

All the Best

Determining the structures of compounds is an important part of organic chemistry. After a compound has been synthesized,

its structure must be confirmed. Chemists who study natural products must determine the structure of a naturally occurring compound before they can design a synthesis to produce the compound in greater quantities than nature can provide or before they can design and synthesize related compounds with modified properties.

Chapter 13 introduced two instrumental techniques used to determine the structure of organic compounds: mass spectrometry and IR spectroscopy. Now we will look at *nuclear magnetic resonance (NMR) spectroscopy*, another 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 we have studied, 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.



## 14.1 Introduction to NMR Spectroscopy

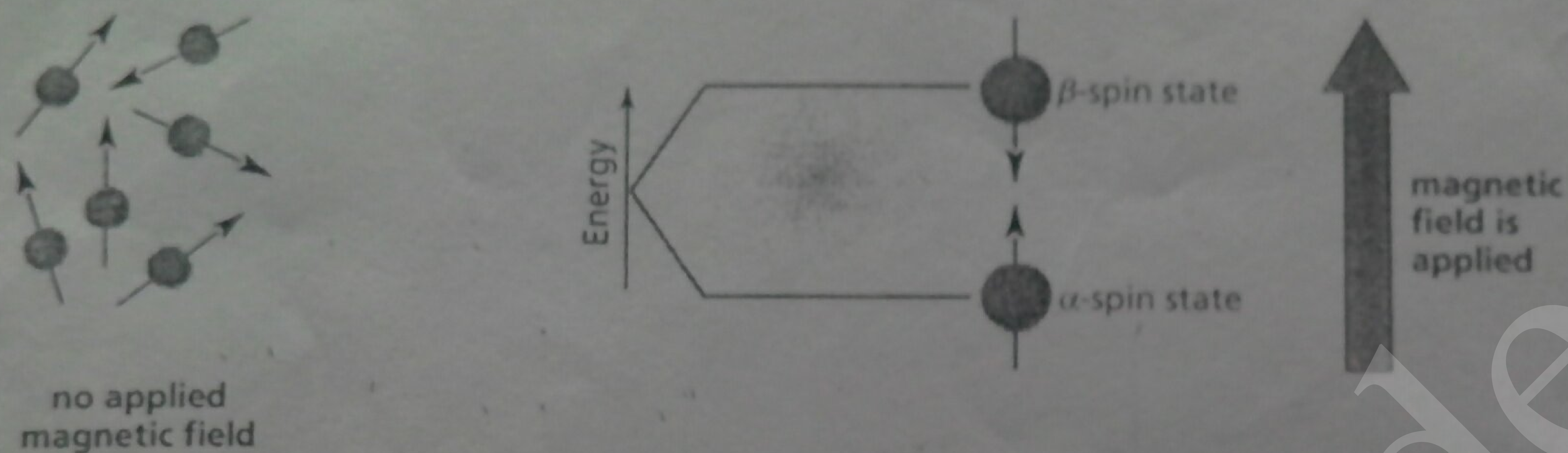
NMR spectroscopy was developed by physical chemists in the late 1940s to study the properties of atomic nuclei. In 1951, chemists realized that NMR spectroscopy could also be used to determine the structures of organic compounds. We have seen that electrons are charged, spinning particles with two allowed spin states:  $+1/2$  and  $-1/2$  (Section 1.2). Certain nuclei also have allowed spin states of  $+1/2$  and  $-1/2$ , and this property allows them to be studied by NMR. Examples of such nuclei are <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, <sup>19</sup>F, and <sup>31</sup>P.

Because hydrogen nuclei (protons) were the first nuclei studied by nuclear magnetic resonance, the acronym "NMR" is generally assumed to mean <sup>1</sup>H NMR (proton



magnetic resonance). Spectrometers were later developed for  $^{13}\text{C}$  NMR,  $^{15}\text{N}$  NMR,  $^{19}\text{F}$  NMR,  $^{31}\text{P}$  NMR, and other magnetic nuclei.

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 (Figure 14.1), the nuclei twist and turn to align themselves with or against the field of the larger magnet. 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  $\alpha$ -spin state; protons that align against the field are in the higher-energy  $\beta$ -spin state. More nuclei are in the  $\alpha$ -spin state than in the  $\beta$ -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.

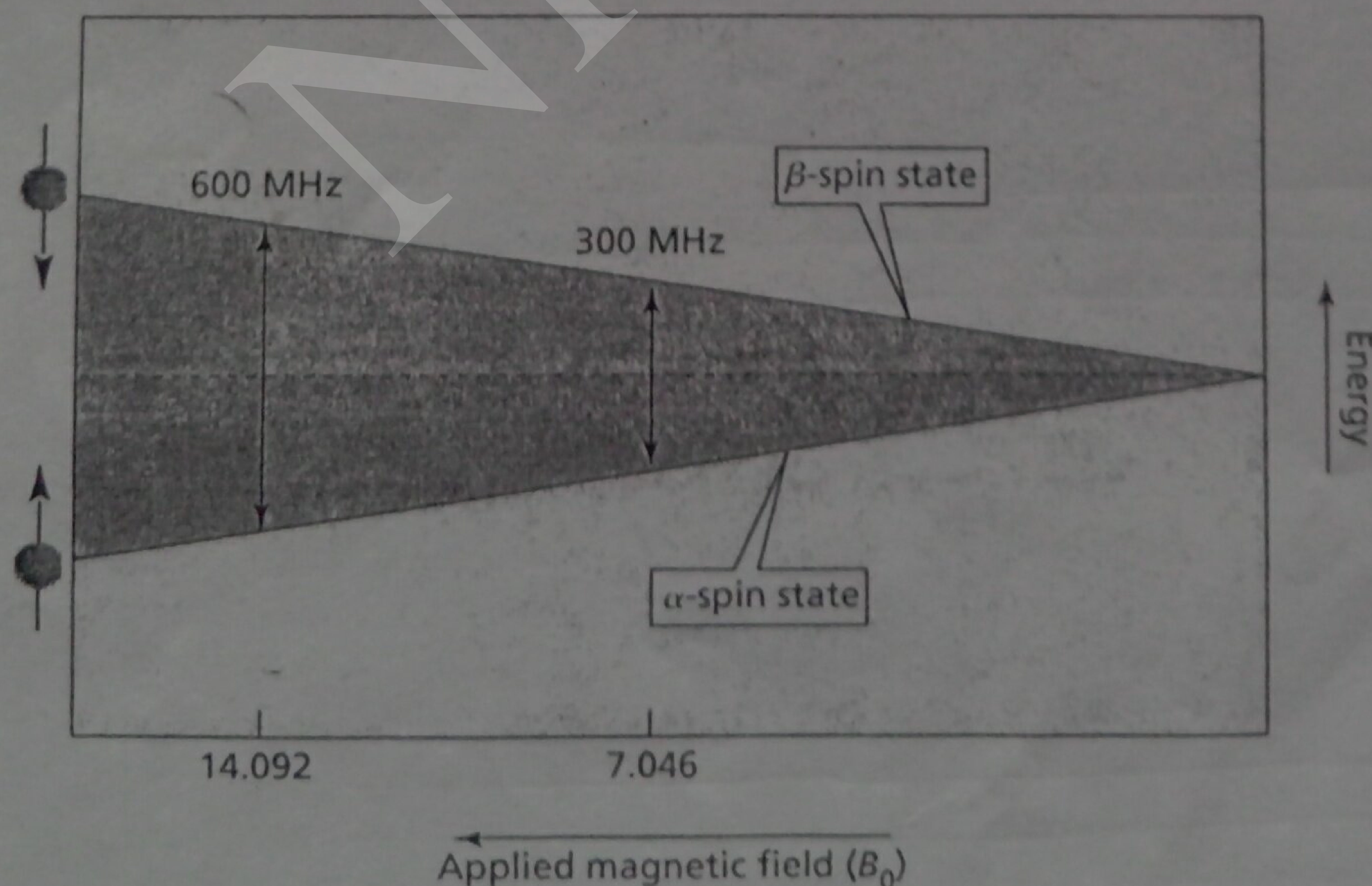


◀ Figure 14.1  
In the absence of an applied magnetic field, the spins of the nuclei are randomly oriented. In the presence of an applied magnetic field, the spins of the nuclei line up with or against the field.

The energy difference ( $\Delta E$ ) between the  $\alpha$ - and  $\beta$ -spin states depends on the strength of the **applied magnetic field ( $B_0$ )**. The greater the strength of the magnetic field to which we expose the nucleus, the greater is the difference in energy between the  $\alpha$ - and  $\beta$ -spin states (Figure 14.2).

When the sample is subjected to a pulse of radiation whose energy corresponds to the difference in energy ( $\Delta E$ ) between the  $\alpha$ - and  $\beta$ -spin states, nuclei in the  $\alpha$ -spin state are promoted to the  $\beta$ -spin state. This transition is called "flipping" the spin. Because the energy difference between the  $\alpha$ - and  $\beta$ -spin 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

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.



▲ Figure 14.2  
The greater the strength of the applied magnetic field, the greater is the difference in energy between the  $\alpha$ - and  $\beta$ -spin states.



the difference in energy ( $\Delta E$ ) between the  $\alpha$ - and  $\beta$ -spin 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  $\alpha$ - and  $\beta$ -spin states in response to the rf radiation.

Recall that Planck’s constant,  $h$ , is the proportionality constant relating the difference in energy ( $\Delta E$ ) to the frequency ( $\nu$ )<sup>1</sup> (Section 13.6). The following equation shows that the energy difference between the spin states ( $\Delta E$ ) depends on the operating frequency of the spectrometer, which in turn depends on the strength of the magnetic field ( $B_0$ ), measured in tesla (T)<sup>1</sup>, and the gyromagnetic ratio ( $\gamma$ ). The gyromagnetic ratio (also called the magnetogyric ratio) is a constant that depends on the magnetic moment of the particular kind of nucleus. In the case of the proton, the value of  $\gamma$  is  $2.675 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$ ; in the case of a  $^{13}\text{C}$  nucleus, it is  $6.688 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}$ .

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

Canceling Planck’s constant on both sides of the equation gives  $\nu = \frac{\gamma}{2\pi} B_0$ .

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

$$\begin{aligned} \nu &= \frac{\gamma}{2\pi} B_0 \\ &= \frac{2.675 \times 10^8}{2(3.1416)} \text{ T}^{-1} \text{ s}^{-1} \times 7.046 \text{ T} \\ &= 300 \times 10^6 \text{ Hz} = 300 \text{ MHz} \end{aligned}$$

Earth’s magnetic field is  $5 \times 10^5 \text{ T}$ , measured at the equator. Its maximum surface magnetic field is  $7 \times 10^5 \text{ T}$ , measured at the south magnetic pole.

The magnetic field is proportional to the operating frequency.

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.

Today’s NMR spectrometers operate at frequencies between 60 and 900 MHz. The operating frequency of a particular spectrometer depends on the strength of the built-in magnet. The greater the operating frequency of the instrument—and the stronger the magnet—the better is the resolution (separation of the signals) of the NMR spectrum (Section 14.17).

Because each kind of nucleus has its own gyromagnetic ratio, different energies are required to bring different kinds of nuclei into resonance. For example, an NMR spectrometer with a magnet requiring a frequency of 300 MHz to flip the spin of an  $^1\text{H}$  nucleus requires a frequency of 75 MHz to flip the spin of a  $^{13}\text{C}$  nucleus. NMR spectrometers are equipped with radiation sources that can be tuned to different frequencies so that they can be used to obtain NMR spectra of different kinds of nuclei ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , etc.).

### 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? 42.5 MHz

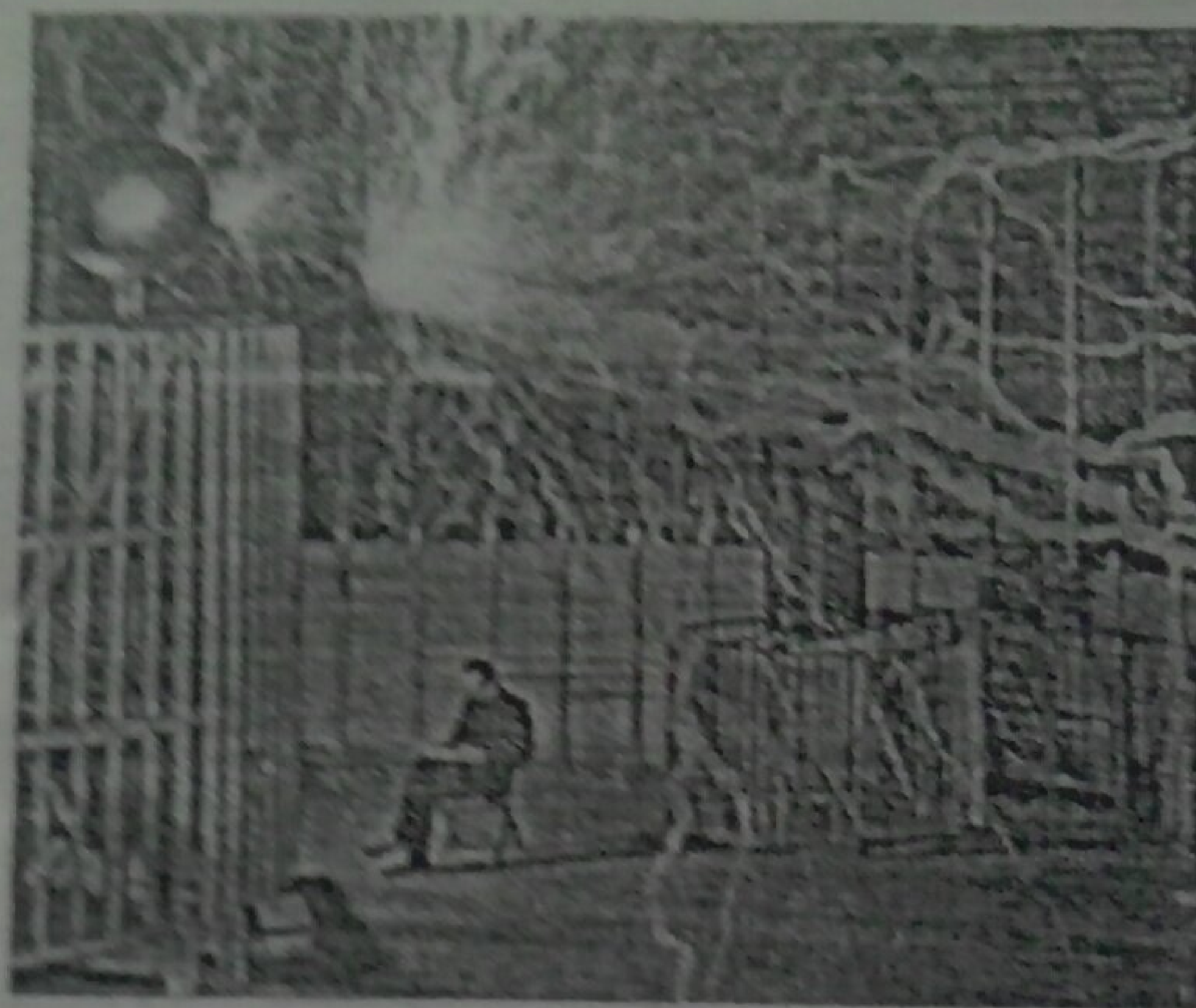
<sup>1</sup>Until recently, the gauss (G) was the unit in which magnetic field strength was commonly measured ( $1 \text{ T} = 10^4 \text{ G}$ ).





### 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

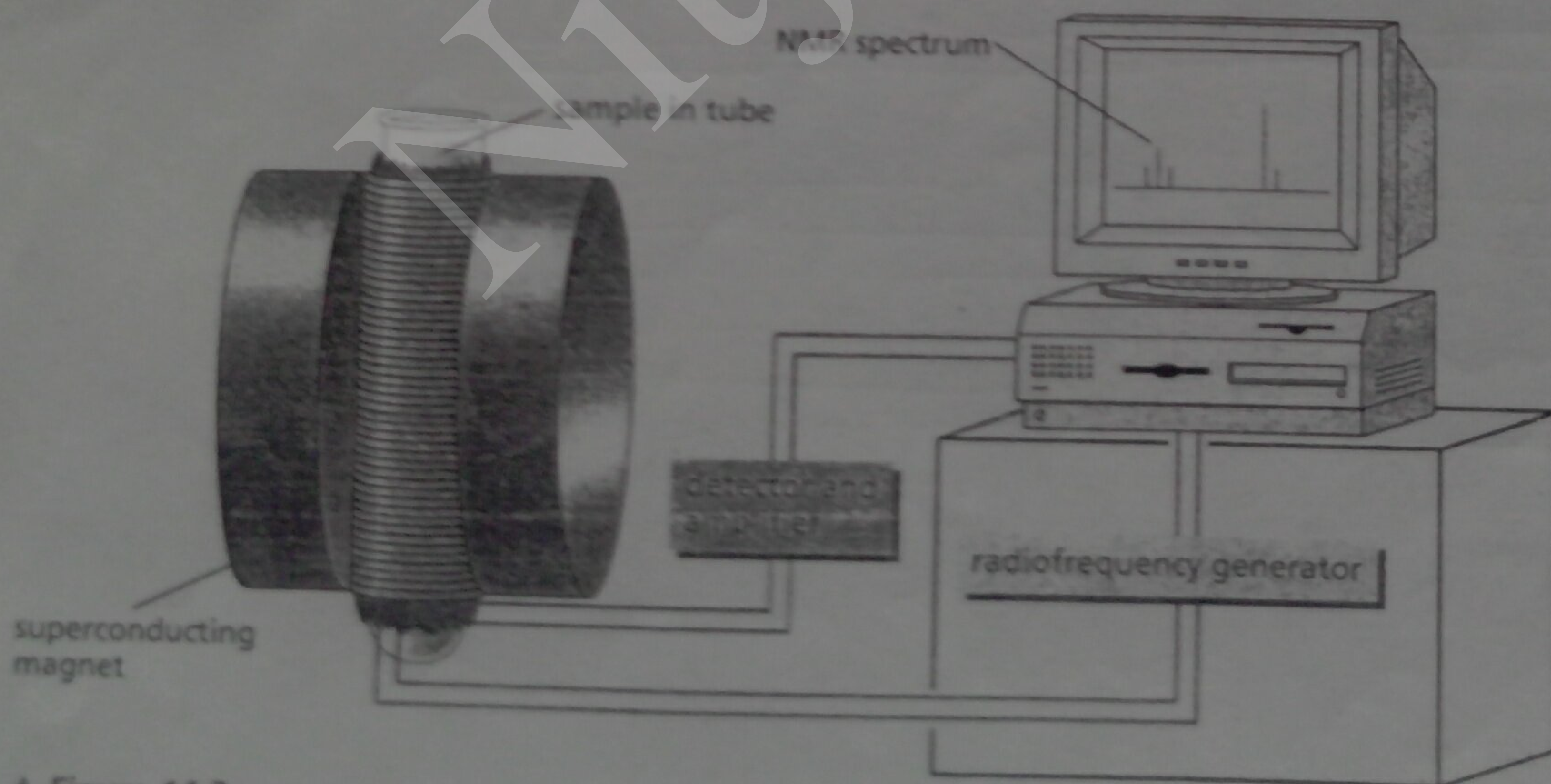
#### PROBLEM 2

- Calculate the magnetic field (in tesla) required to flip an  $^1\text{H}$  nucleus in an NMR spectrometer that operates at 360 MHz.  $8.45\text{ T}$
- What strength magnetic field is required when a 500-MHz instrument is used?  $11.73\text{ T}$

## 14.2 Fourier Transform NMR

To obtain an NMR spectrum, one dissolves a small amount of a compound in about 1 mL of solvent and puts the solution into a long, thin glass tube, which is placed within a powerful magnetic field (Figure 14.3). The solvents used in NMR are discussed in Section 14.16. 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



▲ Figure 14.3  
Schematic of an NMR spectrometer.



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.

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  $\Delta E$ . 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. An FT-NMR spectrum can be recorded in about 2 seconds—and many FIDs can be averaged in a few minutes—using less than 5 mg of compound. The NMR spectra in this book are FT-NMR spectra that were taken on a spectrometer with an operating frequency of 300 MHz. This book discusses the theory behind FT-NMR, rather than that behind the older continuous wave (CW) NMR, because FT-NMR is more modern and is easier to understand.

## ② 14.3 Shielding

We have seen that when a sample in a magnetic field is irradiated with rf radiation of the proper frequency, each proton<sup>2</sup> in an organic compound gives a signal at a frequency that depends on the energy difference ( $\Delta E$ ) between the  $\alpha$ - and  $\beta$ -spin states, where  $\Delta E$  is determined by the strength of the magnetic field (Figure 14.2). If all the protons in an organic compound were in exactly the same environment, they would all give signals with the same frequency in response to a given applied magnetic field. If this were the case, all NMR spectra would consist of one signal, which would tell us nothing about the structure of the compound, except that it contains protons.

A nucleus, however, is embedded in a cloud of electrons that partly shields it from the applied magnetic field. Fortunately for chemists, the shielding varies for different protons within a molecule. In other words, all the protons do not experience the same applied magnetic field.

What causes 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:

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

This means that the greater the electron density of the environment in which the proton is located, the greater  $B_{\text{local}}$  is 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—that is, flip their spin—because  $\Delta E$  is smaller (Figure 14.2). Protons in electron-poor environments sense a larger effective magnetic field and, therefore, will require a higher frequency to come into resonance, because  $\Delta E$  is larger.

We see a signal in an NMR spectrum for each proton in a different environment. Protons in electron-rich environments are more shielded and appear at lower frequencies—on the right-hand side of the spectrum (Figure 14.4). Protons in electron-poor environments are less shielded and appear at higher frequencies—on the left-hand side of the spectrum. (Notice that high frequency in an NMR spectrum is on the left-hand side, just as it is in IR and UV/Vis spectra.)

The terms "upfield" and "downfield," which came into use when continuous wave (CW) spectrometers were used (before the advent of Fourier transform spectrometers), are so entrenched in the vocabulary of NMR that you should know

<sup>2</sup>The terms "proton" and "hydrogen" are both used to describe covalently bonded hydrogen in discussions of NMR spectroscopy.

The larger the magnetic field sensed by the proton, the higher is the frequency of the signal.



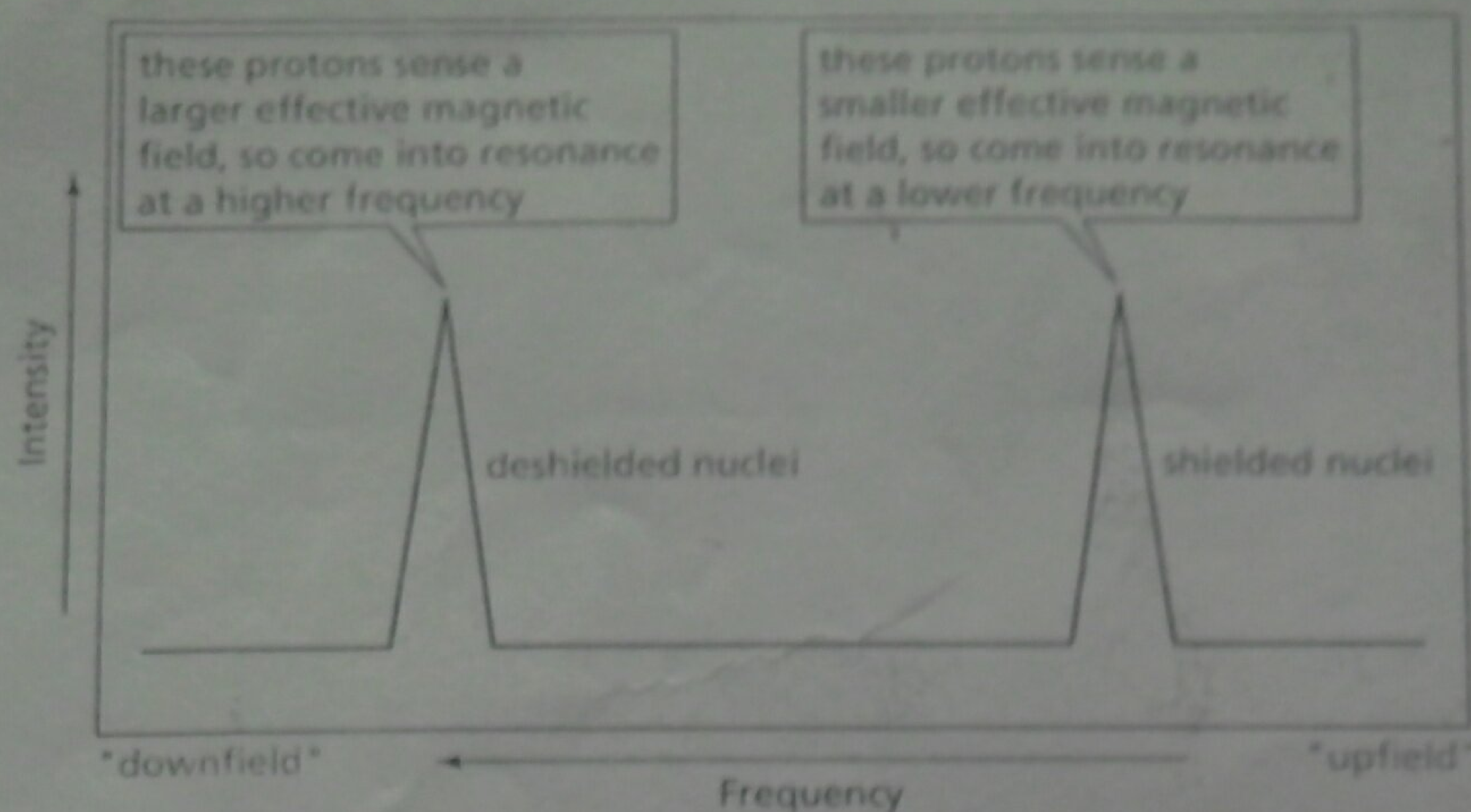
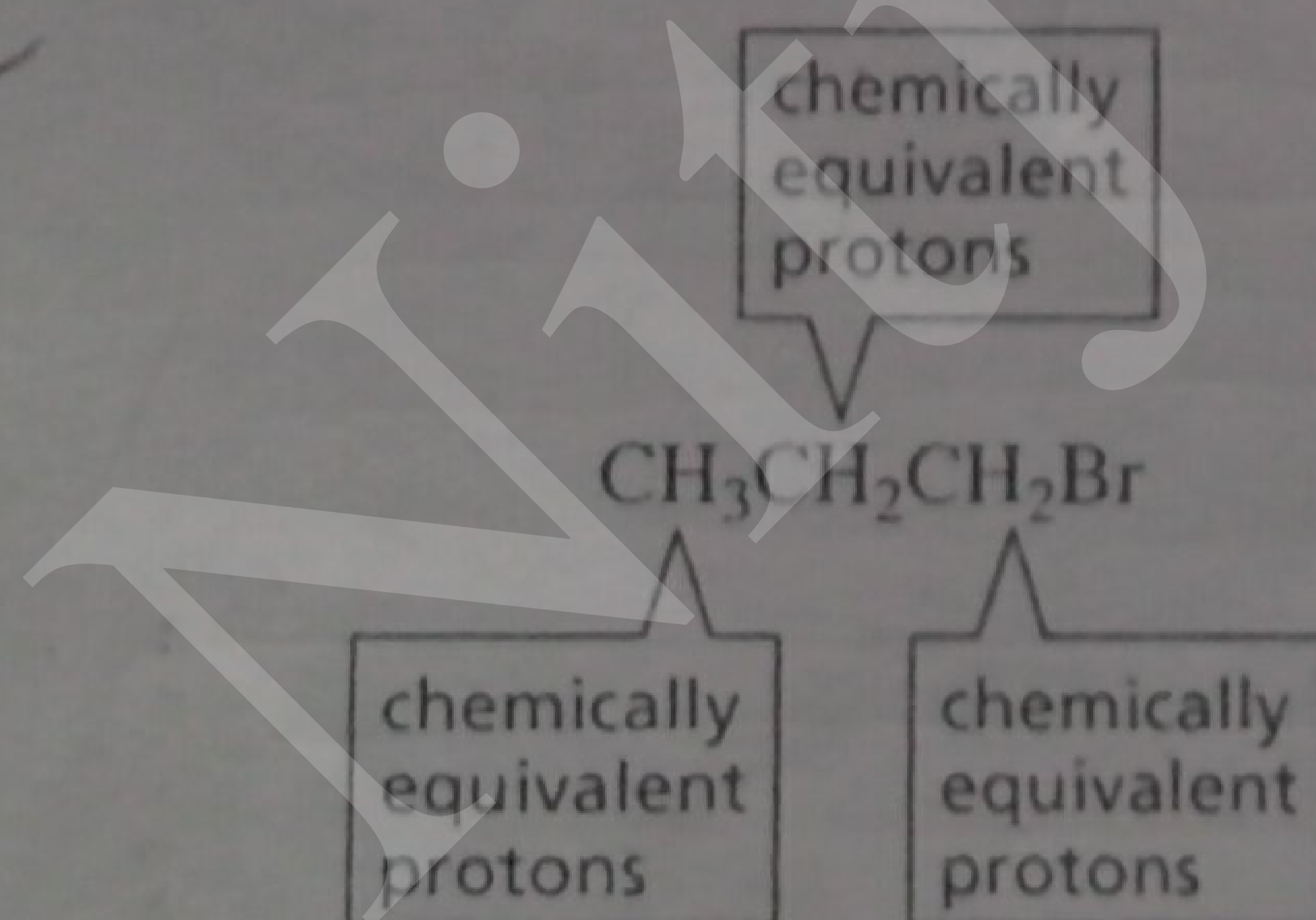


Figure 14.4  
Shielded nuclei come into resonance at lower frequencies than deshielded nuclei.

what they mean. Upfield means farther to the right-hand side of the spectrum, and downfield means farther to the left-hand side of the spectrum. (In contrast to FT-NMR techniques, which hold magnetic field strength constant and vary frequency, continuous-wave techniques hold frequency constant and vary magnetic field. The magnetic field increases from left to right across a spectrum because higher magnetic fields are required for shielded protons to come into resonance at a given frequency (Figure 14.4). Therefore, *upfield* is toward the right and *downfield* is toward the left.)

## 14.4 The Number of Signals in the $^1\text{H}$ NMR Spectrum

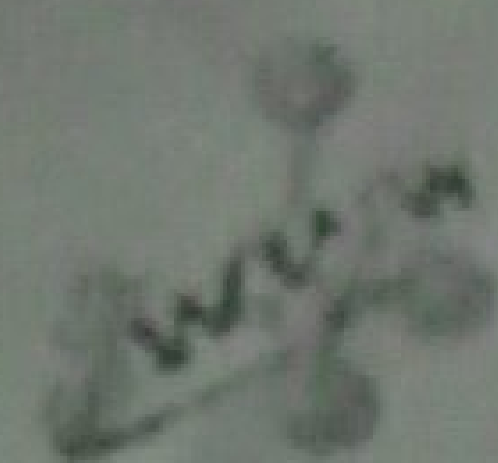
Protons in the same environment are called chemically equivalent protons. (For example, 1-bromopropane has three different sets of chemically equivalent protons. The three methyl protons are chemically equivalent because of rotation about the C—C bond. The two methylene protons on the middle carbon are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



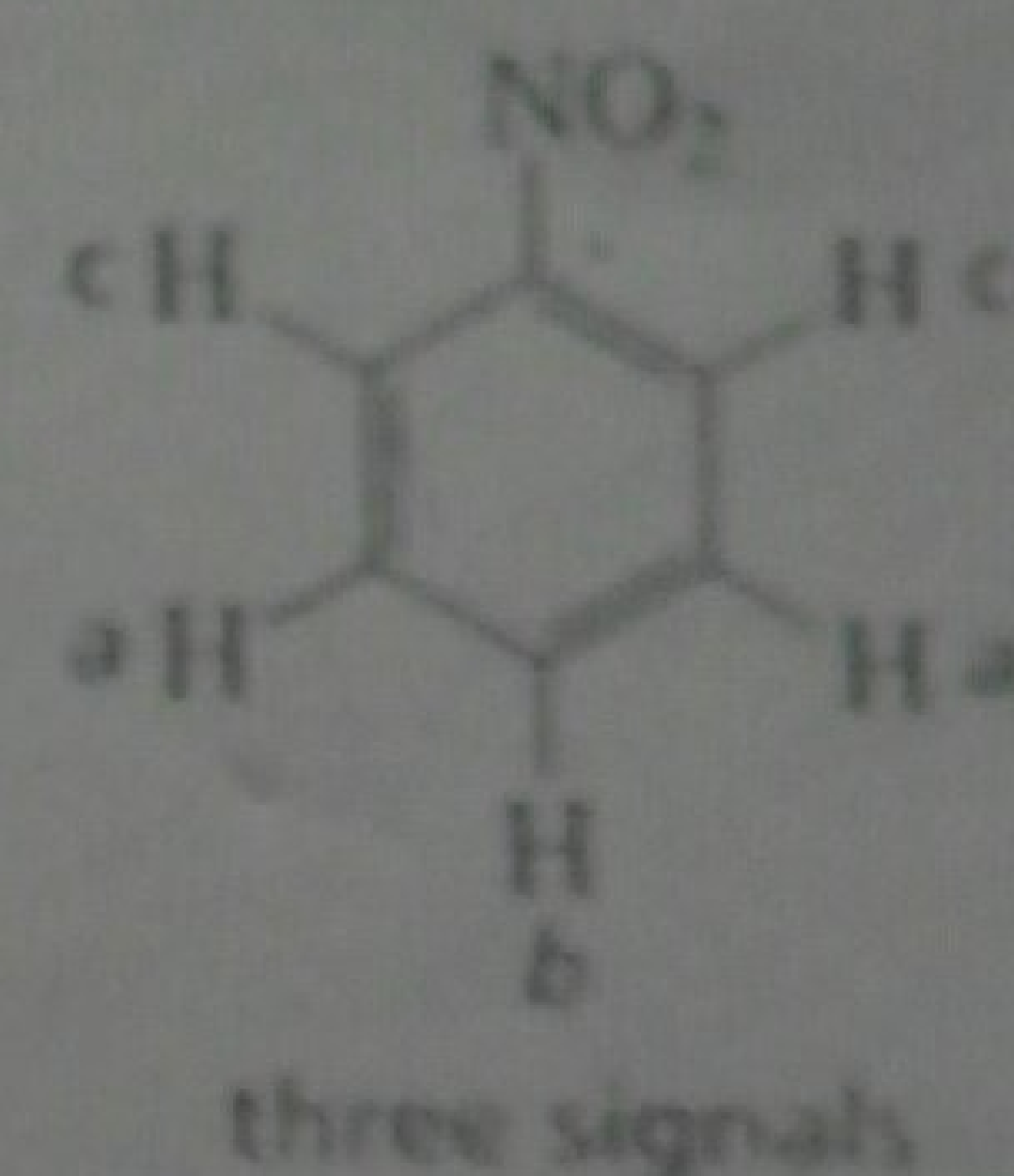
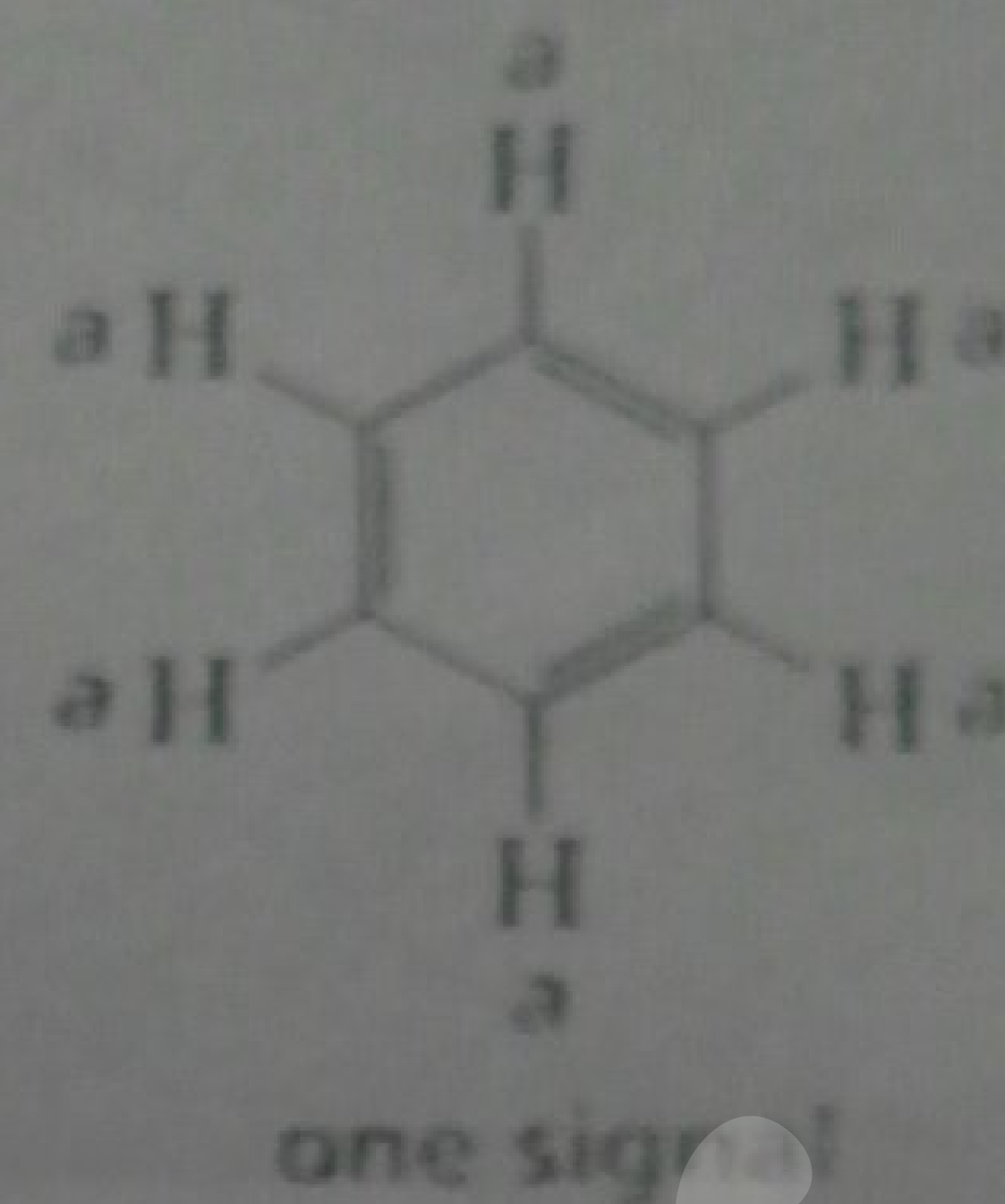
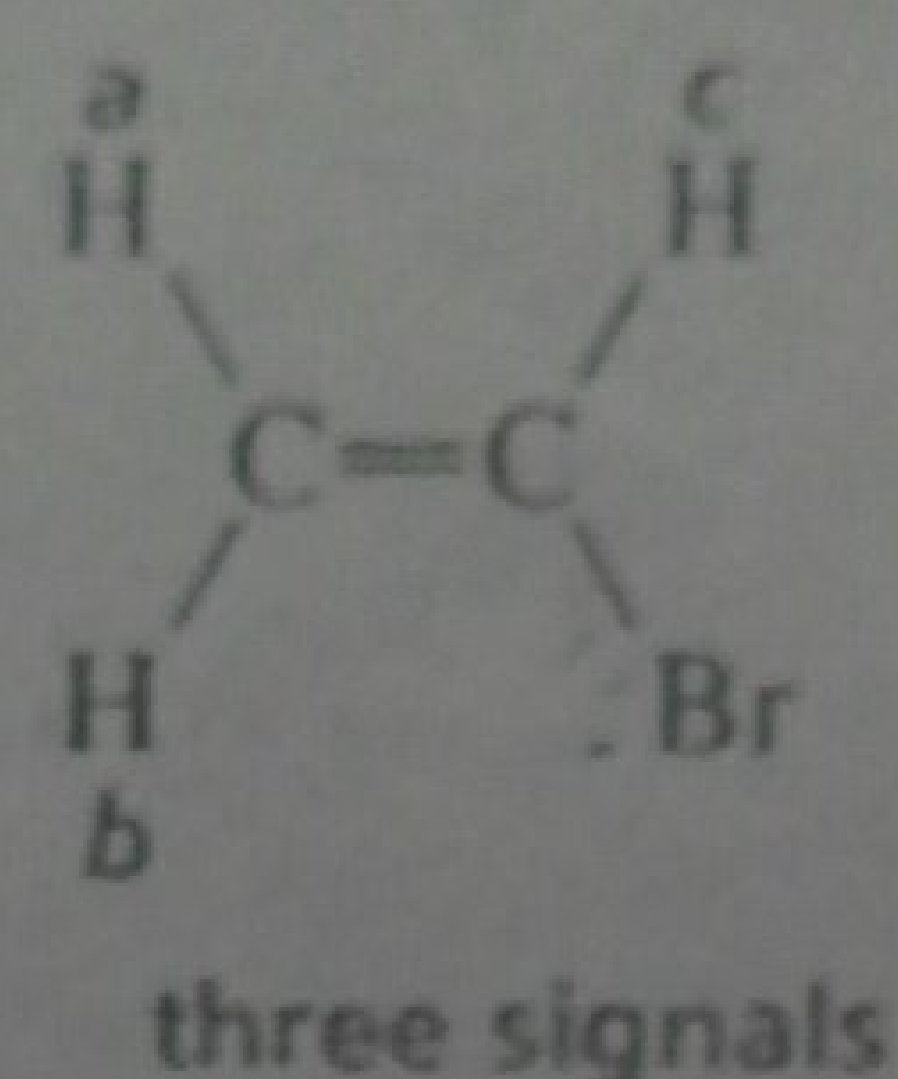
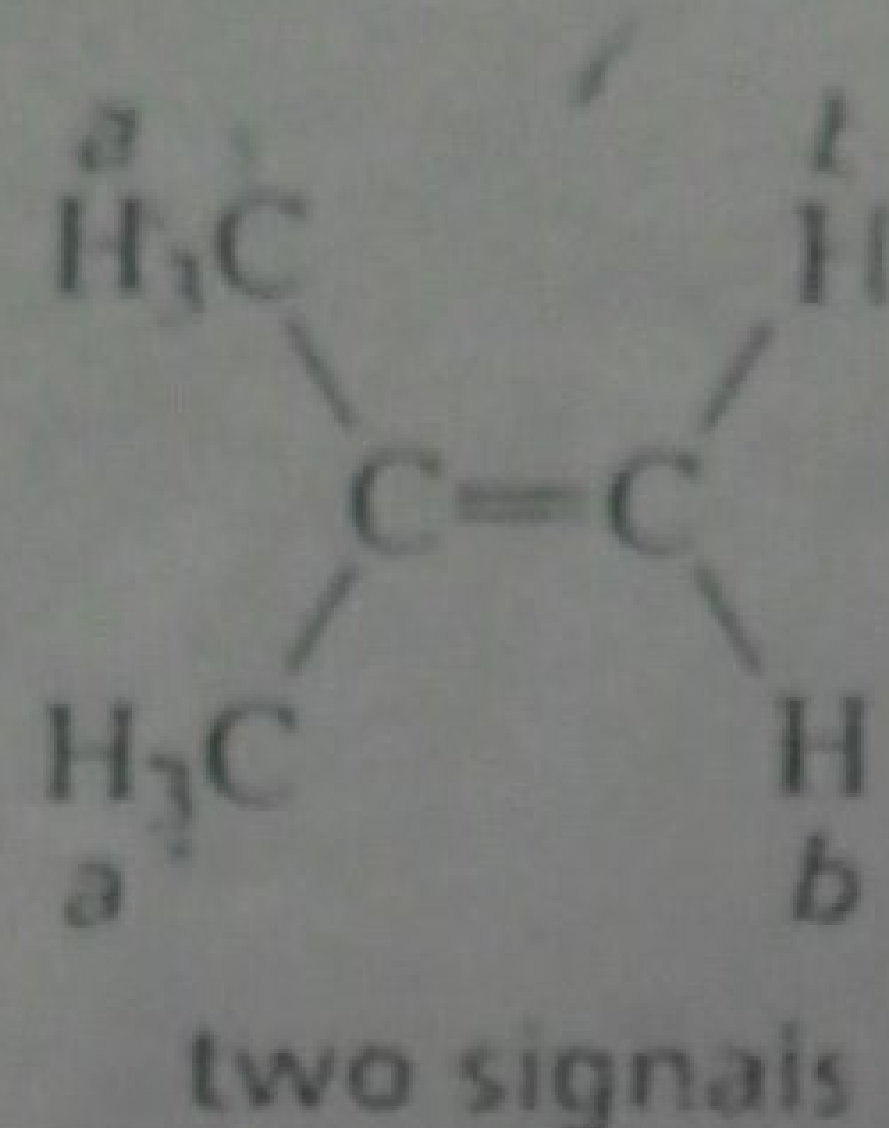
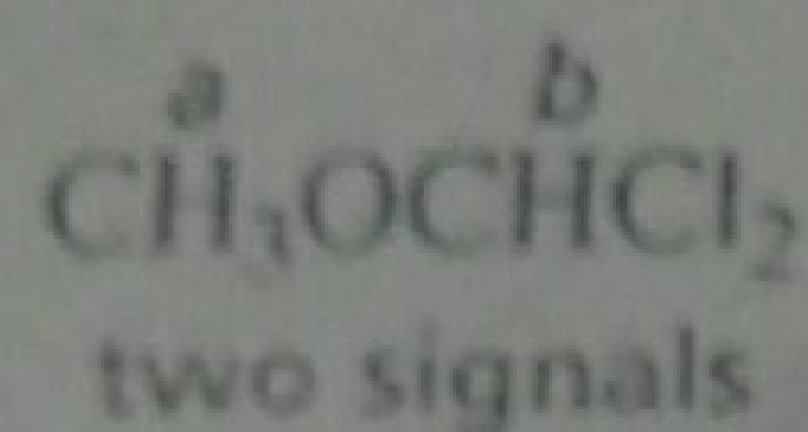
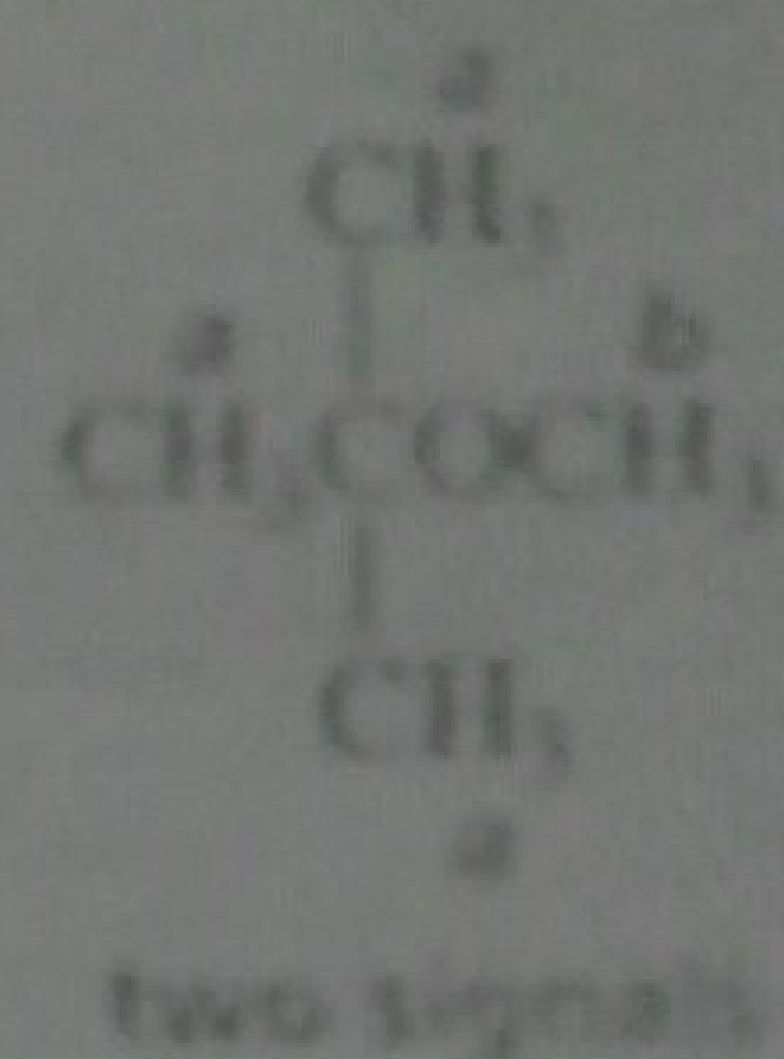
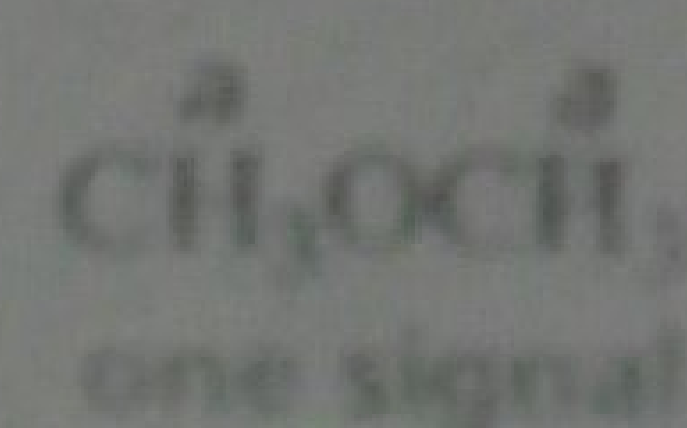
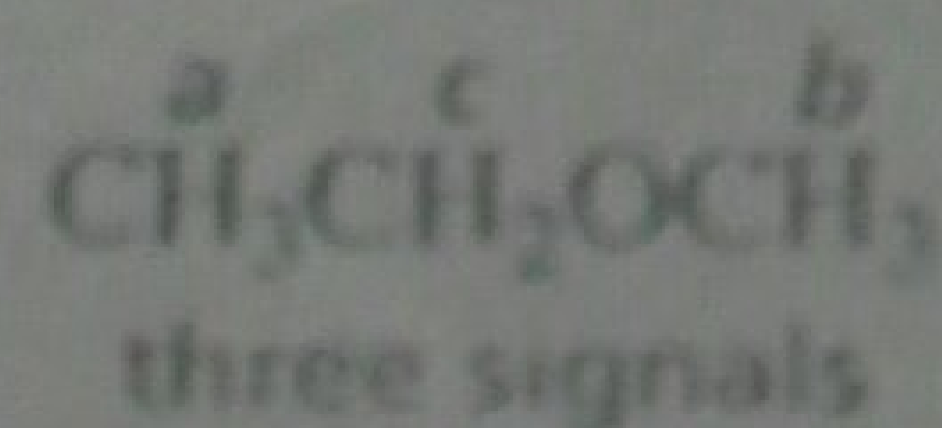
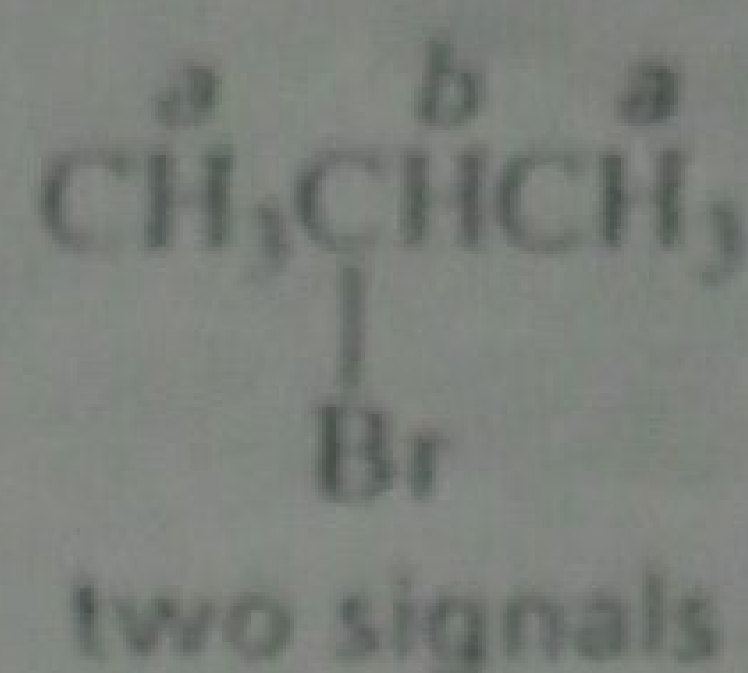
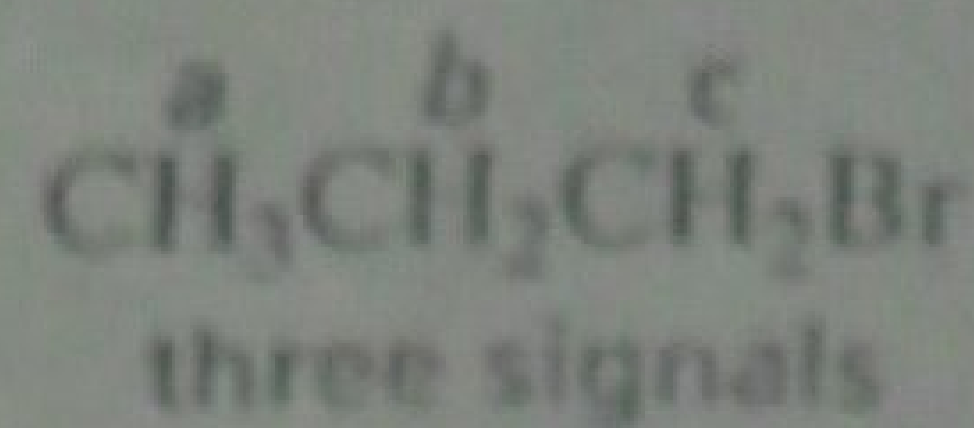
Each set of chemically equivalent protons in a compound gives rise to a signal in the  $^1\text{H}$  NMR spectrum of that compound. (Sometimes the signals are not sufficiently separated and overlap each other. When this happens, one sees fewer signals than anticipated.) Because 1-bromopropane has three sets of chemically equivalent protons, it has three signals in its  $^1\text{H}$  NMR spectrum.

2-Bromopropane has two sets of chemically equivalent protons and, therefore, it has two signals in its  $^1\text{H}$  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,

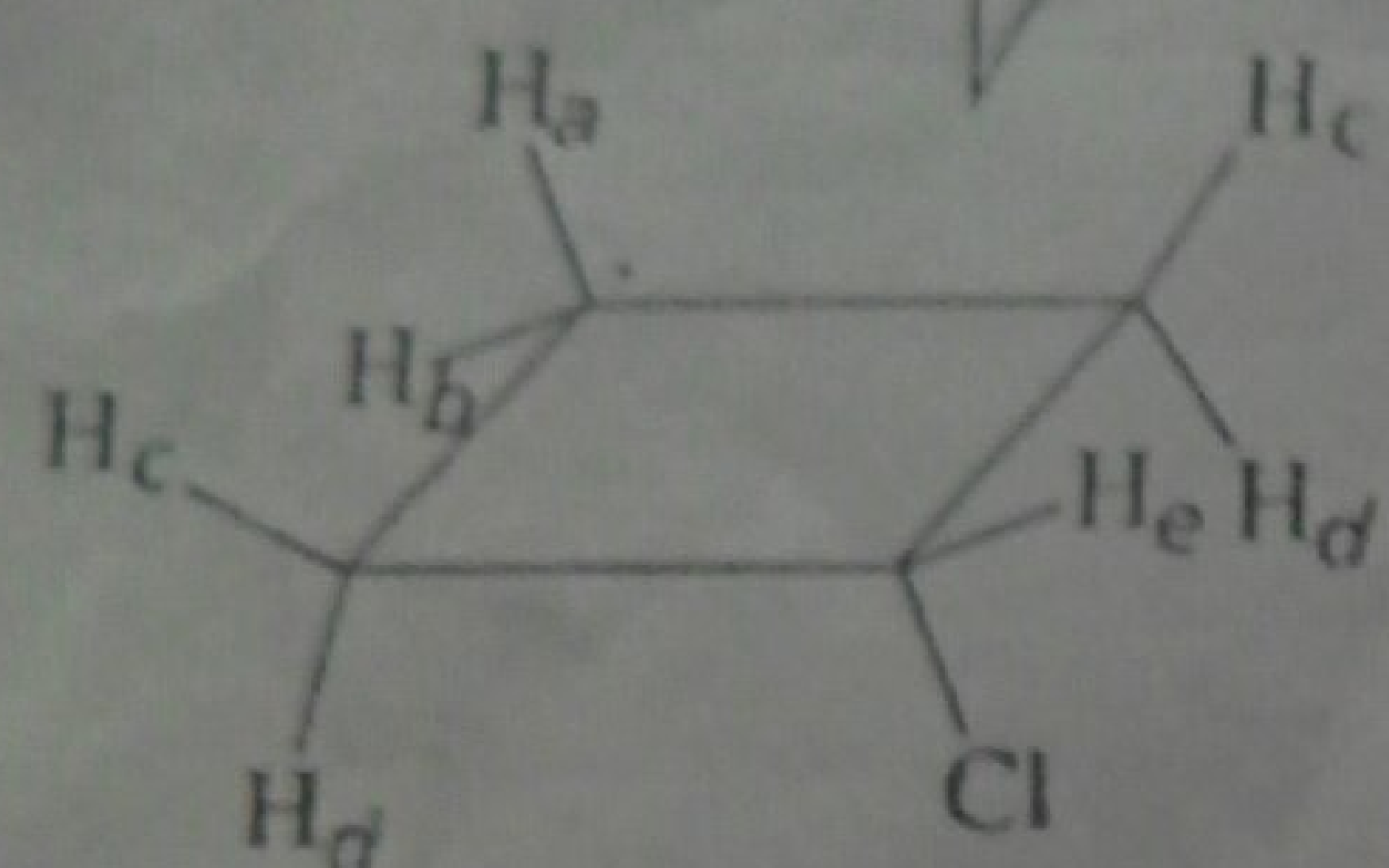


3-D Molecule:  
Chlorocyclobutane

and the methyl protons on the carbon that is one carbon removed from the oxygen. The chemically equivalent protons in the following compounds are designated by the same letter:



its  $^1\text{H}$  NMR spectrum has five signals



chlorocyclobutane

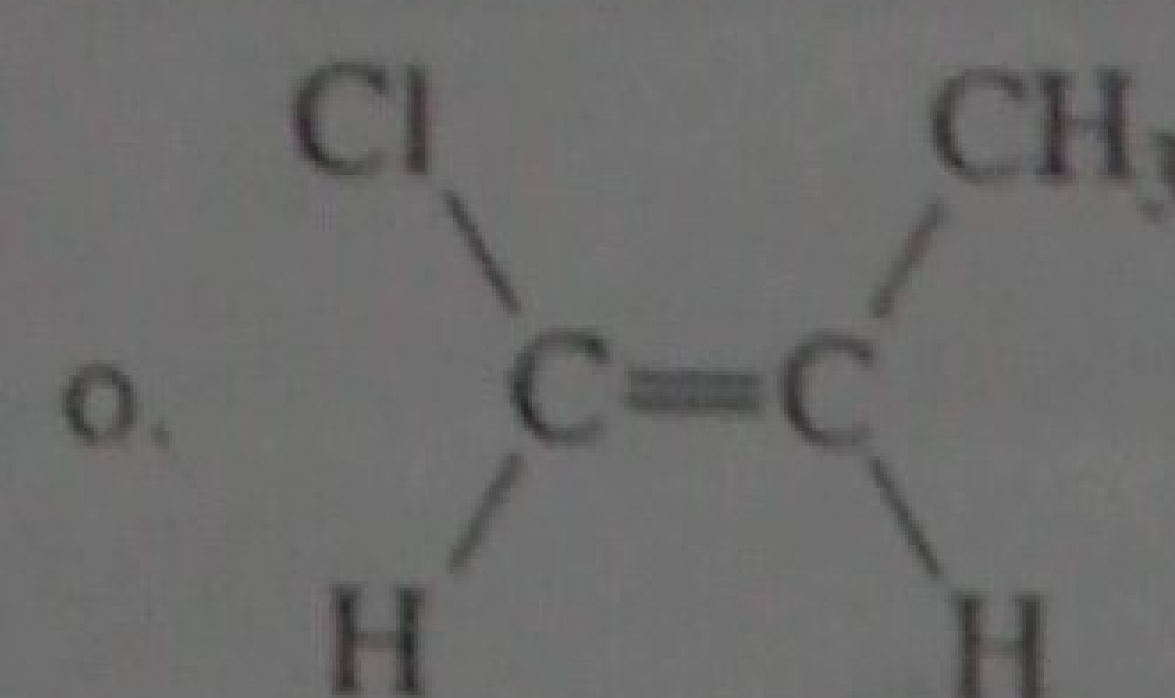
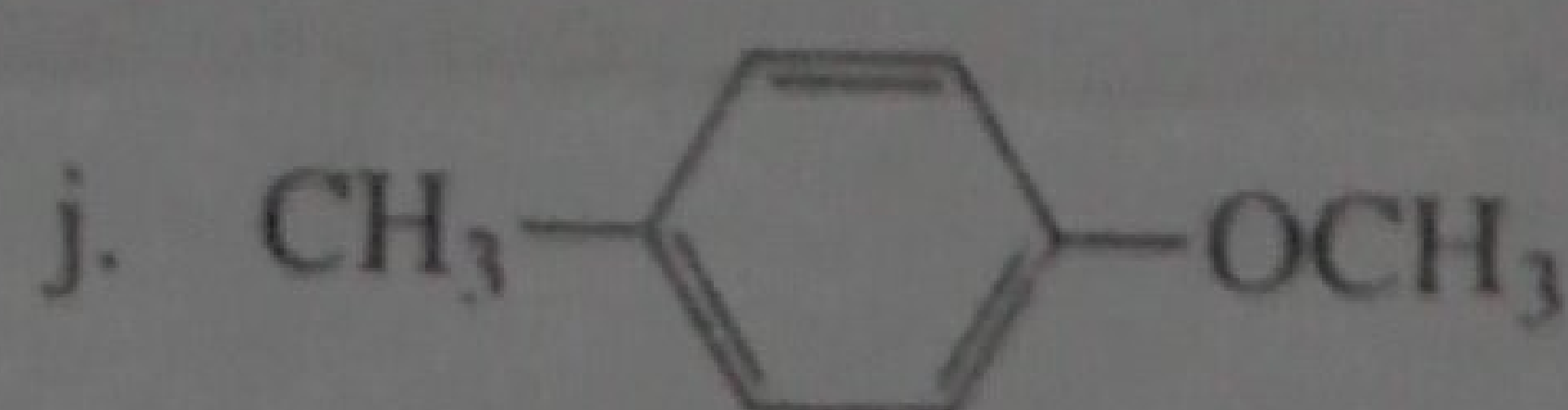
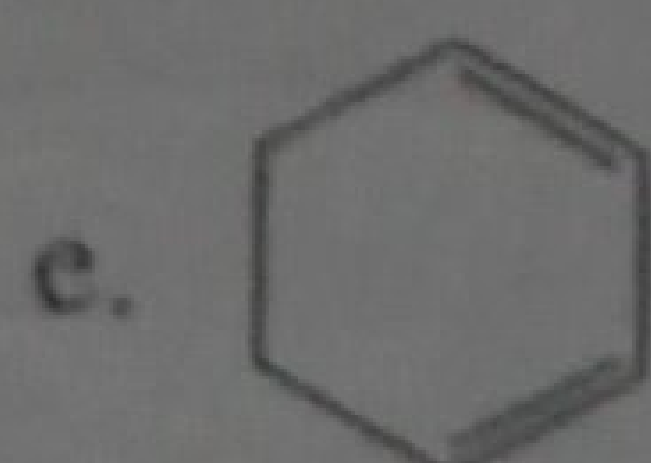
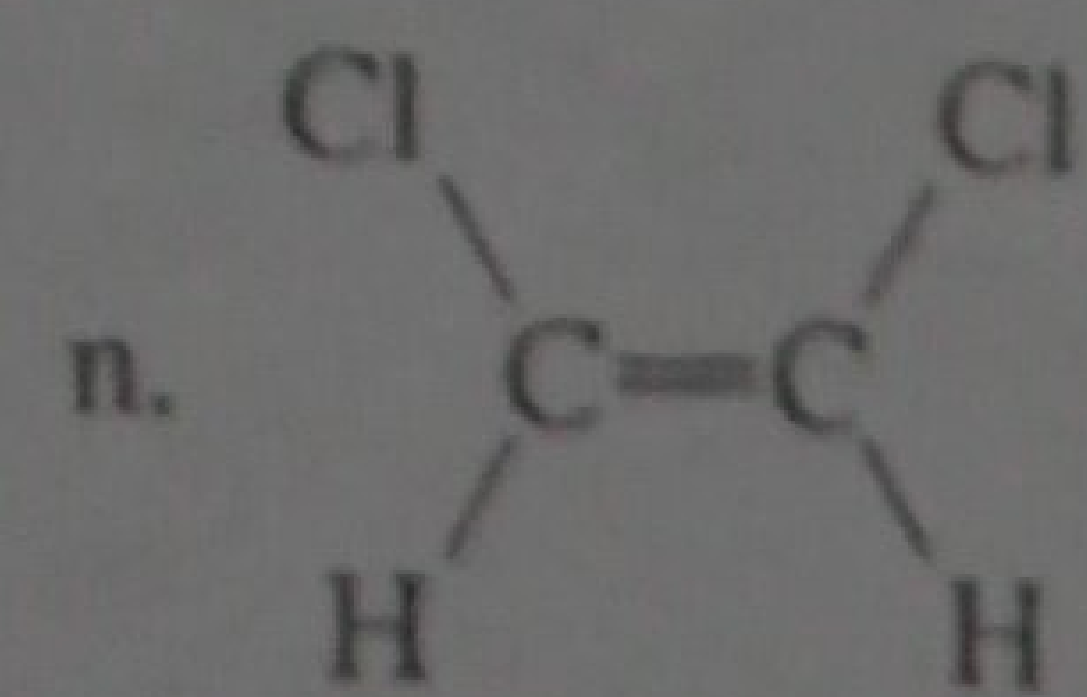
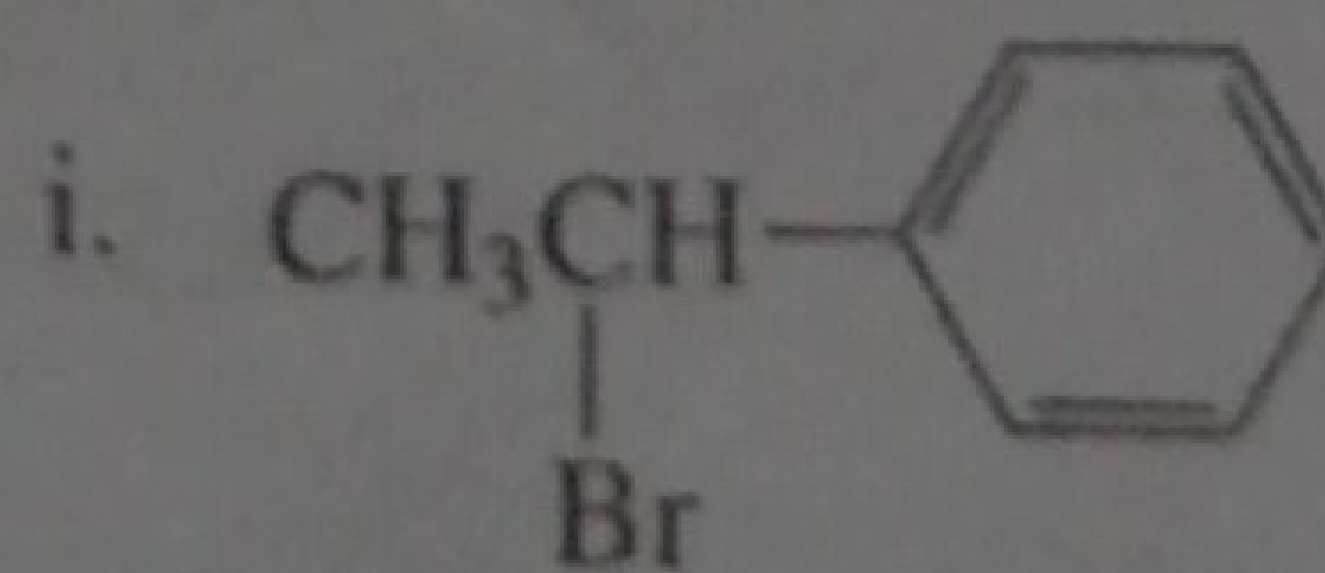
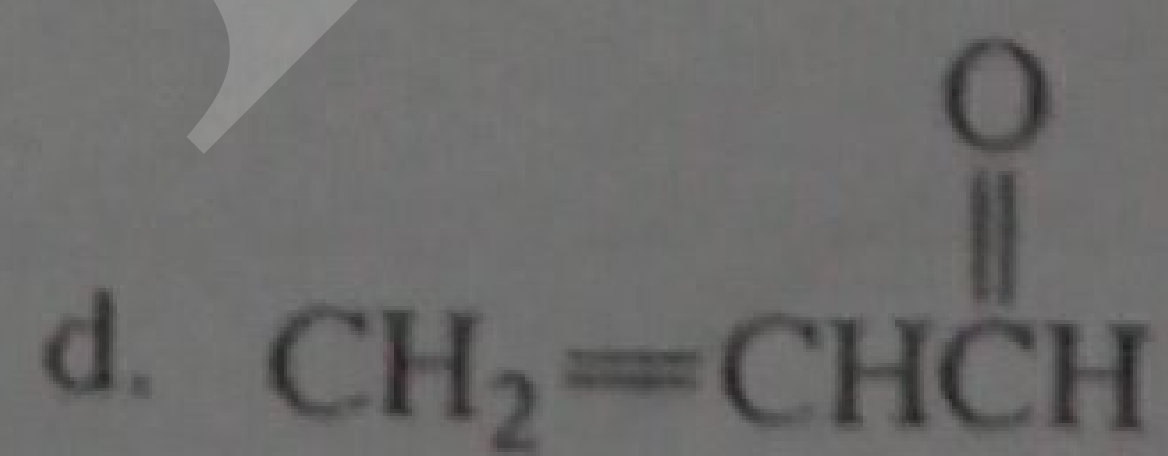
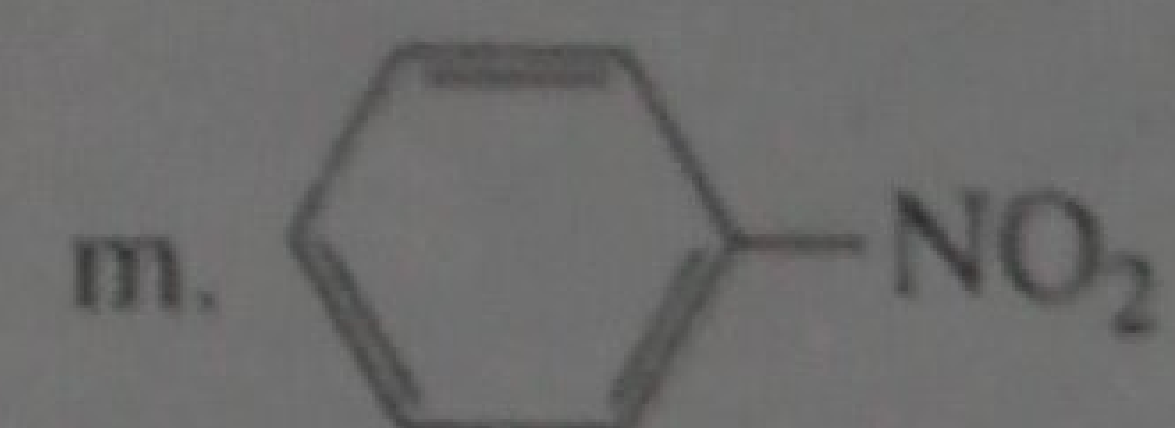
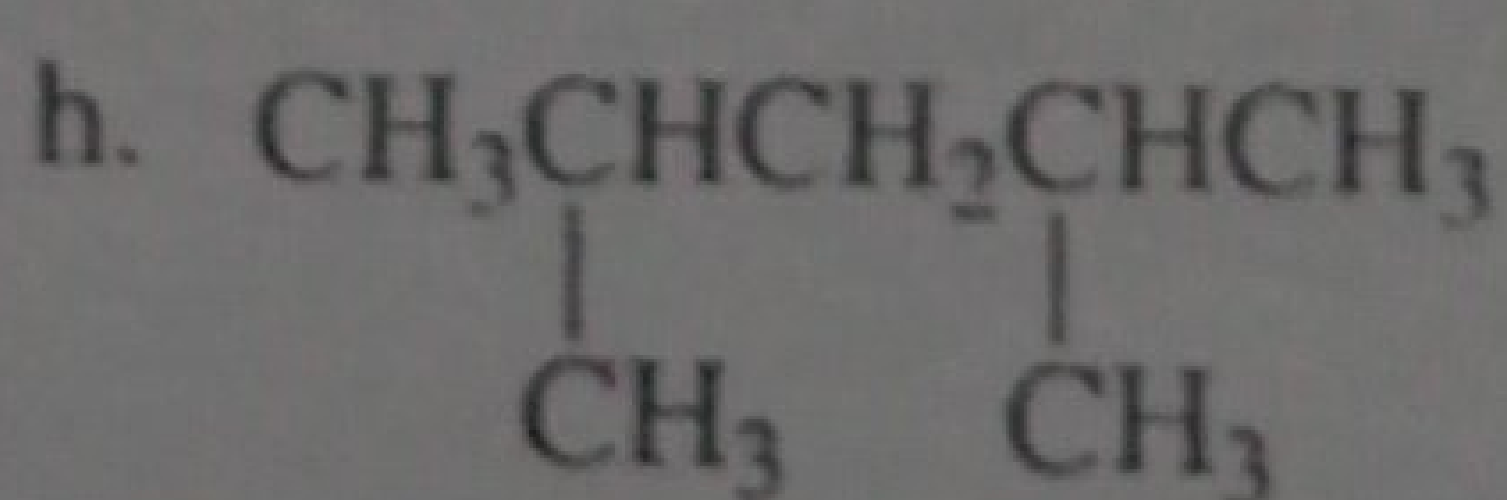
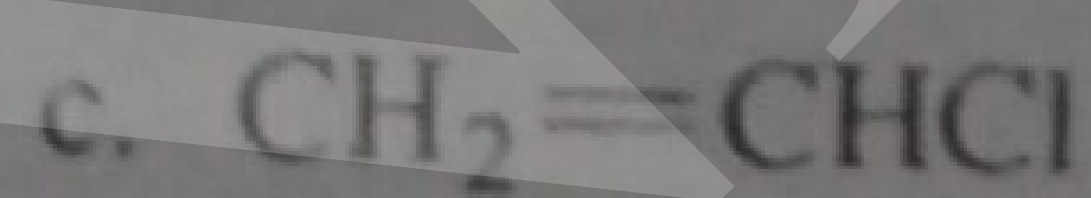
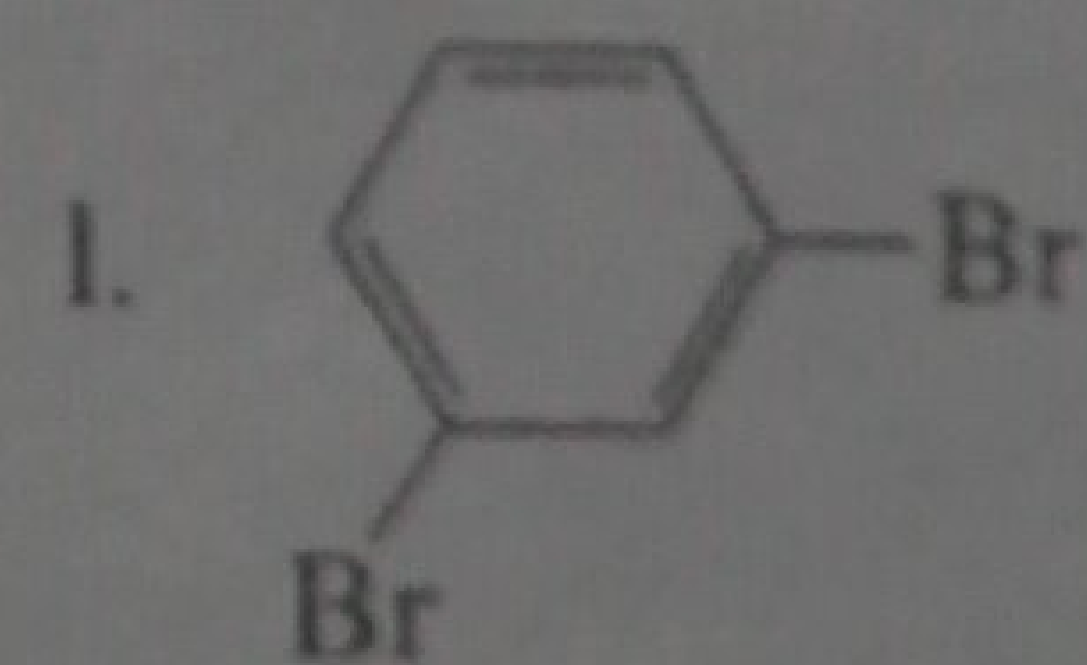
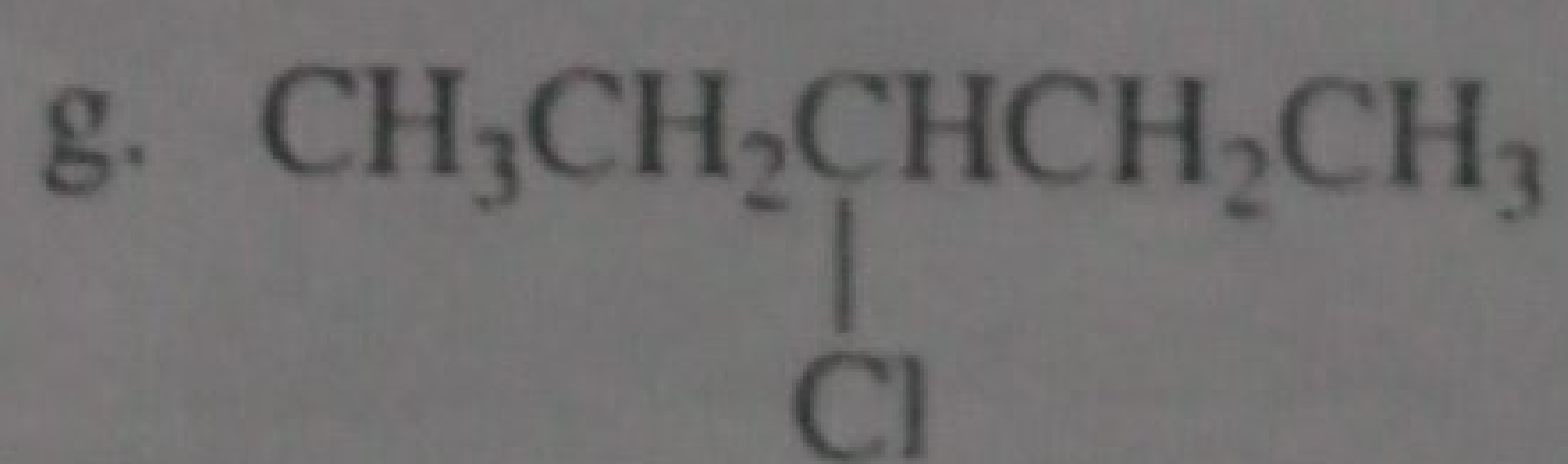
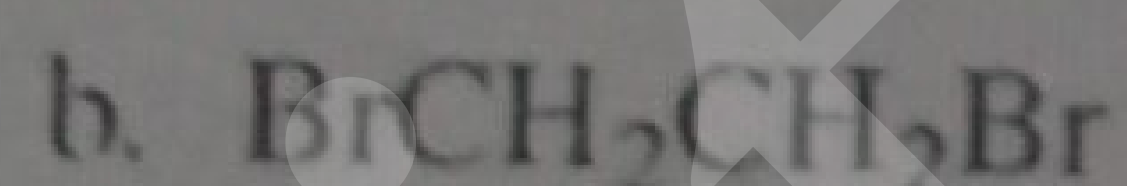
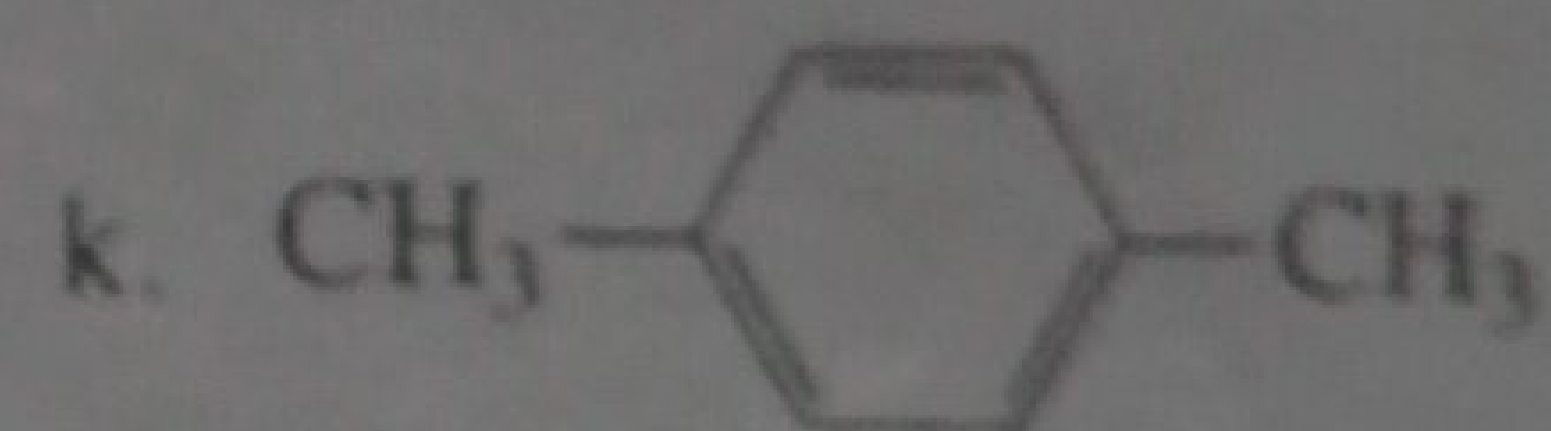
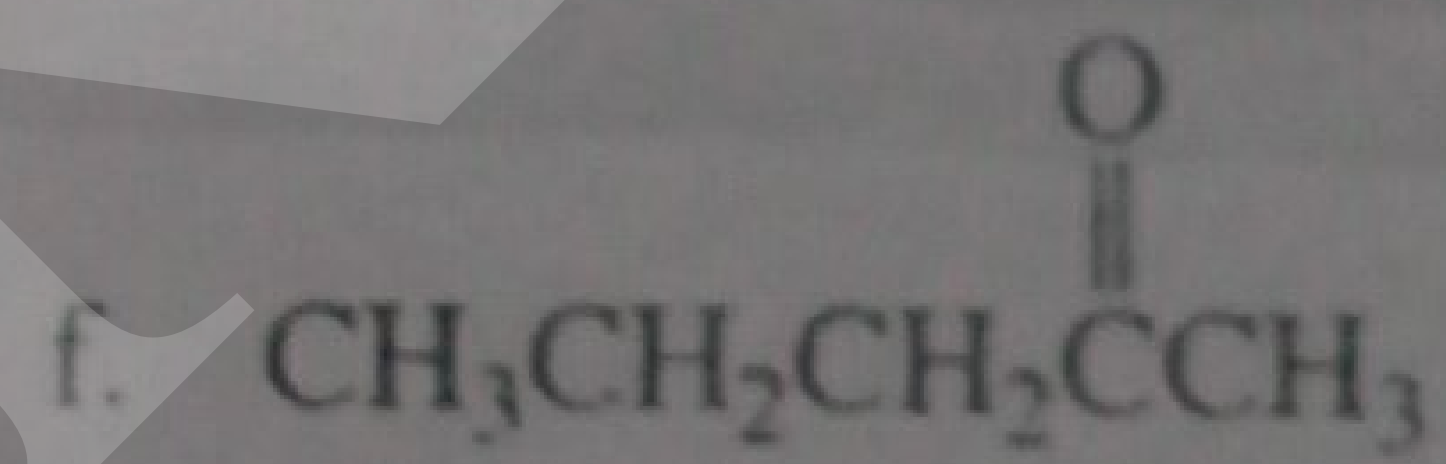
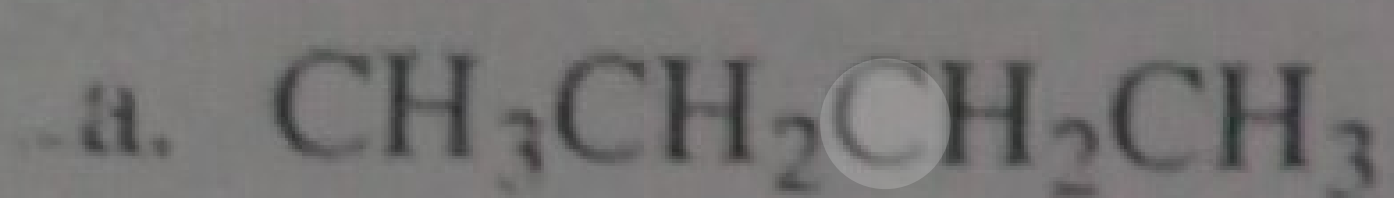
$\text{H}_a$  and  $\text{H}_b$  are not equivalent  
 $\text{H}_c$  and  $\text{H}_d$  are not equivalent

You can tell how many sets of chemically equivalent protons a compound has from the number of signals in its  $^1\text{H}$  NMR spectrum.

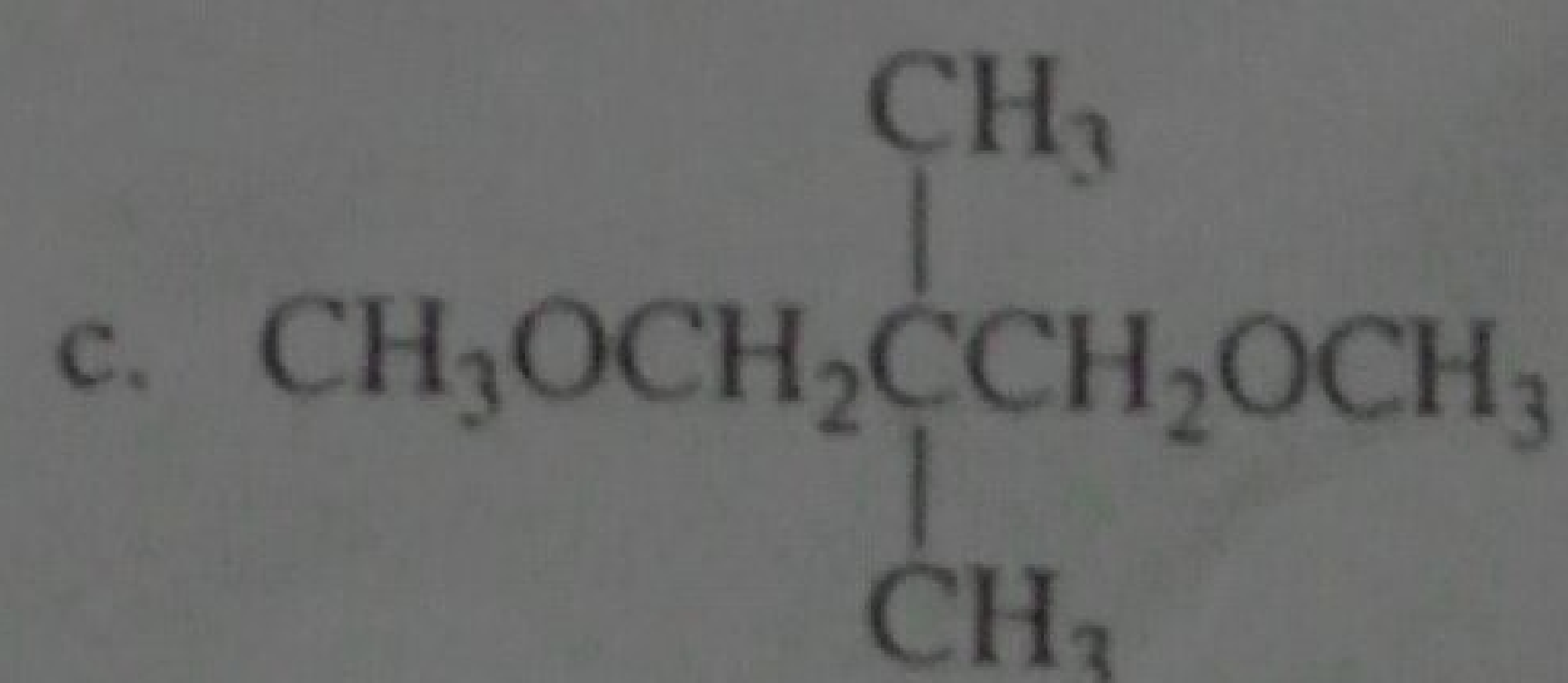
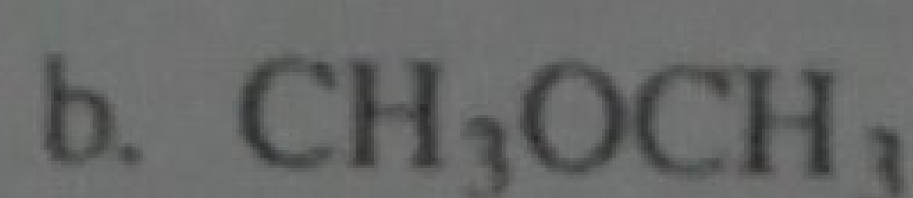
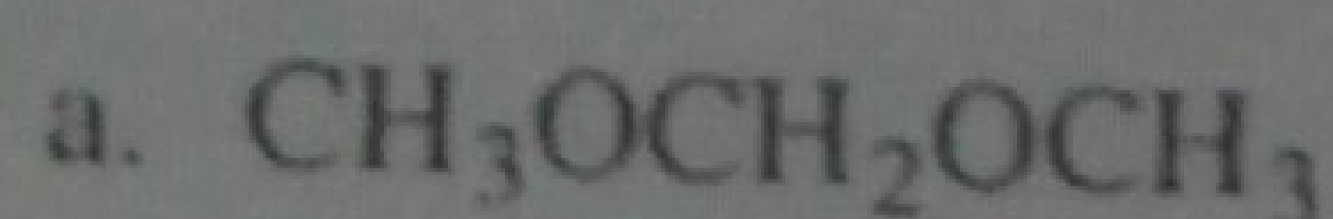
Sometimes, two protons on the same carbon are not equivalent. For example, the  $^1\text{H}$  NMR spectrum of chlorocyclobutane has five signals. Even though they are bonded to the same carbon, the  $\text{H}_a$  and  $\text{H}_b$  protons are not equivalent because they are not in the same environment:  $\text{H}_a$  is trans to Cl and  $\text{H}_b$  is cis to Cl. Similarly, the  $\text{H}_c$  and  $\text{H}_d$  protons are not equivalent.

**PROBLEM 3**

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

**PROBLEM 4**

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





**PROBLEM 5**

There are three isomeric dichlorocyclopropanes. Their  $^1\text{H}$  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.

**14.5 The Chemical Shift**

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). Because TMS is a highly volatile compound, it can easily be removed from the sample by evaporation after the NMR spectrum is taken.

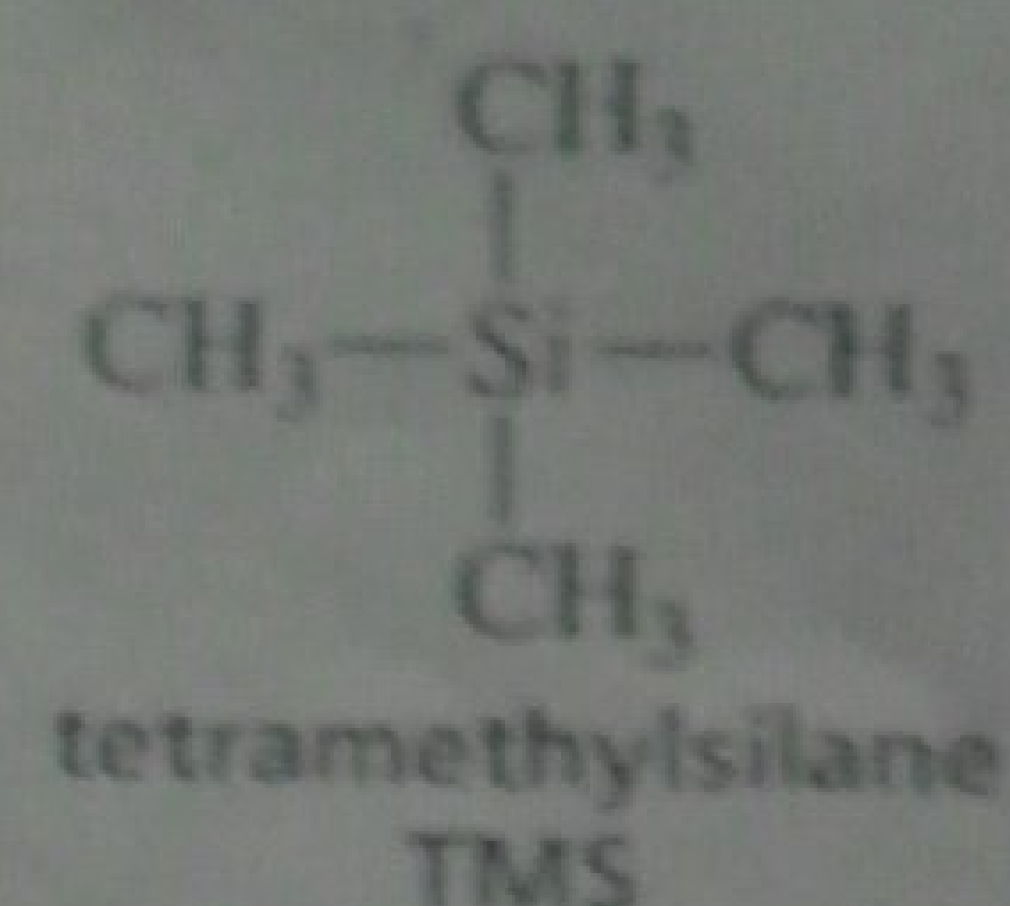
② The methyl protons of TMS are in a more electron-dense environment than are most protons in organic molecules, because silicon is less electronegative than carbon (electronegativities of 1.8 and 2.5, respectively). Consequently, the signal for the methyl protons of TMS is at a lower frequency than most other signals (i.e., it appears to the right of the other signals).

The 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  $\delta$  (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:

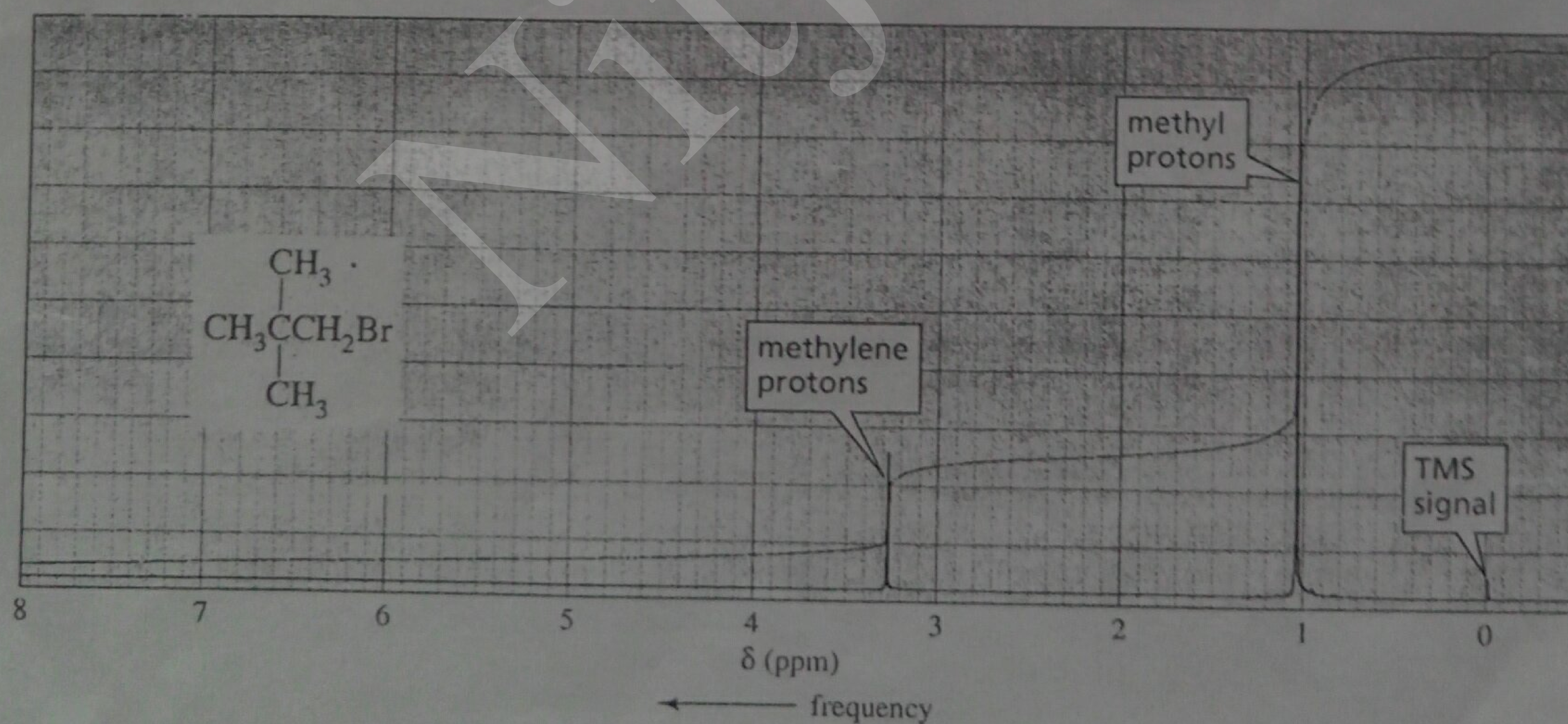
$$\delta = \text{chemical shift (ppm)} = \frac{\text{distance downfield from TMS (Hz)}}{\text{operating frequency of the spectrometer (MHz)}}$$

(Most proton chemical shifts fall in the range from 0 to 10 ppm.)

The  $^1\text{H}$  NMR spectrum for 1-bromo-2,2-dimethylpropane in Figure 14.5 shows that the chemical shift of the methyl protons is at 1.05 ppm and the chemical shift of



3-D Molecule:  
Tetramethylsilane



▲ Figure 14.5

$^1\text{H}$  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 greater the chemical shift ( $\delta$ ), the higher the frequency.

The chemical shift ( $\delta$ ) is independent of the operating frequency of the spectrometer.

the methylene protons is at 3.28 ppm. Notice that low-frequency (upfield, shielded) signals have small  $\delta$  (ppm) values, whereas high-frequency (downfield, deshielded) signals have large  $\delta$  values.

The advantage of the  $\delta$  scale is that the chemical shift of a given nucleus is independent of the operating frequency of the NMR spectrometer. Thus, the chemical shift of the methyl protons of 1-bromo-2,2-dimethylpropane is at 1.05 ppm in both a 60-MHz and a 360-MHz instrument. In contrast, if the chemical shift were reported in hertz, it would be at 63 Hz in a 60-MHz instrument and at 378 Hz in a 360-MHz instrument ( $63/60 = 1.05$ ;  $378/360 = 1.05$ ). The following diagram will help you keep track of the terms associated with NMR spectroscopy:

|                                       |  |
|---------------------------------------|--|
| protons in electron-poor environments | protons in electron-dense environments |
| deshielded protons                    | shielded protons                       |
| downfield                             | upfield                                |
| high frequency                        | low frequency                          |
| large $\delta$ values                 | small $\delta$ values                  |

←  $\delta$   
← 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.

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

#### PROBLEM 7

- If two signals differ by 1.5 ppm in a 300-MHz spectrometer, by how much do they differ in a 100-MHz spectrometer?
- 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  $^1\text{H}$  NMR signal of  $(\text{CH}_3)_2\text{Mg}$  relative to the TMS signal? (Hint: See Table 12.3 on p. 467.)

4

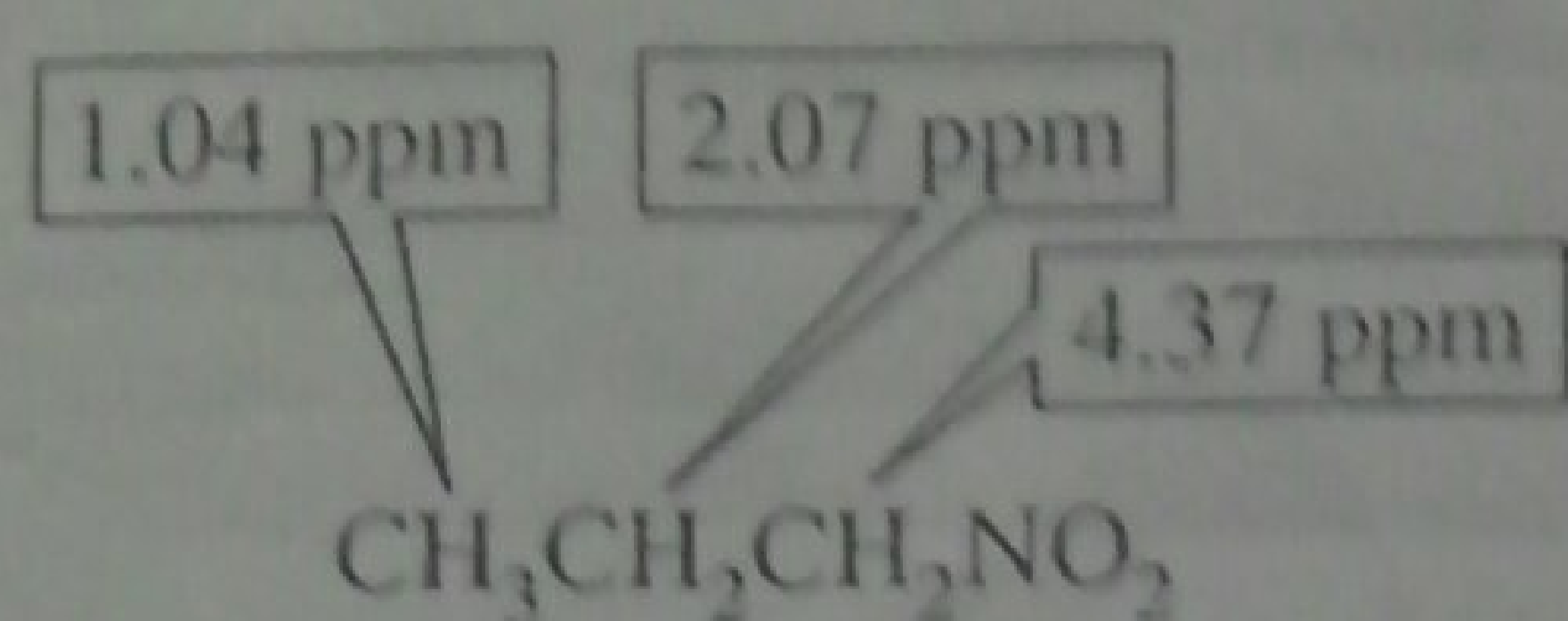
### 14.6 The Relative Positions of $^1\text{H}$ NMR Signals

The  $^1\text{H}$  NMR spectrum of 1-bromo-2,2-dimethylpropane in Figure 14.5 has two signals because the compound has two different kinds of protons. The methylene protons are in a less electron-dense environment than the methyl protons are because the methylene protons are closer to the electron-withdrawing bromine. Because the methylene protons are in a less electron-dense environment, they are less shielded from the applied magnetic field. The signal for these protons therefore occurs at a higher frequency than the signal for the more shielded methyl protons. Remember that the right-hand side of an NMR spectrum is the low-frequency side, where protons in electron-dense environments (more shielded) show a signal. The left-hand side is the high-frequency side, where less shielded protons show a signal (Figure 14.4).

We would expect the  $^1\text{H}$  NMR spectrum of 1-nitropropane to have three signals because the compound has three different kinds of protons. The closer the protons are

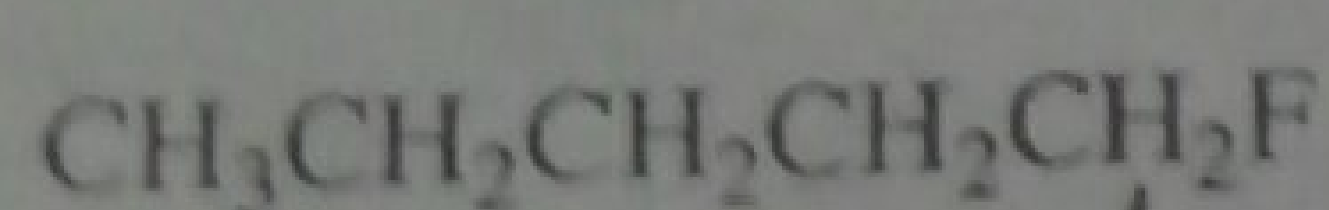


to the electron-withdrawing nitro group, the less they are shielded from the applied magnetic field, so the higher the frequency (i.e., the farther downfield) at which their signals will appear. Thus, the protons closest to the nitro group show a signal at the highest frequency (4.37 ppm), and the ones farthest from the nitro group show a signal at the lowest frequency (1.04 ppm).

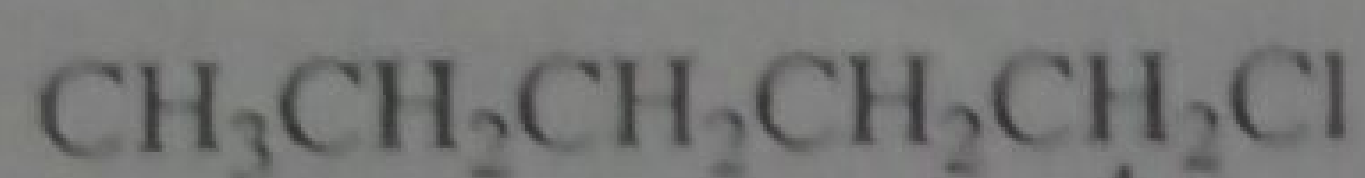


Electron withdrawal causes NMR signals to appear at higher frequencies (at larger  $\delta$  values).

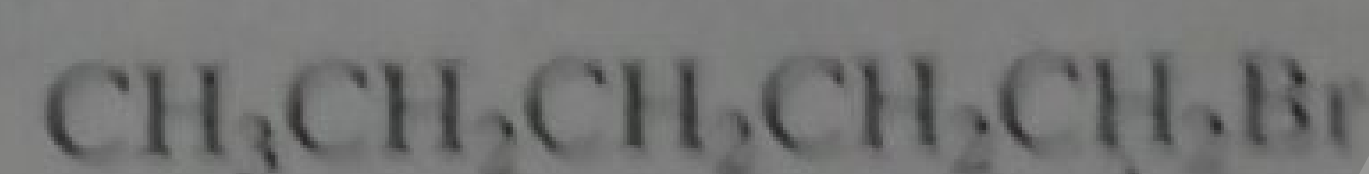
Compare the chemical shifts of the methylene protons immediately adjacent to the halogen in each of the following alkyl halides. The position of the signal depends on the electronegativity of the halogen—the more electronegative the halogen, the higher is the frequency of the signal. Thus, the signal 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.



4.50 ppm



3.50 ppm



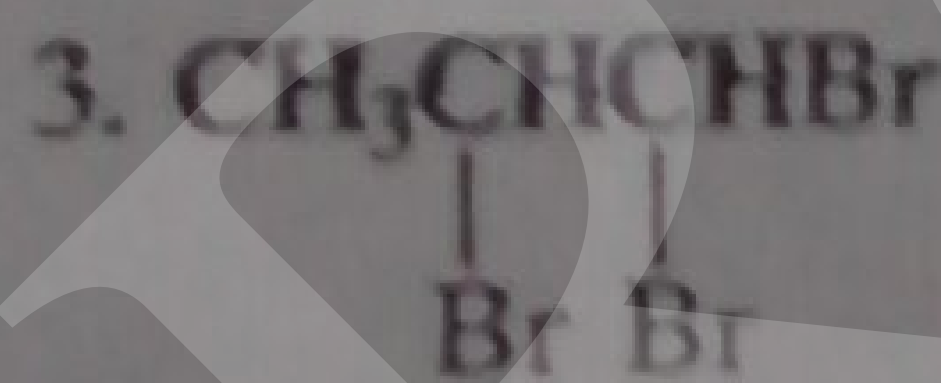
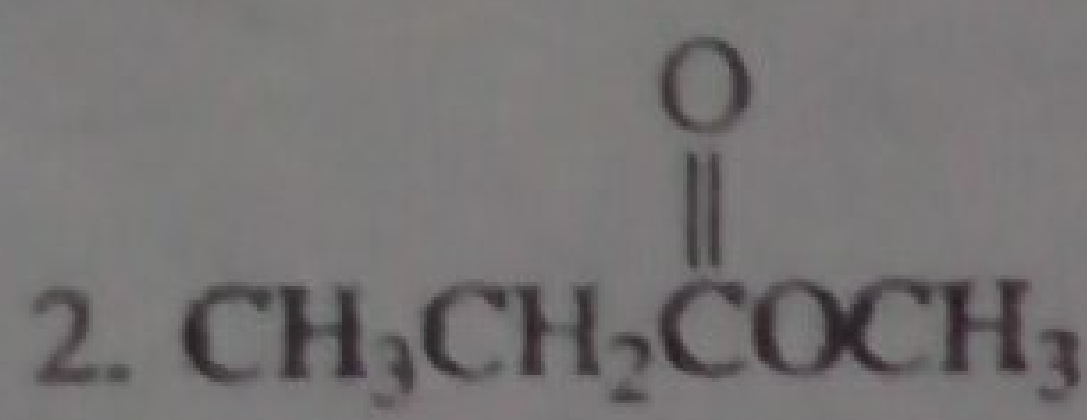
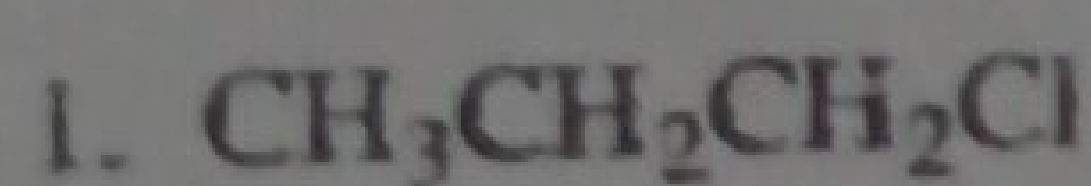
3.40 ppm



3.20 ppm

### PROBLEM 9

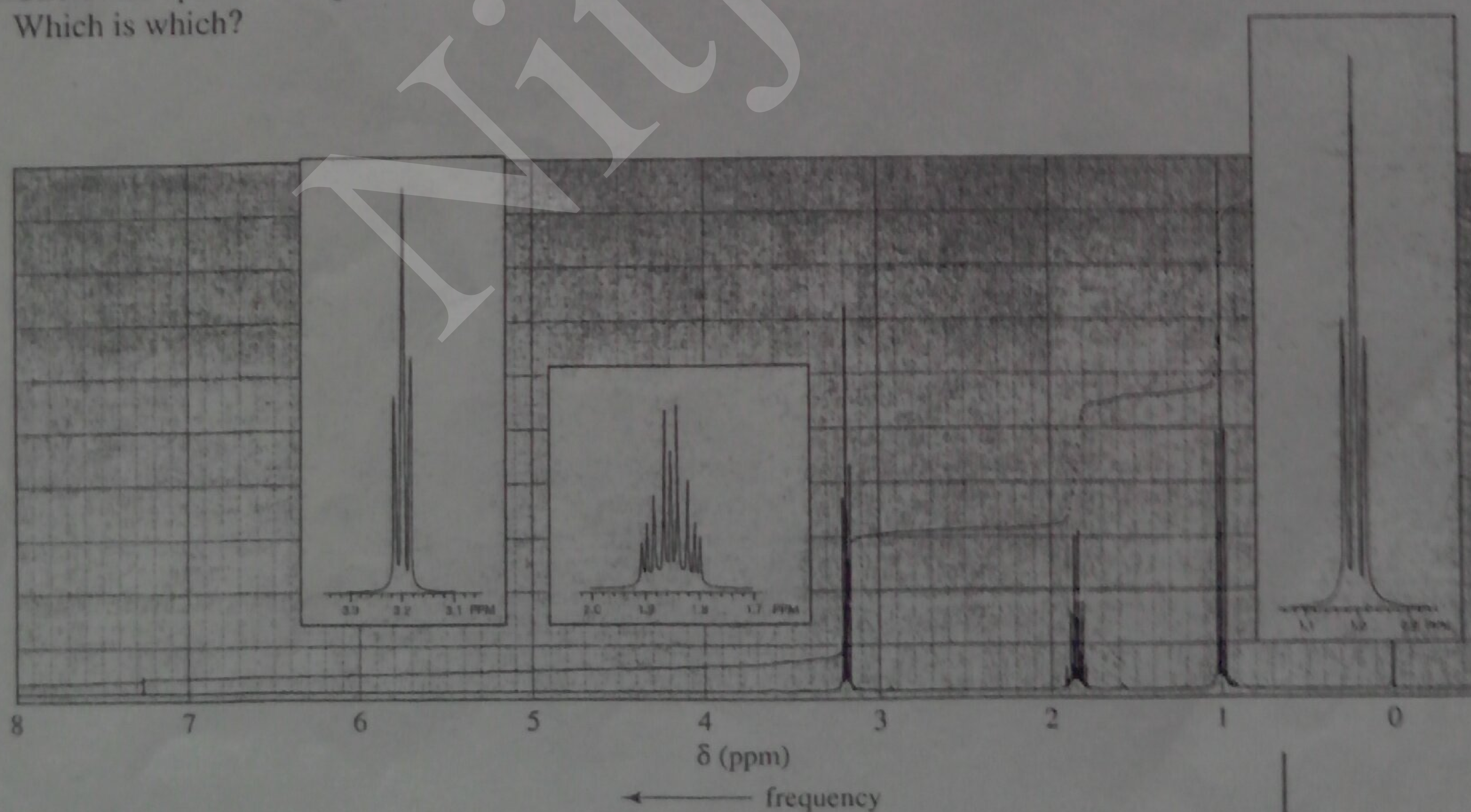
a. Which set of protons in each of the following compounds is the least shielded?



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

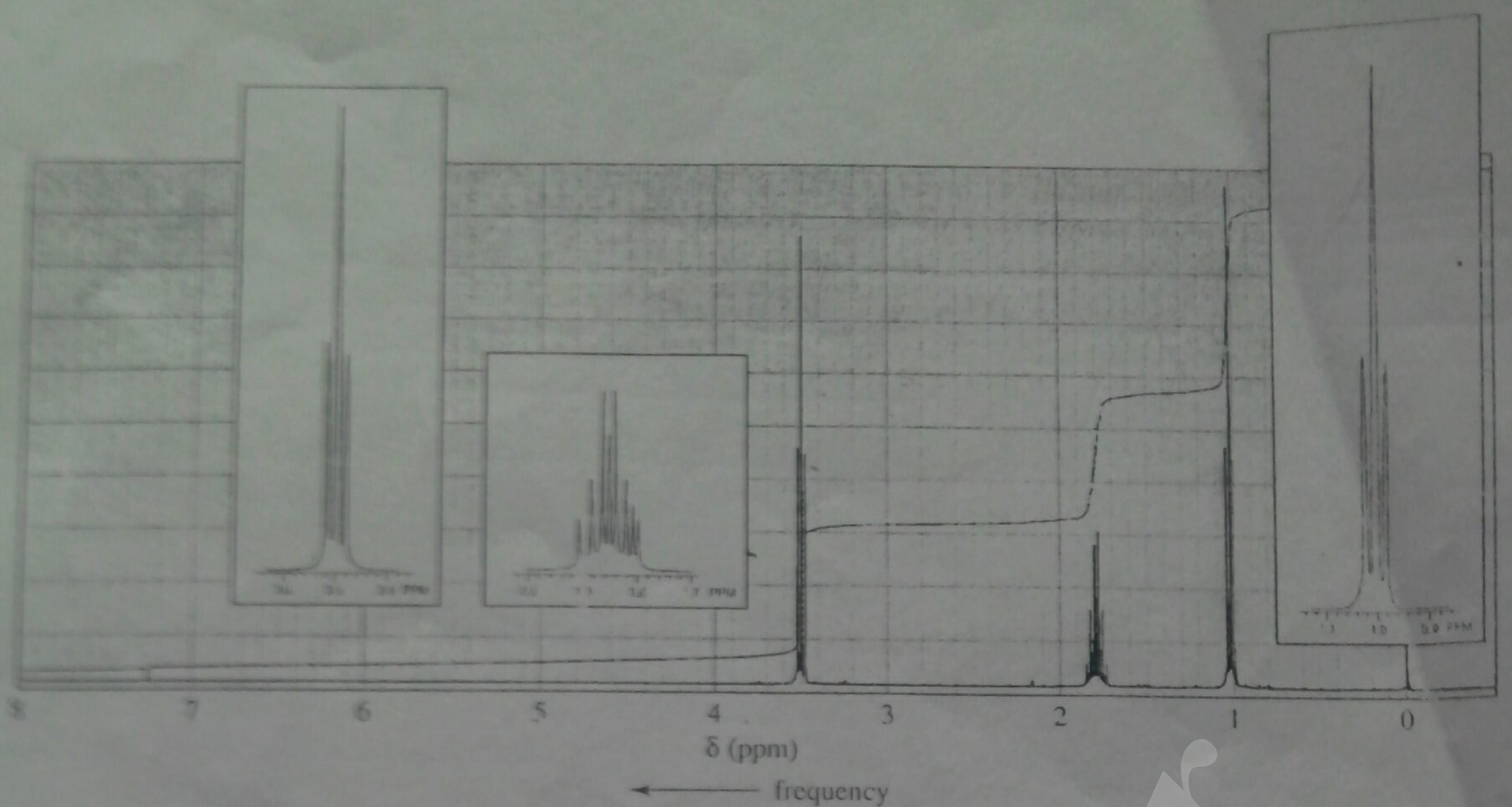
### PROBLEM 10

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



▲ Figure 14.6  
 $^1\text{H}$  NMR spectra for Problem 10.





▲ Figure 14.6 (continued)  
 $^1\text{H}$  NMR spectra for Problem 10.

## 14.7 Characteristic Values of Chemical Shifts


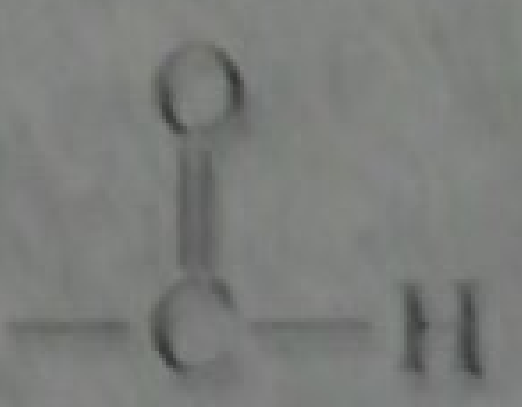
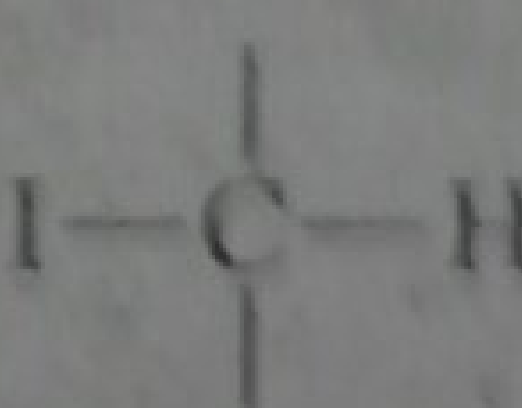
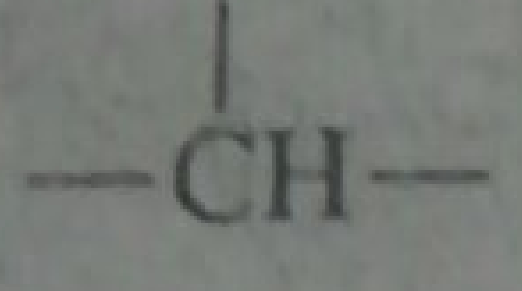
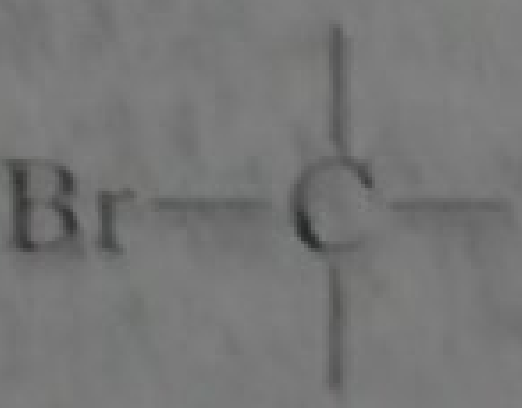
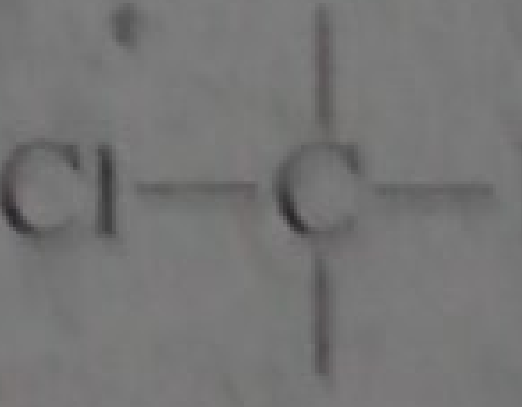
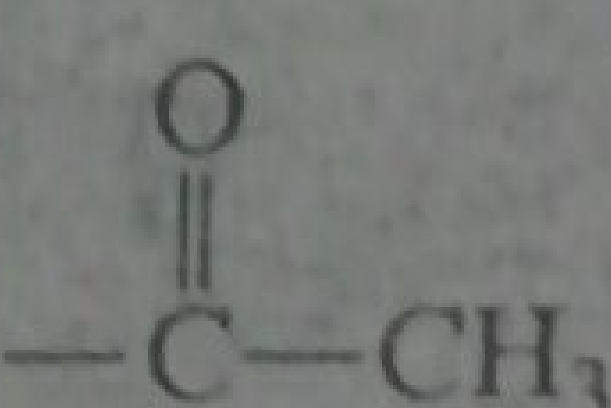
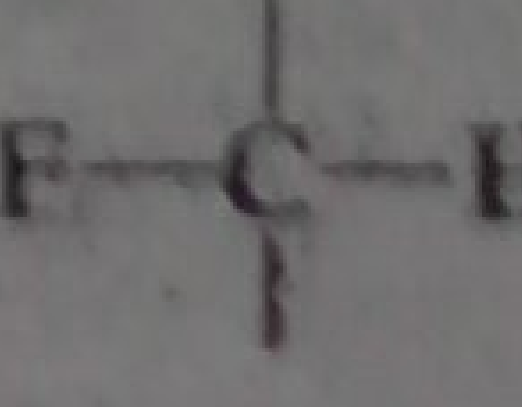
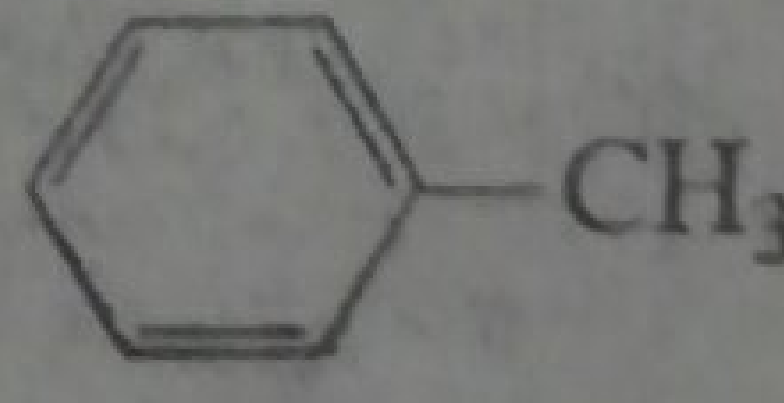
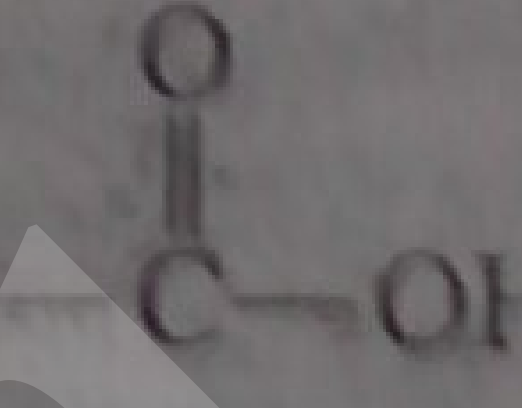
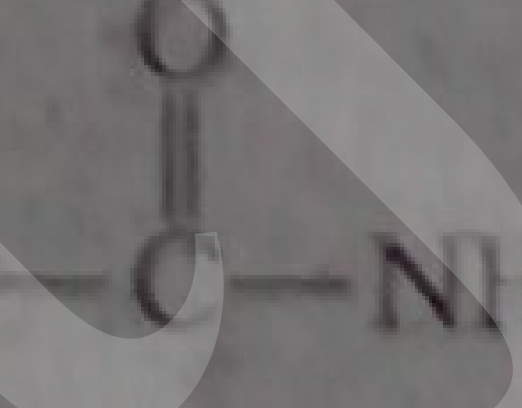
Approximate values of chemical shifts for different kinds of protons are shown in Table 14.1. (A more extensive compilation of chemical shifts is given in Appendix VI.) An  $^1\text{H}$  NMR spectrum can be divided into six regions. Rather than memorizing chemical shift values, if you remember the kinds of protons that are in each region, you will be able to tell what kinds of protons a molecule has from a quick look at its NMR spectrum.

|  |  |   |  |  |   |
|--|--|---|--|--|---|
| $\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{H} \\   \\ -\text{C}-\text{H} \end{array}$ | $\begin{array}{c} \text{H} \\   \\ \text{C}_6\text{H}_5 \end{array}$ | $\begin{array}{c} \text{H} \\   \\ \text{C}=\text{C} \\   \quad   \end{array}$<br>vinylic | $\begin{array}{c} \text{Z} \\   \\ -\text{C}-\text{H} \\   \end{array}$<br>Z = O, N, halogen | $\begin{array}{c} \text{O} \quad \text{H} \\    \quad   \\ \text{C}-\text{C}- \\   \quad   \\ \text{C}=\text{C}-\text{C}- \\   \quad   \end{array}$<br>allylic | $\begin{array}{c}   \quad   \\ -\text{C}-\text{C}-\text{H} \\   \quad   \end{array}$<br>saturated |
| 12   | 8.0  | 6.5   | 4.5  | 2.5  | 1.5   |
| $\delta$ (ppm)   |  |   |  |  |   |

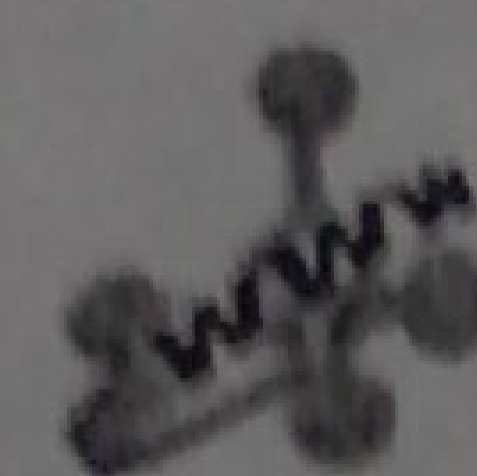
Table 14.1 shows that the chemical shift of methyl protons is at a lower frequency (0.9 ppm) than is the chemical shift of methylene protons (1.3 ppm) in a similar environment and the chemical shift of methylene protons is at a lower frequency than is the chemical shift of a methine proton (1.4 ppm) in a similar environment. (When an  $sp^3$  carbon is bonded to only one hydrogen, the hydrogen is called a methine hydrogen.) For example, the  $^1\text{H}$  NMR spectrum of butanone shows three signals. The signal for the *a* protons of butanone is the signal at the lowest frequency because the protons are farthest from the electron-withdrawing carbonyl group. (In correlating an NMR spectrum with a structure, the set of protons responsible for the signal at the lowest frequency will be labeled *a*, the next set will be labeled *b*, the next set *c*, etc.) The *b* and *c* protons are the same distance from the carbonyl group, but the signal



Table 14.1 Approximate Values of Chemical Shifts for  $^1\text{H}$  NMR<sup>a</sup>

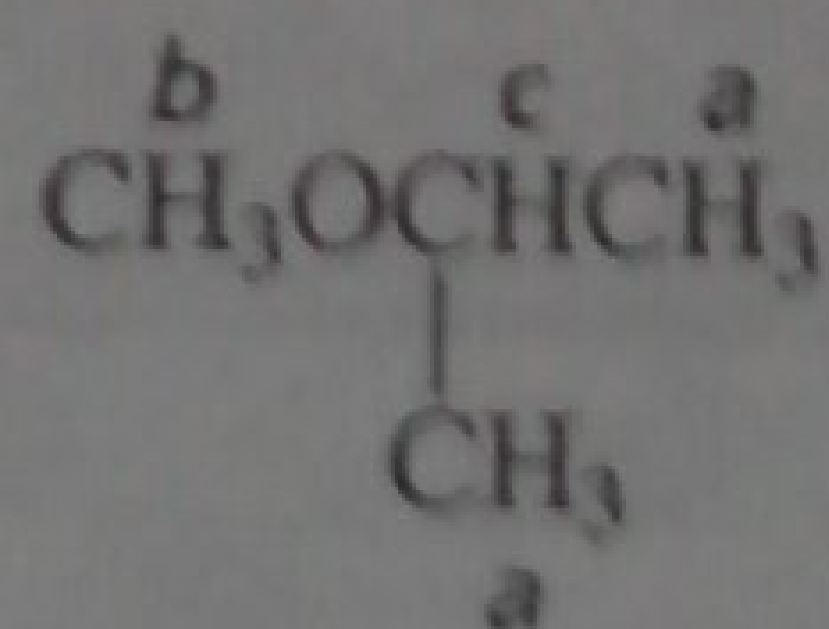
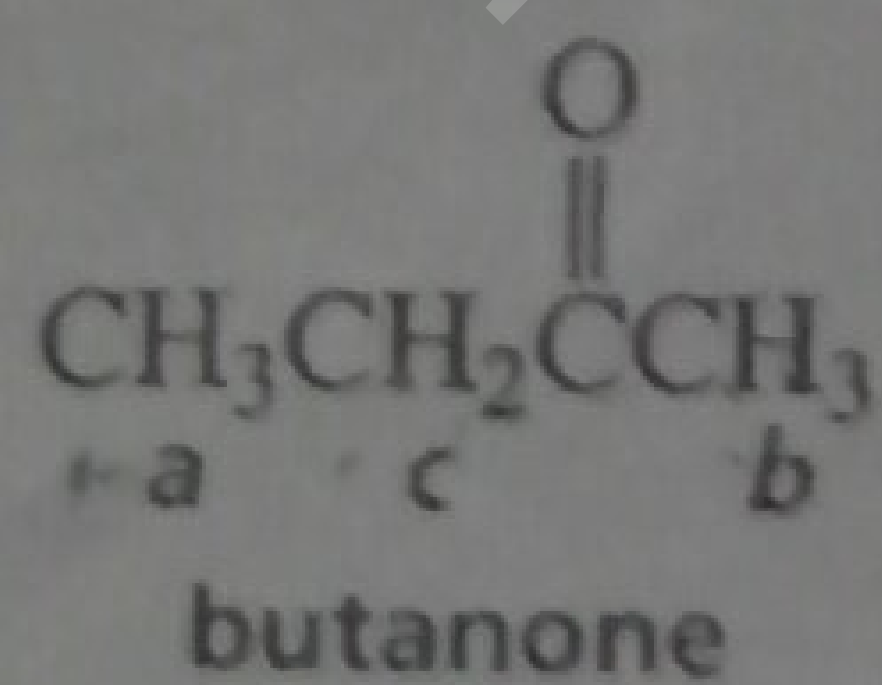
| Type of proton  | Approximate chemical shift (ppm) | Type of proton   | Approximate chemical shift (ppm) |
|---|----------------------------------|--|----------------------------------|
| $(\text{CH}_3)_4\text{Si}$  | 0                                |    | 6.5–8                            |
| $-\text{CH}_3$  | 0.9                              |    | 9.0–10                           |
| $-\text{CH}_2-$   | 1.3                              |    | 2.5–4                            |
|    | 1.4                              |   | 2.5–4                            |
| $-\text{C}=\text{C}-\text{CH}_3$  | 1.7                              |  | 3–4                              |
|   | 2.1                              |  | 4–4.5                            |
|  | 2.3                              | $\text{RNH}_2$   | Variable, 1.5–4                  |
| $-\text{C}\equiv\text{C}-\text{H}$  | 2.4                              | $\text{ROH}$   | Variable, 2–5                    |
| $\text{R}-\text{O}-\text{CH}_3$   | 3.3                              | $\text{ArOH}$  | Variable, 4–7                    |
| $\text{R}-\text{C}=\text{CH}_2$   | 4.7                              |  | Variable, 10–12                  |
| $\text{R}-\text{C}=\text{C}-\text{H}$   | 5.3                              |  | Variable, 5–8                    |

<sup>a</sup>The values are approximate because they are affected by neighboring substituents.



Tutorial:  
NMR chemical shifts

for the *b* protons is at a lower frequency because methyl protons appear at a lower frequency than do methylene protons in a similar environment.



2-methoxypropane

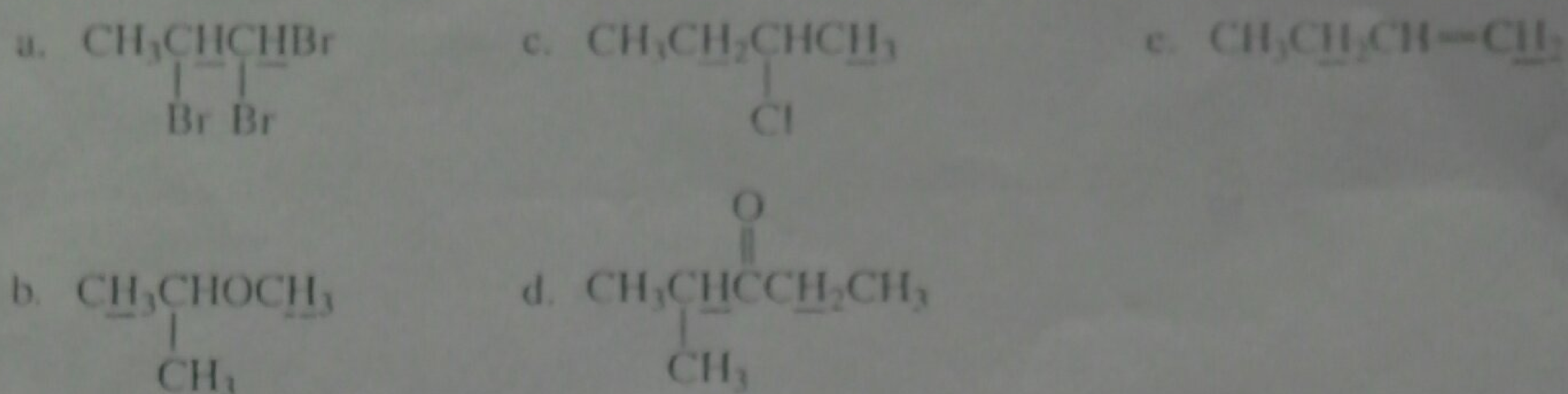
In a similar environment, the signal for methyl protons occurs at a lower frequency than the signal for methylene protons, which in turn occurs at a lower frequency than the signal for a methine proton.

The signal for the *a* protons of 2-methoxypropane is the signal at the lowest frequency in the  $^1\text{H}$  NMR spectrum of this compound because these protons are farthest from the electron-withdrawing oxygen. The *b* and *c* protons are the same distance from the oxygen, but the signal for the *b* protons appears at a lower frequency because, in a similar environment, methyl protons appear at a lower frequency than does a methine proton.

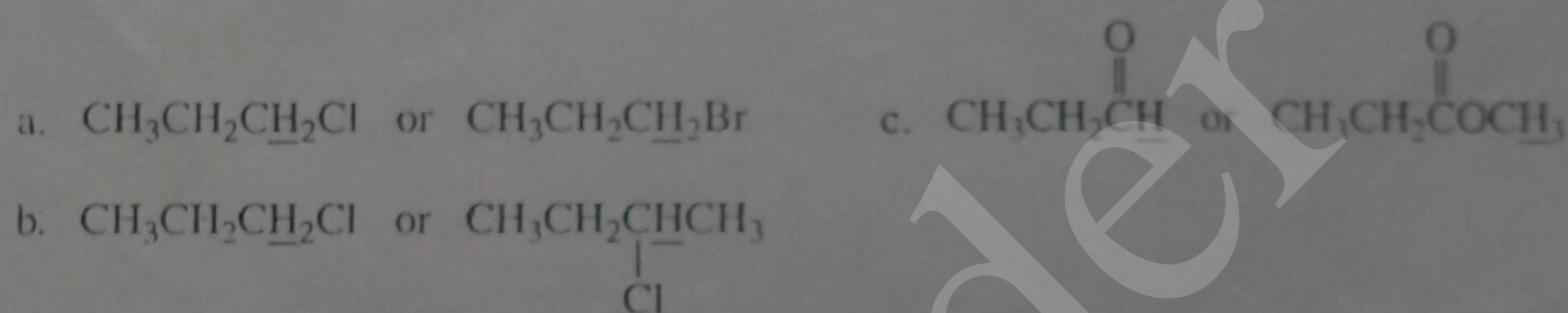


**PROBLEM 11**

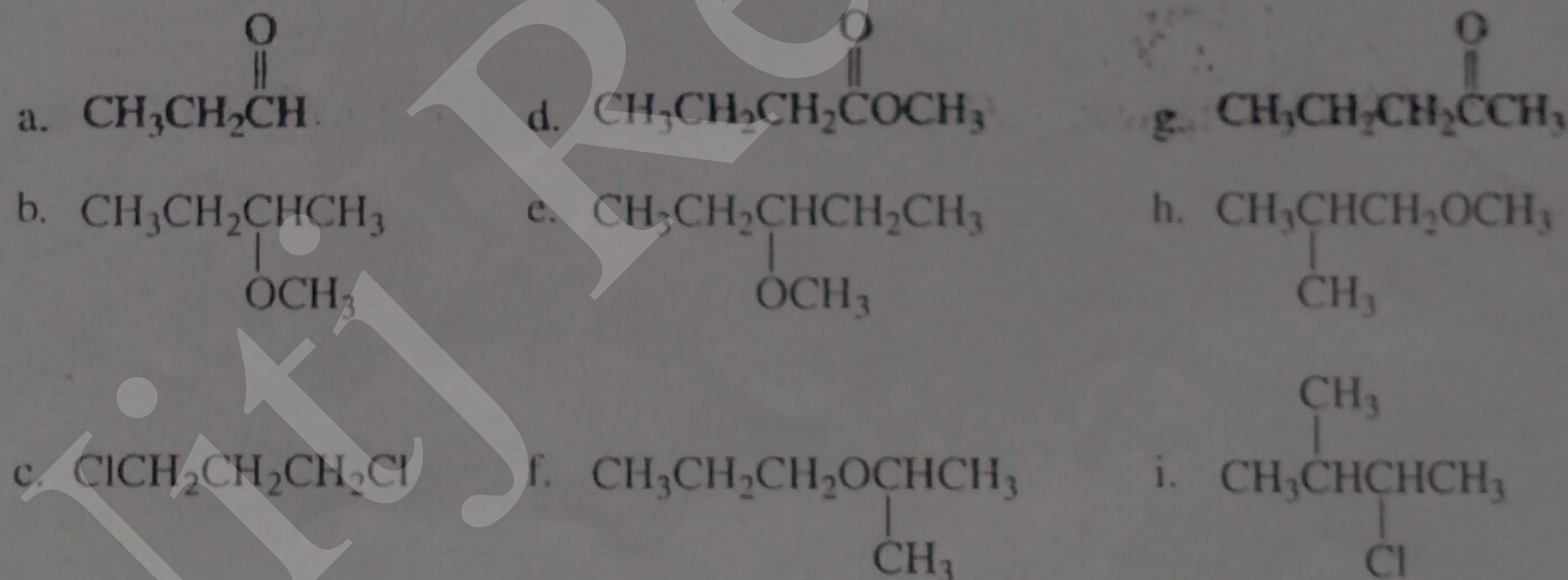
In each of the following compounds, which of the underlined protons has the greater chemical shift (i.e., the farther downfield signal or the higher frequency signal)?

**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)?

**PROBLEM 13**

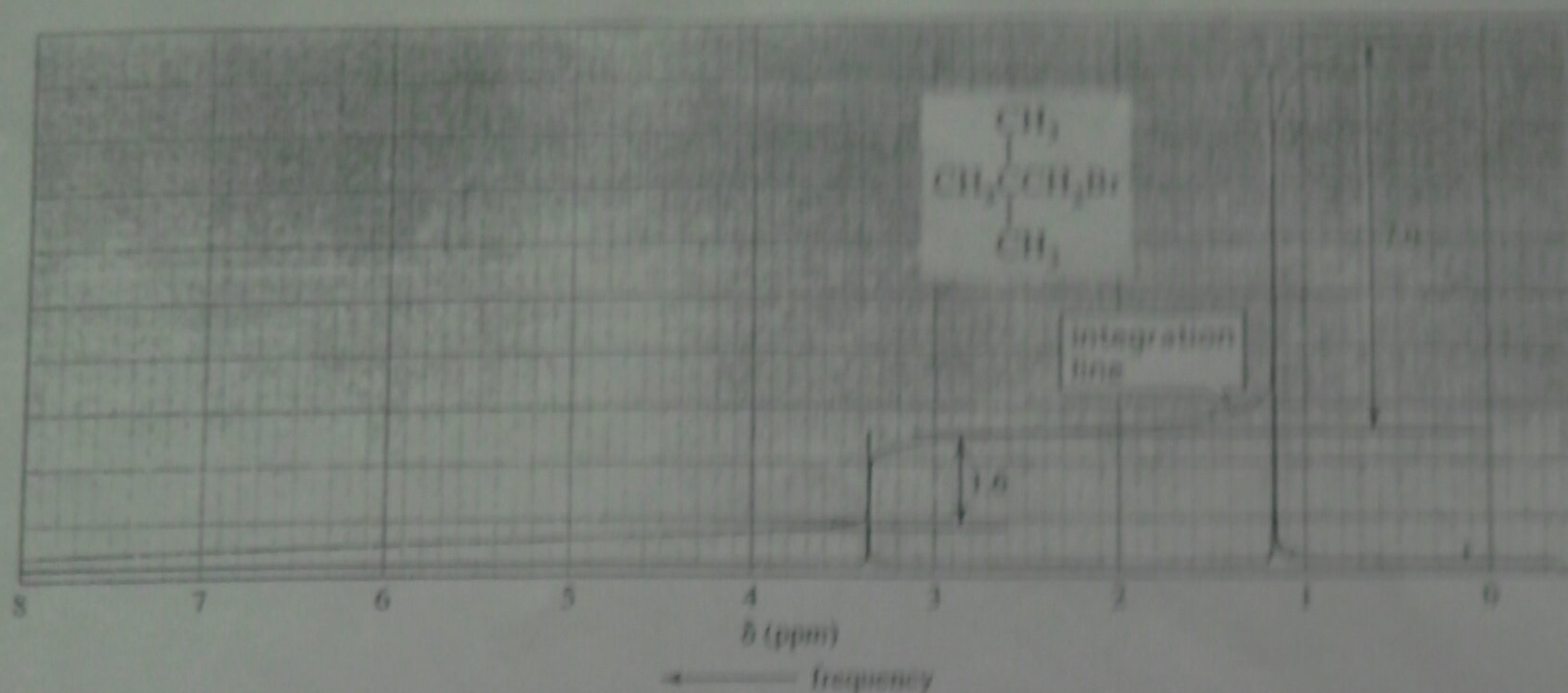
Without referring to Table 14.1, label the protons in the following compounds. The proton that gives the signal at the lowest frequency should be labeled *a*, the next *b*, etc.

**14.8 Integration of NMR Signals**

The two signals in the  $^1\text{H}$  NMR spectrum of 1-bromo-2,2-dimethylpropane in Figure 14.5 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 spectrum is shown again in Figure 14.7.) 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.

You probably remember from a calculus course that the area under a curve can be determined by integration. An  $^1\text{H}$  NMR spectrometer is equipped with a computer that calculates the integrals electronically. Modern spectrometers print out the integrals as numbers on the spectrum. The integrals can also be displayed by a line of integration superimposed on the original spectrum (Figure 14.7). 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

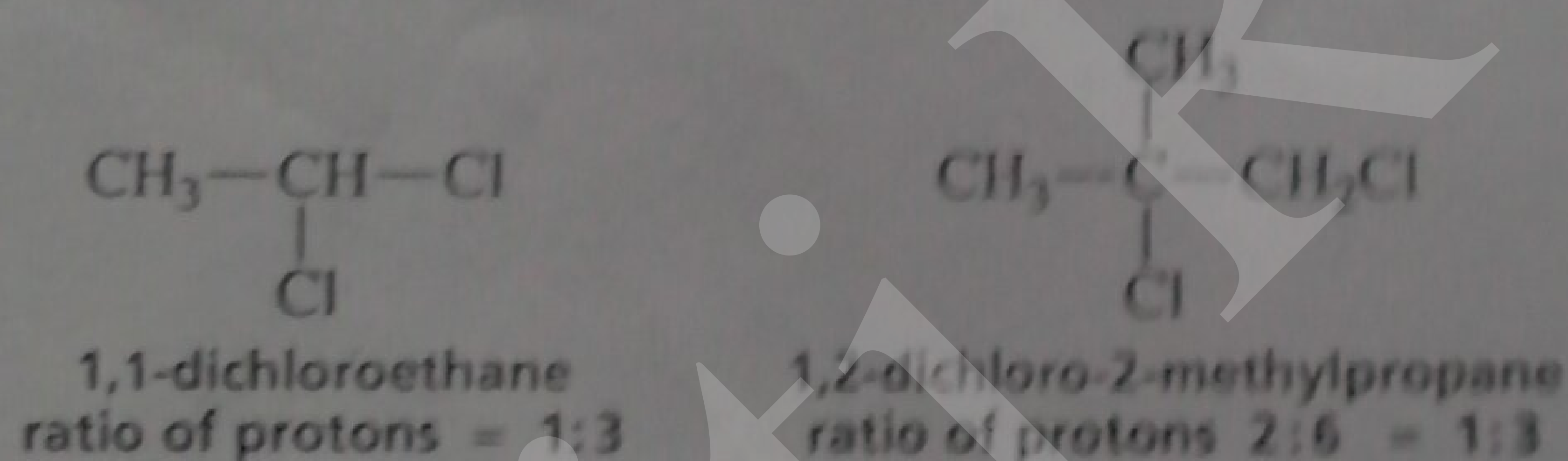




▲ Figure 14.7  
Analysis of the integration line in the  $^1\text{H}$  NMR spectrum of 1-bromo-2,2-dimethylpropane.

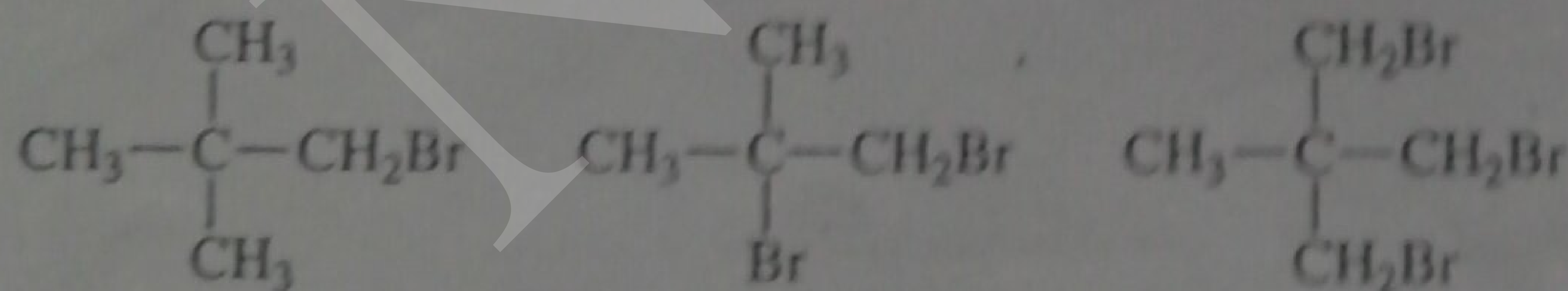
the integration steps, you can determine that the ratio of the integrals is approximately  $1.6:7.0 = 1:4.4$ . (The measured integrals are approximate by as much as 10% because of experimental error.) The ratios are multiplied by a number that will cause all the numbers to be close to whole numbers—in this case, we multiply by 2—because 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.)



### PROBLEM 14

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



### PROBLEM 15 SOLVED

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

#### SOLUTION

- Divide each by the smallest number:

$$\frac{6}{4} = 1.5$$

$$\frac{4}{4} = 1$$

$$\frac{18.4}{4} = 4.6$$



15

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

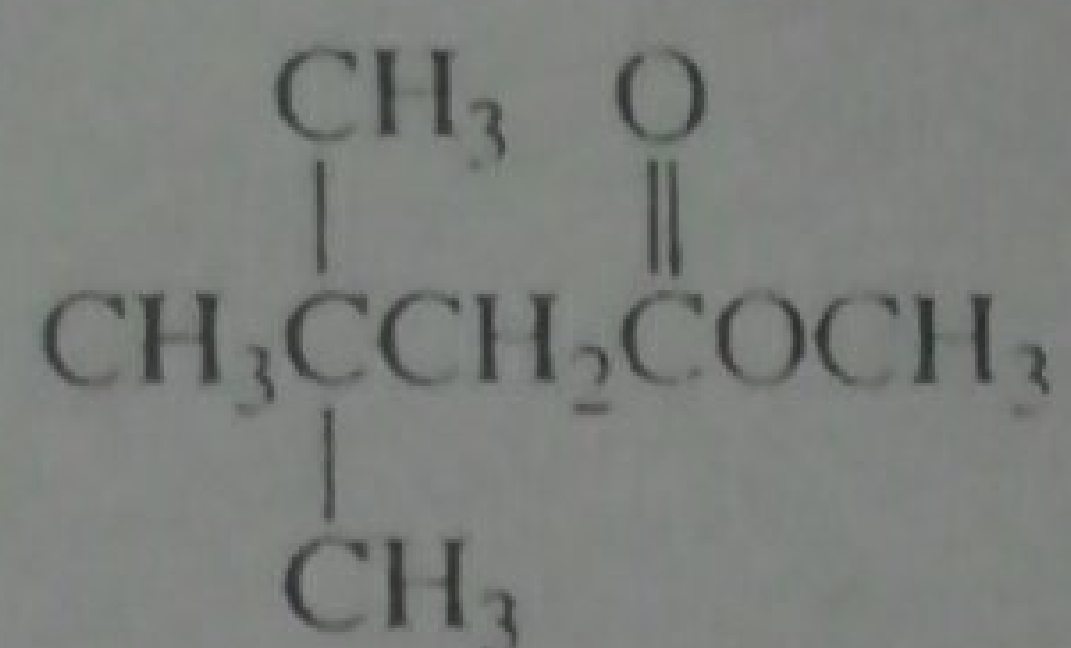
$$1.5 \times 2 = 3$$

$$1 \times 2 = 2$$

$$4.6 \times 2 = 9$$

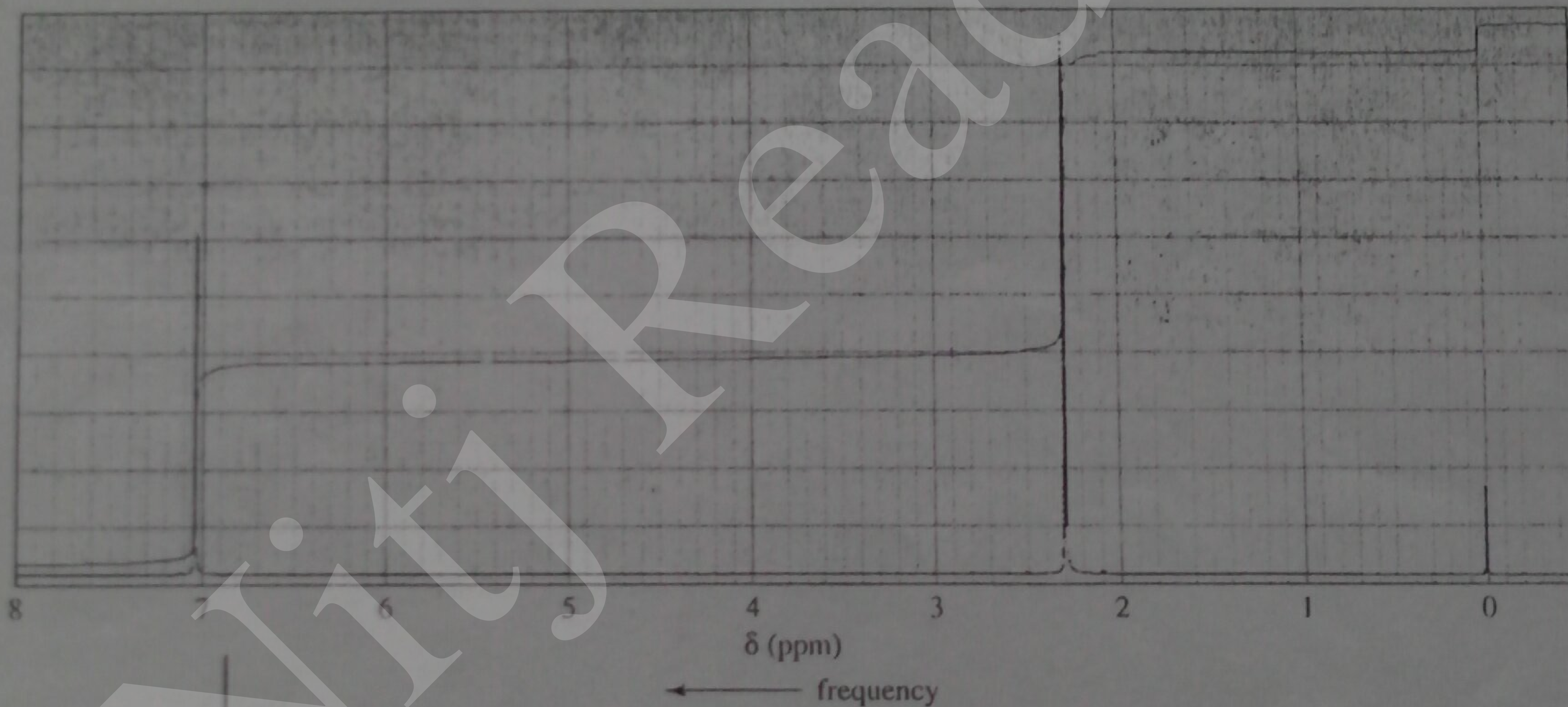
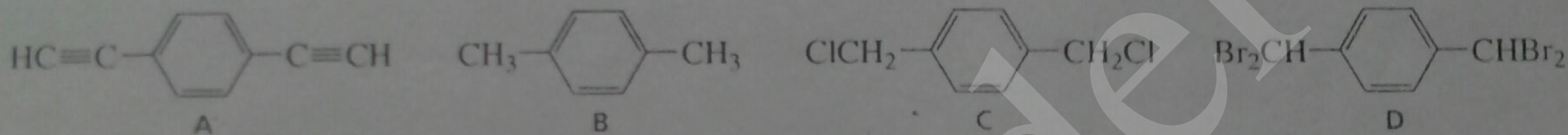
The ratio 3:2:9 gives the relative numbers of the different kinds of protons. The actual ratio could be 6:4:18, or even some higher multiple, but let's not go there if we don't have to.

- 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

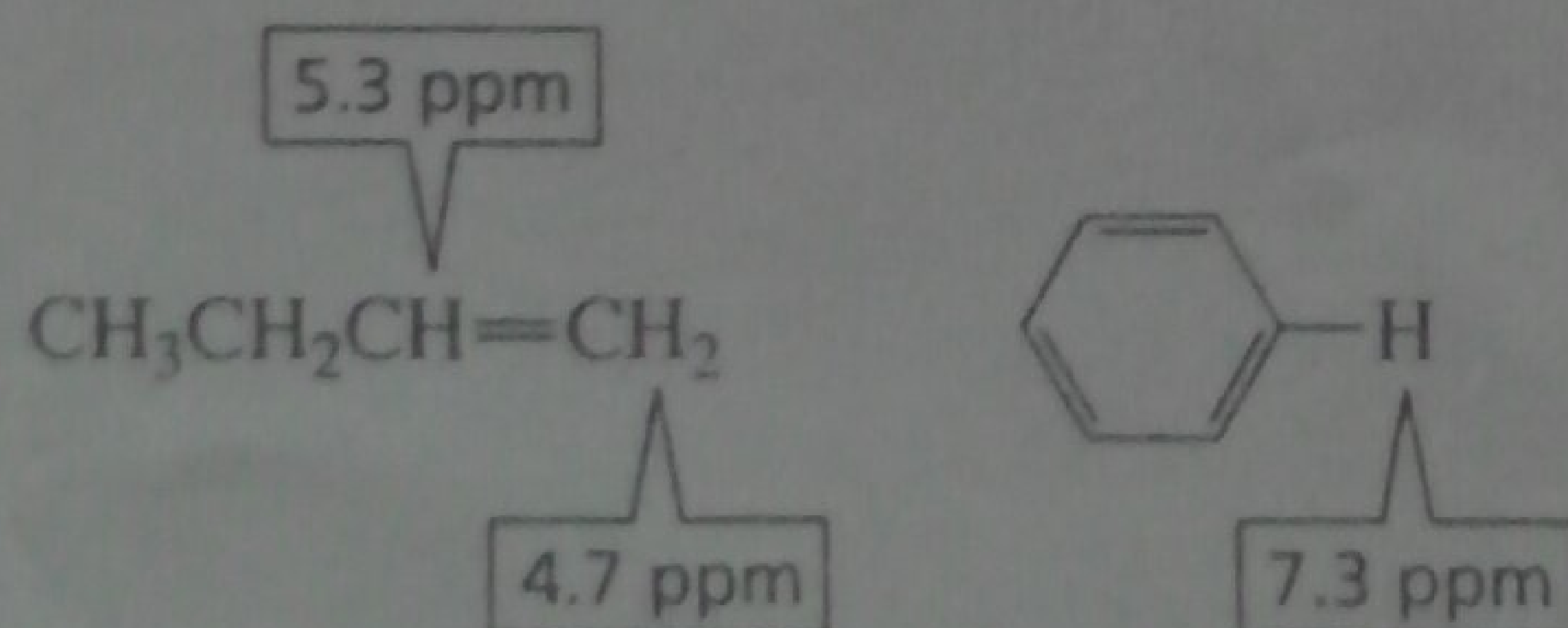
The  $^1\text{H}$  NMR spectrum shown in Figure 14.8 corresponds to one of the following compounds. Which compound is responsible for this spectrum?



▲ Figure 14.8  
 $^1\text{H}$  NMR spectrum for Problem 16.

## 14.9 Diamagnetic Anisotropy

The chemical shifts of hydrogens bonded to  $sp^2$  hybridized carbons are at a higher frequency than one would predict, based on the electronegativity of the  $sp^2$  carbons. For example, a hydrogen bonded to a terminal  $sp^2$  carbon of an alkene appears at 4.7 ppm, a hydrogen bonded to an internal  $sp^2$  carbon appears at 5.3 ppm, and a hydrogen on a benzene ring appears at 6.5–8.0 ppm (Table 14.1).

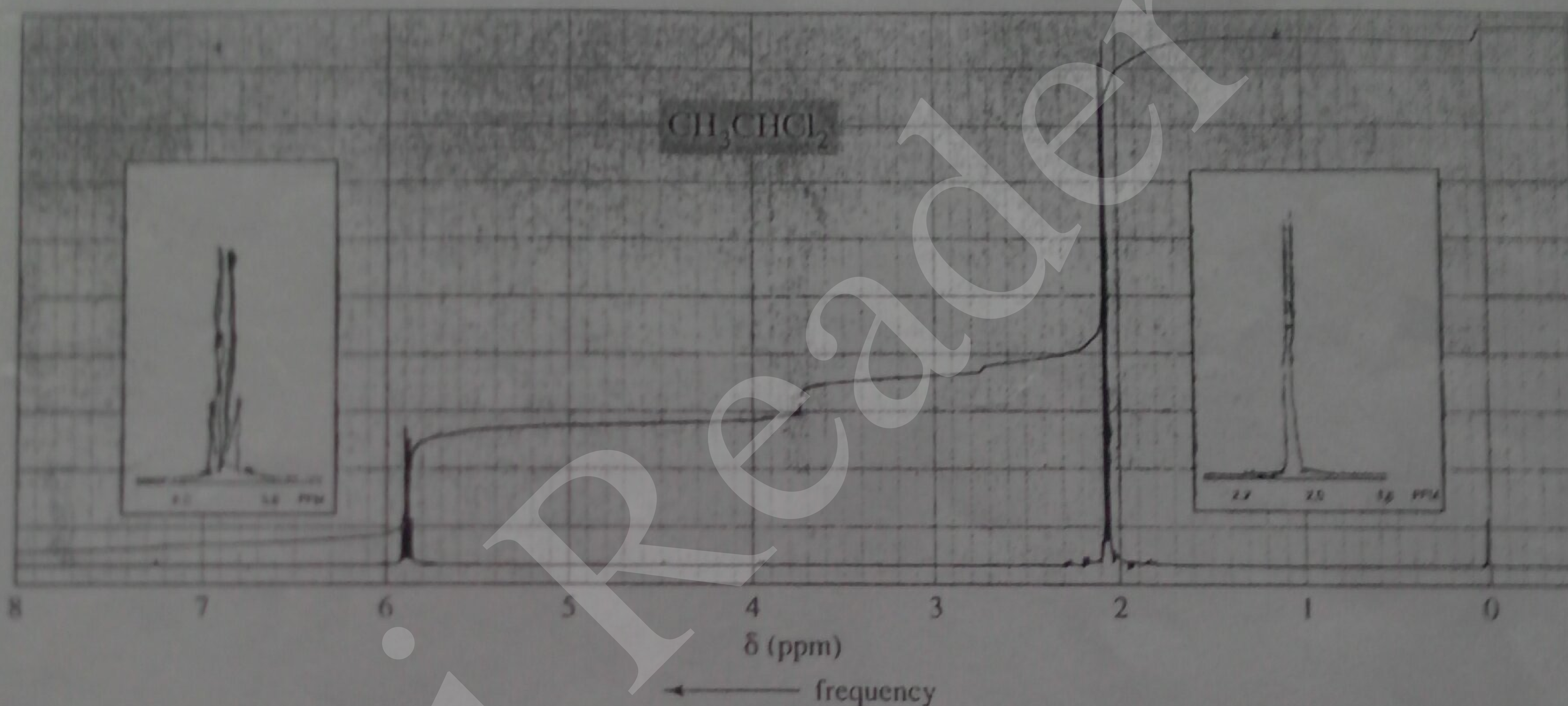




1,1-dichloroethane (the lower-frequency signal) is split into two peaks (a doublet), and the signal for the methine proton is split into four peaks (a quartet). (Magnifications of the doublet and quartet are shown as insets in Figure 14.10.)

Splitting is caused by protons bonded to adjacent (i.e., directly attached) carbons. The splitting of a signal is described by the  $N + 1$  rule, where  $N$  is the number of equivalent protons bonded to adjacent carbons. 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. Both signals in Figure 14.5 are singlets because neither the carbon adjacent to the methyl groups nor that adjacent to the methylene group in 1-bromo-2,2-dimethylpropane is bonded to any protons ( $N + 1 = 0 + 1 = 1$ ). In contrast, in Figure 14.10, 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 ( $N + 1 = 1 + 1 = 2$ ). 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 ( $N + 1 = 3 + 1 = 4$ ). The number of peaks in a signal is called the multiplicity of the signal. 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.

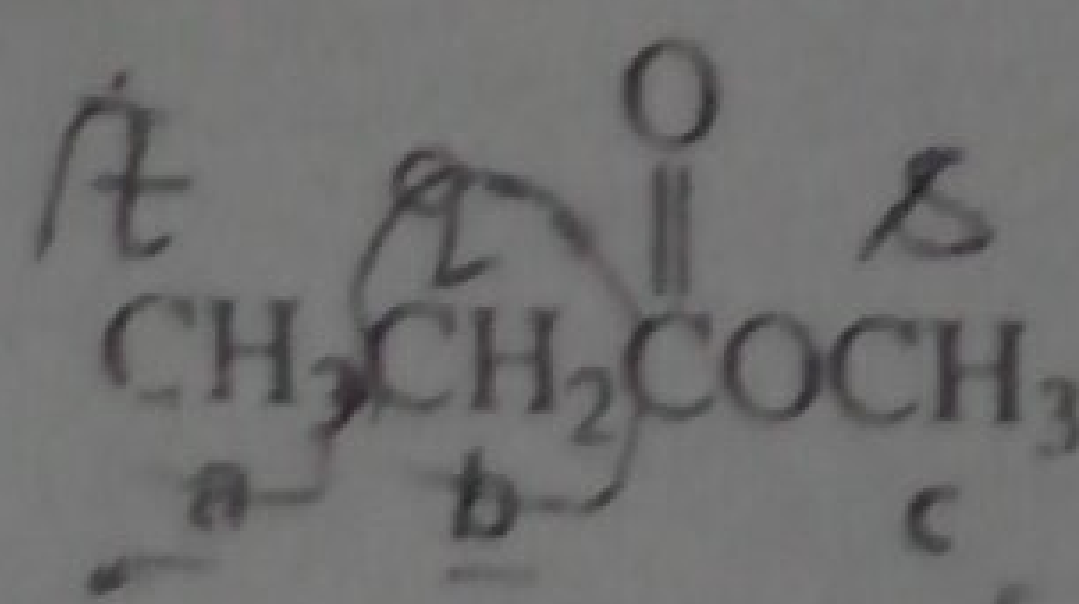
An  $^1\text{H}$  NMR signal is split into  $N + 1$  peaks, where  $N$  is the number of equivalent protons bonded to adjacent carbons.



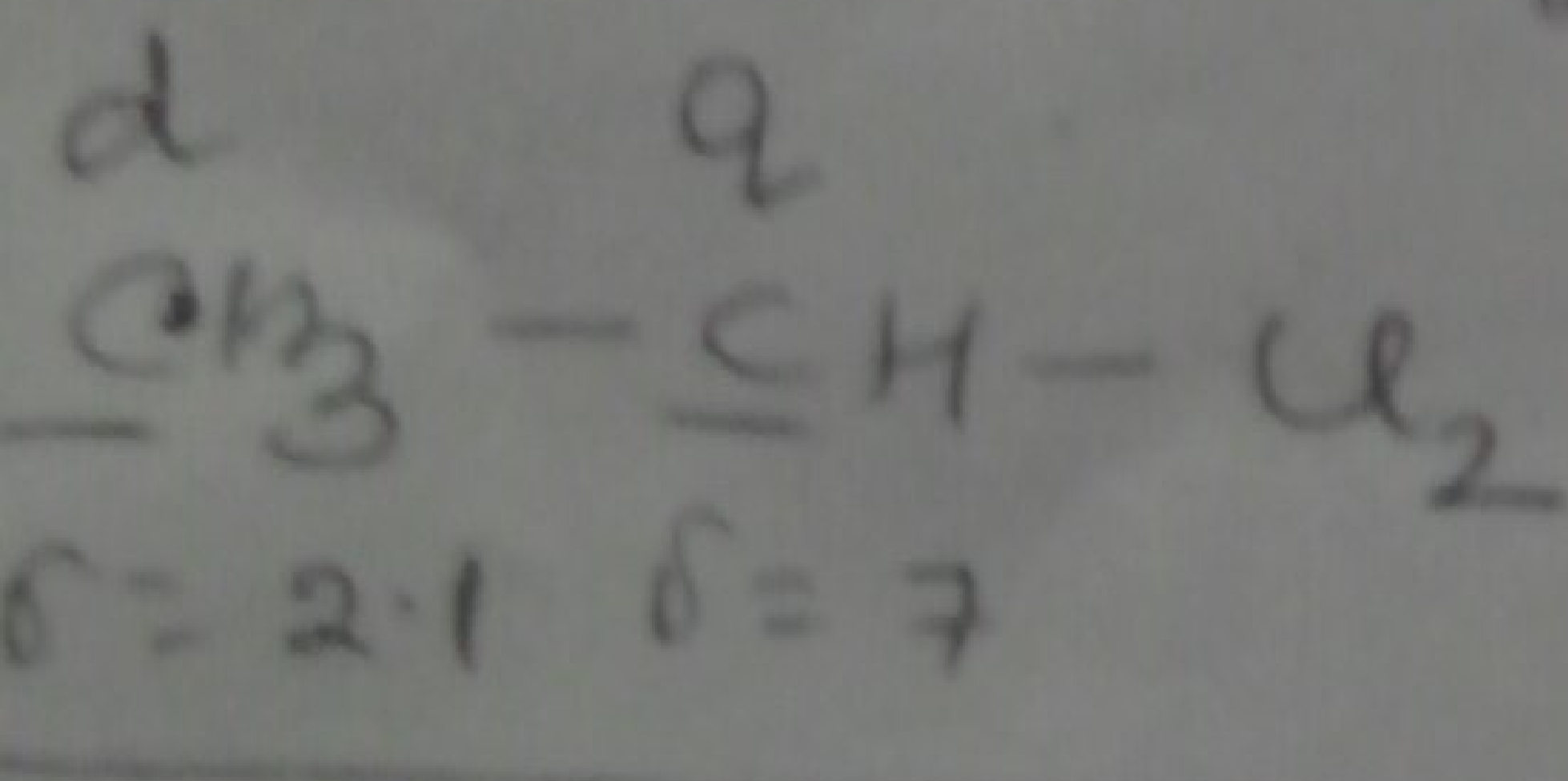
▲ Figure 14.10

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

Keep in mind that 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.

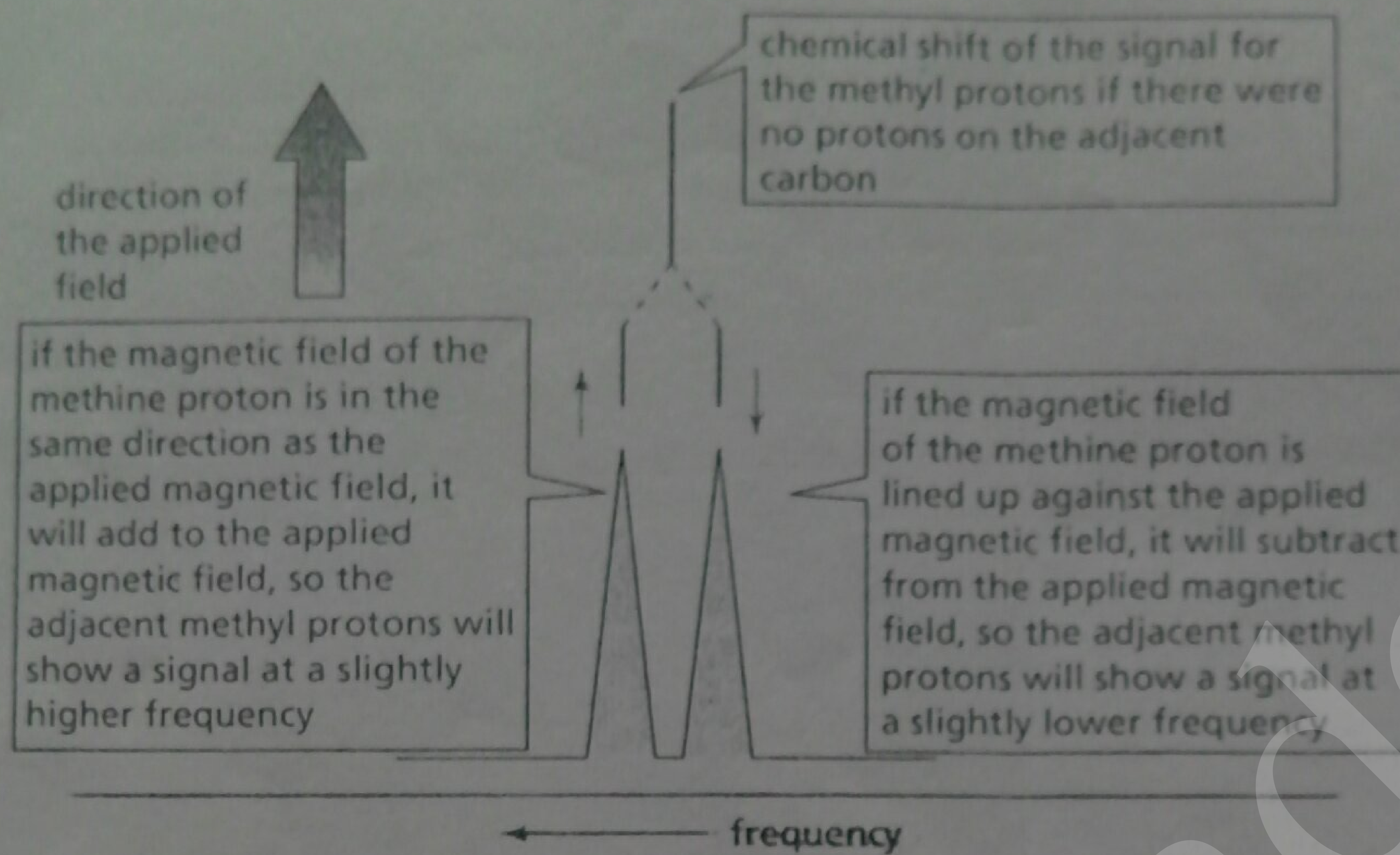


More specifically, the splitting of signals occurs when different kinds of protons are close enough for their magnetic fields to influence one another—called *spin-spin coupling*. For example, the frequency at which the methyl protons of 1,1-dichloroethane show a signal is influenced by the magnetic field of the methine proton. If the magnetic field of the methine proton aligns with that of the applied magnetic field, it will add to the applied magnetic field, causing the methyl protons to show a signal at a





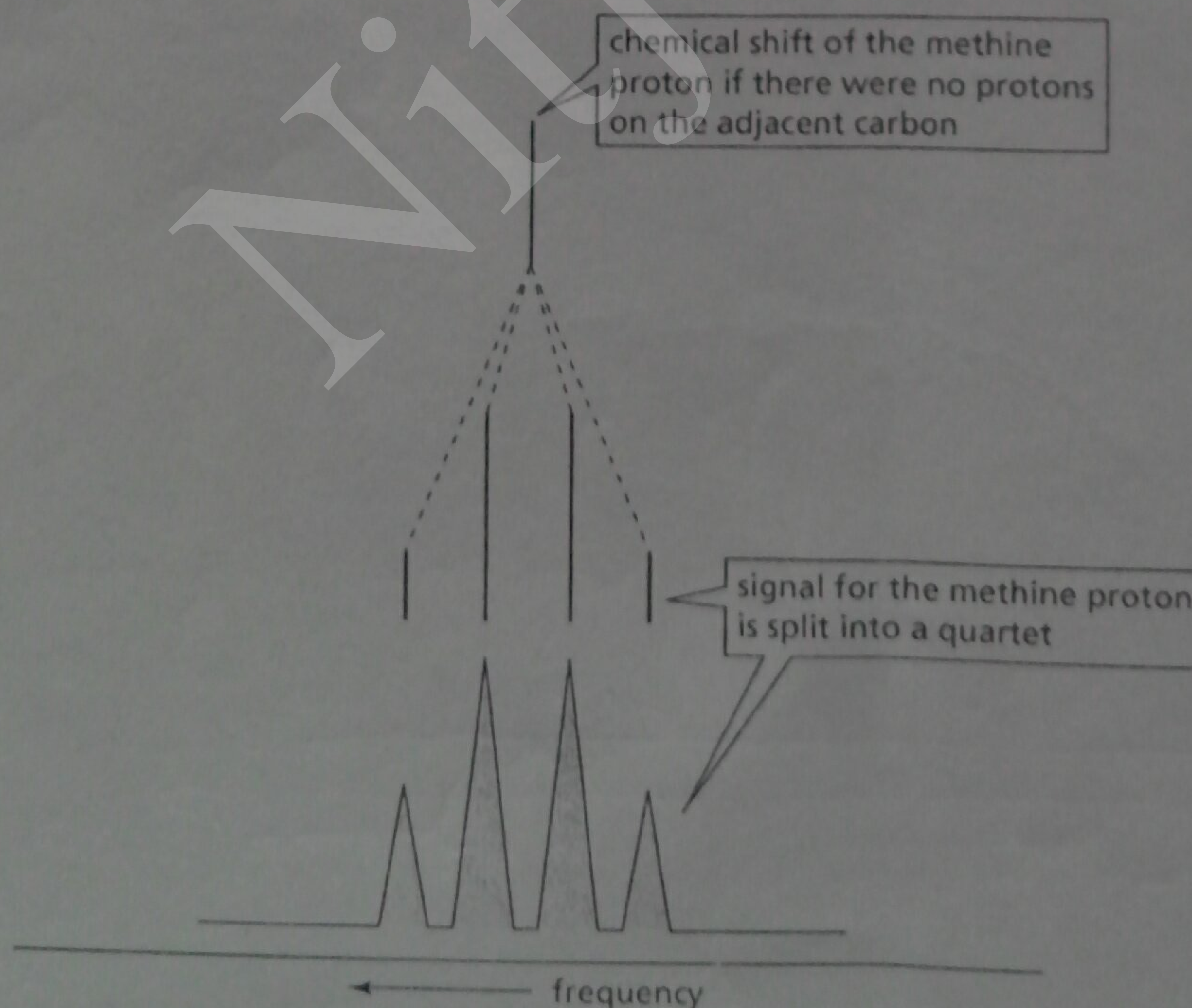
slightly higher frequency. On the other hand, if the magnetic field of the methine proton aligns *against* the applied magnetic field, it will subtract from the applied magnetic field and the methyl protons will show a signal at a lower frequency (Figure 14.11). Therefore, the signal for the methyl protons is split into two peaks, one corresponding to the higher frequency and one corresponding to the 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.



◀ Figure 14.11  
The signal for the methyl protons of 1,1-dichloroethane is split into a doublet by the methine proton.

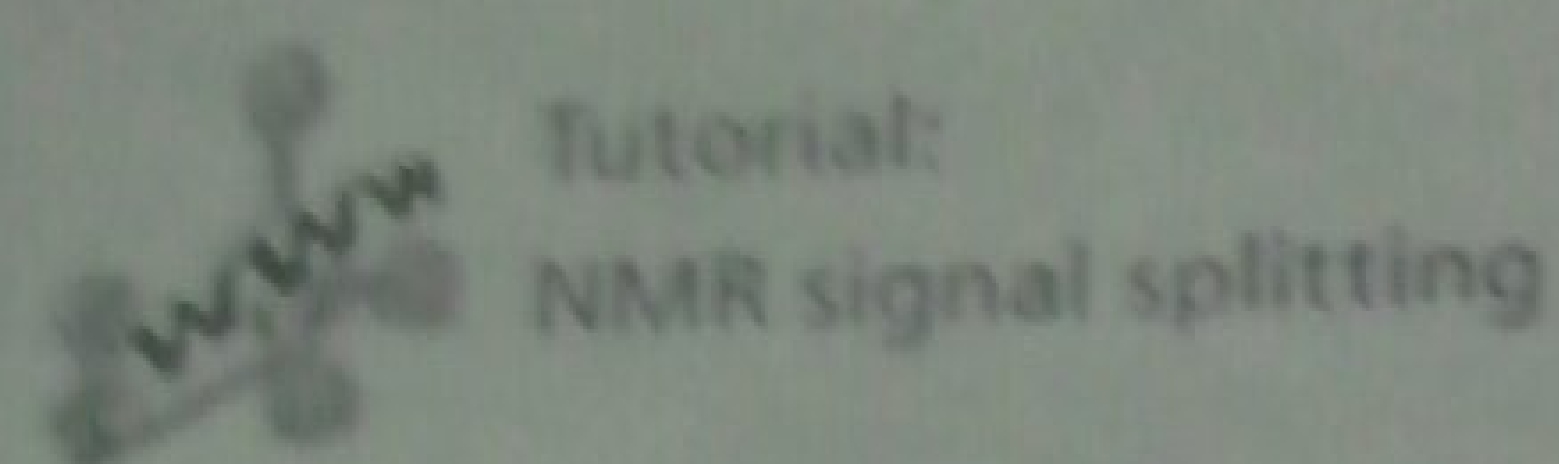
Similarly, the frequency at which the methine proton shows a signal is influenced by the magnetic fields of the three protons bonded to the adjacent carbon. The magnetic fields of each of the three methyl protons can align with the applied magnetic field, two can align with the field and one against it, one can align with it and two against it, or all three can align against it. Because the magnetic field that the methine proton senses is affected in four different ways, its signal is a *quartet* (Figure 14.12).

The relative intensities of the peaks in a signal reflect the number of ways the neighboring protons can be aligned relative to the applied magnetic field. For example, a



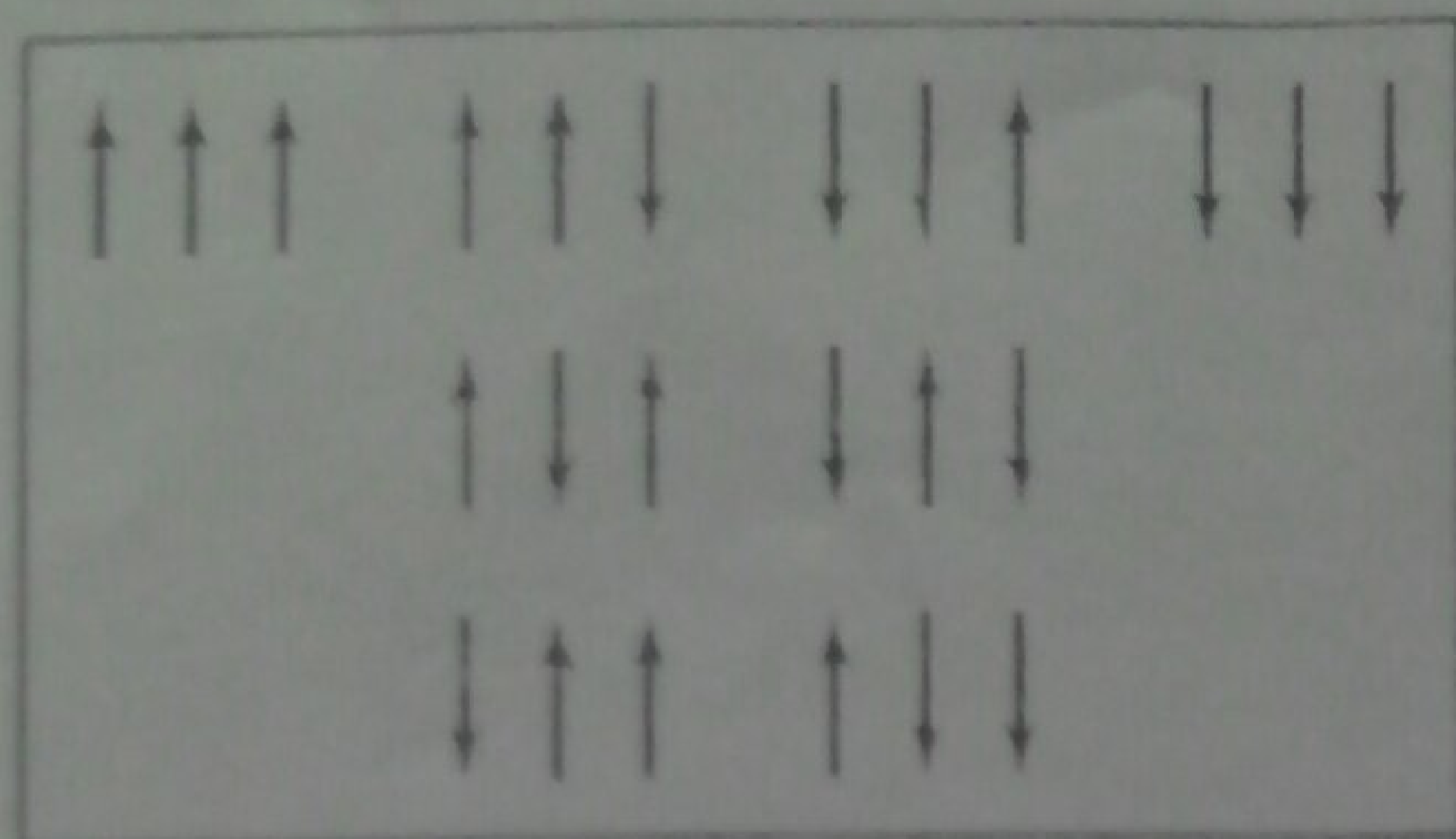
◀ Figure 14.12  
The signal for the methine proton of 1,1-dichloroethane is split into a quartet by the methyl protons.





quartet has relative peak intensities of 1 : 3 : 3 : 1 because there is only one way to align the magnetic fields of three protons so that they are all with the field and only one way to align them so that they are all against the field. However, there are three ways to align the magnetic fields of three protons so that two are lined up with the field and one is lined up against the field (Figure 14.13). Likewise, there are three ways to align the magnetic fields of three protons so that one is lined up with the field and two are lined up against it.)

Figure 14.13 ▶  
The ways in which the magnetic fields of three protons can be aligned.

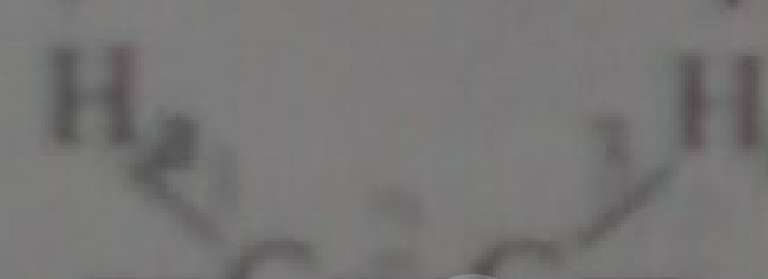


Equivalent protons do not split each other's signal.

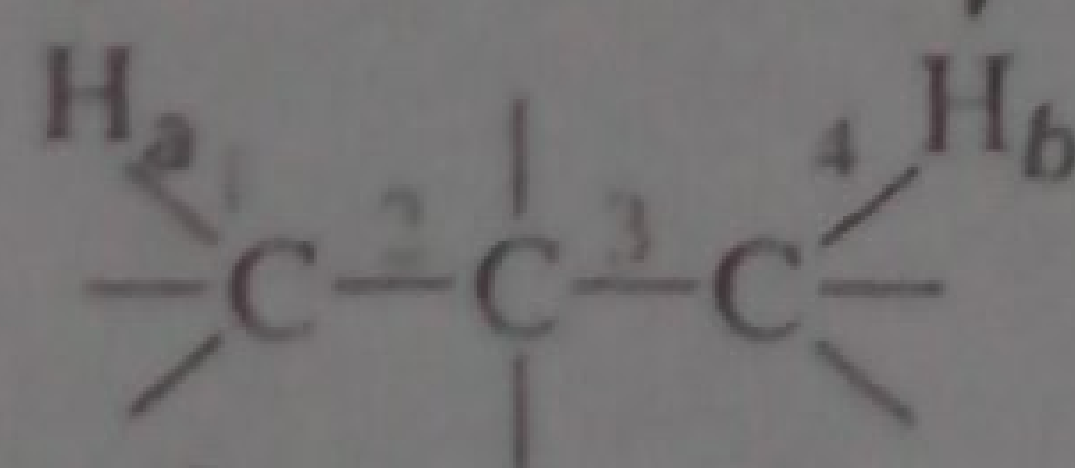
(The relative intensities obey the mathematical mnemonic known as *Pascal's triangle*. (You may remember this mnemonic from one of your math classes.) According to Pascal, each number at the bottom of a triangle in the rightmost column of Table 14.2 is the sum of the two numbers to its immediate left and right in the row above it.)

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*.

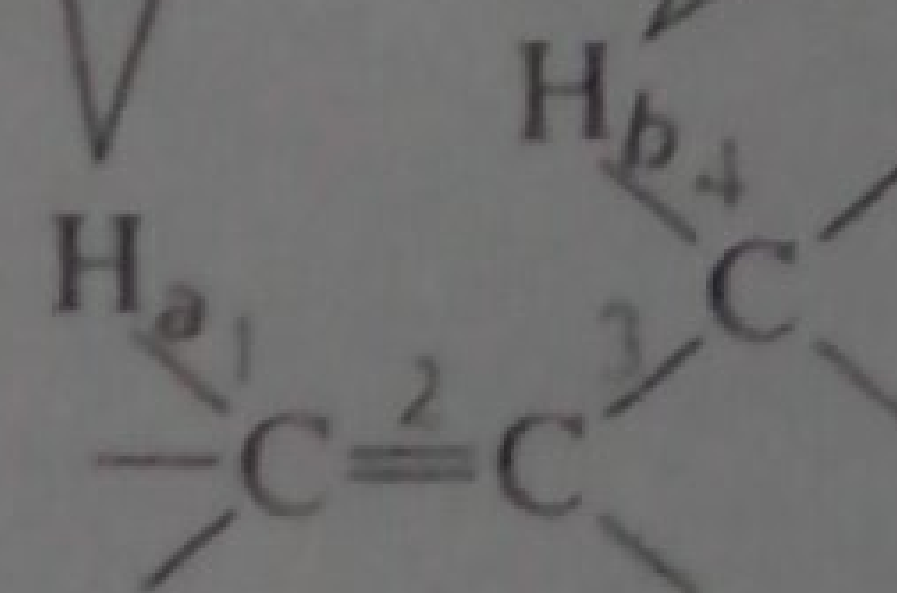
$H_a$  and  $H_b$  split each other's signal because they are separated by three  $\sigma$  bonds



$H_a$  and  $H_b$  do not split each other's signal because they are separated by four  $\sigma$  bonds



$H_a$  and  $H_b$  may split each other's signal because they are separated by four bonds, including one double bond



cond<sup>n</sup> for splitting

1. Non equivalent protons (neighboring)
2. separated by three  $\sigma$  bonds.

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.

Table 14.2 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          |



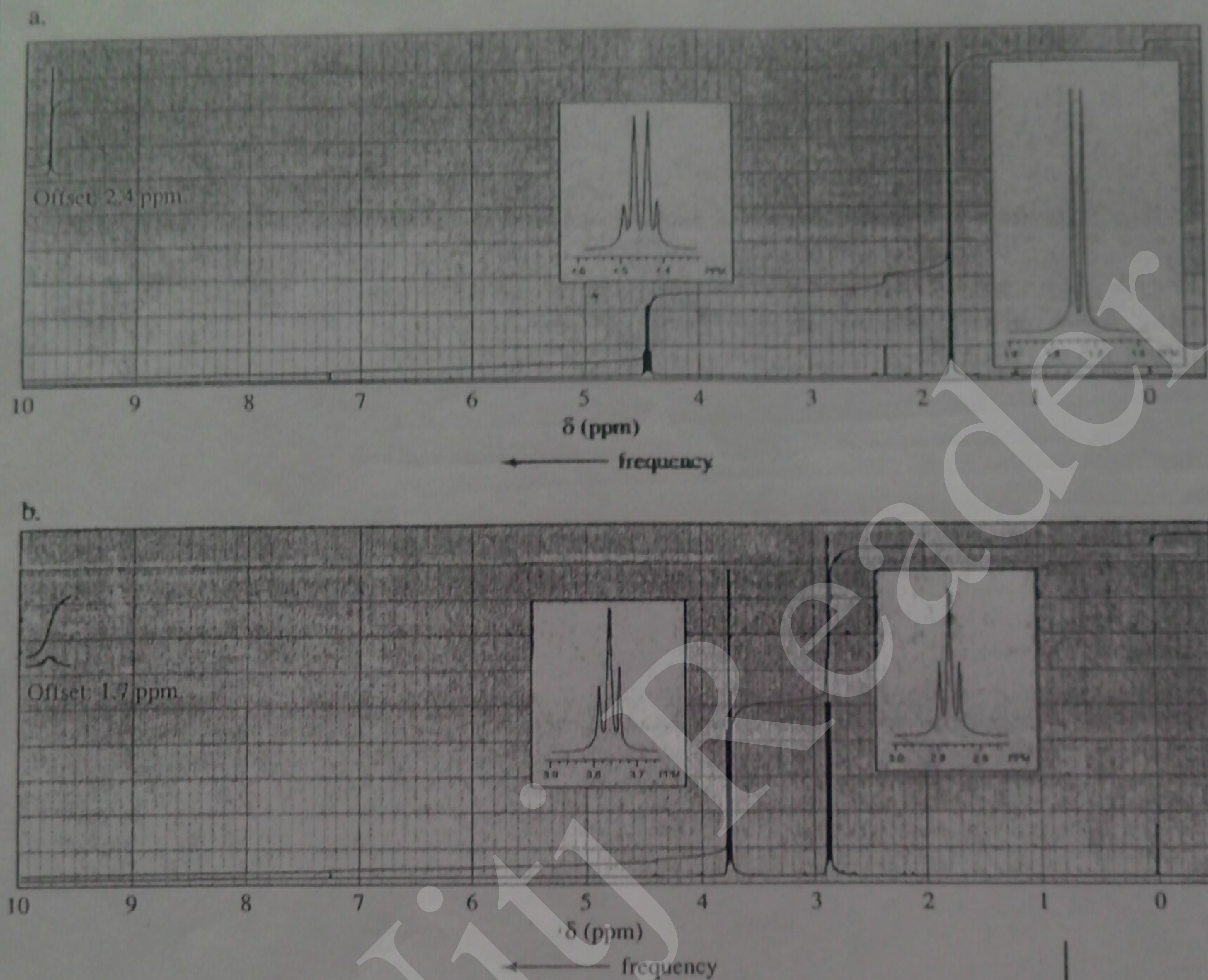
**PROBLEM 18**

Using a diagram like the one in Figure 14.13, predict

- the relative intensities of the peaks in a triplet
- the relative intensities of the peaks in a quintet

**PROBLEM 19**

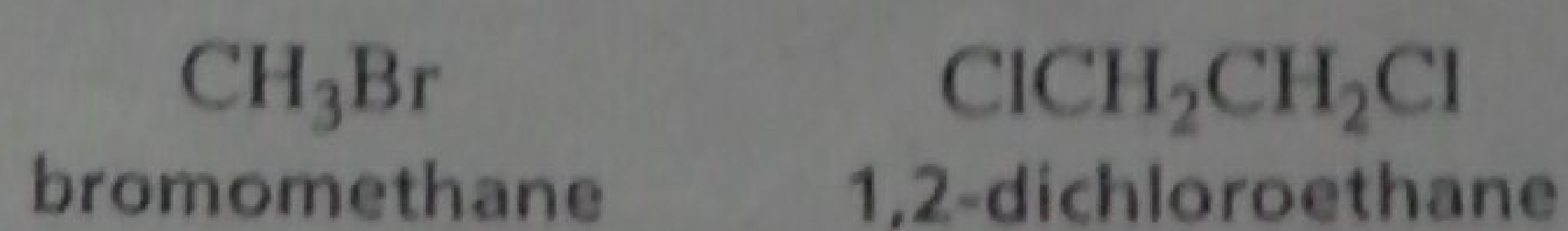
The  $^1\text{H}$  NMR spectra of two carboxylic acids with molecular formula  $\text{C}_3\text{H}_5\text{O}_2\text{Cl}$  are shown in Figure 14.14. Identify the carboxylic acids. (The "offset" notation means that the signal has been moved to the right by the indicated amount).



▲ Figure 14.14  
 $^1\text{H}$  NMR spectra for Problem 19.

**14.11** More Examples of  $^1\text{H}$  NMR Spectra

The  $^1\text{H}$  NMR spectrum of bromomethane shows one singlet. The three methyl protons are chemically equivalent, and chemically equivalent protons do not split each other's signal. The four protons in 1,2-dichloroethane are also chemically equivalent, so its  $^1\text{H}$  NMR spectrum also shows one singlet.

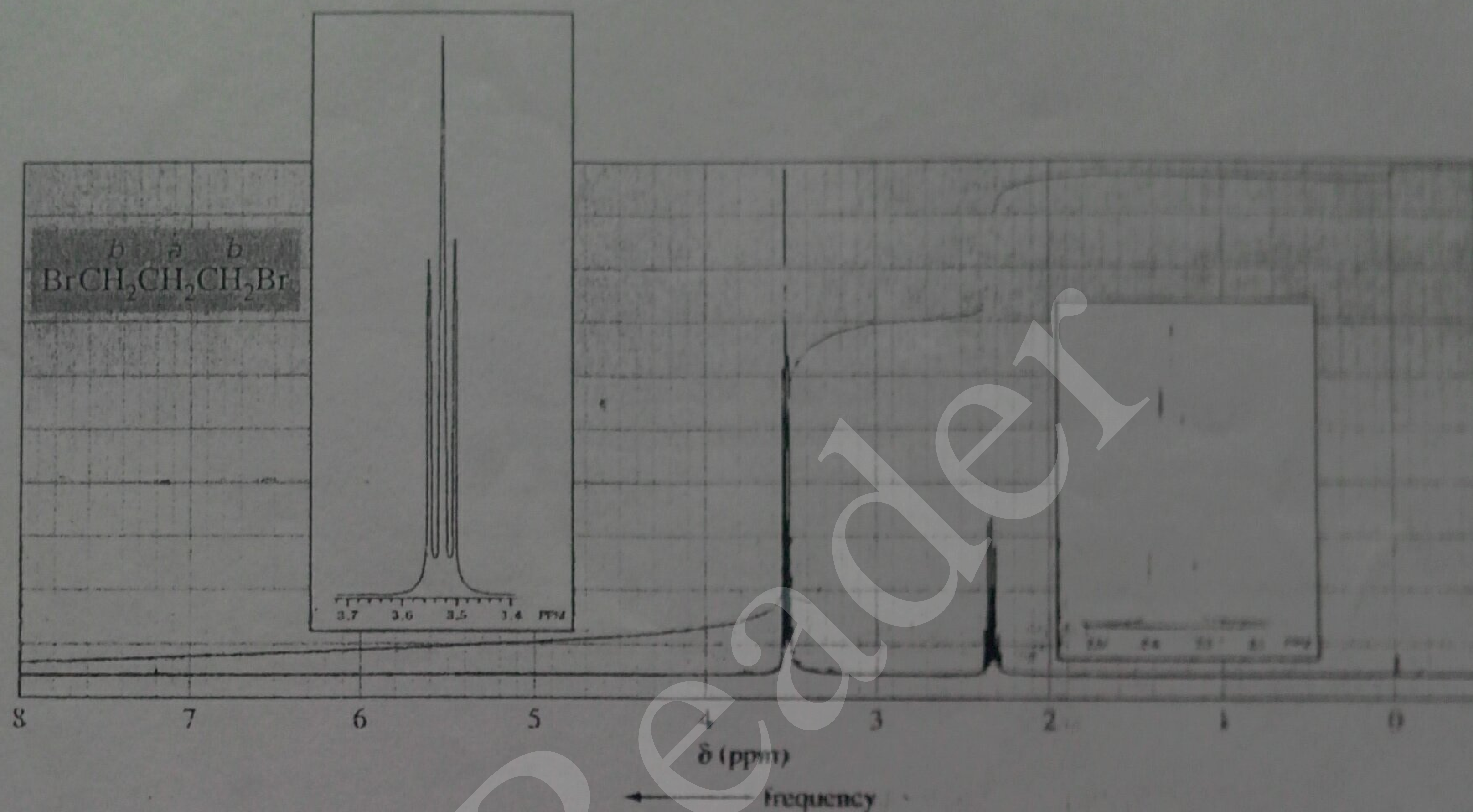


each compound has an NMR spectrum that shows one singlet because equivalent protons do not split each other's signals



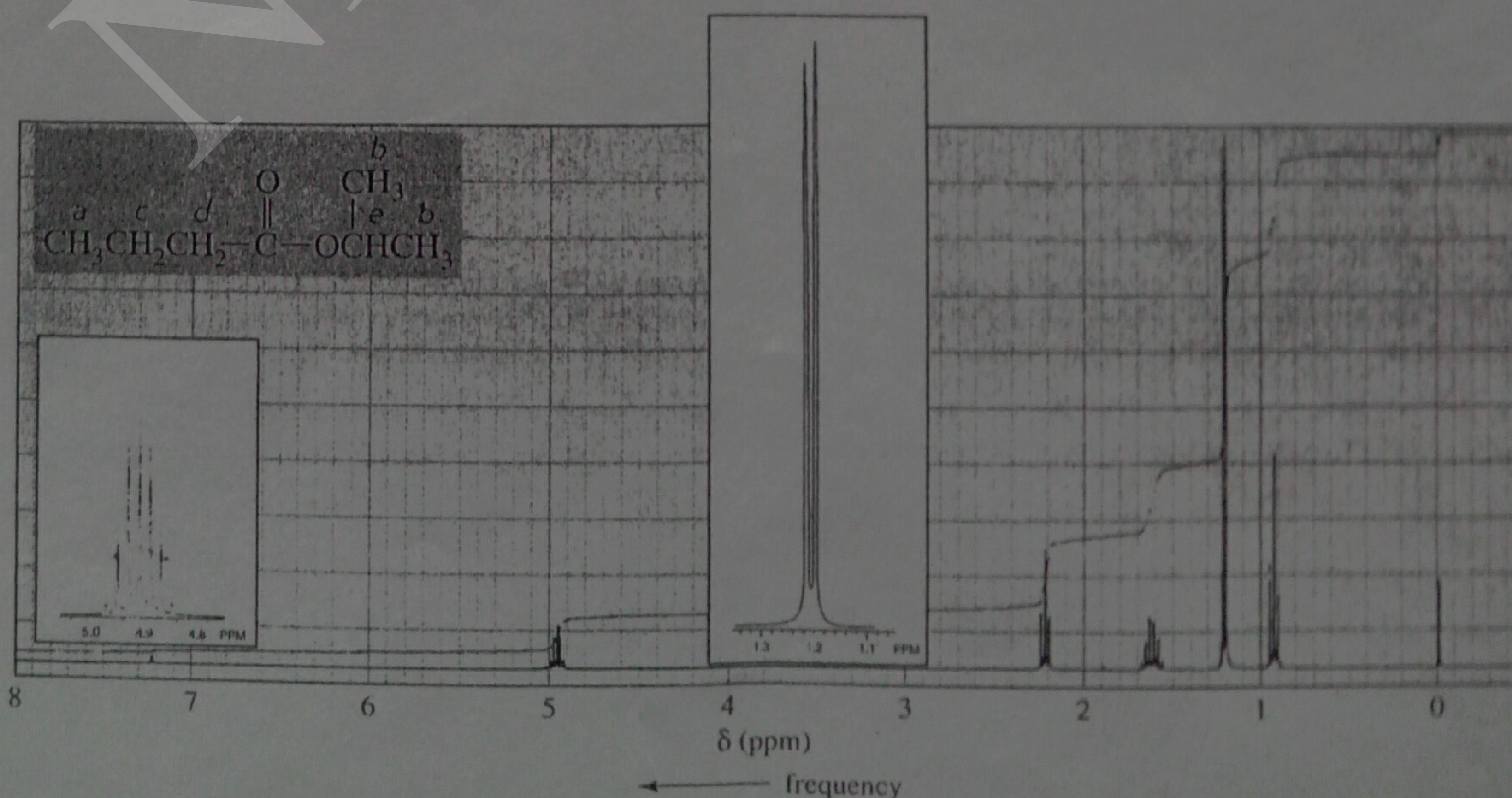
There are two signals in the  $^1\text{H}$  NMR spectrum of 1,3-dibromopropane (Figure 14.15). The signal for the  $\text{H}_b$  protons is split into a triplet by the two hydrogens on the adjacent carbon. The  $\text{H}_a$  protons have two adjacent carbons that are bonded to protons. The protons on one adjacent carbon are equivalent to the protons on the other adjacent carbon. Because the two sets of protons are equivalent, the  $N + 1$  rule is applied to both sets at the same time. In other words,  $N$  is equal to the sum of the equivalent protons on both carbons. So the signal for the  $\text{H}_a$  protons is split into a quintet ( $4 + 1 = 5$ ). Integration confirms that two methylene groups contribute to the  $\text{H}_b$  signal because twice as many protons give rise to the  $\text{H}_b$  signal as to the  $\text{H}_a$  signal.

Figure 14.15 ►  
 $^1\text{H}$  NMR spectrum of  
1,3-dibromopropane.



The  $^1\text{H}$  NMR spectrum of isopropyl butanoate shows five signals (Figure 14.16). The signal for the  $\text{H}_a$  protons is split into a triplet by the  $\text{H}_c$  protons. The signal for the  $\text{H}_b$  protons is split into a doublet by the  $\text{H}_e$  proton. The signal for the  $\text{H}_d$  protons is split into a triplet by the  $\text{H}_c$  protons, and the signal for the  $\text{H}_e$  proton is split into a septet by the  $\text{H}_b$  protons. The signal for the  $\text{H}_c$  protons is split by both the  $\text{H}_a$  and  $\text{H}_d$  protons. Because the  $\text{H}_a$  and  $\text{H}_d$  protons are not equivalent, the  $N + 1$  rule has to be applied separately to each set. Thus, the signal for the  $\text{H}_c$  protons will be split into a

Figure 14.16 ►  
 $^1\text{H}$  NMR spectrum of  
isopropyl butanoate.

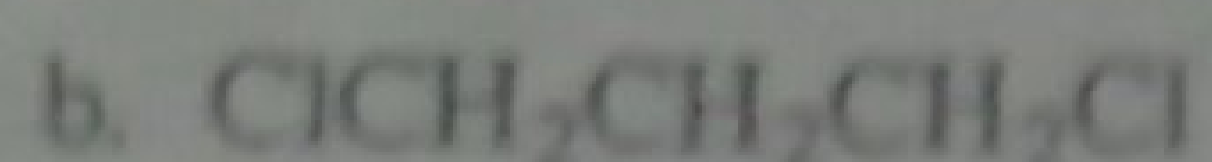




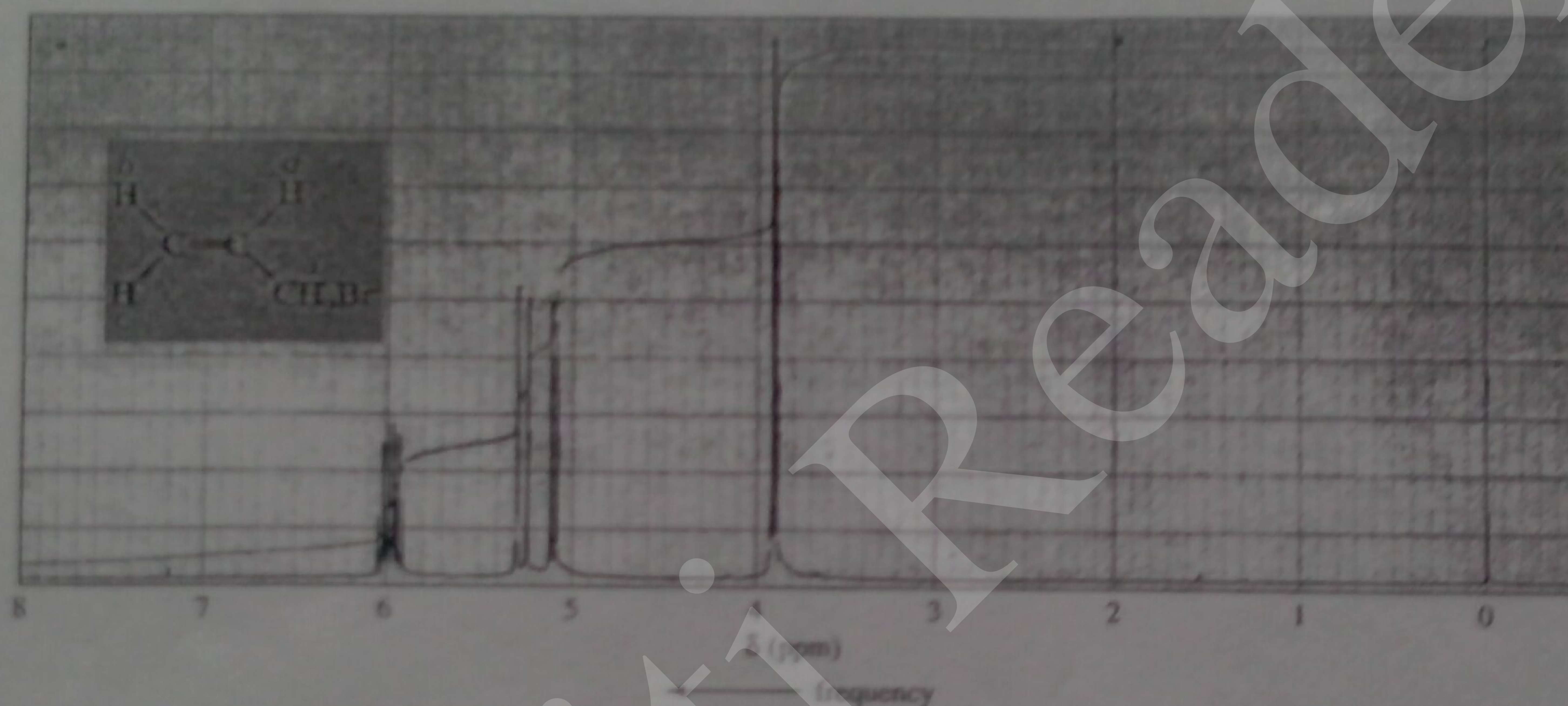
quartet by the  $\text{H}_a$  protons, and each of these four peaks will be split into a triplet by the  $\text{H}_d$  protons:  $(N_a + 1)(N_d + 1) = (4)(3) = 12$ . As a result, the signal for the  $\text{H}_c$  protons is a multiplet (a signal that is more complex than a triplet, quartet, quintet, etc.). The reason we do not see 12 peaks is that some of them overlap (Section 14.13).

**PROBLEM 20**

Indicate the number of signals and the multiplicity of each signal in the  $^1\text{H}$  NMR spectrum of each of the following compounds:



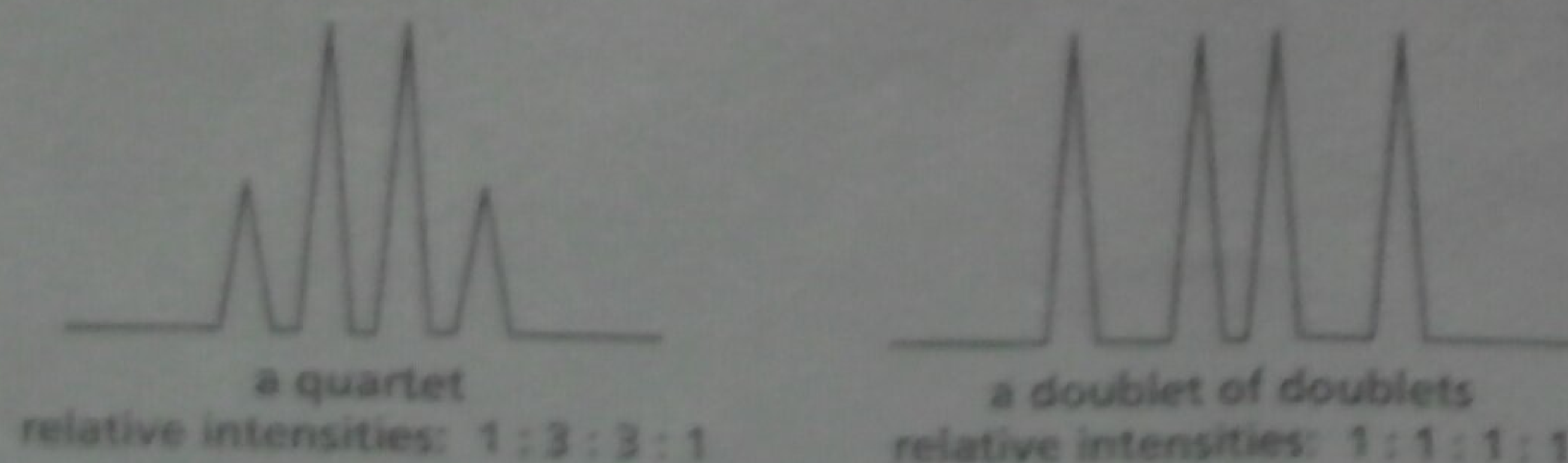
The  $^1\text{H}$  NMR spectrum of 3-bromo-1-propene shows four signals (Figure 14.17). Although the  $\text{H}_b$  and  $\text{H}_c$  protons are bonded to the same carbon, they are not chemically equivalent (one is cis to the bromomethyl group, the other is trans to the bromomethyl group), so each produces a separate signal. The signal for the  $\text{H}_a$  protons is split into a doublet by the  $\text{H}_d$  proton. Notice that the signals for the three vinylic protons are at relatively high frequencies because of diamagnetic anisotropy (Section 14.9). The signal for the  $\text{H}_d$  proton is a multiplet because it is split separately by the  $\text{H}_a$ ,  $\text{H}_b$ , and  $\text{H}_c$  protons.



◀ Figure 14.17  
 $^1\text{H}$  NMR spectrum of  
3-bromo-1-propene.

Because the  $\text{H}_b$  and  $\text{H}_c$  protons are not equivalent, they split one another's signal. This means that the signal for the  $\text{H}_b$  proton is split into a doublet by the  $\text{H}_d$  proton and that each of the peaks in the doublet is split into a doublet by the  $\text{H}_c$  proton. The signal for the  $\text{H}_b$  proton should be what is called a doublet of doublets. The signal for the  $\text{H}_c$  proton should also be a doublet of doublets. However, the mutual splitting of the signals of two nonidentical protons bonded to the same  $sp^2$  carbon, caused by what is called geminal coupling, is often too small to be observed (Section 14.12). Therefore, the signals for the  $\text{H}_b$  and  $\text{H}_c$  protons in Figure 14.17 appear as doublets rather than as doublets of doublets. (If the signals were expanded, the doublet of doublets would be observed.)

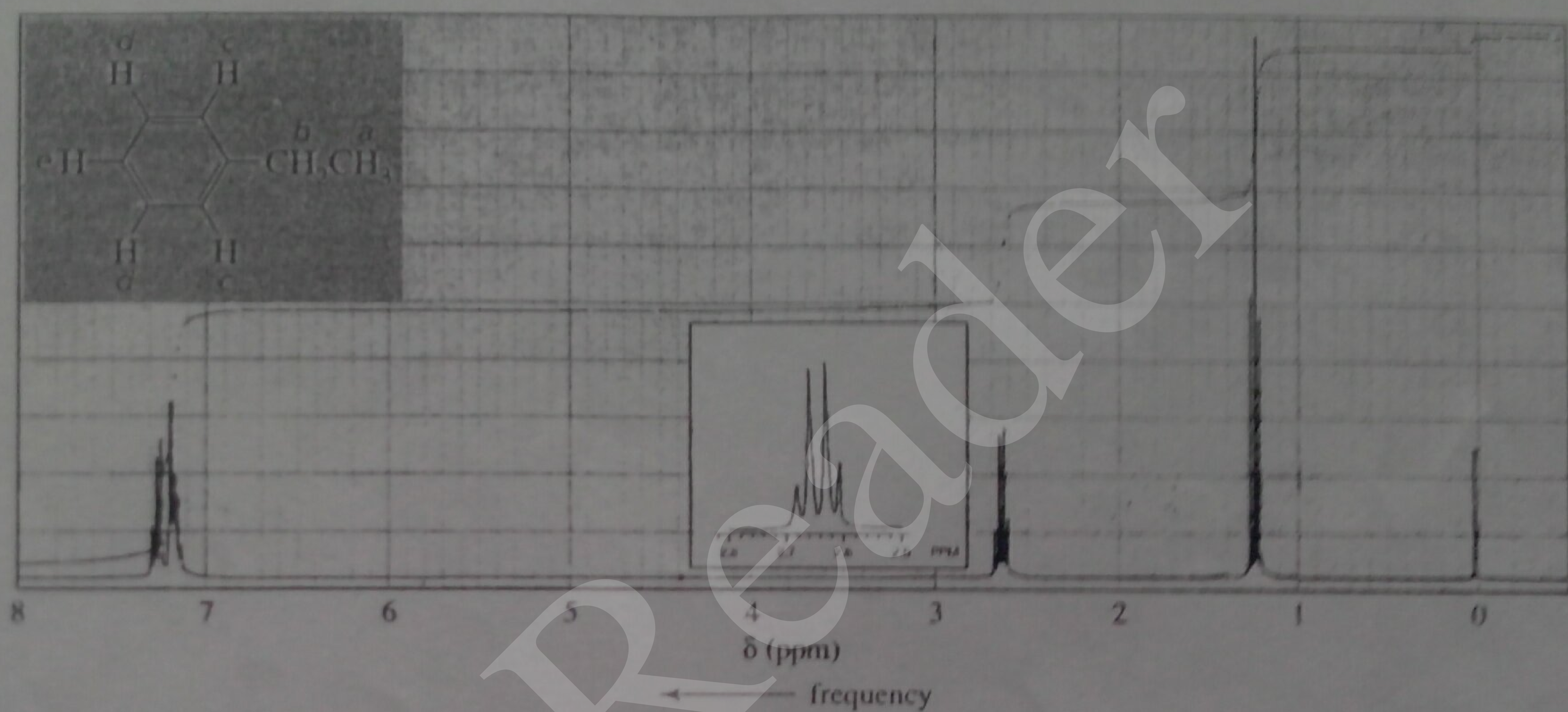
Notice the difference between a quartet and a doublet of doublets. Both have four peaks. A quartet results from splitting by *three equivalent* adjacent protons; it has relative peak intensities of 1 : 3 : 3 : 1, and the individual peaks are equally spaced. A doublet of doublets, on the other hand, results from splitting by *two nonequivalent* adjacent protons; it has relative peak intensities of 1 : 1 : 1 : 1, and the individual peaks are not necessarily equally spaced (see Figure 14.24).





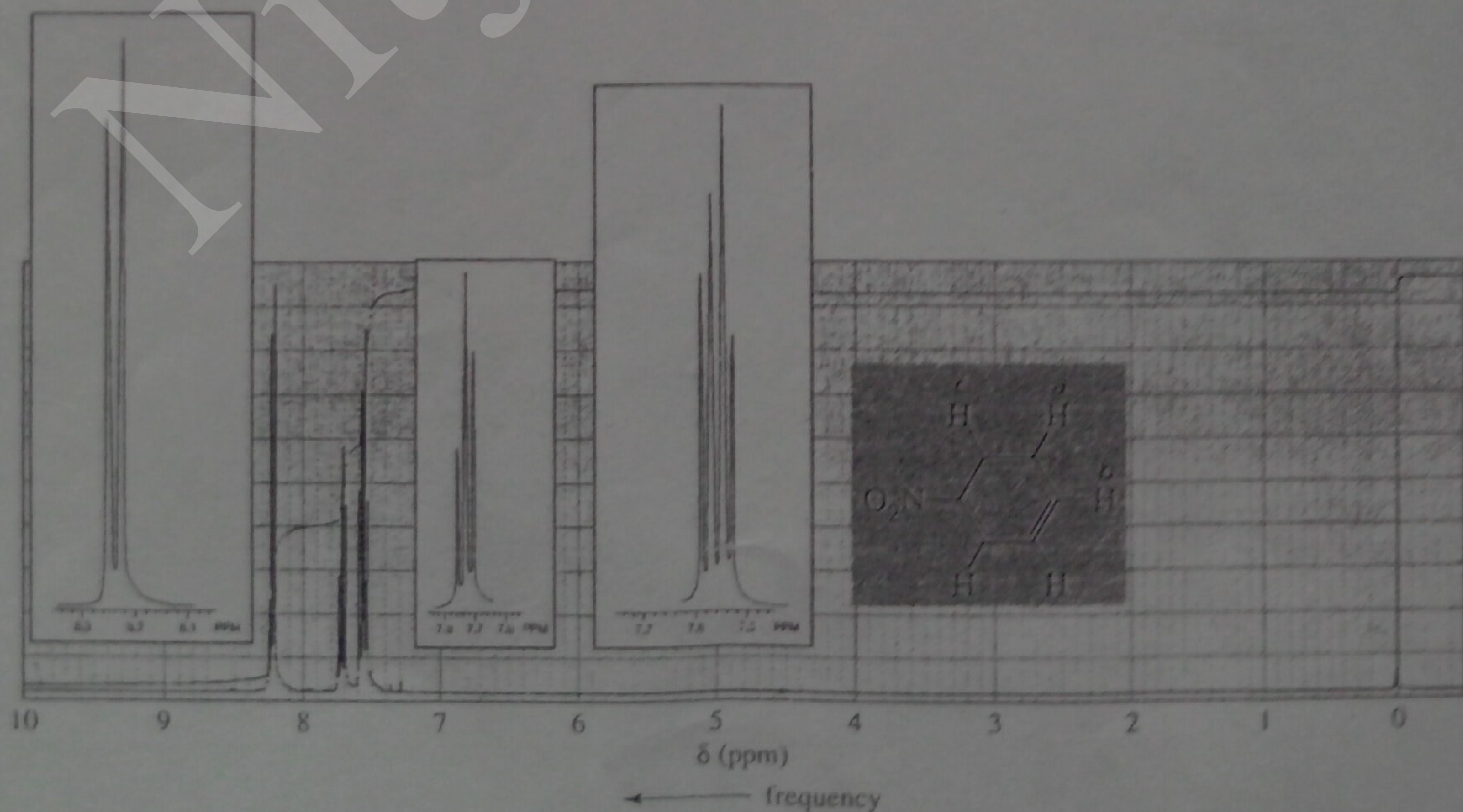
There are five sets of chemically equivalent protons in ethylbenzene (Figure 14.18). We see the expected triplet for the  $H_a$  protons and the quartet for the  $H_b$  protons. (This is a characteristic pattern for an ethyl group.) We expect the signal for the  $H_c$  protons to be a doublet and the signal for the  $H_e$  proton to be a triplet. Because the  $H_c$  and  $H_e$  protons are not equivalent, they must be considered separately in determining the splitting of the signal for the  $H_d$  protons. Therefore, we expect the signal for the  $H_d$  protons to be split into a doublet by the  $H_c$  protons and each peak of the doublet to be split into another doublet by the  $H_e$  proton, forming a doublet of doublets. However, we do not see three distinct signals for the  $H_c$ ,  $H_d$ , and  $H_e$  protons in Figure 14.18. Instead, we see overlapping signals. Apparently, the electronic effect (i.e., the electron-donating/electron-withdrawing ability) of an ethyl substituent is not sufficiently different from that of a hydrogen to cause a difference in the environments of the  $H_c$ ,  $H_d$ , and  $H_e$  protons that is large enough to allow them to appear as separate signals.

Figure 14.18 ▶  $^1\text{H}$  NMR spectrum of ethylbenzene. The signals for the  $H_c$ ,  $H_d$ , and  $H_e$  protons overlap.



In contrast to the  $H_c$ ,  $H_d$ , and  $H_e$  protons of ethylbenzene, the  $H_a$ ,  $H_b$ , and  $H_c$  protons of nitrobenzene show three distinct signals (Figure 14.19), and the multiplicity of each signal is what we predicted for the signals for the benzene ring protons in

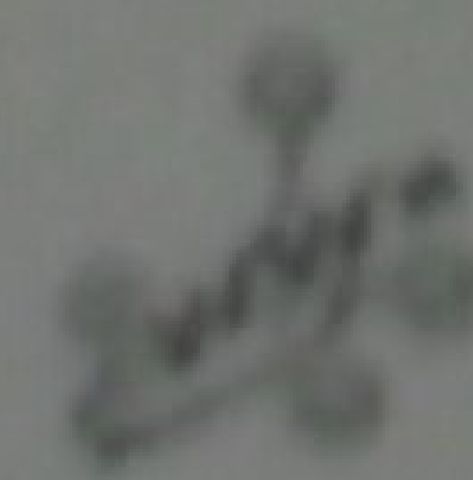
Figure 14.19 ▶  $^1\text{H}$  NMR spectrum of nitrobenzene. The signals for the  $H_a$ ,  $H_b$ , and  $H_c$  protons do not overlap.





ethylbenzene ( $\text{H}_a$  is a doublet,  $\text{H}_b$  is a triplet, and  $\text{H}_c$  is a doublet of doublets). The nitro group is sufficiently electron withdrawing to cause the  $\text{H}_a$ ,  $\text{H}_b$ , and  $\text{H}_c$  protons to be in different enough environments that their signals do not overlap.

Notice that the signals for the benzene ring protons in Figures 14.18 and 14.19 occur in the 7.0–8.5 ppm region. Other kinds of protons usually do not resonate in this region, so signals in this region of an  $^1\text{H}$  NMR spectrum indicate that the compound probably contains an aromatic ring.



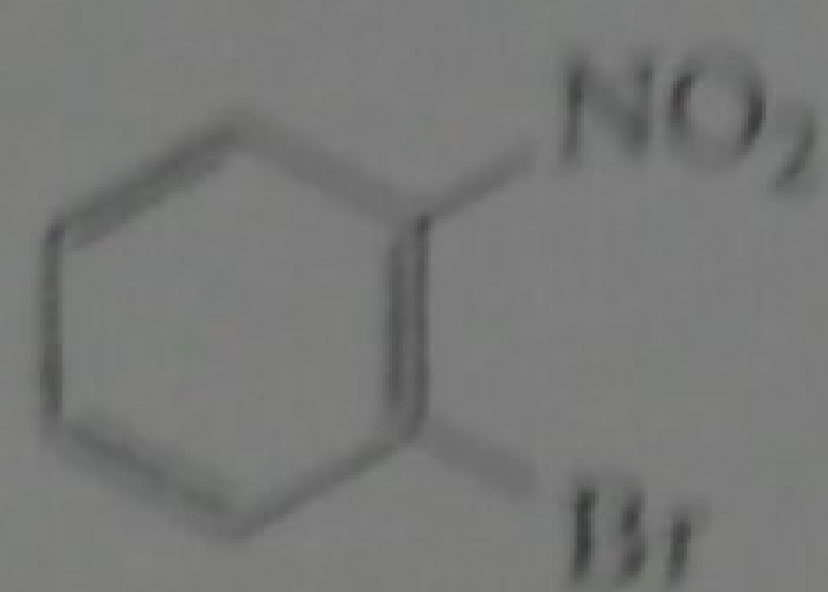
Tutorial:  
NMR spectrum assignment

### PROBLEM 21

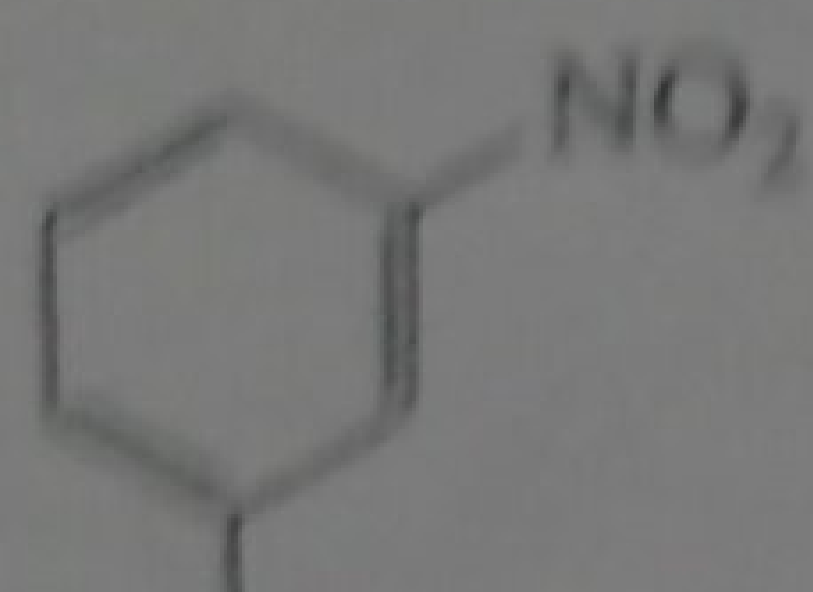
Explain why the signal for the protons identified as  $\text{H}_a$  in Figure 14.19 appears at the lowest frequency and the signal for the protons identified as  $\text{H}_c$  appears at the highest frequency. (*Hint:* Draw the contributing resonance structures.)

### PROBLEM 22

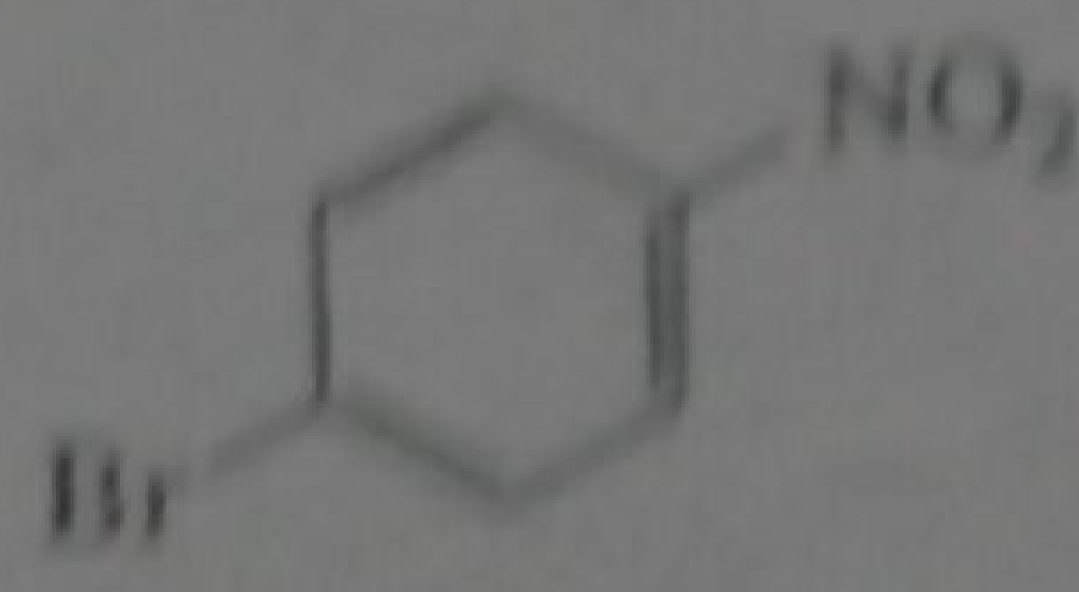
How could  $^1\text{H}$  NMR spectra distinguish the following compounds?



A



B



C

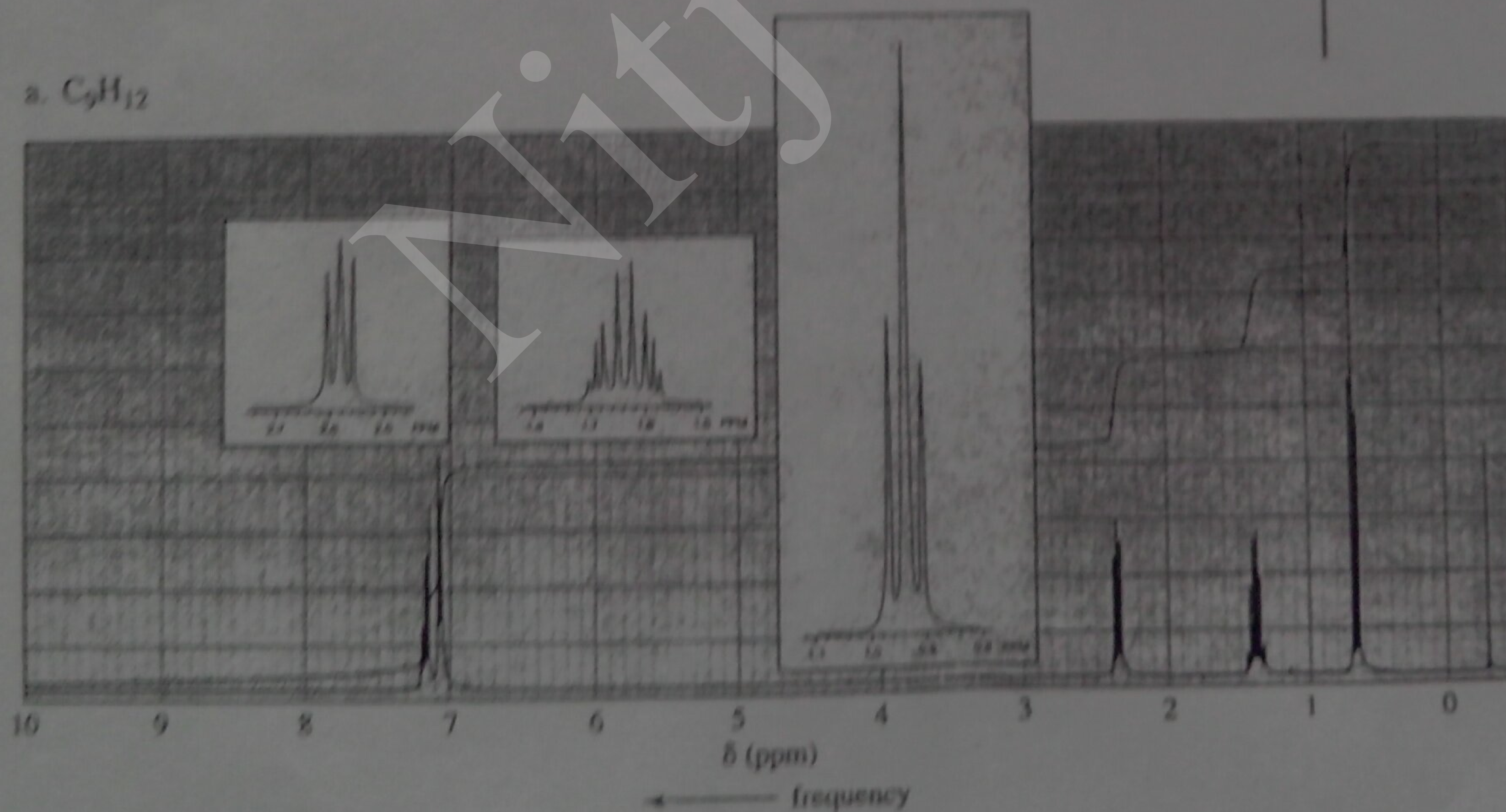
### PROBLEM 23

How would the  $^1\text{H}$  NMR spectra for the four compounds with molecular formula  $\text{C}_3\text{H}_6\text{Br}_2$  differ?

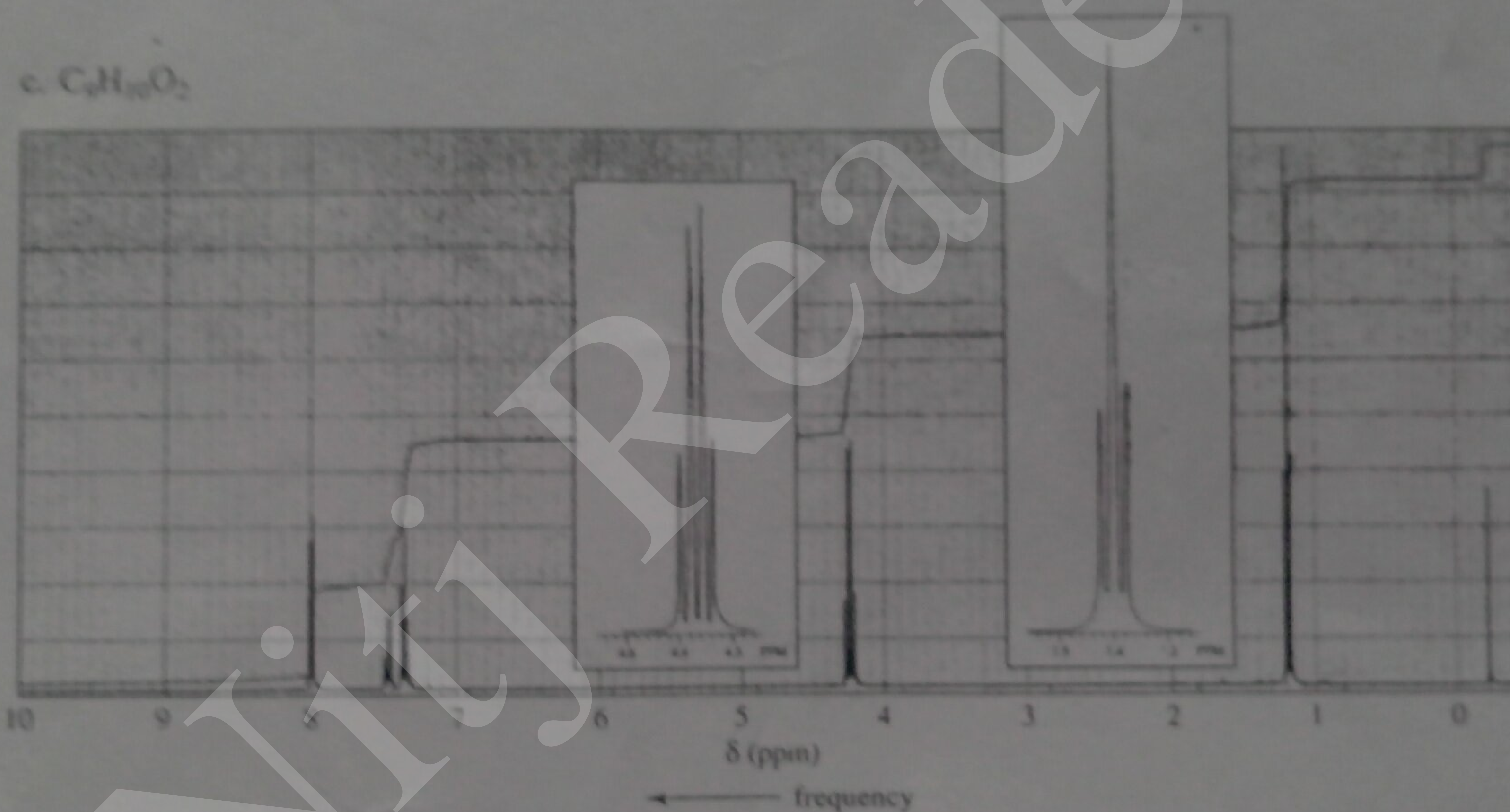
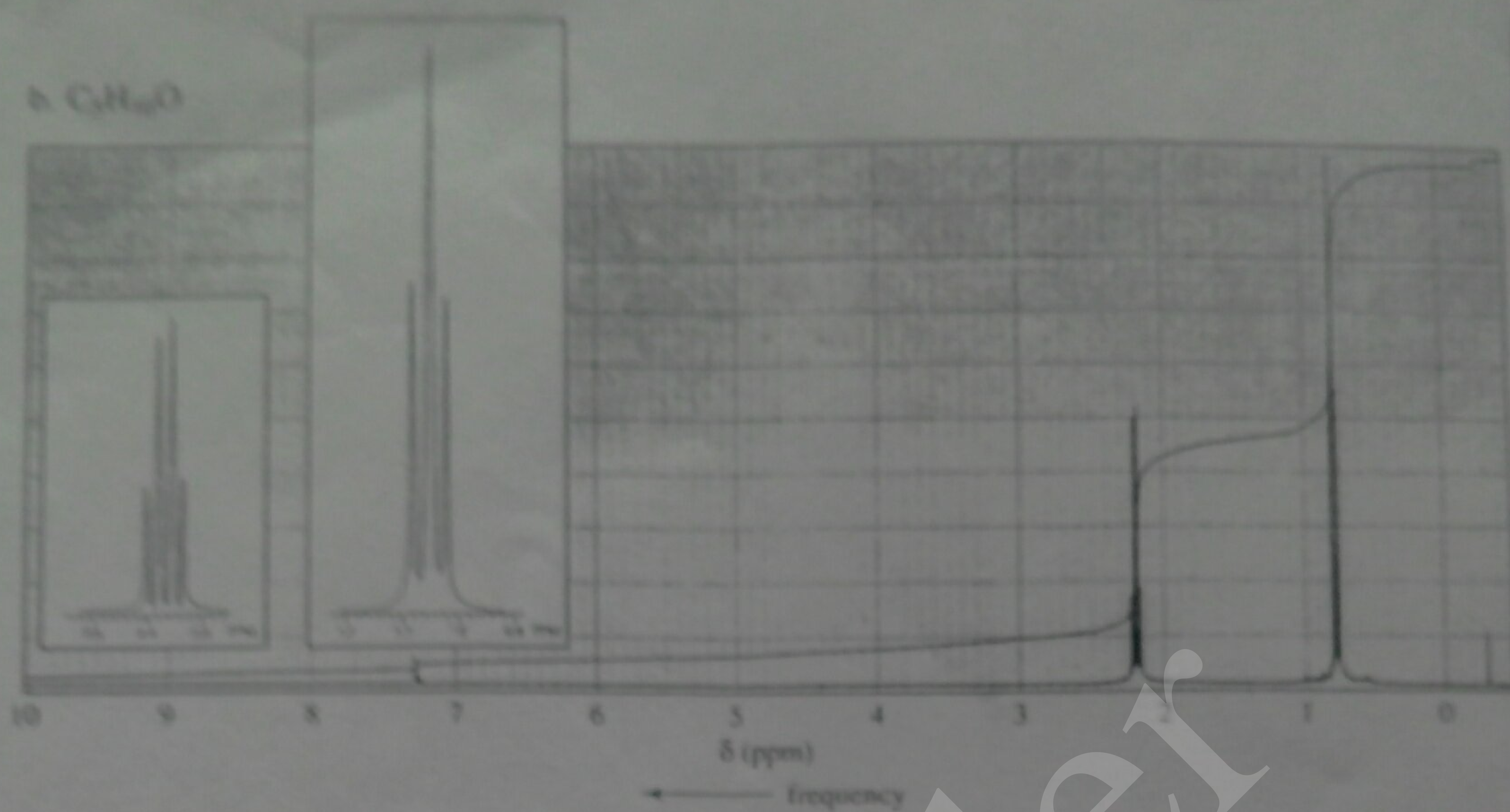
### PROBLEM 24♦

Identify each compound from its molecular formula and its  $^1\text{H}$  NMR spectrum:

a.  $\text{C}_9\text{H}_{12}$





**PROBLEM 25**

Predict the splitting patterns for the signals given by each of the compounds in Problem 3.

**PROBLEM 26♦**

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

- The  $^1\text{H}$  NMR spectrum of a compound with molecular formula  $\text{C}_4\text{H}_{10}\text{O}_2$  has two singlets with an area ratio of 2 : 3.
- The  $^1\text{H}$  NMR spectrum of a compound with molecular formula  $\text{C}_6\text{H}_{10}\text{O}_2$  has two singlets with an area ratio of 2 : 3.
- The  $^1\text{H}$  NMR spectrum of a compound with molecular formula  $\text{C}_8\text{H}_6\text{O}_2$  has two singlets with an area ratio of 1 : 2.

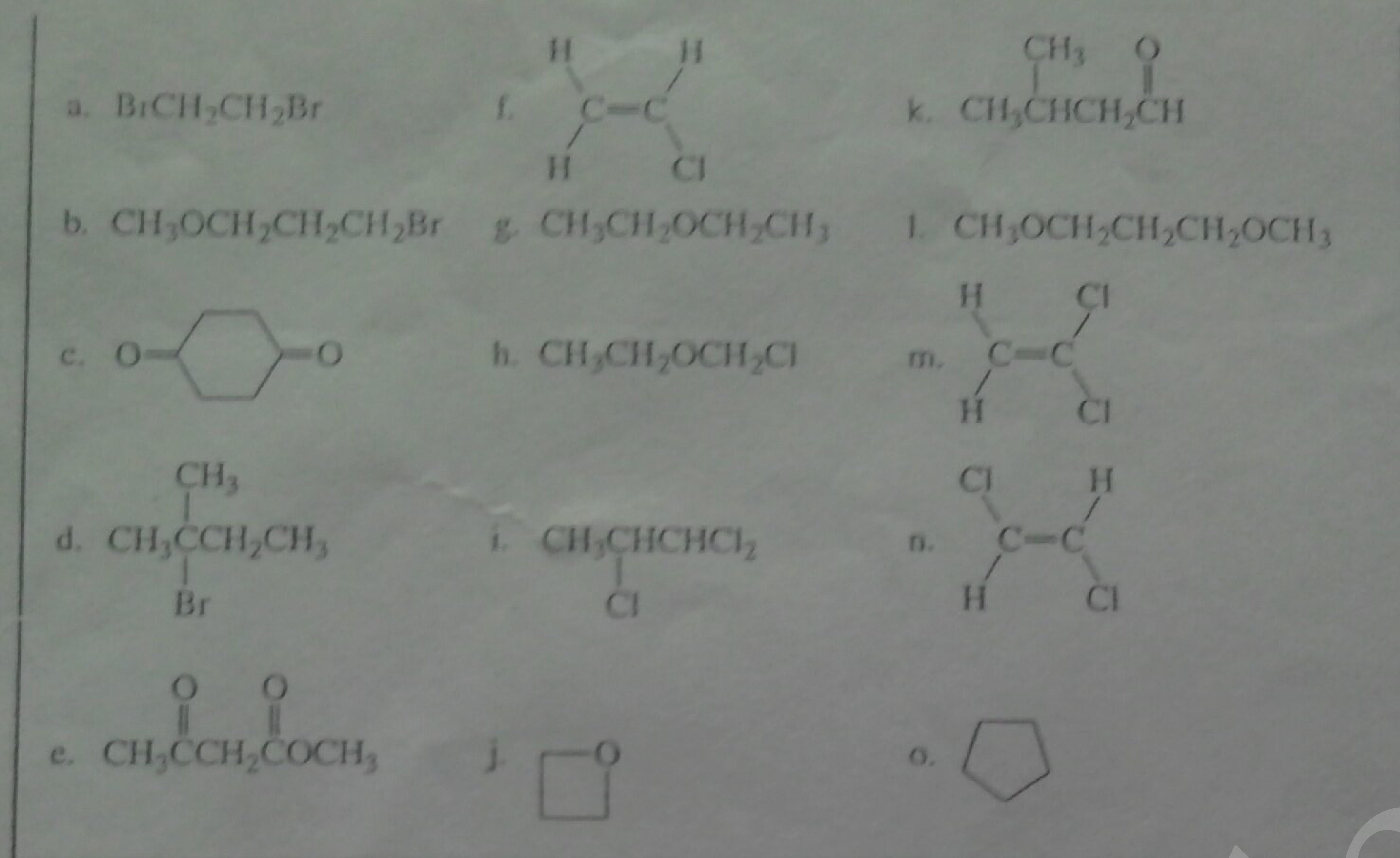
**PROBLEM 27**

Describe the  $^1\text{H}$  NMR spectrum you would expect for each of the following compounds, using relative chemical shifts rather than absolute chemical shifts:



Tutorial:  
NMR spectrum  
interpretation



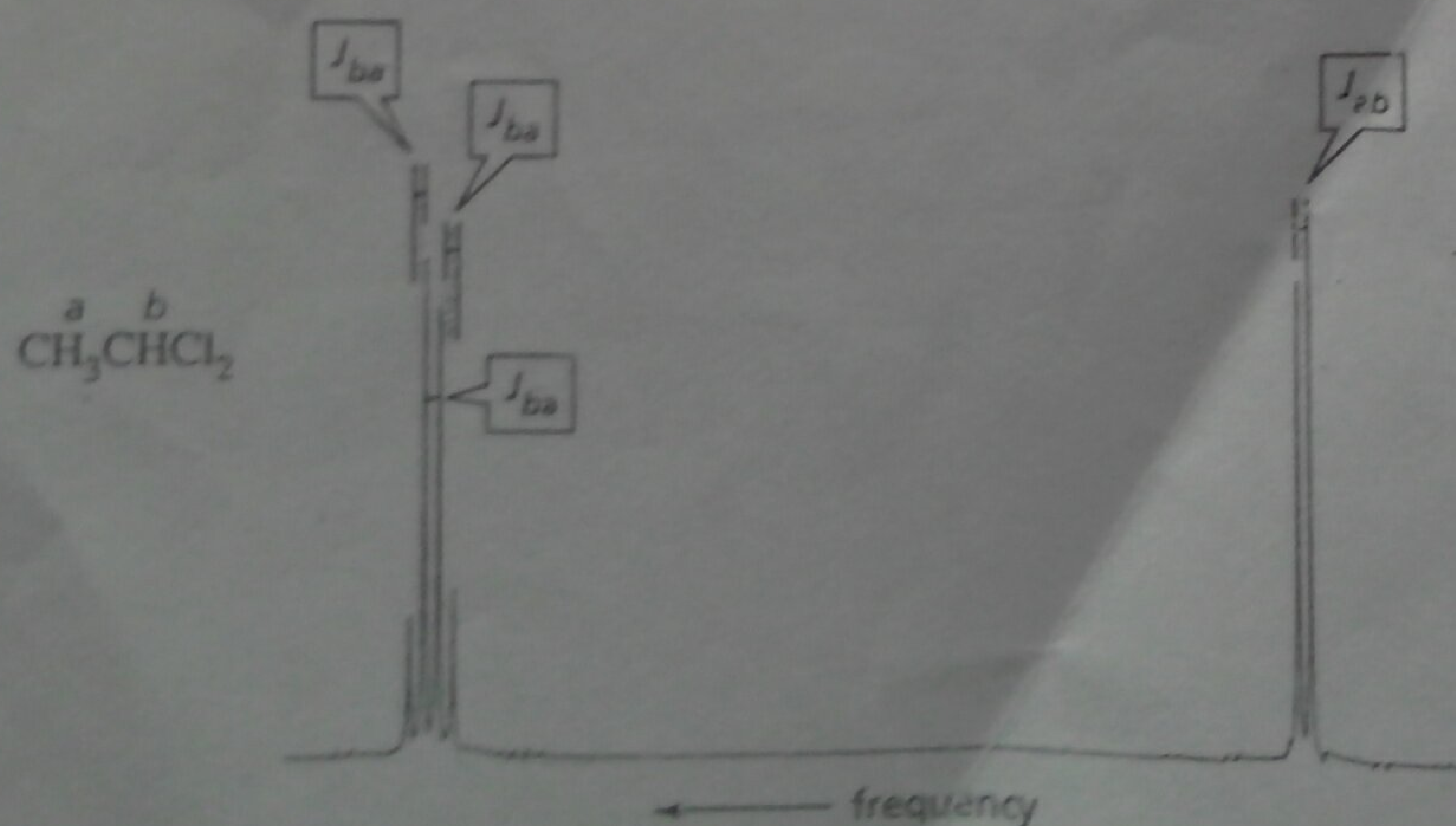


## 14.12 Coupling Constants

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  $\text{H}_a$  being split by  $\text{H}_b$  is denoted by  $J_{ab}$ . The signals of coupled protons (protons that split each other's signal) have the same coupling constant; in other words,  $J_{ab} = J_{ba}$  (Figure 14.20). 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 are given in Table 14.2, and range from 0 to 15 Hz.

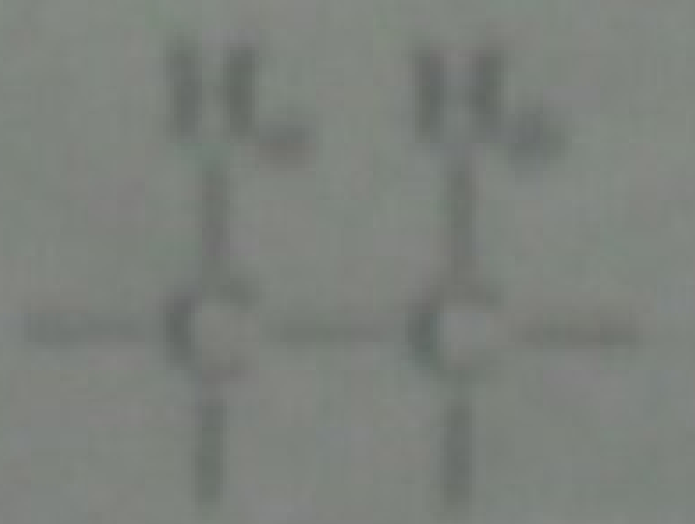
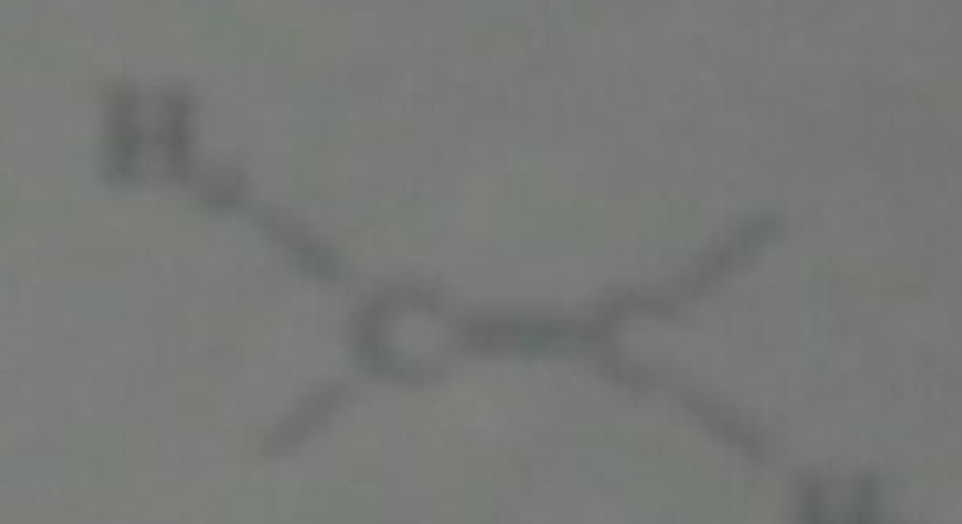
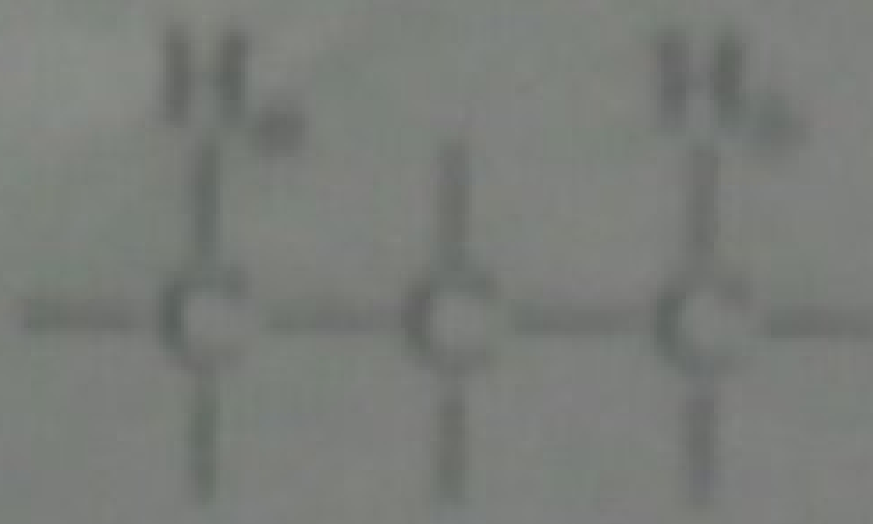
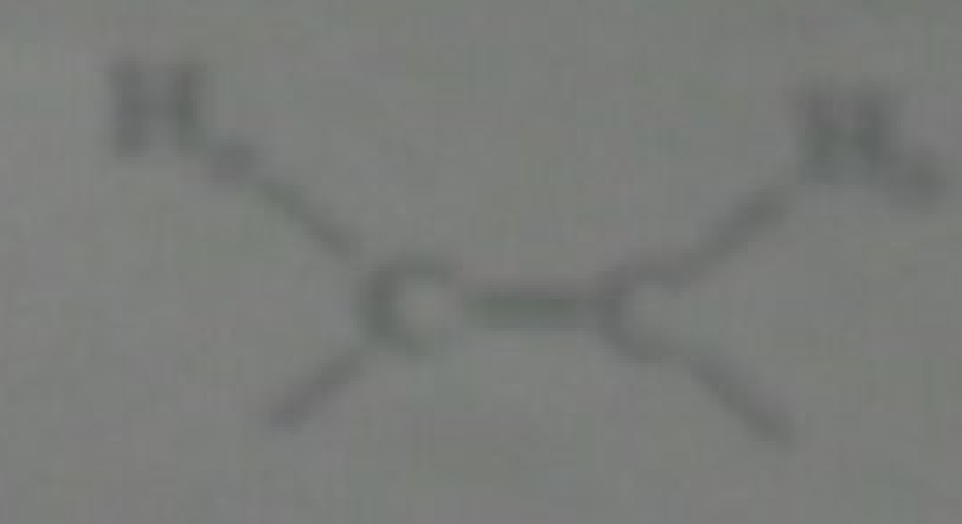
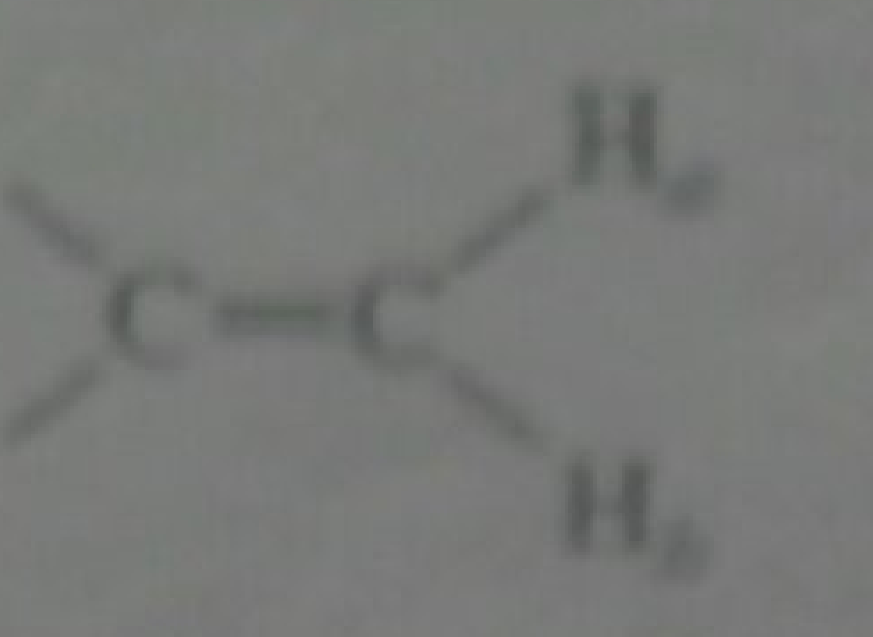
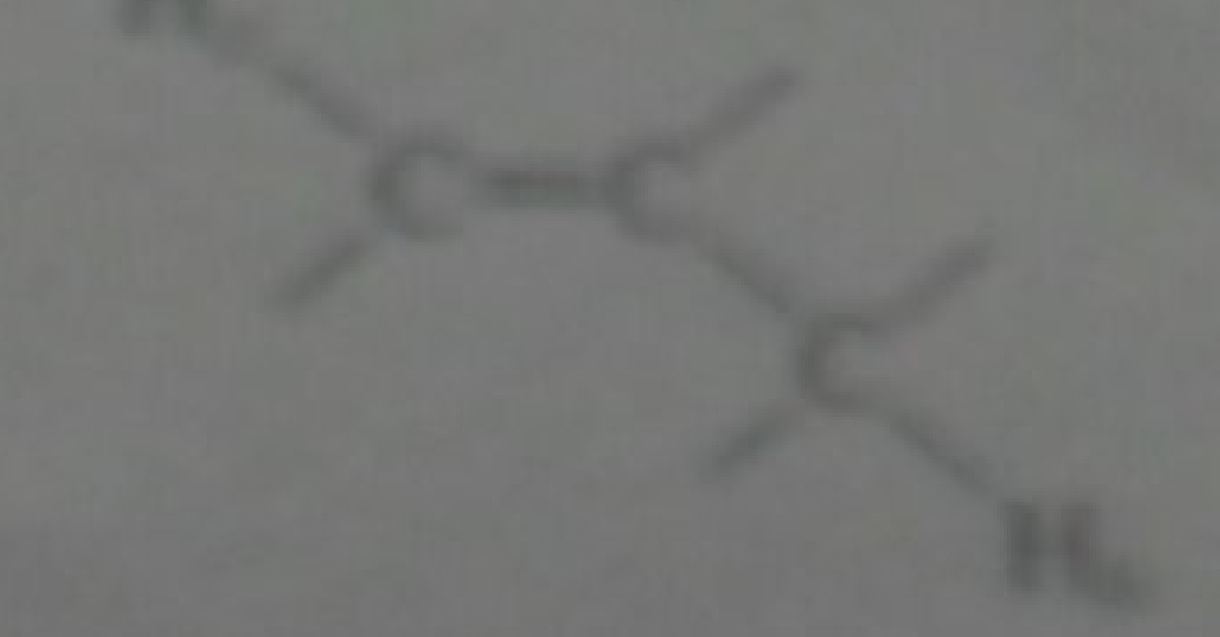
The coupling constant for two nonequivalent hydrogens on the same  $sp^2$  carbon is often too small to be observed (Figure 14.17), but it is large for nonequivalent hydrogens bonded to adjacent  $sp^3$  carbons. Apparently, the interaction between the hydrogens is strongly affected by the intervening  $\pi$  electrons. We have seen that  $\pi$  electrons also allow long-range coupling—that is, coupling through four or more bonds (Section 14.10).



◀ Figure 14.20  
The  $\text{H}_a$  and  $\text{H}_b$  protons of 1,1-dichloroethane are coupled protons, so their signals have the same coupling constant,  $J_{ab} = J_{ba}$ .



27

| Table 14.3 Approximate Values of Coupling Constants   |  |
|---|--|
| Approximate value of $J_{ab}$ (Hz)  | Approximate value of $J_{ab}$ (Hz)   |
| <br>7                    | <br>15 (trans)              |
| <br>0                    | <br>10 (cis)                |
| <br>2 (geminal coupling) | <br>1 (long-range coupling) |

Coupling constants can be used to distinguish between the  $^1\text{H}$  NMR spectra of *cis* and *trans* alkenes. The coupling constant of *trans*-vinylic protons is significantly greater than the coupling constant of *cis*-vinylic protons (Figure 14.21), 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 C—H bonds is  $180^\circ$  (*trans*) and smaller when it is  $0^\circ$  (*cis*). Notice the difference between  $J_{bd}$  and  $J_{cd}$  in the spectrum of 3-bromo-1-propene (Figure 14.17).

The dependence of the coupling constant on the angle between the two C—H 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.

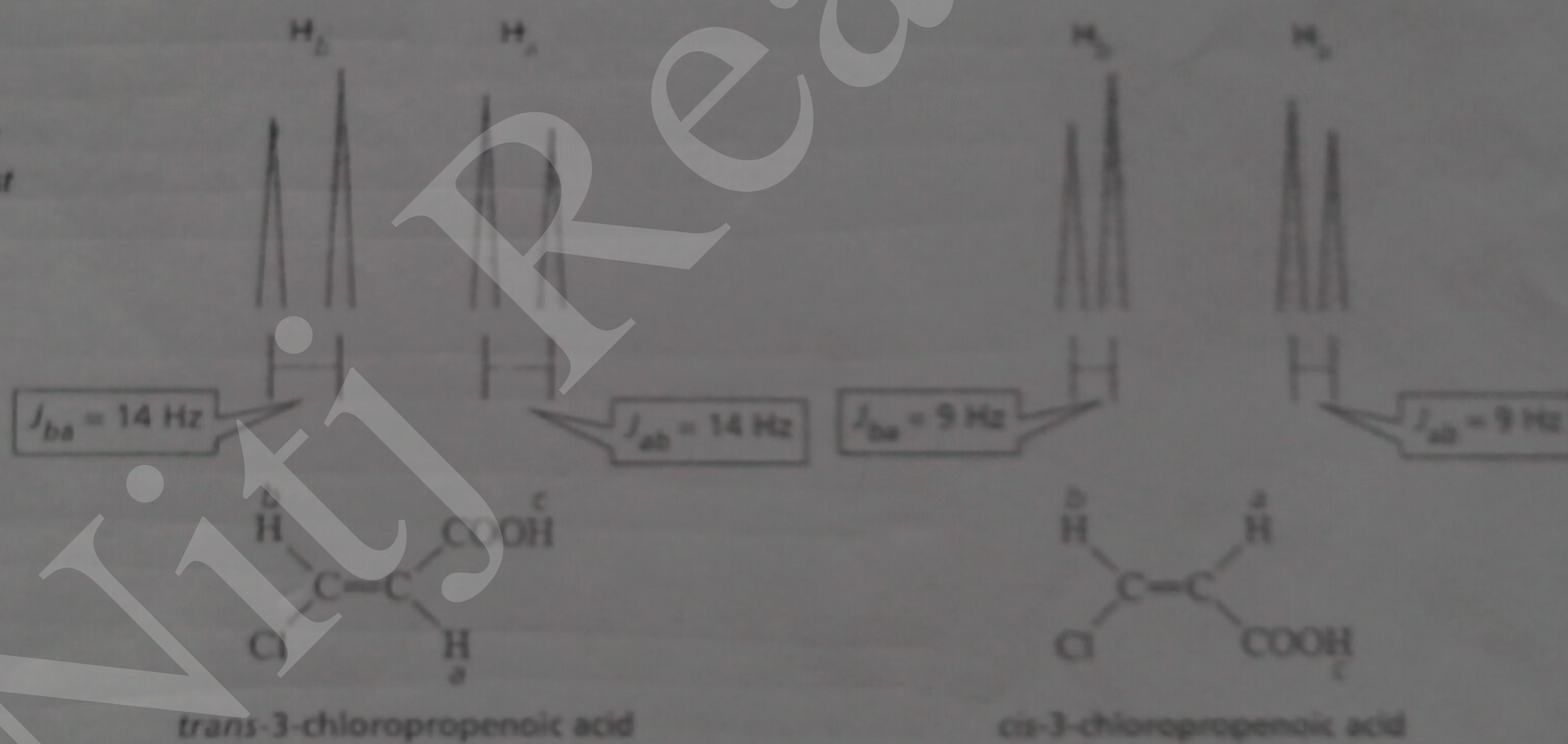


Figure 14.21

The doublets observed for the  $\text{H}_b$  and  $\text{H}_d$  protons in the  $^1\text{H}$  NMR spectra of *trans*-3-chloropropenoic acid and *cis*-3-chloropropenoic acid. The coupling constant for *trans* protons (14 Hz) is greater than the coupling constant for *cis* protons (9 Hz).

The coupling constant for *trans* protons is greater than the coupling constant for *cis* protons.

### PROBLEM 28

Why is there no coupling between  $\text{H}_a$  and  $\text{H}_c$  or between  $\text{H}_b$  and  $\text{H}_d$  in *cis*- or *trans*-3-chloropropenoic acid?

Let's now summarize the kind of information that can be obtained from an  $^1\text{H}$  NMR spectrum:

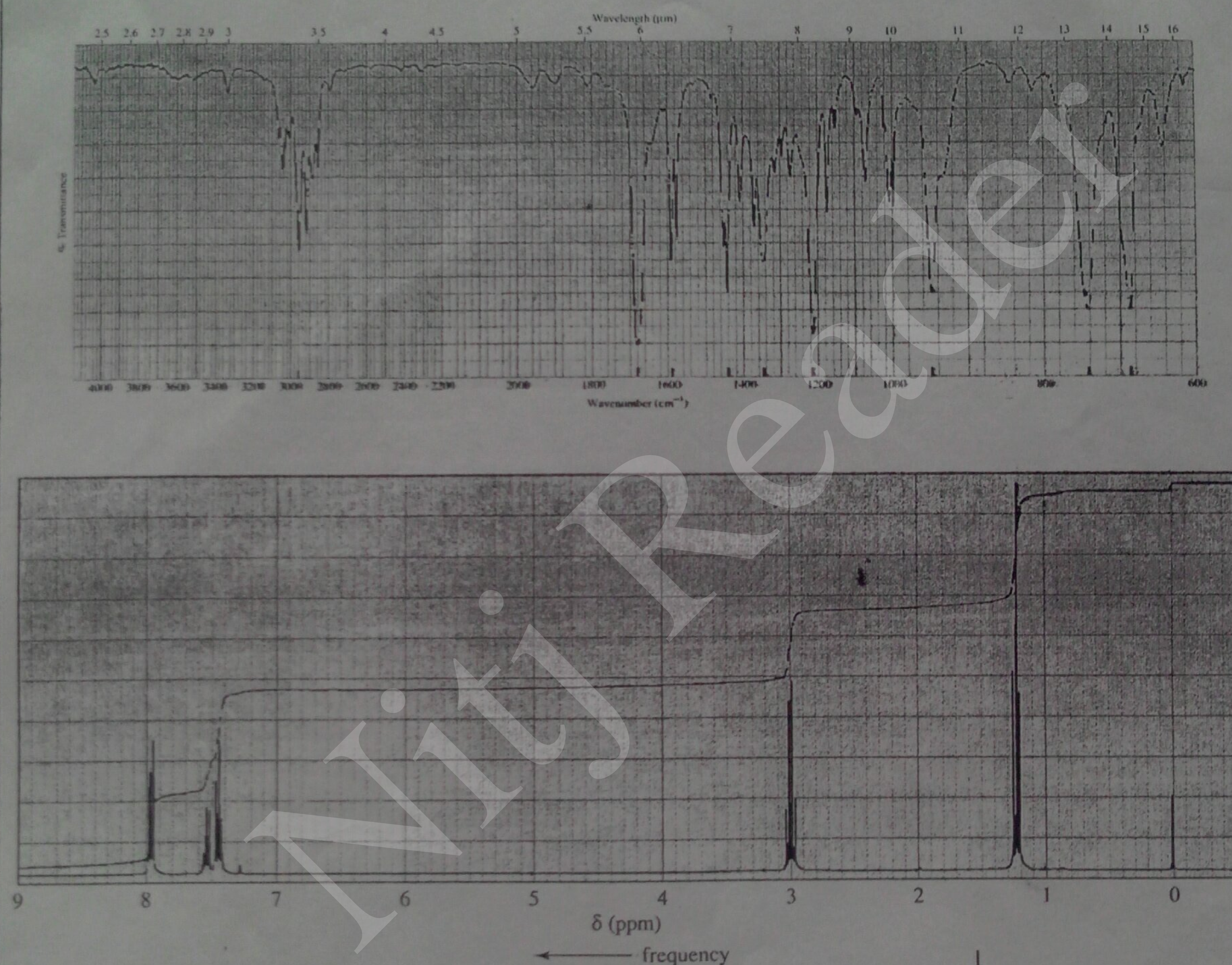
- 1. The number of signals indicates the number of different kinds of protons that are in the compound.



- ✓ 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.

### PROBLEM-SOLVING STRATEGY

Identify the compound with molecular formula  $C_9H_{10}O$  that gives the IR and  $^1H$  NMR spectra in Figure 14.22.

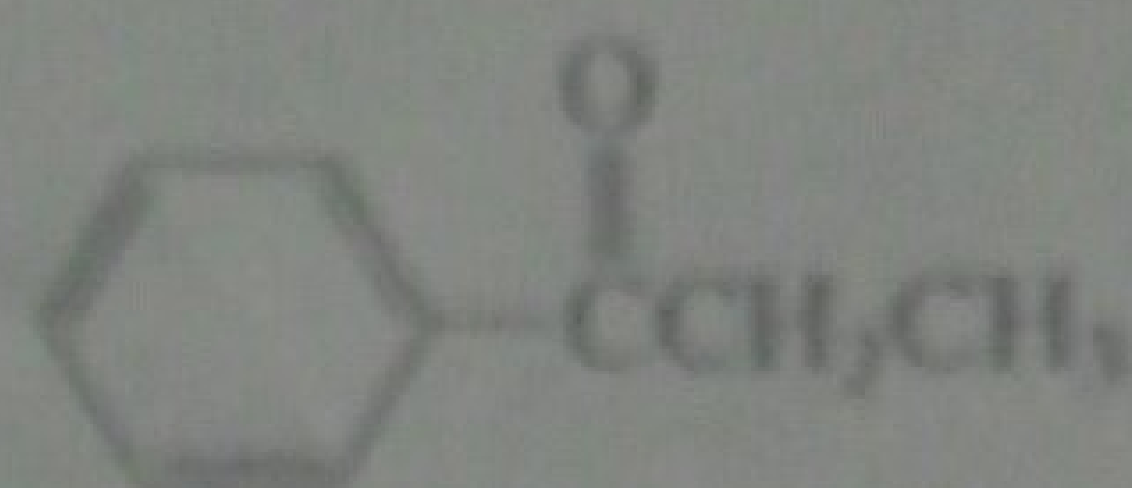


▲ Figure 14.22  
IR and  $^1H$  NMR spectra for this problem-solving strategy.

The best way to approach this kind of problem is to identify whatever structural features you can from the molecular formula and IR spectrum and then use the information from the  $^1H$  NMR spectrum to expand on that knowledge. From the molecular formula and IR spectrum, we learn that the compound is a ketone: It has a carbonyl group at  $\sim 1680\text{ cm}^{-1}$ , only one oxygen, and no absorption bands at  $\sim 2820$  and  $\sim 2720\text{ cm}^{-1}$  that would indicate an aldehyde. That the carbonyl group absorption is at a lower frequency than normal suggests that it has partial single-bond character as a result of electron delocalization—indicating that it is attached to an  $sp^2$  carbon. The compound contains a benzene ring ( $>3000\text{ cm}^{-1}$ ,  $\sim 1600\text{ cm}^{-1}$ , and  $1440\text{ cm}^{-1}$ ), and it has hydrogens bonded to  $sp^3$  carbons ( $<3000\text{ cm}^{-1}$ ). In the NMR spectrum, the triplet at  $\sim 1.2\text{ ppm}$  and the quartet at  $\sim 3.0\text{ ppm}$



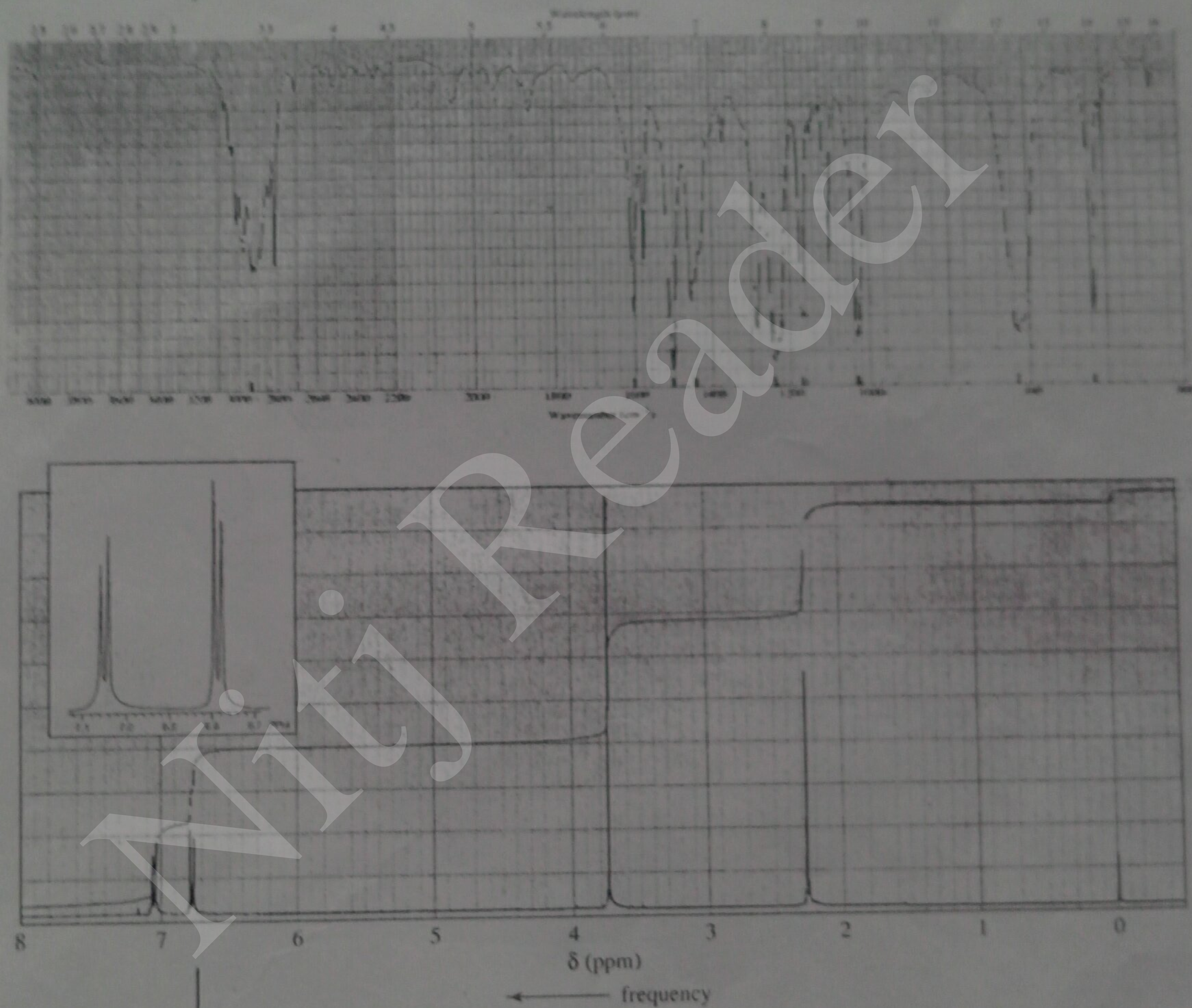
indicate the presence of an ethyl group that is attached to an electron-withdrawing group. The signals in the 7.4–8.0 ppm region confirm the presence of a benzene ring. From this information, we can conclude that the compound is the following ketone. The integration ratio (5:2:3) confirms this answer.



Now continue on to Problem 29.

### PROBLEM 29

Identify the compound with molecular formula  $C_8H_{10}O$  that gives the IR and  $^1H$ NMR spectra shown in Figure 14.23.



▲ Figure 14.23  
IR and  $^1H$  NMR spectra for Problem 29.

## 14.13 Splitting Diagrams

The splitting pattern obtained when a signal is split by more than one set of protons can best be understood by using a splitting diagram. In a **splitting diagram** (also called a **splitting tree**), the NMR peaks are shown as vertical lines and the effect of each of the splittings is shown one at a time. (For example, a splitting diagram is shown in Figure 14.24 for splitting of the signal for the  $H_c$  proton of 1,1,2-trichloro-3-methylbutane into a doublet of doublets by the  $H_b$  and  $H_d$  protons.)



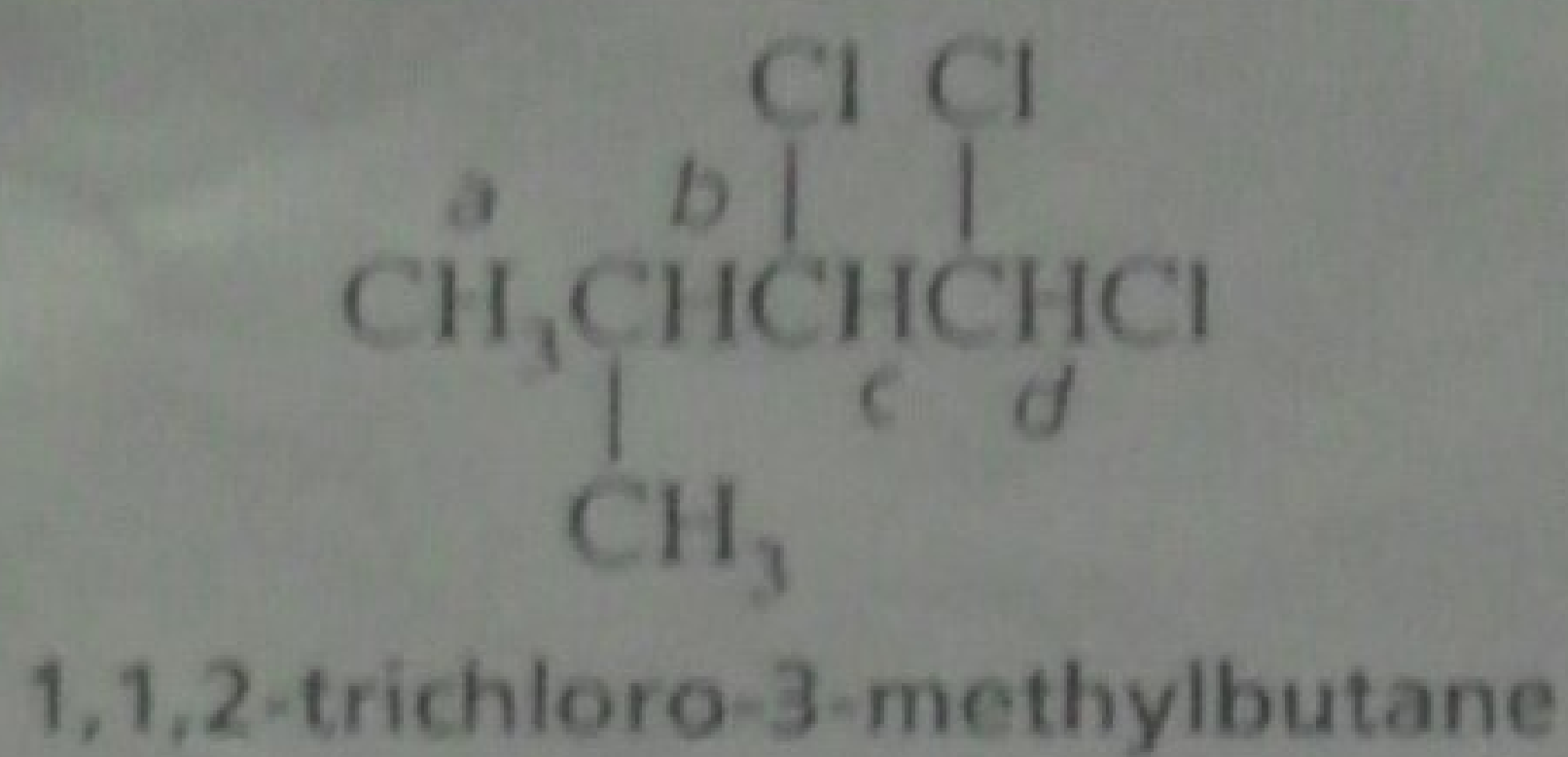
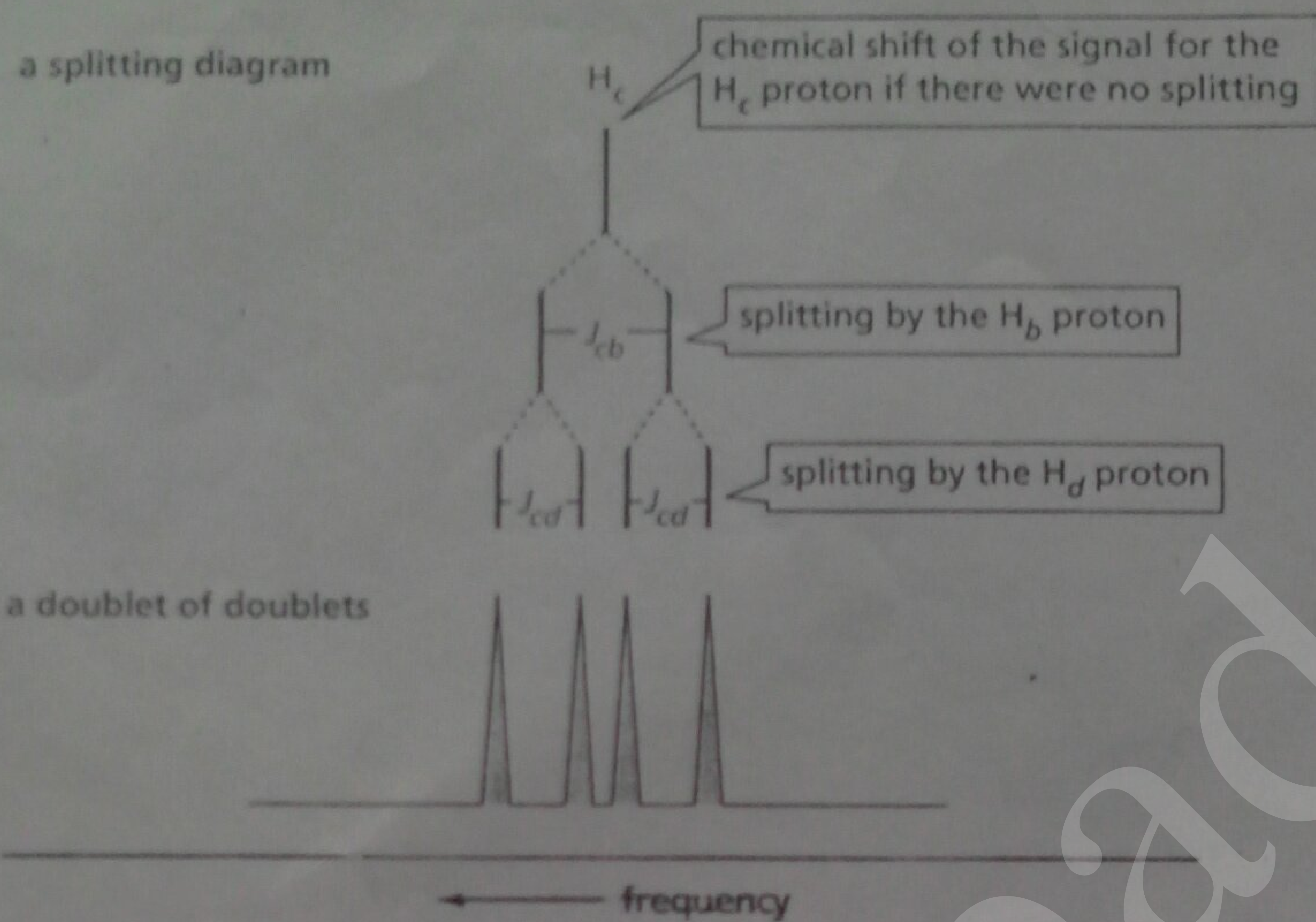


Figure 14.24 A splitting diagram for a doublet of doublets.



(The signal for the  $H_b$  protons of propyl bromide is split into a quartet by the  $H_a$  protons, and each of the resulting four peaks is split into a triplet by the  $H_c$  protons (Figure 14.25). How many of the 12 peaks are actually seen depends on the relative magnitudes of the two coupling constants,  $J_{ba}$  and  $J_{bc}$ . For example, the figure shows that there are 12 peaks when  $J_{ba}$  is much greater than  $J_{bc}$ , 9 peaks when  $J_{ba} = 2J_{bc}$ , and only 6 peaks when  $J_{ba} = J_{bc}$ . As you can see, the number of peaks actually observed depends on how many overlap with one another. When peaks overlap, their intensities add together.)

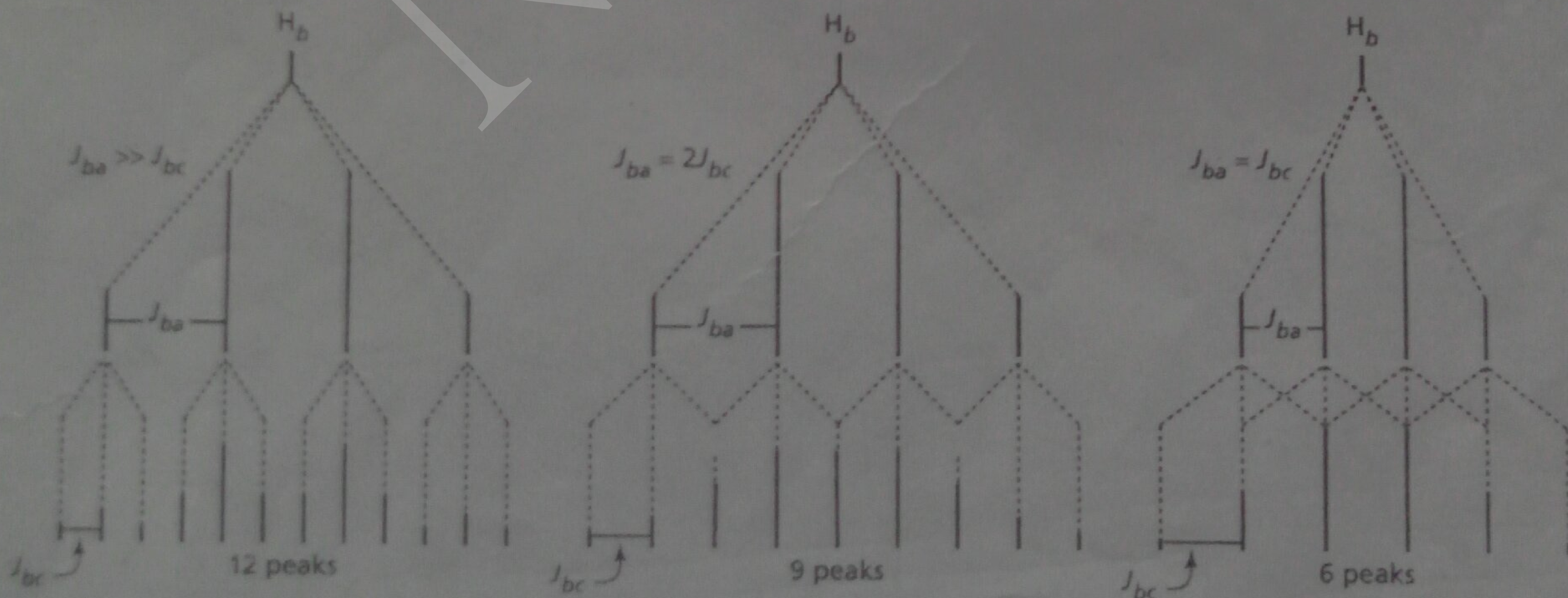
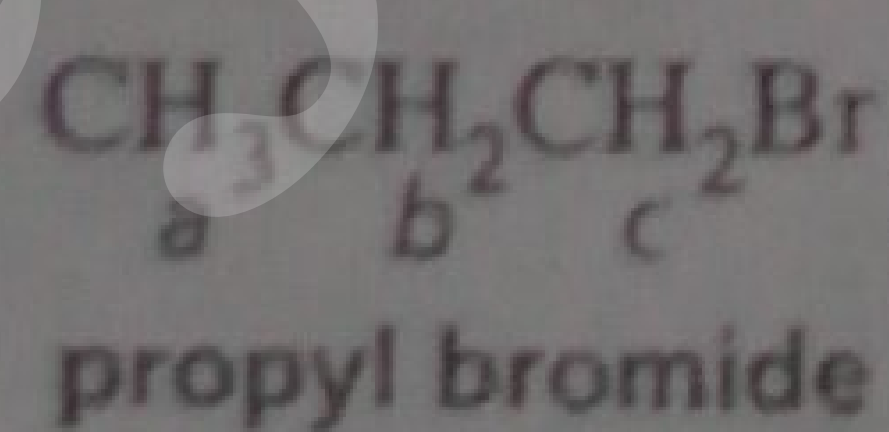


Figure 14.25 A splitting diagram for a quartet of triplets. The number of peaks actually observed when a signal is split by two sets of protons depends on the relative magnitudes of the two coupling constants.