NMR Spectroscopy

(Study Material)

Semester VI **17UCH630215**	**ORGANIC CHEMISTRY-II**	**Hours/Week: 5** **Credits : 4**

Corona – Covid ’19 Quarantine days Work from Home
Online material

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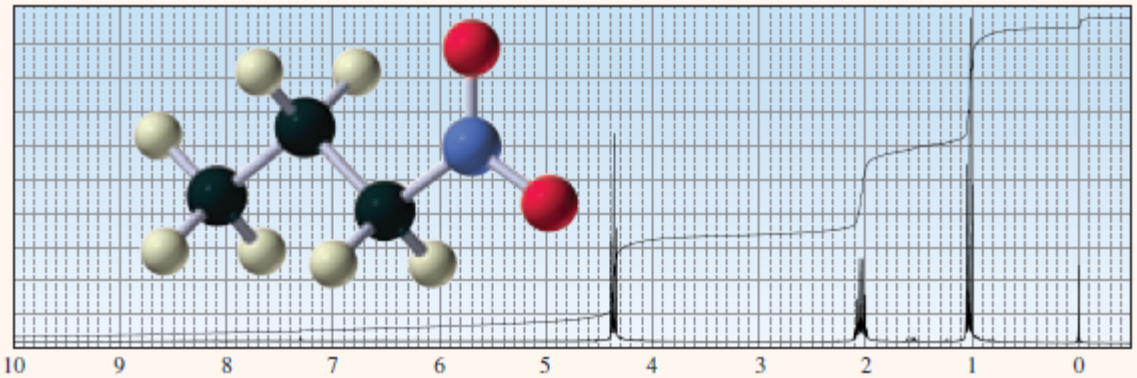
Unit IV: NMR and ESR Spectroscopy (15 Hours)

- NMR-principle, simple instrumentation
- Number of signals, Chemical shift, peak area and proton counting
- Spin-spin coupling and coupling constants,
- Deuteriated solvents
- Interpreting the NMR spectra of some organic
- molecules.
- ^{13}C NMR spectroscopy – types of carbon, splitting and chemical shift
- ESR spectroscopy: Principle and applications to methyl and naphthyl radicals.

Reference book: Paula Yurkanis Bruice, *Organic Chemistry*, (8th edition) University of California, Santa Barbara, Pearson Ltd, (2011).

Nuclear Magnetic Resonance Spectroscopy

- *Nuclear magnetic resonance (NMR) spectroscopy*, is an instrumental technique that chemists use to determine a compound's structure.
- **NMR spectroscopy** helps to identify the carbon–hydrogen framework of an organic compound.
- The power of NMR spectroscopy, compared with that of the other instrumental techniques, is that it not only makes it possible to identify the functionality at a specific carbon but also lets us determine what the neighboring carbons look like.
- In many cases, NMR spectroscopy can be used to determine the entire structure of a molecule.
- NMR spectroscopy was developed by physical chemists in the late 1940s to study the properties of atomic nuclei. In 1951, chemists realized that NMR spectroscopy could also be used to determine the structures of organic compounds.



1-Nitropropane

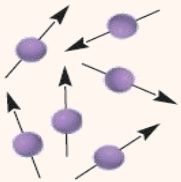
History

Edward Mills Purcell (1912–1997) *and* **Felix Bloch** *did the work on the magnetic properties of nuclei that made the development of NMR spectroscopy possible. They shared the 1952 Nobel Prize in physics. Purcell was born in Illinois. He received a Ph.D. from Harvard University in 1938 and immediately was hired as a faculty member in the physics department.*

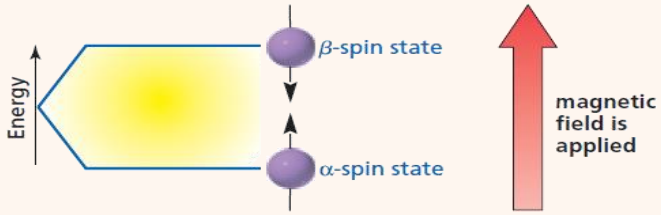
Felix Bloch (1905–1983) *was born in Switzerland. His first academic appointment was at the University of Leipzig. After leaving Germany upon Hitler's rise to power, Bloch worked at universities in Denmark, Holland, and Italy. He eventually came to the United States, becoming a citizen in 1939. He was a professor of physics at Stanford University and worked on the atomic bomb project at Los Alamos, New Mexico, during World War II.*

Principle of NMR Spectroscopy

- Certain nuclei also have allowed spin states of +½ and -1/2. This property allows them to be studied by NMR. Examples of such nuclei are ^{1}H, $1^{3}C$, ^{15}N, ^{19}F, ^{31}P.
- Because hydrogen nuclei (protons) were the first nuclei studied by nuclear magnetic resonance, the acronym "NMR" is generally assumed to mean (**proton ^{1}H NMR**
- Spinning charged nuclei generate a magnetic field, like the field of a small bar magnet. In the absence of an applied magnetic field, the nuclear spins are randomly oriented. However, when a sample is placed in an applied magnetic field, the nuclei twist and turn to align themselves *with* or *against* the field of the larger magnet.

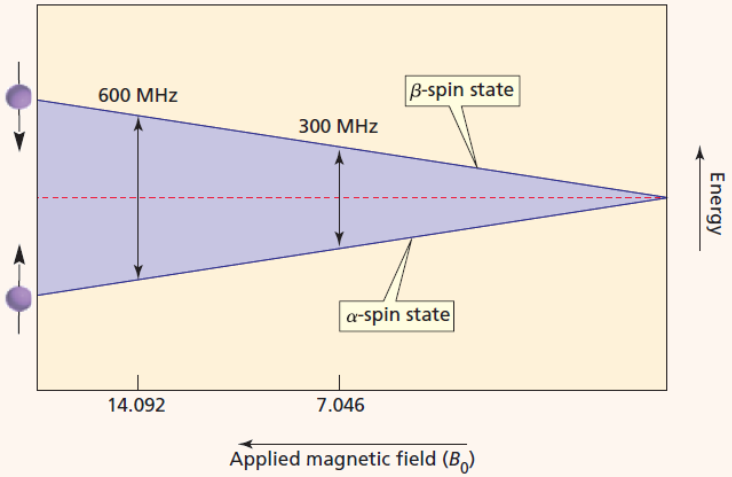


no applied magnetic field



- More energy is needed for a proton to align against the field than with it.
- Protons that align with the field are in the lower-energy **α-spin state** protons that align against the field are in the higher-energy **β-spin state.** More nuclei are in the **α-spin state** than in the **β-spin** state.
- The difference in the populations is very small (about 20 out of a million protons), but is sufficient to form the basis of NMR spectroscopy.

The energy difference between the and states depends on the strength of the ***applied magnetic field*** *The greater the strength of the magnetic field to which we expose the nucleus, the greater is the difference in energy between the and states.*



$$\Delta E = h\nu = h\frac{\gamma}{2\pi}B_0$$

Larmor equation

- When the sample is subjected to a pulse of radiation whose energy corresponds to the difference in energy between the α and β states, nuclei in the α state are promoted to the β state. This transition is called "flipping" the spin.
- Because the energy difference between the α and β states is so small—for currently available magnets—only a small amount of energy is needed to flip the spin.
- The radiation required is in the radiofrequency (rf) region of the electromagnetic spectrum and is called **rf radiation**. When the nuclei undergo relaxation (i.e., return to their original state), they emit electromagnetic signals whose frequency depends on the difference in energy between the α and β states.
- The NMR spectrometer detects these signals and displays them as a plot of signal frequency versus intensity—an NMR spectrum.
- It is because the nuclei are *in resonance* with the rf radiation that the term "nuclear magnetic resonance" came into being.
- In this context, "resonance" refers to the flipping back and forth of nuclei between the and states in response to the rf radiation.

Larmor equation

$$\Delta E = h\nu = h\frac{\gamma}{2\pi}B_0$$

The following calculation shows that if an ^{1}H NMR spectrometer is equipped with a magnet with a magnetic field $(B_0) = 7.046\,\text{T}$, the spectrometer will require an operating frequency of 300 MHz (megahertz):

$$\nu = \frac{\gamma}{2\pi}B_0$$

$$= \frac{2.675 \times 10^8}{2(3.1416)}\,\text{T}^{-1}\,\text{s}^{-1} \times 7.046\,\text{T}$$

$$= 300 \times 10^6\,\text{Hz} = 300\,\text{MHz}$$

The equation shows that the *magnetic field* (B_0) *is proportional to the operating frequency* (MHz). Therefore, if the spectrometer has a more powerful magnet, it must have a higher operating frequency. For example, a magnetic field of 14.092 T requires an operating frequency of 600 MHz.

PROBLEM 1◆

What frequency (in MHz) is required to cause a proton to flip its spin when it is exposed to a magnetic field of 1 tesla?

PROBLEM 2◆

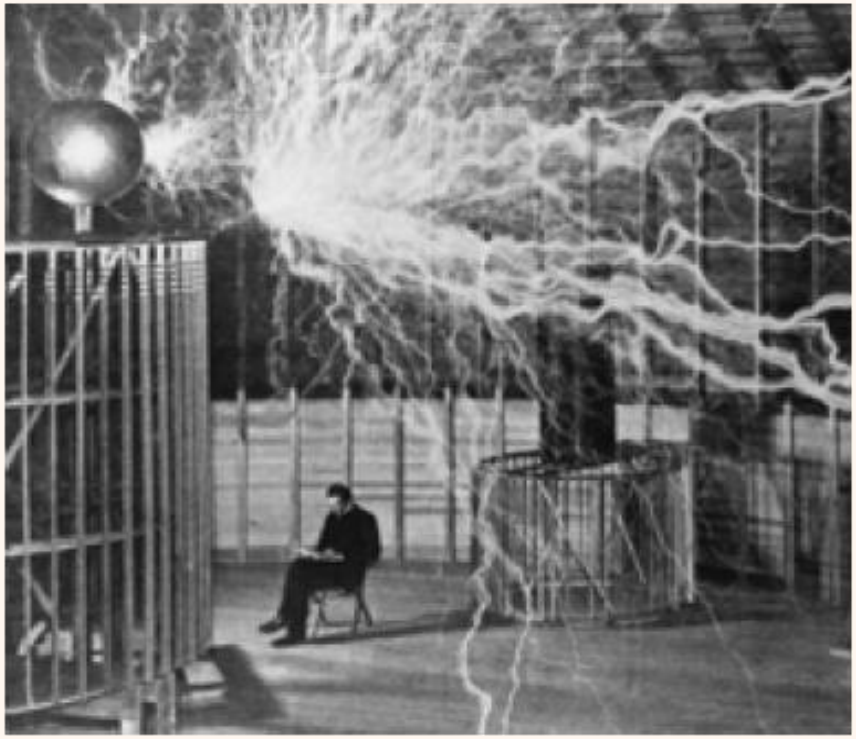
a. Calculate the magnetic field (in tesla) required to flip an ^{1}H nucleus in an NMR spectrometer that operates at 360 MHz.

b. What strength magnetic field is required when a 500-MHz instrument is used?

Nikola Tesla

NIKOLA TESLA (1856–1943)

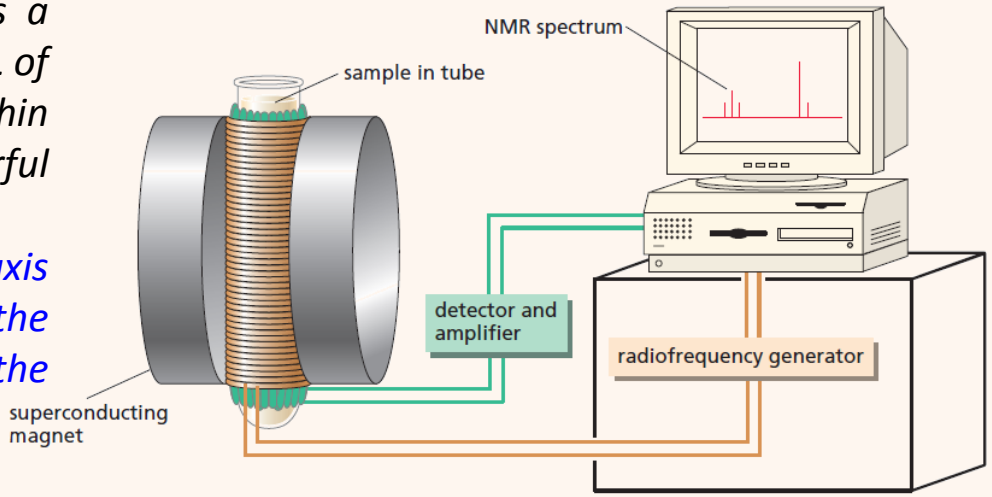
Nikola Tesla was born in Croatia, the son of a clergyman. He emigrated to the United States in 1884 and became a citizen in 1891. He was a proponent of alternating current and bitterly fought Edison, who promoted direct current. Although Tesla did not win his dispute with Marconi over which of them invented the radio, Tesla is given credit for developing neon and fluorescent lighting, the electron microscope, the refrigerator motor, and the Tesla coil, a type of transformer.



Nikola Tesla in his laboratory

NMR INSTRUMENTATION

- *To obtain an NMR spectrum, one dissolves a small amount of a compound in about 0.5 mL of solvent and puts the solution into a long, thin glass tube, which is placed within a powerful magnetic field.*
- *Spinning the sample tube about its long axis averages the position of the molecules in the magnetic field and thus greatly increases the resolution of the spectrum.*



- *In modern instruments called pulsed Fourier transform (FT) spectrometers, the magnetic field is kept constant and an rf pulse of short duration excites all the protons simultaneously. Because the short rf pulse covers a range of frequencies, the individual protons absorb the frequency required to come into resonance (flip their spin).*

- *As the protons relax (i.e., as they return to equilibrium), they produce a complex signal—called a free induction decay (FID)—at a frequency corresponding to The intensity of the signal decays as the nuclei lose the energy they gained from the rf pulse.*

- *A computer collects and then converts the intensity-versus-time data into intensity-versus-frequency information in a mathematical operation known as a Fourier transform, producing a spectrum called a* ***Fourier transform NMR (FT–NMR) spectrum****.*

Richard R Ernst

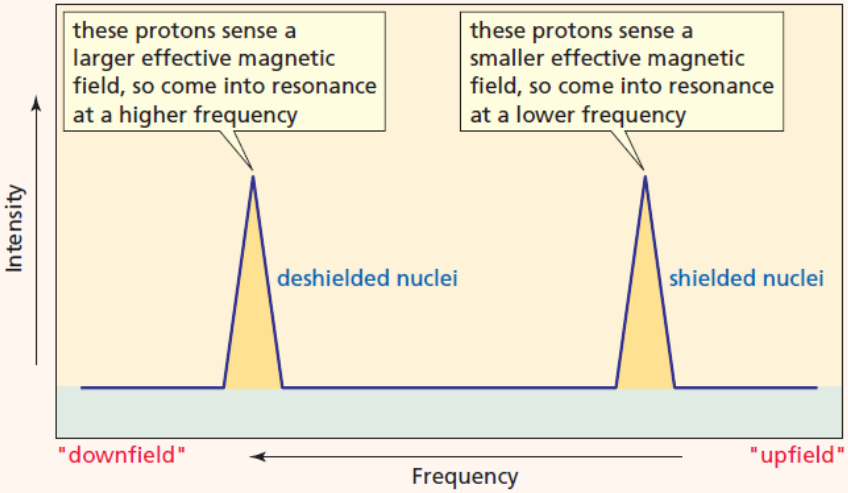
The 1991 Nobel Prize in chemistry was awarded to **Richard R. Ernst** *for two important contributions: FT–NMR spectroscopy and an NMR tomography method that forms the basis of magnetic resonance imaging (MRI). Ernst was born in 1933, received a Ph.D. from the Swiss Federal Institute of Technology [Eidgenössische Technische Hochschule (ETH)] in Zurich, and became a research scientist at Varian Associates in Palo Alto, California. In 1968, he returned to the ETH, where he is a professor of chemistry.*

Shielding

*In a magnetic field, the electrons circulate about the nuclei and induce a local magnetic field that opposes (i.e., that subtracts from) the applied magnetic field. The **effective magnetic field**, therefore, is what the nuclei "sense" through the surrounding electronic environment:*

$$B_{effective} = B_{applied} - B_{local}$$

- *Greater the electron density of the environment in which the proton is located, the greater is B_{local} and the more the proton is shielded from the applied magnetic field. This type of shielding is called **diamagnetic shielding**. Thus, protons in electron-dense environments sense a smaller effective magnetic field. They, therefore, will require a lower frequency to come into resonance.*
- *Protons in electron-poor environments sense a larger effective magnetic field and, therefore, will require a higher frequency to come into resonance., because ΔE is larger.*

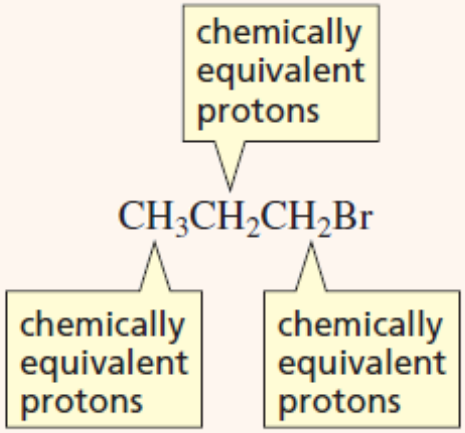


Shielded nuclei come into resonance at lower frequencies than deshielded nuclei.

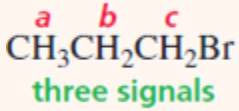
Protons in electron-rich environments are more shielded and appear at lower frequencies—on the right-hand side of the spectrum. Protons in electron-poor environments are less shielded and appear at higher frequencies—on the left-hand side of the spectrum.

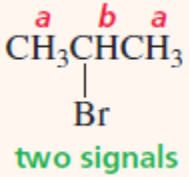
The Number of Signals in the ^{1}H NMR Spectrum

- Protons in the same environment are called **chemically equivalent protons**. For example, 1-bromopropane has three different sets of chemically equivalent protons.
- The three methyl protons are chemically equivalent because of rotation about the bond.
- The two methylene protons on the middle carbon are chemically equivalent, and the two methylene protons on the carbon bonded to the bromine atom make up the third set of chemically equivalent protons.

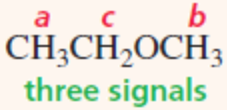


- Each set of chemically equivalent protons in a compound gives rise to a signal in the ^{1}H NMR spectrum of that compound. Because 1-bromopropane has three sets of chemically equivalent protons, it has three signals in its ^{1}H NMR spectrum.





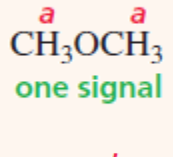
- 2-Bromopropane has two sets of chemically equivalent protons and, therefore, it has two signals in its NMR spectrum. The six methyl protons in 2-bromopropane are equivalent, so they give rise to only one signal.



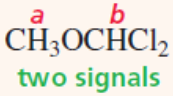
Ethyl methyl ether has three sets of chemically equivalent protons: the methyl protons on the carbon adjacent to the oxygen, the methylene protons on the carbon adjacent to the oxygen, and the methyl protons on the carbon that is one carbon removed from the oxygen.

The Number of Signals in the ^{1}H NMR Spectrum

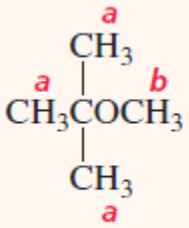
The chemically equivalent protons in the following compounds are designated by the same letter:



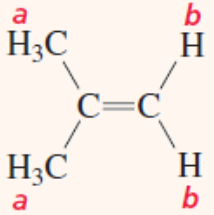
one signal



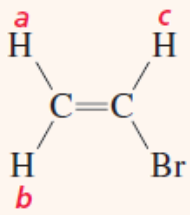
two signals



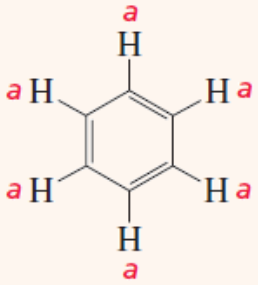
two signals



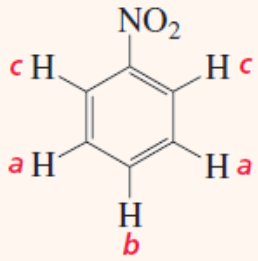
two signals



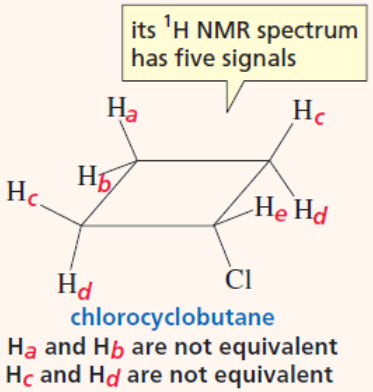
three signals



one signal



three signals



- Sometimes, two protons on the same carbon are not equivalent.
- For example, the ^{1}H NMR spectrum of chlorocyclobutane has five signals.
- Even though they are bonded to the same carbon, the H_a and H_b protons are not equivalent because they are not in the same environment: H_a is trans to Cl and H_b is cis to Cl.
- Similarly, the H_c and H_d protons are not equivalent.

PROBLEM 3◆

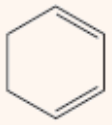
How many signals would you expect to see in the ^1H NMR spectrum of each of the following compounds?

a. $CH_3CH_2CH_2CH_3$

b. $BrCH_2CH_2Br$

c. $CH_2{=}CHCl$

d. $CH_2{=}CHCH{=}O$

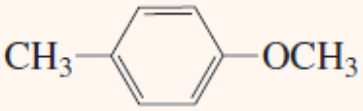
e. 

f. $CH_3CH_2CH_2CCH_3$ (O)

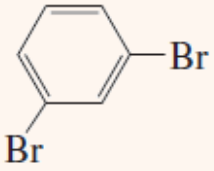
g. $CH_3CH_2CHCH_2CH_3$ (Cl)

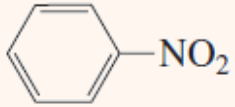
h. $CH_3CHCH_2CHCH_3$ (CH_3, CH_3)

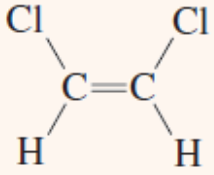
i. CH_3CH(Br)–C$_6$H$_5$

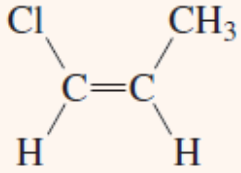
j. 

k. 

l. 

m. 

n. 

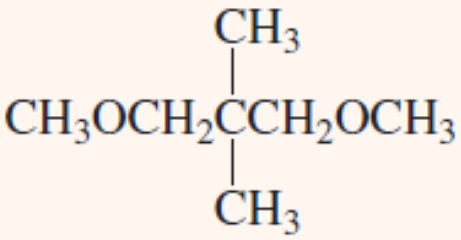
o. 

PROBLEM 4

How could you distinguish the ^{1}H NMR spectra of the following compounds?

a. $CH_3OCH_2OCH_3$

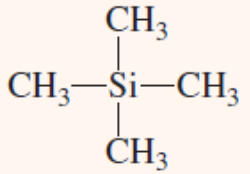
b. CH_3OCH_3

c. 

PROBLEM 5◆

There are three isomeric dichlorocyclopropanes. Their ^{1}H NMR spectra show one signal for isomer 1, two signals for isomer 2, and three signals for isomer 3. Draw the structures of isomers 1, 2, and 3.

The Chemical Shift



tetramethylsilane
TMS

- The position at which a signal occurs in an NMR spectrum is called the *chemical shift.*
- The **chemical shift** is a measure of how far the signal is from the reference TMS signal.
- The most common scale for chemical shifts is the δ (delta) scale.
- The TMS signal is used to define the zero position on this scale.
- The chemical shift is determined by measuring the distance from the TMS peak (in hertz) and dividing by the operating frequency of the instrument (in megahertz).
- Because the units are Hz/MHz, a chemical shift has units of parts per million (ppm) of the operating frequency:

$$\delta = \text{chemical shift (ppm)} = \frac{\text{distance downfield from TMS (Hz)}}{\text{operating frequency of the spectrometer (MHz)}}$$

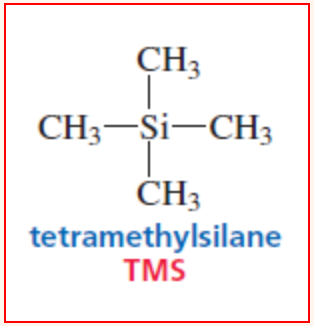
- Most proton chemical shifts fall in the range from 0 to 10 ppm.
- The advantage of the δ scale is that the chemical shift of a given nucleus is *independent of the operating frequency of the NMR spectrometer*.

protons in electron-poor environments	protons in electron-dense environments
deshielded protons	shielded protons
downfield	upfield
high frequency	low frequency
large δ values	small δ values

← δ
← frequency

Tetramethylsilane TMS – An internal standard

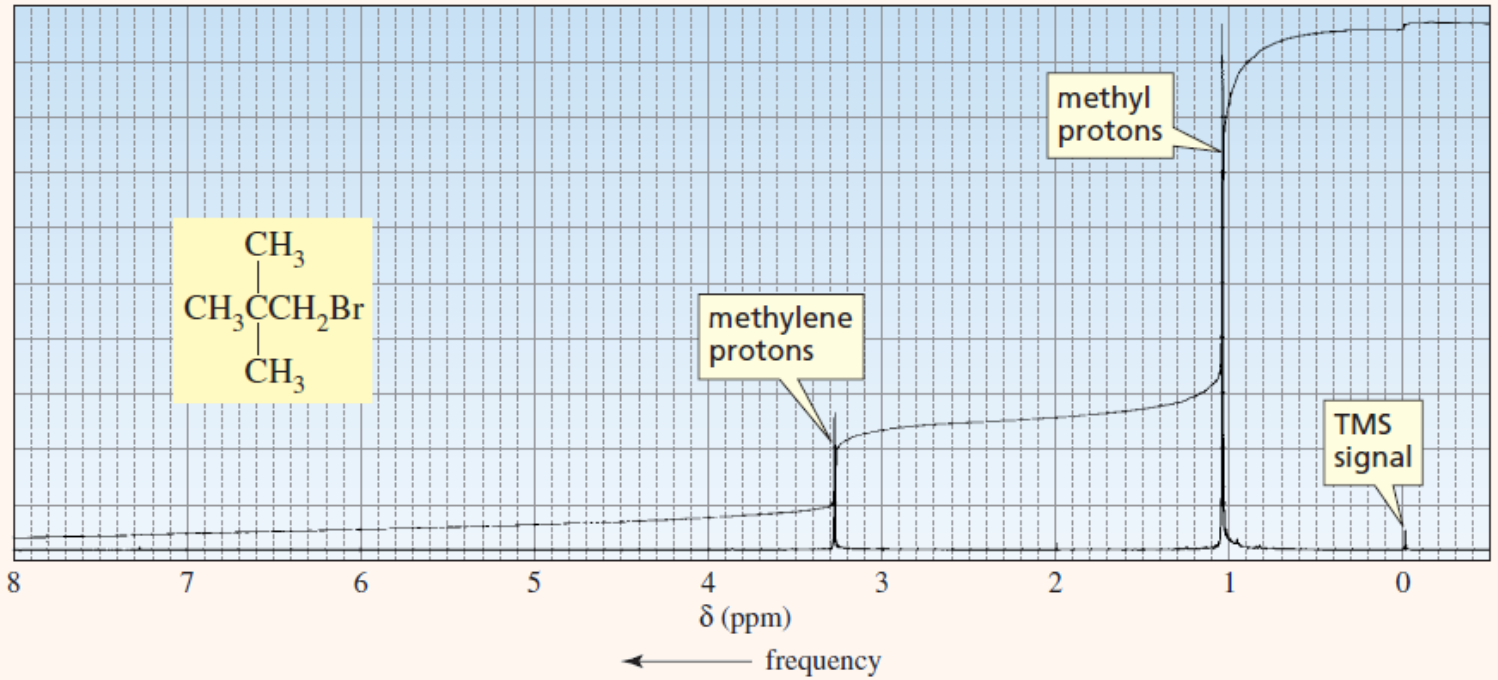
- A small amount of an inert **reference compound** is added to the sample tube containing the compound whose NMR spectrum is to be taken.
- The positions of the signals in an NMR spectrum are defined according to how far they are from the signal of the reference compound.



The most commonly used reference compound is **tetramethylsilane (TMS)**.

1. Because TMS is a highly volatile compound, it can easily be removed from the sample by evaporation after the NMR spectrum is taken.
2. The methyl protons of TMS are in a more electron-dense environment than are most protons in organic molecules, because silicon is less electronegative than carbon (electronegativities of 1.8 and 2.5, respectively).
3. Consequently, the signal for the methyl protons of TMS is at a lower frequency than most other signals (i.e., it appears to the right of the other signals).

The Relative Positions of ^{1}H NMR Signals

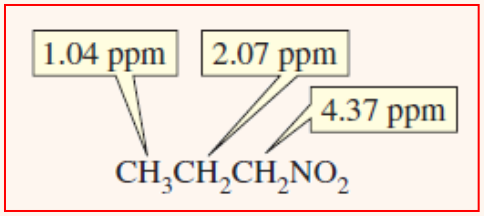


- 1H NMR spectrum of 1-bromo-2,2-dimethylpropane.
- The TMS signal is a reference signal from which chemical shifts are measured; it defines the zero position on the scale.

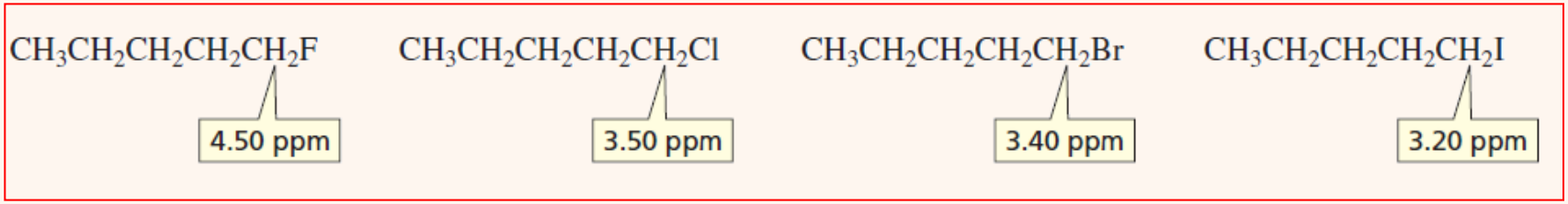
- *The ^{1}H NMR spectrum for 1-bromo-2,2-dimethylpropane shows that the chemical shift of the methyl protons is at δ 1.05 ppm and the chemical shift of the methylene protons is at δ 3.28 ppm. Notice that low-frequency (upfield, shielded) signals have small (ppm) δ values, whereas high-frequency (downfield, deshielded) signals have large δ values.*

The Relative Positions of ^{1}H NMR Signals

- The ^{1}H NMR spectrum of 1-nitropropane to have three signals because the compound has three different kinds of protons. The closer the protons are to the electron-withdrawing nitro group, the less they are shielded from the applied magnetic field, so the higher the frequency *(i.e.*, the farther downfield) at which their signals will appear. Thus, the protons closest to the nitro group show a signal at the highest frequency (4.37 ppm), and the ones farthest from the nitro group show a signal at the lowest frequency (1.04 ppm).



- The position of the signal depends on the electronegativity of the halogen—the more electronegative the halogen, the higher is the frequency of the signal. Thus, the signal for the methylene protons adjacent to fluorine (the most electronegative of the halogens) occurs at the highest frequency, whereas the signal for the methylene protons adjacent to iodine (the least electronegative of the halogens) occurs at the lowest frequency.



PROBLEM 6◆

A signal has been reported to occur at 600 Hz downfield from TMS in an NMR spectrometer with a 300-MHz operating frequency.

a. What is the chemical shift of the signal?
b. What would its chemical shift be in an instrument operating at 100 MHz?
c. How many hertz downfield from TMS would the signal be in a 100-MHz spectrometer?

PROBLEM 7◆

a. If two signals differ by 1.5 ppm in a 300-MHz spectrometer, by how much do they differ in a 100-MHz spectrometer?
b. If two signals differ by 90 hertz in a 300-MHz spectrometer, by how much do they differ in a 100-MHz spectrometer?

PROBLEM 8◆

Where would you expect to find the ^{1}H NMR signal of $(CH_3)_2Mg$ relative to the TMS signal? (*Hint:* See Table 12.3 on p. 467.)

PROBLEM 9◆

a. Which set of protons in each of the following compounds is the least shielded?

1. $CH_3CH_2CH_2Cl$

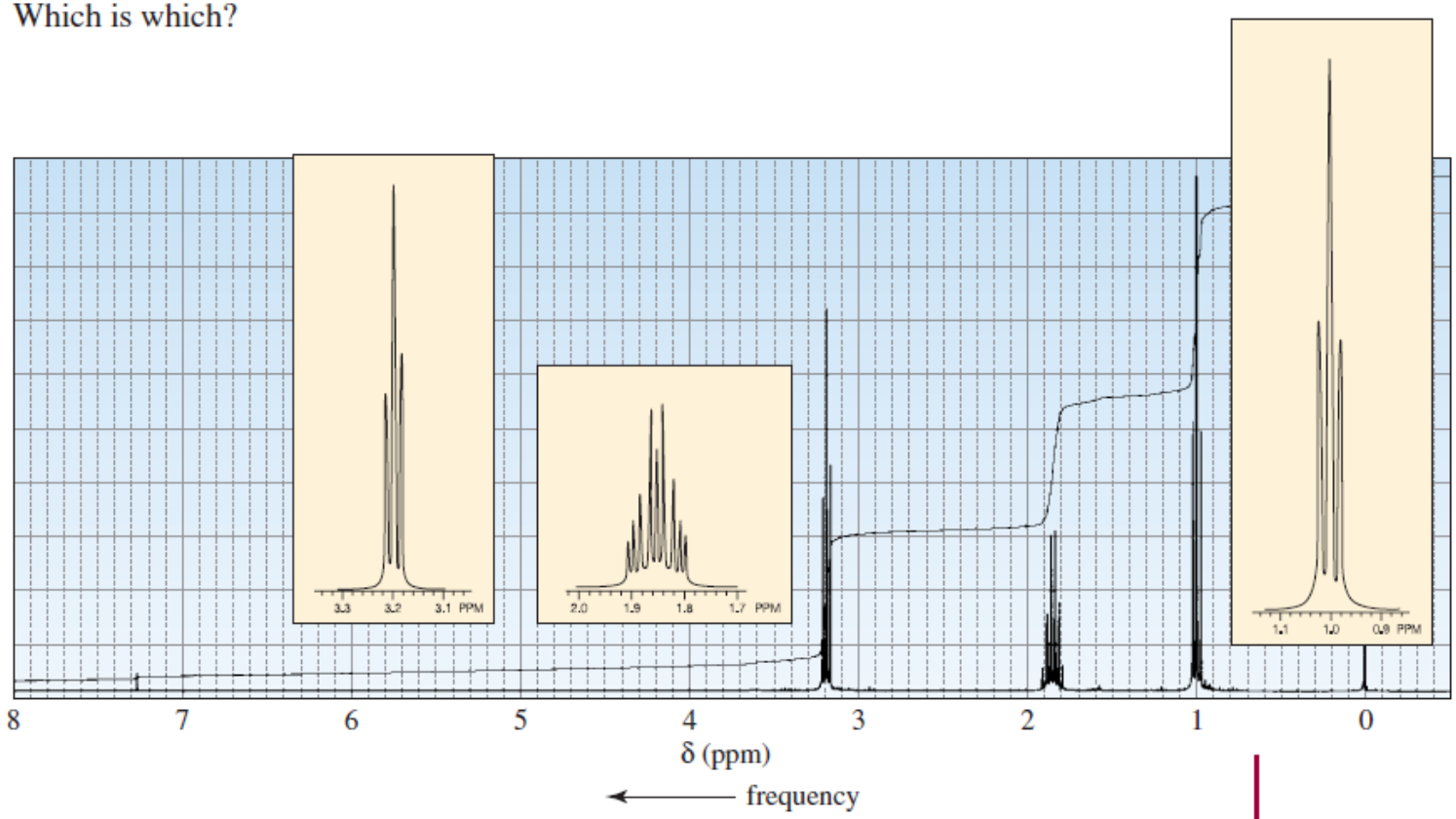
2. $CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_3$

3. $CH_3\underset{\underset{Br}{|}}{CH}\underset{\underset{Br}{|}}{CH}Br$

b. Which set of protons in each compound is the most shielded?

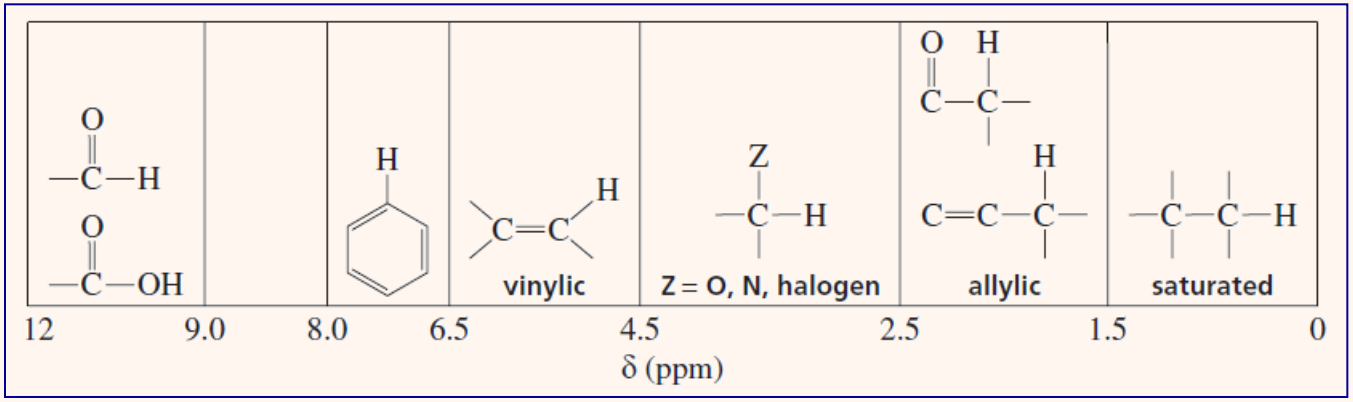
PROBLEM 10◆

One of the spectra in Figure 14.6 is due to 1-chloropropane, and the other to 1-iodopropane. Which is which?



Characteristic Values of Chemical Shifts

Approximate values of chemical shifts for different kinds of protons are shown in the Table. An NMR spectrum can be divided into six regions.



The chemical shift of methyl protons is at a lower frequency (0.9 ppm) than is the chemical shift of methylene protons (1.3 ppm) in a similar environment and that the chemical shift of methylene protons is at a lower frequency than is the chemical shift of a methine proton (1.4 ppm) in a similar environment.

PROBLEM 11◆

In each of the following compounds, which of the underlined protons has the greater chemical shift (i.e., the farther downfield signal or the higher frequency signal)?

a. $CH_3\underline{C}H(Br)\underline{C}HBrBr$

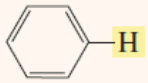
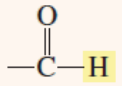
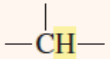
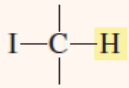
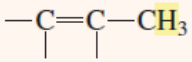
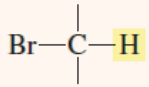
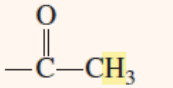
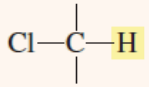
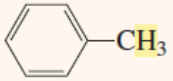
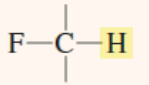
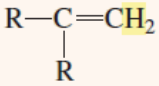
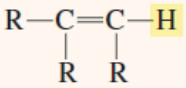
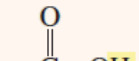
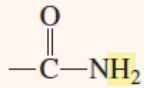
c. $CH_3\underline{C}H_2CH(Cl)\underline{C}H_3$

e. $CH_3\underline{C}H_2CH{=}\underline{C}H_2$

b. $CH_3\underline{C}H(OCH_3)\underline{C}H_3$

d. $CH_3\underline{C}H(\underline{C}H_3)C(=O)\underline{C}H_2CH_3$

Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0		6.5–8
$-CH_3$	0.9		
$-CH_2-$	1.3		9.0–10
	1.4		2.5–4
	1.7		2.5–4
	2.1		3–4
	2.3		4–4.5
$-C\equiv C-H$	2.4	RNH_2	Variable, 1.5–4
$R-O-CH_3$	3.3	ROH	Variable, 2–5
	4.7	ArOH	Variable, 4–7
	5.3		Variable, 10–12
			Variable, 5–8

[a]The values are approximate because they are affected by neighboring substituents.

PROBLEM 12◆

In each of the following pairs of compounds, which of the underlined protons has the greater chemical shift (i.e., the farther downfield signal or the higher frequency signal)?

a. $CH_3CH_2\underline{C}H_2Cl$ or $CH_3CH_2\underline{C}H_2Br$

b. $CH_3CH_2\underline{C}H_2Cl$ or $CH_3CH_2\underline{C}HCH_3$ (Cl)

c. $CH_3CH_2\underline{C}H(=O)$ or $CH_3CH_2C(=O)OCH_3$ (underlined CH_3)

PROBLEM 13

Without referring to Table 14.1, label the protons in the following compounds. The proton that gives the signal at the lowest frequency should be labeled *a*, the next *b*, etc.

a. $CH_3CH_2CH(=O)$

b. $CH_3CH_2CHCH_3$ (OCH_3)

c. $ClCH_2CH_2CH_2Cl$

d. $CH_3CH_2CH_2COCH_3$

e. $CH_3CH_2CHCH_2CH_3$ (OCH_3)

f. $CH_3CH_2CH_2OCHCH_3$ (CH_3)

g. $CH_3CH_2CH_2CCH_3$ (=O)

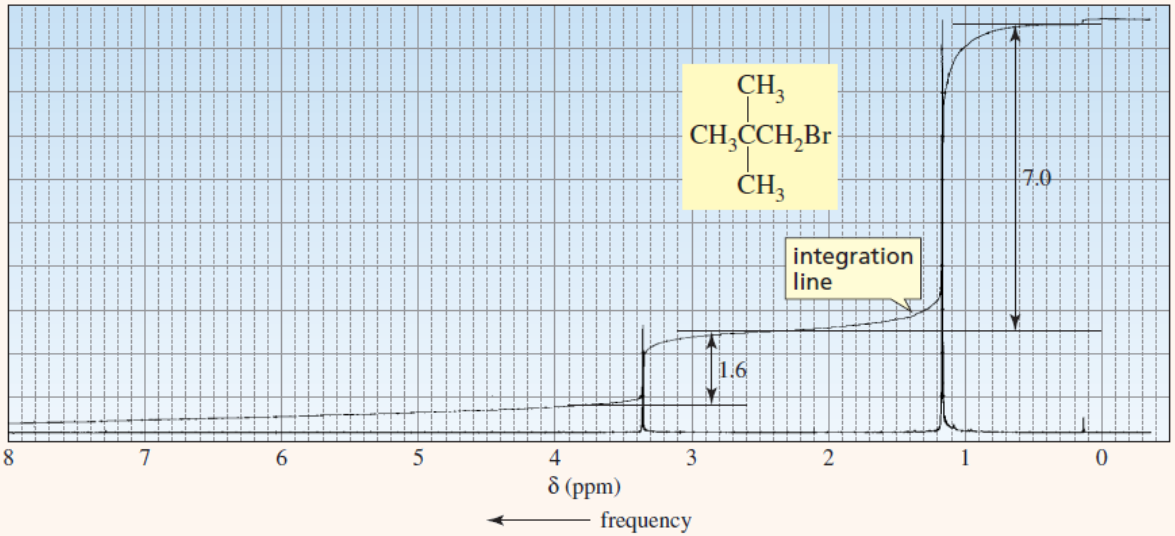
h. $CH_3CHCH_2OCH_3$ (CH_3)

i. $CH_3CHCHCH_3$ (CH_3, Cl)

Integration of NMR Signals

The **integration** tells us the *relative* number of protons that give rise to each signal, not the *absolute* number.

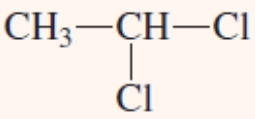
The two signals in the ^1H NMR spectrum of 1-bromo-2,2-dimethylpropane in the figure are not the same size because *the area under each signal is proportional to the number of protons that gives rise to the signal*.



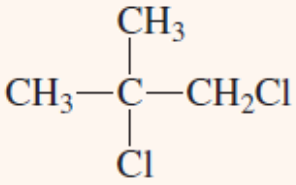
- The area under the signal occurring at the lower frequency is larger because the signal is caused by *nine* methyl protons, while the smaller, higher-frequency signal results from *two* methylene protons.
- The height of each integration step is proportional to the area under that signal, which, in turn, is proportional to the number of protons giving rise to the signal.

- By measuring the heights of the integration steps, the ratio of the integrals is approximately 1.6:7.0 = 1: 4.4.
- The ratios are multiplied by a number that will cause all the numbers to be close to whole numbers—in this case, we multiply by 2—as there can be only whole numbers of protons. That means that the ratio of protons in the compound is 2 : 8.8 which is rounded to 2 : 9.

The **integration** tells us the *relative* number of protons that give rise to each signal, not the *absolute* number. For example, integration could not distinguish between 1,1-dichloroethane and 1,2-dichloro-2-methylpropane because both compounds would show an integral ratio of 1 : 3.



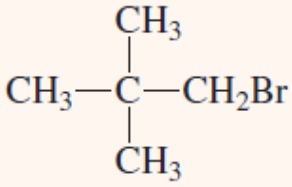
1,1-dichloroethane
ratio of protons = 1:3

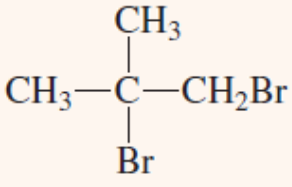


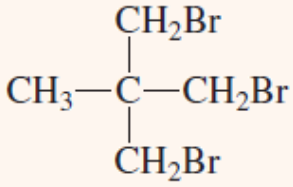
1,2-dichloro-2-methylpropane
ratio of protons 2:6 = 1:3

PROBLEM 14◆

How would integration distinguish the ^{1}H NMR spectra of the following compounds?







PROBLEM 15 SOLVED

a. Calculate the ratios of the different kinds of protons in a compound with an integral ratio of 6 : 4 : 18.4 (going from left to right across the spectrum).

b. Determine the structure of a compound that would give these relative integrals in the observed order.

SOLUTION

a. Divide each by the smallest number:

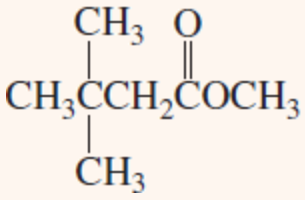
$$\frac{6}{4} = 1.5 \qquad \frac{4}{4} = 1 \qquad \frac{18.4}{4} = 4.6$$

Multiply by a number that will cause all the numbers to be close to whole numbers:

$$1.5 \times 2 = 3 \qquad 1 \times 2 = 2 \qquad 4.6 \times 2 = 9$$

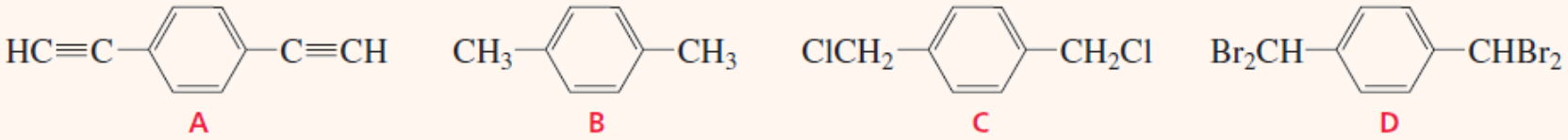
The ratio 3 : 2 : 9 gives the relative numbers of the different kinds of protons. The actual ratio could be 6 : 4 : 18, or even some higher multiple, but let's not go there if we don't have to.

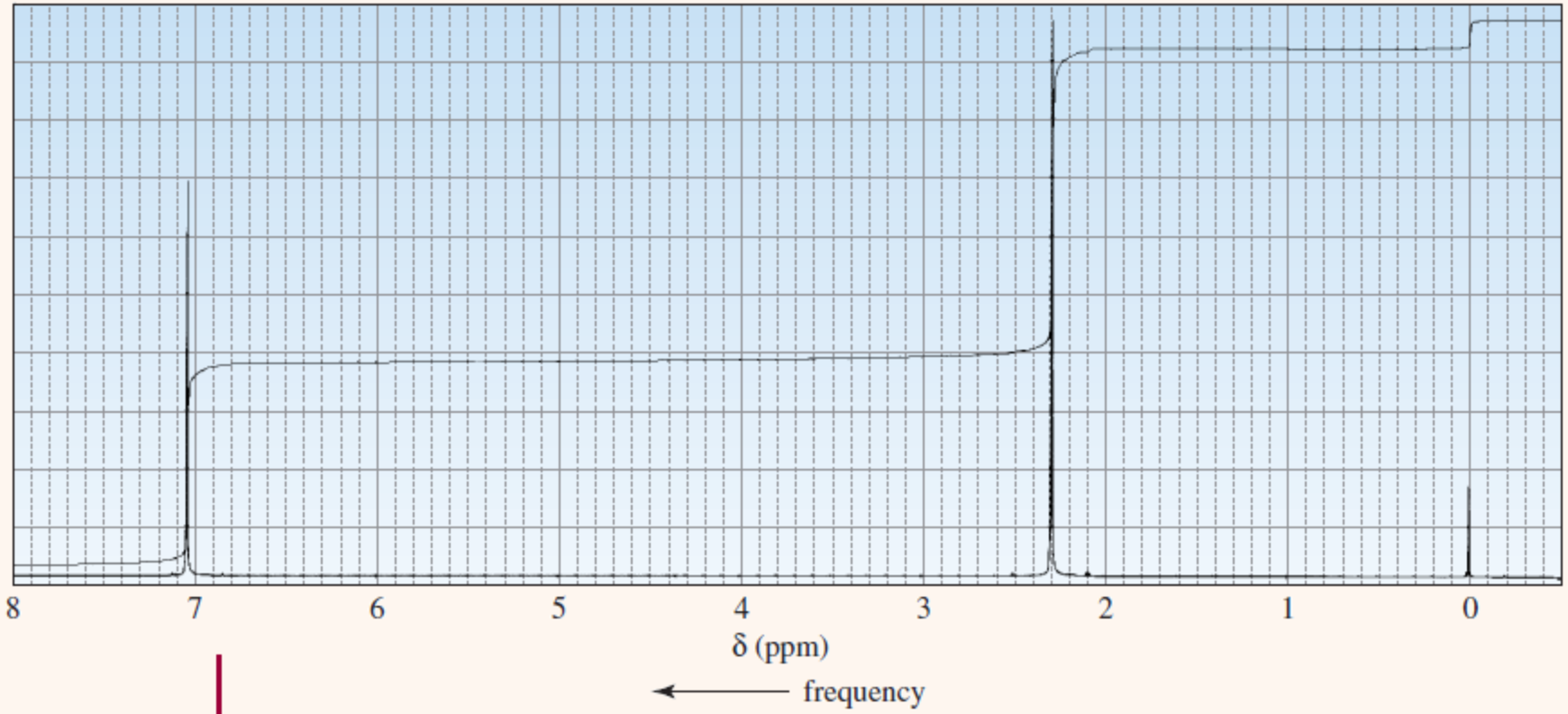
b. The "3" suggests a methyl, the "2" a methylene, and the "9" a *tert*-butyl. The methyl is closest to a group causing deshielding, and the *tert*-butyl group is farthest away from the group causing deshielding. The following compound meets these requirements:



PROBLEM 16◆

The ^{1}H NMR spectrum shown in Figure 14.8 corresponds to one of the following compounds. Which compound is responsible for this spectrum?

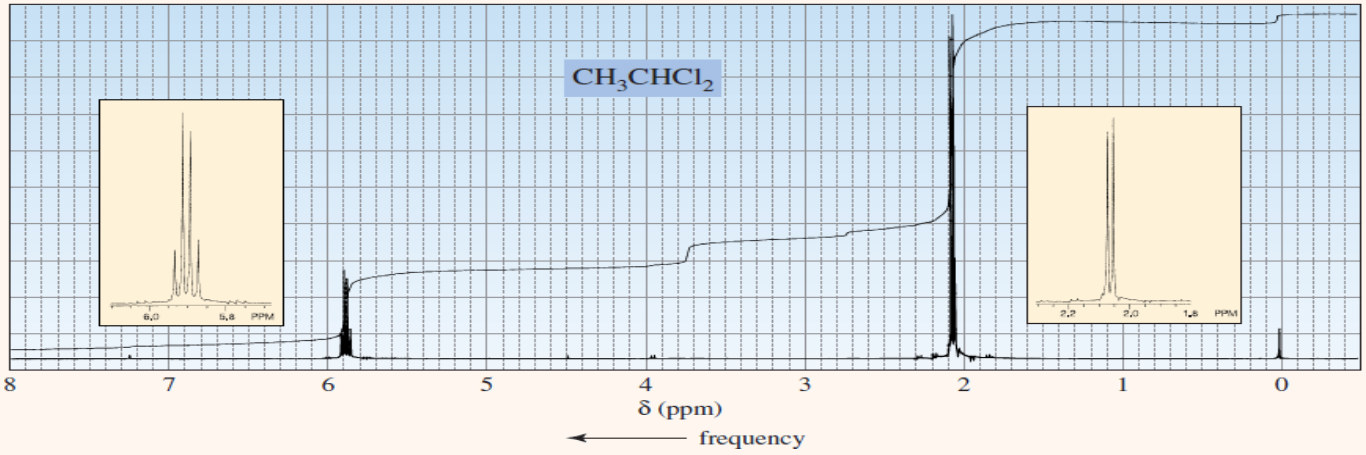




▲ **Figure 14.8**
^{1}H NMR spectrum for Problem 16.

Splitting of the Signals

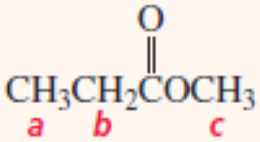
1. Splitting is caused by protons bonded to adjacent (i.e., directly attached) carbons.
2. The splitting of a signal is described by ***N* + 1 rule**, the where *N* is the number of *equivalent* protons bonded to *adjacent* carbons.
3. By "equivalent protons," we mean that the protons bonded to an adjacent carbon are equivalent to each other, but not equivalent to the proton giving rise to the signal.
4. The carbon adjacent to the methyl group in 1,1-dichloroethane is bonded to one proton, so the signal for the methyl protons is split into a doublet.
5. The carbon adjacent to the carbon bonded to the methine proton is bonded to three equivalent protons, so the signal for the methine proton is split into a quartet.
6. The number of peaks in a signal is called the **multiplicity** of the signal.
7. Splitting is always mutual: If the ***a*** protons split the ***b*** protons, then the ***b*** protons must split the ***a*** protons. The methine proton and the methyl protons are an example of *coupled protons*. **Coupled protons** split each other's signal.



^{1}H NMR spectrum of 1,1-dichloroethane.
The higher-frequency signal is an example of a quartet;
the lower-frequency signal is a doublet.

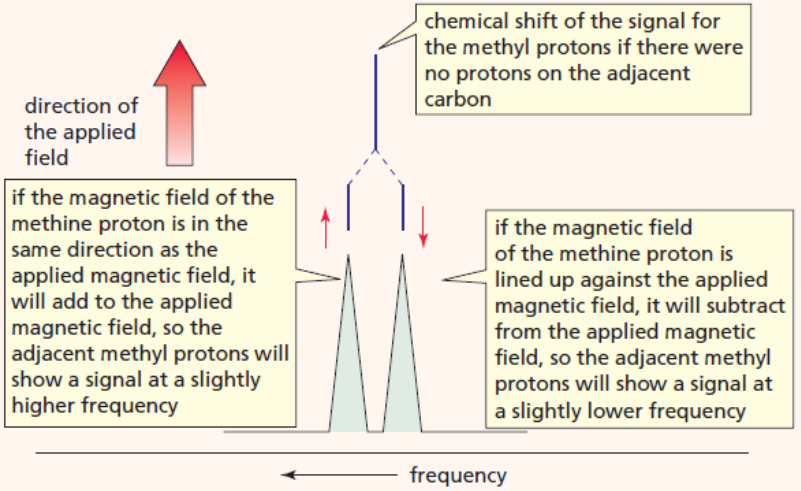
Splitting of the Signals

- *It is not the number of protons giving rise to a signal that determines the multiplicity of the signal; rather, it is the number of protons bonded to the immediately adjacent carbons that determines the multiplicity.*
- For example, the signal for the ***a*** protons in the following compound will be split into three peaks (a **triplet**) because the adjacent carbon is bonded to two hydrogens. The signal for the ***b*** protons will appear as a quartet because the adjacent carbon is bonded to three hydrogens, and the signal for the ***c*** protons will be a singlet.



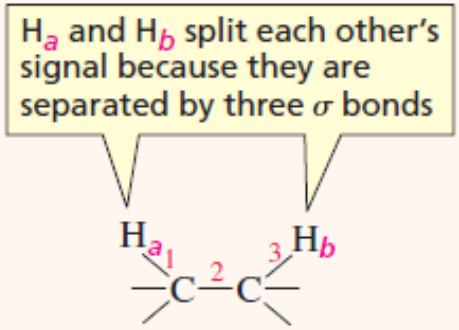
- The splitting of signals occurs when different kinds of protons are close enough for their magnetic fields to influence one another—called **spin–spin coupling**.
- For example, the frequency at which the methyl protons of 1,1-dichloroethane show a signal is influenced by the magnetic field of the methine proton.

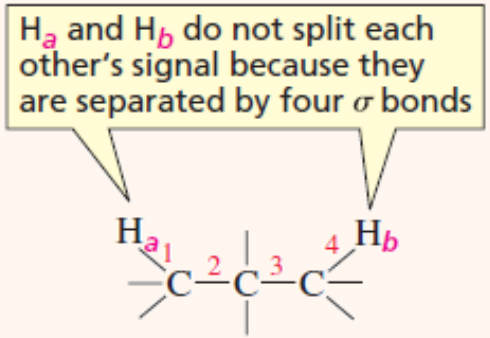
- Therefore, the signal for the methyl protons is split into two peaks, one at higher frequency and one at lower frequency.
- Because each spin state has almost the same population, about half the methine protons are lined up with the applied magnetic field and about half are lined up against it. Therefore, the two peaks of the *doublet* have approximately the same height and area.

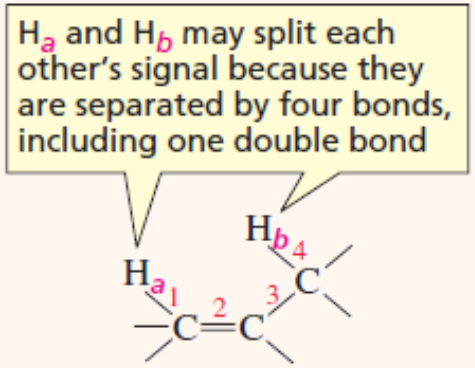


Long-range coupling

- A signal for a proton is never split by *equivalent* protons. Normally, *nonequivalent* protons split each other's signal only if they are on *adjacent* carbons.
- Splitting is a "through-bond" effect, not a "through-space" effect; it is rarely observed if the protons are separated by more than three **sigma** bonds.
- If, however, they are separated by more than three bonds and one of the bonds is a double or triple bond, a small splitting is sometimes observed. This is called **long-range coupling**.







Multiplicity of the Signal and Relative Intensities of the Peaks in the Signal

The relative intensities obey the mathematical mnemonic known as *Pascal's triangle*. According to Pascal, each number at the bottom of a triangle in the rightmost column of Table is the sum of the two numbers to its immediate left and right in the row above it.

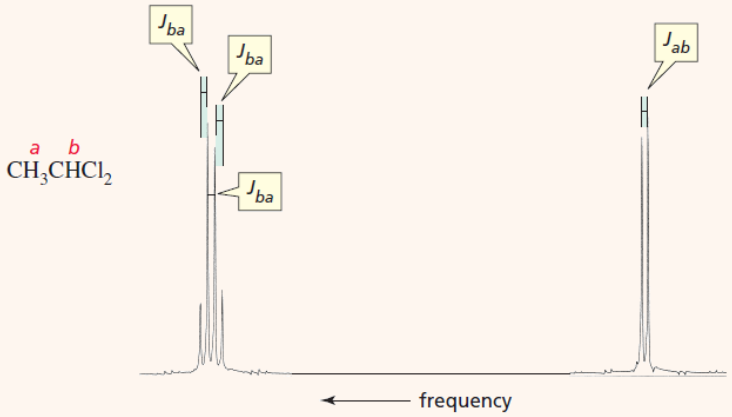
Number of equivalent protons causing splitting	Multiplicity of the signal	Relative peak intensities
0	singlet	1
1	doublet	1:1
2	triplet	1:2:1
3	quartet	1:3:3:1
4	quintet	1:4:6:4:1
5	sextet	1:5:10:10:5:1
6	septet	1:6:15:20:15:6:1

Blaise Pascal (1623–1662) *was born in France. At age 16, he published a book on geometry, and at 19, he invented a calculating machine. He propounded the modern theory of probability, developed the principle underlying the hydraulic press, and showed that atmospheric pressure decreases as altitude increases.*

In 1644, he narrowly escaped death when the horses leading a carriage in which he was riding bolted. That scare caused him to devote the rest of his life to meditation and religious writings.

Coupling Constants: The distance, in hertz, between two adjacent peaks of a split NMR signal is called the **coupling constant** (denoted by ***J***).

- The coupling constant for H_a being split by H_b is denoted by J_{ab}
- The signals of coupled protons (protons that split each other's signal) have the same coupling constant, $J_{ab} = J_{ba}$.
- Coupling constants are useful in analyzing complex NMR spectra because protons on adjacent carbons can be identified by identical coupling constants.

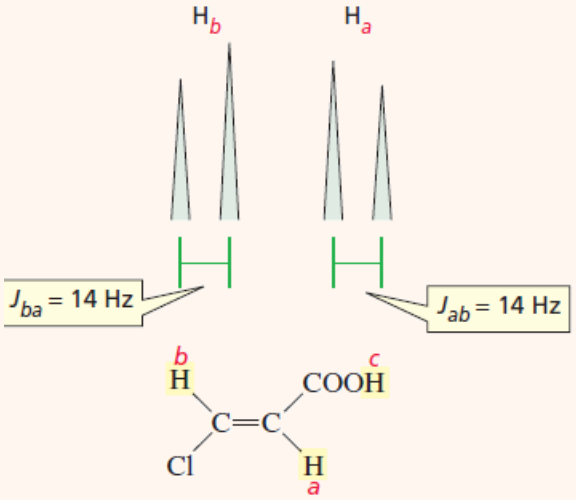


- *The magnitude of a coupling constant is independent of the operating frequency of the spectrometer*—the same coupling constant is obtained from a 300-MHz instrument as from a 600-MHz instrument.
- The magnitude of a coupling constant is a measure of how strongly the nuclear spins of the coupled protons influence each other. It, therefore, depends on the number and type of bonds that connect the coupled protons, as well as the geometric relationship of the protons.
- Characteristic coupling constants range from 0 to 15 Hz.

The dependence of the coupling constant on the angle between the two bonds is called the Karplus relationship after **Martin Karplus**, *who first observed the relationship. Karplus was born in 1930. He received a B.A. from Harvard University and a Ph.D. from the California Institute of Technology. He is currently a professor of chemistry at Harvard University.*

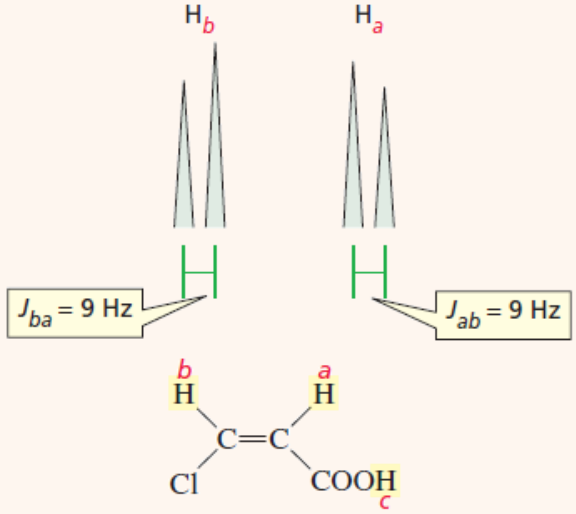
Approximate Values of Coupling Constants

Approximate value of J_{ab} (Hz)		Approximate value of J_{ab} (Hz)	
H_a H_b —C—C—	7	H_a C=C H_b	15 (trans)
H_a H_b —C—C—C—	0	H_a H_b C=C	10 (cis)
H_a C=C H_b	2 (geminal coupling)	H_a C=C C H_b	1 (long-range coupling)



trans-3-chloropropenoic acid

- Coupling constants can be used to distinguish between the spectra of *cis* and *trans* alkenes.
- The coupling constant of *trans*-vinylic protons is significantly greater than the coupling constant of *cis*-vinylic protons because the coupling constant depends on the dihedral angle between the two C-H bonds in the H¬C=C¬H unit.
- The coupling constant is greatest when the angle between the two bonds is 180° (*trans*) and smaller when it is 0° (*cis*).
- Notice the difference between J_{bd} and J_{cd} in the spectrum of 3-bromo-1-propene.



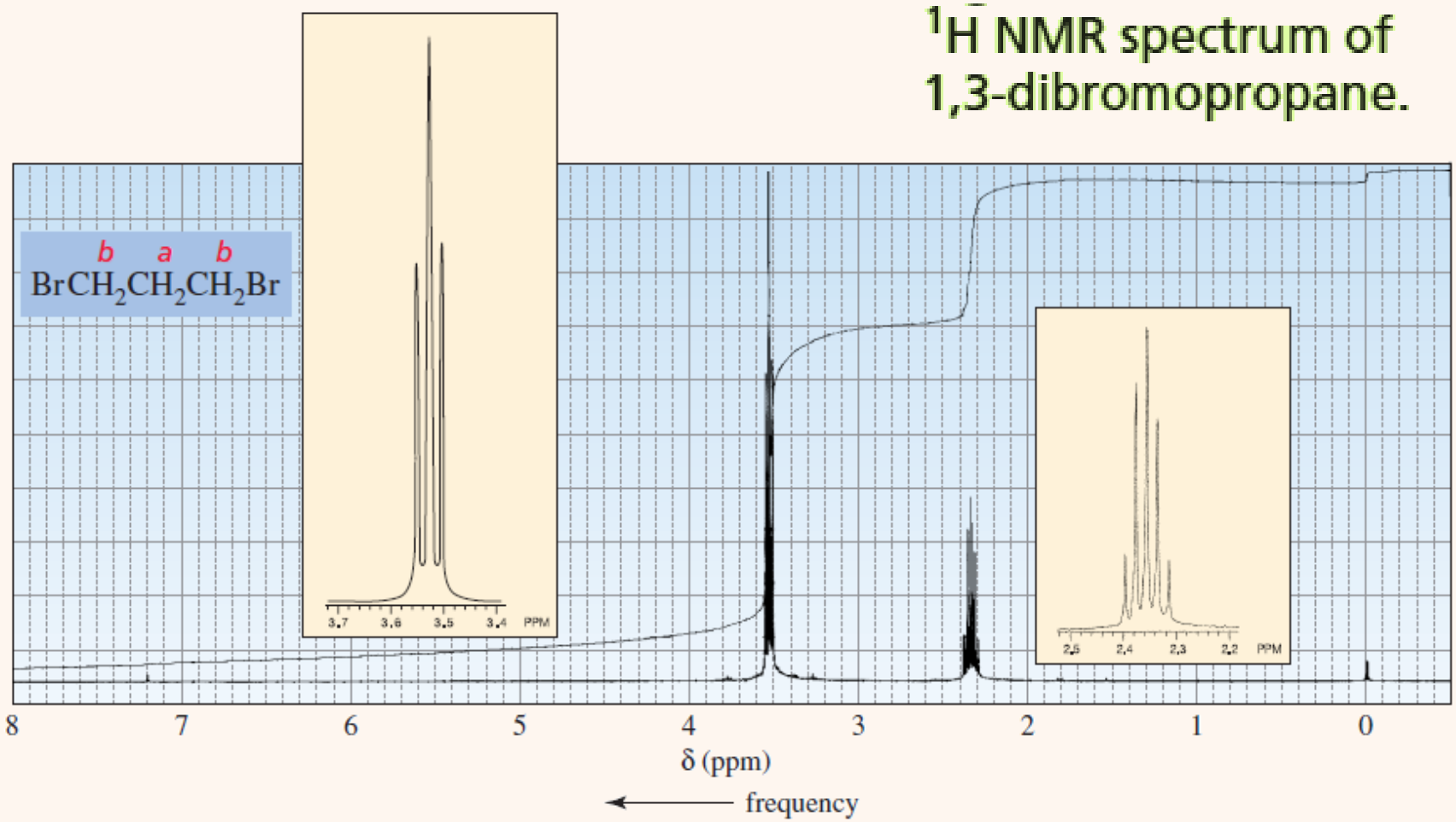
cis-3-chloropropenoic acid

Information from NMR spectrum

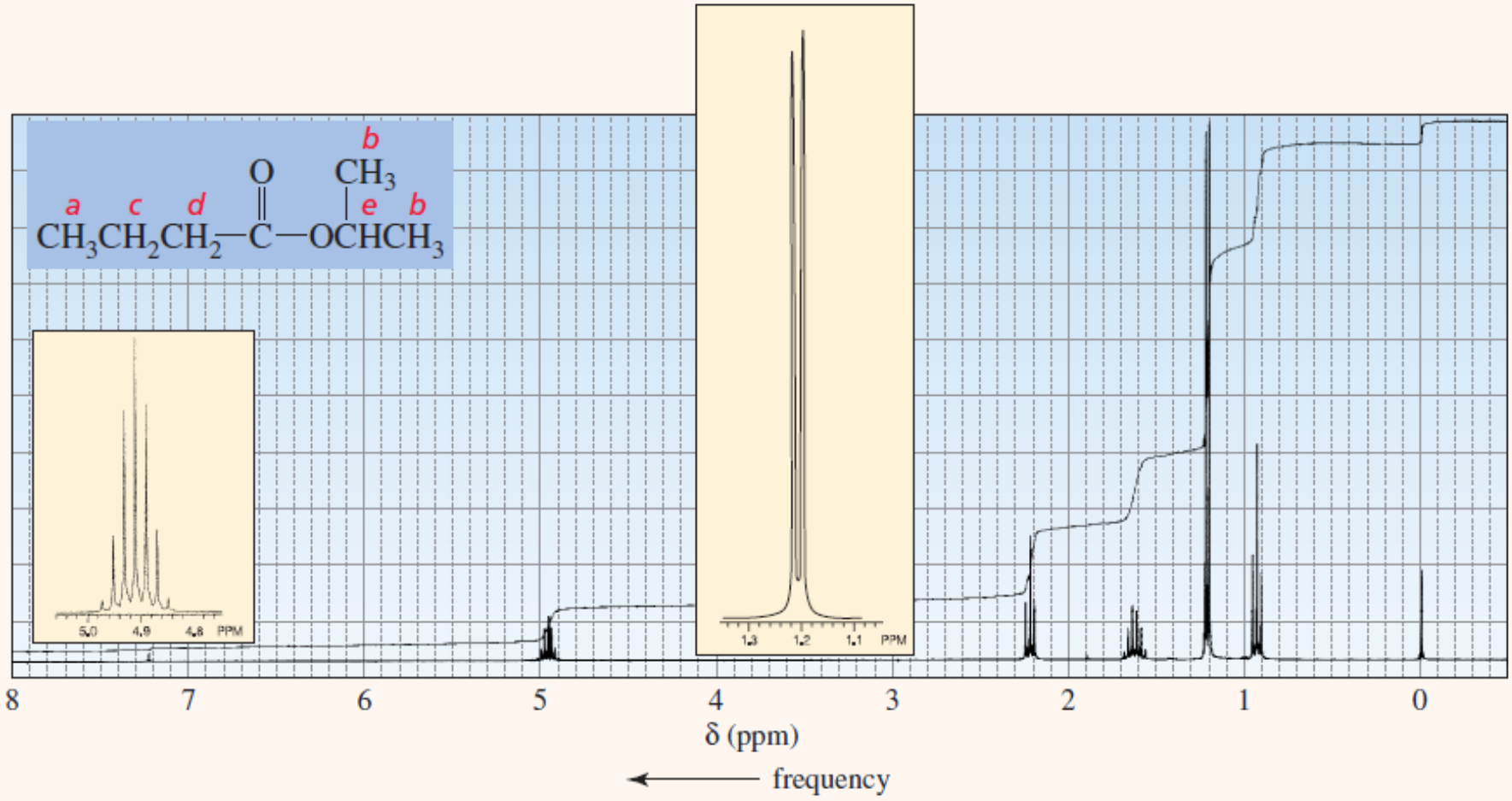
1. The number of signals indicates the number of different kinds of protons that are in the compound.

2. The position of a signal indicates the kind of proton(s) responsible for the signal (methyl, methylene, methine, allylic, vinylic, aromatic, etc.) and the kinds of neighboring substituents.
3. The integration of the signal tells the relative number of protons responsible for the signal.
4. The multiplicity of the signal $(N + 1)$ tells the number of protons (N) bonded to adjacent carbons.
5. The coupling constants identify coupled protons.

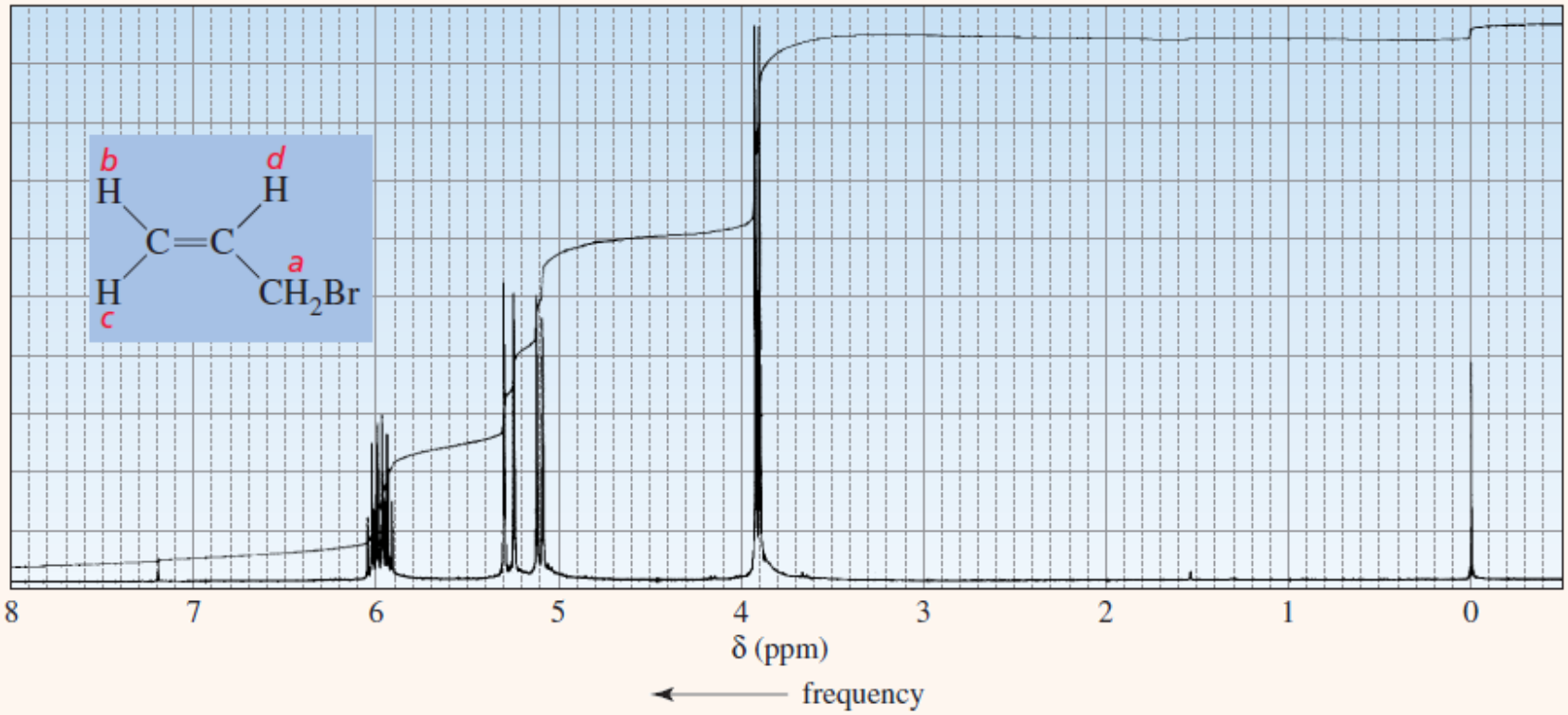
More Examples of ^{1}H NMR Spectra



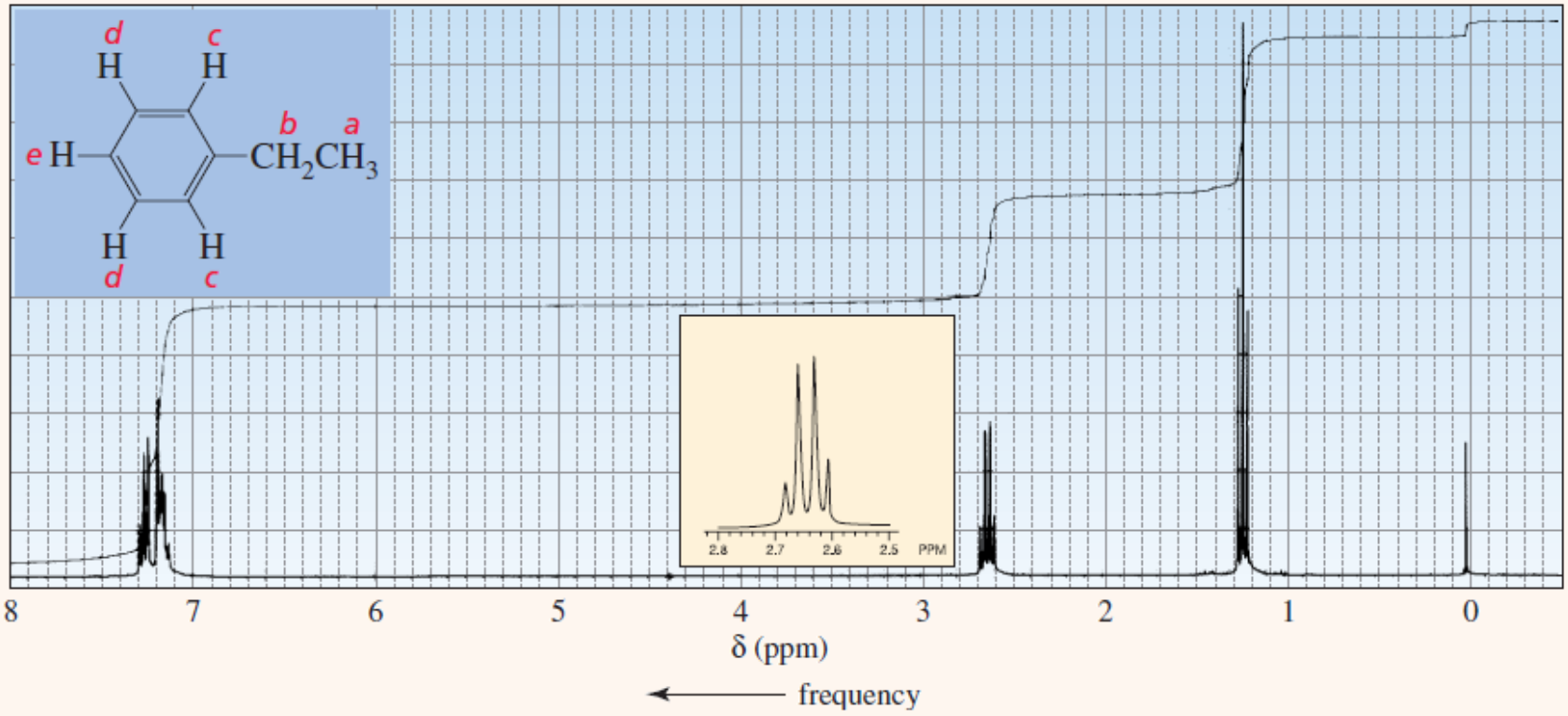
^{1}H NMR spectrum of isopropyl butanoate.



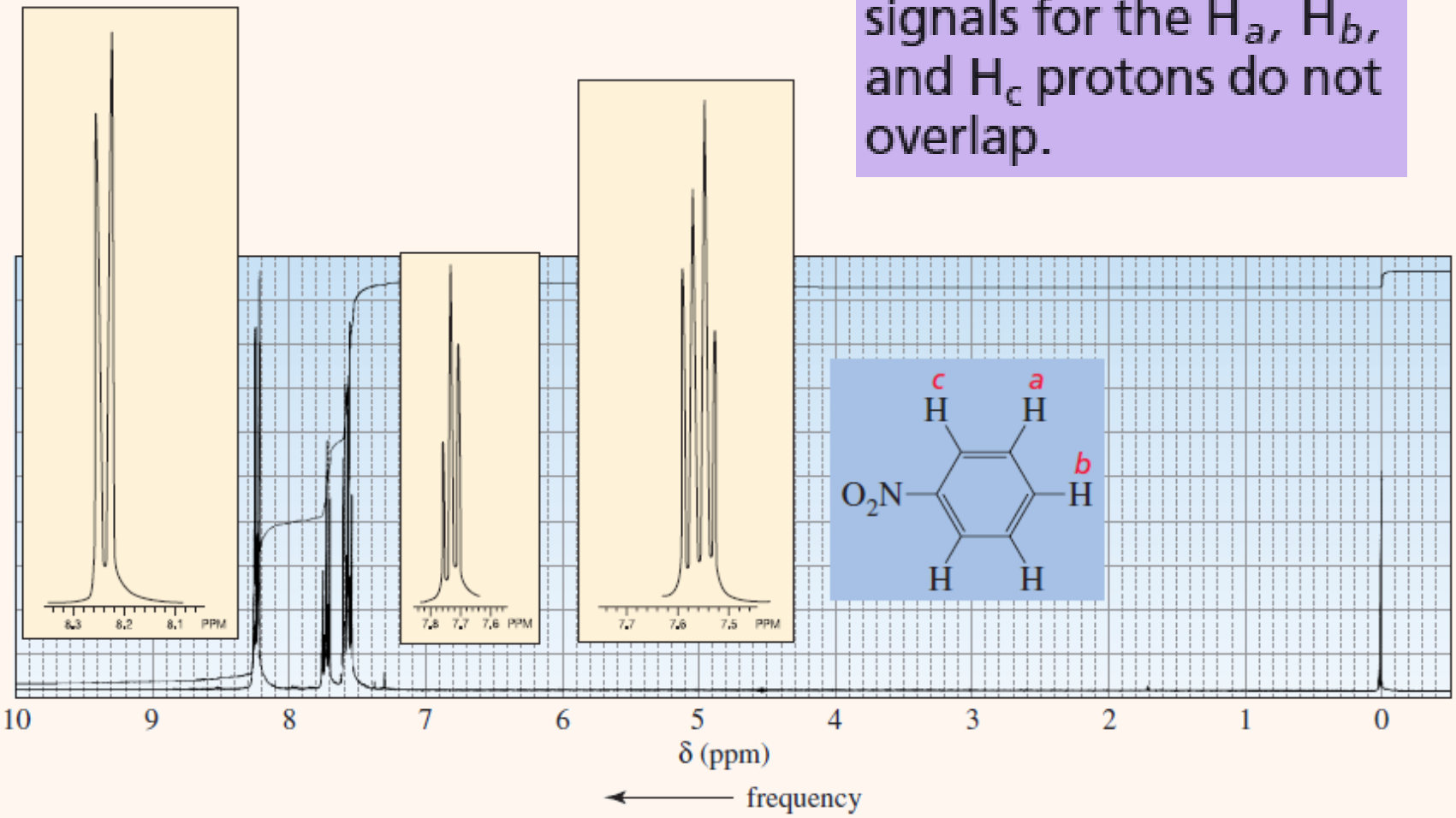
^{1}H NMR spectrum of 3-bromo-1-propene.



^{1}H NMR spectrum of ethylbenzene. The signals for the H_c, H_d, and H_e protons overlap.



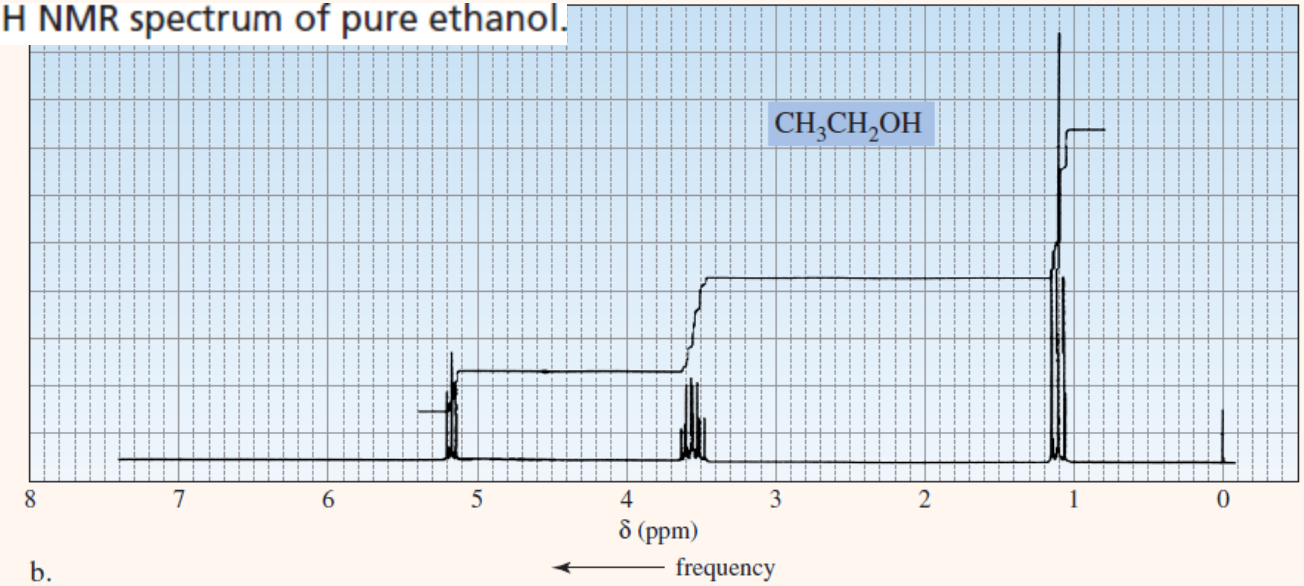
^{1}H NMR spectrum of nitrobenzene. The signals for the H_a, H_b, and H_c protons do not overlap.



Protons Bonded to Oxygen and Nitrogen

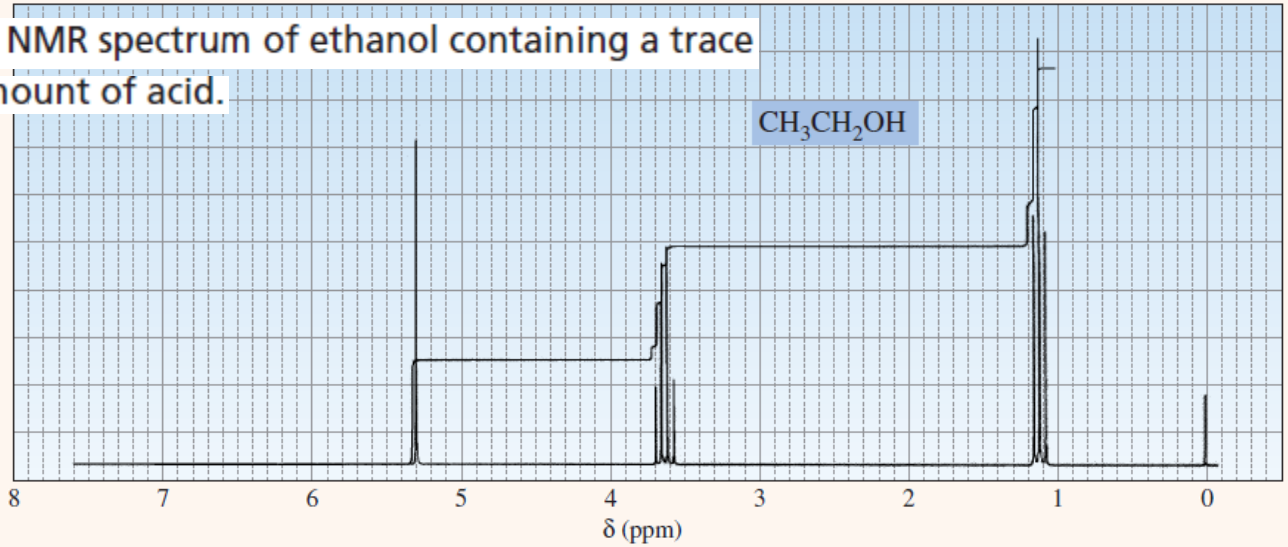
a.

(a) ^{1}H NMR spectrum of pure ethanol.

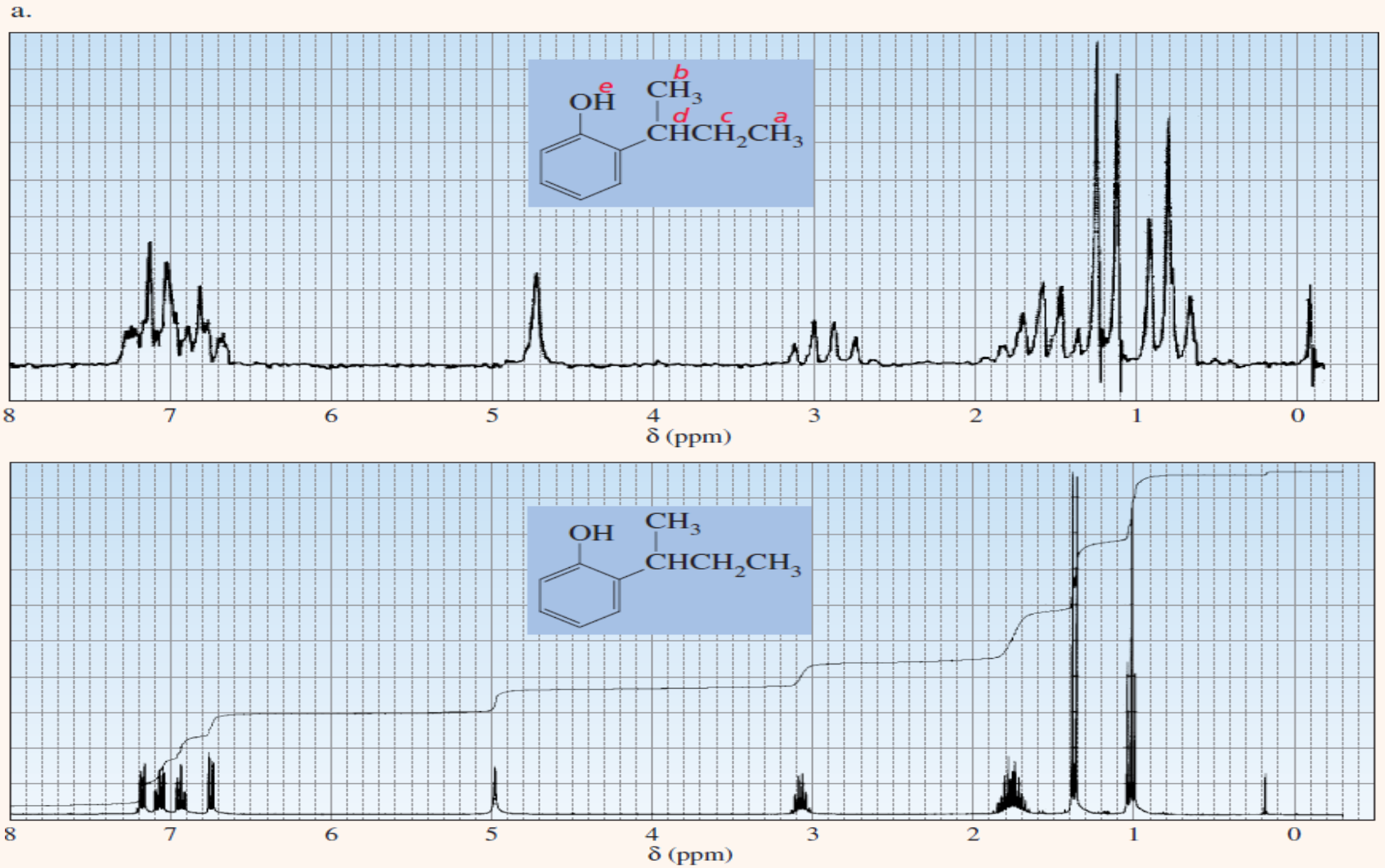


b.

(b) ^{1}H NMR spectrum of ethanol containing a trace amount of acid.



Resolution of ^{1}H NMR Spectra



(a) 60-MHz ^{1}H NMR spectrum of 2-*sec*-butylphenol. (b) 300-MHz ^{1}H NMR spectrum of 2-*sec*-butylphenol.

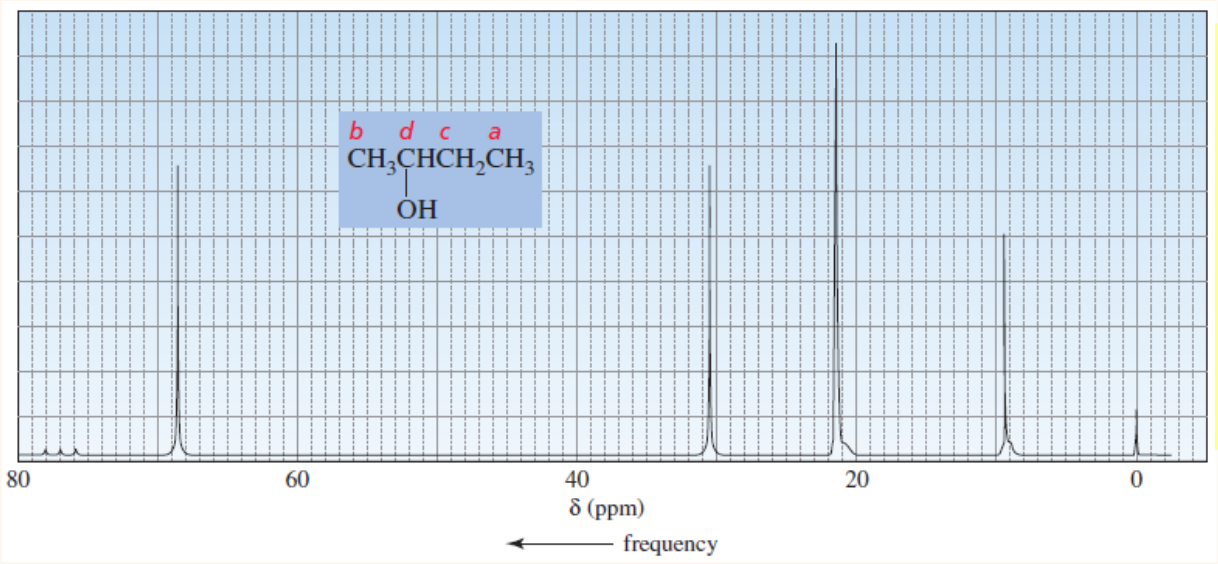
^{13}C NMR Spectroscopy

- The number of signals in a ^{13}C NMR spectrum tells you how many different kinds of carbons a compound has—just as the number of signals in an ^{1}H NMR spectrum tells you how many different kinds of hydrogens a compound has.
- The principles behind ^{13}C NMR and ^{1}H NMR spectroscopy are essentially the same. There are, however, some differences that make ^{13}C NMR easier to interpret.

The individual ^{13}C signals are weak because the isotope of carbon (^{13}C) that gives rise to ^{13}C NMR signals constitutes only 1.11% of carbon atoms (Section 13.3). (The most abundant isotope of carbon, ^{12}C, has no nuclear spin and therefore cannot produce an NMR signal.) The low abundance of ^{13}C means that the intensities of the signals in ^{13}C NMR compared with those in ^{1}H NMR are reduced by a factor of approximately 100. In addition, the gyromagnetic ratio (γ) of ^{13}C is about one-fourth that of ^{1}H, and the intensity of a signal is proportional to γ^3. Therefore, the overall intensity of a ^{13}C signal is about 6400 times ($100 \times 4 \times 4 \times 4$) less than the intensity of an ^{1}H signal.

One advantage to ^{13}C NMR spectroscopy is that the chemical shifts range over about 220 ppm, compared with about 12 ppm for ^{1}H NMR (Table 14.1). This means that signals are less likely to overlap. The ^{13}C NMR chemical shifts of different kinds of carbons are shown in Table 14.4. The reference compound used in ^{13}C NMR is TMS, the reference compound also used in ^{1}H NMR. Notice that ketone and aldehyde carbonyl groups can be easily distinguised from other carbonyl groups.

A disadvantage of ^{13}C NMR spectroscopy is that, unless special techniques are used, the area under a NMR signal is not proportional to the number of atoms giving rise to the signal. Thus, the number of carbons giving rise to a ^{13}C NMR signal cannot routinely be determined by integration.

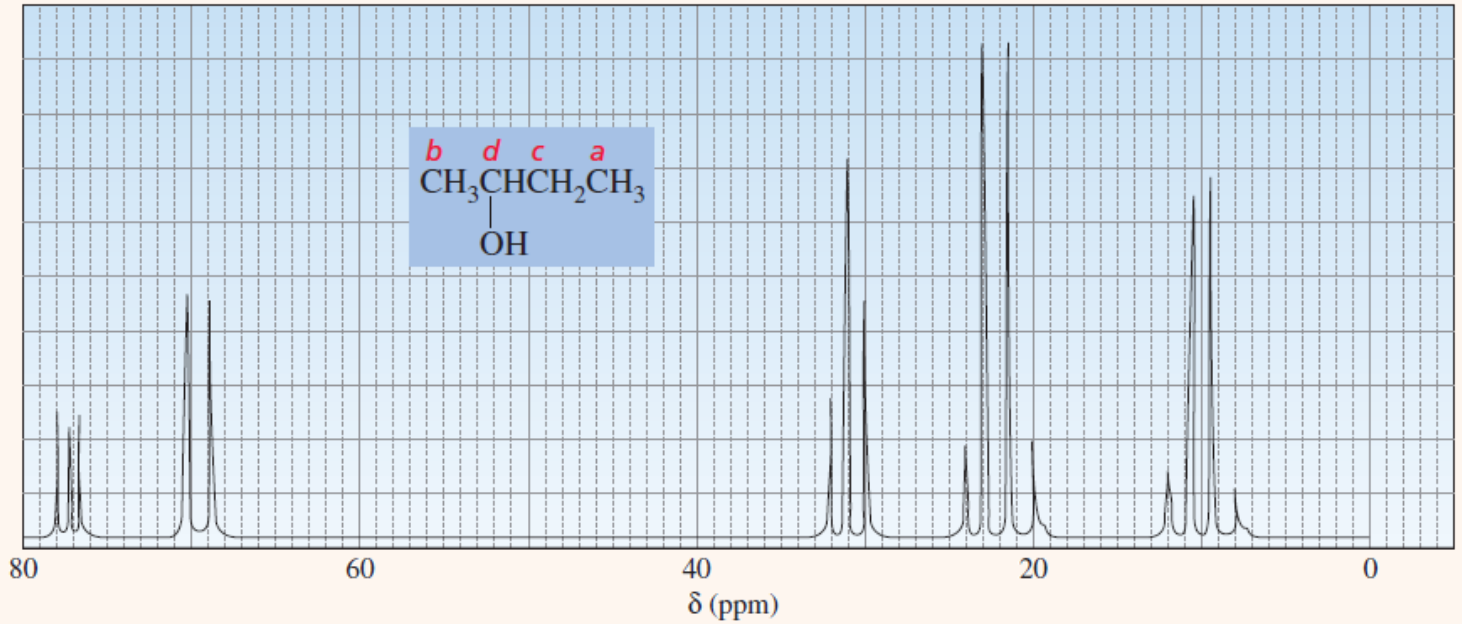


The signals in a NMR spectrum can be split by nearby hydrogens. However, this splitting is not usually observed because the spectra are recorded using spin-decoupling, which obliterates the carbon–proton interactions. Thus, all the signals are singlets in an ordinary NMR spectrum.

- 2-Butanol has carbons in four different environments, so there are four signals in the spectrum.
- Carbons in electron-dense environments produce low-frequency signals, and carbons close to electron-withdrawing groups produce high-frequency signals. This means that the signals for the carbons of 2-butanol are in the same relative order that we would expect for the signals of the protons on those carbons in the ^{1}H NMR spectrum.
- Thus, the carbon of the methyl group farther away from the electron-withdrawing OH group gives the lowest-frequency signal.
- As the frequency increases, the other methyl carbon comes next, followed by the methylene carbon; and the carbon attached to the OH group gives the highest-frequency signal.

Proton-coupled ^{13}C NMR spectrum

- If the spectrometer is run in a *proton-coupled* mode, the signals show spin–spin splitting.
- The splitting is not caused by adjacent carbons, but by the hydrogens bonded to the
- carbon that produces the signal. The multiplicity of the signal is determined by the N + 1 rule.
- The **proton-coupled ^{13}C NMR spectrum** of 2-butanol is shown below.
- The triplet at 78 ppm is produced by the solvent, $CDCl_3$.
- The signals for the methyl carbons are each split into a quartet because each methyl carbon is bonded to three hydrogens **(3 + 1 = 4).**
- The signal for the methylene carbon is split into a triplet **(2+ 1 = 3),** and the signal for the carbon bonded to the OH group is split into a doublet **(1 + 1 = 1).**



PROBLEM 36

Answer the following questions for each of the compounds:

a. How many signals are in the ^{13}C NMR spectrum?

b. Which signal is at the lowest frequency?

1. $CH_3CH_2CH_2Br$

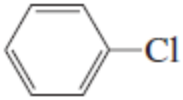
2. $(CH_3)_2C{=}CH_2$

3. $CH_3CH_2OCH_3$

4. $CH_2{=}CHBr$

5. $CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_3$

6. $CH_3\overset{\overset{O}{\|}}{C}HCH(CH_3)$

7. 

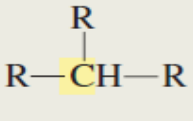
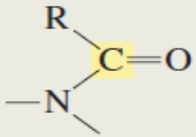
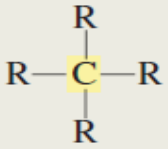
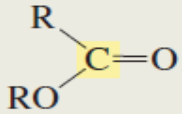
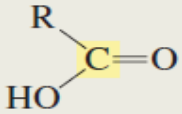
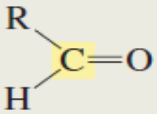
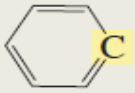
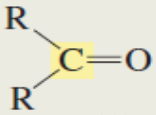
8. $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

9. $CH_3C(CH_3)(CH_3)COCH_3$

10. $CH_3CH(Br)CH_3$

^{13}C NMR Spectroscopy

Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	C—I	0–40
R—CH_3	8–35	C—Br	25–65
R—CH_2—R	15–50	C—Cl C—N C—O	35–80 40–60 50–80
	20–60		165–175
	30–40		165–175
≡C	65–85		175–185
=C	100–150		190–200
	110–170		205–220

Answer the following questions for each of the compounds:

a. How many signals are in the ^{13}C NMR spectrum?

b. Which signal is at the lowest frequency?

1. $CH_3CH_2CH_2Br$

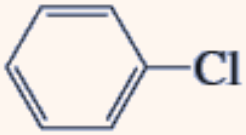
2. $(CH_3)_2C{=}CH_2$

3. $CH_3CH_2OCH_3$

4. $CH_2{=}CHBr$

5. $CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_3$

6. $CH_3\overset{\overset{O}{\|}}{C}HCH$ with CH_3 branch

7. 

8. $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

9. $CH_3\overset{\overset{CH_3}{|}}{C}OCH_3$ with CH_3 branch

10. CH_3CHCH_3 with Br branch

THANK YOU

Stay home. Stay safe.

Continue learning!