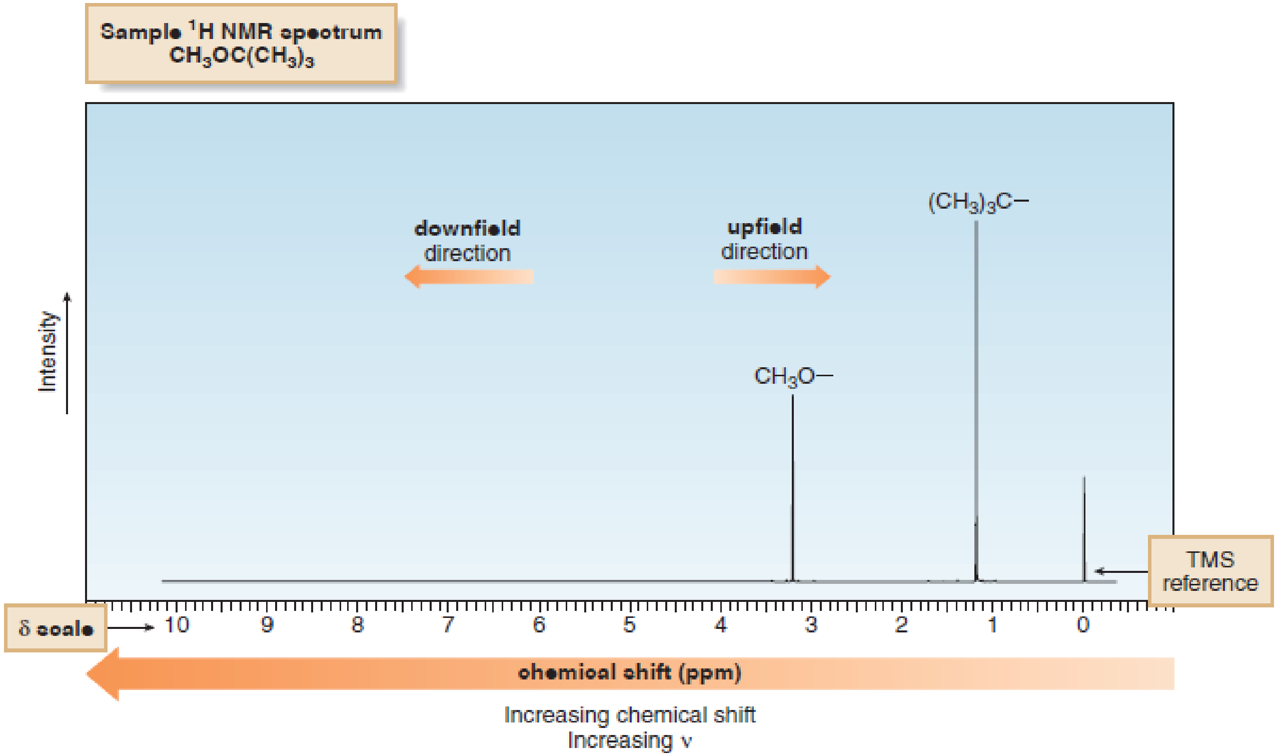
A ^{1}H NMR Spectrum

An NMR spectrum plots the **intensity of a signal** against its **chemical shift** measured in **parts per million (ppm)**. The common scale of chemical shifts is called the **δ (delta) scale.** The proton NMR spectrum of *tert*-butyl methyl ether [$CH_3OC(CH_3)_3$] illustrates several important features:

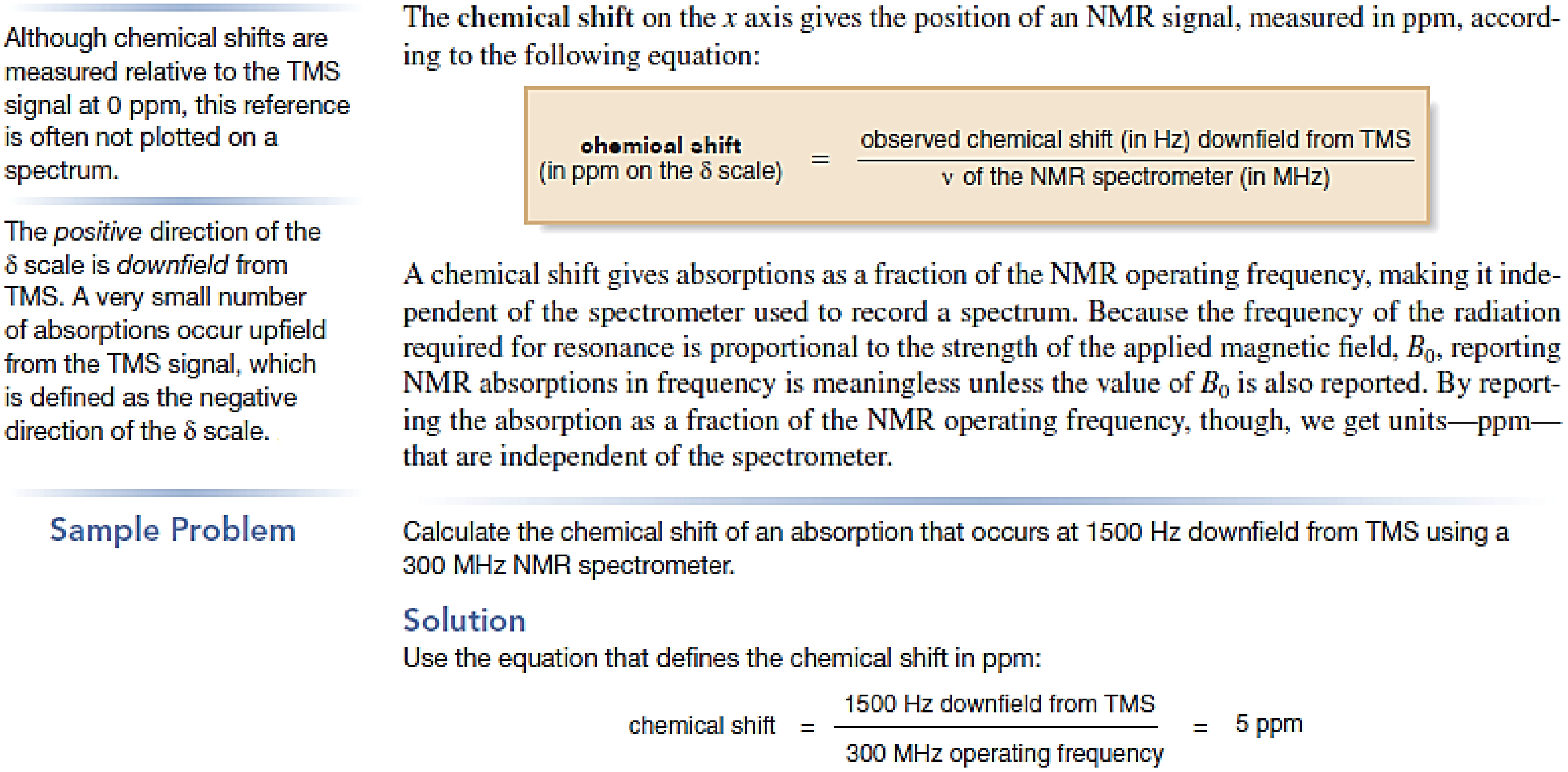


tert-Butyl methyl ether (MTBE) is the high-octane gasoline additive that has contaminated the water supply in some areas (Section 3.4).

- NMR absorptions generally appear as sharp signals. The ^{1}H NMR spectrum of $CH_3OC(CH_3)_3$ consists of two signals: a tall peak at 1.2 ppm due to the $(CH_3)_3C-$ group, and a smaller peak at 3.2 ppm due to the CH_3O- group.
- **Increasing chemical shift is plotted from *right to left*.** Most protons absorb somewhere from 0–12 ppm.
- The terms **upfield** and **downfield** describe the relative location of signals. Upfield means to the *right*. The $(CH_3)_3C-$ peak is upfield from the CH_3O- peak. Downfield means to the *left*. The CH_3O- peak is downfield from the $(CH_3)_3C-$ peak.

NMR absorptions are measured relative to the position of a reference signal at 0 ppm on the δ scale due to **tetramethylsilane (TMS). TMS** is a volatile and inert compound that gives a single peak upfield from other typical NMR absorptions.

$(CH_3)_4Si$
tetramethylsilane
TMS



Although chemical shifts are measured relative to the TMS signal at 0 ppm, this reference is often not plotted on a spectrum.

The *positive* direction of the δ scale is *downfield* from TMS. A very small number of absorptions occur upfield from the TMS signal, which is defined as the negative direction of the δ scale.

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

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

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

Sample Problem

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

Solution

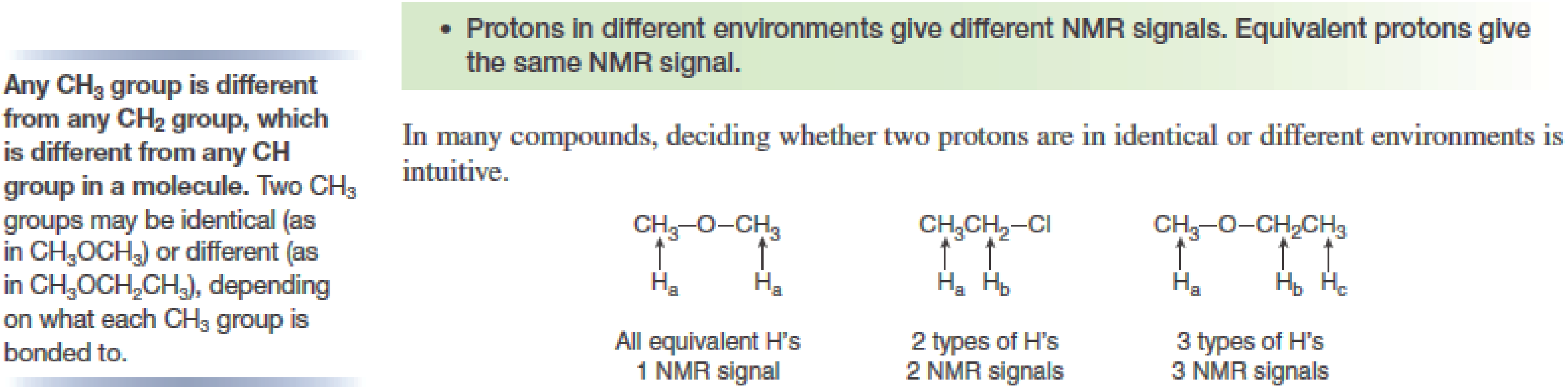
Use the equation that defines the chemical shift in ppm:

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

^{1}H NMR: Number of Signals

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

General Principles



Any CH_3 group is different from any CH_2 group, which is different from any CH group in a molecule. Two CH_3 groups may be identical (as in CH_3OCH_3) or different (as in $CH_3OCH_2CH_3$), depending on what each CH_3 group is bonded to.

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

In many compounds, deciding whether two protons are in identical or different environments is intuitive.

$\underset{H_a}{CH_3}\text{–O–}\underset{H_a}{CH_3}$

All equivalent H's
1 NMR signal

$\underset{H_a}{CH_3}\underset{H_b}{CH_2}\text{–Cl}$

2 types of H's
2 NMR signals

$\underset{H_a}{CH_3}\text{–O–}\underset{H_b}{CH_2}\underset{H_c}{CH_3}$

3 types of H's
3 NMR signals

- **CH_3OCH_3:** Each CH_3 group is bonded to the same group (–OCH_3), making both CH_3 groups equivalent.

- **CH_3CH_2Cl:** The protons of the CH^3 group are different from those of the CH_2 group.

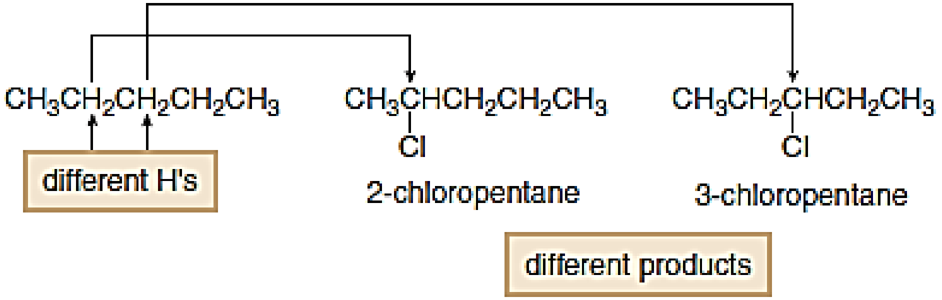
- **$CH_3OCH_2CH_3$:** The protons of the CH_2 group are different from those in each CH_3 group. The two CH_3 groups are also different from each other; one CH_3 group is bonded to –OCH_2CH_3 and the other is bonded to –CH_2OCH_3.

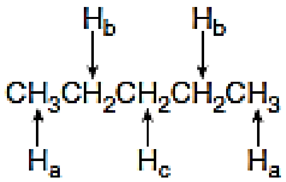
In some cases, it is less obvious by inspection if two protons are equivalent or different. To rigorously determine whether two protons are in identical environments (and therefore give rise to one NMR signal), replace each H atom in question by another atom Z (for example, Z = Cl). If substitution by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

How many different kinds of H atoms does $CH_3CH_2CH_2CH_2CH_3$ contain?

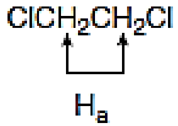
Solution

In comparing two H atoms, replace each H by Z (for example, Z = Cl), and examine the substitution products that result. The two CH_3 groups are identical because substitution of one H by Cl gives $CH_3CH_2CH_2CH_2CH_2Cl$ (1-chloropentane). There are two different types of CH_2 groups, because substitution of one H by Cl gives two different products:

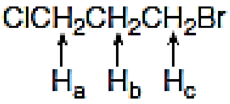




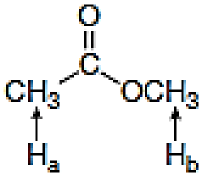
Thus, $CH_3CH_2CH_2CH_2CH_3$ has three different types of protons and gives three NMR signals.



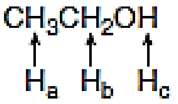
1 type of H
1 NMR signal



3 types of H's
3 NMR signals



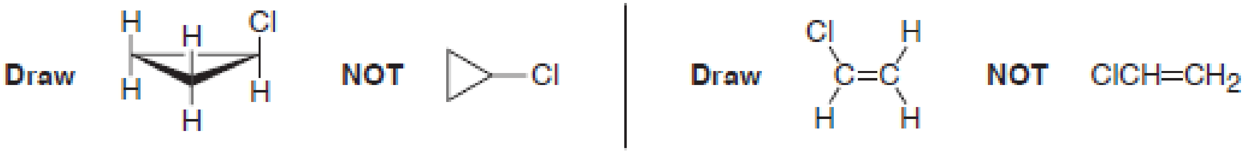
2 types of H's
2 NMR signals



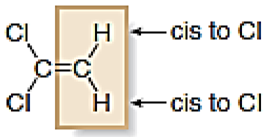
3 types of H's
3 NMR signals

Determining Equivalent Protons in Alkenes and Cycloalkanes:

To determine equivalent protons in cycloalkanes and alkenes that have restricted bond rotation, always draw in all bonds to hydrogen.

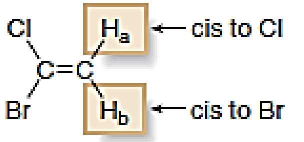


Then, in comparing two H atoms on a ring or double bond, **two protons are equivalent only if they are cis (or trans) to the same groups,** as illustrated with 1,1-dichloroethylene, 1-bromo-1-chloroethylene, and chloroethylene.



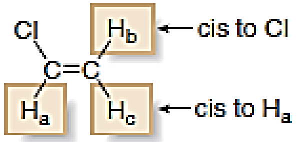
1,1-dichloroethylene

1 type of H
1 NMR signal



1-bromo-1-chloroethylene

2 types of H's
2 NMR signals

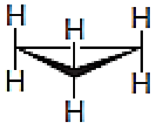


chloroethylene

3 types of H's
3 NMR signals

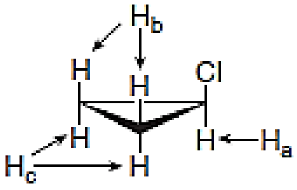
- **1,1-Dichloroethylene:** The two H atoms on the C=C are both cis to a Cl atom. Thus, both H atoms are equivalent.
- **1-Bromo-1-chloroethylene:** Ha is cis to a Cl atom and Hb is cis to a Br atom. Thus, Ha and
Hb are different, giving rise to two NMR signals.
- **Chloroethylene:** Ha is bonded to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

Proton equivalency in cycloalkanes can be determined similarly.



cyclopropane

All H's are equivalent.
1 NMR signal



chlorocyclopropane

3 types of H's
3 NMR signals

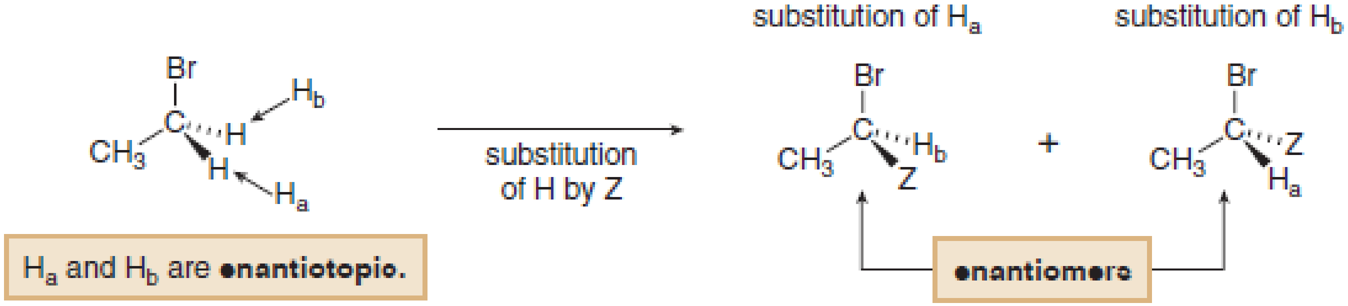
- **Cyclopropane:** All H atoms are equivalent, so there is only one NMR signal.

- **Chlorocyclopropane:** There are now three kinds of H atoms: Ha is bonded to a carbon bonded to a Cl; both Hb protons are cis to the Cl whereas both Hc protons are cis to another H.

Enantiotopic and Diastereotopic Protons

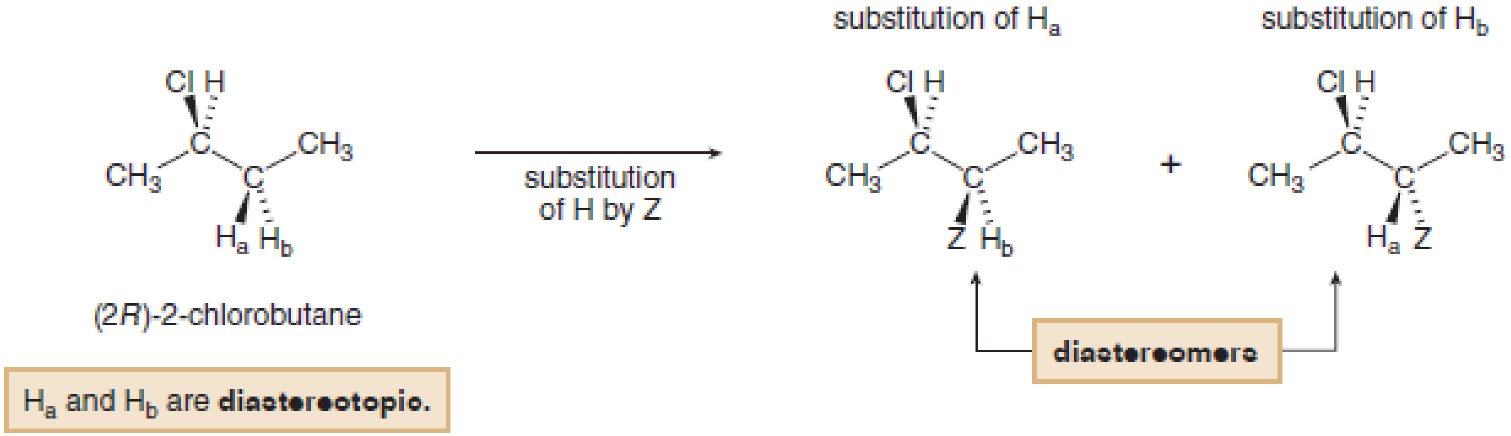
Let's look more closely at the protons of a single *sp*^{3} hybridized CH_2 group to determine whether these two protons are always equivalent to *each other*. Two examples illustrate different outcomes.

CH_3CH_2Br has two different types of protons—those of the CH_3 group and those of the CH_2 group—meaning that the two H atoms of the CH_2 group are *equivalent to each other*. To confirm this fact, we replace each H of the CH_2 group by an atom Z and examine the products of substitution. In this case, substitution of each H by Z creates a new stereogenic center, forming two products that are **enantiomers.**



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

In contrast, the two H atoms of the CH_2 group in (2*R*)-2-chlorobutane, which contains one stereogenic center, are *not* equivalent to each other. Substitution of each H by Z forms two **diastereomers**, and thus, these two H atoms give *different* NMR signals.

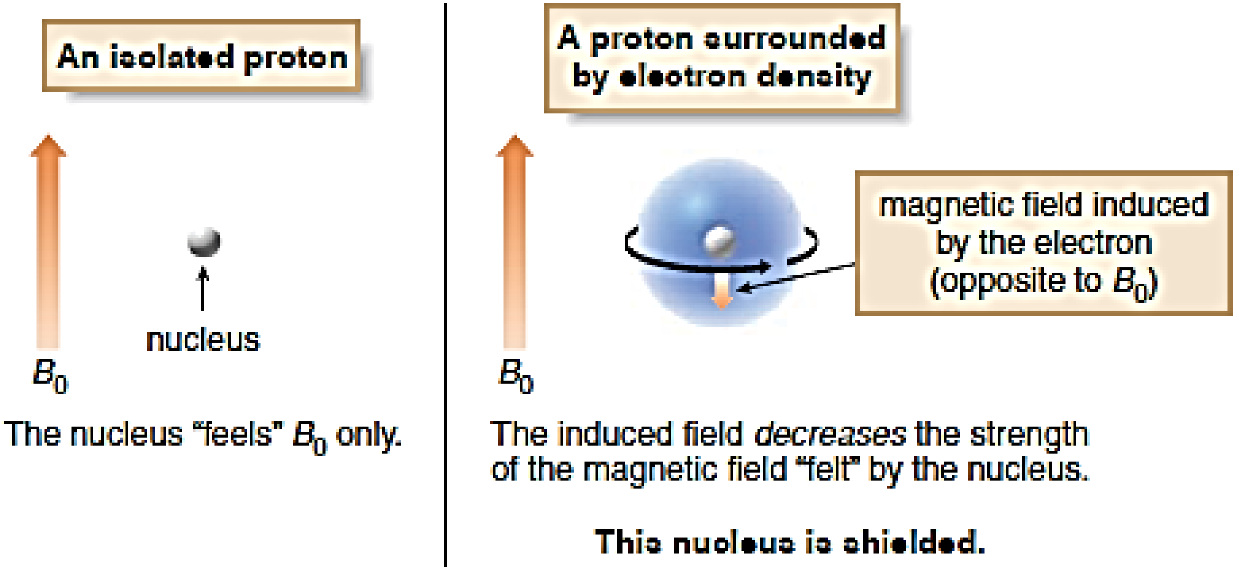


- When substitution of two H atoms by Z forms diastereomers, the two H atoms are not equivalent, and give two NMR signals. These two H atoms are called *diastereotopic* protons.

^{1}H NMR: Position of Signals

Shielding and Deshielding Effects

To understand how the electronic environment around a nucleus affects its chemical shift, recall that in a magnetic field, an electron creates a small magnetic field that opposes the applied magnetic field, B_0. Electrons are said to *shield* the nucleus from B_0.



The nucleus "feels" B_0 only.

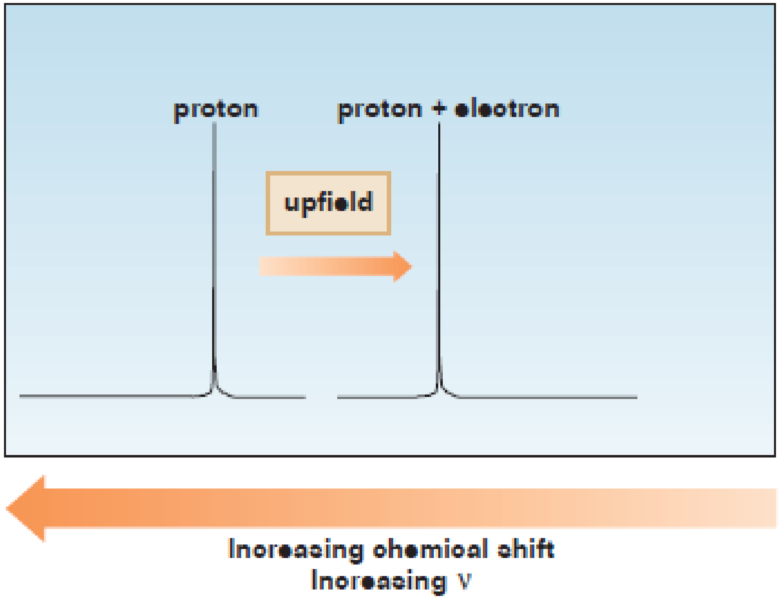
The induced field *decreases* the strength of the magnetic field "felt" by the nucleus.

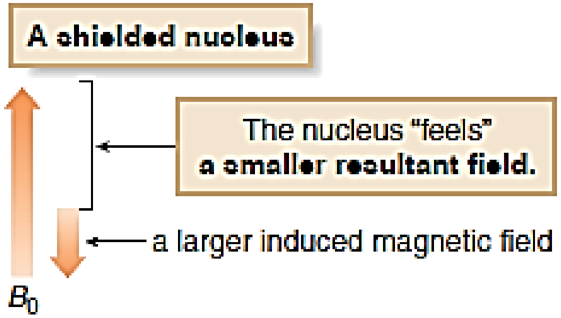
This nucleus is shielded.

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

a. Shielding effects

- An electron shields the nucleus.
- The absorption shifts *upfield*.

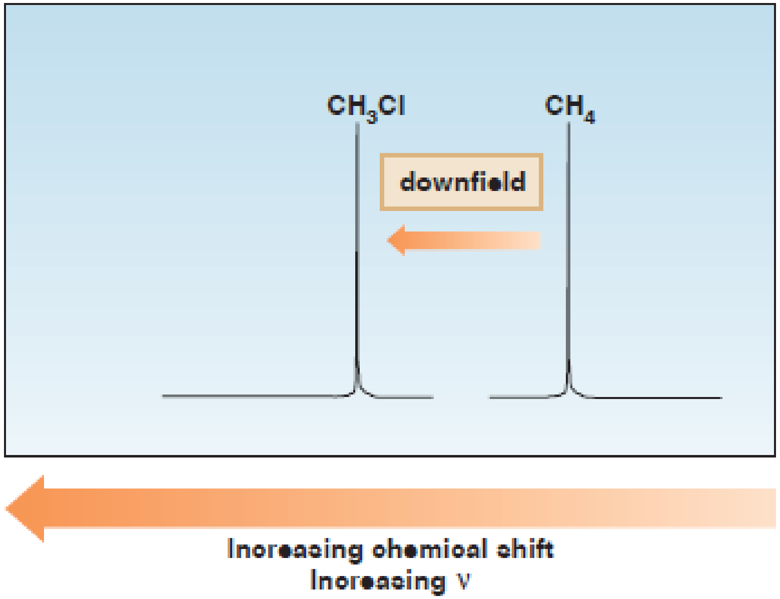


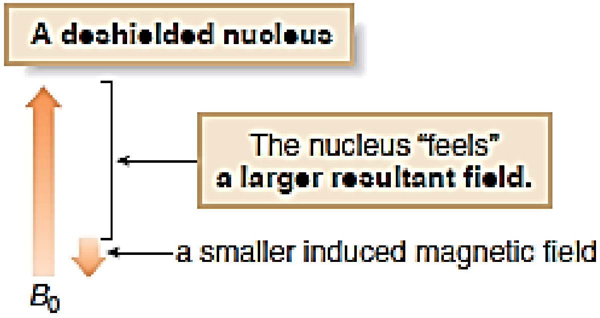


- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.
- **The absorption shifts upfield.**

b. Deshielding effects

- Decreased electron density deshields a nucleus.
- The absorption shifts *downfield*.





- 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.**

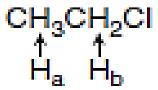
What happens if the electron density around a nucleus is *decreased,* instead? For example, how do the chemical shifts of the protons in CH_4 and CH_3Cl compare?

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.**

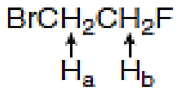
. The electronegative Cl atom withdraws electron density from the carbon and hydrogen atoms in CH_3Cl, thus deshielding them relative to those in CH_4.

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

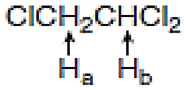
These electron density arguments explain the relative position of NMR signals in many compounds.


$\underset{\overset{\uparrow}{H_a}}{CH_3}\underset{\overset{\uparrow}{H_b}}{CH_2}Cl$

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


$Br\underset{\overset{\uparrow}{H_a}}{CH_2}\underset{\overset{\uparrow}{H_b}}{CH_2}F$

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


$Cl\underset{\overset{\uparrow}{H_a}}{CH_2}\underset{\overset{\uparrow}{H_b}}{CH}Cl_2$

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

Which of the underlined protons in each pair absorbs farther downfield: (a) $CH_3CH_2C\underline{H}_3$ or $CH_3OC\underline{H}_3$; (b) $CH_3OC\underline{H}_3$ or $CH_3SC\underline{H}_3$?

Solution

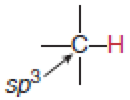
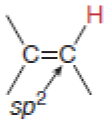
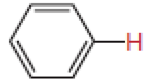
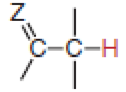
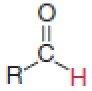
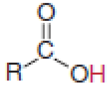
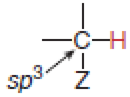
a. The CH_3 group in CH_3OCH_3 is deshielded by the electronegative O atom. **Deshielding shifts the absorption downfield.**
b. Because oxygen is more electronegative than sulfur, the CH_3 group in CH_3OCH_3 is more **deshielded and absorbs downfield.**

Chemical Shift Values

Not only is the *relative* position of NMR absorptions predictable, but it is also possible to predict the approximate chemical shift value for a given type of proton.

This Table illustrates that absorptions for a given type of C – H bond occur in a narrow range of chemical shift values, usually 1–2 ppm. For example, all *sp*3 hybridized C – H bonds in alkanes and cycloalkanes absorb between 0.9 and 2.0 ppm. By contrast, absorptions due to N – H and O– H protons can occur over a broader range. For example, the OH proton of an alcohol is found anywhere in the 1–5 ppm range. The position of these absorptions is affected by the extent of hydrogen bonding, making it more variable.

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

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
	0.9–2		4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7		6.5–8
 Z = C, O, N	1.5–2.5		9–10
—C≡C—H	~2.5		10–12
 Z = N, O, X	2.5–4	RO—H or R—N—H	1–5

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

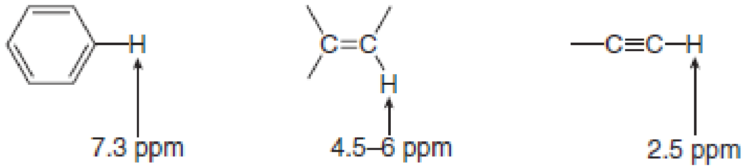
RCH_2—H	R_2CH—H	R_3C—H
~ 0.9 ppm	~ 1.3 ppm	~ 1.7 ppm

Increasing alkyl substitution
Increasing chemical shift

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

The Chemical Shift of Protons on sp^2 and sp Hybridized Carbons

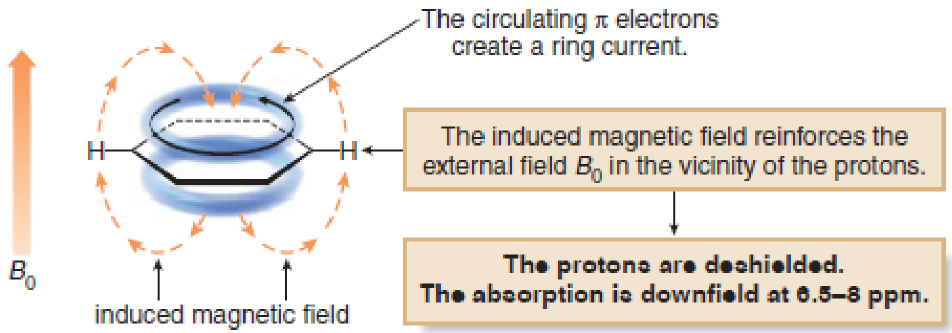
The chemical shift of protons bonded to benzene rings, C–C double bonds, and C–C triple bonds merits additional comment.



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

Protons on Benzene Rings

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



The circulating π electrons create a ring current.

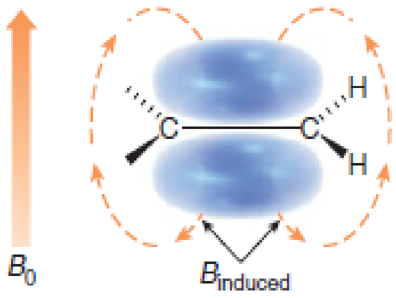
The induced magnetic field reinforces the external field B_0 in the vicinity of the protons.

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

Organic Chemistry, J. G. Smith, 3rd Ed.

Protons on Carbon–Carbon Double Bonds

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



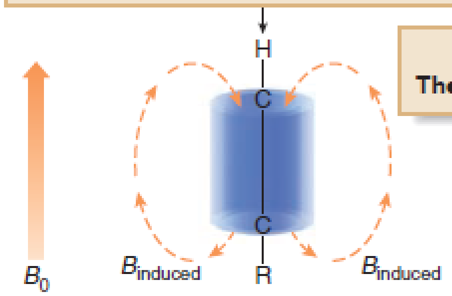
The induced magnetic field reinforces the external field B_0 in the vicinity of the protons.

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

Protons on Carbon–Carbon Triple Bonds

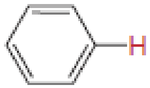
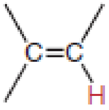
In a magnetic field, the π electrons of a carbon–carbon triple bond are induced to circulate, but in this case the induced magnetic field *opposes* the applied magnetic field (B_0). The proton thus feels a weaker magnetic field, so a lower frequency is needed for resonance. **The nucleus is shielded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

The induced magnetic field opposes the external field B_0 in the vicinity of the proton.

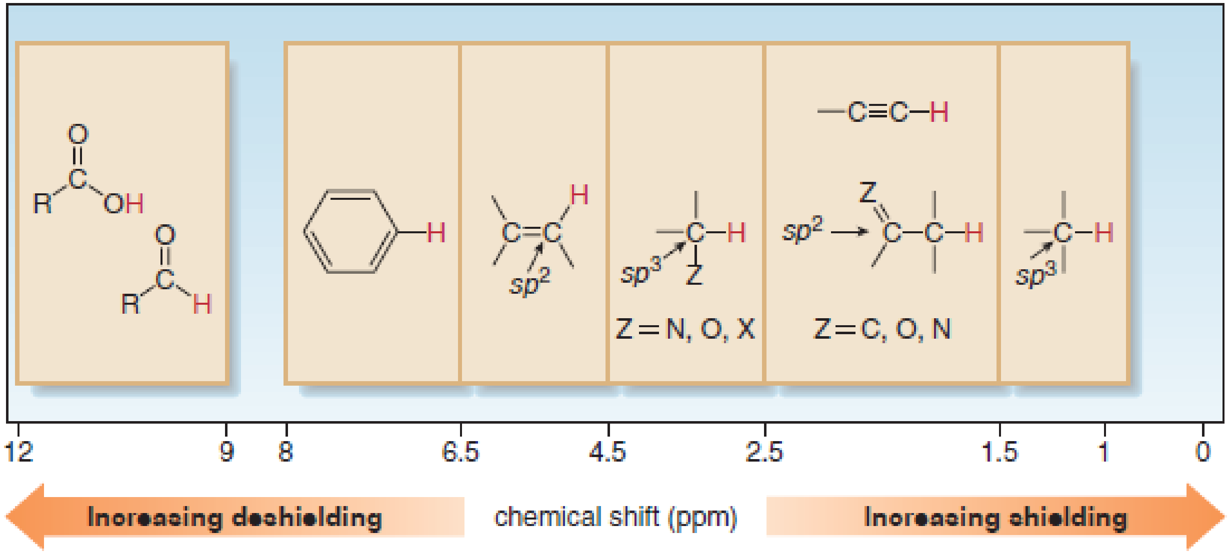


The proton is shielded.
The absorption is upfield at ~2.5 ppm.

Effect of π Electrons on Chemical Shift Values

Proton type	Effect	Chemical shift (ppm)
	highly deshielded	6.5–8
	deshielded	4.5–6
—C≡C—H	shielded	~2.5

Regions in the ^1H NMR spectrum



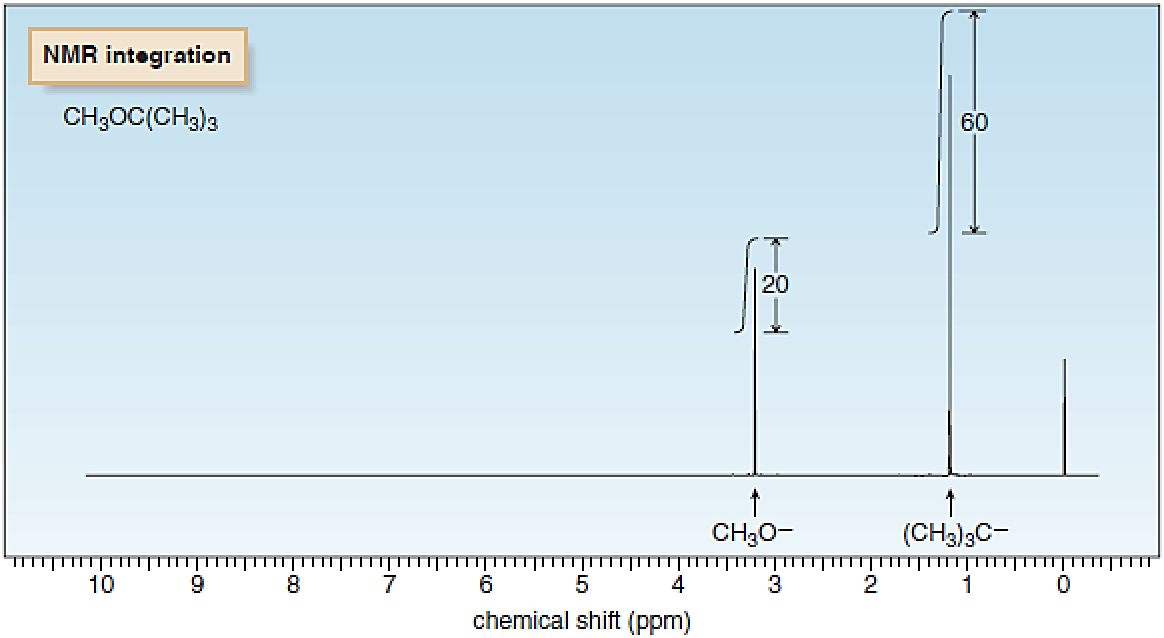
- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).
- Note: The drawn chemical shift scale is not linear.

^{1}H NMR: Intensity of Signals

The relative intensity of ^{1}H NMR signals also provides information about a compound's structure.

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

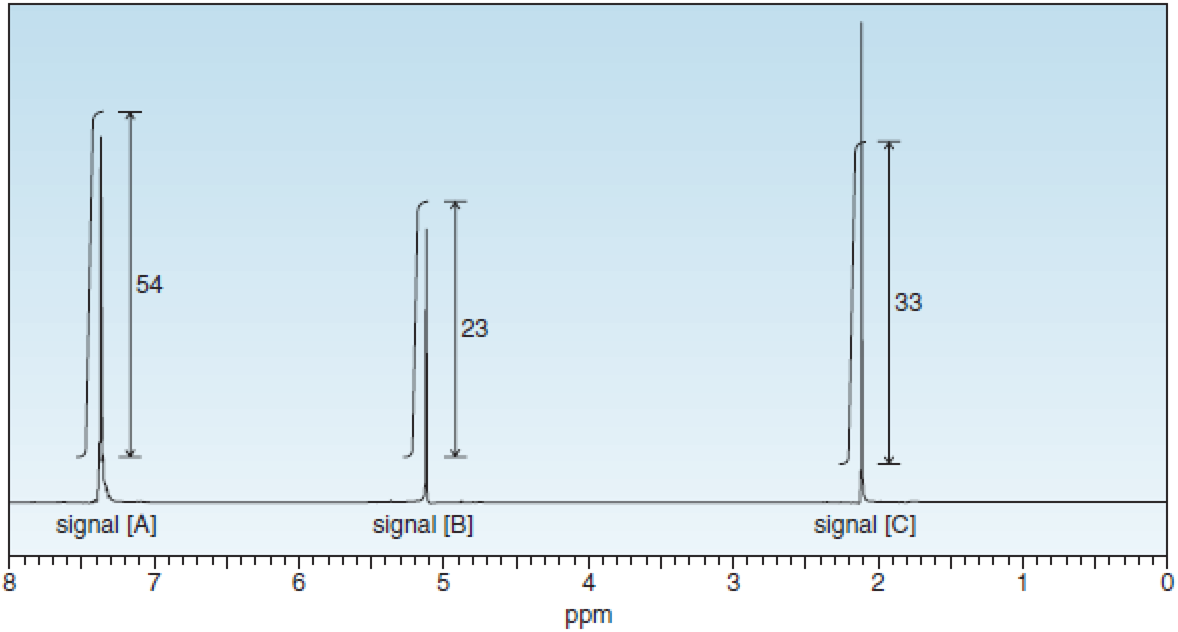
For example, in the ^{1}H NMR spectrum of $CH_3OC(CH_3)_3$, the ratio of the area under the downfield peak (due to the CH_3O- group) to the upfield peak [due to the $-C(CH_3)_3$ group] is 1:3. An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (an **integral**) on the spectrum. **The height of each step is proportional to the area under the peak, which is in turn proportional to the number of absorbing protons.**



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

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 ^1H NMR spectrum. How many protons give rise to each signal?



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.

Answer:

Signal [A]: $\frac{54}{11} = 4.9 \approx$ **5 H**

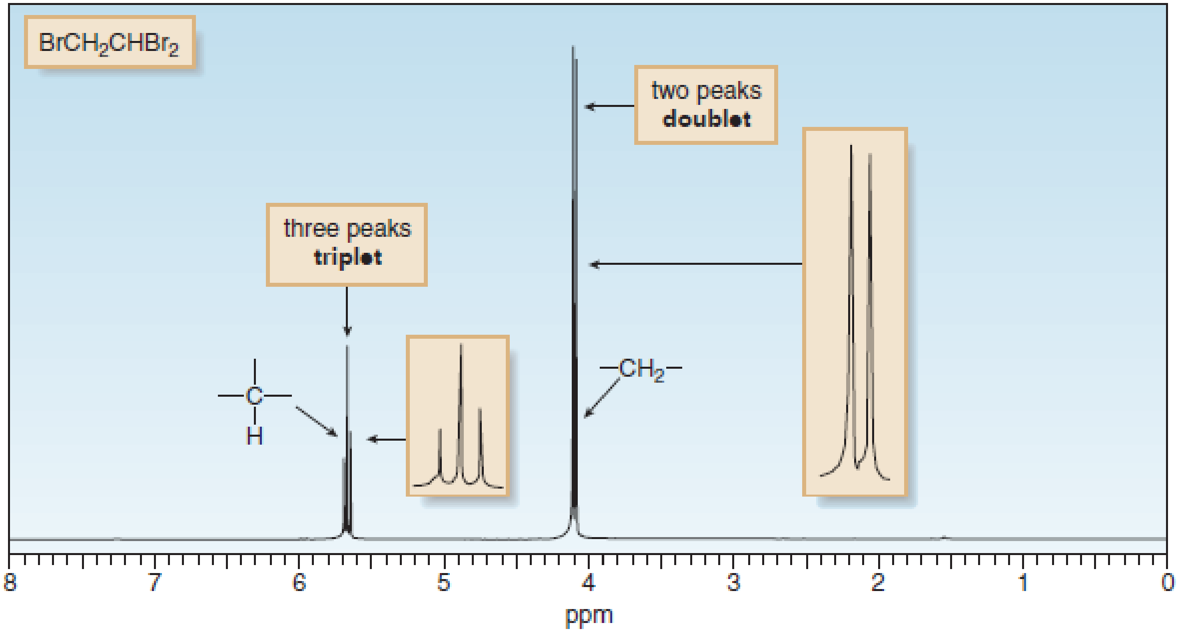
Signal [B]: $\frac{23}{11} = 2.1 \approx$ **2 H**

Signal [C]: $\frac{33}{11} =$ **3 H**

^{1}H NMR: Spin–Spin Splitting

The ^{1}H NMR spectra you have seen up to this point have been limited to one or more single absorptions called **singlets.** In the ^{1}H NMR spectrum of $BrCH_2CHBr_2$, however, the two signals for the two different kinds of protons are each split into more than one peak. The splitting patterns, the result of **spin–spin splitting,** can be used to determine how many protons reside on the carbon atoms near the absorbing proton.

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



- The CH_2 signal appears as **two peaks,** called a ***doublet.*** The relative area under the peaks of a doublet is 1:1.
- The CH signal appears as **three peaks,** called a ***triplet.*** The relative area under the peaks of a triplet is 1:2:1.

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

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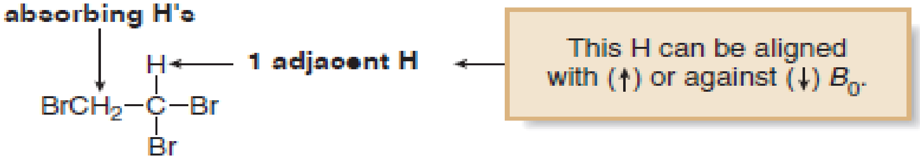
Splitting: How a Doublet Arises

First, let's examine how the doublet due to the CH_2 group in $BrCH_2CHBr_2$ arises. The CH_2 group contains the absorbing protons and the CH group contains the adjacent proton that causes the splitting.

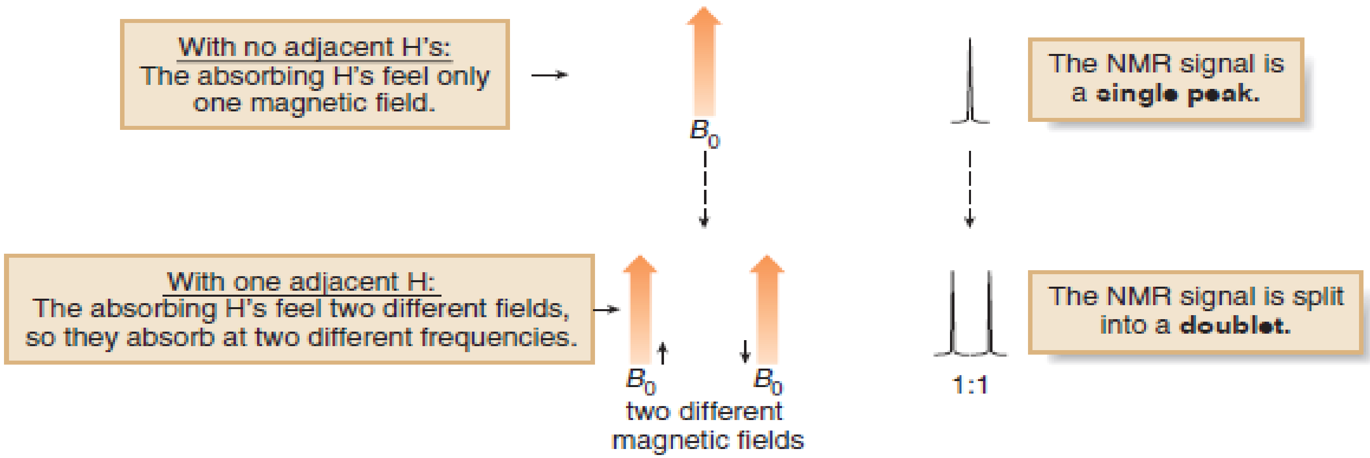


$BrCH_2-CHBr_2$

This H can be aligned with (↑) or against (↓) B_0.

When placed in an applied magnetic field (B_0), the adjacent proton ($CHBr_2$) can be aligned with (↑) or against (↓) B_0. As a result, the absorbing protons (CH_2Br) feel two slightly different magnetic fields—one slightly larger than B_0 and one slightly smaller than B_0. Because the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.

How a doublet arises



With no adjacent H's:
The absorbing H's feel only one magnetic field.

The NMR signal is a **single peak.**

With one adjacent H:
The absorbing H's feel two different fields, so they absorb at two different frequencies.

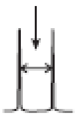
The NMR signal is split into a **doublet.**

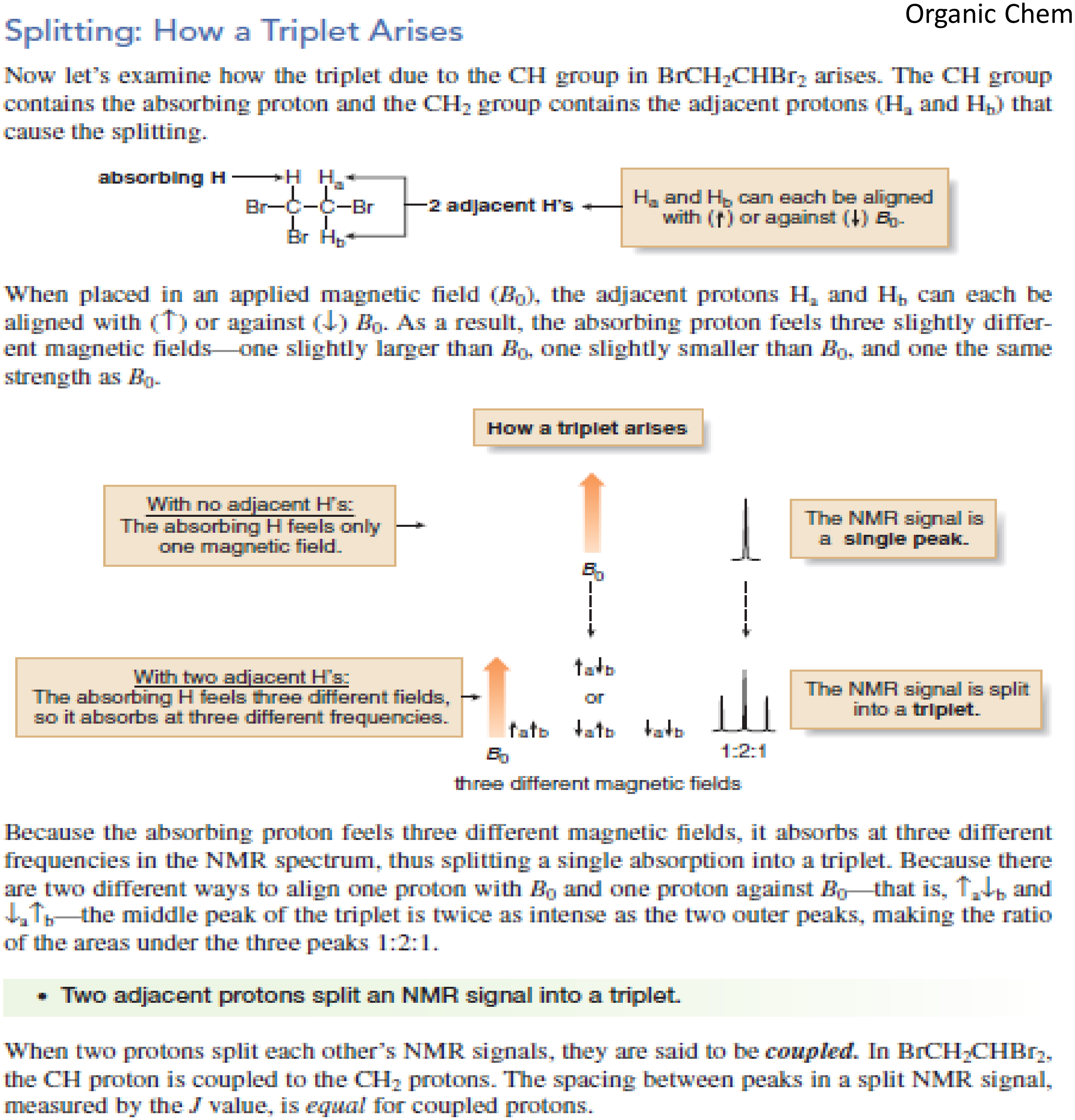
Keep in mind the difference between an **NMR signal** and an **NMR peak.** An NMR signal is the entire absorption due to a particular kind of proton. NMR peaks are contained within a signal. A doublet constitutes one signal that is split into two peaks.

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

The two peaks of a doublet are approximately equal in area. The area under both peaks—the entire NMR signal—is due to both protons of the CH_2 group of $BrCH_2CHBr_2$.

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





Splitting: How a Triplet Arises

Now let's examine how the triplet due to the CH group in $BrCH_2CHBr_2$ arises. The CH group contains the absorbing proton and the CH_2 group contains the adjacent protons (H_a and H_b) that cause the splitting.

H_a and H_b can each be aligned with (↑) or against (↓) B_0.

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. As a result, the absorbing proton feels three slightly different magnetic fields—one slightly larger than B_0, one slightly smaller than B_0, and one the same strength as B_0.

How a triplet arises

<u>With no adjacent H's:</u> The absorbing H feels only one magnetic field.

The NMR signal is a **single peak.**

<u>With two adjacent H's:</u> The absorbing H feels three different fields, so it absorbs at three different frequencies.

The NMR signal is split into a **triplet.**

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's NMR signals, they are said to be ***coupled.*** In $BrCH_2CHBr_2$, the CH proton is coupled to the CH_2 protons. The spacing between peaks in a split NMR signal, measured by the J value, is *equal* for coupled protons.

Splitting: The Rules and Examples

Three general rules describe the splitting patterns commonly seen in the ^{1}H NMR spectra of organic compounds.

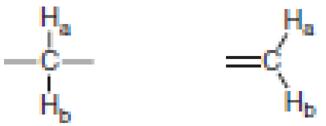
Rule [1] **Equivalent protons don't split each other's signals.**

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

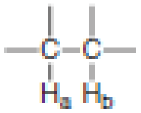
- In $BrCH_2CHBr_2$, for example, *one* adjacent CH proton splits an NMR signal into *two* peaks (a doublet), and *two* adjacent CH_2 protons split an NMR signal into *three* peaks (a triplet).
- The inside peaks of a split NMR signal are always most intense, with the area under the peaks decreasing from the inner to the outer peaks in a given splitting pattern.

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

If H_a and H_b are not equivalent, splitting is observed when:

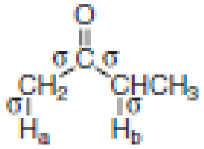


H_a and H_b are on the **same** carbon.



H_a and H_b are on **adjacent** carbons.

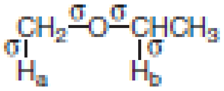
Splitting is not generally observed between protons separated by more than three σ bonds. Although H_a and H_b are not equivalent to each other in 2-butanone and ethyl methyl ether, H_a and H_b are separated by four σ bonds and so they are too far away to split each other's NMR signals.



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

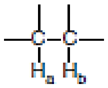
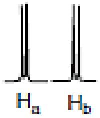
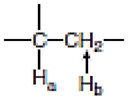
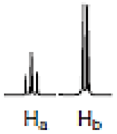
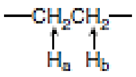
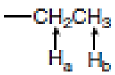
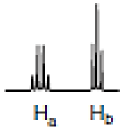
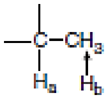
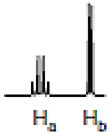
Names for a Given Number of Peaks in an NMR Signal

Number of peaks	Name	Number of peaks	Name
1	singlet	5	quintet
2	doublet	6	sextet
3	triplet	7	septet
4	quartet	> 7	multiplet

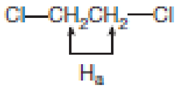
Predicting splitting is always a two-step process:

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

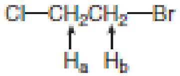
Several examples of spin–spin splitting in specific compounds illustrate the result of this two-step strategy.

Example	Pattern	Analysis (H_a and H_b are not equivalent.)
[1] 		H_a: one adjacent H_b proton ----→ two peaks ----→ **a doublet** H_b: one adjacent H_a proton ----→ two peaks ----→ **a doublet**
[2] 		H_a: two adjacent H_b protons ----→ three peaks ----→ **a triplet** H_b: one adjacent H_a proton ----→ two peaks ----→ **a doublet**
[3] 		H_a: two adjacent H_b protons ----→ three peaks ----→ **a triplet** H_b: two adjacent H_a protons ----→ three peaks ----→ **a triplet**
[4] 		H_a: three adjacent H_b protons ----→ four peaks ----→ **a quartet*** H_b: two adjacent H_a protons ----→ three peaks ----→ **a triplet**
[5] 		H_a: three adjacent H_b protons ----→ four peaks ----→ **a quartet*** H_b: one adjacent H_a proton ----→ two peaks ----→ **a doublet**

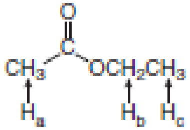
*The relative area under the peaks of a quartet is 1:3:3:1.


$Cl{-}CH_2CH_2{-}Cl$

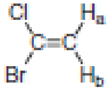
- All protons are equivalent (H$_a$), so there is no splitting and the NMR signal is one singlet.


$Cl{-}CH_2CH_2{-}Br$

- There are two NMR signals. H$_a$ and H$_b$ are nonequivalent protons bonded to adjacent C atoms, so they are close enough to split each other's NMR signals. The H$_a$ signal is split into a triplet by the two H$_b$ protons. The H$_b$ signal is split into a triplet by the two H$_a$ protons.

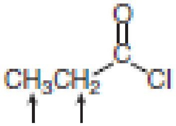


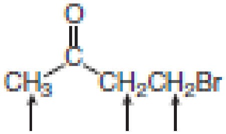
- There are three NMR signals. H$_a$ has no adjacent nonequivalent protons, so its signal is a singlet. The H$_b$ signal is split into a quartet by the three H$_c$ protons. The H$_c$ signal is split into a triplet by the two H$_b$ protons.

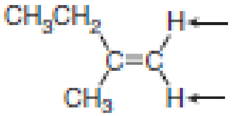


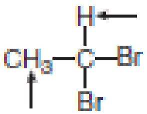
- There are two NMR signals. H$_a$ and H$_b$ are nonequivalent protons on the same carbon, so they are close enough to split each other's NMR signals. The H$_a$ signal is split into a doublet by H$_b$. The H$_b$ signal is split into a doublet by H$_a$.

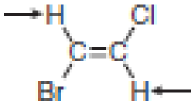
Into how many peaks will each indicated proton be split?

a.


c.


e.


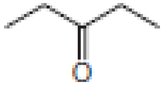
b.


d.


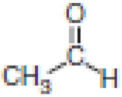
f.

$ClCH_2CH(OCH_3)_2$

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

a.


b.

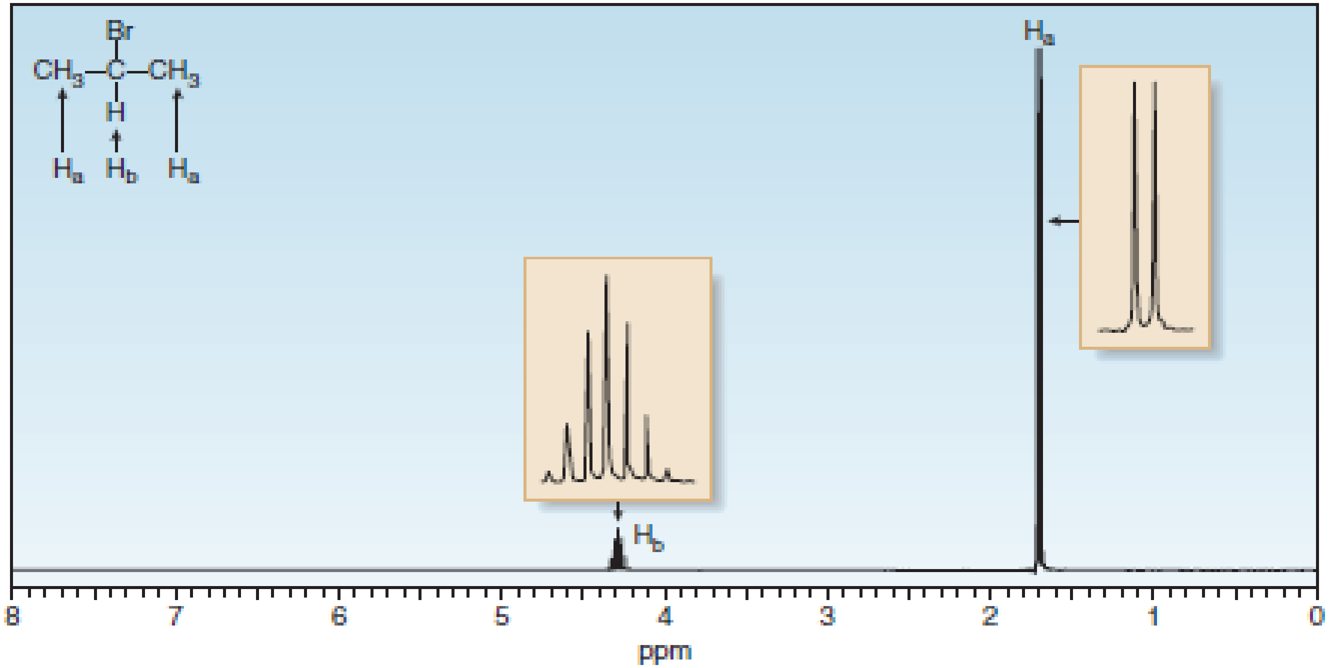

c.


d. $Cl_2CHCH_2CO_2CH_3$

Sketch the NMR spectrum of CH_3CH_2Cl, giving the approximate location of each NMR signal.

More Complex Examples of Splitting

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



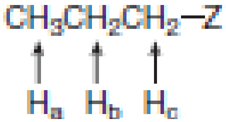
- The H_a protons have only one adjacent nonequivalent proton (H_b), so they are split into two peaks, a **doublet.**
- H_b has three H_a protons on each side. Because the six H_a protons are *equivalent to each other,* the ***n*** **+ 1** rule can be used to determine splitting: 6 + 1 = 7 peaks, a **septet.**

This is a specific example of a general rule:

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

A different outcome results when an absorbing proton is flanked by adjacent protons that are *not equivalent to each other.* Consider the splitting pattern expected for the H_b protons in the

^{1}H NMR spectrum of $CH_3CH_2CH_2Z$. H_b has protons on both adjacent carbons, but since H_a and H_c are *not equivalent to each other,* we cannot merely add them together and use the *n* + 1 rule.



$$\underset{H_a}{\underset{\uparrow}{CH_3}}\underset{H_b}{\underset{\uparrow}{CH_2}}\underset{H_c}{\underset{\uparrow}{CH_2}}-Z$$

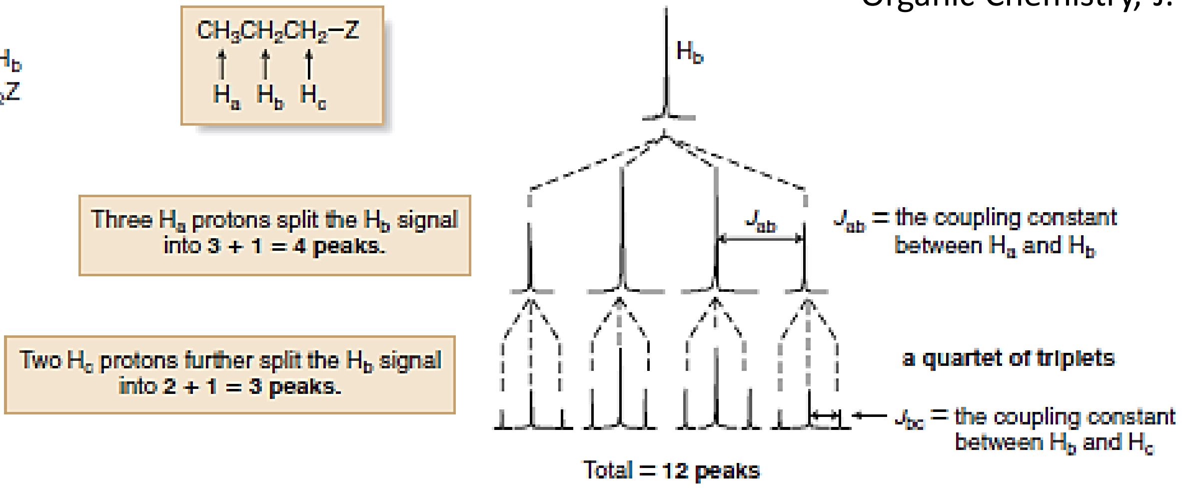
Instead, to determine the splitting of H_b, we must consider the effect of the H_a protons and the H_c protons *separately.* The three H_a protons split the H_b signal into four peaks, and the two H_c protons split each of these four peaks into three peaks—that is, the NMR signal due to H_b consists of $4 \times 3 = 12$ **peaks.**

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

It is only possible to see 12 peaks in an NMR spectrum when the coupling constants between each set of nonequivalent protons—that is, J_{ab} and J_{bc} in this example—are different; in other words, $J_{ab} \neq J_{bc}$.

In practice, with flexible alkyl chains it is more common for J_{ab} and J_{bc} to be very similar or identical. In this case, peaks overlap and many fewer than 12 peaks are observed.

A splitting diagram for the H_b protons in $CH_3CH_2CH_2Z$



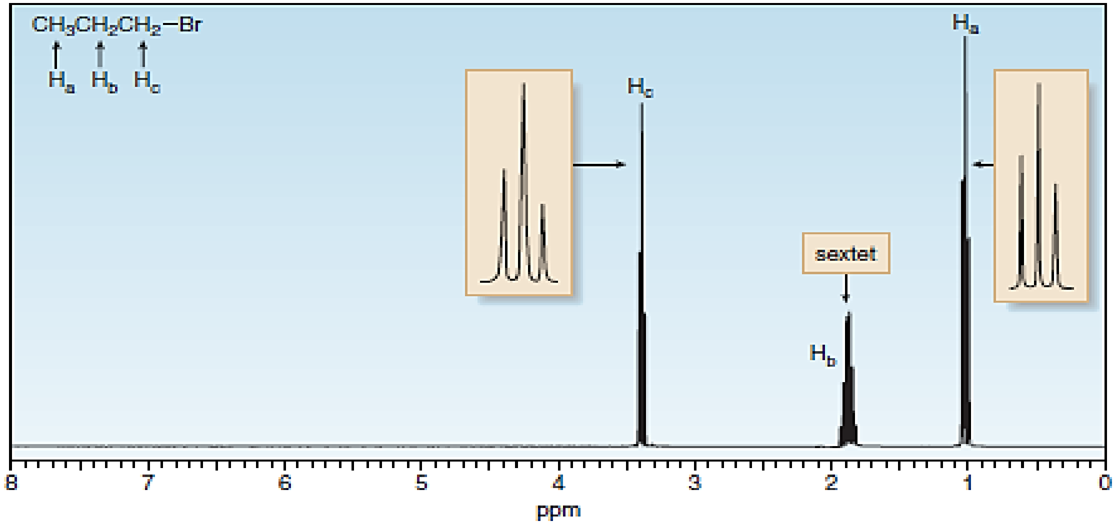
Three H_a protons split the H_b signal into 3 + 1 = **4 peaks.**

Two H_c protons further split the H_b signal into 2 + 1 = **3 peaks.**

Total = **12 peaks**

- 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.

The ^{1}H NMR spectrum of 1-bromopropane, $CH_3CH_2CH_2Br$

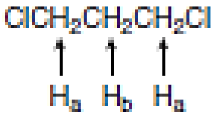


In $CH_3CH_2CH_2Br$, the *n* protons on one adjacent carbon and the *m* protons on the other adjacent carbon split the observed signal into *n* + *m* + 1 peaks. In other words, the 3 H_a protons and 2 H_c protons split the NMR signal into 3 + 2 + 1 = 6 peaks, How many peaks are present in the NMR signal of each indicated proton?

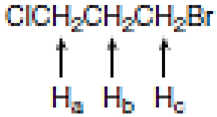
a. 
$ClCH_2CH_2CH_2Cl$

b. 
$ClCH_2CH_2CH_2Br$

Solution

a. 
$ClCH_2CH_2CH_2Cl$

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

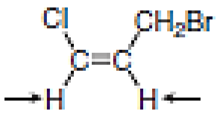
b. 
$ClCH_2CH_2CH_2Br$

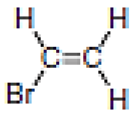
- H_b has two H_a protons on one adjacent C and two H_c protons on the other. Because H_a and H_c are not equivalent to each other, the maximum number of peaks for $H_b = (n + 1)(m + 1) = (2 + 1)(2 + 1) =$ **9 peaks.** However, since this molecule has a flexible alkyl chain, it is likely that J_{ab}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

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

a. 
$(CH_3)_2CHCO_2CH_3$

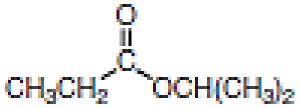
b. 
$CH_3CH_2CH_2CH_2CH_3$

c. 

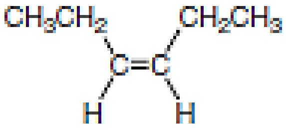
d. 
(all H atoms)

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

a. $CH_3OCH_2CH_3$

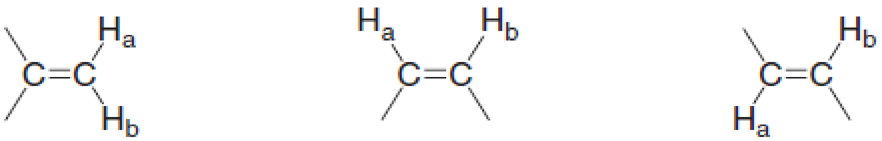
b. 

c. $CH_3OCH_2CH_2CH_2OCH_3$

d. 

Spin–Spin Splitting in Alkenes

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



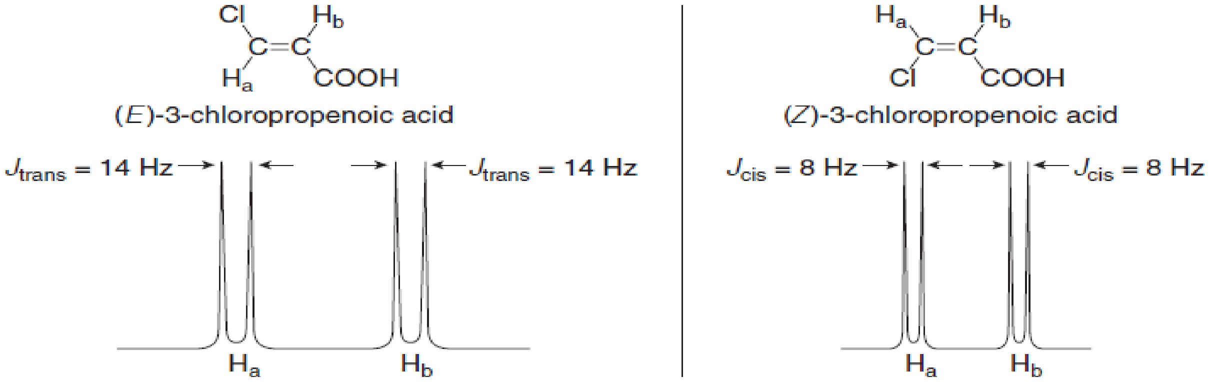
geminal H's | cis H's | trans H's

$J_{geminal}$ < J_{cis} < J_{trans}

0–3 Hz | 5–10 Hz | 11–18 Hz

characteristic coupling constants for three types of disubstituted alkenes

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



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

When a double bond is monosubstituted, there are three nonequivalent protons, and the pattern is more complicated because all three protons are coupled to each other. For example, vinyl acetate ($CH_2{=}CHOCOCH_3$) has four different types of protons, three of which are bonded to the double bond. Besides the singlet for the CH_3 group, each proton on the double bond is coupled to two other different protons on the double bond, giving the spectrum in Figure 14.10.

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

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

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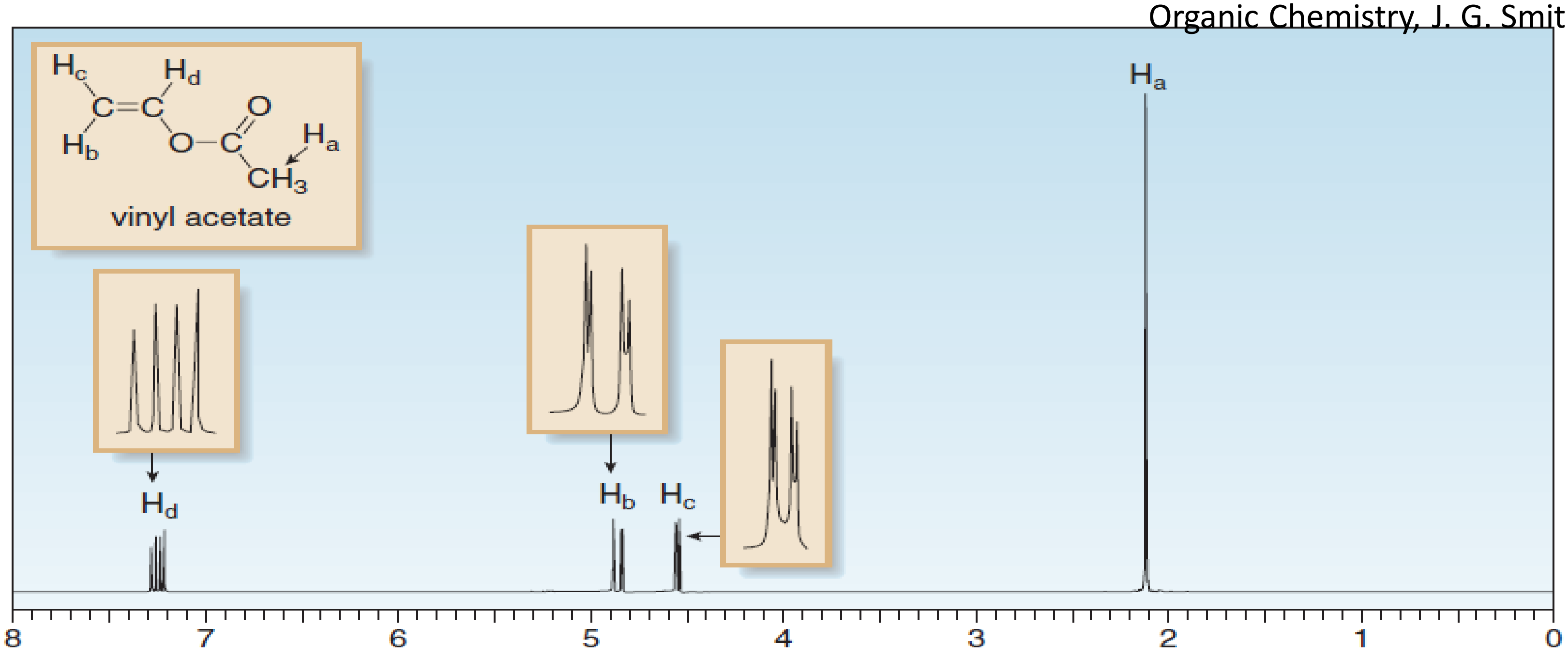
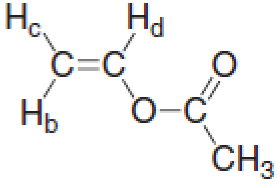
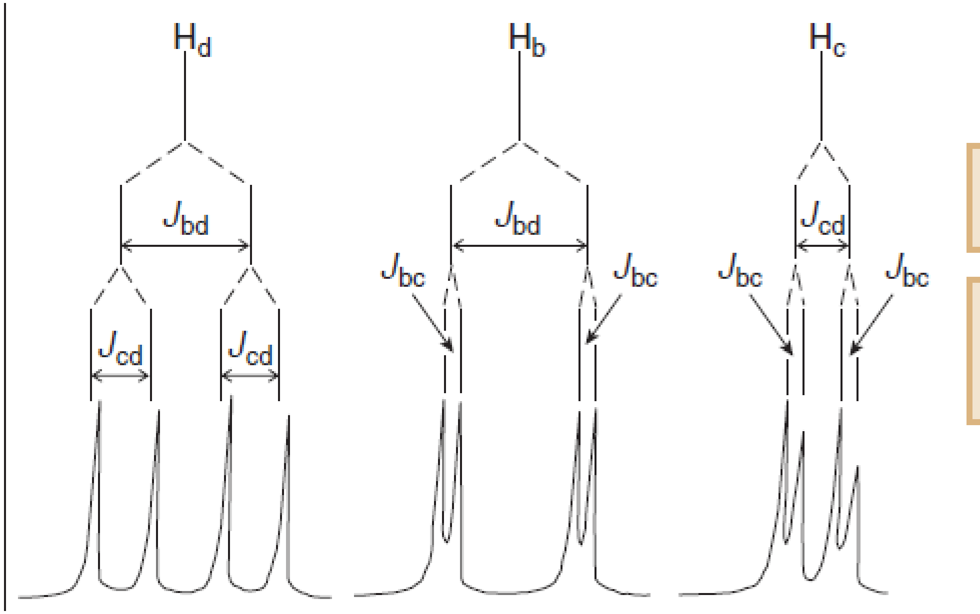




J_{bc} = 1.2 Hz (geminal)
J_{cd} = 6.5 Hz (cis)
J_{bd} = 14 Hz (trans)



doublet of doublets for H_d

doublet of doublets for H_b

doublet of doublets for H_c

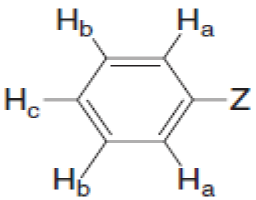
One nearby H splits the signal into a doublet.

The second nearby H splits the doublet into a doublet of doublets.

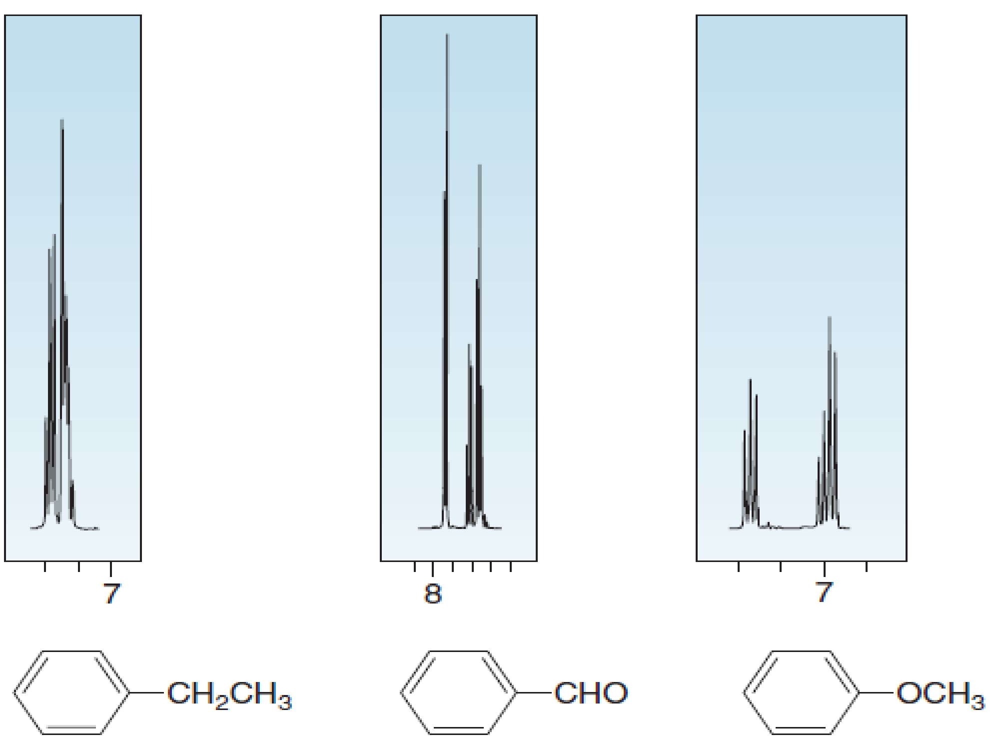
Protons on Benzene Rings

Benzene has six equivalent, deshielded protons and exhibits a single peak in its ^1H NMR spectrum at 7.27 ppm. Monosubstituted benzene derivatives—that is, benzene rings with one H atom replaced by another substituent Z—contain five deshielded protons that are no longer all equivalent to each other. The identity of Z determines the appearance of this region of a ^1H NMR spectrum (6.5–8 ppm), as shown in Figure 14.13. We will not analyze the splitting patterns observed for the ring protons of monosubstituted benzenes.

A benzene ring with one substituent Z

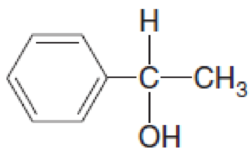


A monosubstituted benzene ring has three different types of H atoms: H_a, H_b, and H_c.

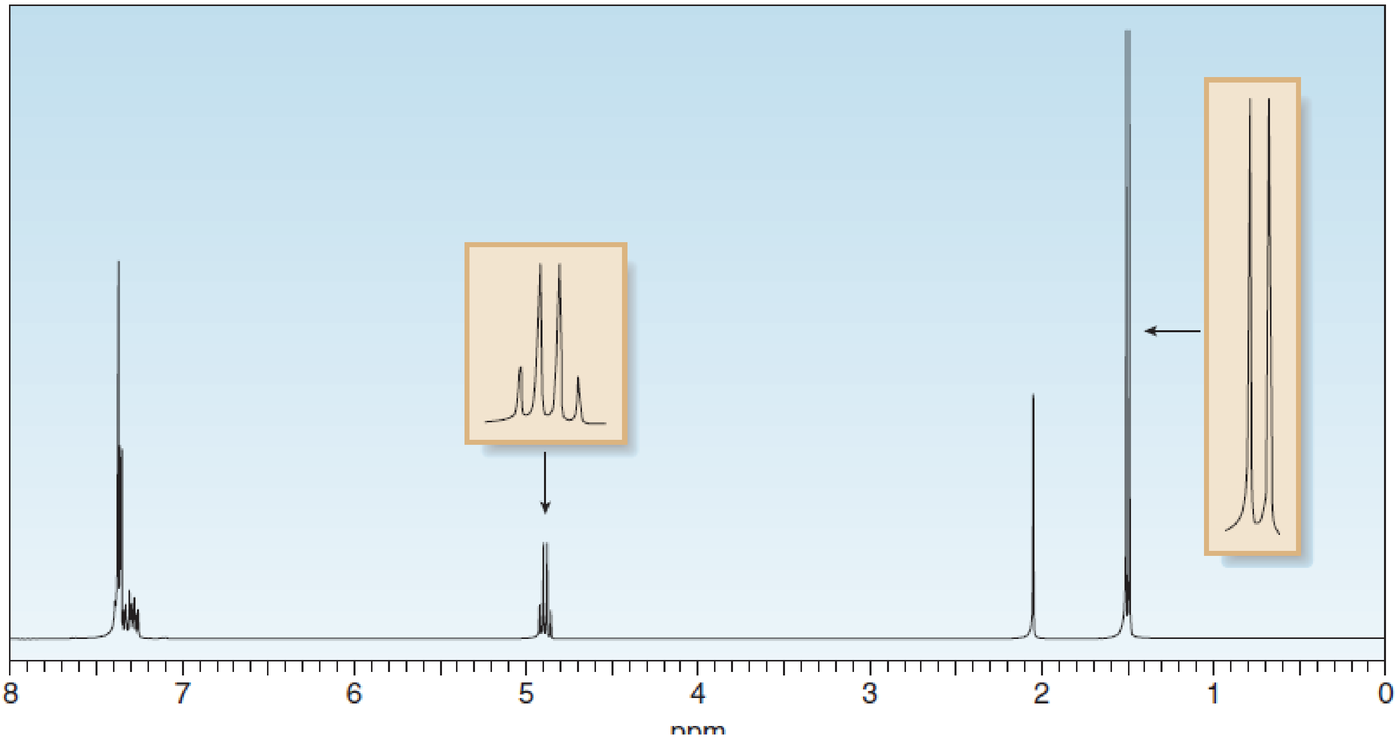


- The appearance of the signals in the 6.5–8 ppm region of the ^1H NMR spectrum depends on the identity of Z in C_6H_5Z.

Problem 14.23 What protons in alcohol **A** give rise to each signal in its ^{1}H NMR spectrum? Explain all splitting patterns observed for absorptions between 0–7 ppm.

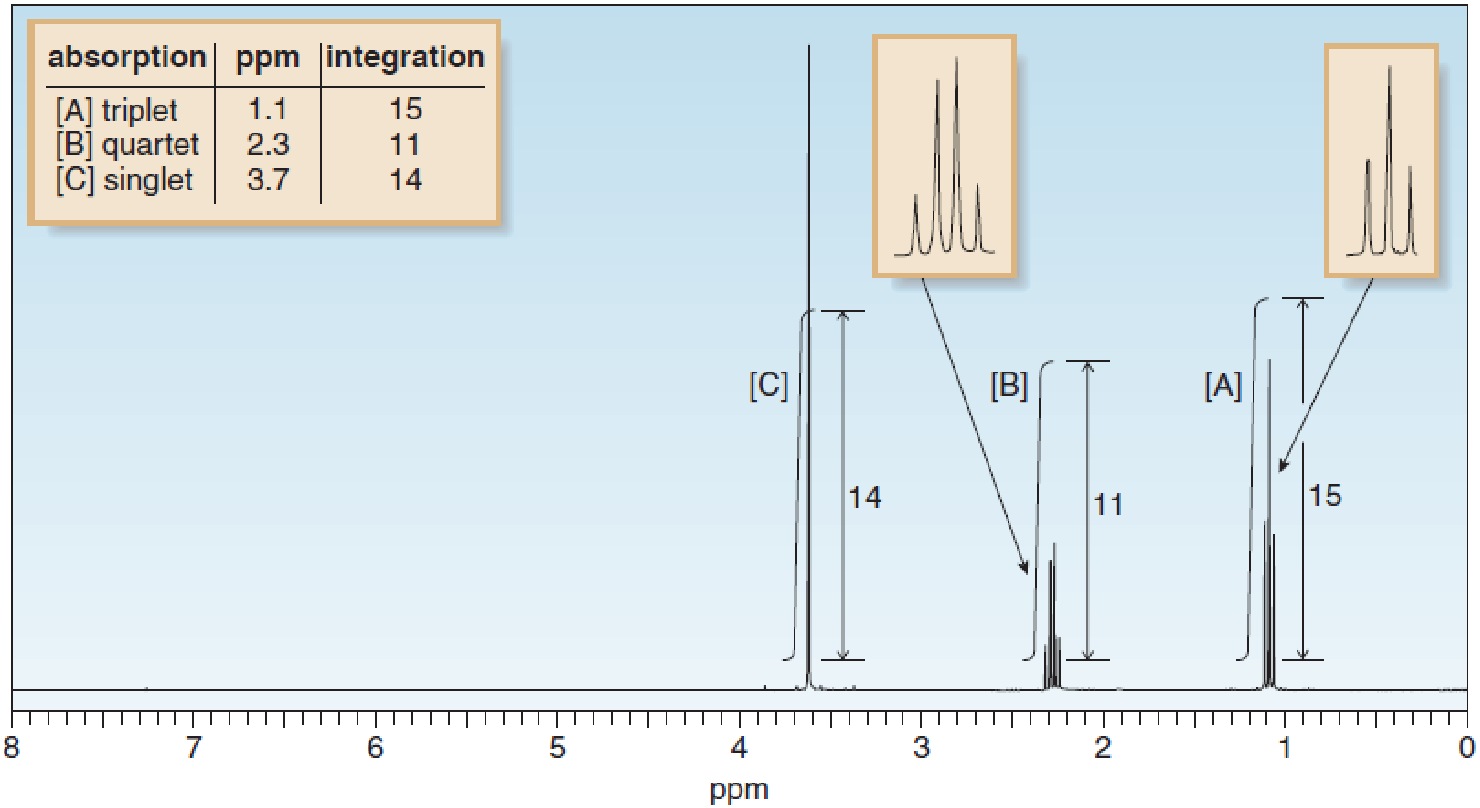


A



HOW TO Use ^1H NMR Data to Determine a Structure

Example Using its ^1H 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).

Step [2] Use the integration data to determine the number of H atoms giving rise to each signal (Section 14.5).

- Total number of integration units: 14 + 11 + 15 = 40 units
- Total number of protons = 8
- Divide: 40 units/8 protons = **5 units per proton**
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.

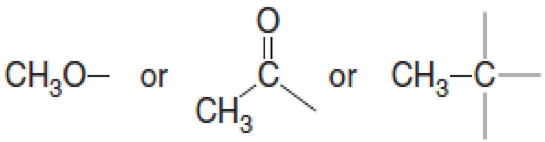
$\frac{15}{5} = 3\ H_a$ protons — signal [A] → Three equivalent H's usually means a **CH_3** group.

$\frac{11}{5} = 2.2 \approx 2\ H_b$ protons — signal [B] → Two equivalent H's usually means a **CH_2** group.

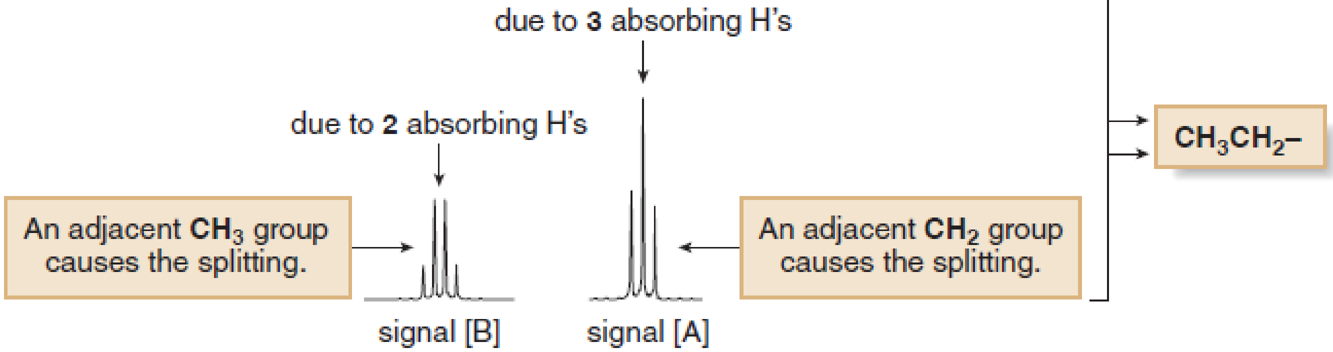
$\frac{14}{5} = 2.8 \approx 3\ H_c$ protons — signal [C] → Three equivalent H's usually means a **CH_3** group.

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

- Start with the singlets. Signal [C] is due to a CH_3 group with no adjacent nonequivalent H atoms. Possible structures include:



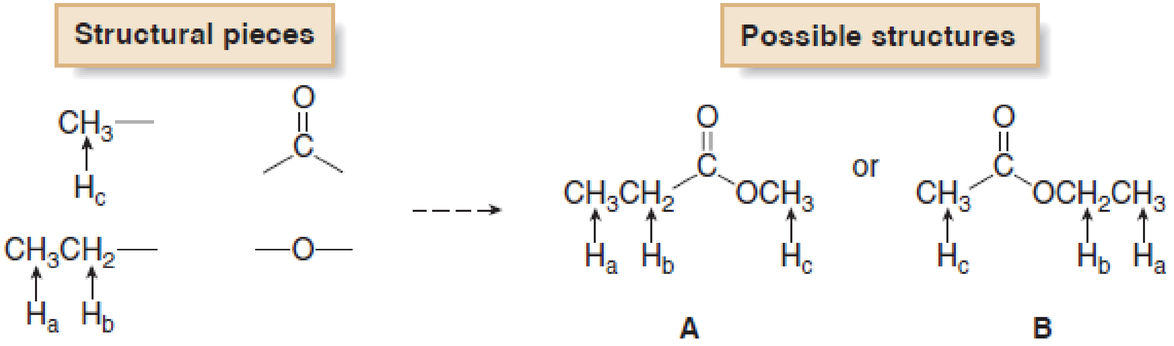
- Because signal [A] is a **triplet,** there must be **2 H's** (CH_2 group) on the adjacent carbon.
- Because signal [B] is a **quartet,** there must be **3 H's** (CH_3 group) on the adjacent carbon.
- This information suggests that **X** has an **ethyl** group ----→ CH_3CH_2-.



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:



- 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.**