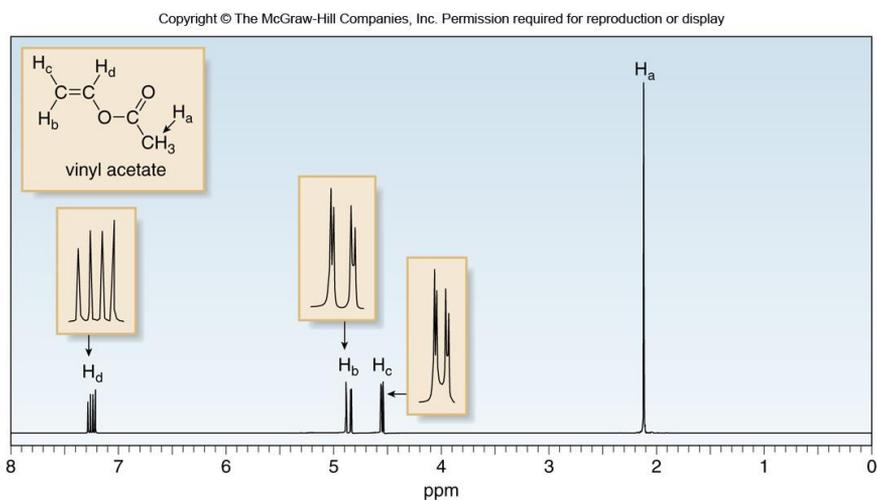


- Although both (*E*)- and (*Z*)-3-chloropropenoic acid show two doublets in their  $^1\text{H}$  NMR spectra for their alkenyl protons,  $J_{\text{trans}} > J_{\text{cis}}$ .

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# $^1\text{H}$ NMR of Vinyl Acetate

Figure 14.10

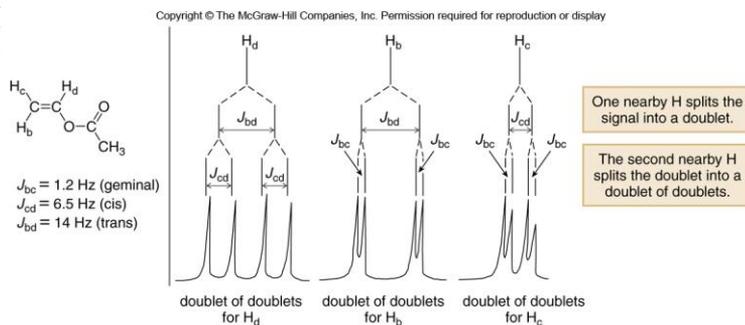


48

## Splitting Diagram for Vinyl Acetate

- Splitting diagrams for the alkenyl protons in vinyl acetate are shown below.
- 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 ( $\text{CH}_2=\text{CHOCHOCH}_3$ )

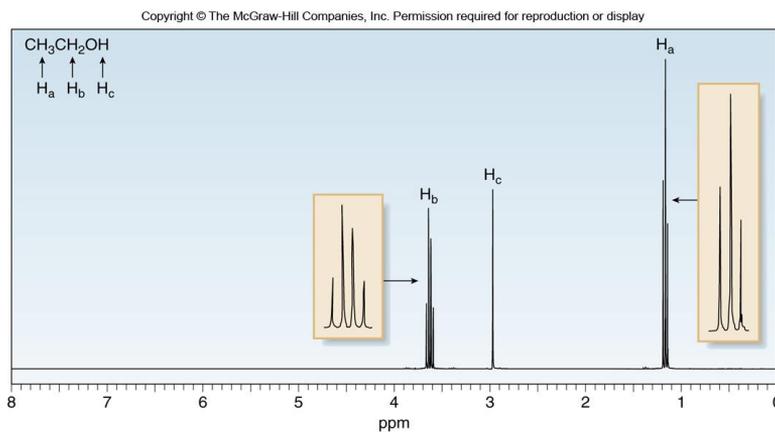


49

## $^1\text{H}$ NMR of 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



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## $^1\text{H}$ NMR of Ethanol

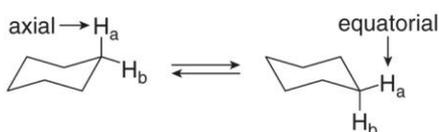
- Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) has three different types of protons, so there are three signals in its NMR spectrum.
  - The  $\text{H}_a$  signal is split by the two  $\text{H}_b$  protons into three peaks (a triplet).
  - The  $\text{H}_b$  signal is split only by the three  $\text{H}_a$  protons into four peaks, a quartet.
  - The adjacent OH proton does not split the signal due to  $\text{H}_b$ .
  - $\text{H}_c$  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  $\text{CH}_2$  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.

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## 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.
- 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.”

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

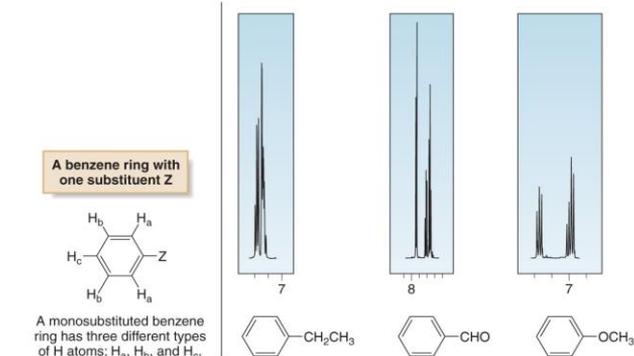
52

# Protons on Benzene Rings

- Benzene has six equivalent deshielded protons and exhibits a single peak in its  $^1\text{H}$  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.

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Figure 14.13



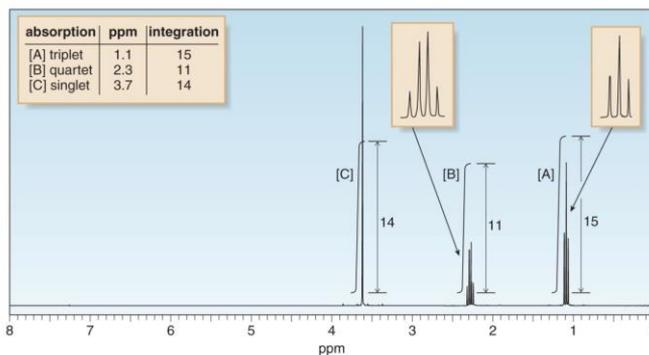
- The appearance of the signals in the 6.5–8 ppm region of the  $^1\text{H}$  NMR spectrum depends on the identity of Z in  $\text{C}_6\text{H}_5\text{Z}$ .

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## How To Use $^1\text{H}$ NMR Data to Determine a Structure

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



### 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 ( $\text{H}_a$ ,  $\text{H}_b$ , and  $\text{H}_c$ ).

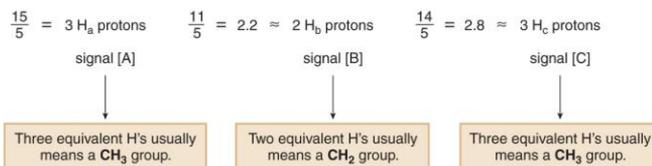
54

## <sup>1</sup>H NMR—Structure Determination, *continued*

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**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:  $40 \text{ units} / 8 \text{ protons} = 5 \text{ units per proton}$
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.



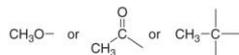
55

## <sup>1</sup>H NMR—Structure Determination, *continued*

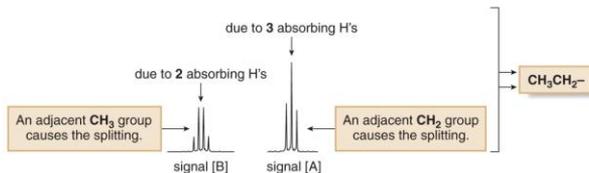
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**Step [3]** Use individual splitting patterns to determine what carbon atoms are bonded to each other.

- Start with the singlets. Signal [C] is due to a CH<sub>3</sub> group with no adjacent nonequivalent H atoms. Possible structures include:



- Because signal [A] is a **triplet**, there must be **2 H's** (CH<sub>2</sub> group) on the adjacent carbon.
- Because signal [B] is a **quartet**, there must be **3 H's** (CH<sub>3</sub> group) on the adjacent carbon.
- This information suggests that X has an **ethyl** group  $\text{---CH}_2\text{CH}_2\text{---}$ .



To summarize, X contains CH<sub>3</sub>-, CH<sub>3</sub>CH<sub>2</sub>-, 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 <sup>1</sup>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.

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## Splitting in $^{13}\text{C}$ NMR

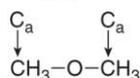
- The lack of splitting in a  $^{13}\text{C}$  spectrum is a consequence of the low natural abundance of  $^{13}\text{C}$ .
- Splitting occurs when two NMR active nuclei—like two protons—are close to each other.
  - Because of the low natural abundance of  $^{13}\text{C}$  nuclei (1.1%), the chance of two  $^{13}\text{C}$  nuclei being bonded to each other is very small (0.01%), and so no carbon-carbon splitting is observed.
- A  $^{13}\text{C}$  NMR signal can also be split by nearby protons.
  - This  $^1\text{H}$ - $^{13}\text{C}$  splitting is usually eliminated from the spectrum by using an instrumental technique that decouples the proton-carbon interactions, so that every peak in a  $^{13}\text{C}$  NMR spectrum appears as a singlet.

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## Details of $^{13}\text{C}$ NMR

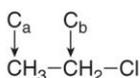
- The two features of a  $^{13}\text{C}$  NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.
- The number of signals in a  $^{13}\text{C}$  spectrum gives the number of different types of carbon atoms in a molecule.
- Because  $^{13}\text{C}$  NMR signals are not split, the number of signals equals the number of lines in the  $^{13}\text{C}$  spectrum.
- In contrast to the  $^1\text{H}$  NMR situation, peak intensity is not proportional to the number of absorbing carbons, so  $^{13}\text{C}$  NMR signals are not integrated.

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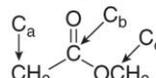
dimethyl ether

1  $^{13}\text{C}$  NMR signal  
Both C's are equivalent.



chloroethane

2  $^{13}\text{C}$  NMR signals



methyl acetate

3  $^{13}\text{C}$  NMR signals

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## Chemical Shifts in $^{13}\text{C}$ NMR

- In contrast to the small range of chemical shifts in  $^1\text{H}$  NMR (1-10 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.

Table 14.5 Common  $^{13}\text{C}$  Chemical Shift Values

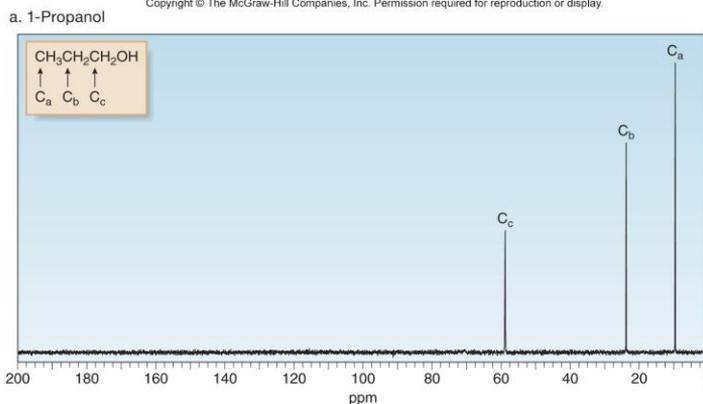
Type of carbon	Chemical shift (ppm)	Type of carbon	Chemical shift (ppm)
	5-45		100-140
 Z = N, O, X	30-80		120-150
	65-100		160-210

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## $^{13}\text{C}$ NMR of 1-Propanol

Figure 14.14

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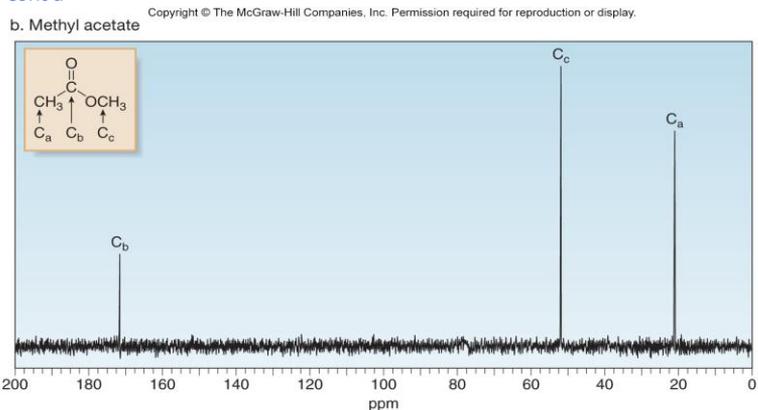


- The three types of C's in 1-propanol—identified as C<sub>a</sub>, C<sub>b</sub>, and C<sub>c</sub>—give rise to three  $^{13}\text{C}$  NMR signals.
- Deshielding increases with increasing proximity to the electronegative O atom, and the absorption shifts downfield; thus, in order of increasing chemical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

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# <sup>13</sup>C NMR of Methyl Acetate

Figure 14.14 cont'd



- The three types of C's in methyl acetate—identified as C<sub>a</sub>, C<sub>b</sub>, and C<sub>c</sub>—give rise to three <sup>13</sup>C NMR signals.
- The carbonyl carbon (C<sub>b</sub>) is highly deshielded, so it absorbs farthest downfield.
- C<sub>a</sub>, an sp<sup>3</sup> 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<sub>a</sub> < C<sub>c</sub> < C<sub>b</sub>.

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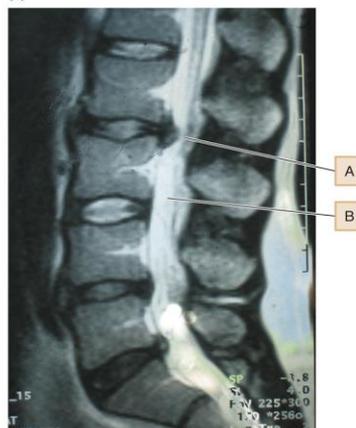
# Magnetic Resonance Imaging (MRI)

Figure 14.15 (a)



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(b)



- An MRI instrument: 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.
- An MRI image of the lower back: **A** labels spinal cord compression from a herniated disc. **B** labels the spinal cord, which would not be visualized with conventional X-rays.

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