Qualitative Organic Analysis – CH 351

NMR Spectroscopy

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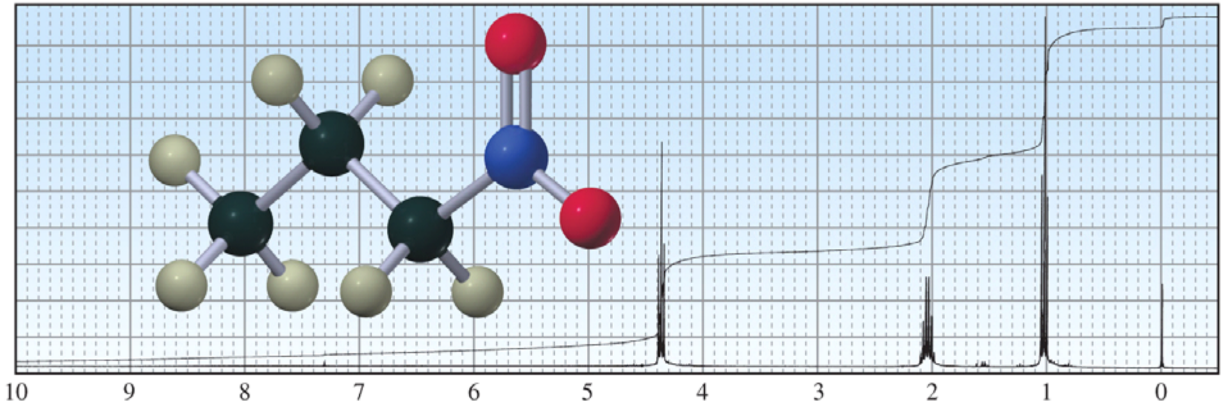
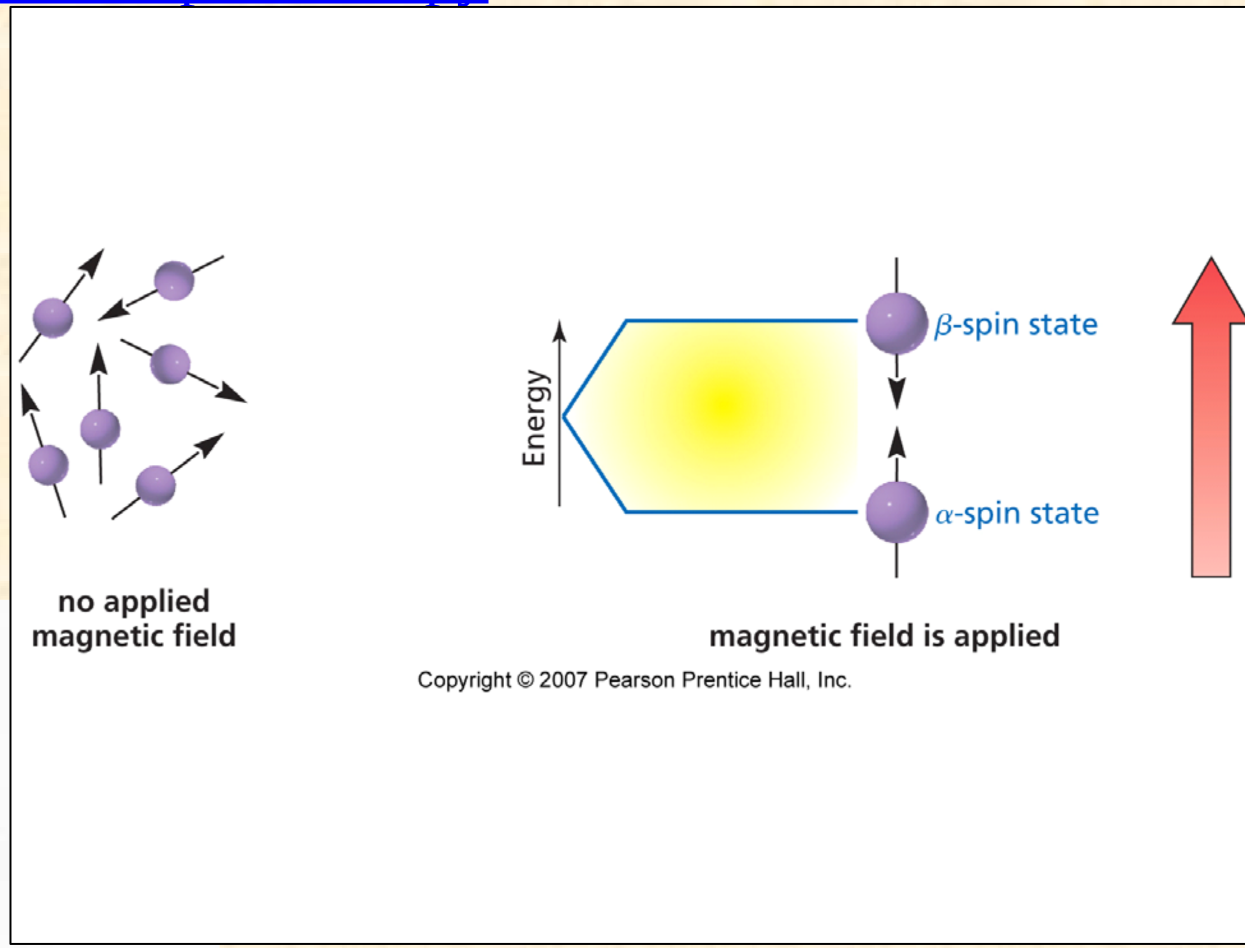
General Aspects



1-Nitropropane

General Aspects

Theoretical base of NMR spectroscopy



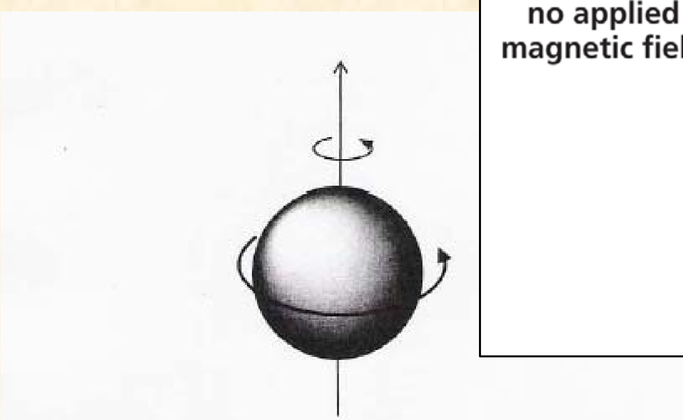


FIGURE 3.1 Spinning charge on proton generates magnetic dipole.

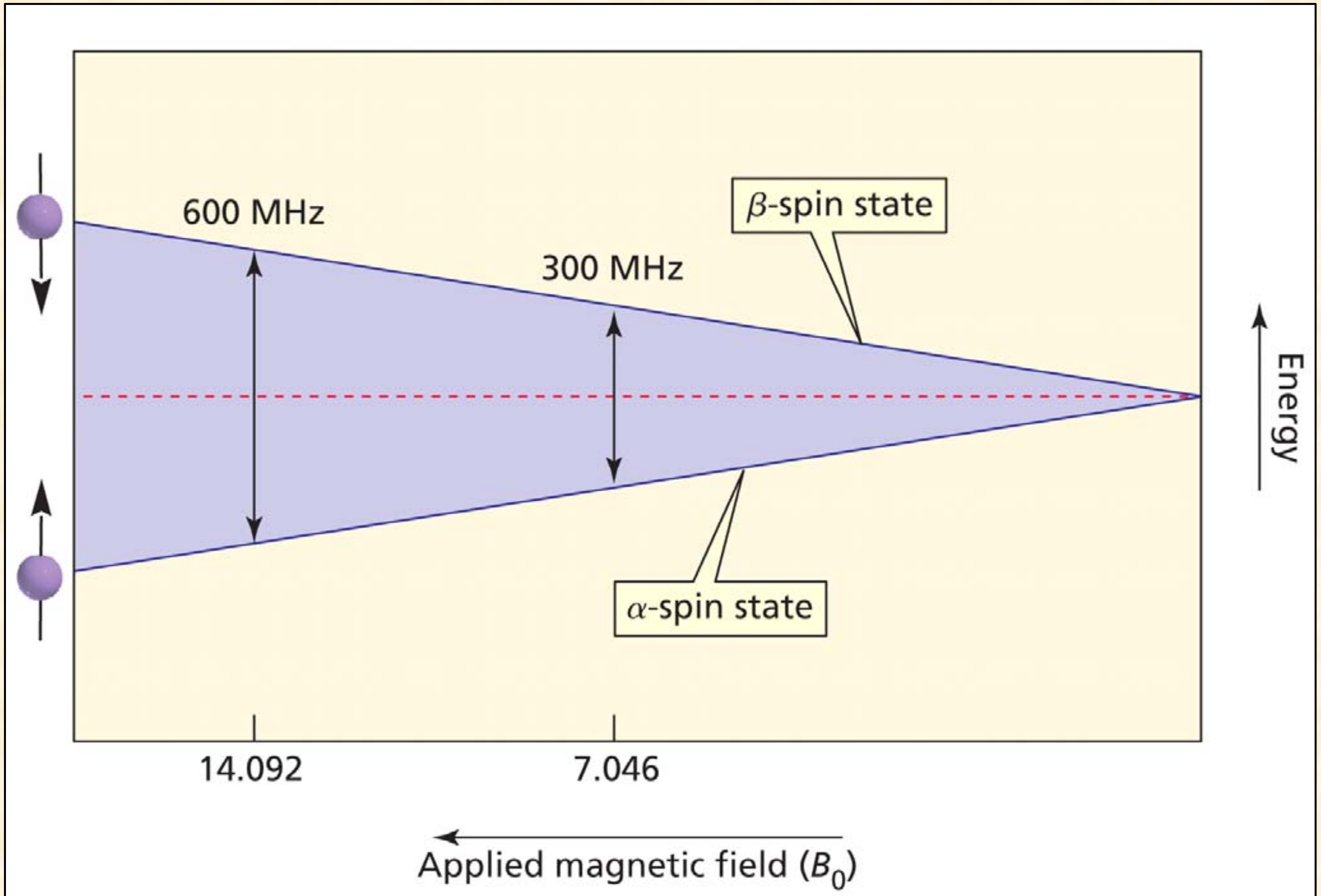
General Aspects

Theoretical base of NMR spectroscopy

$$\Delta E = (h\gamma/2\pi)B_0$$

$$\Delta E = h\nu$$

$$\nu_1 = (\gamma/2\pi)\,B_0$$



UMASS BOSTON

Theoretical base of NMR spectroscopy

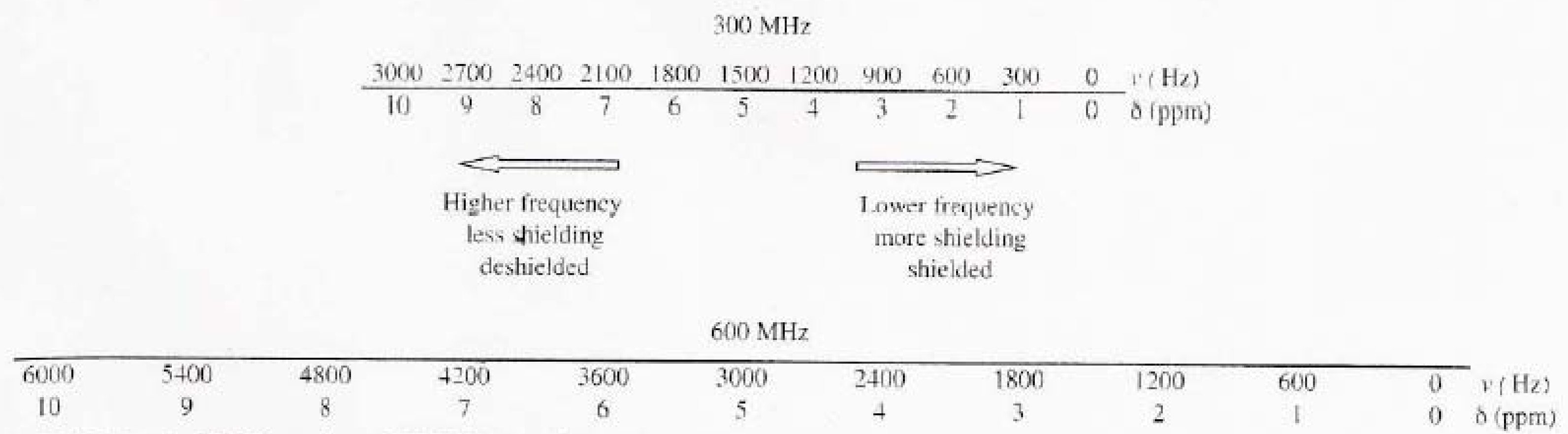
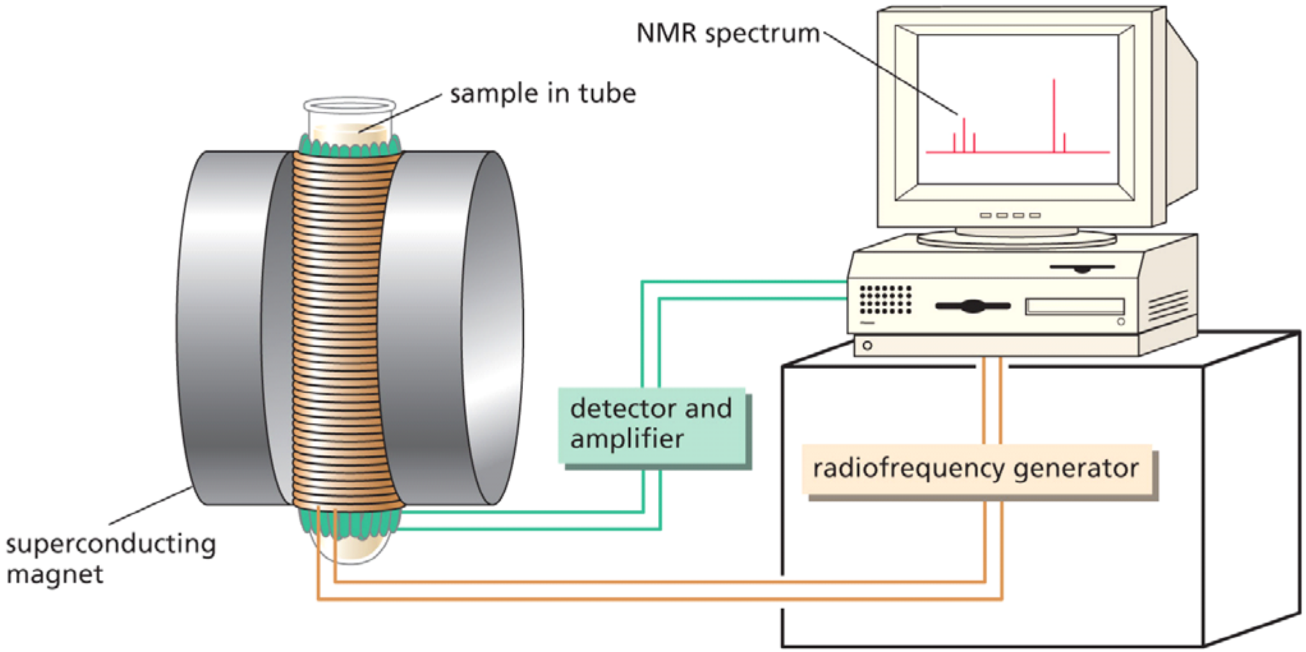


FIGURE 3.18 NMR scale at 300 MHz and 600 MHz. Relatively few organic compounds show absorption peaks to the right of the TMS peak. These lower frequency signals are designated by negative numbers to the right (not shown in the Figure).

$$\nu_1 = (\gamma/2\pi)\, \boldsymbol{B}_0$$

General Aspects

[Schematic diagram of an NMR spectrometer]



General Aspects

Handling

General Aspects

Magnetic field

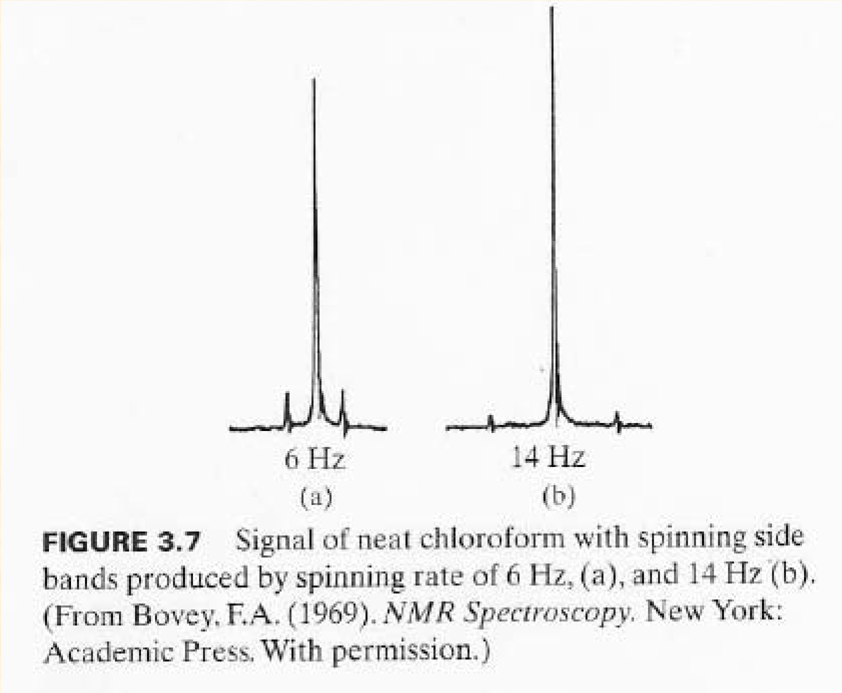
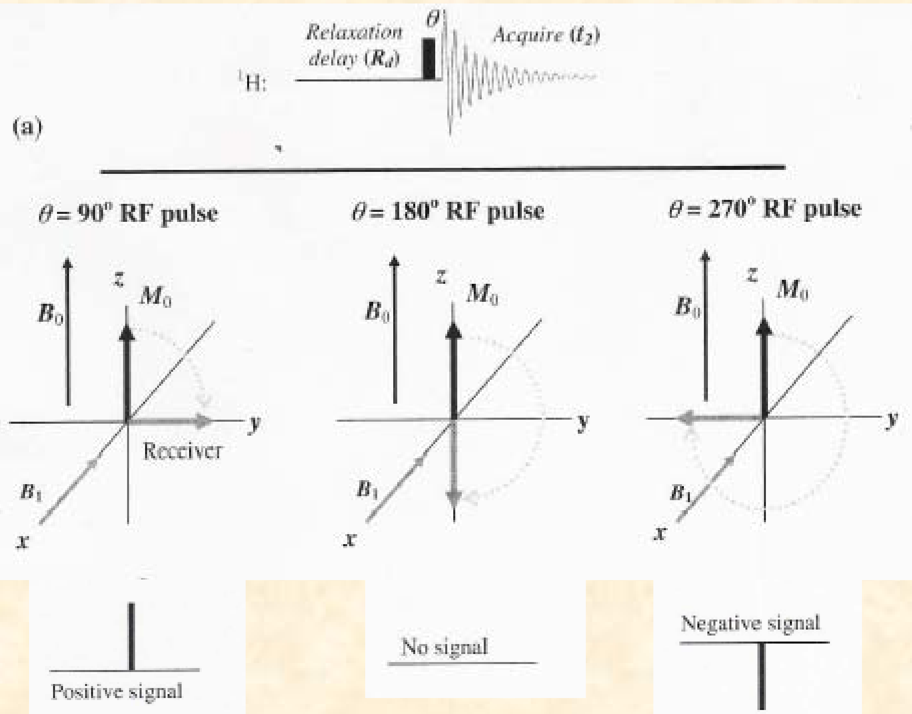


FIGURE 3.7 Signal of neat chloroform with spinning side bands produced by spinning rate of 6 Hz, (a), and 14 Hz (b). (From Bovey, F.A. (1969). *NMR Spectroscopy.* New York: Academic Press. With permission.)

General Aspects

Pulsed NMR



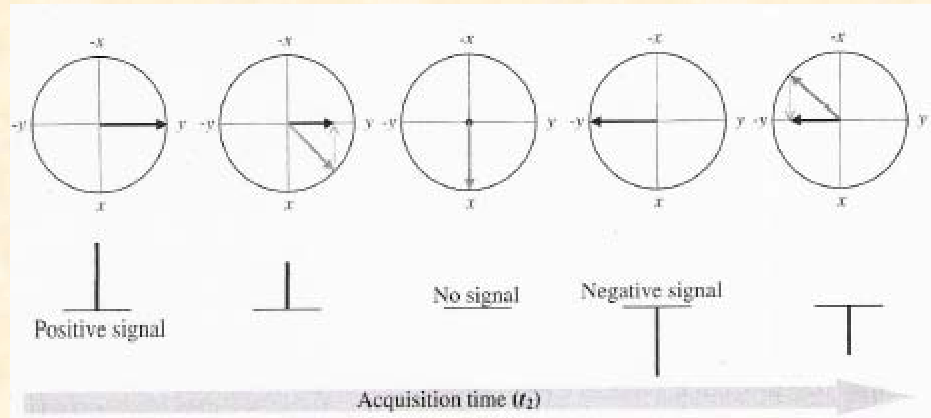
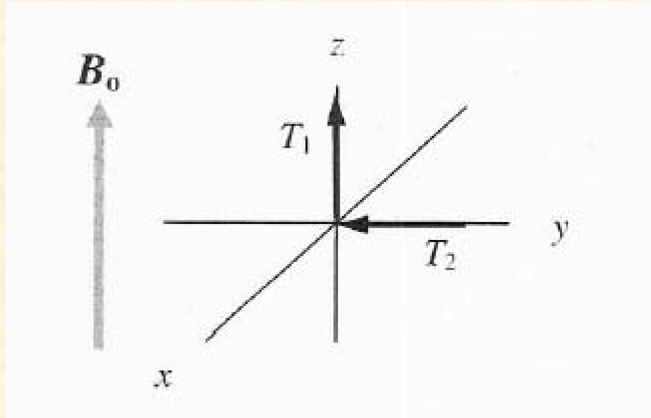


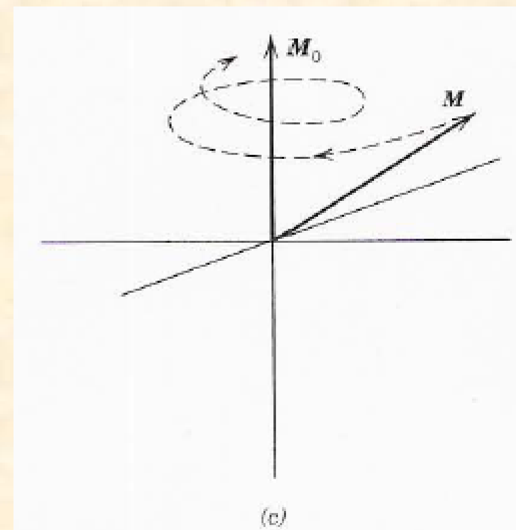
FIGURE 3.9 (A) Pulse sequence for a standard ^{1}H experiment (θ) is a variable radio frequency pulse. (B) shows the effect of various pulse angles (θ) and expected signal. (C) shows the rotation of the signal in the xy plane after the 90° pulse.

General Aspects

Relaxation



Spin-Lattice
Relaxation
(longitudinal or T_1)



Relaxation

Spin-Spin
Relaxation (T_2)

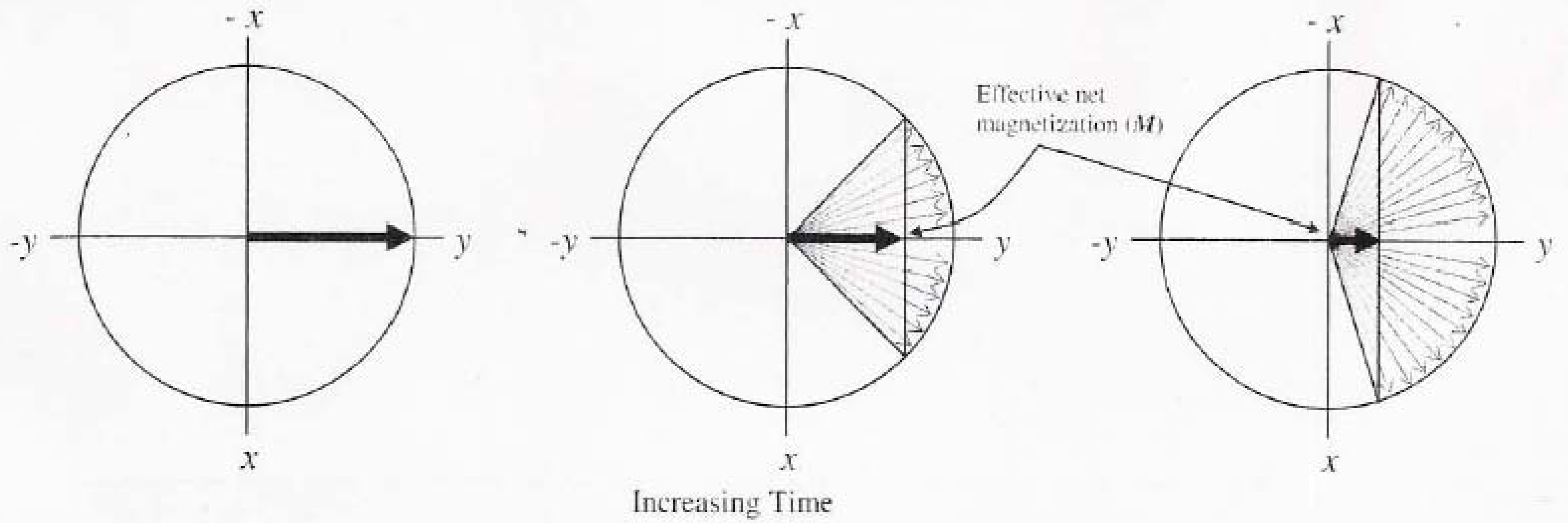
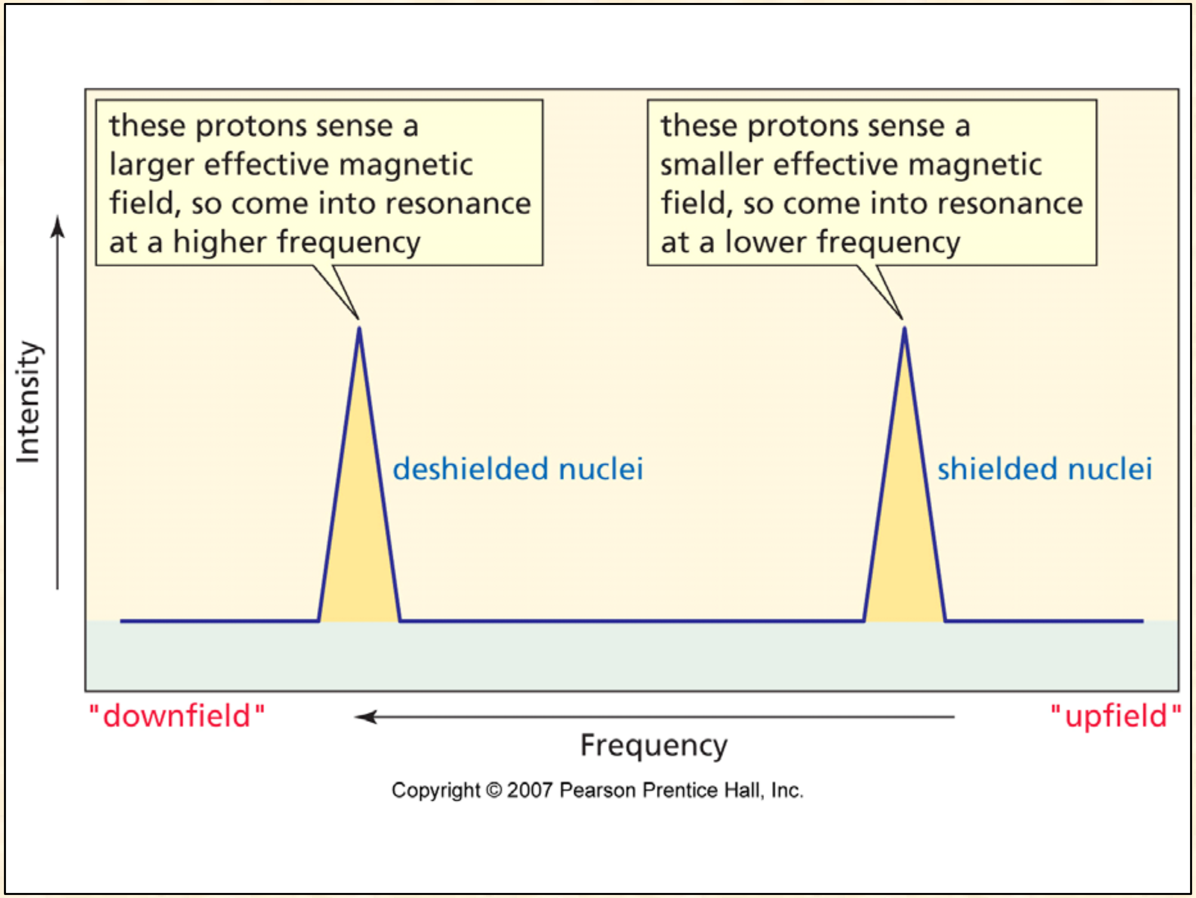


FIGURE 3.10 One spin, rotating at the same frequency as the rotating frame of reference with T_2 relaxation in the xy plane. T_2 relaxation will dephase or spread the magnetization in the xy plane, which causes line broadening and decay of the signals. T_2 effects are partially due to inhomogeneous magnetic fields.

General Aspects

Shielding



General Aspects

NMR active nucleii (elements)

Odd number of protons and/or neutrons

^{1}H , ^{2}H (^{3}H)

^{13}C

^{15}N

^{18}O check!

^{19}F

^{31}P

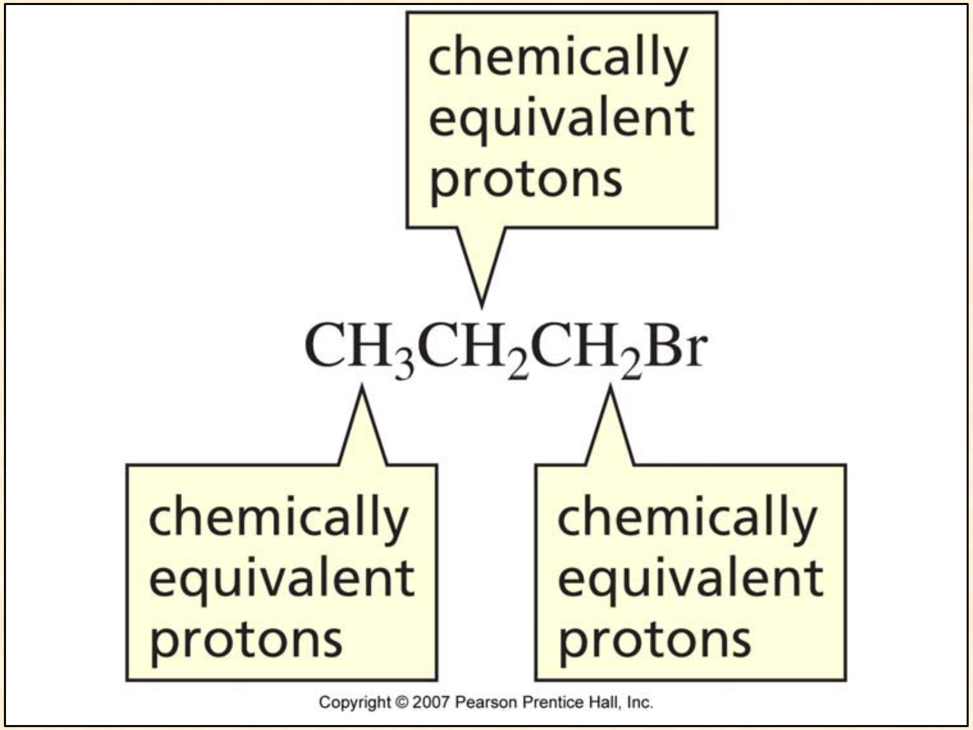
and many others

(strongly depends on natural abundance)

TABLE 3.1 Type of nuclear spin number, *I*, with various combinations of atomic mass and atomic number.

I	Atomic Mass	Atomic Number	Example of Nuclei
Half-integer	Odd	Odd	${}^{1}_{1}H(\frac{1}{2})$, ${}^{3}_{1}H(\frac{1}{2})$, ${}^{15}_{7}N(\frac{1}{2})$, ${}^{19}_{9}F(\frac{1}{2})$, ${}^{31}_{15}P(\frac{1}{2})$
Half-integer	Odd	Even	${}^{13}_{6}C(\frac{1}{2})$, ${}^{17}_{8}O(\frac{1}{2})$, ${}^{29}_{14}Si(\frac{1}{2})$
Integer	Even	Odd	${}^{2}_{1}H(1)$, ${}^{14}_{7}N(1)$, ${}^{10}_{5}B(3)$
Zero	Even	Even	${}^{12}_{6}C(0)$, ${}^{16}_{8}O(0)$, ${}^{34}_{16}S(0)$

Equivalent vs. Nonequivalent nucleii

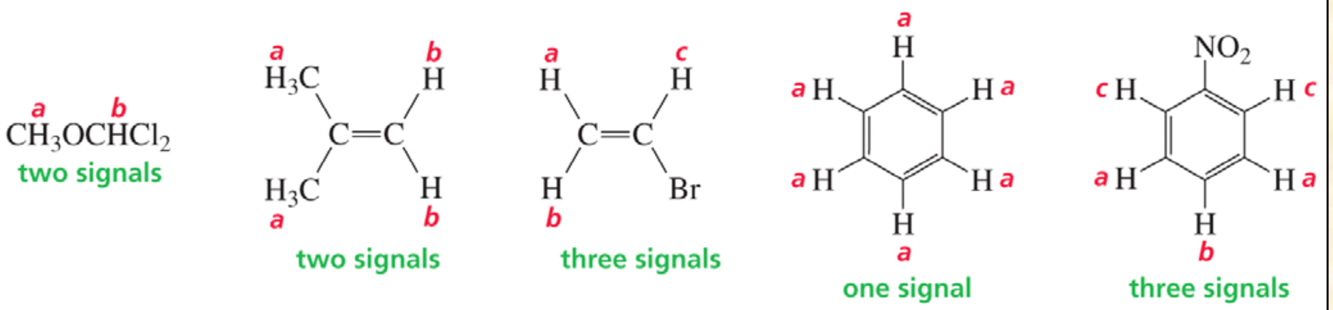


General Aspects – ^{1}H NMR Spectroscopy

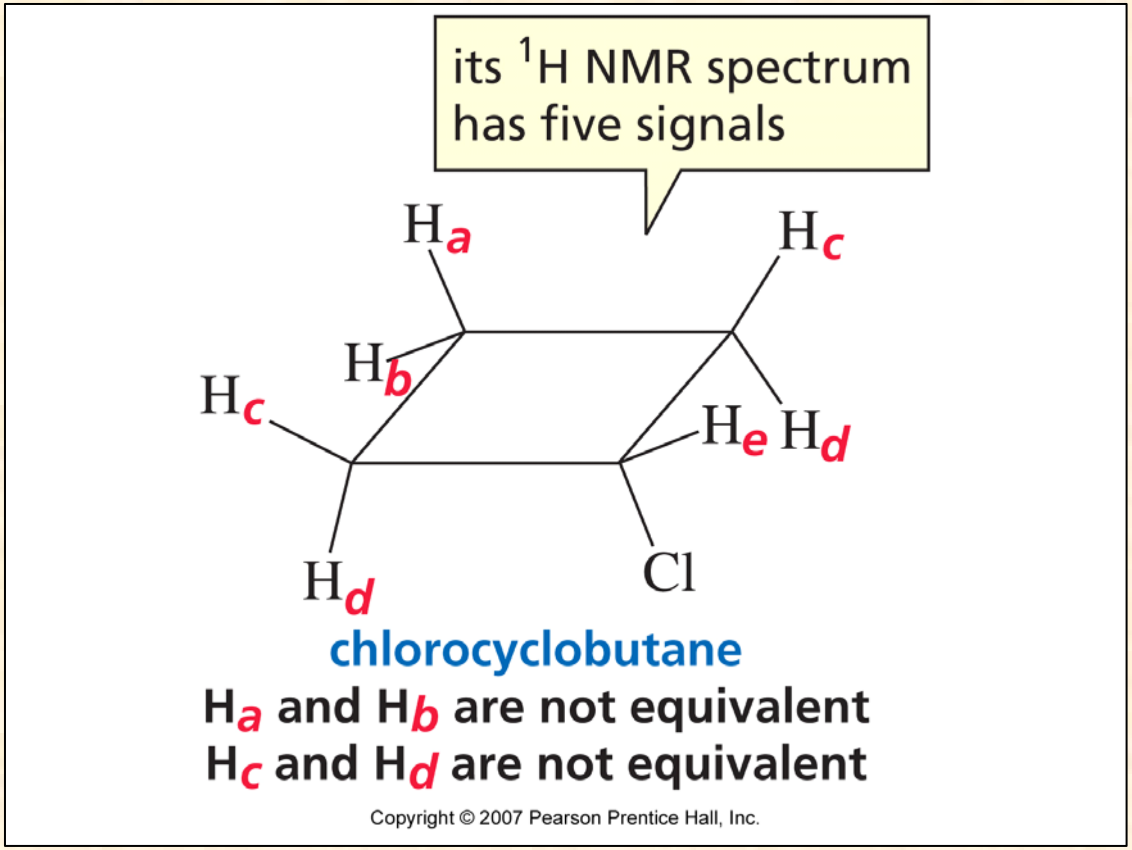
Equivalent vs. Nonequivalent nucleii

General Aspects – [1]H NMR Spectroscopy

Equivalent vs. Nonequivalent nucleii



Equivalent vs. Nonequivalent nuclei



General Aspects – ^{1}H NMR Spectroscopy

Equivalent vs. Nonequivalent nucleii

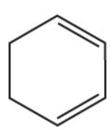
PROBLEM 3◆

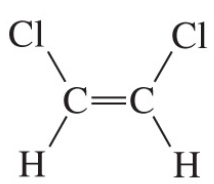
How many signals would you expect to see in the ^{1}H NMR spectrum of each of the following compounds?

a. $CH_3CH_2CH_2CH_3$

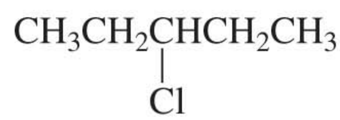
b. $BrCH_2CH_2Br$

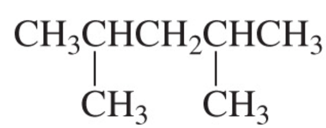
c. $CH_2{=}CHCl$

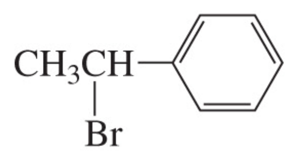
d. 

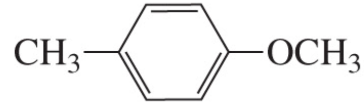
e. 

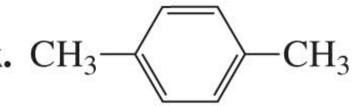
f. 

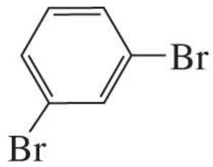
g. 

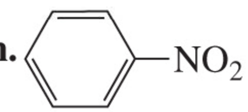
h. 

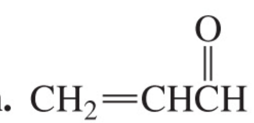
i. 

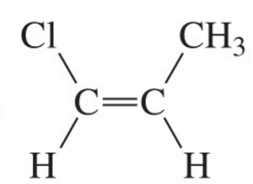
j. 

k. 

l. 

m. 

n. 

o. 

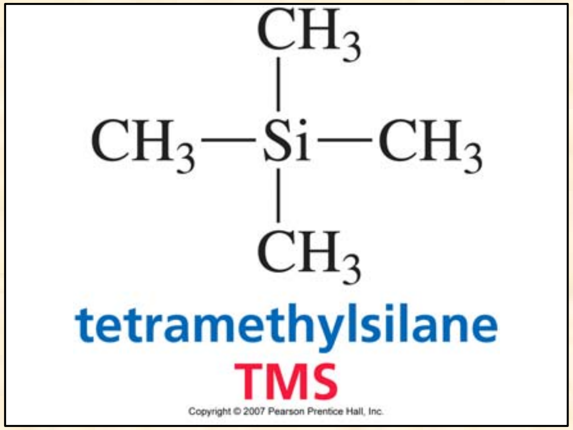
Equivalent vs. Nonequivalent nucleii

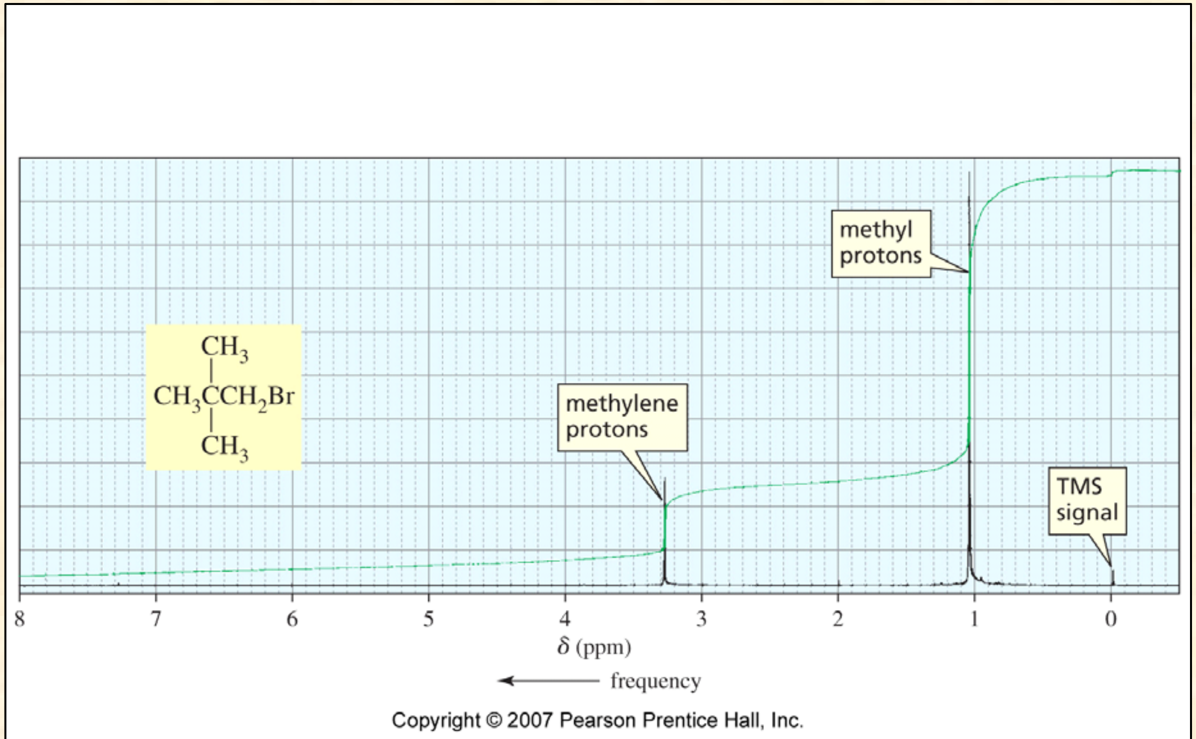
PROBLEM 5◆

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.

General Aspects – ¹H NMR Spectroscopy

Chemical Shift





$$\nu_1 = (\gamma/2\pi) B_0$$

Chemical Shift

δ = dist. down field from TMS (Hz) / op. frequency (MHz)

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 ppm

← frequency

Chemical Shift

PROBLEM 7◆

A signal is seen at 600 Hz downfield from the TMS signal 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?

Chemical Shift

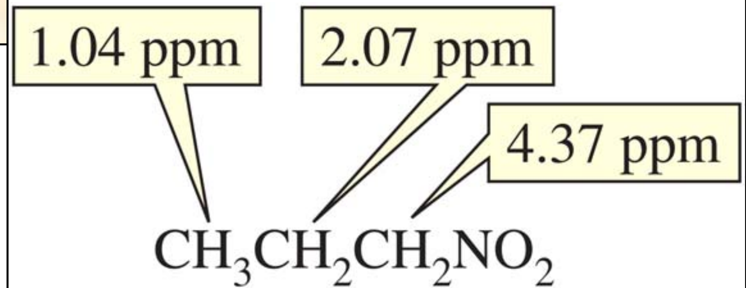
PROBLEM 8◆

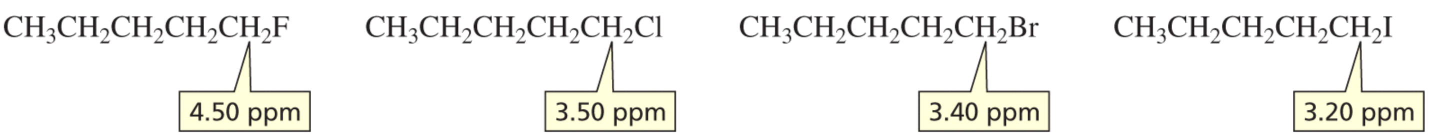
a. If two signals differ by 1.5 ppm in a 300-MHz spectrometer, by how much do they differ in a 100-MHz spectrometer?

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

General Aspects – ^{1}H NMR Spectroscopy

Chemical Shift



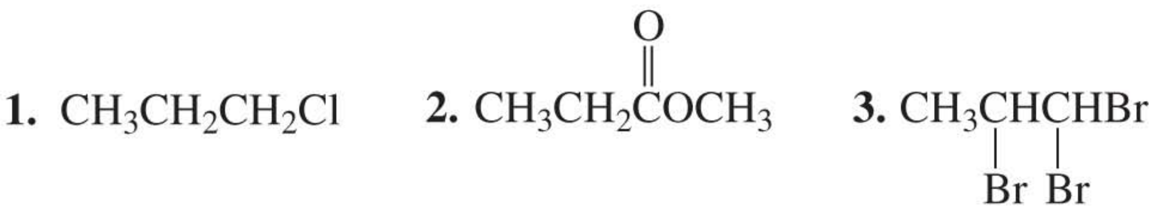


$$\nu_1 = (\gamma/2\pi)\, \boldsymbol{B}_0$$

Chemical Shift

PROBLEM 10◆

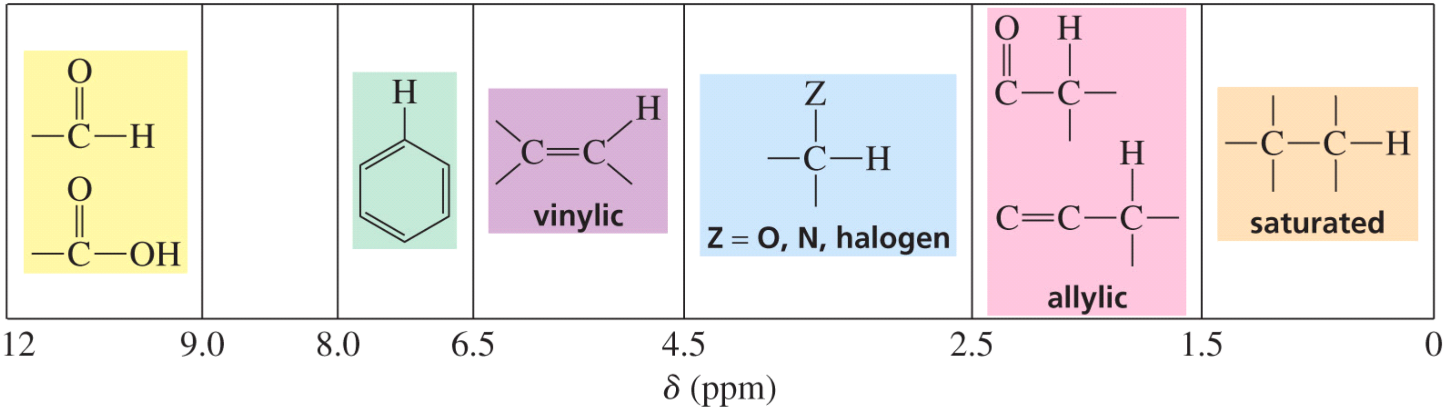
a. Which set of protons in each of the following compounds is the least shielded?



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

General Aspects – ^{1}H NMR Spectroscopy

Chemical Shift



General Aspects – ^{1}H NMR Spectroscopy

Chemical Shift

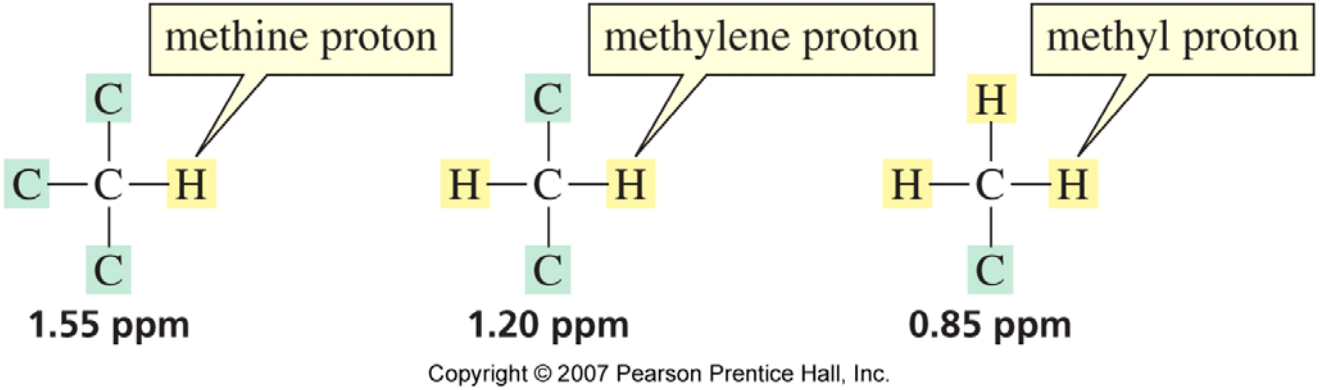
Table 13.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$-CH_3$	0.85	$I-\overset{\vert}{\underset{\vert}{C}}-H$	2.5–4
$-CH_2-$	1.20	$Br-\overset{\vert}{\underset{\vert}{C}}-H$	2.5–4
$-\overset{\vert}{CH}-$	1.55	$Cl-\overset{\vert}{\underset{\vert}{C}}-H$	3–4
$-\underset{\vert}{C}=\underset{\vert}{C}-CH_3$	1.7	$F-\overset{\vert}{\underset{\vert}{C}}-H$	4–4.5
$-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.1	RNH_2	Variable, 1.5–4
$C_6H_5-CH_3$	2.3	ROH	Variable, 2–5
$-C\equiv C-H$	2.4	$ArOH$	Variable, 4–7
$R-O-CH_3$	3.3	C_6H_5-H	6.5–8
$R-\underset{R}{\underset{\vert}{C}}=CH_2$	4.7	$-\overset{O}{\overset{\Vert}{C}}-H$	9.0–10
$R-\underset{R}{\underset{\vert}{C}}=\underset{R}{\underset{\vert}{C}}-H$	5.3	$-\overset{O}{\overset{\Vert}{C}}-OH$	Variable, 10–12
		$-\overset{O}{\overset{\Vert}{C}}-NH_2$	Variable, 5–8

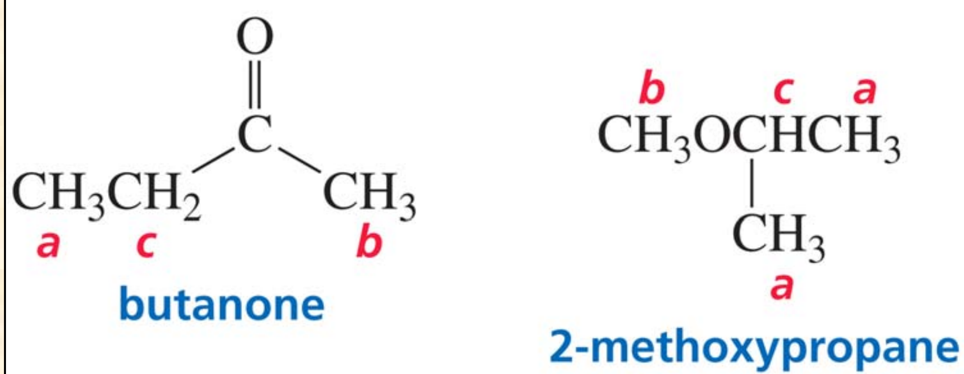
[a]The values are approximate because they are affected by neighboring substituents.

General Aspects – ^{1}H NMR Spectroscopy

Chemical Shift



Chemical Shift



General Aspects – ^{1}H NMR Spectroscopy

Chemical Shift

PROBLEM 11◆

In each of the following compounds, which of the underlined protons (or sets of protons) has the greater chemical shift (that is, the higher frequency signal)?

a. $CH_3C\underline{H}C\underline{H}Br$
$\quad\quad |\quad |$
$\quad\quad Br\ Br$

b. $C\underline{H}_3CHOC\underline{H}_3$
$\quad\quad |$
$\quad\quad CH_3$

c. $CH_3C\underline{H}_2CHC\underline{H}_3$
$\quad\quad\quad |$
$\quad\quad\quad Cl$

d.
$\quad\quad\quad O$
$\quad\quad\quad \|$
$CH_3C\underline{H}CC\underline{H}_2CH_3$
$\quad\quad |$
$\quad\quad CH_3$

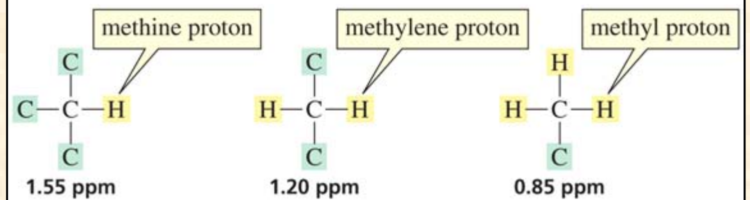
e. $CH_3C\underline{H}_2CH{=}C\underline{H}_2$

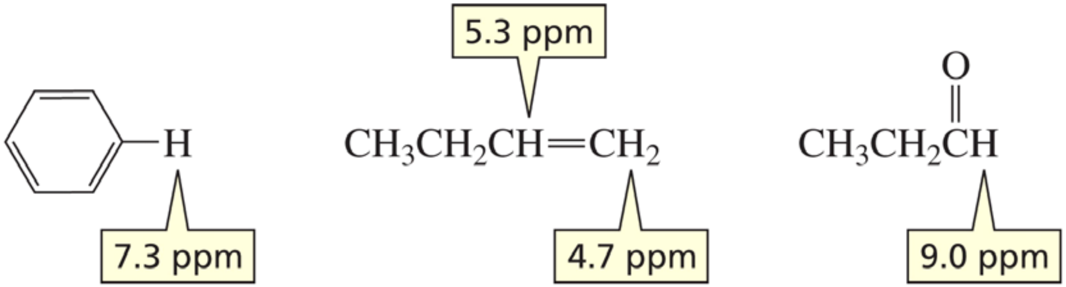
f. $C\underline{H}_3OC\underline{H}_2CH_2CH_3$

General Aspects – ¹H NMR Spectroscopy

Chemical Shift

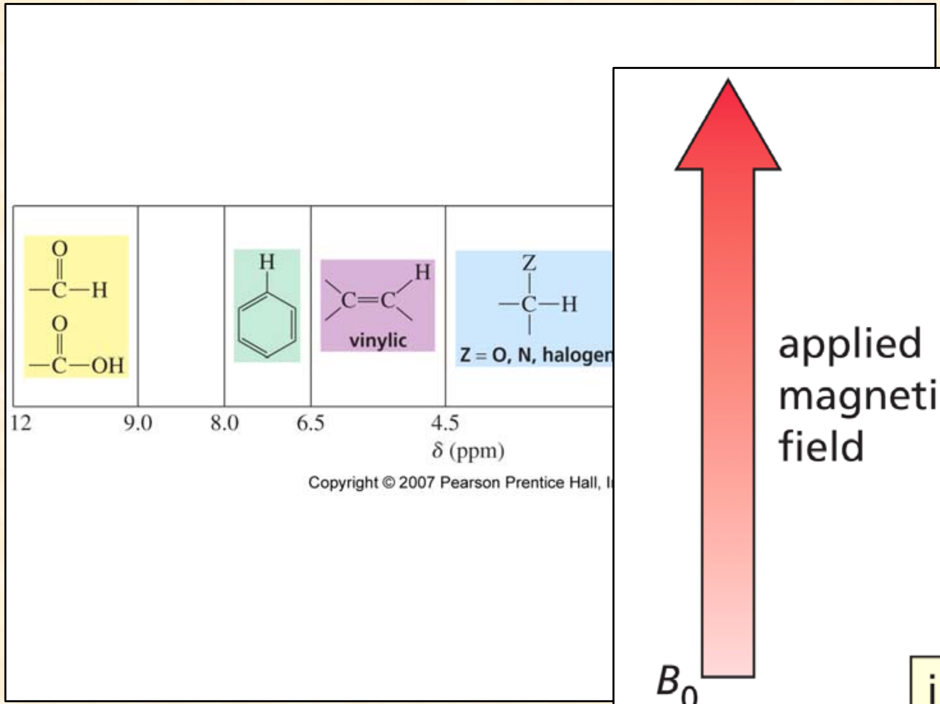
Diamagnetic anisotropy



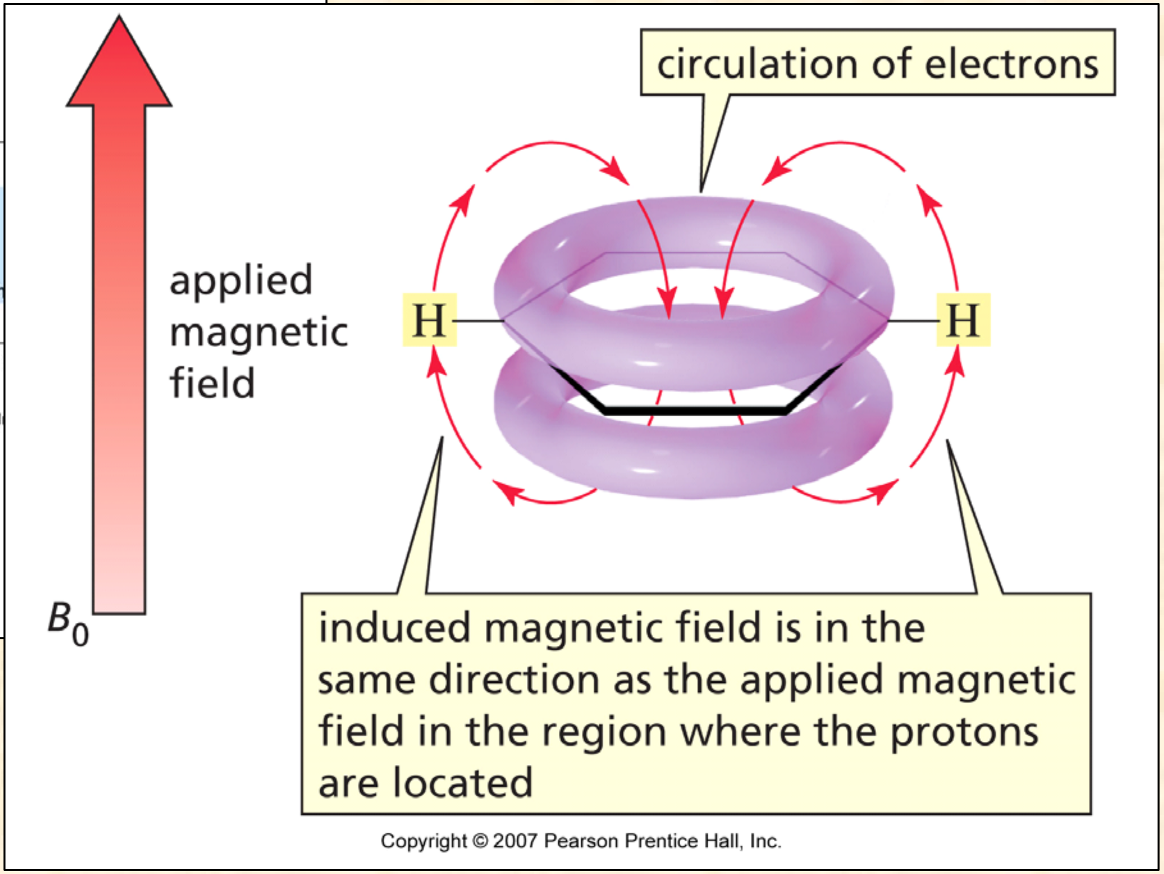


General Aspects – ^{1}H NMR Spectroscopy

Chemical Shift



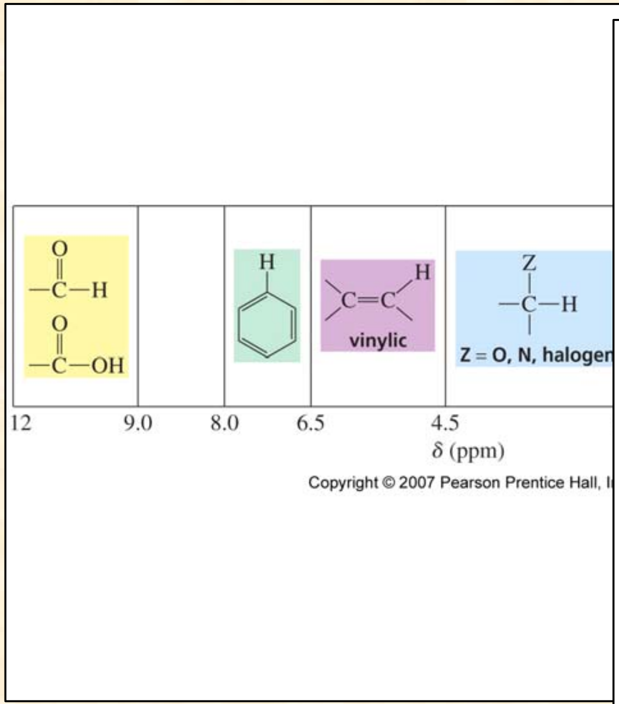
$$\nu_1 = (\gamma/2\pi)\,\boldsymbol{B}_0$$

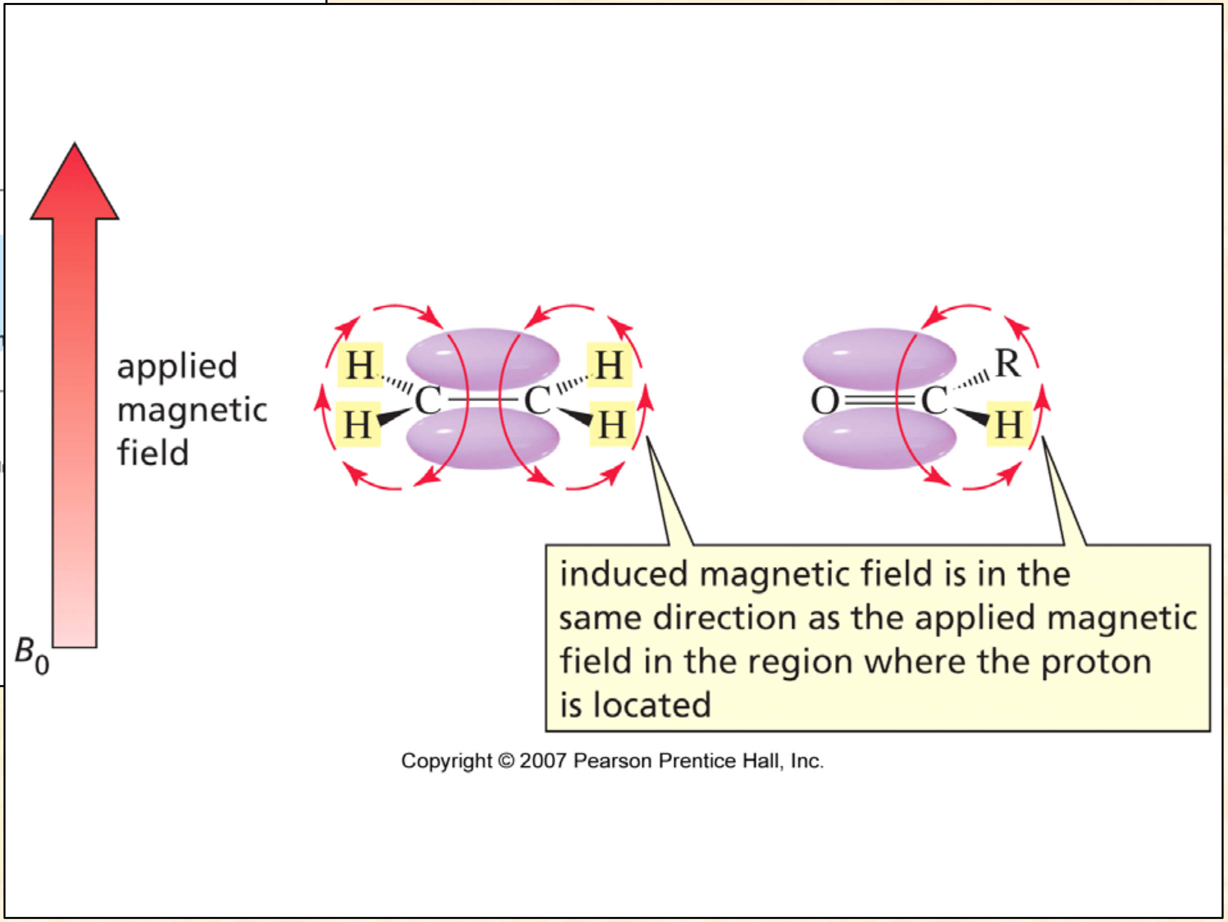


General Aspects – ^{1}H NMR Spectroscopy

Chemical Shift

Diamagnetic anisotropy





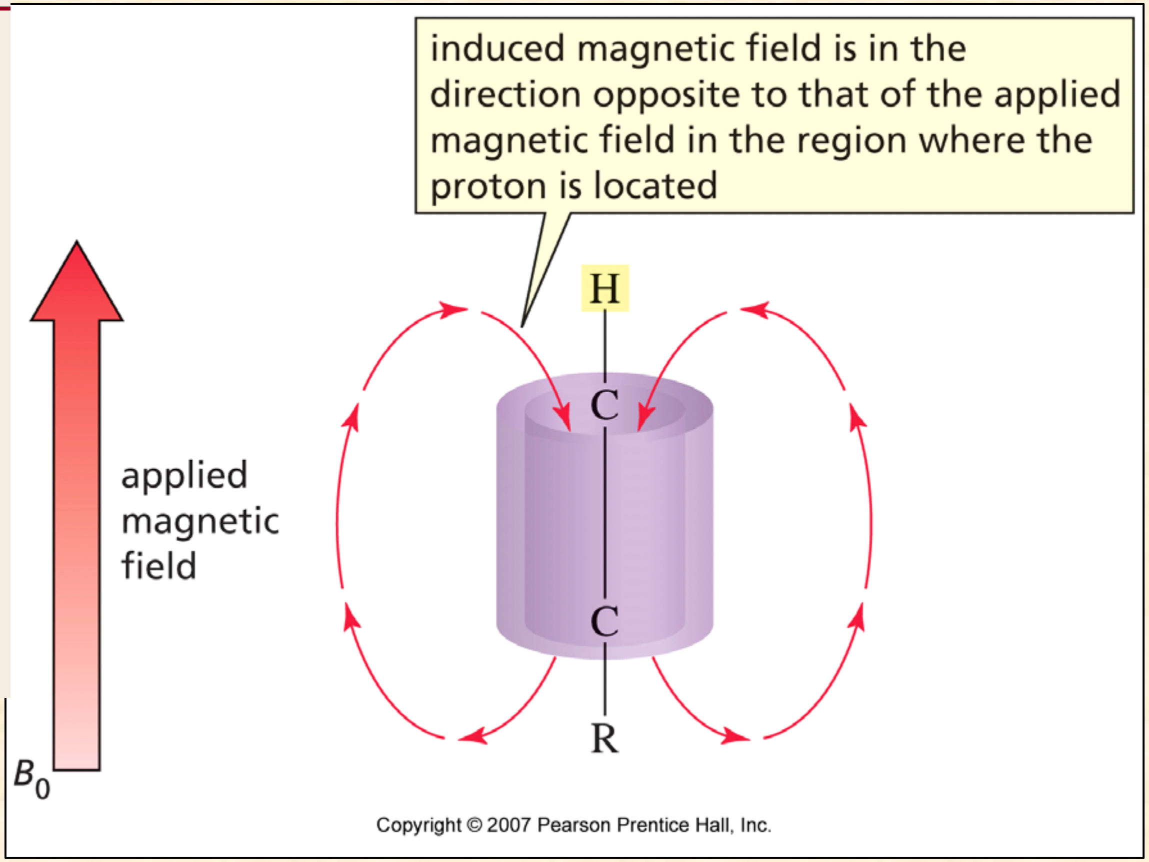
$$\nu_1 = (\gamma/2\pi)\, B_0$$

General Aspects – [1]H NMR Spectroscopy

Chemical Shift

Diamagnetic anisotropy

Type of proton	Approximate chemical shift (ppm)
$—CH_3$	0.85
$—CH_2—$	1.20
$—\overset{\vert}{C}H—$	1.55
$—C{=}C—CH_3$	1.7
$—C(=O)—CH_3$	2.1
$C_6H_5—CH_3$	2.3
$—C{\equiv}C—H$	2.4

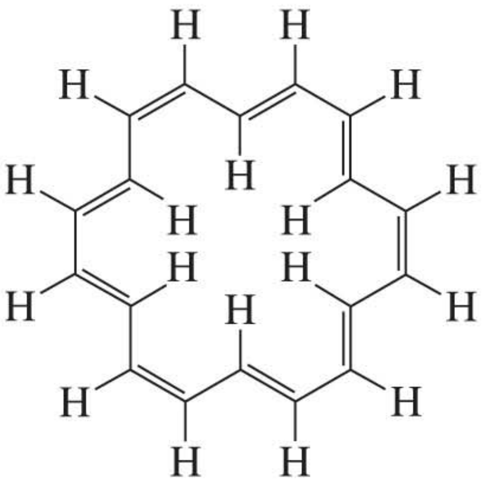


Chemical Shift

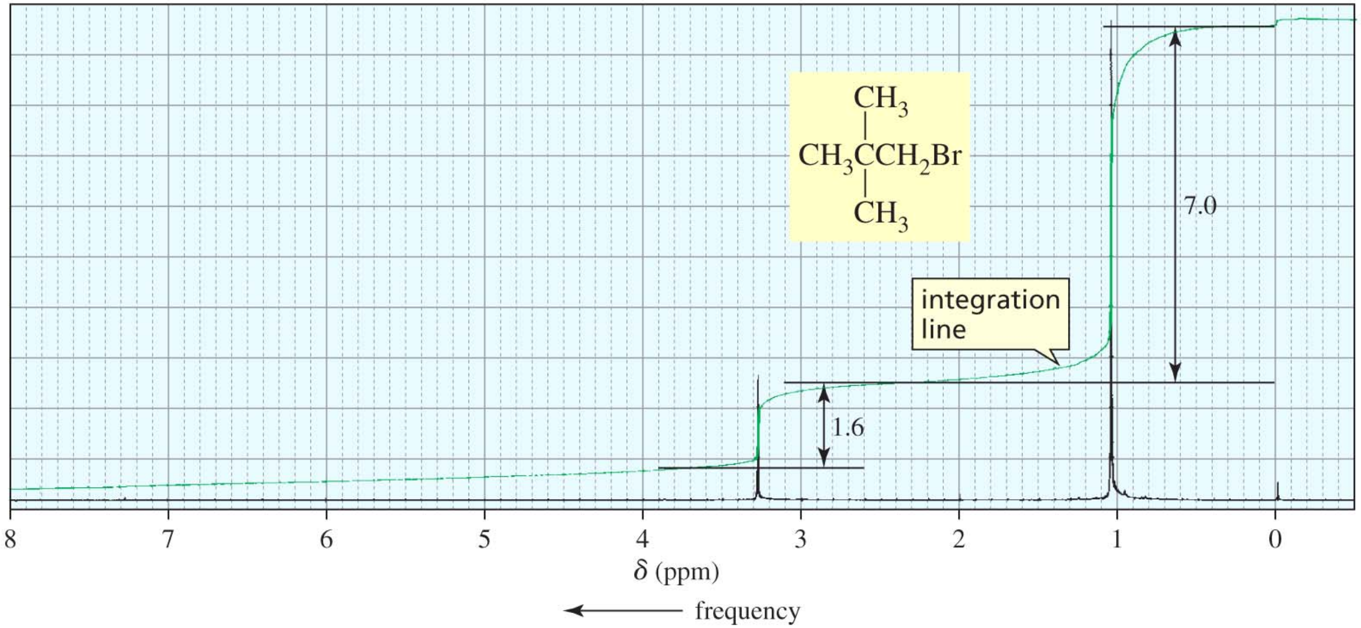
Diamagnetic anisotropy

PROBLEM 14◆

[18]-Annulene shows two signals in its ^{1}H NMR spectrum: one at 9.25 ppm and the other very far upfield (to the right of the TMS signal) at −2.88 ppm. What hydrogens are responsible for each of the signals? (*Hint:* Look at the direction of the induced magnetic field outside and inside the benzene ring in Figure 13.6.)



Integration



General Aspects – ¹H NMR Spectroscopy

Integration

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

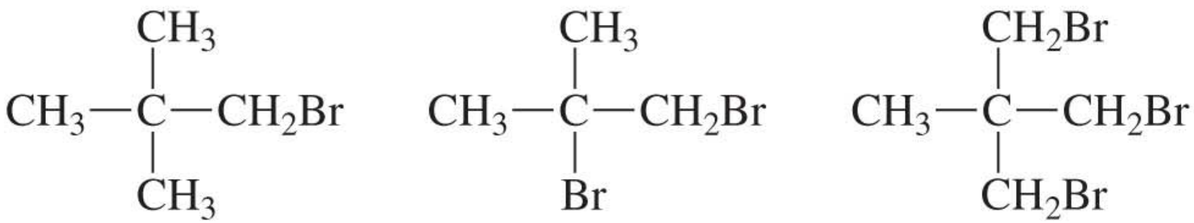
1,2-dichloro-2-methylpropane
ratio of protons 2:6 = 1:3

General Aspects – ^{1}H NMR Spectroscopy

Integration

PROBLEM 15◆

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



General Aspects – ^{1}H NMR Spectroscopy

Integration

PROBLEM 17◆

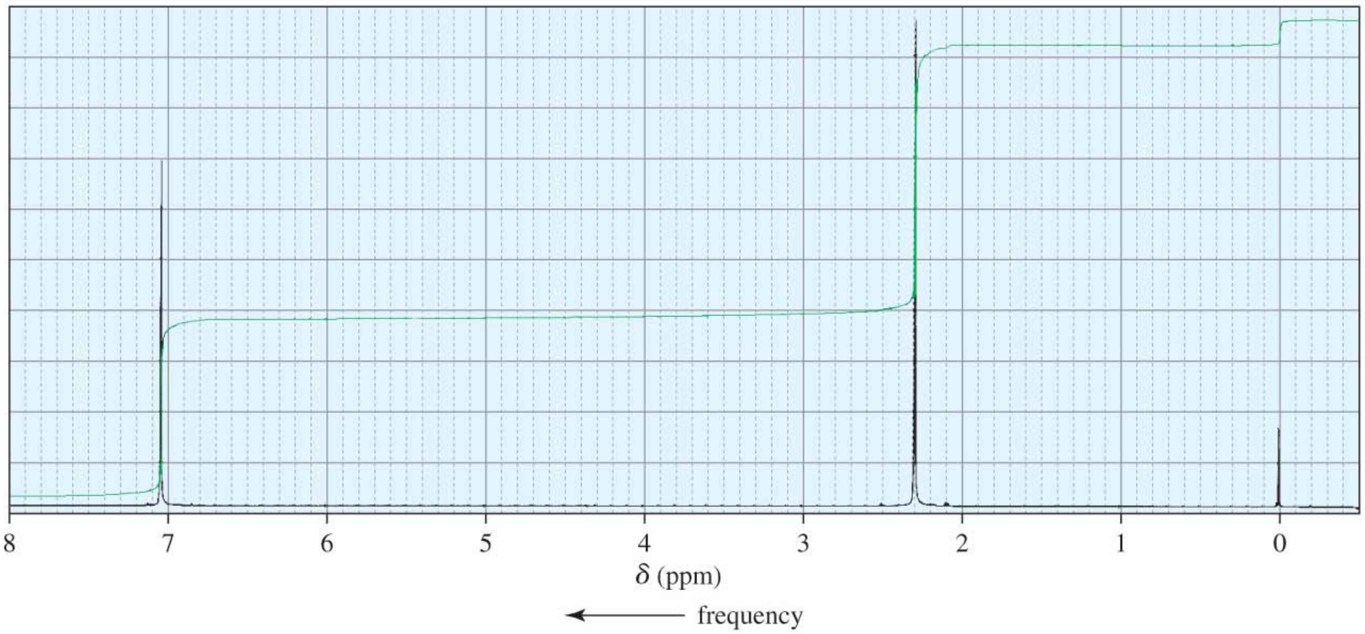
The ^{1}H NMR spectrum shown in Figure 13.10 corresponds to one of the following compounds. Which compound is responsible for this spectrum?


A


B


C

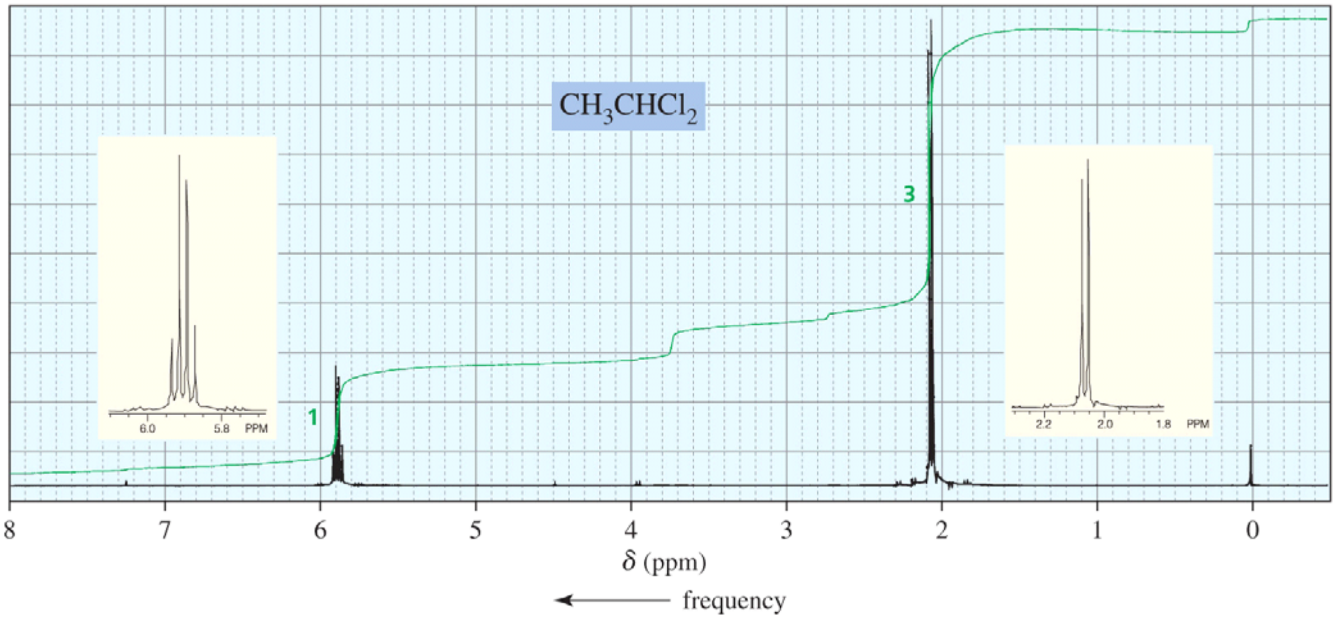

D



▲ Figure 13.10
The ^{1}H NMR spectrum for Problem 17.

General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling splitting of the signals

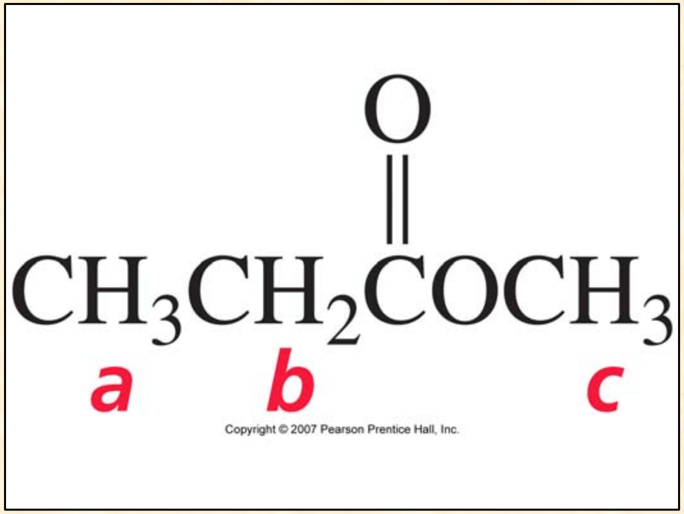


General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling   splitting of the signals

N+1 rule

(2I+1 in general)



General Aspects – ^{1}H NMR Spectroscopy

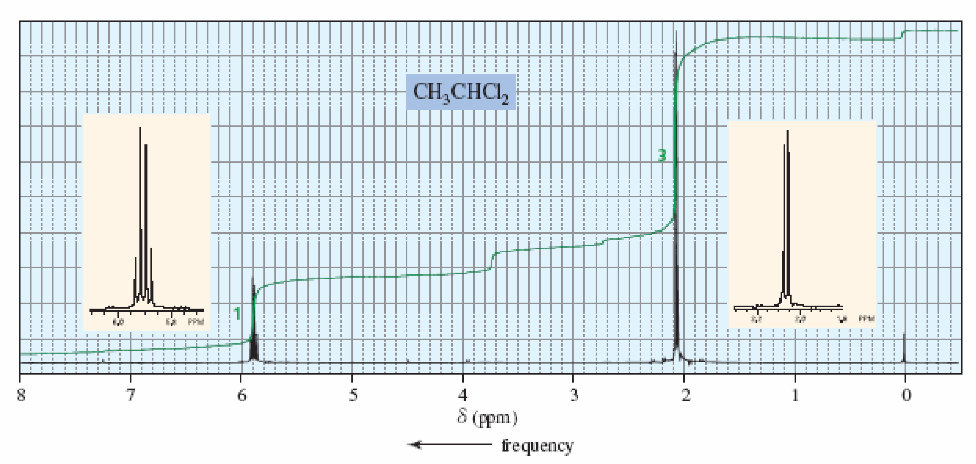
Spin-Spin Coupling   splitting of the signals

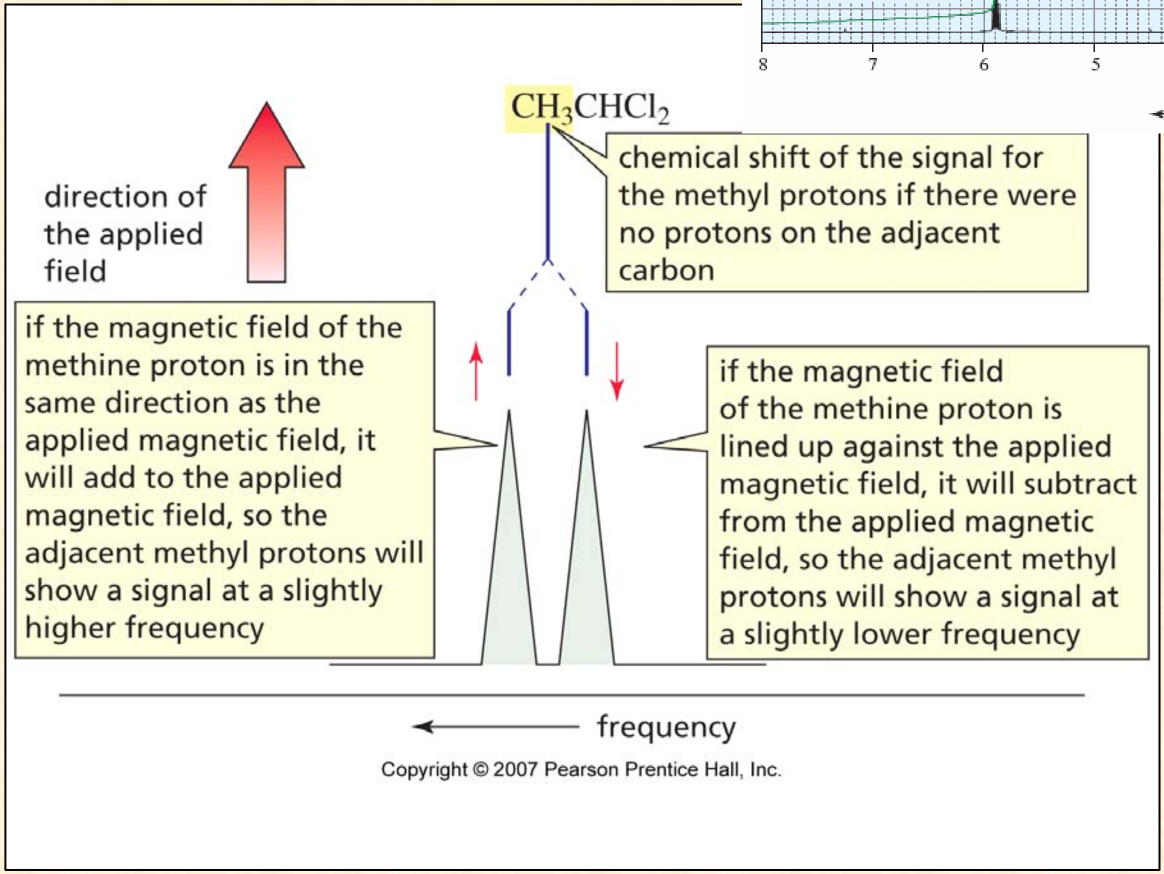
CH_3Br
bromomethane

$ClCH_2CH_2Cl$
1,2-dichloroethane

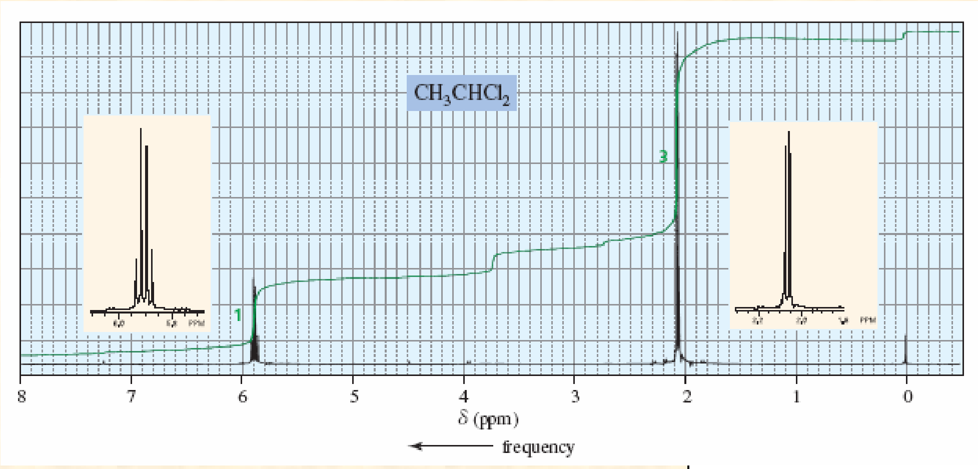
each compound has an NMR spectrum that shows one singlet because equivalent protons do not split each other's signals

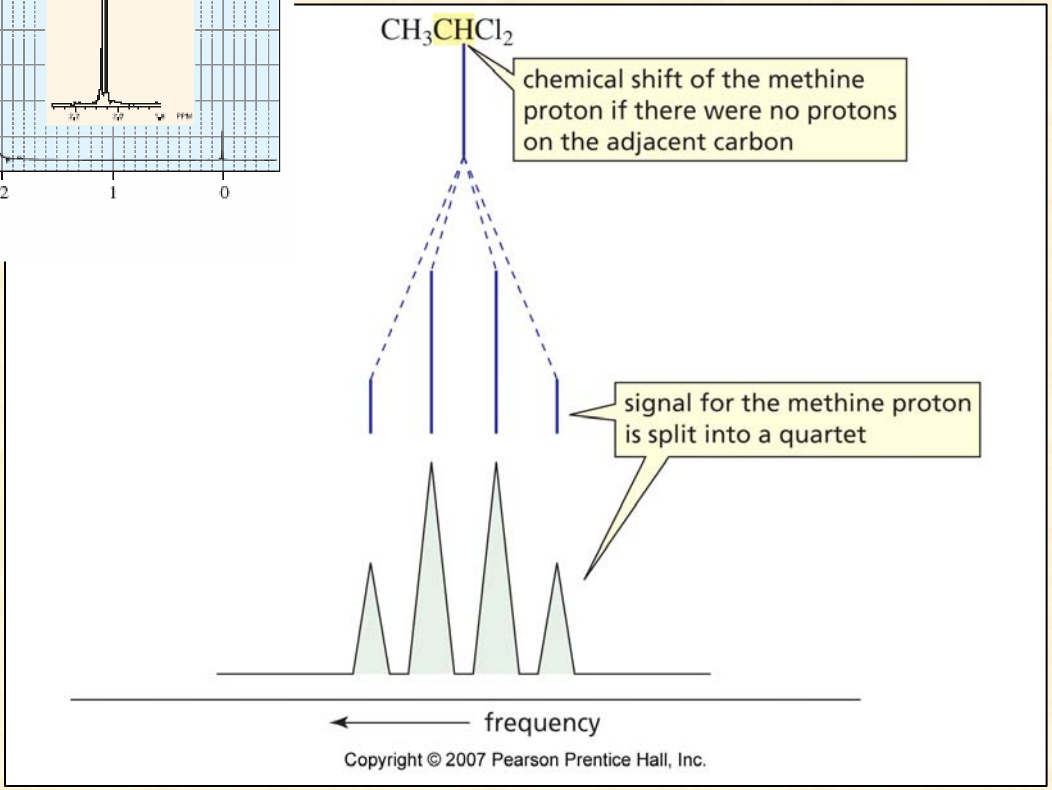
Spin-Spin Coupling



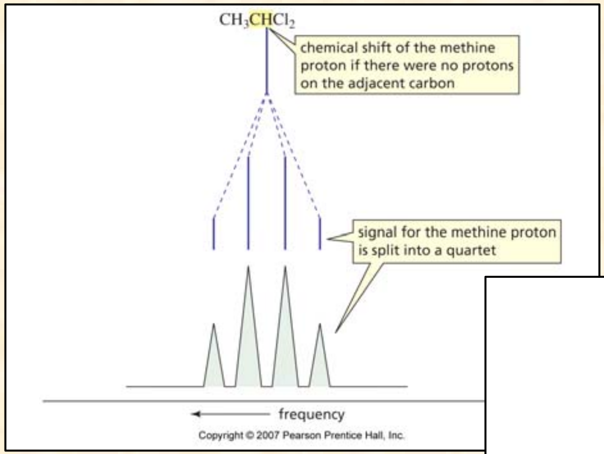


Spin-Spin Coupling

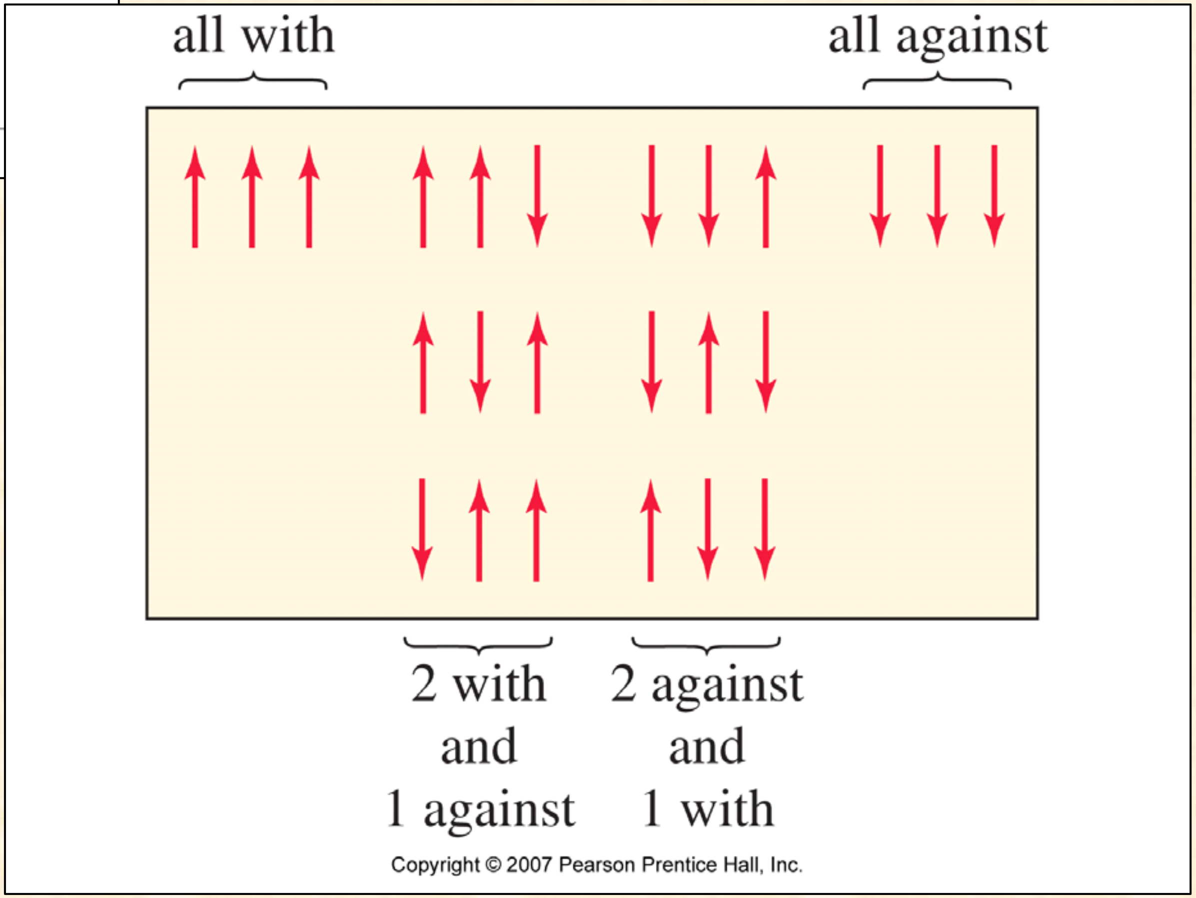




General Aspects – ^{1}H NMR Spectroscopy



Spin-Spin Coupling



General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling

Table 13.2 Multiplicity of the Signal and Relative Intensities of the Peaks in the Signal

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

Spin-Spin Coupling

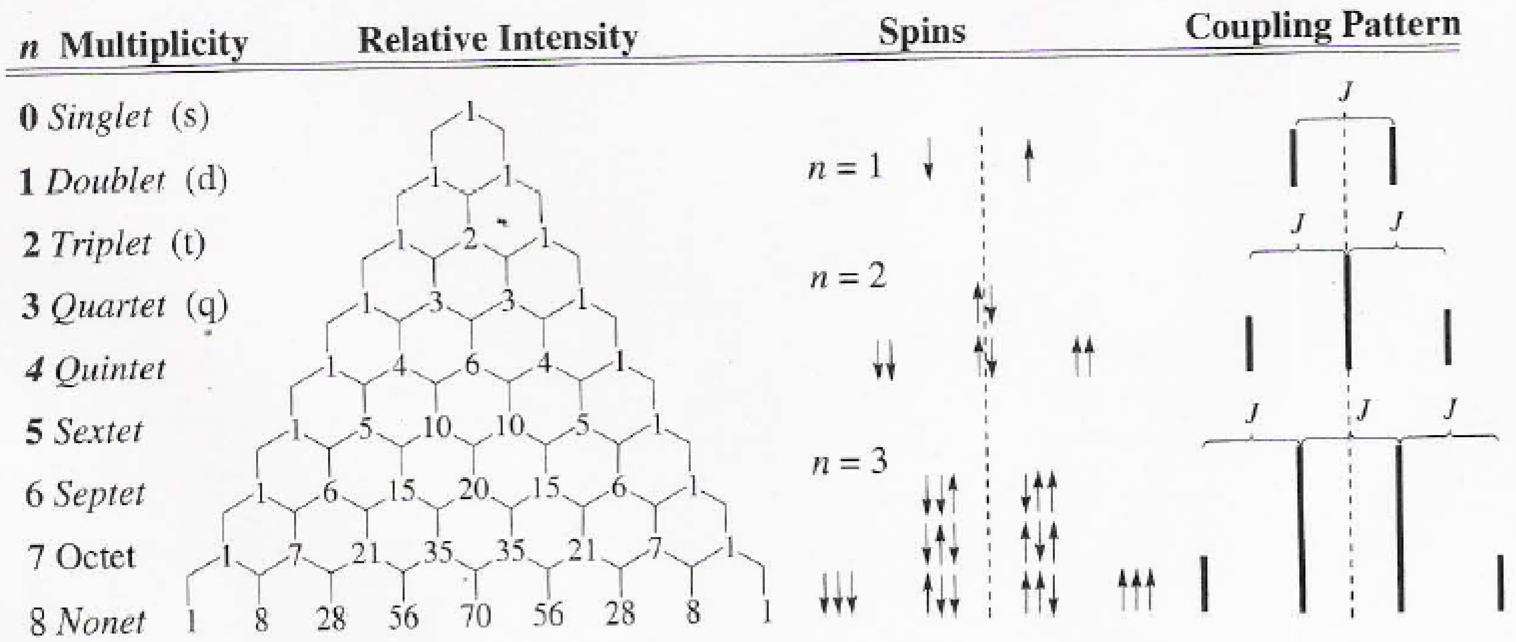
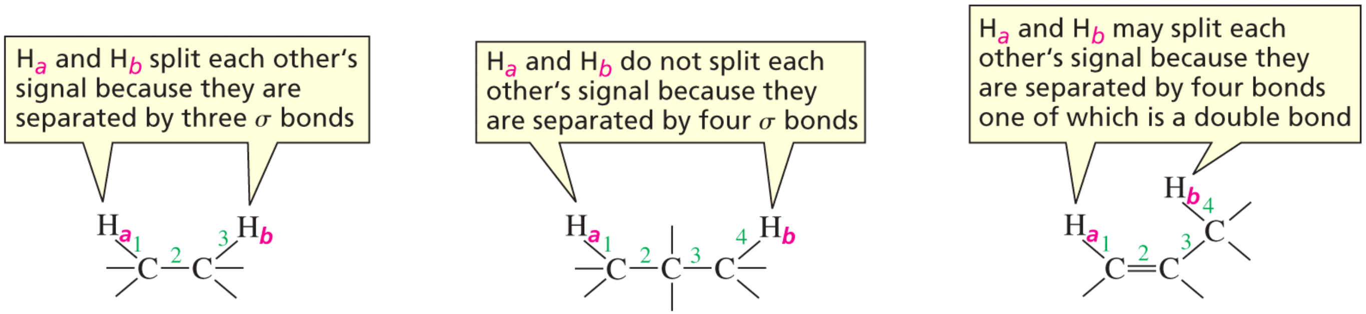


FIGURE 3.32 Pascal's triangle. Relative intensities of first-order multiplets; *n* = number of equivalent coupling nuclei of spin 1/2 (e.g., protons).

General Aspects – ^{1}H NMR Spectroscopy

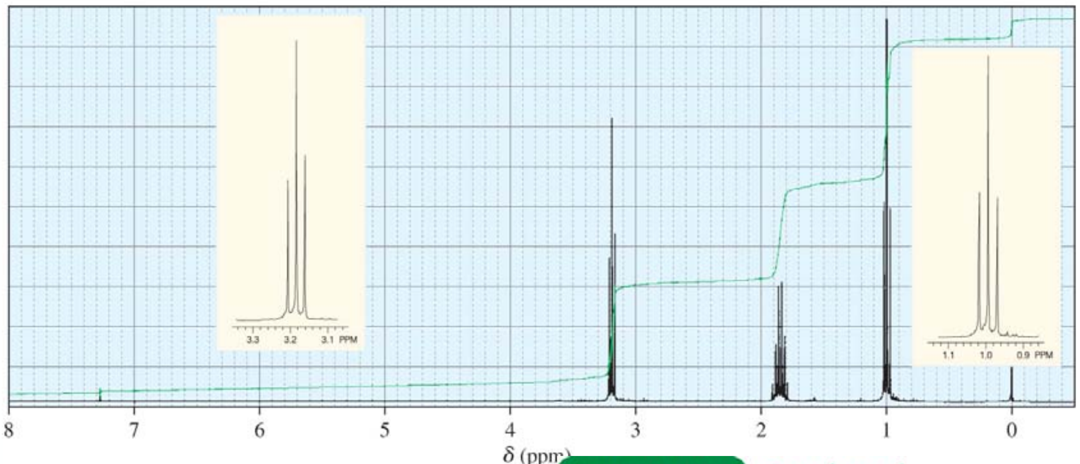
Spin-Spin Coupling   long range splitting



General Aspects – ^{1}H NMR Spectroscopy

PROBLEM 18◆

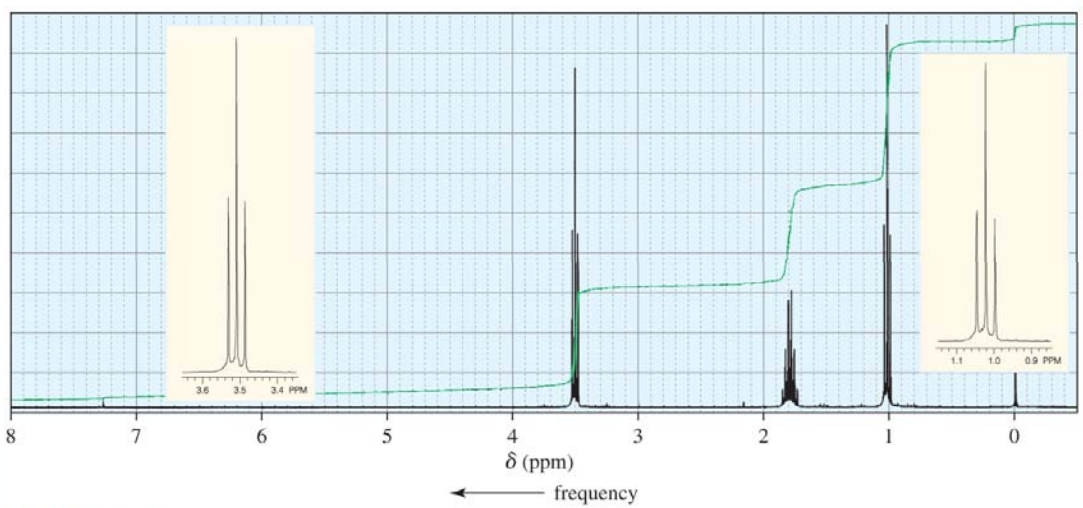
One of the spectra in Figure 13.15 is produced by 1-chloropropane, and the other by 1-iodopropane. Which is which?



▲ Figure 13.15
The ^{1}H NMR spectrum for Problem 18.

Spin-Spin Coupling

PROBLEM 18◆ *Continued*



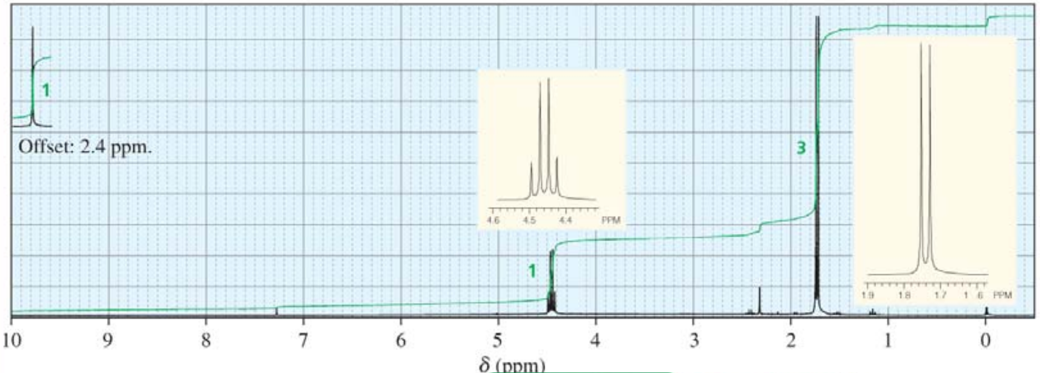
▲ Figure 13.15
Continued

General Aspects – ^{1}H NMR Spectroscopy

PROBLEM 20◆

The ^{1}H NMR spectra of two carboxylic acids with molecular formula $C_3H_5O_2Cl$ are shown in Figure 13.16. Identify the carboxylic acids. (The "offset" notation means that the farthest-left signal has been moved to the right by the indicated amount in order to fit on the spectrum; thus, the signal at 9.8 ppm offset by 2.4 ppm has an actual chemical shift of 12.2 ppm.)

a.

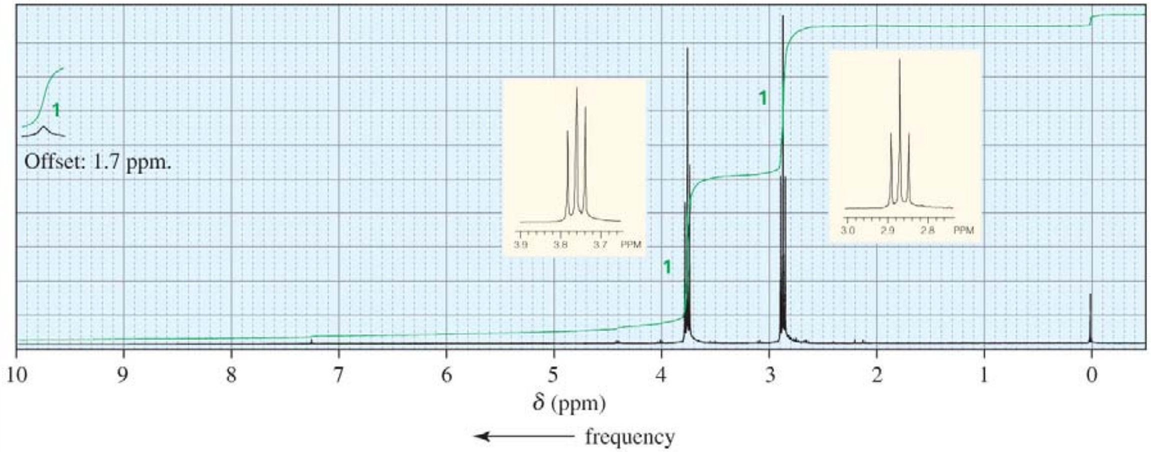


▲ **Figure 13.16a**
The ^{1}H NMR spectra for Problem 20.

[Spin-Spin Coupling](#)

PROBLEM 20◆ ***Continued***

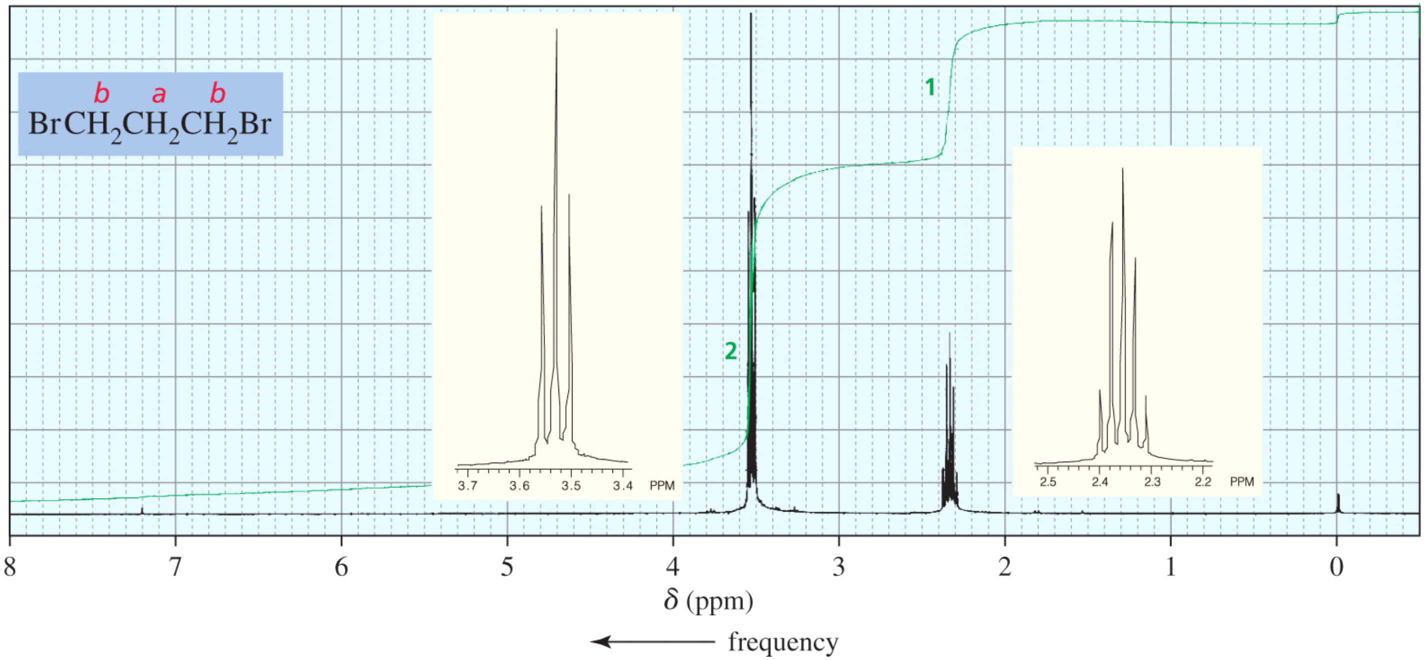
b.



▲ **Figure 13.16b**

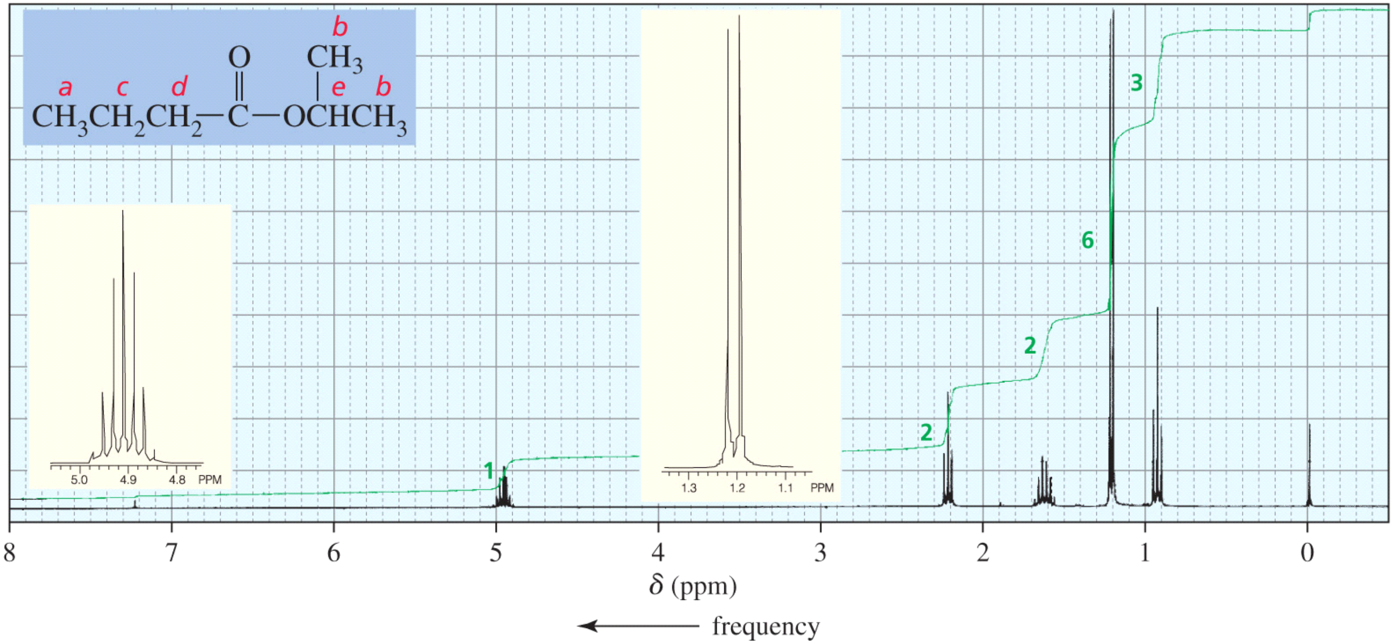
General Aspects – ¹H NMR Spectroscopy

Spin-Spin Coupling

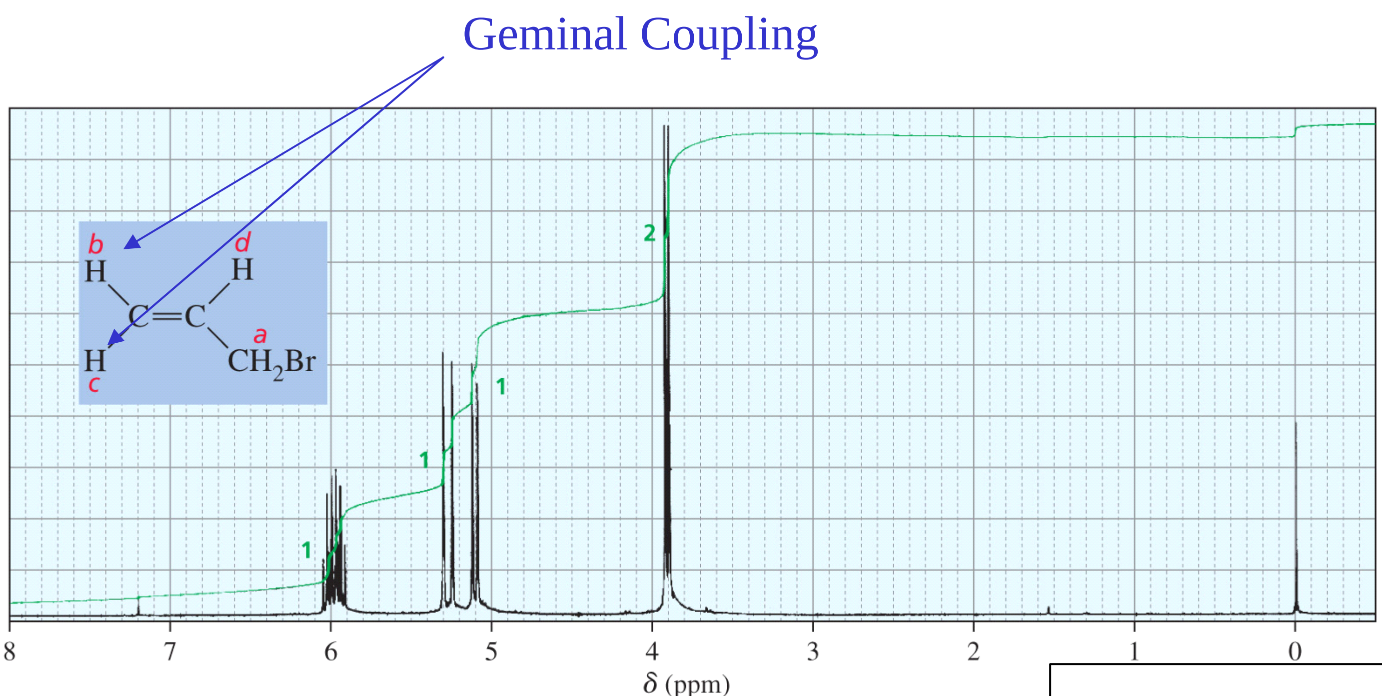


General Aspects – ¹H NMR Spectroscopy

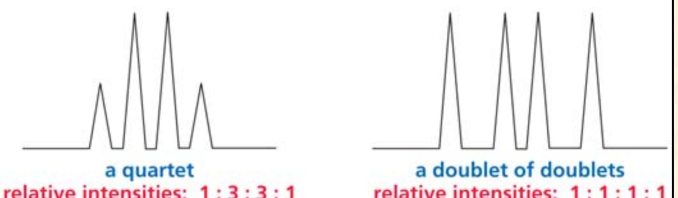
Spin-Spin Coupling



General Aspects – ^{1}H NMR Spectroscopy

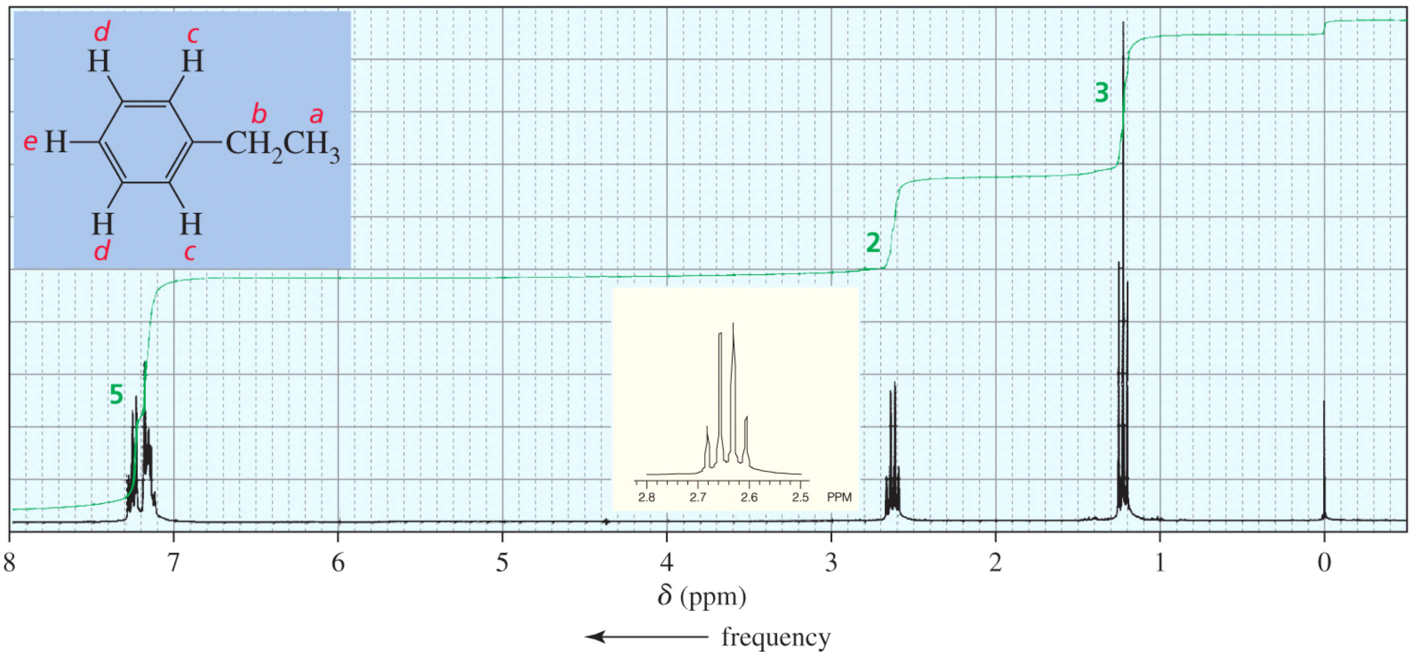


Spin-Spin Coupling



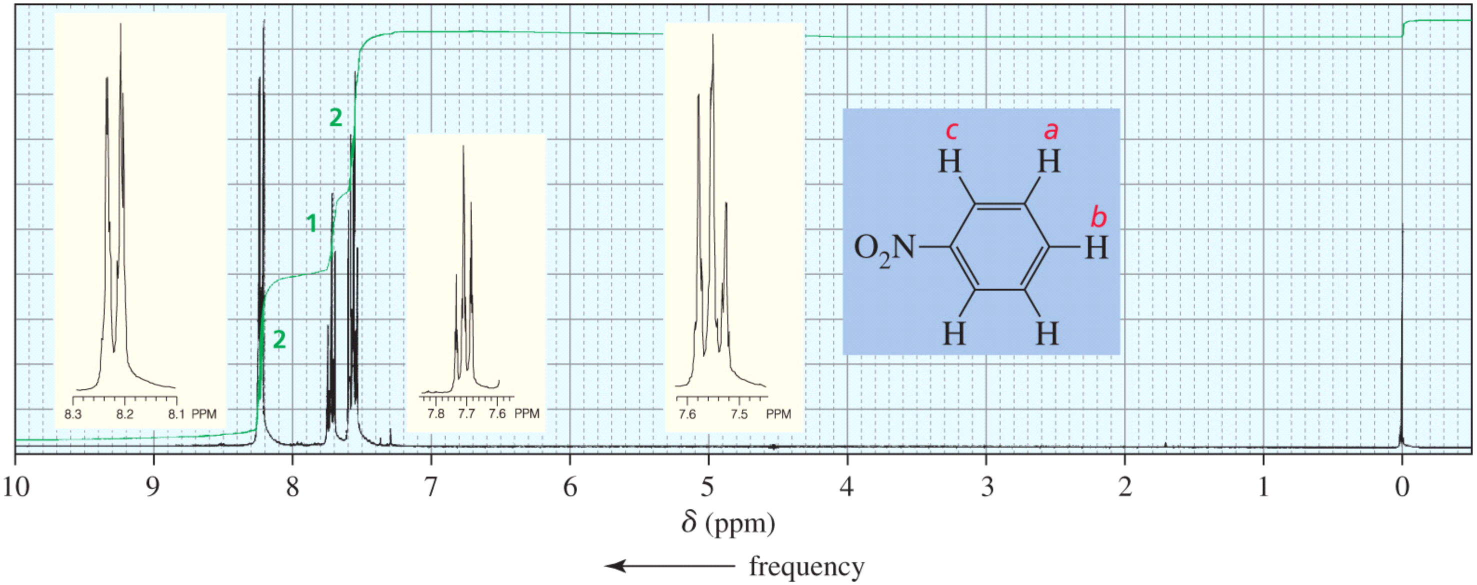
General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling



General Aspects – ¹H NMR Spectroscopy

Spin-Spin Coupling



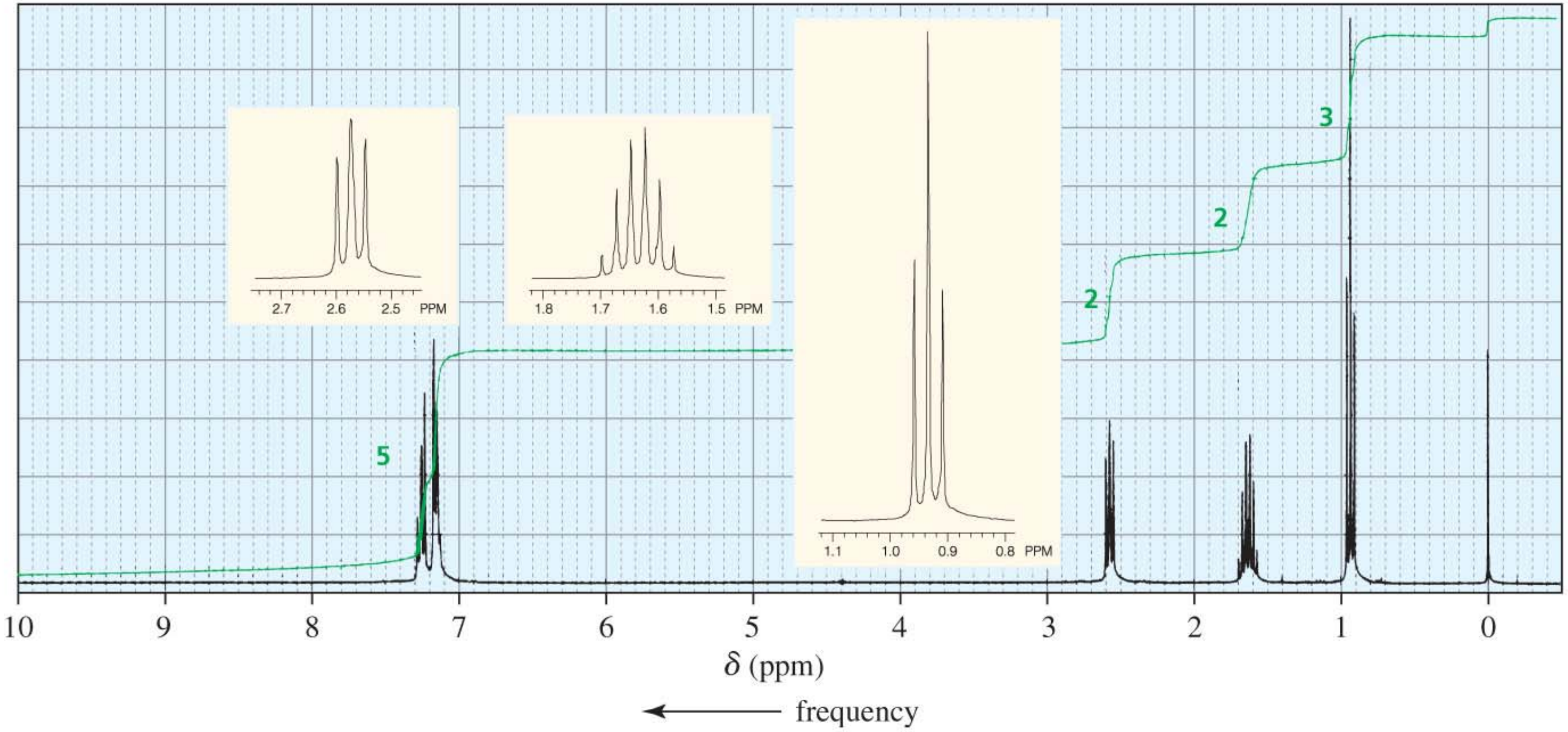
General Aspects – ¹H NMR Spectroscopy

Spin-Spin Coupling

PROBLEM 25◆

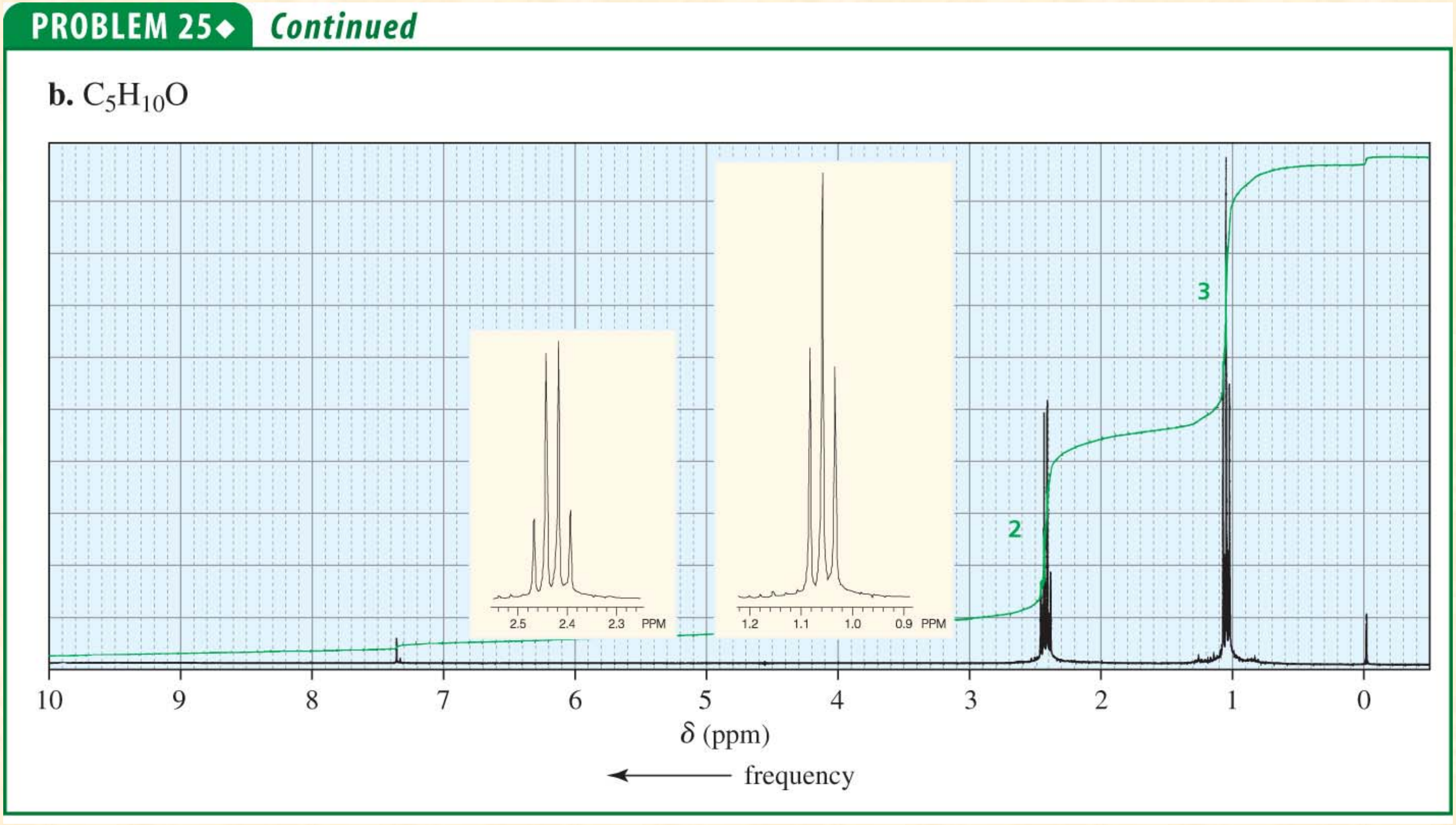
Identify each compound from its molecular formula and its ¹H NMR spectrum:

a. C_9H_{12}



General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling



Spin-Spin Coupling

PROBLEM 27◆

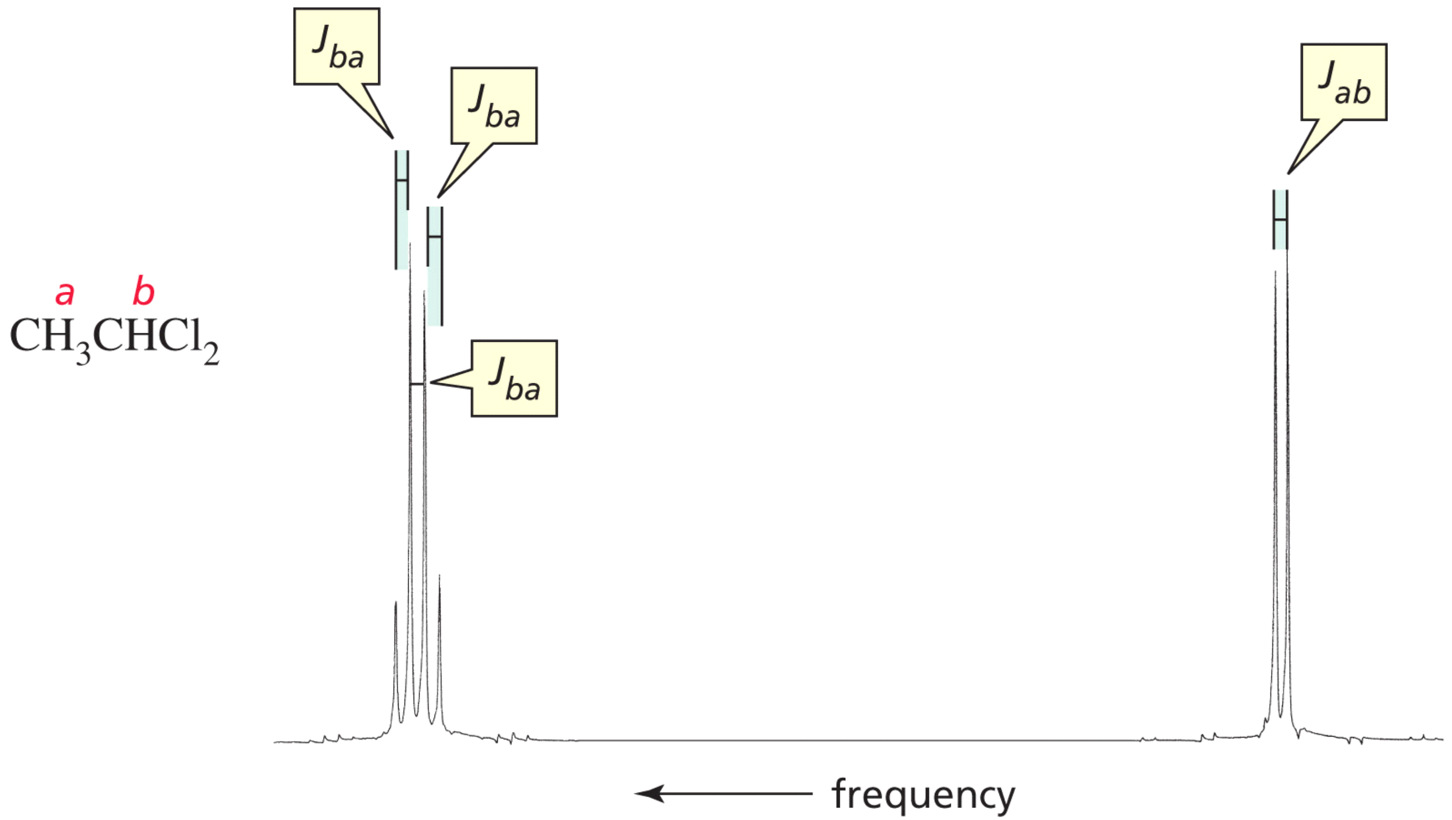
Identify the following compounds. (Relative integrals are given from left to right across the spectrum.)

a. The ^{1}H NMR spectrum of a compound with molecular formula $C_4H_{10}O_2$ has two singlets with an area ratio of 2 : 3.

b. The ^{1}H NMR spectrum of a compound with molecular formula $C_6H_{10}O_2$ has two singlets with an area ratio of 2 : 3.

c. The ^{1}H NMR spectrum of a compound with molecular formula $C_8H_6O_2$ has two singlets with an area ratio of 1 : 2.

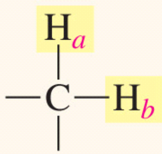
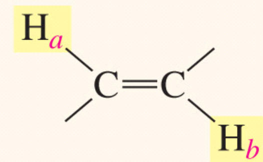
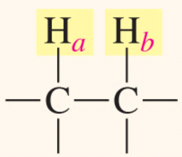
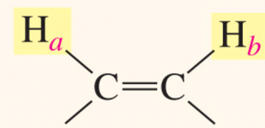
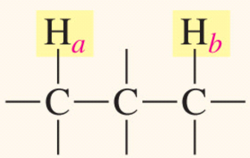
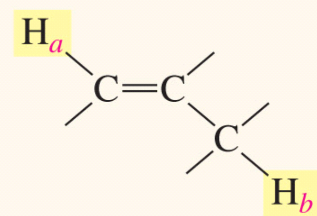
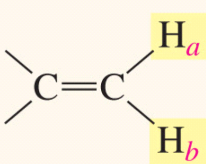
Spin-Spin Coupling – Coupling Constant



General Aspects – ¹H NMR Spectroscopy

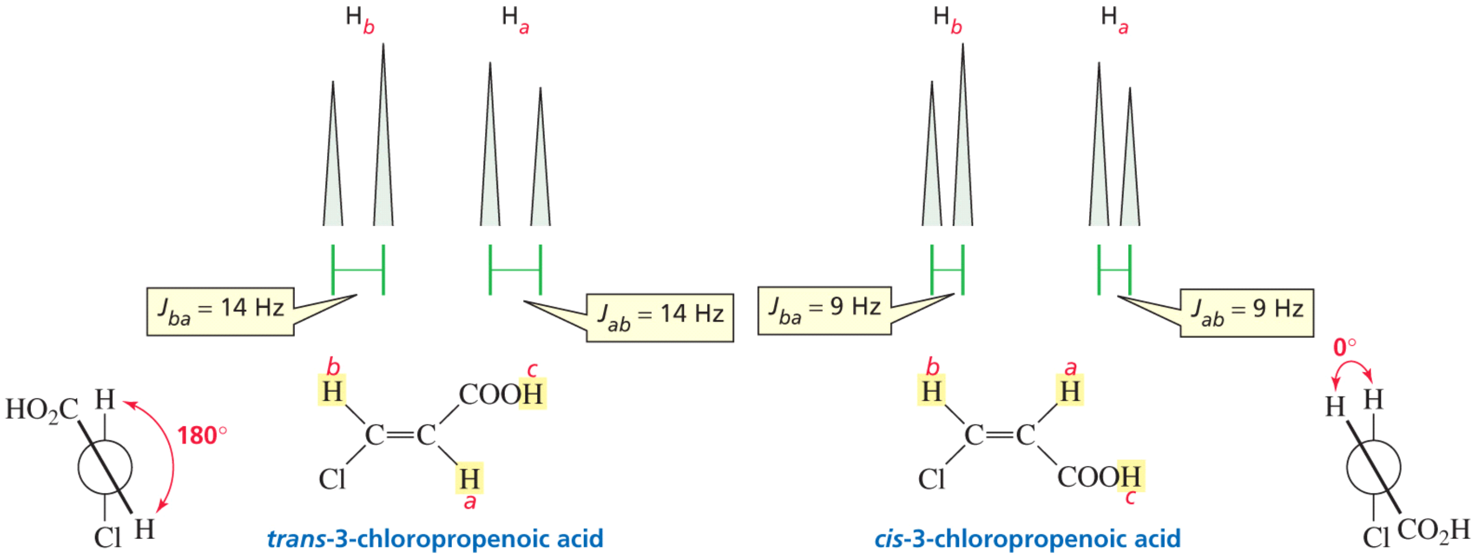
Spin-Spin Coupling – Coupling Constant

Table 13.3 Approximate Values of Coupling Constants

Approximate value of J_{ab} (Hz)		Approximate value of J_{ab} (Hz)	
	12		15 (trans)
	7		10 (cis)
	0		1 (long-range coupling)
	2 (geminal coupling)		

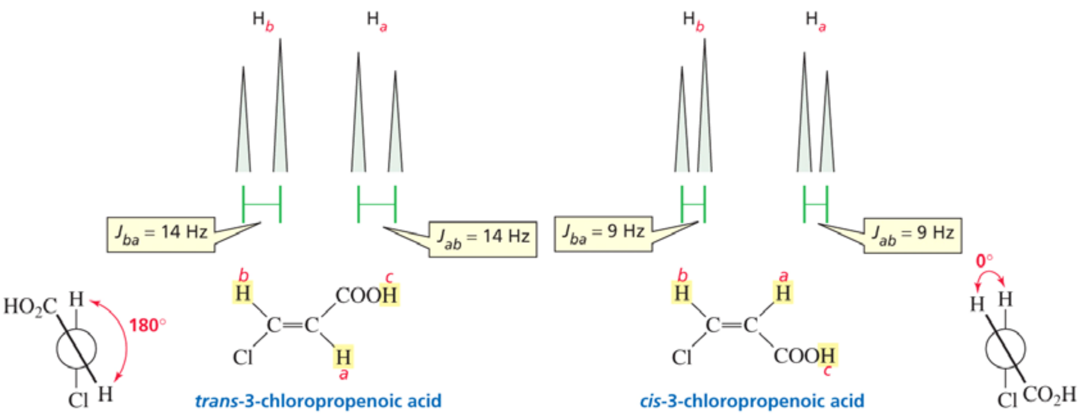
General Aspects – ¹H NMR Spectroscopy

Spin-Spin Coupling – Coupling Constant



General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling – Coupling Constant

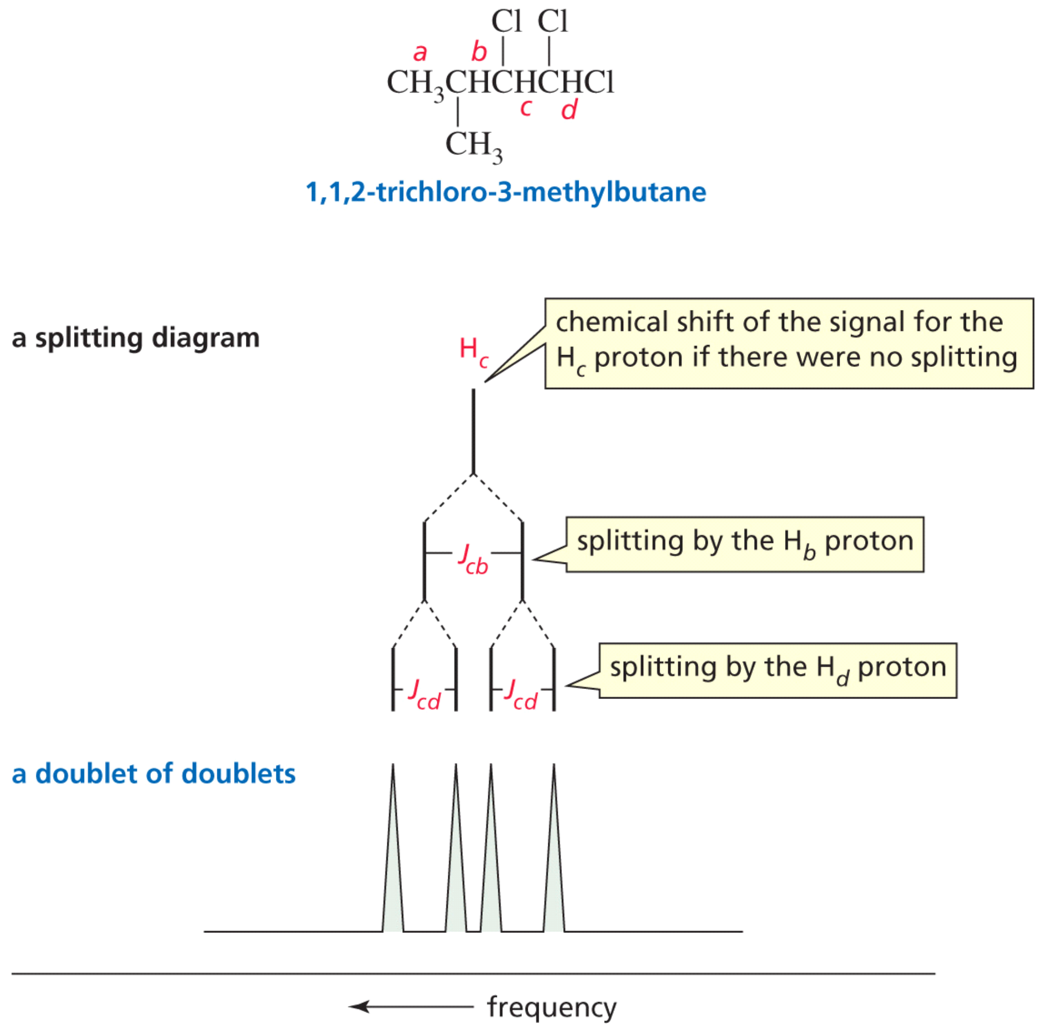


PROBLEM 29

Why is there no coupling between H_a and H_c or between H_b and H_c in *cis*- or *trans*-3-chloropropenoic acid?

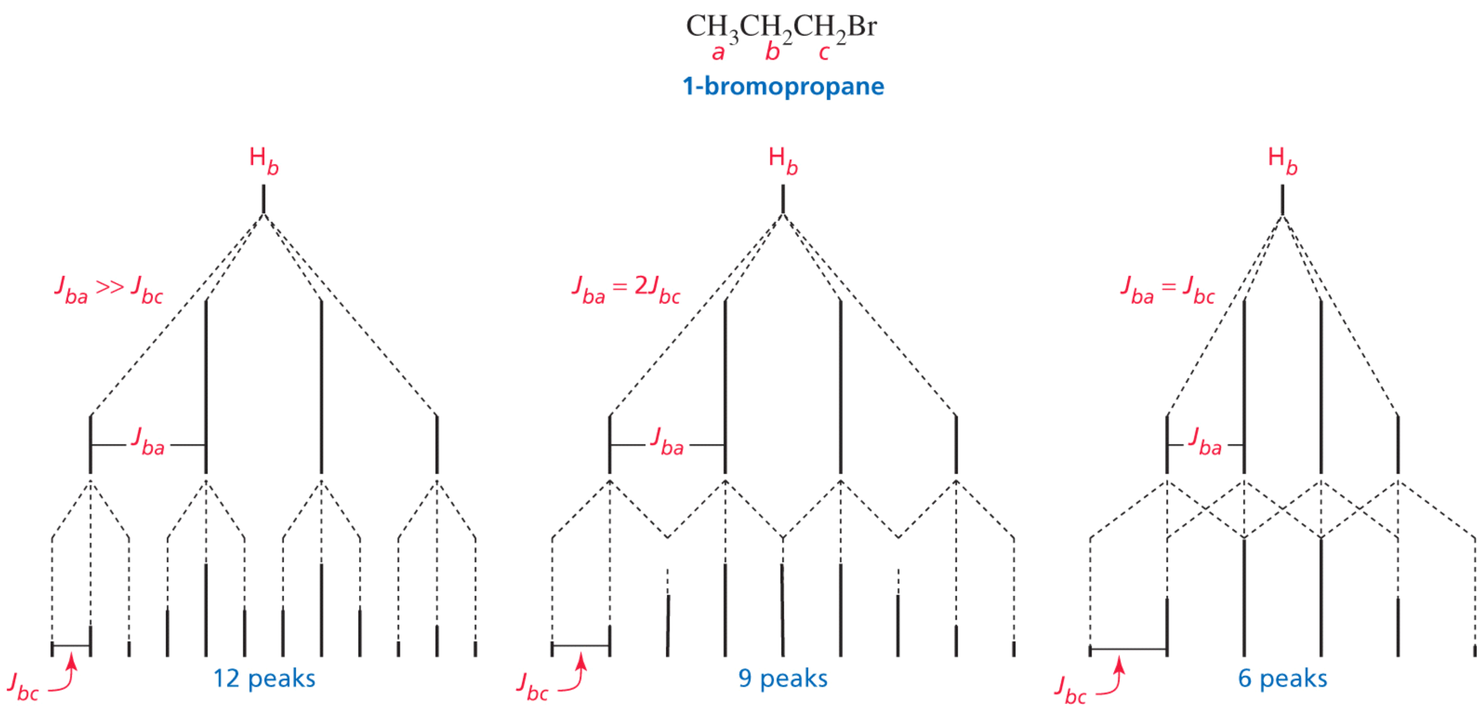
General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling – Splitting Diagram



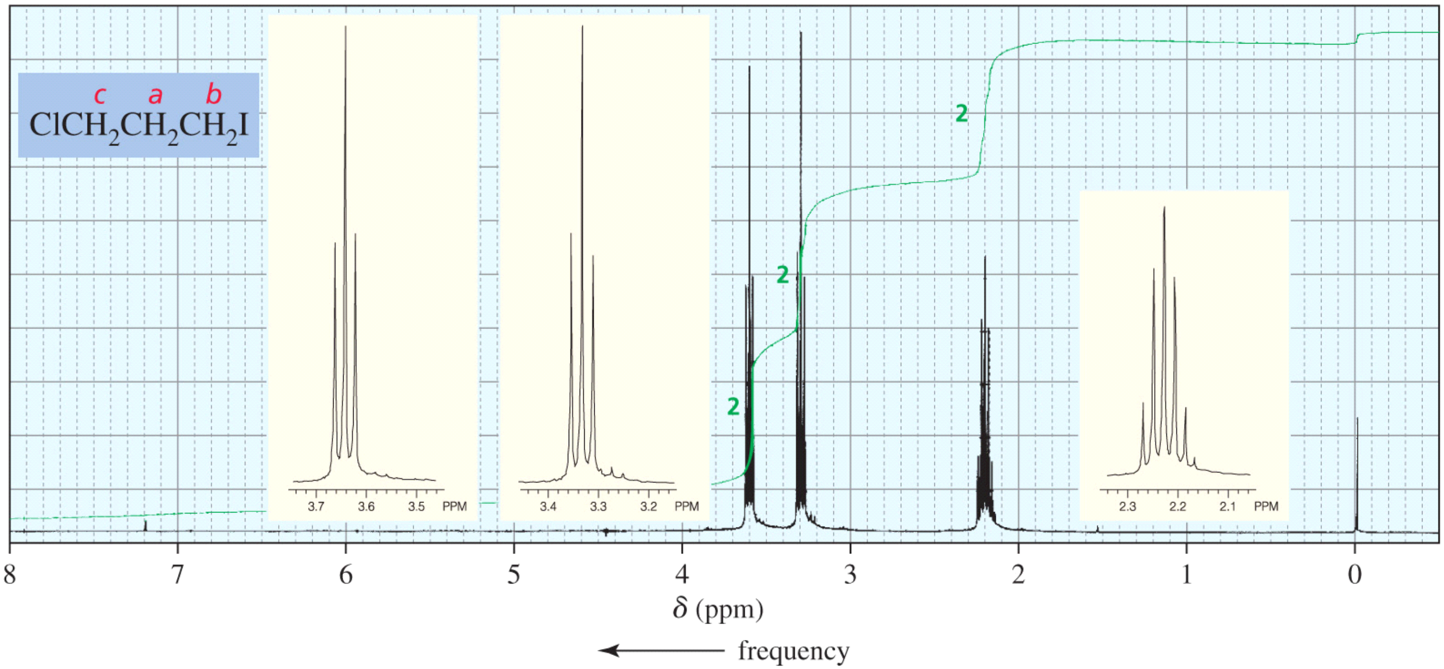
General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling – Splitting Diagram



General Aspects – ^{1}H NMR Spectroscopy

Spin-Spin Coupling – Splitting Diagram



General Aspects – ^{1}H NMR Spectroscopy

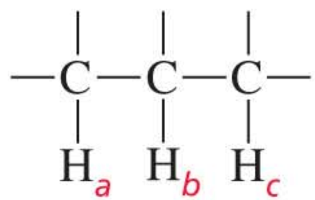
Spin-Spin Coupling – Splitting Diagram

PROBLEM 31

Draw a splitting diagram for H_b, where

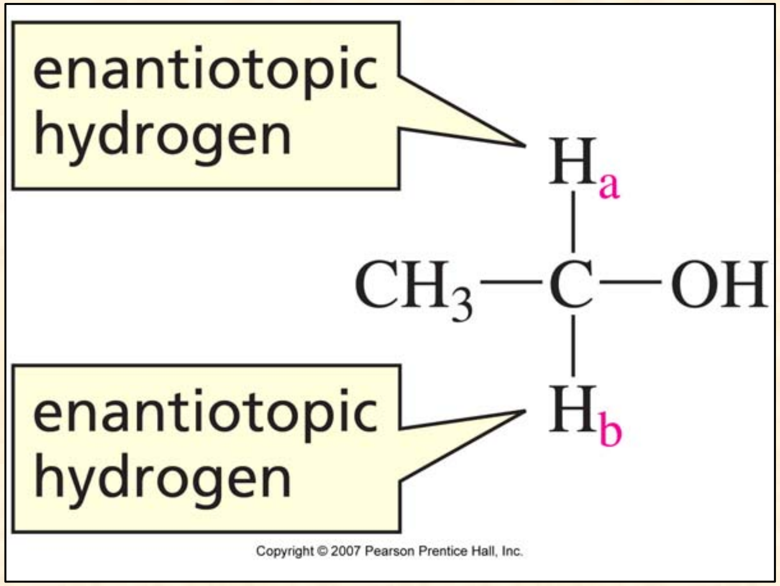
a. J_{ba} = 12 Hz and J_{bc} = 6 Hz.

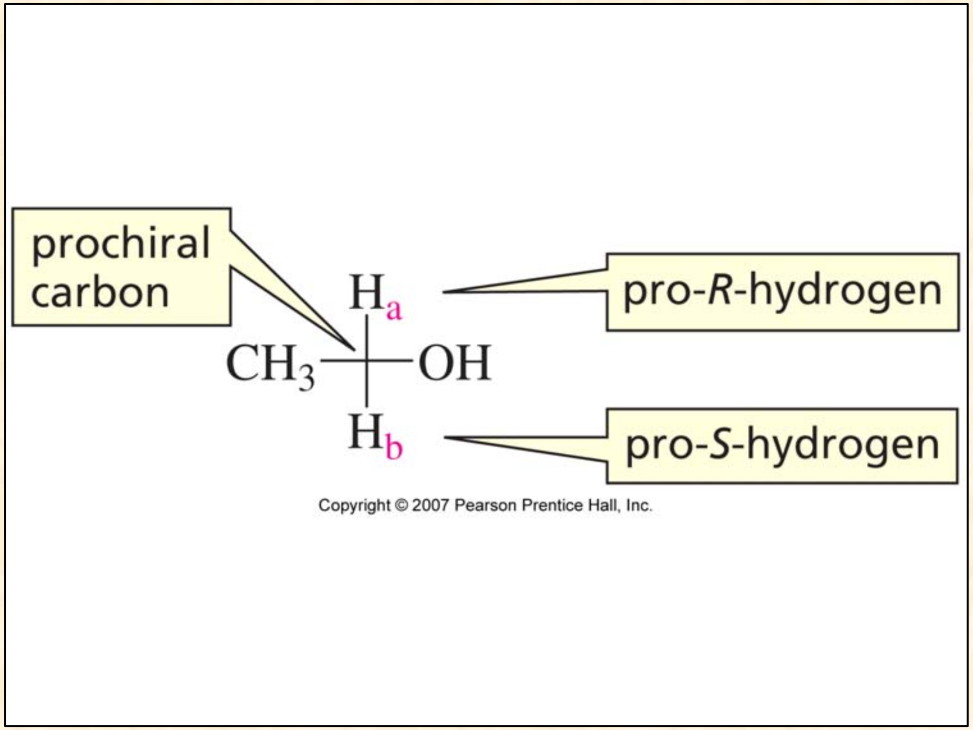
b. J_{ba} = 12 Hz and J_{bc} = 12 Hz.



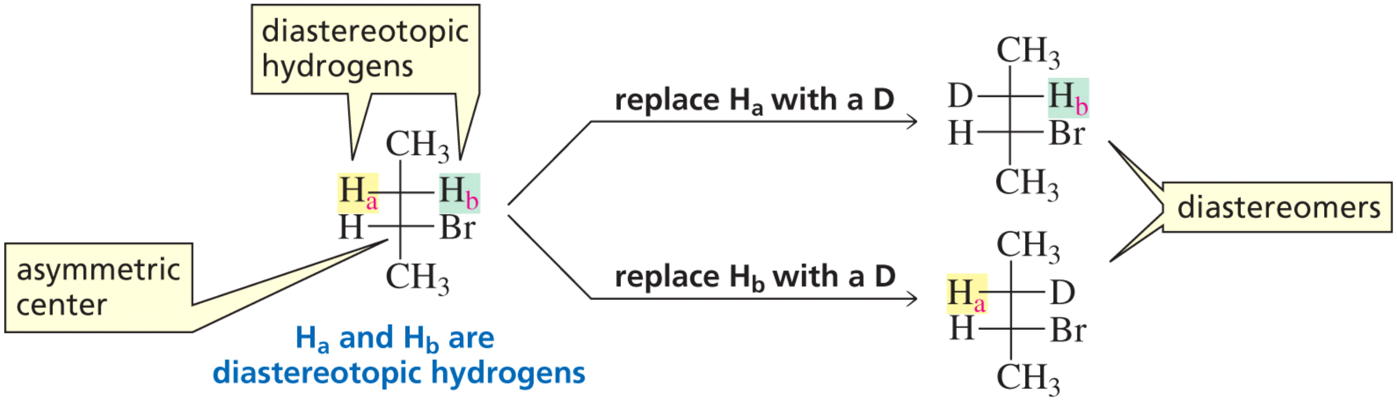
General Aspects – ¹H NMR Spectroscopy

Enantiotopic hydrogens



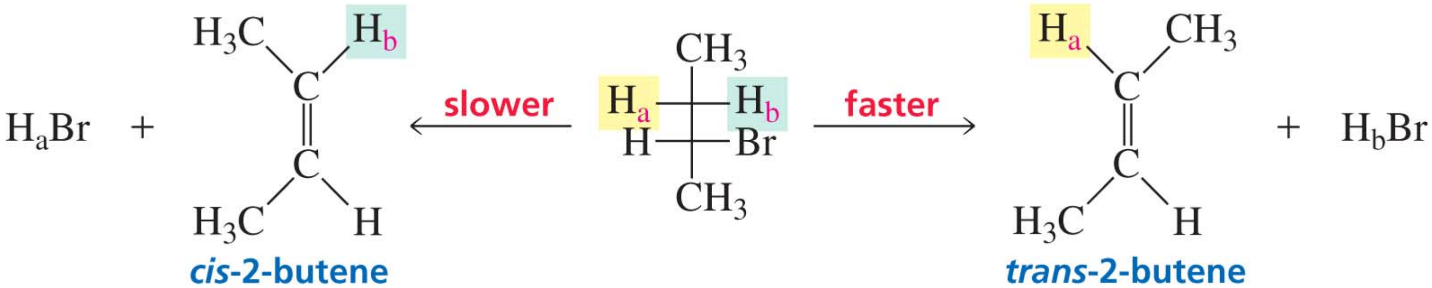


Diastereotopic hydrogens



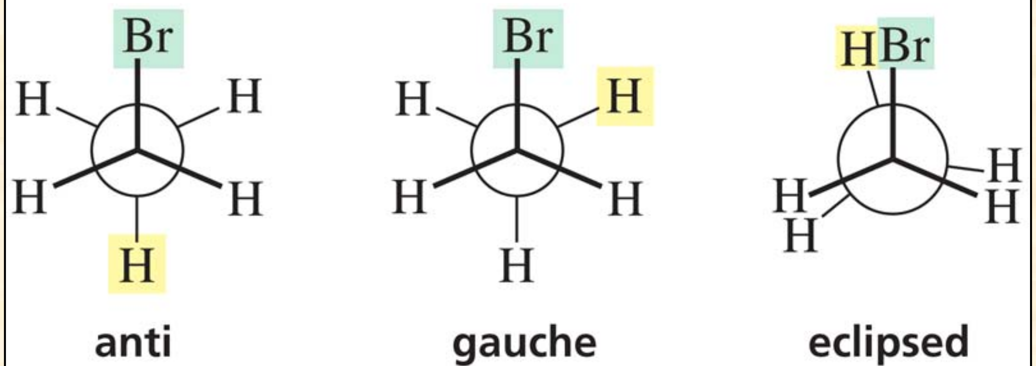
General Aspects – ¹H NMR Spectroscopy

Diastereotopic hydrogens



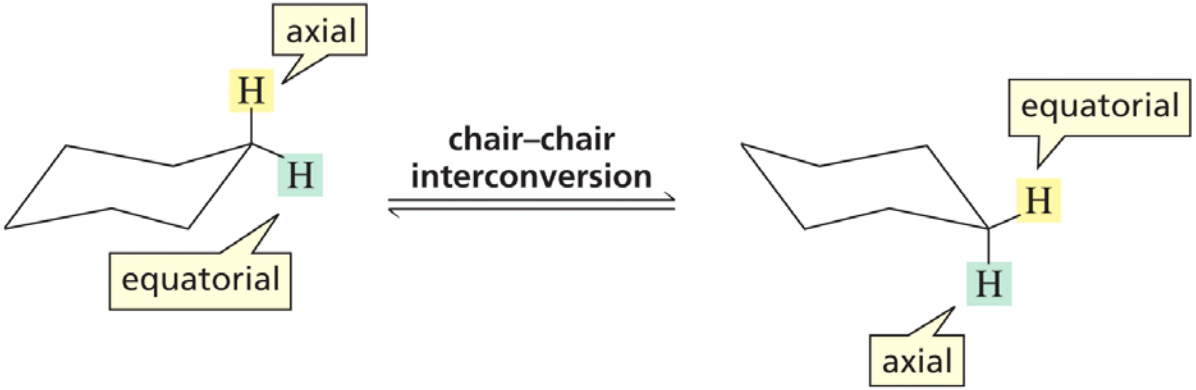
General Aspects – ^{1}H NMR Spectroscopy

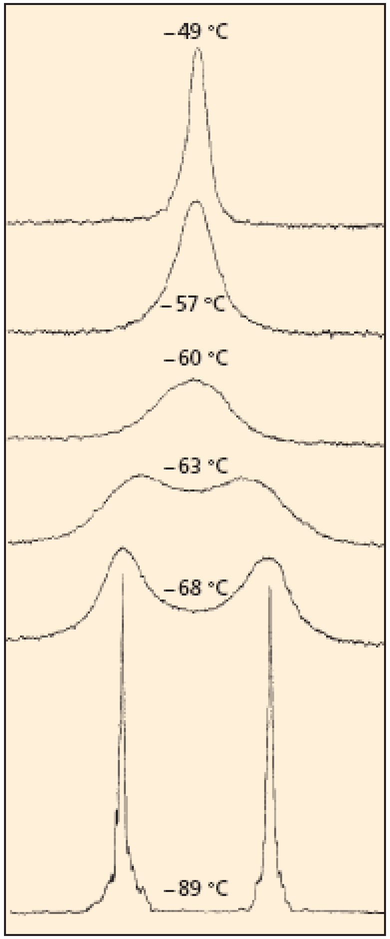
Time dependence - slow method



General Aspects – ^{1}H NMR Spectroscopy

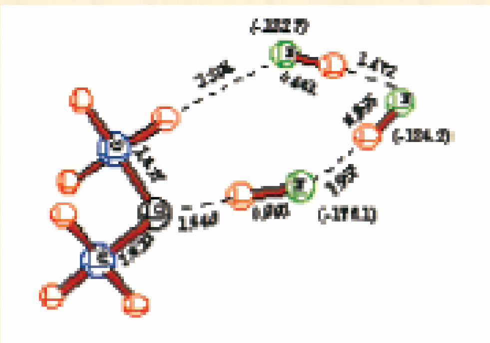
Time dependence - slow method





General Aspects – ^{1}H NMR Spectroscopy

Time dependence - slow method



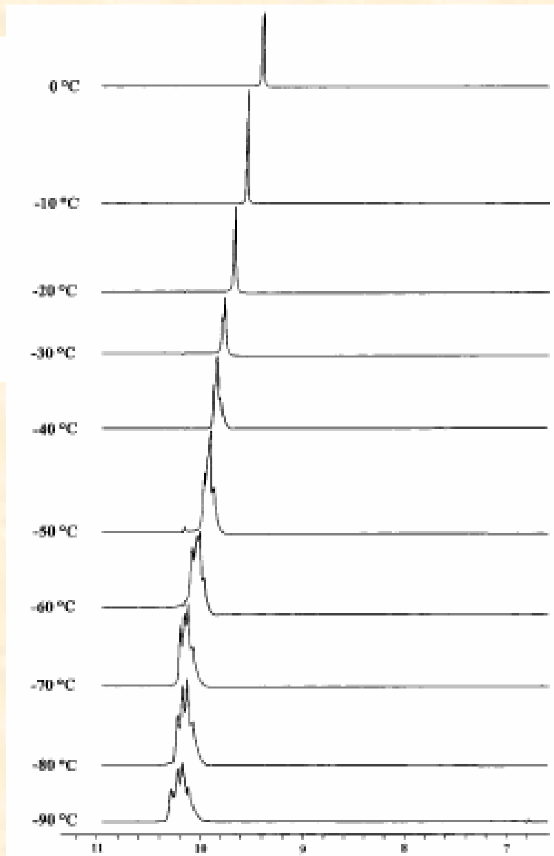


Figure 1. ^{1}H NMR signals of H(F) in DMEHF complex (HF:DME = 3:1) as a function of temperature.

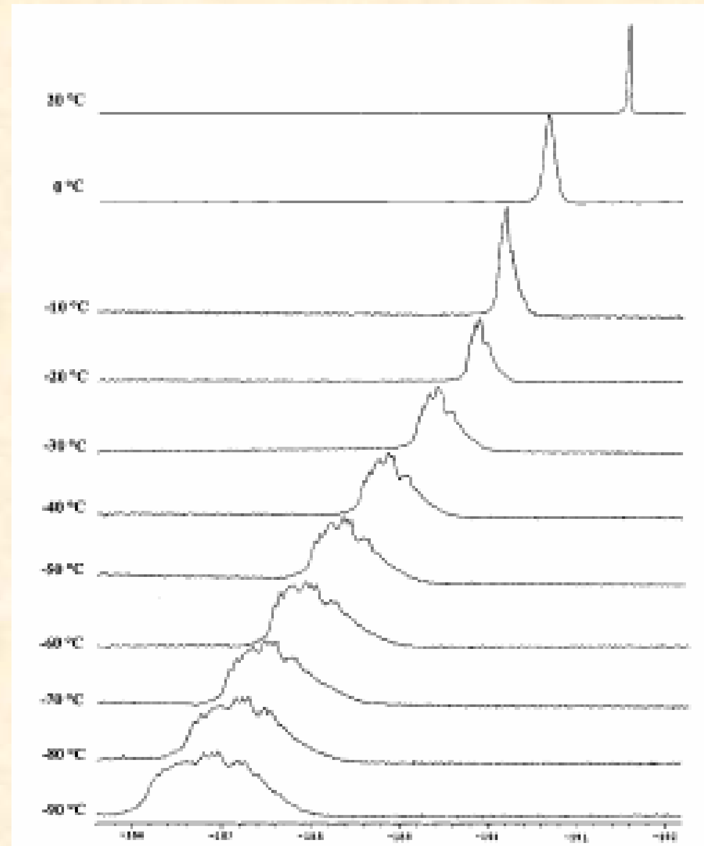
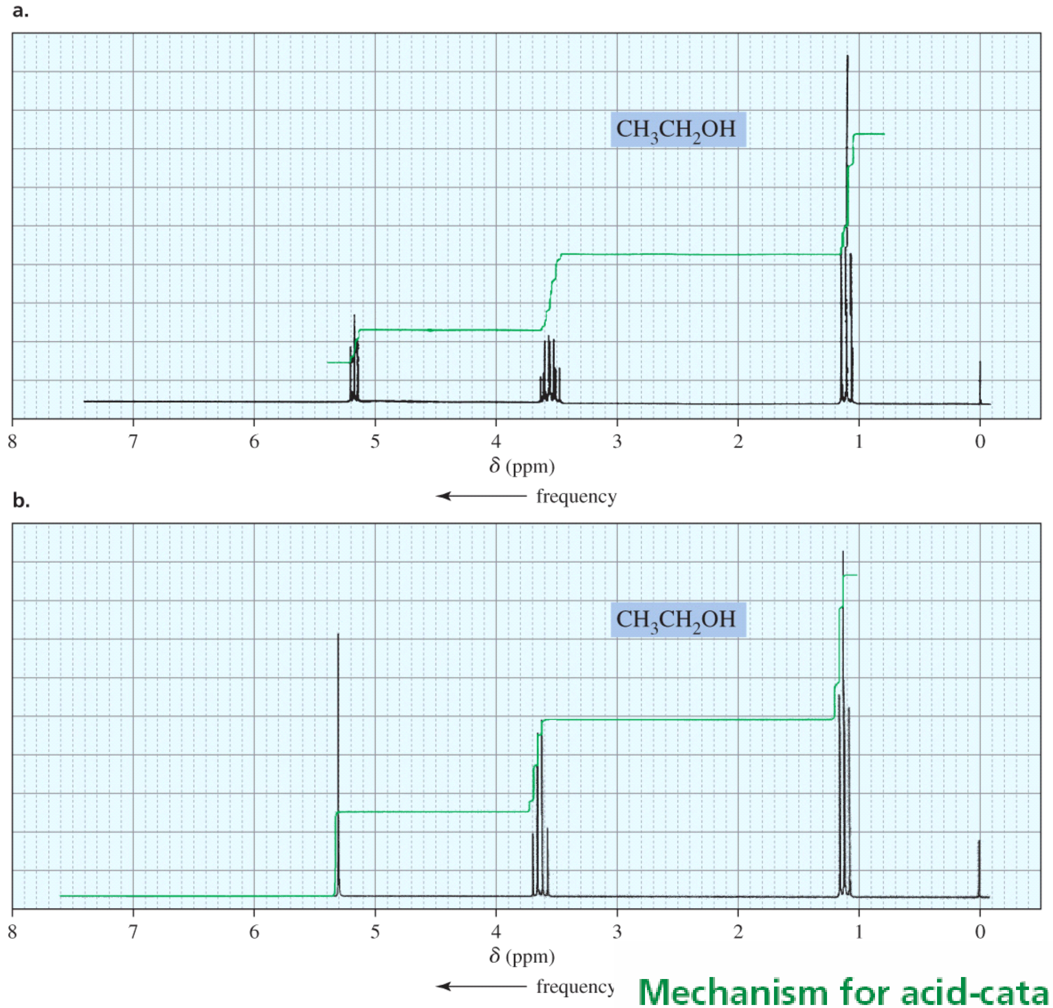


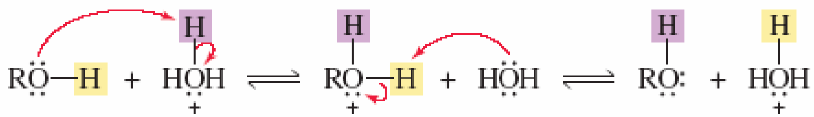
Figure 2. ^{19}F NMR signals of DMEHF complex (HF:DME = 3:1) as a function of temperature.

General Aspects – ^{1}H NMR Spectroscopy

Effect of the medium



Mechanism for acid-catalyzed proton exchange



General Aspects – ^{1}H NMR Spectroscopy

Resolution of spectra

$$\nu_1 = (\gamma/2\pi)\, B_0$$

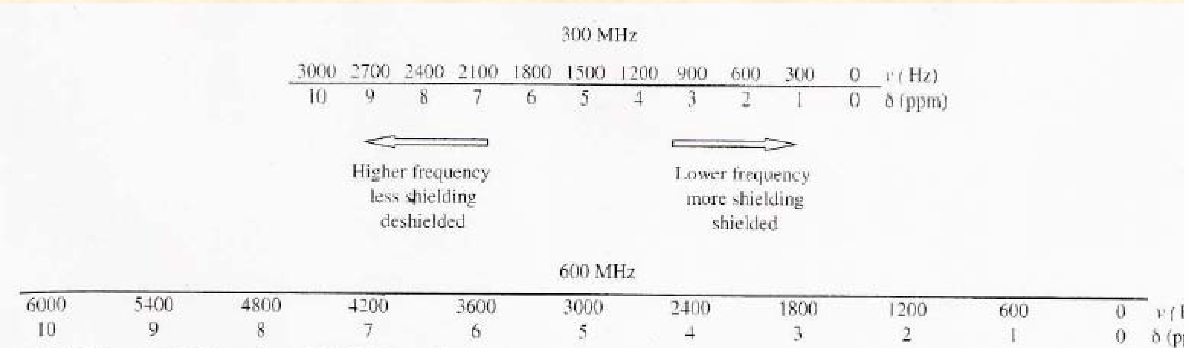


FIGURE 3.18 NMR scale at 300 MHz and 600 MHz. Relatively few organic compounds show absorption peaks to the rig
of the TMS peak. These lower frequency signals are designated by negative numbers to the right (not shown in the Figure).