11

Infrared Absorption Spectroscopy

Infrared absorption spectroscopy is the measure of the amount of radiation absorbed by compounds within the infrared region of the electromagnetic spectrum. The infrared region consists of radiation with wavelengths between 2.5 and 15 μm (1 μm = 1 micrometer or micron = 10^{-6} m), which corresponds to frequencies between 4000 and 650 cm^{-1} (cm^{-1} = "reciprocal centimeters" or wave numbers). An infrared spectrometer measures the amount of radiation absorbed as a function of the frequency of the radiation and provides absorption spectra such as those shown in Figures 11.2 through 11.8. Spectrometers can be constructed with a chart drive that is linear in either frequency or wavelength; the latter is in common use. The wavelength and frequency scales have a reciprocal relationship, and conversion from one to the other is very simple:

$$\nu(cm^{-1}) = \frac{1}{\lambda(cm)} = \frac{10{,}000}{\lambda(\mu m)}$$

$$\lambda(\mu m) = \frac{10{,}000}{\nu(cm^{-1})}$$

When electromagnetic radiation in the infrared region is absorbed by molecules, the molecules are excited to a higher energy state. Infrared radiation absorption causes energy changes on the order of 2 to 10 kcal/mole, and the excited state is one involving a greater amplitude of molecular vibration. Each absorption band or peak in the spectrum corresponds to the excitation of a different type (mode) of vibration of the atoms, and the positions of these peaks (measured in μm or cm^{-1}) provide useful information about the structure of the molecule. The intensity of the absorbance is proportional to the change in dipole moment for the motion, so a C = O stretch will, for instance, be much more intense than a C=C stretch.

For simple molecules containing few atoms, the number and position of peaks in the infrared spectrum can be calculated, and the spectrum can be completely analyzed. The major use of infrared spectra in organic chemistry, however, depends on empirical correlations of band positions with structural units. These correlations have been derived from spectra of a large number of compounds of known structure. By the use of this information, the presence or absence of certain functional groups or other structural features of a new compound can be determined.

Two types of vibrations, stretching and bending, are responsible for most of the peaks of importance in the identification of organic compounds. A few of the types of vibrations observed are shown in Figure 11.1, using CH_2 as a typical group. Also shown are the approximate frequencies of the radiation absorbed in exciting each type of vibration. When expressed in cycles per second (Hz), these are also the vibrational frequencies of the indicated motions. The vibrational frequency, and thus the frequency of radiation absorbed, is determined by the force constant for the deformation (i.e., the rigidity or strength of the bond) and the masses of the atoms that are involved in the vibration; specifically, the stronger the bond and the lighter the atoms,

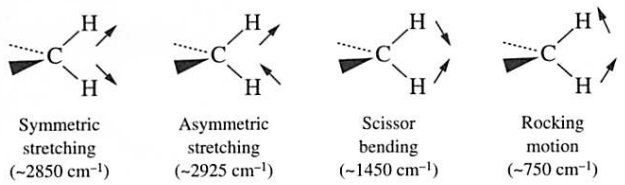


Figure 11.1 Normal modes of CH_2 vibration.

the higher is the vibration frequency. Bending motions are easier than stretching motions, so the former absorb at lower frequencies. These trends are illustrated in Table 11.1, which lists the types of vibrations that appear in various regions of the infrared spectrum.

Peaks in the first four regions listed in Table 11.1 are largely due to vibrations of specific types of bonds, and these are by far the most useful in compound classification. A few of the peaks appearing below 1500 cm^{-1} are characteristic of certain functional groups, but most of the absorption bands in this region are associated with vibrations of larger groups or the molecule as a whole. An infrared spectrum can be divided into two portions for examination. The region 4000 to 1500 cm^{-1} is useful for the identification of various functional groups. The region from 1500 to 600 cm^{-1}, sometimes called the "fingerprint region," is quite complex yet represents a unique pattern for each organic compound and, so, is useful for comparing two compounds for identification.

Table 11.1 Absorption Frequencies and Types of Vibrations

FREQUENCY (CM^{-1})	VIBRATION
3600–2700	X—H single bond stretching: O—H, N—H, C—H
3300–2500	Hydrogen-bonded O—H--X stretching
	Ammonium ion $-\overset{+}{N}-H$ stretching
2400–2000	Triple bond and cumulated double bond stretching:
	C≡C, C≡N, N=C=O, C=C=O, N=C=N
1850–1550	Double bond stretching: C=O, C=N, C=C
1600–650	Single bond bending: NH_2, CH_3, C—C—C
	Single bond stretching: C—C, C—O, C—N

Fourier transform infrared spectroscopy (FTIR) is now being widely used. In this method, the electromagnetic radiation is split into two beams and one is made to travel a longer path than the other. Recombination of the two beams creates an interference pattern or **interferogram.** Mathematical manipulation (Fourier transformation) of this interference pattern by a computer converts it into the usual infrared (IR) spectrum. The advantages of FTIR are that the whole spectrum is measured in a few seconds, very small samples can be analyzed, and high resolution is obtained.

STRUCTURAL GROUP ANALYSIS

Extensive correlations exist between absorption peak positions and structural units of organic molecules; the most useful of these are summarized in Table 11.2. In spectra to be presented

later, the vertical scale is percent transmittance, 100% being the top of the spectrum and 0% the bottom. Thus, absorption of radiation at a certain frequency results in a decrease in transmittance and appears as a dip in the curve (Figs. 11.2 through 11.8).

Table 11.2 Structural Units and Absorption Frequencies

BOND		TYPE OF COMPOUND	FREQUENCY (CM^{-1})
	(stretch)	Alkane	2800–3000
	(stretch)	Alkenes, aromatics	3000–3100
	(stretch)	Alkynes	3300
	(stretch)	Alcohols, phenols	3600–3650 (free) 3200–3500 (H-bonded) (broad)
	(stretch)	Carboxylic acids	2500–3300
	(stretch)	Amines	3300–3500 (doublet for NH_2)
	(stretch)	Aldehyde	2720 and 2820
	(stretch)	Alkenes	1600–1680
	(stretch)	Aromatic	1500 and 1600
	(stretch)	Alkynes	2100–2270
	(stretch)	Aldehydes, ketones	1680–1740
	(stretch)	Nitriles	2220–2260
	(stretch)	Amines	1180–1360
	(bending)	Alkane	1375 (methyl)
	(bending)	Alkane	1460 (methyl and methylene)
	(bending)	Alkane	1370 and 1385 (isopropyl split)
	(bending)	R—CH=CH_2	1000–960 and 940–900
	(bending)	R_2C=CH_2	915–870
	(bending)	*cis* RCH=CHR	790–650
	(bending)	*trans* RCH=CHR	990–940
	(out-of-plane bending)	*mono* subst. benzene	770–730 and 710–690
	(out-of-plane bending)	*o*-subst. benzene	770–735
	(out-of-plane bending)	*m*-subst. benzene	810–750 and 710–690
	(out-of-plane bending)	*p*-subst. benzene	860–800
	(stretch)	Primary alcohol	1050–1085
	(stretch)	Secondary alcohol	1085–1125
	(stretch)	Tertiary alcohol	1125–1200
	(stretch)	Phenol	1180–1260

For the more common structural units shown in Table 11.2, more specific assignments and deductions may often be made. Some of these are discussed in the following sections. For even more specific correlations and for similar data on the other functional groups, any of several books on this subject can be consulted (see References).

ALKANES

The most prominent peaks in infrared spectra of saturated hydrocarbons and from saturated portions of more complicated organic compounds are those due to C—H stretching and bending (see Fig. 11.2). The stretching frequencies are in the regions 3000 to 2800 cm^{-1} and are usually rather strong. Since most organic compounds contain several CH_3, CH_2, and/or CH groupings, the presence or absence of peaks in this region is simply taken to indicate the presence or absence of aliphatic C—H bonds in the molecule. The major bending modes of CH_2 and CH_3 groups appear in the 1470 to 1420 cm^{-1} and 1340 to 1380 cm^{-1} regions, but interpretation is usually complicated by the presence of several bands of this type or additional bands from other sources. The usually large number of different C—C bonds in an organic molecule makes the C—C stretching vibrations in the 1300 to 1100 cm^{-1} region uninterpretable in most cases. The "breathalyzer" sometimes used to check motorists for inebriation is an infrared device that measures "C—H" stretch on the breath.

ALKENES

Olefinic C—H stretching peaks generally appear in the region 3100 to 3000 cm^{-1}, thus differentiating between saturated and unsaturated hydrocarbons. Of the C—H bending modes, the out-of-plane vibrations in the 1000 to 650 cm^{-1} region were, before the advent of ^1H and ^{13}C-NMR, often used to deduce the substitution pattern of a double bond. This is illustrated in Table 11.2. The C=C stretching frequency in the 1600 to 1675 cm^{-1} region also varies with substitution, but to a lesser degree. The out-of-plane bending and C=C stretching absorptions of an alkene are illustrated in Figure 11.2.

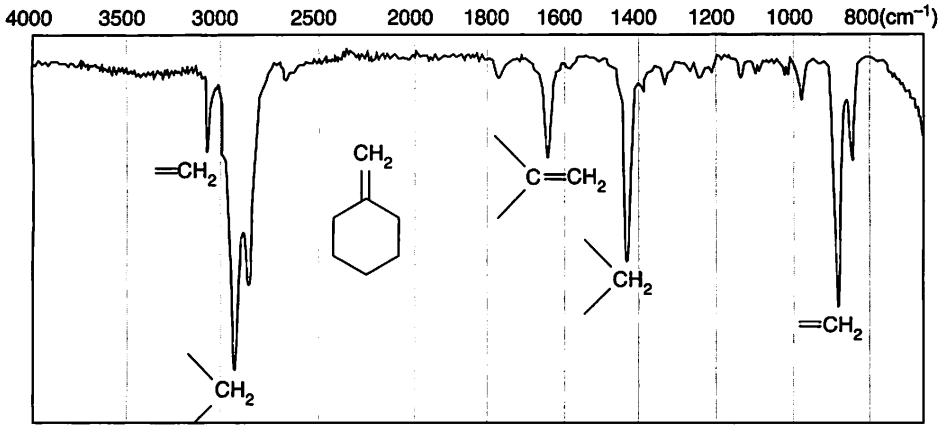


Figure 11.2 Infrared spectrum of an alkene.

ALKYNES

The C—H stretching vibration of terminal acetylenes generally appears at about 3300 cm^{-1} as a strong sharp band. The C≡C stretching band is found in the region 2150 to 2100 cm^{-1} if the alkyne is monosubstituted (Fig. 11.3) and at 2270 to 2150 cm^{-1} if disubstituted. Because the

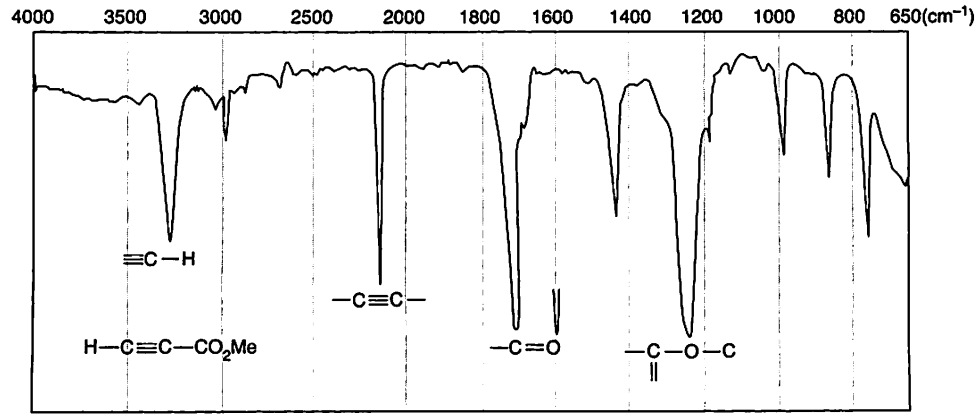


Figure 11.3 Infrared spectrum of an alkyne.

change in dipole moment is small, the latter are usually quite weak absorptions, unless the alkyne has a polarizing substituent such as an alcohol nearby (the partial peak at 1601 cm^{-1} in the figure is a frequency marker, from a polystyrene standard).

AROMATIC RINGS

Aromatic C—H stretching absorption appears in the region 3100 to 3000 cm^{-1}. This fact, taken with the corresponding frequencies of aliphatic and olefinic C—H stretching bands, allows a reliable determination of the types of carbon-bound hydrogen in the molecule. Aromatic C—H out-of-plane bending bands in the 900 to 690 cm^{-1} region are reasonably well determined by the substitution pattern of the benzene ring, as indicated in Table 11.2. In the absence of other interfering absorptions, such as those from nitro groups, these strong, usually sharp bands can be used in distinguishing positional isomers of substituted benzenes. Sharp peaks at approximately 1600 and approximately 1500 cm^{-1} are very characteristic of all benzenoid compounds; a band at 1580 cm^{-1} appears when the ring is conjugated with a substituent (Fig. 11.4).

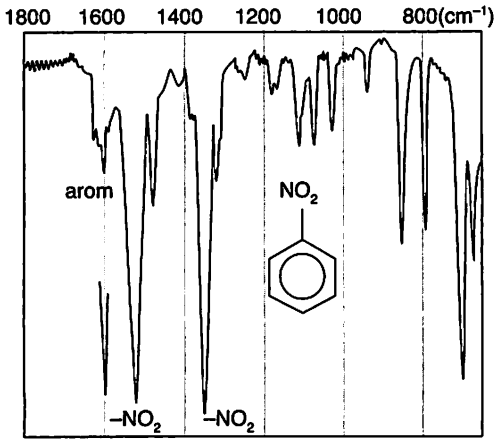


Figure 11.4 Infrared spectrum of an aromatic compound.

ALCOHOLS, PHENOLS, AND ENOLS

The very characteristic infrared band due to O—H stretching appears at 3650 to 3600 cm^{-1} in dilute solutions. In spectra of neat (undiluted) liquids or solids, intermolecular hydrogen bonding broadens the band and shifts its position to lower frequency (3500 to 3200 cm^{-1}) (Fig. 11.5). Intramolecular hydrogen bonding (to C=O, $—NO_2$ groups), as in enols, lowers the frequency and broadens the absorption even more. Strong bands due to O—H bending and C—O stretching are observed at 1500 to 1300 cm^{-1} and 1220 to 1000 cm^{-1}, respectively. In simple alcohols and phenols, the exact position of the latter is useful in classification of the hydroxyl group (see Table 11.2). Within the range given, typical frequencies observed are phenols > tertiary > secondary > primary. Further branching and unsaturation also affect the frequency somewhat.

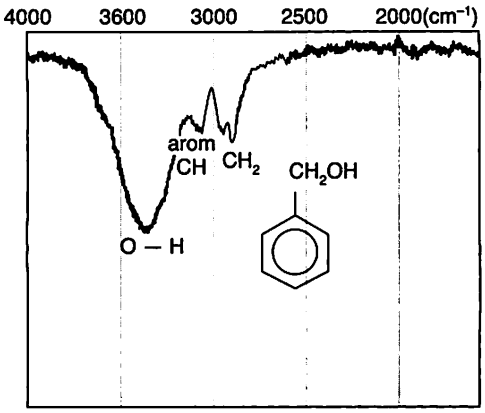


Figure 11.5 Infrared spectrum of an alcohol.

ALDEHYDES AND KETONES

The C=O stretching frequencies of saturated aldehydes and acyclic ketones are observed at 1735 to 1710 cm^{-1} and 1725 to 1700 cm^{-1}, respectively. Adjacent unsaturation lowers the frequency by 25 to 50 cm^{-1}. Thus, aryl aldehydes generally absorb at 1700 to 1690 cm^{-1} and diaryl ketones at 1670 to 1660 cm^{-1}. Intramolecular hydrogen bonding to the carbonyl oxygen also lowers the frequency by 25 to 50 cm^{-1}. Aldehydes are also recognizable by the C—H stretching vibration, which appears as two peaks in the 2850 to 2700 cm^{-1} region (Fig. 11.6). The former may be obscured by aliphatic C—H stretching, but the latter is usually quite prominent. Cyclic ketones (four- or five-membered rings) absorb at higher frequencies (in the area of 1780 and 1745 cm^{-1}, respectively).

CARBOXYLIC ACIDS

The most characteristic absorption of carboxylic acids is a broad peak extending from 3300 to 2500 cm^{-1} due largely to hydrogen-bonded O—H stretching (Fig. 11.7). The C—H stretching vibrations appear as small peaks on top of this band. The carbonyl group of aliphatic acids appears at 1730 to 1700 cm^{-1} and is shifted to 1720 to 1680 cm^{-1} by adjacent unsaturation.

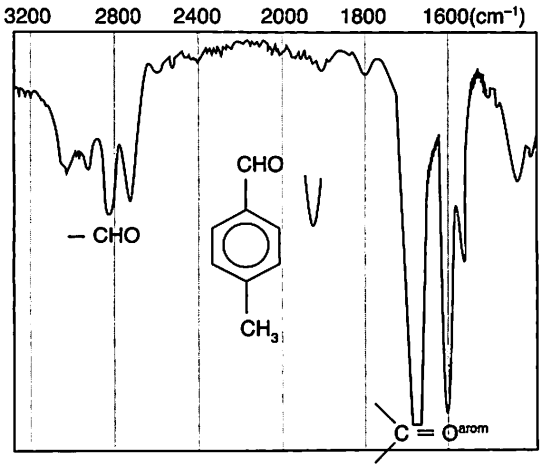


Figure 11.6 Infrared spectrum of an aldehyde.

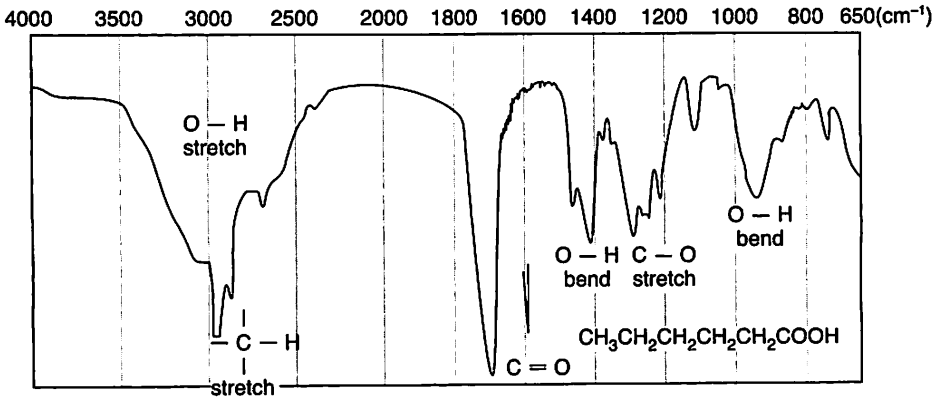


Figure 11.7 Infrared spectrum of a carboxylic acid.

CARBOXYLIC ESTERS AND LACTONES

Saturated ester carbonyl stretching is observed at 1750 to 1730 cm^{-1}. Unsaturation adjacent to the carbonyl group lowers the frequency by 10 to 15 cm^{-1} (see Fig. 11.3), whereas unsaturation adjacent to the oxygen (enol and phenol esters) increases the frequency by 20 to 30 cm^{-1}. The C—O—C stretching of esters appears as two bands in the 1280 to 1050 cm^{-1} region. The asymmetric stretching peak at 1280 to 1150 cm^{-1} is usually strong and varies with substitution, much as does the corresponding ether band. Cyclic esters (lactones), like cyclic ketones, absorb at higher frequencies as the ring size decreases: five-membered rings (γ-lactones) absorb around 1770 cm^{-1}, and four-membered rings (β-lactones) around 1820 cm^{-1}. **The most important use of infrared spectroscopy in deducing the structure of an organic unknown is the assignment of the ring size of a cyclic carbonyl compound.**

ANHYDRIDES

Acid anhydrides are readily recognized by the presence of two high-frequency (1830 to 1800 cm^{-1} and 1775 to 1740 cm^{-1}) carbonyl absorptions. As with other carbonyl stretching vibrations, the frequency is increased by incorporating the group in a ring and decreased by adjacent unsaturation. Cyclic anhydrides differ from acyclic anhydrides also in that the lower frequency band is stronger in the former, while the reverse is true of the latter.

AMIDES AND LACTAMS

Amide carbonyl stretching is observed in the 1700 to 1630 cm^{-1} region. In contrast to other carbonyl groups, both adjacent unsaturation and ring formation (lactams) cause the absorption to shift to higher frequencies. Primary and secondary amides also show N—H stretching at 3500 to 3100 cm^{-1} (see discussion of amines), and N—H bending at 1640 to 1550 cm^{-1}.

ETHERS

The asymmetric C—O stretching absorption of ethers appears in the region 1280 to 1050 cm^{-1}. As in alcohols, the exact position of this strong peak is dependent on the nature of the attached groups. Phenol and enol ethers generally absorb at 1275 to 1200 cm^{-1} and dialkyl ethers at 1150 to 1050 cm^{-1}. Epoxides have three characteristic absorptions in the 1270 to 1240, 950 to 810, and 850 to 750 cm^{-1} regions of the spectrum.

AMINES

Primary and secondary amines show N—H stretching vibrations in the 3500 to 3300 cm^{-1} region (Fig. 11.8). Primary amines generally have two bands approximately 70 cm^{-1} apart due to asymmetric and symmetric stretching modes. Secondary amines show only one band. Intermolecular or intramolecular hydrogen bonding broadens the absorptions and lowers the frequency. In general, the intensities of N—H bands are less than of O—H bands. The N—H bending and C—N stretching absorptions are not as strong as the corresponding alcohol bands and occur at approximately 100 cm^{-1} higher frequencies. In addition, NH_2 groups give an additional broad band at 900 to 700 cm^{-1} caused by out-of-plane bending.

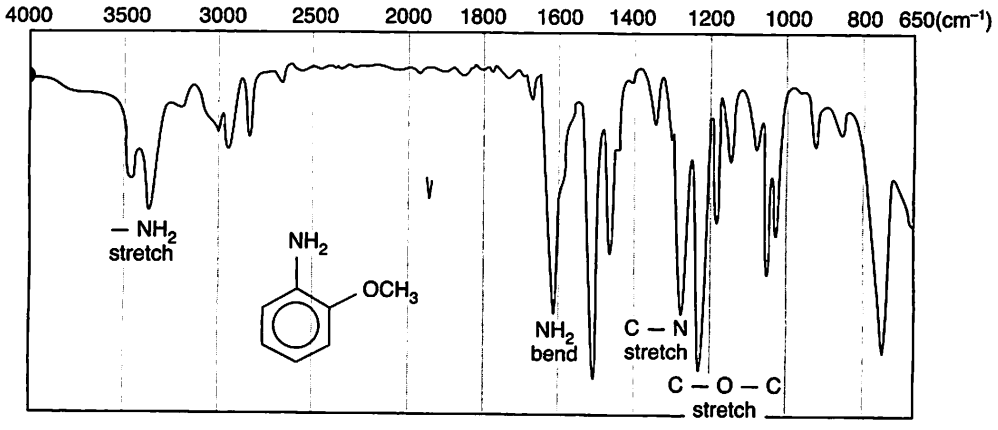


Figure 11.8 Infrared spectrum of an amine.

NITRO GROUPS

Due to the high polarity of the N—O bonds in nitro compounds, the absorptions at the N—O stretching frequencies are very strong. In nitroaromatics, the asymmetric stretching band appears at 1560 to 1520 cm^{-1}, and the symmetric stretching at 1360 to 1320 cm^{-1} (see Fig. 11.4). Since peaks due to several groups other than NO_2 appear in these regions, the presence or absence of a nitro group often cannot be determined with certainty from infrared data alone.

NITRILES

A sharp, usually strong absorption at 2260 to 2220 cm^{-1} due to C≡N stretching is very characteristic of nitriles.

SAMPLE PREPARATION

FILMS

Infrared spectroscopy is quite convenient for the identification of films such as cellophane, Saran Wrap, and so forth. To do this, cut a hole (approximately 2 × 3 cm) in a 3 × 5-inch file card and tape the film over the hole in the card, taking care that none of the tape overlaps the hole. The sample is then ready for insertion in the sample beam.

LIQUIDS

The simplest method for mounting a liquid sample consists of placing a thin film of the liquid between two transparent windows. The most common material used for the windows is NaCl, which is transparent throughout the normally used region of the infrared spectrum (10,000 to 650 cm^{-1}). Large polished plates ground from single crystals are used, *and it is important to remember when handling them that NaCl is water soluble.* They should be picked up *only* by the edges, preferably with gloves, to avoid marring the polished surface with moisture from your fingers.

For mounting the salt plates with the liquid sample between them, the holder illustrated in Figure 11.9 may be used. The bottom metal plate is placed on a flat surface, and one of the rubber gaskets is placed around the opening in the plate. This serves to cushion the relatively fragile salt plate, which is placed on top of it. A drop of the liquid compound is placed in the center of the lower window, and the second salt plate is placed carefully on top, spreading the drop into a thin film. The other rubber gasket and the face plate are then added to the top of the "sandwich" and the entire stack is held together by the thumb nuts on the threaded studs as shown. All four nuts should be tightened firmly *but not excessively.* The assembly is placed in the holder provided on the instrument.

After obtaining the spectrum, disassemble the cell and rinse the windows well with a dry, volatile solvent (CH_2Cl_2, hexane, or the like). Let the solvent evaporate, and store them in a desiccator to protect them from atmospheric moisture.

As alternatives to the cell illustrated in Figure 11.9, smaller circular salt plates may be used and held together in threaded holders that simply screw together or, if the liquid is somewhat viscous, the two plates will stick together by themselves and can be set in the sample beam without mounting brackets.

SOLIDS

Solutions

Sealed cells are available for volatile samples or solutions of compounds in volatile solvents. Solution spectra in nonpolar liquids are useful for minimizing intermolecular association of polar groups in the molecule.

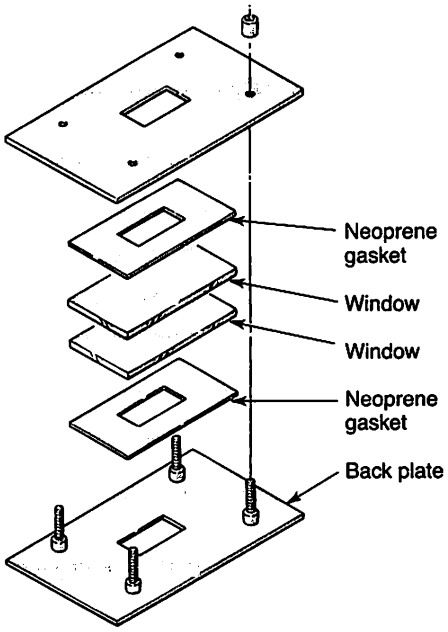


Figure 11.9 Infrared salt plate assembly.

An approximately 10% solution of the compound is prepared using a solvent such as carbon tetrachloride, and the solution is placed in the sealed cell through an injection port. Another (carefully matched) cell is filled with pure solvent and placed in the reference beam. In this manner the absorption of the solvent in the reference beam and in the sample will cancel each other.

KBr Pellet

As an alternative to measuring the spectrum of a liquid solution of a solid compound, a solid solution or dispersion in KBr can be prepared. A 1- to 2-mg sample of the compound is ground together with 50 to 100 mg of dry KBr powder. The mixing must be complete and vigorous enough to reduce the particle size below which it will diffract or scatter the light (less than 2 microns). This can be accomplished by grinding the mixture thoroughly with an agate mortar and pestle or by using the pounding action of a miniature ball mill. The latter technique is preferable because it minimizes the possibility of contamination with moisture. It will be described here.

Weigh the specified quantities of material into the dry plastic vial provided and add a glass ball that fits loosely into the vial. Place the stoppered vial in the shaker and mix for 30 seconds at full speed. Remove the ball from the vial and loosen the powder from the sides of the vial by tapping or by scraping with a spatula.

The powder is formed into a transparent pellet by pressure in a small die. One type of die that may be used consists of a threaded metal block and two bolts with polished end surfaces (Fig. 11.10). To use the die, screw one of the bolts in five or six turns, so that one or two threads remain showing. Pour the powder into the open end and distribute it evenly over the end of the bolt by tapping gently. Screw the other bolt down on top of the sample and tighten the bolts securely with the wrenches provided (use of a torque wrench is recommended). Let the die stand for about 1 minute, during which time the KBr flows to fill the empty spaces between the original particles.

Figure 11.10 Pellet press.

Gently loosen the bolts with the wrenches and remove them, leaving the KBr as a window in the middle of the die. If the pellet is very cloudy, either the compound was not ground well or the bolts were not tightened enough, and a poor spectrum will result due to light scattering. Slight scattering due to a translucent pellet can be partially compensated for with an attenuating device in the reference beam of the instrument. In the absence of a commercial attenuator, a piece of wire screen works adequately to balance the lowered transmittance of the pellet.

Nujol Mull

The infrared spectra of solid compounds can also be measured in a Nujol (a trade name for a purified grade of mineral oil) mull, prepared by grinding 5 mg of the solid to a fine dispersion in a drop of Nujol. The mixture is then placed between salt plates and the spectrum of the thin film is measured. Since Nujol consists of a mixture of saturated hydrocarbons, absorption bands will be present at 2850 to 3000, 1460, and 1375 cm^{-1} in all Nujol mull spectra.

Use of IR in Deducing Unknown Organic Structures

While a typical IR spectrum will cover 600–4500 cm^{-1}, there are two areas of particular interest: 1600–2800 cm^{-1} and 3000–3600 cm^{-1}. The area 2800–3000 cm^{-1} is dominated by the C—H stretch. Pertinent absorptions are summarized in the table in this chapter. IR is diagnostic. If there is a terminal alkyne in the molecule, for instance, then there should be a band between 2100 and 2150 cm^{-1}. The corollary is particularly important. If a structure that could otherwise fit the ^{13}C and ^{1}H NMR data includes a four-membered ring ketone, there should be a band around 1780 cm^{-1}. If there is not, then that structure is *not* acceptable.

While IR is diagnostic for a variety of functional groups, it is especially valuable for establishing the ring size of cyclic esters ("lactones"), and cyclic ketones. Note that α,β-unsaturated carbonyl compounds in general absorb 20–40 cm^{-1} lower frequency than the saturated analogues.

To work a problem with IR data, note which of the (often many!) reported absorptions fall in the key diagnostic areas outlined above, and try to assign *those absorptions.* Note also that any functional groups thought to be present must be consistent with the molecular formula, including the Index of Hydrogen Deficiency (see Chapter 12). At the end, check prospective solutions against the IR. It may be possible that several of the otherwise acceptable alternative ways of assembling the unknown molecule will be seen to be not compatible with the IR spectrum.

EXPERIMENTS

Precautions

1. No aqueous solution or other material that may dissolve the sodium chloride optics should be brought near the instrument.

2. The sample holders (except for film holders) are sodium chloride crystals and should be treated with extreme care! Avoid using water or hydroxylic solvents because these dissolve sodium chloride, and avoid mechanical shock because the salt crystals break easily.
3. Do not operate the instrument without prior detailed instructions. You may inadvertently cause considerable damage.
4. Keep the instrument clean.

SAFETY NOTE

Nothing in this experiment is particularly hazardous; however, usual precautions should be taken to avoid excessive exposure to vapors of solvents and/or samples. Chloroform and carbon tetrachloride, sometimes used as solvents, are suspected carcinogens.

PROCEDURE

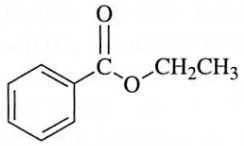
A demonstration of the use of IR spectrophotometers will be given. Students are reminded to sign the log book when using instruments and to promptly label each spectrum (date, sample identity, instrument number, etc.) for future use.

A. Determine the infrared spectrum of polystyrene film. The 1601 cm^{-1} band is often used as a frequency marker (e.g., see Figs. 11.3 and 11.7); note particularly its location on your spectrum (it is important to correctly position the chart paper before recording a spectrum). Label this spectrum and secure it in your laboratory notebook.

B. Determine the infrared spectrum of mineral oil (Nujol). Note the simplicity of the spectrum and the location of the absorption bands near 3000 cm^{-1} (above or below 3000 cm^{-1}?). Use this spectrum for future reference should you have occasion to measure a spectrum in a Nujol mull.

C. Determine the infrared spectrum of cyclohexanol. Examine this spectrum and identify the absorption bands due to the O—H stretch, the C—O stretch, and the C—H stretching.

D. Determine the spectrum of ethyl benzoate:



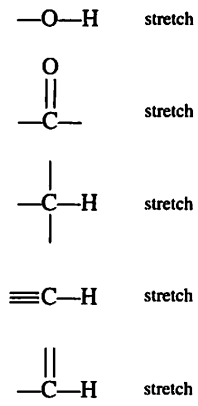
Examine this spectrum and note the location of the absorption band due to the

stretch. Does absorption occur above and below 3000 cm^{-1}? Note the absence of absorption above 3100 cm^{-1} (O—H stretch). Attempt to identify the C—O—C stretching bands and as many of the aromatic absorption bands as you can. Label the spectrum and secure it in your laboratory notebook.

E. You will be given an unknown to characterize. It will be either an alkane, aromatic hydrocarbon, alcohol, or ketone. Assign the major peaks in your spectrum and conclude from your data the nature of your sample.

QUESTIONS

1. Show the following conversions to the units requested.
   2.5 microns = _____ cm^{-1}
   1700 cm^{-1} = _____ μm
2. Give absorption frequency ranges (in cm^{-1}) for each of the following.



3. How could you distinguish between cyclohexane and cyclohexene using IR?
4. In general, how could you identify a compound as an alkane, alkene, alkyne, or arene using IR?
5. An unknown has the following physical data:
   Elemental analysis: 60.0% C, 13.3% H, 26.7% O
   Molecular weight = 60
   IR: 3400, 2950, 1460, 1385, 1365, 1100 cm^{-1}.
   Draw three structures consistent with the analysis and molecular weight data. Which one is consistent with the IR data? Assign absorptions to support your answer.
6. Figure 11.11 A($C_{10}H_{12}O$) is the infrared spectrum of one of the essential oils in Chapter 10. Interpret the spectrum for functional groups, and if possible, suggest the structure of this compound.

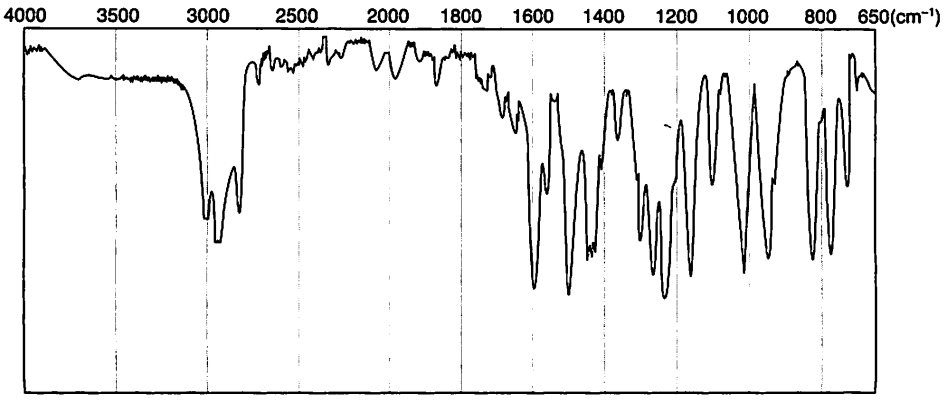


Figure 11.11 Compound A.

PRELABORATORY QUESTIONS

1. Why should aqueous solutions not be used in infrared cells?
2. Describe the procedure to prepare a liquid sample for infrared examination.
3. What is Nujol? What is a Nujol mull?
4. What is a "KBr pellet"? Why not just dissolve a solid sample in a suitable solvent to take its IR spectrum?
5. How could you tell if an unknown is an alcohol by examining its IR spectrum?

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12

Spectroscopic Structure Determination: A Lifelong Quest

INTRODUCTION

Why are there wiggles?
And why are there squiggles?
It's all in the quantum mechanics...

Assume that you have a pure organic compound. How can you tell what it is? You can't tell just by looking at it—it usually looks like a blob of vegetable oil, or like crystals of sugar. Instead, you apply several spectroscopic techniques, and deduce from the data—the squiggles that the machine made on a piece of chart paper—what the structure is. This is immediately enjoyable, as within a week you will learn to decipher simple structures—and it can become a lifelong quest, figuring out more and more complicated structures.

THE QUEST, LEVEL ONE: FINDING THE PIECES

This I know, that whereas I was blind, now I see.

The pieces that make up an organic molecule are the **organic functional groups** and the **hydrocarbon framework.** You will be able to find both the organic functional groups and the pieces of the hydrocarbon framework from the ^{13}C NMR (nuclear magnetic resonance), the theory and practice of which are explained in detail in your lecture text.

As it comes from the spectrometer, a ^{13}C NMR spectrum might look like Figure 12.1.

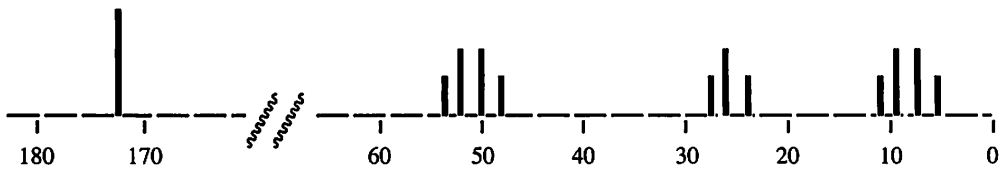

Figure 12.1 ^{13}C NMR spectrum of methyl propanoate.

Altogether, there are twelve lines in this spectrum. These can be divided into four sets: a single line at 173, four lines centered at 51, three lines centered at 27, and four lines centered at 9. The structure that gave rise to this spectrum is shown in Figure 12.2.

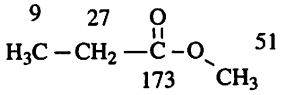

Figure 12.2 ^{13}C NMR Chemical shifts of methyl propanoate.

There are four different carbons in this structure, labelled respectively 9, 27, 173 and 51. It can be seen that 173 gave a single line (a singlet, s) in the ^{13}C NMR spectrum, 51 gave four lines (quartet, q), 27 gave three lines (triplet, t), and 9 also gave four lines (q). If there had been a carbon atom with one H on it, it would have given two lines (doublet, d).

This spectrum introduces two new terms, **chemical shift** and **multiplicity**. Chemical shift is the distance removed from zero at which the center of the pattern of lines appears (in this case 9, 27, 51, and 173). Multiplicity is the number of lines in each pattern. We will summarize ^{13}C NMR spectra as shown in Figure 12.3.

9, q
27, t
51, q
173, s

Figure 12.3 ^{13}C spectrum the way it will be reported.

So . . . how do we use this information to find the **organic functional groups** in the molecule? Actually, there are two kinds of organic functional groups, those that have sp^2- or sp-hybridized carbons and those that have only sp^3-hybridized carbons. We will call the former **unsaturated functional groups** and the latter **saturated functional groups**. Representative samples of each of these kinds of organic functional groups are depicted in Figure 12.4.

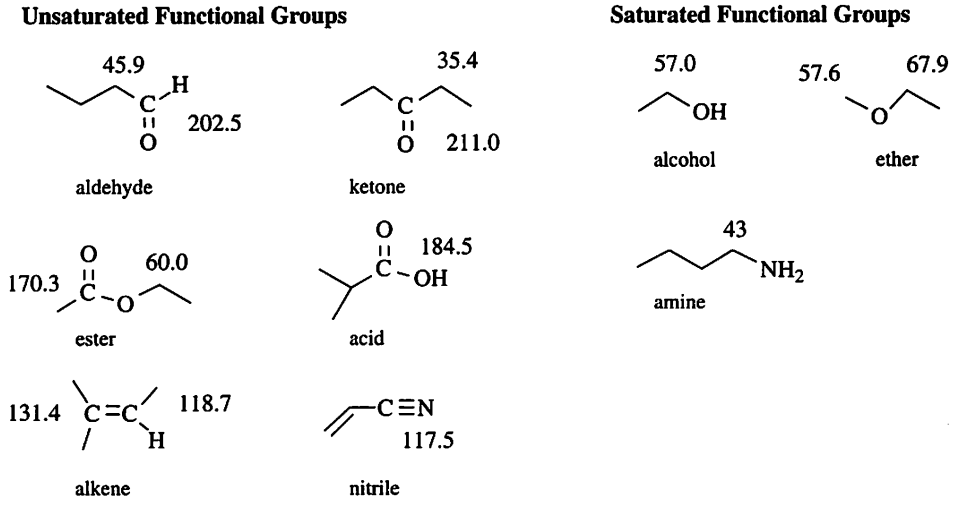

Figure 12.4 Unsaturated and saturated organic functional groups.

It is easy to tell if a molecule has any **unsaturated functional groups** by considering the **molecular formula**. In this example, the molecular formula is $C_4H_8O_2$. A saturated hydrocarbon will have the formula C_nH_{2n+2}. If the ends of the hydrocarbon meet to form a ring, or if two H's are removed to make an alkene, the formula becomes C_nH_{2n}. This count is not affected by oxygen. In our example, one pair of H's is missing, so there is one ring or double bond in the molecule—we can be sure that we have one unsaturated functional group. The IHD (Index of Hydrogen Deficiency) is the number of double bonds plus rings in the molecule. For $C_{13}H_{16}O_2$ for instance, the IHD = 6. There are other considerations. While oxygen does not affect the IHD, nitrogen does. Because N is trivalent, each nitrogen brings with it an extra hydrogen. For instance, the IHD of $C_9H_{14}N_2O_2$ is four. The H_{14} includes two extra H's, one for each of the N's. Halogens (F, Cl, Br, I) in a formula count as H's.

A double bond can be either a C=C bond or a C=O bond. There is O in the formula of our example, so there could be a C=O bond. From the examples above (there are more examples in Tables 12.8 and 12.9), we know that the C=O carbon of a ketone or aldehyde will come around 210, while the C=O carbon of an ester or acid will come around 170. Since we observe a singlet at 173, and we have two O's in the formula, we know that we have either an ester or an acid (Fig. 12.5)—but, which is it?

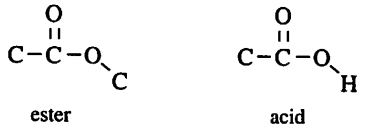

Figure 12.5 Is it an ester or an acid?

A key difference between an ester and an acid is that with an ester, all of the H's are attached to C. With an acid, one of the H's is attached to an O. We can count in the ^{13}C NMR spectrum how many H's are attached to each C by the multiplicity: s = 0 H, d = 1 H, t = 2 H, q = 3 H. In this example, when we add up all the H's attached to C the total comes to 8. That is the same number of H's as in the formula, so there are no H's attached to O. Therefore, the **unsaturated functional group** in this example must be an ester.

Next, we **explore around** the unsaturated functional group. An ester has two carbons attached to it, one connected to the sp^2-hybridized C and one connected to the sp^3-hybridized O. We would like to know how many H's are attached to each of these two C's. From the pictures in Table 12.9, we find that the C that is attached to the sp^3-hybridized O comes around 50 or 60. That must be the signal in our data at 51. That signal is a quartet (q), so there must be three H's attached to the C that is attached to the sp^3-hybridized O. From the same pictures in Table 12.9, we find that the C connected to the sp^2-hybridized C comes in the range 20–35. We can conclude that this must be the signal from our data at 27. That signal is a triplet (t), so there must be two H's attached to the C that is connected to the sp^2-hybridized C of the carbonyl. Putting all of this together gives us the **partial structure** shown in Figure 12.6.

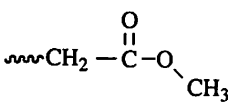

Figure 12.6 The partial structure of the ester.

SATURATED FUNCTIONAL GROUPS: After you are finished with all of the unsaturated functional groups, are there heteroatoms (O, N, S) in the formula that you have not yet dealt with? If so, now would be the time to find the saturated functional groups. In this example, we had 2 O's in the formula, and we have already accounted for both of them, so in this case there are no saturated functional groups.

HYDROCARBON FRAMEWORK: Which signals in the carbon spectrum have you not yet accounted for? In this case, all that is left is "9, q"—so there is one more -CH_3 to attach to the structure.

PUTTING IT ALL TOGETHER: In this case, there is only one way to connect the pieces, so the structure must be as shown in Figure 12.7.

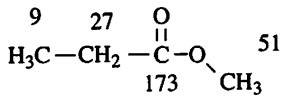

Figure 12.7 The full structure of the ester.

Note that there is a pattern to ^{13}C chemical shifts—the fewer the H atoms on a carbon, the larger the chemical shift. Consider ethyl methyl ether. (Figure 12.8) The methyl carbon directly attached to the oxygen comes at 57.6, whereas the methylene carbon directly attached to oxygen comes at 67.9. If you study the examples in Table 12.7, you will see that this is a general pattern.

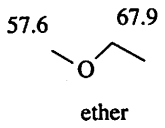

Figure 12.8 Chemical shifts of the carbons attached to the oxygen of an ether.

To solve a given structure, it is necessary to assemble a significant amount of data in an orderly way. To aid in this process, we will use a worksheet. A sample of the worksheet is reproduced on the following page. Especially in the early going, you may find it useful to make several copies of this worksheet and write directly on them in working the problems.

You should now be ready to work through Examples A–C. It would probably work best to do Example A on your own, then study the way it is worked out in the book before going on to Example B. After you have worked Example B on your own, study the way it is worked out in the book before going on to Example C.

Example A		**Example B**		**Example C**	
23, q (2)	$C_7H_{14}O$	11, q (2)	$C_6H_{14}O$	16, t (2)	$C_5H_6N_2$
28, d		23, t (2)		22, t	
29, q		44, d		119, s (2)	
33, t		65, t			
42, t					
206, s					

WORKSHEET

Step 1. Molecular formula and IHD. Any OH or N-H?

Step 2. Exploring around the unsaturated functional groups

C=O (160–220):

C=C (100–160):

R-CN (105–120, s):

Alkyne (65–90):

Number of rings:

IHD =

Step 3. Other heteroatoms—Exploring around the saturated functional groups

Step 4. Other pieces

a. Methyl groups:

b. ^{1}H NMR greater than 2.0 □:

c. Other carbons:

Step 5. Putting it all together

Solution for A

Step 1. (The steps here are the same as the steps on the worksheet.)

From the molecular formula, $C_7H_{14}O$, the IHD is one, so we have one ring or multiple bond. All 14 H's are attached to C.

Step 2.

We know from the signal at 206 that we have either an aldehyde or a ketone (see Table 12.8). Because it is a singlet, it must be a ketone. That means that there is a carbon on either side of the carbonyl. The question is, how many H's are on each of the two carbons? Again from Table 12.8, we can observe that a methyl attached to a ketone carbonyl comes at about 30 (this would be a quartet) and a methylene comes at about 40 (this would be a triplet). Methines (doublet) and carbons with no H's (quaternary carbons, singlets) would be further downfield (larger numbers) than that.

Looking at the data, we see that we do indeed have a quartet at 29 and a triplet at 42, so we can draw the following partial structure as shown in Figure 12.9.

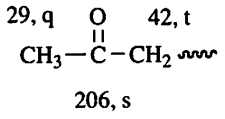

Figure 12.9 Partial structure of the unknown ketone.

We draw the wiggly line to remind ourselves that there is more to attach—we just don't know what it is yet.

Step 3.

There is only one heteroatom in the molecular formula, and we have already found it.

Step 4.

Since we are not yet using ^1H NMR, only 4c is relevant. From the ^{13}C NMR, there are four carbons we have not yet accounted for, two methyls, a methylene, and a methine. Note, however, that the two methyl groups have the same chemical shift. This makes it likely that there is a plane of symmetry in the molecule. This gives us the pictures in Figure 12.10:

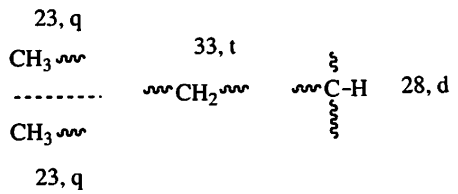

Figure 12.10 The pieces of the hydrocarbon skeleton of the unknown ketone.

Step 5.

In this step we put the pieces together, like assembling a jigsaw puzzle. Because the methyl groups must be symmetrical, and nothing else in the molecule is symmetrical (none of the other carbon signals are doubled), there is only one way to assemble the final structure. (See Fig. 12.11.)

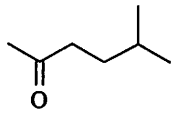

Figure 12.11 The final structure of the unknown ketone.

Solution for B

Step 1. From the molecular formula, $C_6H_{14}O$, the IHD is zero—there are no rings or double bonds in this molecule. From the hydrogen count, there are only 13 H's attached to carbon, so one must be attached to some other atom. The only other atom in this example is the O, so we must have an alcohol.

Step 2.

As the IHD is zero, there are no unsaturated functional groups, and there is no need to look for rings.

Step 3.

Following the examples in Table 12.6, the carbon directly attached to -OH comes around 60 or 70. Looking at the data, we have 65, t, which gives us the partial structure in Figure 12.12.

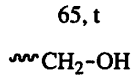

Figure 12.12 Partial structure of the unknown alcohol.

Step 4.

Both the methyl (11, q) and the methylene (23, t) carbon signals are doubled, so we must have symmetrical ethyl groups. We also have a methine. (See Fig. 12.13.)

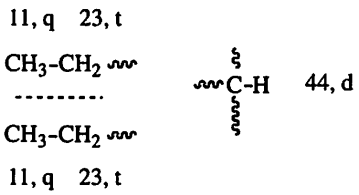

Figure 12.13 The pieces of the hydrocarbon skeleton of the unknown alcohol.

Step 5.

There is only one way to assemble the molecule. (See Fig. 12.14.)

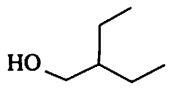

Figure 12.14 The final structure of the unknown alcohol.

Solution for C

Step 1.

From the molecular formula, $C_5H_6N_2$, the IHD is 4. Remember, each N brings an extra H with it, so to calculate the IHD, this is "C_5H_4". From the ^{13}C NMR, all 6 H's are attached to carbon.

Step 2.

The presence of N in the molecule, and the carbon singlet at 119, together suggest a nitrile. There are two of them, and they are symmetrical. This accounts for all of the IHD.(See Fig. 12.15.)

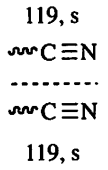

Figure 12.15 The unknown is a symmetrical nitrile.

Step 3.

All heteroatoms are already accounted for.

Step 4.

There are three methylenes. Two of them are symmetrical. (See Fig. 12.16.)

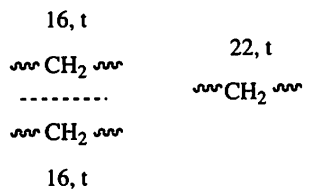

Figure 12.16 The pieces of the hydrocarbon skeleton of the unknown nitrile.

Step 5.

There is only one way to combine these fragments. (See Fig. 12.17.)

Figure 12.17 The final structure of the unknown nitrile.

PROBLEMS

Using this same approach, you should be able to figure out the structures of unknowns 1–20 using the molecular formula and the ^{13}C NMR.

1. $C_3H_8O_2$

   ^{13}C NMR

   57.5, q
   60.1, t
   73.1, t

2. $C_5H_{10}O$

   ^{13}C NMR

   29.6, q (2)
   70.9, s
   110.6, t
   146.8, d

3. $C_5H_{10}O_2$

   ^{13}C NMR

   19.3, q (2)
   34.4, d
   51.4, q
   176.9, s

4. $C_5H_{10}O$

   ^{13}C NMR

   212.5, s
   41.6, d
   27.4, q
   18.1, q (2)

5. $C_6H_{12}O$

   ^{13}C NMR

   80.0, s
   41.3, t
   28.2, q
   24.1, t

6. $C_5H_{11}N$

^{13}C NMR

56.3, t (2)
42.2, q
24.1, t (2)

7. C_4H_9NO

^{13}C NMR

170.4, s
34.4, t
23.1, q
14.7, q

8. $C_6H_{12}O$

^{13}C NMR

211.5, s
44.3, t
35.9, t
17.4, t
13.8, q
7.8, q

9. $C_9H_{16}O$

^{13}C NMR

204.7, d
50.7, d
26.7, t (2)
26.2, t (2)
25.6, t
25.3, t (2)

10. $C_5H_{12}O$

^{13}C NMR

73.4, t
32.6, s
26.0, q (3)

11. $C_5H_{10}O$

^{13}C NMR

135.5, d
125.5, d
68.8, d
23.3, q
17.5, q

12. $C_6H_{14}O$

^{13}C NMR

70.5, t
66.1, t
32.0, t
19.5, t
15.3, q
14.0, q

13. $C_5H_{10}O$

^{13}C NMR

205.2, d
47.7, d
23.6, t
12.9, q
11.4, q

14. C_3H_8O

^{13}C NMR

68.3, d
67.8, t
18.7, q

15. $C_5H_{10}O$

^{13}C NMR

67.2, t
37.4, d
24.5, t (2)
18.4, t

16. C_4H_8O

^{13}C NMR

145.7, s
110.5, t
67.4, t
19.9, q

17. $C_5H_{12}O$

^{13}C NMR

72.7, t
58.5, q
31.8, t
19.4, t
13.9, q

18. $C_5H_{12}O$

^{13}C NMR

67.0, d
41.6, t
23.3, q
19.1, t
14.0, q

19. C_4H_9NO

^{13}C NMR

170.5, s
38.0, q
35.1, q
21.5, q

20. $C_{11}H_{20}O_2$

^{13}C NMR

173.8, s
64.5, t
34.4, t
26.1, t
24.8, t
24.5, t
24.0, t
23.9, t
23.5, t
23.3, t
22.1, t

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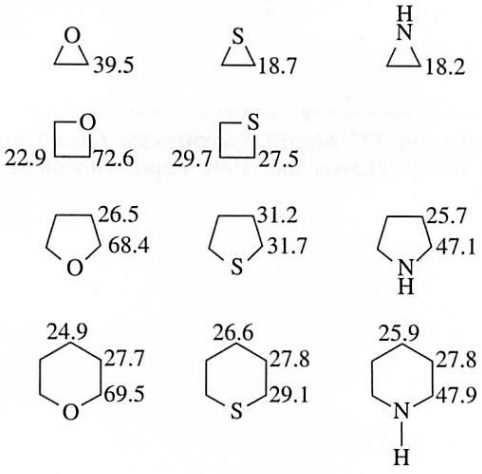
Table 12.1 Chemical Shifts of Cycloalkanes (ppm from TMS)

C_3H_6	−2.9	C_7H_{14}	28.4
C_4H_8	22.4	C_8H_{16}	26.9
C_5H_{10}	25.6	C_9H_{18}	26.1
C_6H_{12}	26.9	$C_{10}H_{20}$	25.3

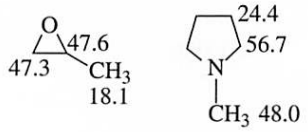
From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.4, p. 237.

Table 12.2 Chemical Shifts for Saturated Heterocyclics (ppm from TMS, neat)

Unsubstituted

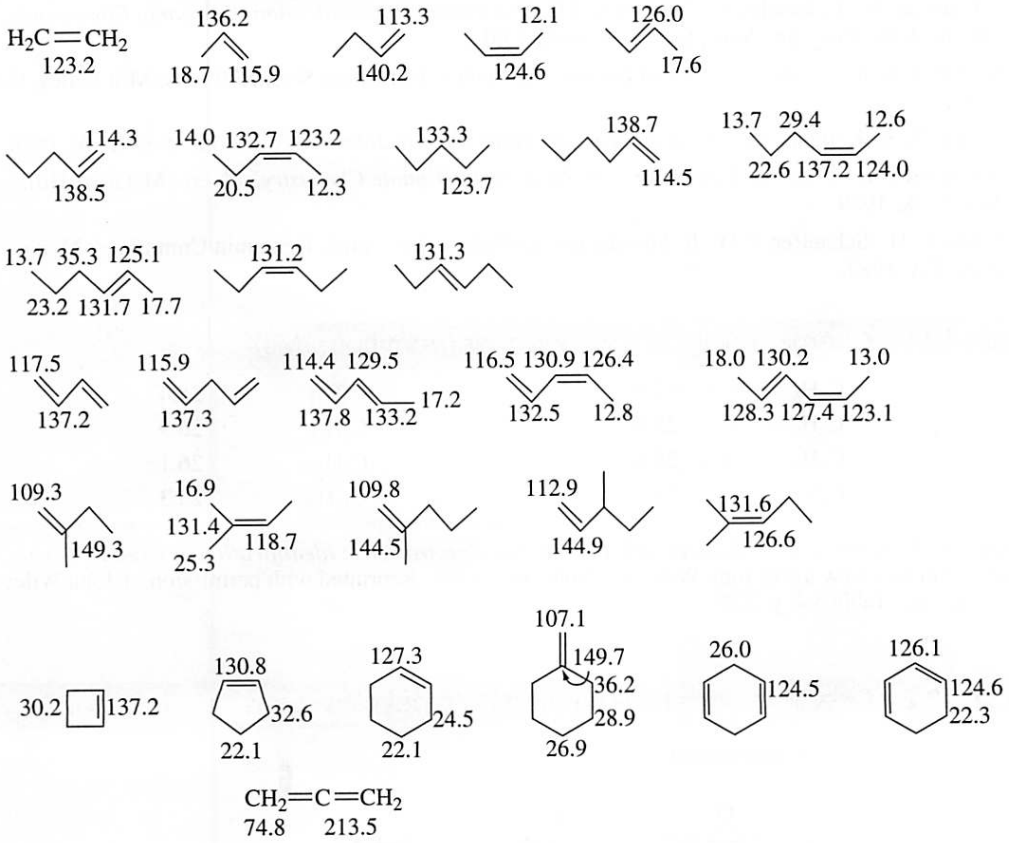


Substituted



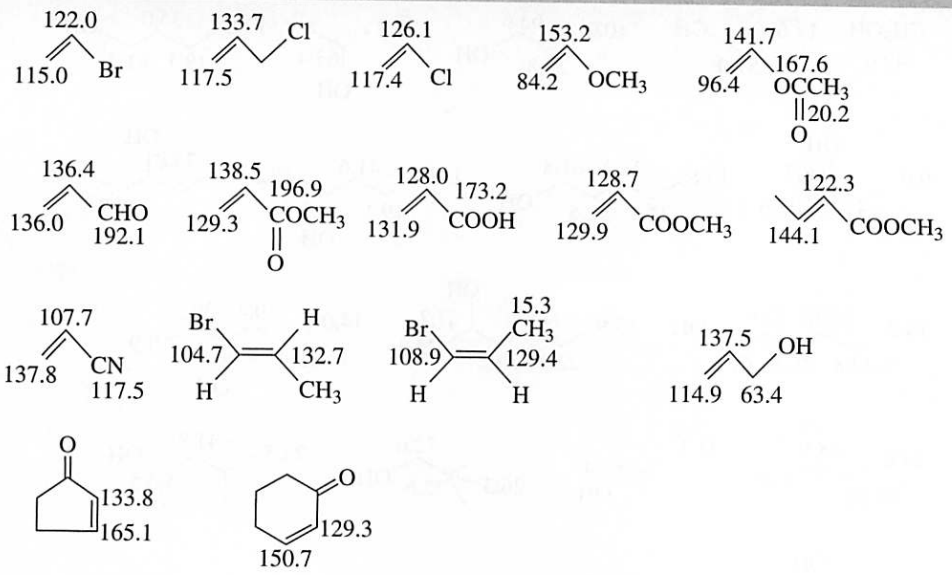
From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.5, p. 237.

Table 12.3 Alkene and Cycloalkene Chemical Shifts (ppm from TMS)



From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.6, p. 238.

Table 12.4 Chemical Shifts of Substituted Alkenes (ppm from TMS)



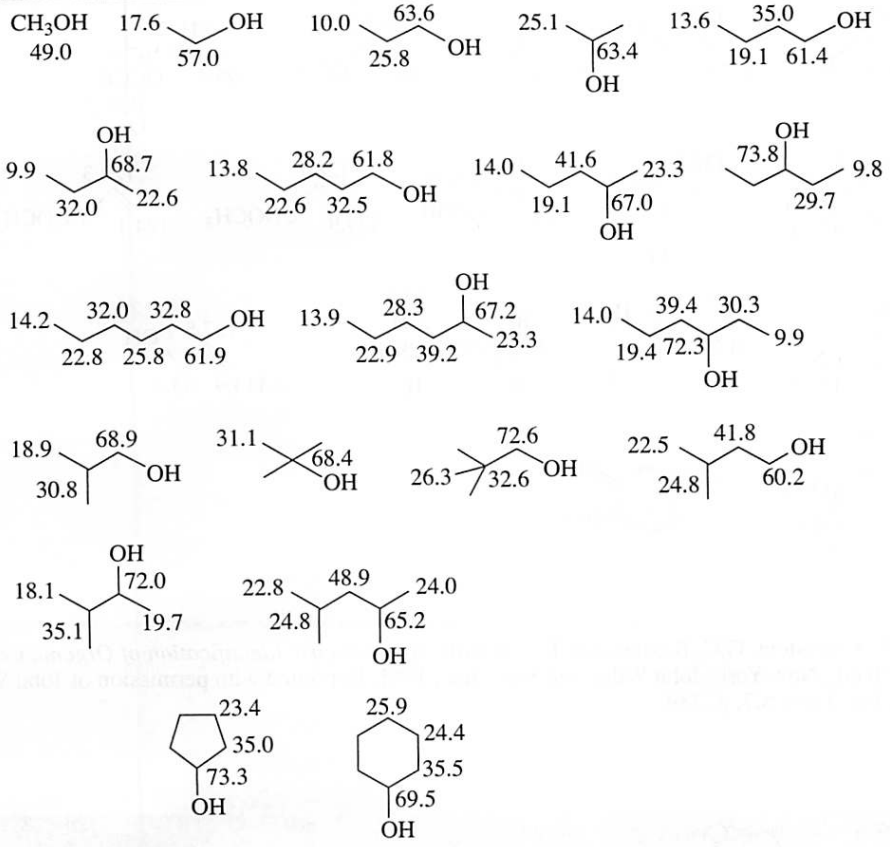
From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.7, p. 239.

Table 12.5 Alkyne Chemical Shifts (ppm)

COMPOUND	C-1	C-2	C-3	C-4	C-5	C-6
1-Butyne	67.0	84.7				
2-Butyne		73.6				
1-Hexyne	67.4	82.8	17.4	29.9	21.2	12.9
2-Hexyne	1.7	73.7	76.9	19.6	21.6	12.1
3-Hexyne	14.4	12.0	79.9			

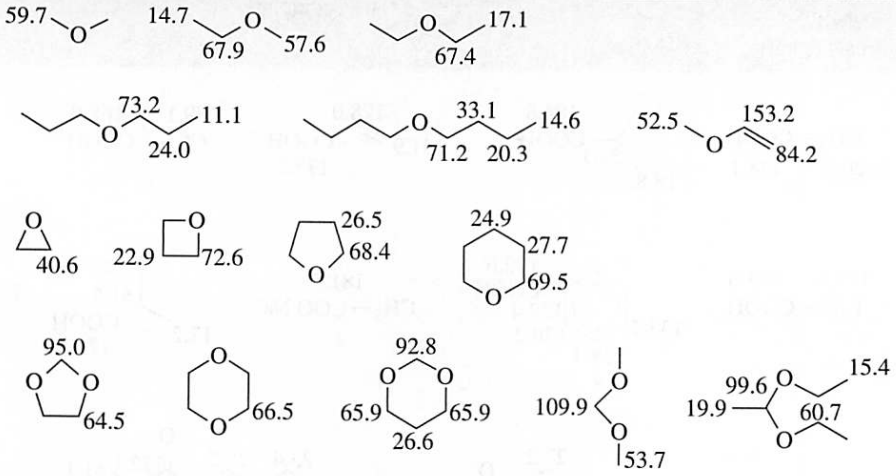
From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.8, p. 239.

Table 12.6 Chemical Shifts of Alcohols (neat, ppm from TMS)



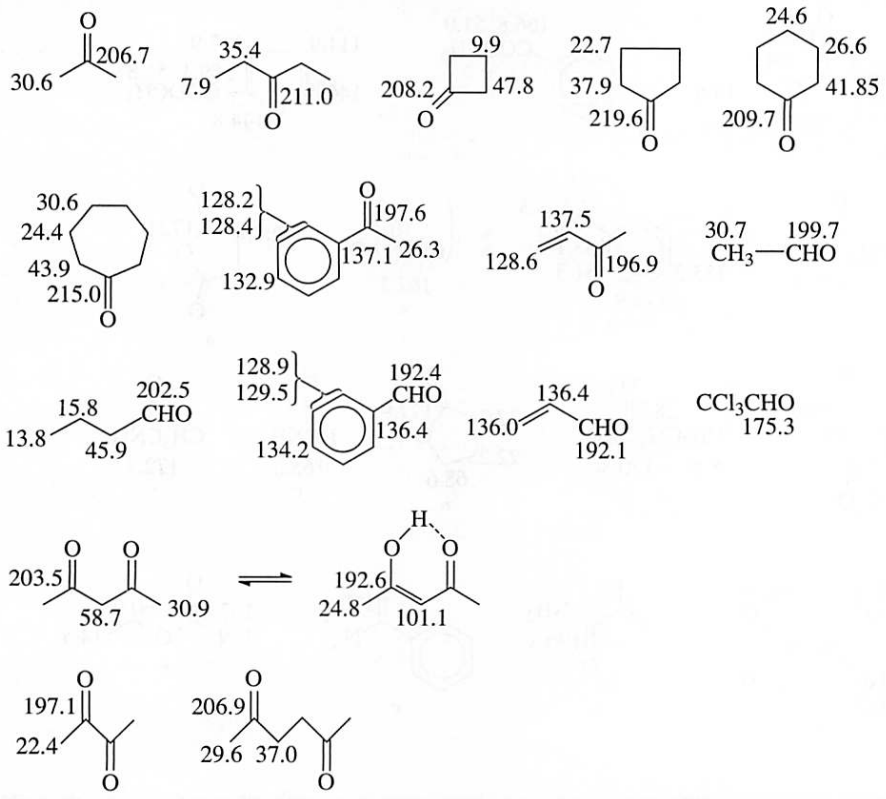
From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.11, p. 242.

Table 12.7 Chemical Shifts of Ethers, Acetals, and Epoxides (ppm from TMS)



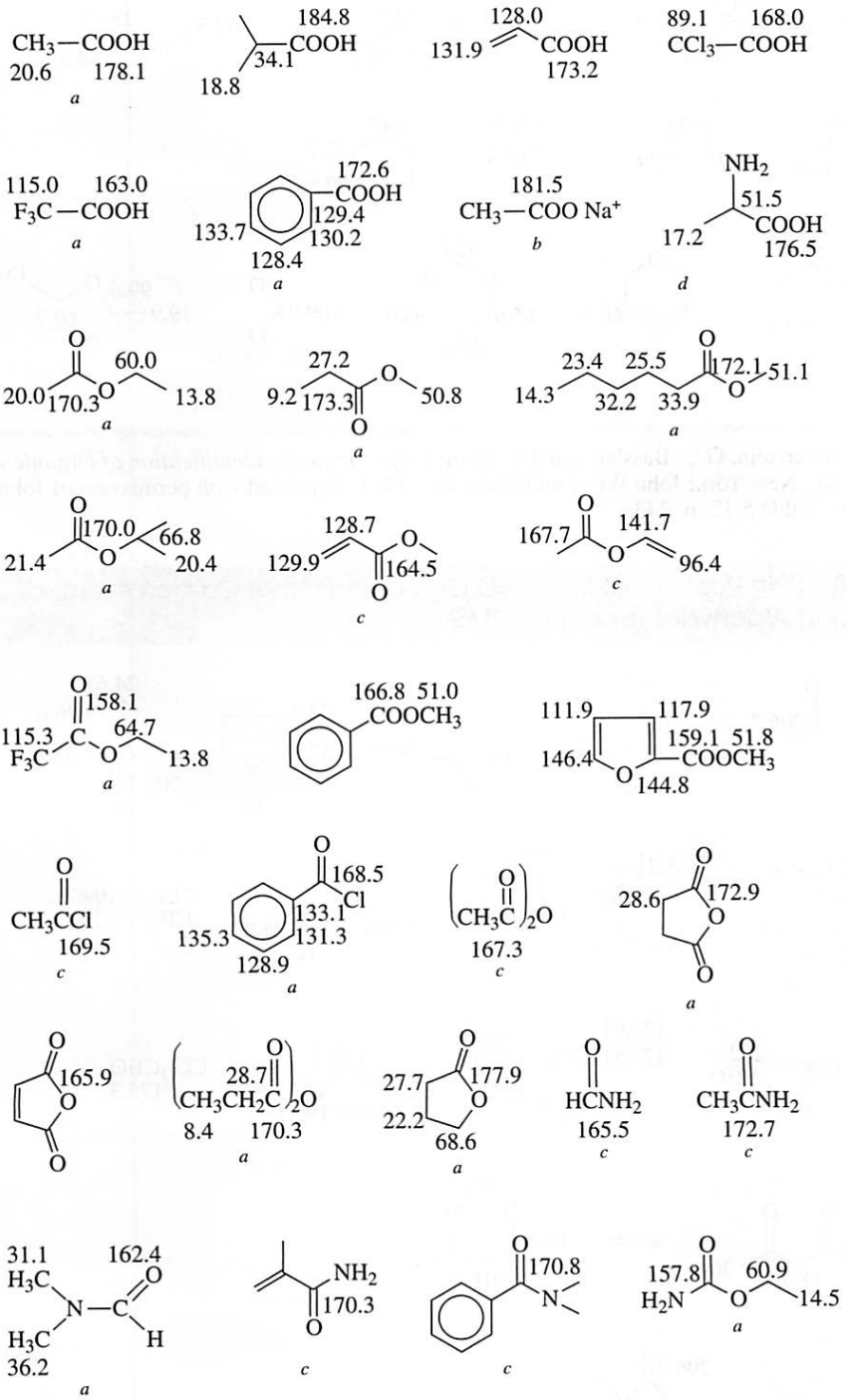
From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.12, p. 243.

Table 12.8 Shift Positions of the C=O Group and Other Carbon Atoms of Ketones and Aldehydes (ppm from TMS)



From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.15, p. 245.

Table 12.9 Shift Positions for the C=O Group and Other Carbon Atoms of Carboxylic Acids, Esters, Lactones, Chlorides, Anhydrides, Amides, Carbamates, and Nitriles (ppm from TMS)



From R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.16, p. 246.

13

^{1}H Nuclear Magnetic Resonance

THE QUEST, LEVEL TWO: CONNECTING THE PIECES TOGETHER

Hip bone connected to the thigh bone ...

So far, you have learned how to find the functional groups in an unknown molecule. You have also learned to find the pieces of the molecule, and in some cases you have been able to find the carbons directly attached to the functional groups. For the compounds you have done so far, once you found the pieces, it was easy to put them together to get the final structure. With more advanced compounds, you will also need information from the ^{1}H NMR spectrum to settle on the structure. With ^{1}H NMR, you will be able to see how one piece of the unknown structure is connected to the other pieces. The theory of ^{1}H NMR (proton magnetic resonance) is discussed in detail in your organic text.

A typical ^{1}H NMR spectrum can be seen in Figure 13.1.

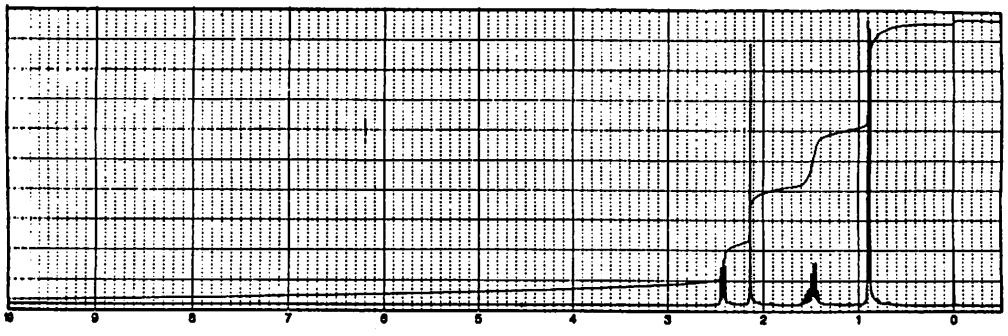


Figure 13.1 A typical ^{1}H nuclear magnetic resonance spectrum.

In this text, a ^{1}H NMR spectrum will be summarized as shown in Figure 13.2.

^{1}H NMR
0.90, d, 6H, J = 6.5 Hz
1.2–1.6, m, 3H
2.13, s, 3H
2.40, t, 2H, J = 6.8 Hz

Figure 13.2 Summary of a typical ^{1}H nuclear magnetic resonance spectrum.

ANALYZING THE ^{1}H SPECTRUM

Taking the first entry of this spectrum as an example, with each entry you will see the chemical shift (0.90), the multiplicity (d), the number of protons at that chemical shift (6), and the coupling constants (J values, in this case = 6.5 Hz).

THE CHEMICAL SHIFT

The chemical shift δ (parts per million downfield from the internal standard, tetramethylsilane) of the protons attached to a carbon is a function of the environment of those protons. These effects are summarized in Table 13.1 on page 138. In this case, 0.90 is typical for a methyl group that is not shifted by some other functional group.

THE MULTIPLICITY

The multiplicity (d, in this case) is the number of lines in the signal. As with Chapter 12, s = singlet, one line; d = doublet, two lines; t = triplet, three lines; q = quartet, four lines. In addition, you will see examples such as dd = doublet of doublets, and m = multiplet. In the ^{1}H NMR spectrum, multiple lines tell you the number of **H's** on neighboring carbons. In this case, there would be one H on a neighboring carbon, which would suggest the partial structure shown in Figure 13.3. **Multiplicity** is explained in more detail under "Coupling Constant (J)" below.

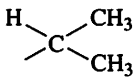


Figure 13.3 A fragment of the unknown structure.

THE NUMBER OF PROTONS—INTEGRATION

In the ^{1}H spectrum, it is typical to have two, three, or even more protons with the same chemical shift. The vertical distance on the integral of the signal at a given chemical shift is proportional to the peak area, and thus also to the number of protons having that chemical shift. If the total number of hydrogens is known, one can divide the total vertical integration by that number to get the vertical distance per hydrogen. In the summaries, you will be given the actual number of protons in the signal. In this first entry, there are 6 H's, so you might guess (correctly!) that this represents two methyl groups (see Fig. 13.3).

COUPLING CONSTANT (J)

The effective magnetic field at a given nucleus is the sum of the imposed external magnetic field, H_0, added to all the smaller magnetic fields from surrounding nuclei. Consider the case (Fig. 13.4) of H_a, attached to carbon A, with one proton, H_b, on the adjacent carbon. The actual magnetic field experienced by H_a will be the sum of H_0 plus the field due to spin of H_b. On average, half the H_a's will see an H_b having a spin aligned with the external field, and half the H_a's will see an H_b with the spin opposed to the magnetic field. Thus, there will be two populations of H_a, and so two resonances. We say that the signal due to H_a is **split,** because of coupling to H_b. The magnitude of the coupling, the **coupling constant (J),** is measured in **Hertz** (= one cycle per second). For values of J in different situations, see Table 13.2 on page 140–141.

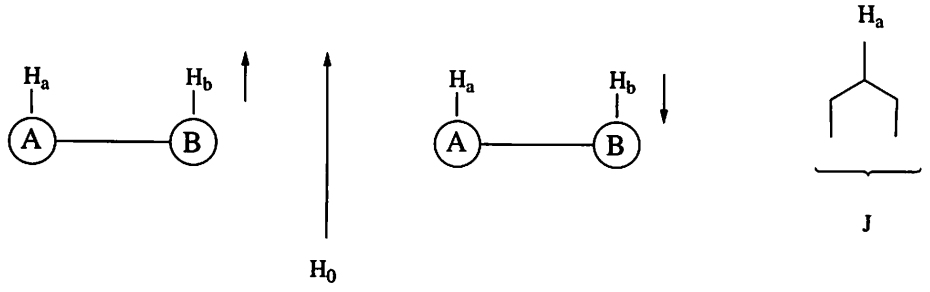


Figure 13.4 Illustration of ^{1}H NMR coupling.

Protons with the same chemical shift will not show coupling. Protons on the same carbon ("geminal") **will** show coupling if they have different chemical shifts, as, for instance, if the carbon is part of a ring (Fig. 13.5).

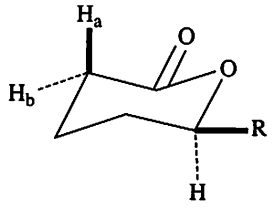


Figure 13.5 H_a and H_b are not equivalent. They will have different chemical shifts, and will couple to each other.

If protons are coupled to each other, they will show the same numerical value for J (J_{AB} = J_{BA}). This is very useful for following connectivity in an unknown structure.

MULTIPLICITY—THE NUMBER OF NEIGHBORS

If a proton is coupled to more than one other proton, the J values may or may not be equal. If they are equal, then the multiplicity of the signal for that first proton will be the number of hydrogens to which it is coupled with that J value, plus one (Fig. 13.6).

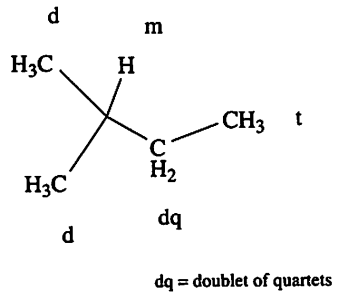


Figure 13.6 The multiplicity of a ^{1}H NMR signal is the number of neighbors, plus one.

If there are no protons attached to the neighboring carbons, the ^{1}H signal will appear as a singlet.

OTHER INFORMATION IN THE ^{1}H SPECTRUM

In general, you should look for signals that stand out from the others (Step 4). Methyl groups often stand out, as do protons shifted downfield by adjacent functional groups. It is often possible to make a reasonable guess as to what that functional group is, first based on the ^{13}C data, and then using the ^{1}H chemical shift data in Table 13.1. It should be remembered that a given proton could be adjacent to two or even three functional groups. As you will see, the proton shifts due to the nearness of two or more functional groups are very nearly additive.

SUMMARY

The proton spectrum can be used in two ways: (a) confirming deductions from the ^{13}C spectrum about the presence and substitution pattern of organic functional groups in the molecule, and (b) establishing carbon–carbon connectivity.

EXAMPLE A

^{13}C NMR	$C_7H_{14}O$
22.3, q (2)	
27.8, d	
29.7, q	
32.8, t	
41.8, t	
206.8, s	

^{1}H NMR
0.90, d, 6H, J = 6.5 Hz
1.2–1.6, m, 3H
2.13, s, 3H
2.40, t, 2H, J = 6.8 Hz

The spectrum shown in Figure 13.1 is, in fact, for the same substance as Example A in Chapter 12. From the ^{13}C spectrum, we had deduced that a ketone was present. Using approximate carbon shifts, we had concluded that the carbons flanking the ketone were a methyl and a methylene. From the data in Table 13.1, we can read that a methyl group directly adjacent to a ketone should have a chemical shift of 2.1 δ. The signal should integrate for three protons. Because there are no protons attached to adjacent carbons, it should appear as a singlet. In fact, there is just such a signal in the ^{1}H NMR spectrum listed above: 2.13, s, 3H

The other carbon flanking the carbonyl carbon was a methylene. Referring to the data in Table 13.1, that methylene should have a chemical shift of about 2.3 δ. In fact, we do have a signal at 2.40 δ. It integrates for two hydrogens, as we would expect. The critical information is that this signal appears as a **triplet.** That means that there are **two** protons on the adjacent carbon. In other words, the adjacent carbon is a methylene. That gives us the partial structures illustrated in Figure 13.7 (We know that we have two methyls attached to a C-H from 0.90, d, 6H, as discussed above).

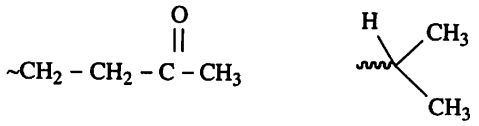


Figure 13.7 Partial structures of Example A.

It is helpful to use a wiggly line on partial structures, to remind yourself of where an additional fragment will eventually be attached. In this case, there is only one way to put the molecule together (Fig. 13.8). Note that undifferentiated H's, often with more than one coupling, appear as a **multiplet, "M".**

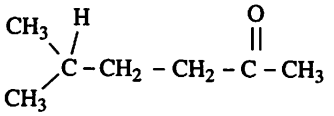


Figure 13.8 Complete Structure of Example A.

EXAMPLE B

^{13}C NMR	$C_6H_{14}O$
11.1, q (2)	
22.9, t (2)	
43.6, d	
64.8, t	

^{1}H NMR
0.90, t, 6H, J = 7.0 Hz
1.2–1.6, m, 5H
1.95, 1H, bs (exchanges)
3.52, d, 2H, J = 6.5 Hz

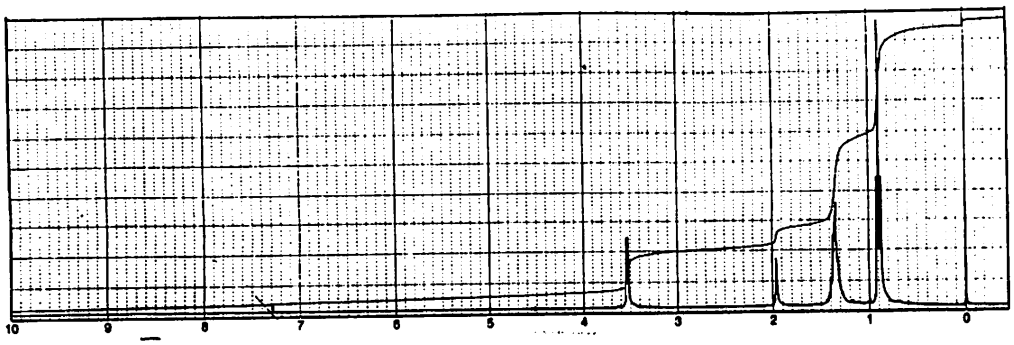


Figure 13.9 ^{1}H NMR spectrum for Example B.

This is the same substance as Example B in Chapter 12. By counting that there were 13 protons bonded to carbon in the ^{13}C data, we deduced that the other proton must be bonded to oxygen, and that we therefore have an alcohol functional group. That we have one proton attached to a heteroatom is also apparent from the proton spectrum. When a $CDCl_3$ solution of a sample having such a proton is shaken with D_2O, the signal for the O-H proton disappears, having exchanged with the D_2O. Further, because such protons are rapidly exchanging with each other, broadening the signal somewhat, one does not usually observe coupling of O-H or N-H to protons attached to adjacent carbon atoms. Thus, protons attached to heteroatoms appear, as in this problem, "bs, 1H, exchanges," where "bs" stands for "broadened singlet" and "exchanges" means "exchanges with D_2O."

Using approximate carbon shifts, we had concluded that the carbon to which the alcohol was attached was a $-CH_2-$. From the data in Table 13.1, this methylene should have a chemical shift of about 3.4 δ. It should integrate for two protons. In fact, we do have a two-proton signal at 3.52 δ. Now we look at the multiplicity of that signal. It is a doublet. That means that the group of two protons at 3.4 δ has exactly one proton on a neighboring carbon. We can thus discern the partial structure shown in Figure 13.10.

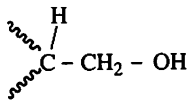


Figure 13.10 Partial structure for Example B.

Methyl groups also stand out in the proton spectrum, because they are intense signals (three hydrogens each) that can have at most only two protons on neighboring carbons. We know from the ^{13}C spectrum that there are two methyl groups in this molecule, with the same apparent chemical shift. Further, we know that these methyl groups are not near any heteroatoms, so they should have a normal hydrocarbon shift. Consulting the data in Table 13.1, we would expect the signal for these methyl groups at about 0.9 δ. In fact, we do observe a six-proton signal at 0.90 δ. This signal has a multiplicity of t, a triplet. We can thus discern that there must be a methylene adjacent to each methyl. From the ^{13}C spectrum, the methylenes must also be symmetrical. This analysis gives us the partial structures illustrated in Figure 13.11.

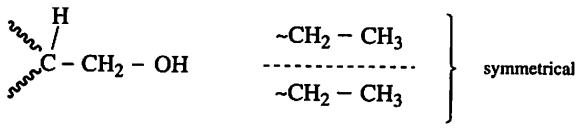


Figure 13.11 All the partial structures for Example B.

There is only one way to assemble these partial structures, so the final structure is that illustrated in Figure 13.12.

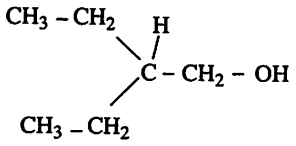


Figure 13.12 Complete structure for Example B.

THE QUEST, LEVEL THREE: RINGS

Around and around and around we go . . .

You have assigned all of the unsaturated functional groups, but you still have IHD for which you have not accounted—you must have a ring! So . . . how do we approach rings?

Branch Points and End Groups: Imagine three cartoon rings. These cartoons are drawn as eight-membered rings, but are meant to be generic, "any rings". The rings (Fig. 13.13) could be unbranched (A), singly branched (B), or multiply branched (C). How are you going to be able to tell?

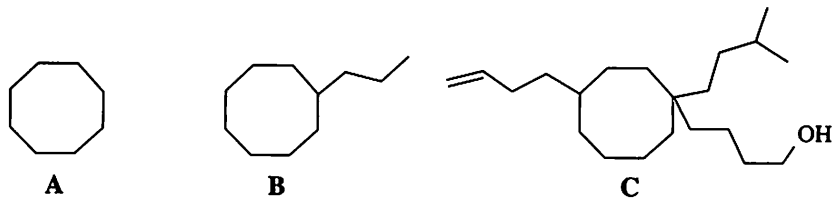


Figure 13.13 Representative rings.

We will use branch points and end groups to narrow down the possibilities for our unknown ring. An end group is a group that ends a chain, such as a methyl group or a primary alcohol. A branch point is a methine, such as that in B. Example C also includes a methine, and it also includes an sp^3-hybridized quaternary carbon, a double branch point. Ring A has no methine or

quaternary carbons, and it has no end groups, so there could not be any branches off the ring. Ring B has one branch point and one end group, so it must have one branch off the ring. Ring C has multiple branch points and end groups, including a branch point on a chain away from the ring. By considering how many branch points and end groups a molecule has, it is possible to more quickly come to a beginning idea of how to assemble the structure.

Problems 13.1-13.10, beginning on page 133, will give further practice in deducing structures from spectra.

EXPERIMENTS

SAFETY NOTE

All samples should be prepared in a well-ventilated area to avoid unnecessary breathing of solvent vapors. Although the capped NMR tubes are reasonably resilient, care must be taken not to crush the thin walls inadvertently.

For all of the experiments listed below, the instructor should demonstrate the proper use of the spectrometer and explain the precautions to be taken in determining a spectrum. A Varian model 360EM or any more powerful spectrometer would be appropriate.

The amount of sample used will depend on the spectrometer. With a modern Fourier transform instrument, 30 mg of sample is ample for both ^{1}H and ^{13}C spectra. In general, spectra are acquired using a 5-mm NMR tube. Make sure that the tube and its plastic cap are clean and dry. Take up the sample in 0.3 mL of deuterated NMR solvent (usually $CDCl_3$ containing 0.1% tetramethylsilane as an internal standard) and add the solution to the tube. If the solution appears turbid, filter it through a small plug of glass wool and then into the NMR tube. Cap the NMR tube securely.

A. PROTON SPECTRUM OF ETHYLBENZENE

In a 5-mm NMR tube, prepare a solution of ethylbenzene in deuterated chloroform containing TMS. Place the cap on the tube, and mix the contents well by inverting the tube several times. Wipe the sample tube clean with a disposable tissue. Place the sample tube in the spectrometer and allow it to come to the temperature of the instrument. Determine and record the spectrum and integration curve over the range of 10 ppm. Record the instrument parameters on the spectrum and identify all of the peaks. Secure the spectra in your laboratory notebook using staples or tape.

B. PROTON SPECTRA OF ALCOHOLS

The purpose of this experiment is to illustrate the effect of proton exchange on the splitting patterns of nearest neighbor hydrogens by the hydroxyl hydrogens of alcohols. A suitable deuterated nonhydroxylic solvent such as dimethylsulfoxide (DMSO-d_6), dimethylformamide (DMF-d_7), or chloroform ($CDCl_3$) is necessary. When sufficiently rapid hydrogen exchange involving the hydroxyl hydrogen occurs, the nearest-neighbor splitting patterns due to this hydrogen disappear and the hydroxyl hydrogen itself appears as a broad singlet. Other compounds with exchangeable hydrogens will also demonstrate this effect.

Determine the spectra of the following samples:

1. Neat absolute ethanol and 3 drops of TMS.
2. A 25% solution of absolute ethanol in DMSO-d_6.
3. Sample 2 plus 10 drops of water.

Identify each peak and comment on the utility of this effect in the interpretation of NMR spectra. Repeat the experiment using 2-propanol or 2-methyl-2-propanol.

C. CARBON-13 SPECTRUM OF ETHYLBENZENE

This experiment is designed to illustrate the effect of proton decoupling on a carbon-13 spectrum. Decoupled spectra are less complex than "nondecoupled" spectra because the splitting of the carbon signal by hydrogen is absent.

1. Determine the ^{13}C spectrum of the ethylbenzene sample used in Experiment A using the following conditions:
   a. Normal, decoupled power applied.
   b. Decoupling power turned off.

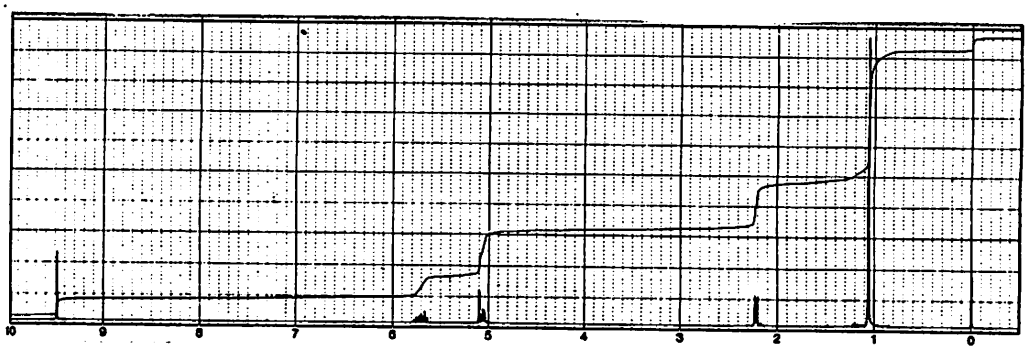
Overlay the two spectra, line up the TMS peaks, and record the identity and splitting patterns for each peak of the sample.

D. ACQUIRE THE SPECTRA OF AN UNKNOWN COMPOUND SUPPLIED BY YOUR INSTRUCTOR, AND DETERMINE THE STRUCTURE

PROBLEM 13.1

$C_7H_{12}O$

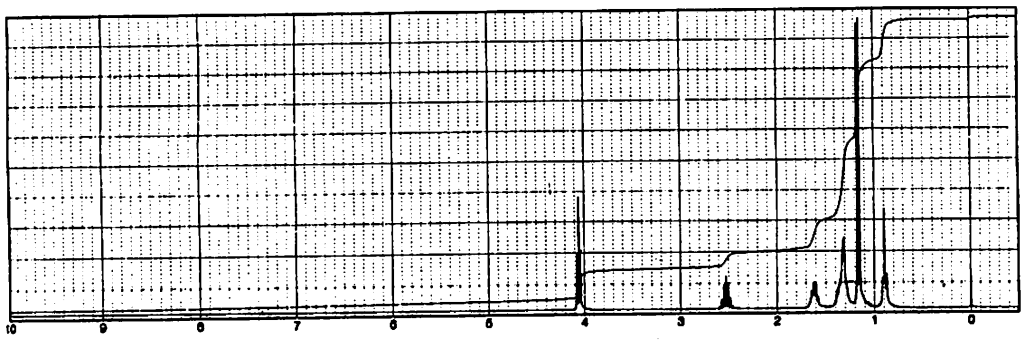
^{13}C NMR	^{1}H NMR
206.7, d	1.08, s, 6H
133.1, d	2.21, d, J = 7.2 Hz, 2H
118.4, t	5.08, d, J = 11.8 Hz, 1H
45.7, s	5.11, d, J = 15.5 Hz, 1H
41.5, t	5.75, ddt, J = 11.8, 15.5, 7.2 Hz, 1H
21.2, q (2)	9.49, s, 1H



PROBLEM 13.2

$C_{10}H_{20}O_2$

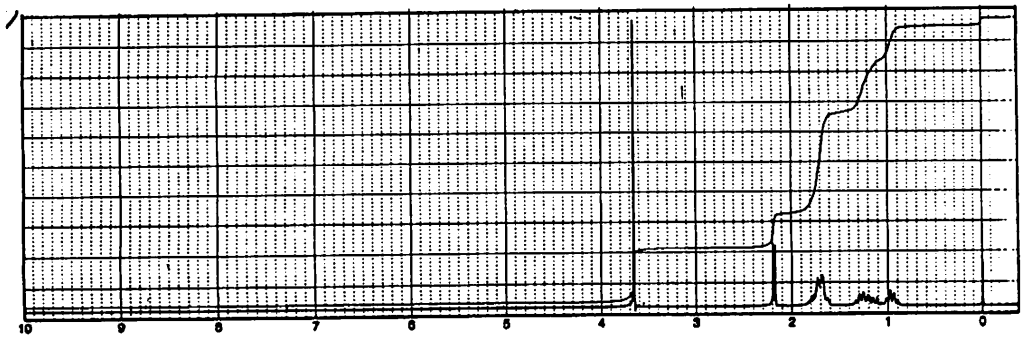
^{13}C NMR	^{1}H NMR
177.0, s	0.89, t, J = 7.3 Hz, 3H
64.4, t	1.26, d, J = 6.5 Hz, 6H
34.1, d	1.4, m, 6H
31.6, t	1.64, m, 2H
28.8, t	2.52, m, 1H
25.7, t	4.05, t, J = 7.1 Hz, 2H
22.6, t	
19.1, q (2)	
14.0, q	



PROBLEM 13.3

$C_9H_{16}O_2$

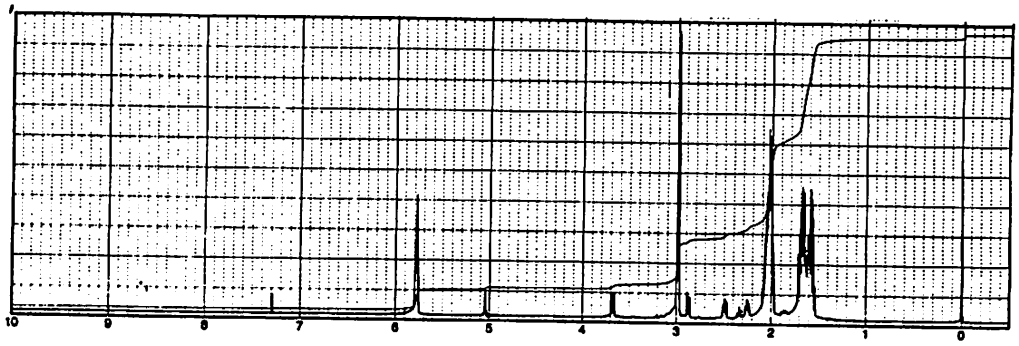
^{13}C NMR	^{1}H NMR
173.6, s	3.67, s, 3H
51.3, q	2.19, d, J = 6.4 Hz, 2H
42.0, t	1.70, m, 6H
34.9, d	0.9–1.3, m, 5H
33.1, t (2)	
26.2, t (2)	
26.1, t	



PROBLEM 13.4

$C_8H_{11}N$

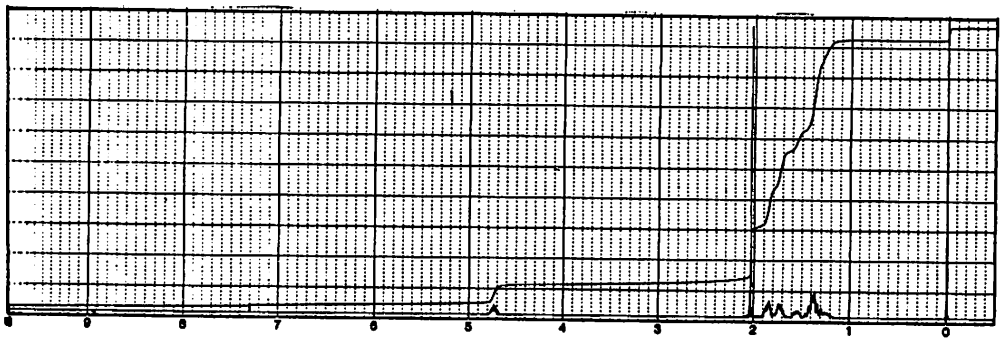
^{13}C NMR	^{1}H NMR
127.1, s	5.79, t, J = 6.2 Hz, 1H
126.3, d	2.97, s, 2H
117.7, s	2.02, m, 4H
28.0, t	1.70, m, 4H
25.8, t	
25.1, t	
22.5, t	
21.8, t	



PROBLEM 13.5

$C_8H_{14}O_2$

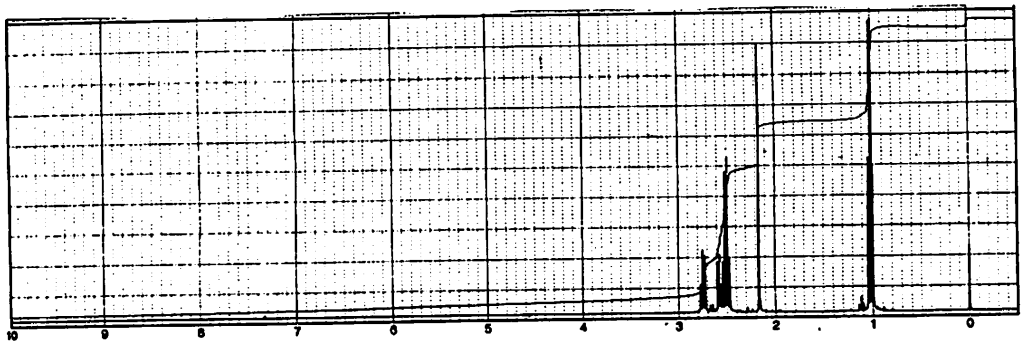
^{13}C NMR	^{1}H NMR
170.5, s	4.75, m, 1H
72.6, d	2.03, s, 3H
31.7, t (2)	1.2–1.7, m, 10H
25.4, t	
23.8, t (2)	
21.4, q	



PROBLEM 13.6

$C_8H_{17}NO$

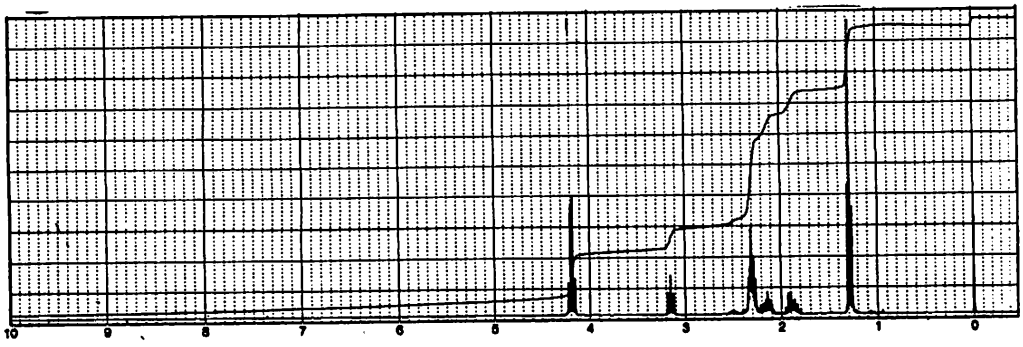
^{13}C NMR	^{1}H NMR
208.2, s	1.02, t, J = 7.1, 6H
47.5, t	2.16, s, 3H
46.9, t	2.52, t, J = 7.1 Hz, 4H
41.6, t (2)	2.61, t, J = 7.6 Hz, 2H
30.2, q	2.75, t, J = 7.6 Hz, 2H
11.8, q (2)	



PROBLEM 13.7

$C_8H_{12}O_3$

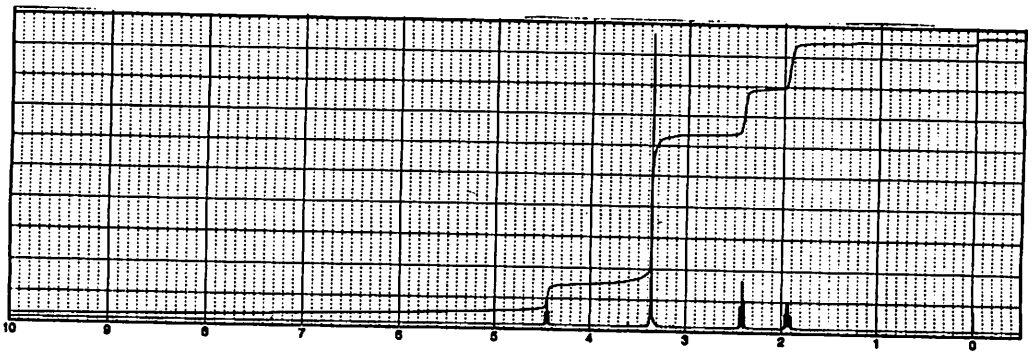
^{13}C NMR	^{1}H NMR
212.3, s	1.28, t, J = 7.2 Hz, 3H
169.4, s	1.9–2.1, m, 2H
61.3, t	2.3, m, 4H
54.8, d	3.15, t, J = 8.4 Hz, 1H
38.0, t	2.39, q, J = 7.2 Hz, 2H
27.4, t	
21.0, t	
14.2, q	



PROBLEM 13.8

$C_6H_{11}NO_2$

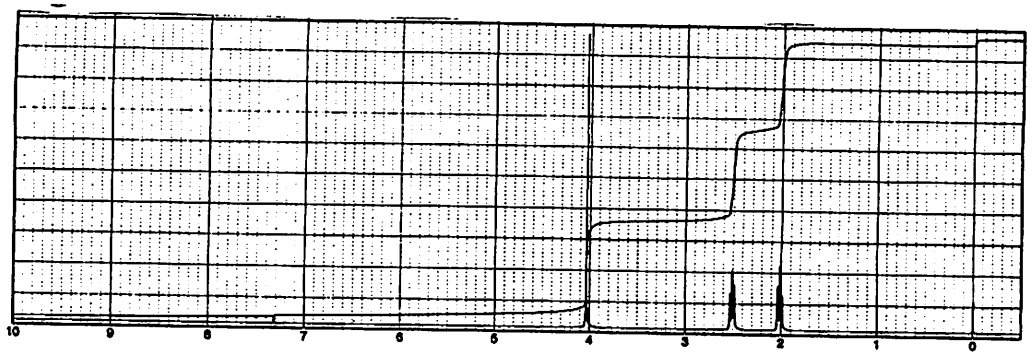
^{13}C NMR	^{1}H NMR
119.4, s	4.46, t, J = 6.2 Hz, 1H
102.7, d	3.36, s, 6H
53.8, q (2)	2.41, t, J = 7.4 Hz, 2H
28.5, t	1.92, dt, J = 6.2, 7.4 Hz, 2H
12.4, t	



PROBLEM 13.9

$C_8H_{12}O_3$

^{13}C NMR	^{1}H NMR
210.1, s	4.04, s, 4H
107.1, s	2.50, t, J = 6.6 Hz, 4H
64.6, t (2)	2.02, t, J = 6.6 Hz, 4H
38.2, t (2)	
33.9, t (2)	



PROBLEM 13.10

$C_9H_{17}NO$

^{13}C NMR
171.1, s
46.8, t (2)
43.7, t
26.1, t (2)
25.5, d
22.7, q (2)

^{1}H NMR
0.96, d, J = 7.8 Hz, 6H
1.9, m, 4H
2.18, d, J = 6.8 Hz, 2H
2.40, m, 1H
3.44, m, 4H

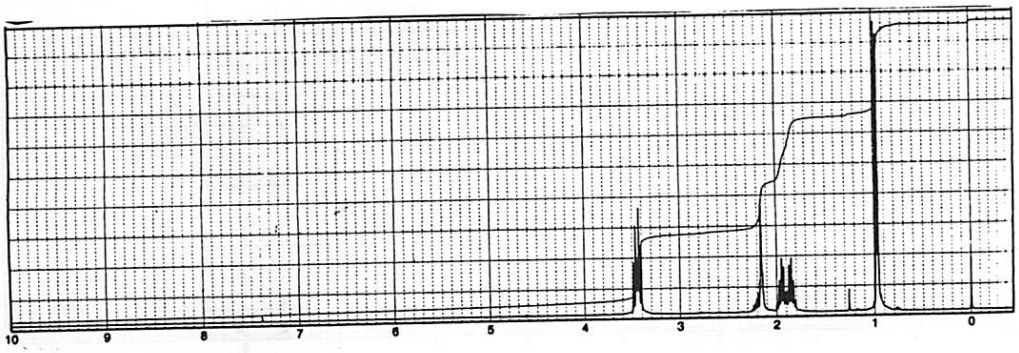


Table 13.1 Chemical Shifts of Protons on a Carbon Atom Adjacent (α Position) to a Functional Group in Aliphatic Compounds (M—Y)

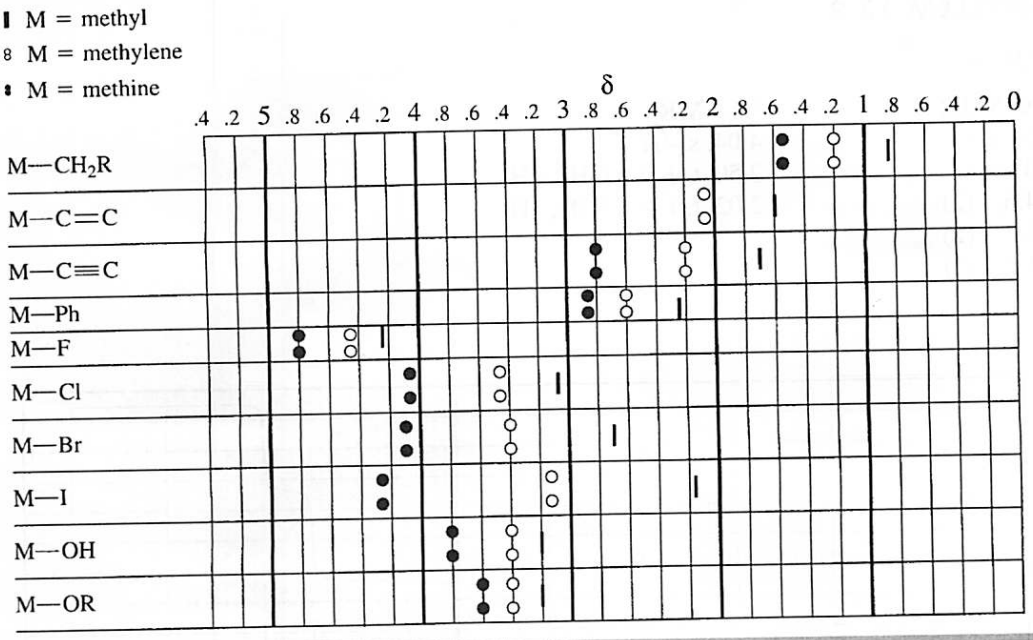


Table 13.1 (Continued)

▮ M = methyl
▮ M = methylene
▮ M = methine

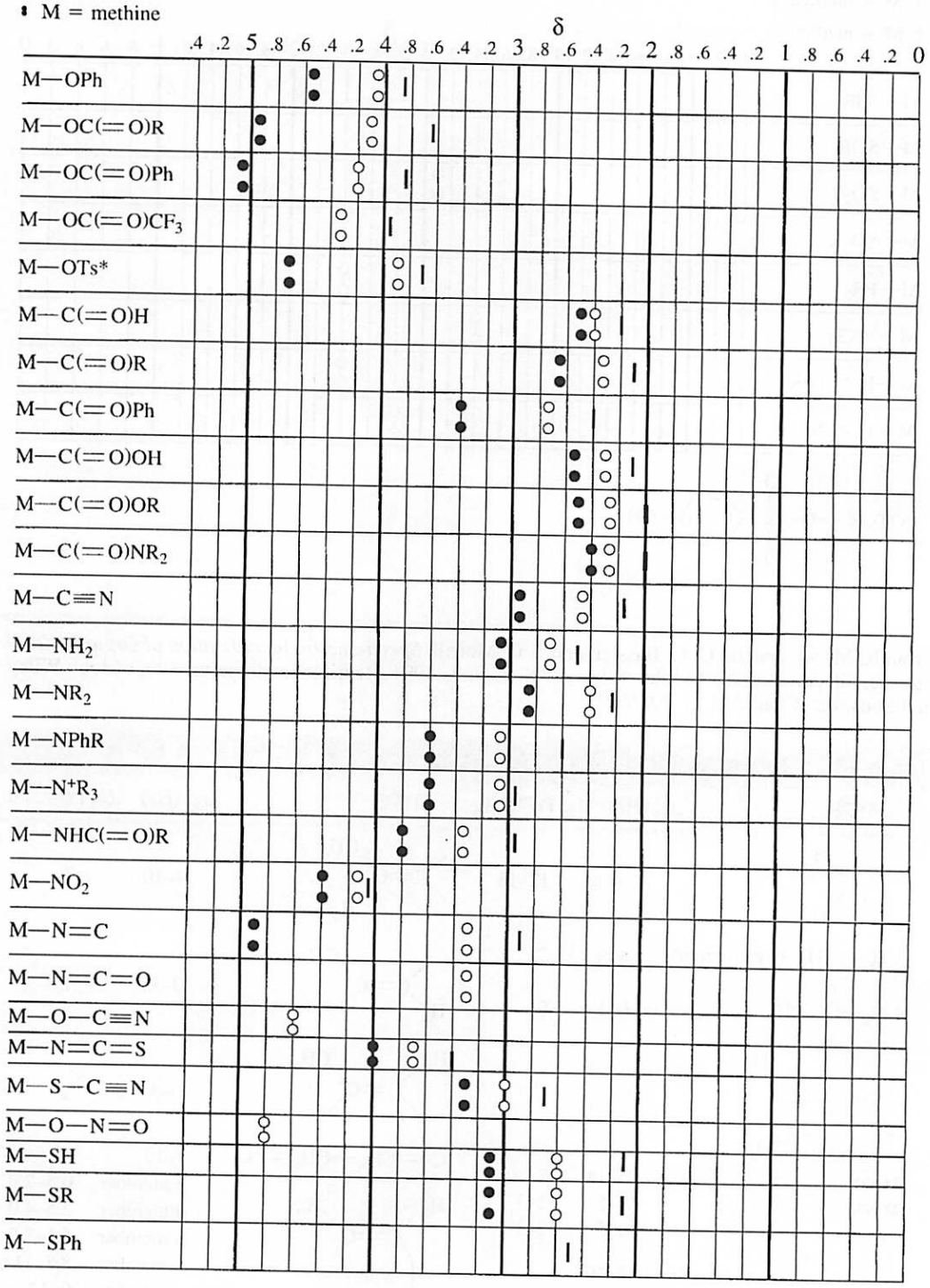
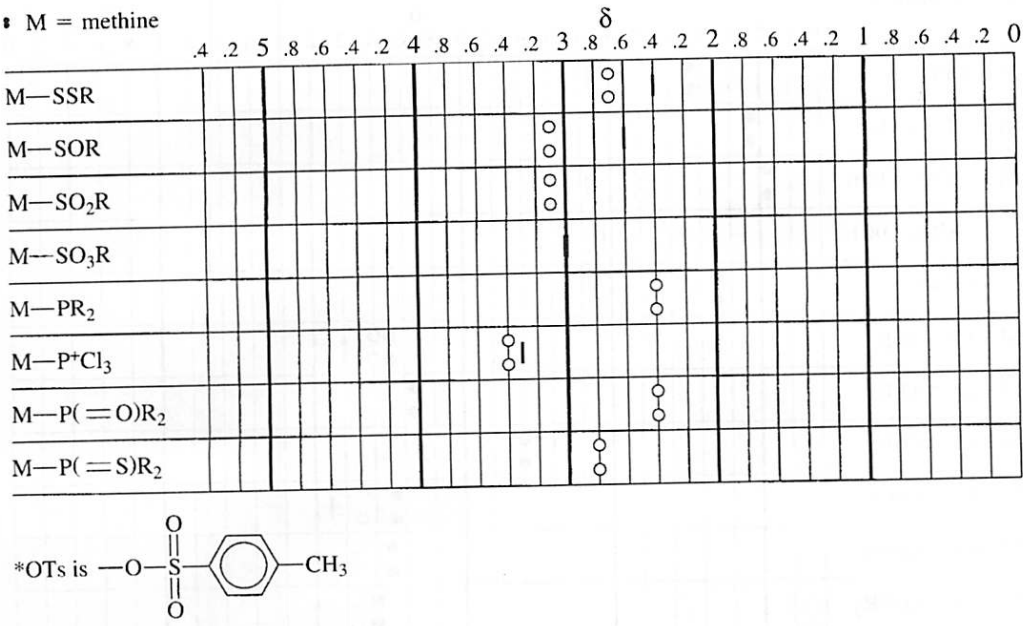


Table 13.1 (Continued)



From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Chart A. 1, p. 208/209.

Table 13.2 Proton Spin-Coupling Constants

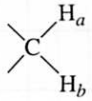
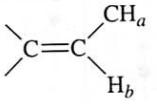
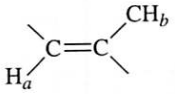
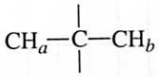
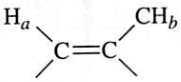
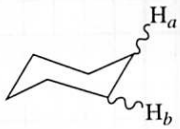
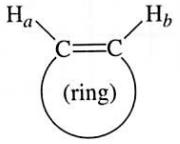
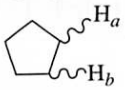
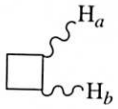
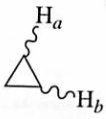
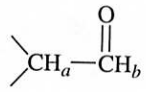
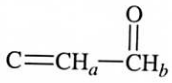
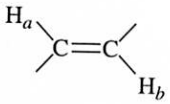
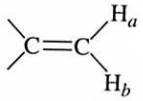
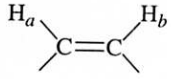
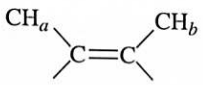
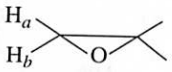
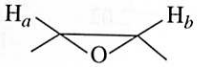
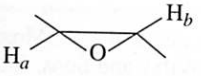
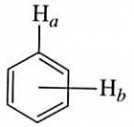
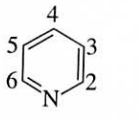
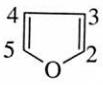
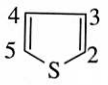
TYPE	J_{ab} (Hz)	J_{ab} TYPICAL	TYPE	J_{ab} (Hz)	J_{ab} TYPICAL
	0–30	12–15		4–10	7
$CH_a—CH_b$ (free rotaion)	6–8	7		0–3	1.5
	0–1	0		0–3	2
			$C{=}CH_a—CH_b{=}C$	9–13	10
ax–ax	6–14	8–10		3 member	0.5–2.0
ax–eq	0–5	2–3		4 member	2.5–4.0
eq–eq	0–5	2–3		5 member	5.1–7.0
	*cis* 5–10			6 member	8.8–11.0
	trans 5–10			7 member	9–13
(cis or trans)				8 member	10–13

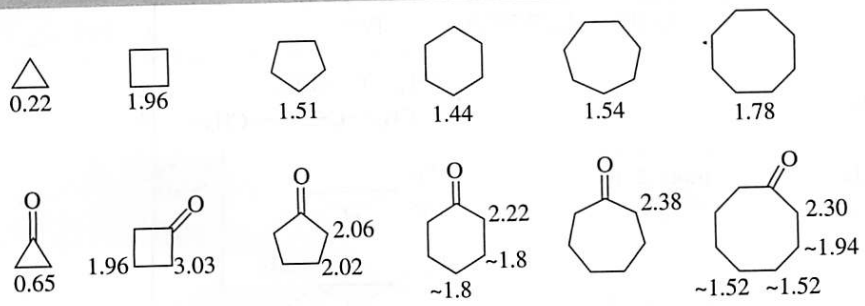
Table 13.2 (Continued)

TYPE	J_{ab} (Hz)	J_{ab} TYPICAL
 (cis or trans)	*cis* 4–12 *trans* 2–10	
 (cis or trans)	*cis* 7–13 *trans* 4–9	
$CH_a—OH_b$ (no exchange)	4–10	5
	1–3	2–3
	5–8	6
	12–18	17
	0–3	0–2
	6–12	10
	0–3	1–2

TYPE	J_{ab} (Hz)	J_{ab} TYPICAL
$CH_a—C\equiv CH_b$	2–3	
$—CH_a—C\equiv C—CH_b—$	2–3	
		6
		4
		2.5
	*J* (ortho) *J* (meta) *J* (para)	6–10 1–3 0–1
		9 3 ~0
	*J* (2–3) *J* (3–4) *J* (2–4) *J* (3–5) *J* (2–5) *J* (2–6)	(5–6) (7–9) (1–2) (1–2) (0–1) (0–1)
		5 8 1.5 1.5 1 ~0
	*J* (2–3) *J* (3–4) *J* (2–4) *J* (2–5)	1.3–2.0 3.1–3.8 0–0 1–2
		1..8 3.6 ~0 1.5
	*J* (2–3) *J* (3–4) *J* (2–4) *J* (2–5)	4.9–6.2 3.4–5.0 1.2–1.7 3.2–3.7
		5.4 4.0 1.5 3.4

From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Chart Appendix F, p. 221, and compiled by Varian Associates.

Table 13.3 Chemical Shifts in Alicyclic Rings



From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table C.1, p. 214.

14

Advanced Structure Determination

... down the rabbit hole, into Wonderland ...

In this chapter, you will learn about more advanced concepts in structural elucidation, including the use of spectroscopic tables to predict ^{13}C and ^{1}H chemical shifts. These concepts, however, are just the beginning. Every day, the detailed three-dimensional structures of complex natural products are elucidated by professionals in the field. Leading references to this work, including detailed instruction on the several useful variations of NMR pulse sequences, are listed at the end of this chapter and at the end of Chapter 12.

THE QUEST, LEVEL FOUR: CALCULATING ^{13}C CHEMICAL SHIFTS

... hear the calculators clicking ...

Consider the unknown listed in Figure 14.1. Using the approach outlined in Chapter 12, it is easy to arrive at the fragments listed in Figure 14.2. The question is, how to assemble those fragments? Two structures are possible, A and B, illustrated in Figure 14.3. How can we tell which it is?

14.1 $C_6H_{14}O$

^{13}C NMR

72.3, d
39.4, t
30.3, t
19.4, t
14.0, q
9.9, q

Figure 14.1 The data for unknown 14.1.

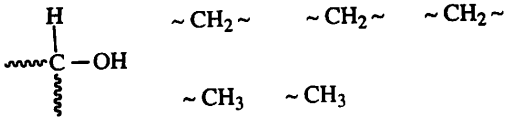


Figure 14.2 Structural fragments for unknown 14.1.

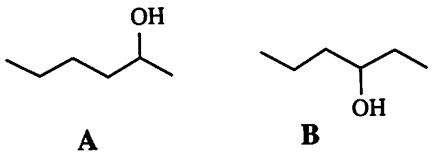


Figure 14.3 Possible structures for unknown 14.1.

To calculate ^{13}C chemical shifts, you will use the data in Tables 14.1 and 14.2. Table 14.1 lists chemical shifts of representative hydrocarbons. Table 14.2 lists the changes in chemical shifts induced by the attachment of functional groups.

To illustrate, both structure A and structure B (Fig. 14.3) are derived from *n*-hexane. The chemical shifts for *n*-hexane are listed in Figure 14.4.

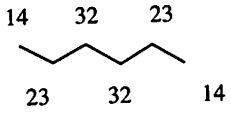


Figure 14.4 The chemical shifts for *n*-hexane.

Using the data in Table 14.2, we can calculate the chemical shifts expected for structure A (Fig. 14.5). Note that we use the internal shifts for the alcohol functional group, since we know that it is attached in the middle of the chain. The α shift refers to the carbon where the functional group is attached. The β carbon is next to the α carbon, and the γ carbon is next to the β carbon.

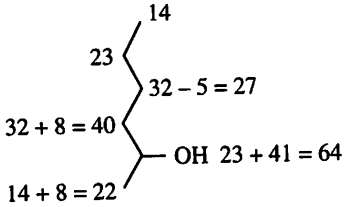


Figure 14.5 Calculated ^{13}C chemical shifts for 2-hexanol (A).

Using this same approach, we can calculate the chemical shifts expected for structure B (Fig. 14.6).

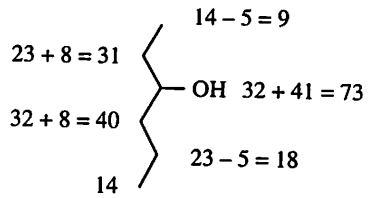


Figure 14.6 Calculated ^{13}C chemical shifts for 3-hexanol (B).

With both sets of data calculated, it is easy to list each set in order and compare each list to the unknown (Fig. 14.6). It is apparent that B fits much more closely, so unknown 14.1 is 3-hexanol.

A	B	unknown 14.1
14, q	9, q	9.9, q
22, q	14, q	14.0, q
23, t	18, t	19.4, t
27, t	31, t	30.3, t
40, t	40, t	39.4, t
64, d	73, d	72.3, d

Figure 14.7 Comparison of calculated ^{13}C chemical shifts for A and B with unknown 14.1.

It would be a useful exercise at this point to practice by calculating the ^{13}C chemical shifts of the unknowns in Chapters 12 and 13. In addition to the data in Table 14.1, the structures in Tables 12.1–12.9 can be used as "starting hydrocarbons."

THE QUEST, LEVEL FIVE: RING SIZE

... around and around and around again ...

While IR is diagnostic for a variety of functional groups, it is especially valuable for ring size of cyclic esters (known as "lactones") and cyclic ketones. Note that α,β-unsaturated carbonyl compounds in general absorb at 20 to 40 cm^{-1} lower frequency than the saturated analogues.

Many of the problems from here on will have IR data. In Step 5, check prospective solutions against the IR. It may be possible that several otherwise acceptable alternative ways of assembling the unknown molecule will not be compatible with the IR spectrum.

We will practice this approach with unknown 14.2, the data for which is in Figure 14.8. The ^{13}C signal at 176.6, s tells us that we have an ester or a carboxylic acid. Since all the H's are attached to carbon, it must be an ester. That accounts for one IHD, but the calculated IHD = 2. There are no other sp^2- or sp-hybridized atoms, so the molecule must also have a ring. The only branch point (see Chapter 12) is the methine, so the ester must be included in the ring, making a lactone. There is one branch off the ring, terminating in a methyl group that must be adjacent to a $-CH_2-$(^{13}C δ 13.1, q; ^1H δ 0.96, t, J = 6.8, 3H). The unknown, then, is either **C** or **D** (Fig. 14.9).

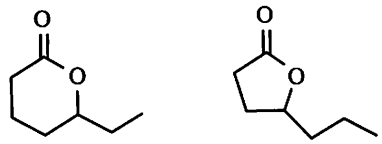
Unknown 14.2

$C_7H_{12}O_2$

IR: 2980, 2890, 1775, 1470, 1370, 1350, 1190, 1020, 980, 925 cm^{-1}

^{13}C NMR	^{1}H NMR
13.1, q	0.96, t, J = 6.8, 3H
17.9, t	1.4–1.9, m, 6H
27.3, t	2.4-2.6, m, 2H
28.1, t	4.5, m, 1H
36.9, t	
80.1, d	
176.6, s	

Figure 14.8 The data for unknown 14.2.



C D

Figure 14.9 Possible structures for unknown 14.2.

Referring to "Carboxylic Esters and Lactones" in Chapter 11, we learn that **C** would be expected to have a carbonyl stretch in the range 1730 to 1750 cm^{-1}, whereas **D** would be expected to have a carbonyl stretch around 1770 cm^{-1}. We can therefore conclude that the structure of unknown 14.2 is **D.**

THE QUEST, LEVEL SIX: ALKENES

How to find the number of alkenes?
Count the number of alkene carbons, and divide by two!

The ^{13}C chemical shifts of representative alkenes are summarized in Tables 12.3 and 12.4. A careful perusal of Table 12.3 reveals a consistent pattern: alkene carbons bearing two hydrogens resonate in the range 105 to 120, those bearing one hydrogen resonate in the range 120 to 140, and those bearing no hydrogen resonate in the range 130 to 150.

In Table 12.6, one observes some carbons that fall in the ranges specified, but many that do not. This is because these alkenes have either heteroatoms or electron-withdrawing groups directly attached to ("conjugated with") them. The chemical shift of a carbon is a function of the electron density observed at that carbon. An increase in electron density will cause a carbon to resonate at higher field (smaller numbers), while a decrease in electron density will cause the carbon to resonate at lower field (larger numbers). A carbonyl conjugated with an alkene shifts

the β-carbon downfield. It does not affect the α-carbon. This can be rationalized by considering the polarization of the bonding electrons. The β-carbon has lost electron density, so it will resonate at lower field (larger numbers). The α-carbon is unchanged (Figure 14.10).

A heteroatom conjugated with an alkene shifts *both* carbons. The α-carbon is shifted downfield (larger chemical shift) and the β-carbon is shifted upfield (smaller chemical shift). This can be rationalized by considering that the alkene electron cloud is repelled by the nonbonding electrons of the heteroatom, while at the same time the electronegative heteroatom withdraws electron density from the α-carbon.

Figure 14.10 Polarization of alkenes by electron-withdrawing and electron-donating groups.

These effects are summarized by Figure 14.11. Remember that "normal" chemical shift for an alkene carbon depends on how many alkyl groups are attached. From Table 12.5, we can see that a "normal" alkene carbon with two protons attached would come at 105–120 δ, a "normal" alkene with one proton attached would come at 120–140 δ, and a "normal" alkene with no protons attached would come at 130–150 δ.

Note that each alkene has two carbons. If you think a signal upfield (e.g., 100 δ) might be half of a heteroatom-polarized alkene, look for the other alkene carbon shifted downfield. If it is not there, then that signal at 100 δ is not an alkene carbon.

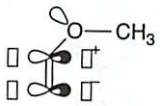


Figure 14.11 Expected chemical shift ranges for polarized and nonpolarized alkenes.

CALCULATING THE ^{1}H NMR CHEMICAL SHIFTS OF ALKENES

^{1}H NMR shifts of alkenes are easily calculated using Table 14.4. You will note that for polarized alkenes, the protons are shifted the same way as the carbons. For carbonyl-polarized alkenes, the β-protons are shifted downfield and the α-protons are normal. For heteroatom-polarized alkenes, the α-protons are shifted downfield and the β-protons are shifted upfield. Note (Table 13.2) that protons *trans* on an alkene share a J value of about 17 Hz, whereas protons *cis* on an alkene usually share a J value of about 10 Hz. Figure 14.12 is the diagram on which Table 14.4 is based, and Figure 14.13 is an example that illustrates the use of the data in Table 14.4.

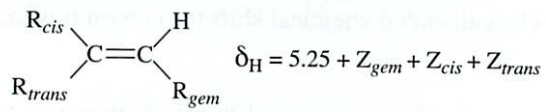


Figure 14.12 Diagram on which Table 14.4 is based.

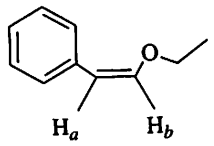


Figure 14.13 Using Table 14.4 to calculate the ^{1}H NMR chemical shifts of an alkene.

Practice using Table 14.4 with the alkene illustrated (Fig. 14.13). The starting value is always 5.25 δ. H substituents neither add to nor subtract from this value. For H_a and H_b, then, we need only to consider the shifts due to the geminal substituent and to the trans substituent. The predicted chemical shift for H_a is then 5.25 + 1.04 − 1.28 = 5.32 δ, and for H_b the predicted chemical shift is 5.25 + 1.18 − 0.10 = 6.33 δ.

THE QUEST, LEVEL SEVEN: BENZENE DERIVATIVES

^{13}C of Benzene Derivatives: The ^{13}C chemical shift of a carbon in a benzene derivative can be calculated using the data in Table 14.5. This can best be illustrated with an example (Fig. 14.14).

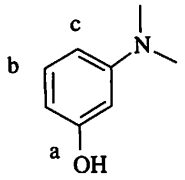


Figure 14.14 Using Table 14.5 to calculate the ^{13}C NMR chemical shifts of a benzene derivative.

Carbon a: The starting value for any benzene carbon is 128.5 δ, from the data in Table 14.5. We then add the incremental contribution from each substituent. The increment shift from H is zero, so we only need to account for effects due to substituents on the ring. For carbon a there are two substituents, a C-1 OH and a C-3 -NMe_2. The C-1 OH contributes +26.6. The C-3 -NMe_2 contributes +0.8. The calculated chemical shift for carbon a is therefore 128.5 + 26.6 + 0.8 = 155.9 δ.

Carbon b: The starting value for carbon b is 128.5 δ. With regard to b, the -OH is at C-3, and so contributes +1.6. The -NMe_2 substituent is at the other C-3, and so contributes an increment of +0.8. The calculated chemical shift for carbon b is therefore 128.5 + 1.6 + 0.8 = 130.9 δ.

Carbon c: The starting value for carbon c is 128.5 δ. With regard to c, the -OH is at C-4, and so contributes −7.3. The -NMe_2 substituent is at C-2, and so contributes an increment of −15.7. The calculated chemical shift for carbon c is therefore 128.5 − 7.3 − 15.7 = 105.5 δ.

Often, the only way to decipher the substitution pattern on a highly substituted benzene derivative is to calculate the chemical shifts of the aromatic carbons for each possible substitution pattern, and compare the calculated values to the data given. Remember to consider multiplicity as well as chemical shift in making these comparisons.

^1H NMR OF BENZENE DERIVATIVES

The ^1H NMR chemical shifts of a benzene derivative can be calculated using the data in Table 14.6. These are approximately additive. Again, the use of this table can best be illustrated with an example (Fig. 14.15).

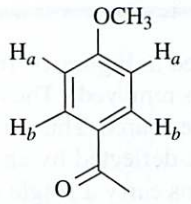


Figure 14.15 Using Table 14.6 to calculate the ^1H NMR chemical shifts of a benzene derivative.

The protons on an unsubstituted or alkyl-substituted benzene (first entries in Table 14.6) come at about 7.26 δ. A proton *ortho* ("1,2-") to an -OCH_3 would, according to this table, come at about 7.0 δ, a shift upfield of 0.26 δ. A proton *meta* ("1,3") to a ketone carbonyl would come at 7.5 δ, a downfield shift of 0.24 δ. It follows that H_a should resonate at about 7.26 − 0.26 + 0.24 = 7.24 δ. For H_b, a proton *meta* to an -OCH_3 would, according to Table 14.6, come at about 7.35 δ, a shift downfield of 0.09 δ. A proton *ortho* to a ketone carbonyl would come at 7.9 δ, a downfield shift from 7.26 of 0.64 δ. It follows that H_b should resonate at about 7.26 + 0.09 + 0.64 = 7.99 δ.

Protons *ortho* to each other (Table 13.2) have a 9-Hz coupling constant, protons *meta* to each other have a 3-Hz coupling constant, and protons *para* to each other do not couple. Remember that protons with the same chemical shift (even if not chemically the same) do *not* couple to each other.

For the example illustrated, H_a and H_b would share a 9-Hz coupling constant. There would be no *meta* coupling, since protons with the same chemical shift do not couple to each other. The aromatic portion of the ^1H spectrum would then be summarized: 7.24, 2H, d, J = 9.0 Hz; 7.99, 2H, d, J = 9.0 Hz.

SOLVING PROBLEMS WITH ALKENES AND ARENES

The key to solving problems with alkenes and arenes is in Step 2 on the worksheet, "assigning and exploring around the unsaturated functional groups." First establish the alkene carbon count, and, where possible, try to pair the alkene carbons. The first clue that an unknown might contain a benzene ring will come when the unknown has at least one ring and at least three double bonds. Confirmation comes if there are also arene-type protons (6.5–8.0 δ).

It is important at this point to figure out the substitution pattern of the arene, especially if there are more than three double bonds in the molecule. Count the arene-type hydrogens. There are six positions on the benzene ring. If there are only three aromatic protons, then there must also be three substituents on the ring.

Once you know how many substituents there are, look for symmery. For instance, a disubstituted aromatic that has only two bands of protons (two doublets, each 2H, J = 9 Hz) must be *para*-disubstituted. Then, decide what the substituents might be. This can often be deduced from the chemical shifts of the arene protons, and other information about functional groups in the molecule. Once the substituents on the benzene ring are known and you have deduced the pattern of attachment, it should be possible to calculate the approximate chemical shifts (and multiplicity) of the arene carbons. Once these carbon signals are subtracted from the spectrum, assignment of the residual alkenes should be more straightforward.

THE QUEST, LEVEL EIGHT: MASS SPECTROMETRY

A typical mass spectrometer is illustrated in Figure 14.16. A sample introduced into the source is vaporized, then ionized (an electron is removed). The resultant group of ions (some of which are falling apart!) is accelerated from the source. This group of ions then encounters a magnetic field. In that field, the moving ions are deflected by an amount inversely proportional to the mass/charge (m/z) ratio. Since most ions carry a single charge, they are thus separated, when they reach the detector, according to mass. An ion current is then measured at each value of m/z, and the result tabulated. That tabulated result is the **mass spectrum.**

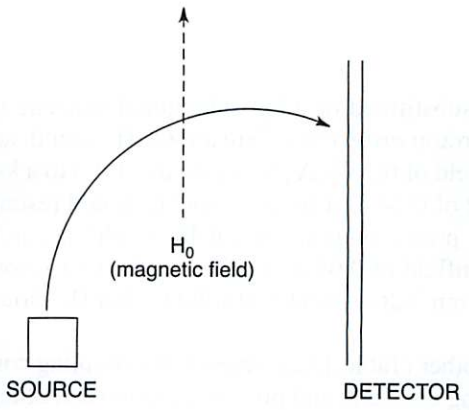


Figure 14.16 Diagram of a mass spectrometer.

Some portion of that ion current will be due to the molecular ion, the ion that is the entire molecule. Other "fragment" ions are also generated. In this section, we will learn how to use these fragment ions to assist in deducing the structure of an unknown. There are four processes that are important to understand: α-cleavage, β-cleavage, McLafferty rearrangement, and decarbonylation.

α-Cleavage: In the ionization process, an electron is removed from the molecule. If there is a heteroatom in the molecule, one of the nonbonding electrons on the heteroatom is most easily removed. This gives a radical cation, the molecular ion. Radical cleavage (Fig. 14.17) of the adjacent carbon-carbon bond then gives a stable carbocation, a fragment ion.

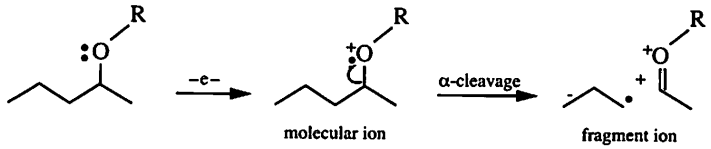


Figure 14.17 Illustration of α-cleavage.

β-Cleavage: Another process that is important, especially in cyclic systems, is β-cleavage. For example, α-cleavage of the molecular ion in a cyclic ketone, as shown in Figure 14.18, gives a new species that has the same molecular weight as the molecular ion. Radical cleavage of the carbon-carbon bond β to the radical center then gives a fragment ion. β-cleavage can proceed whenever there is a carbon-carbon bond β to a radical center.

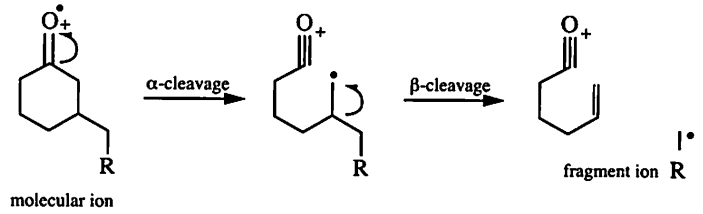


Figure 14.18 Illustration of β-cleavage.

McLafferty Rearrangement: When a carbonyl derivative has a proton on a carbon three carbons from the carbonyl, McLafferty rearrangement can proceed (Fig. 14.19). The product fragment ion rearrangement from McLafferty rearrangement is itself the molecular ion of a new ketone, which can then proceed with α-cleavage, β-cleavage, or McLafferty rearrangement. The fragments resulting from McLafferty rearrangement stand out in the mass spectrum, because (if the starting molecular weight is even) they are of **even mass.** Ions resulting from α-cleavage and β-cleavage, while more abundant, are all **odd mass.**

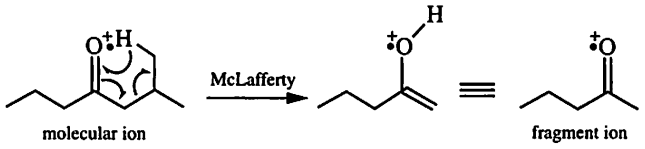


Figure 14.19 Illustration of McLafferty rearrangement.

Decarbonylation: The product of α-cleavage of a ketone, as shown in Figure 14.20, is an acylium ion. Such an ion will often go on to lose carbon monoxide ("decarbonylation"), to give a new fragment ion. This can then further lose methylene units, as illustrated.

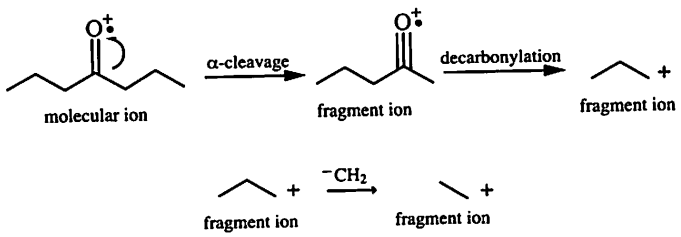


Figure 14.20 Illustration of decarbonylation.

Analysis of the Mass Spectrum: While a variety of other fragmentation and rearrangement processes can and do proceed in the mass spectrometer, the four processes outlined above will often be sufficient to rationalize most of the prominent fragment ions. Use the mass spectrum in Step 5, focusing on fragmentations that differentiate between alternative structures. This is illustrated by unknown 14.3 (Fig. 14.21).

Unknown 14.3

$C_{19}H_{39}N$

MS: 280 ($M^+ - H$, 4), 266 (10), 124 (3), 111 (5), 98 (100)

^{13}C NMR

50.7, d
45.7, d
33.9, t
32.8, t
31.8, t
30.6, t
30.4, t (2)
29.7, t (2)
29.6, t (2)
29.2, t (2)
26.3, t
22.6, t
21.0, q
19.4, t
14.0, q

^1H NMR

3.07, 1H, m
2.88, 1H, m
2.05, 1H, bs (exchanges)
1.6, 8H, m
1.3, 22H, m
1.07, 3H, d, J = 7.1 Hz
0.88, 3H, t, J = 6.6 Hz

Figure 14.21 The data for unknown 14.3.

From the data, this is a secondary amine, with two methines (C-H) attached to the N. The methyl group that is a doublet must also be attached to one of those same methines. Unknown 14.3 has a ring, and a side chain that ends in a methyl that is attached to a $-CH_2-$. This approximate structure is summarized in Figure 14.22. The question is, how many methylenes are in the ring, and how many are in the side chain?

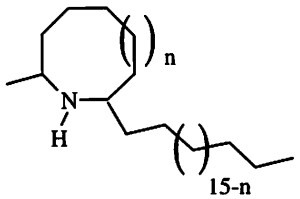
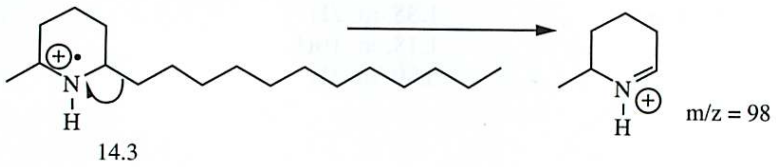


Figure 14.22 The approximate structure of unknown 14.3.

The final structure can be found by analyzing the mass spectrum. α-cleavage of the radical cation derived from the amine would proceed on either side. When the methyl group is lost, an ion of m/z = 266 will be generated. This is observed, but that does not tell us anything new—we already knew that the methyl group was attached to one of the methines.

Loss of the other side chain would mean loss of the terminal methyl on that side chain, plus the accompanying methylenes. If the side chain were ethyl, for instance, α-cleavage would generate a fragment having m/z = 252. Loss of a propyl group would give m/z = 238. Working down, we eventually come to m/z = 98. This is loss of a C_{12} sidechain, so the structure of unknown 14.3 must be as depicted in Figure 14.23.



14.3

Figure 14.23 The structure of unknown 14.3, and its α-cleavage.

PROBLEMS

Problems 14.1–14.10 will give further practice in deducing structures using spectroscopic data.

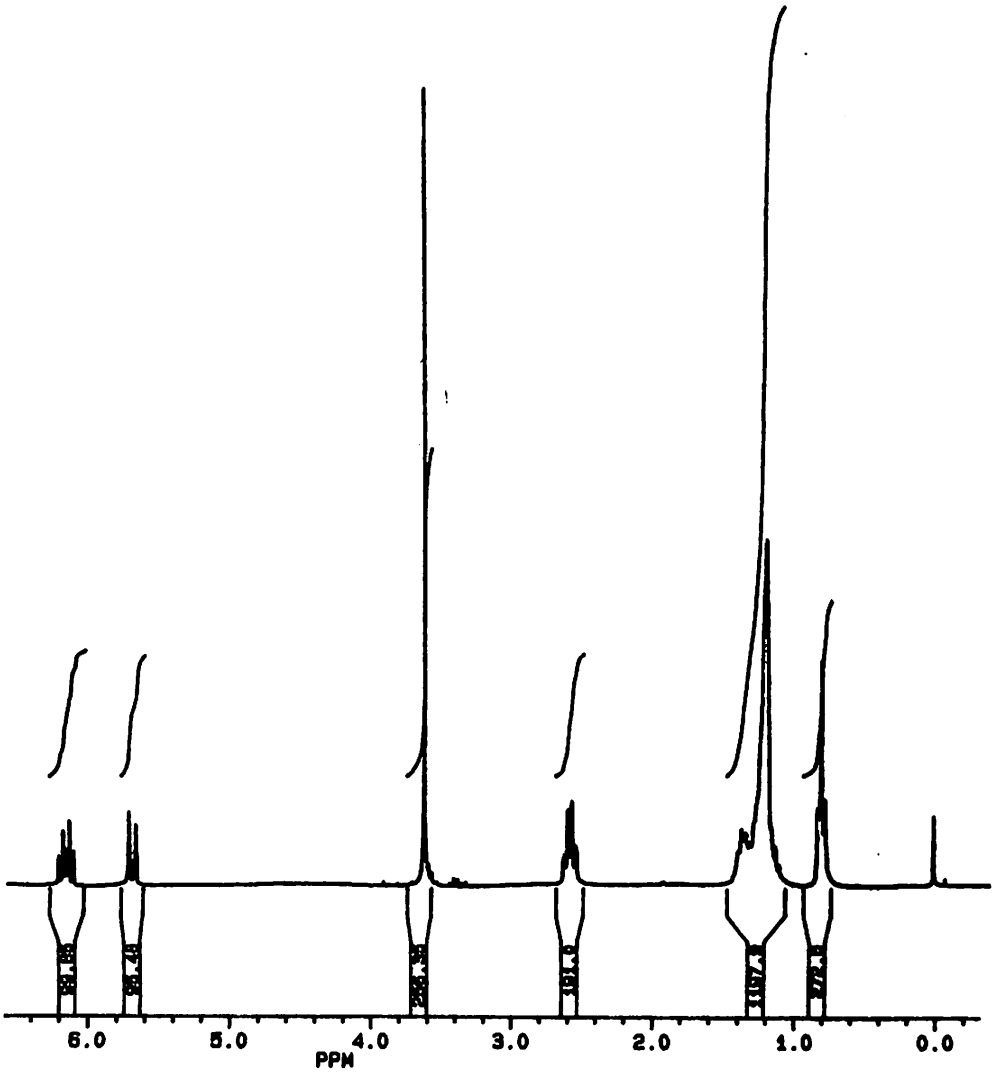
REFERENCE

Crews, P.; Rodriguez, J.; Jaspars, M. *Organic Structure Analysis;* Oxford University Press: New York, 1998.

PROBLEM 14.1

$C_{12}H_{22}O_2$
IR: 2926, 2856, 1728, 1645, 1436, 1197, 1175, 819 cm^{-1}
MS: 198 (M^+, 2), 167 (7), 124 (9), 113 (100), 100 (33), 87 (47), 74 (43)

^{13}C NMR		^1H NMR
166.5, s	29.0, t	6.14, dt, 1H, J = 7.5, 11.5 Hz
150.7, d	28.9, t	5.68, d, 1H, J = 11.5 Hz
119.0, d	28.8, t	3.61, s, 3H
50.6, q	22.5, t	2.57, dq, 2H, J = 1.4, 7.4 Hz
31.7, t	13.9, q	1.35, m, 2H
29.3, t		1.18, m, 10H
29.1, t		0.80, m, 3H

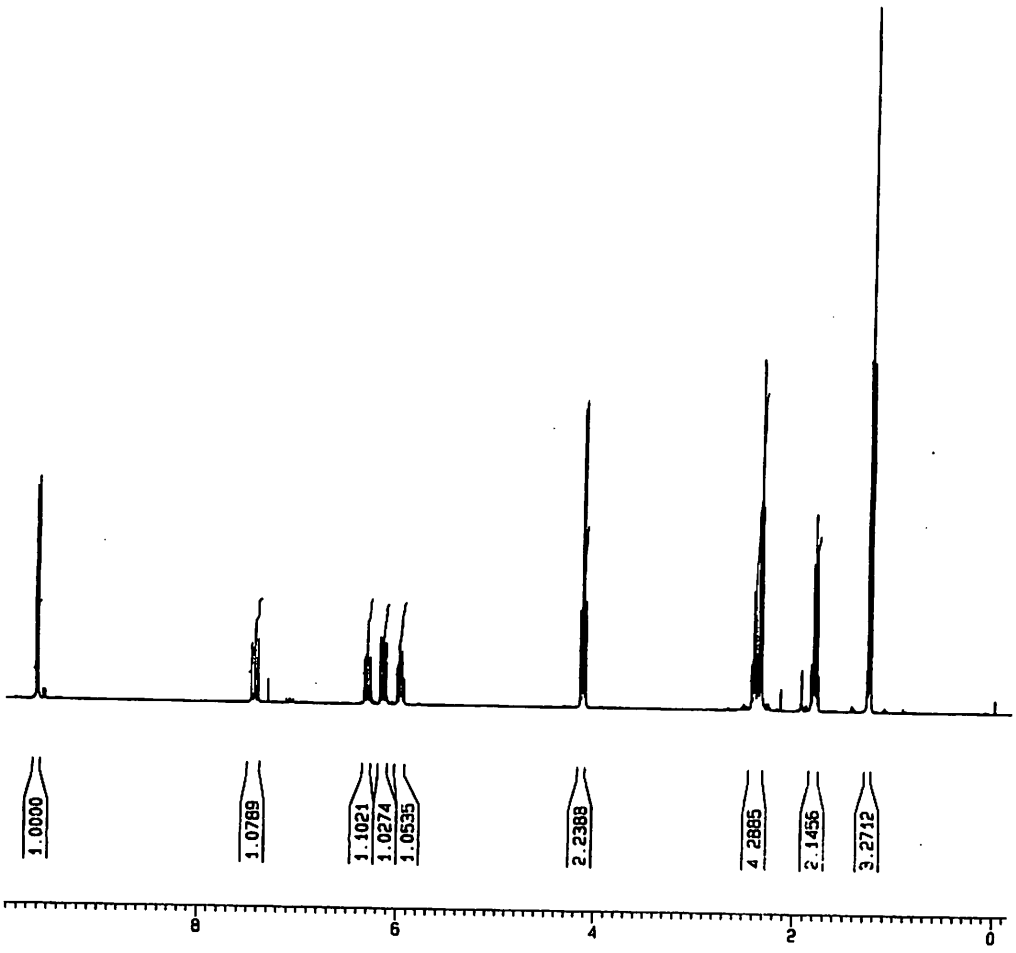


PROBLEM 14.2

$C_{11}H_{16}O_3$

IR (film) 2982, 1732, 1377, 1183, 1023 cm^{-1}
MS: 196 (M^+, 2), 150 (20), 122 (35), 108 (36), 107 (28), 104 (36), 81 (100)

^{13}C NMR	^1H NMR
193.8, d	9.61, d, 1H, J = 7.9 Hz
173.0, s	7.44, ddd, 1H, J = 0.9, 11.1, and 15.2 Hz
146.3, d	6.32, t, 1H, J = 11.1 Hz
142.1, d	6.16, dd, 1H, J = 7.9 and 15.2 Hz
132.0, d	5.99, dt, 1H, J = 7.9 and 11.1 Hz)
127.5, d	4.14, q, 2H, J = 7.1 Hz
60.3, t	2.41, q, 2H, J = 7.9 Hz
33.3, t	2.36, t, 2H, J = 7.3 Hz
27.5, t	1.81, quint, 2H, J = 7.3 Hz
24.2, t	1.26, t, 3H, J = 7.1 Hz
14.1, q	



PROBLEM 14.3

$C_{14}H_{16}O_3$

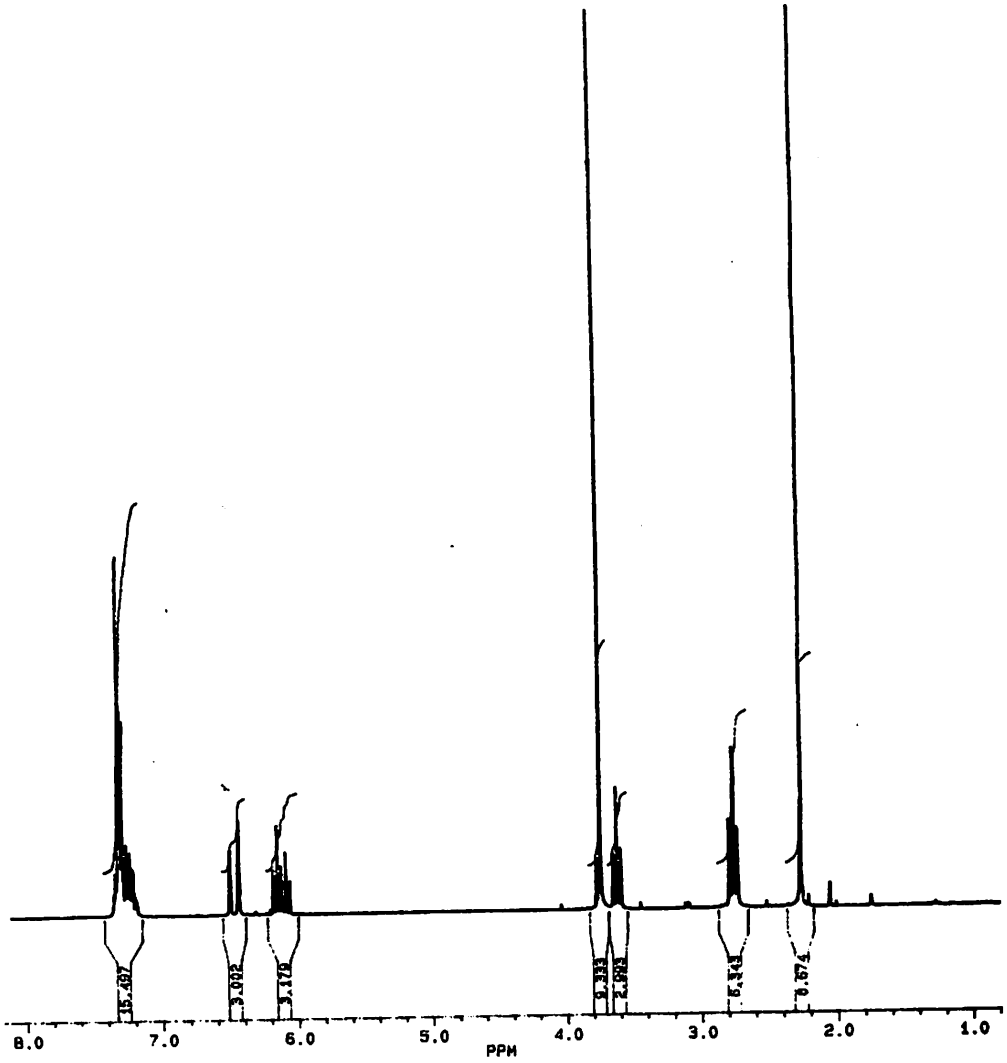
IR: 2926, 2855, 1743, 1718, 1644, 1466, 1358, 1242, 1151, 1120 cm^{-1}
MS: 232 (M^+, 34), 190 (26), 189 (51), 168 (33), 156 (100), 131 (54), 130 (39), 119 (69), 116 (56), 104 (18), 91 (88), 77 (18)

^{13}C NMR

202.1, s
169.6, s
136.9, s
132.7, d
128.4 , d (2)
127.3, d
126.1, d (2)
125.6, d
57.3, q
52.3, d
31.5, t
29.2, q

^1H NMR

7.31, m, 5H
6.46, d, 1H, J = 15.8 Hz
6.12, dt, 1H, J = 7.1, 15.8 Hz
3.74, s, 3H
3.62, t, 1H, J = 7.4 Hz
2.76, t, 2H, J = 7.3 Hz
2.26, s, 3H

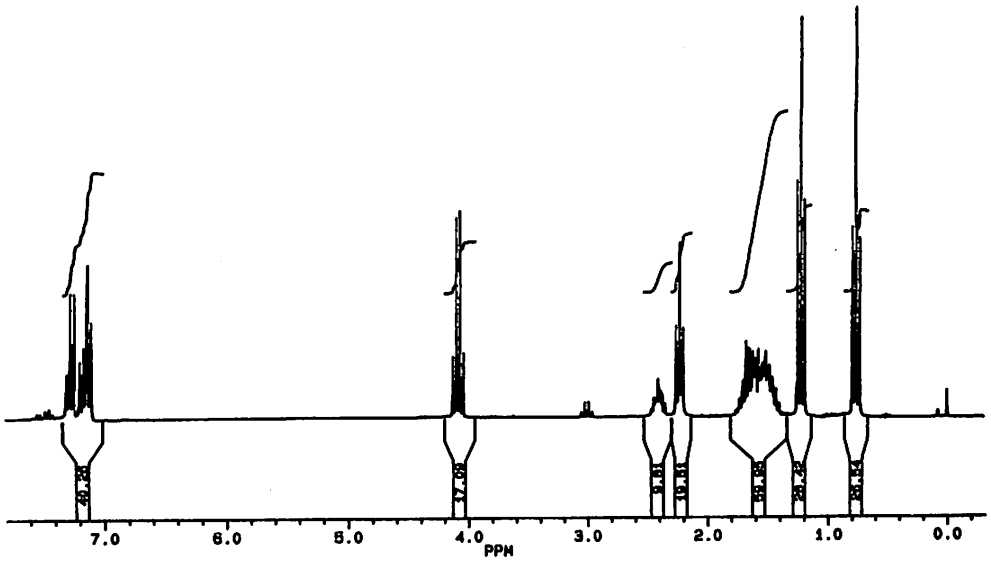


PROBLEM 14.4

$C_{15}H_{22}O_2$

IR: 2931, 1733, 1692, 1452, 1373, 1155, 1036, 757 cm^{-1}
MS: 234 (M^+, 10), 206 (63), 188 (30), 156 (26), 131 (21), 117 (100)

^{13}C NMR		^{1}H NMR
173.6, s	35.8, t	7.2, m, 5H
145.3, s	34.4, t	4.09, 2H, q, J = 7.1 Hz
128.2, d (2)	29.6, t	2.40, 1H, m
127.7, d	23.1, t	2.22, 2H, t, J = 7.5 Hz
125.9, d (2)	14.2, q	1.60, 6H, m
60.1, t	12.1, q	1.21, 3H, t, J = 7.1 Hz
47.6, d		0.76, 3H, t, J = 7.4 Hz

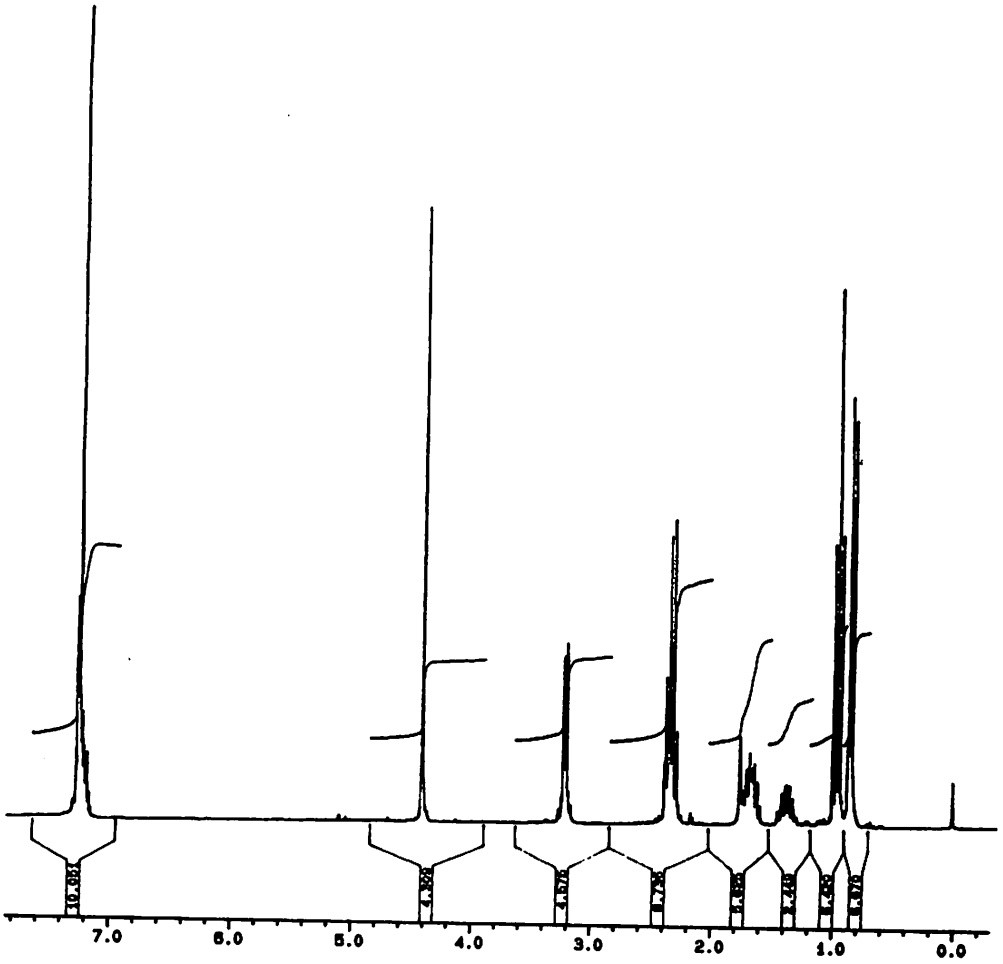


PROBLEM 14.5

$C_{15}H_{22}O_2$

IR : 2931, 2872, 1713, 1455, 1414, 1367, 1102, 738, 697 cm^{-1}
MS: 234 (0.28), 143 (28), 128 (24), 127 (26), 107 (24), 99 (23), 97 (12), 91 (100),

^{13}C NMR		^{1}H NMR
212.1, s	36.1, t	7.30, 5H, m
138.5, s	32.1, d	4.49, 2H, s
129.2, d (2)	27.5, t	3.29, 2H, dd, J =1.8, 6.0 Hz
128.2, d	15.5, q	2.38, 4H, m
127.5, d (2)	9.5, q	1.74, 2H, m
75.7, t		1.42, 1H, m
72.8, t		0.98, 3H, t, J = 7.3 Hz
39.0, t		0.93, 3H, d, J = 6.6 Hz



PROBLEM 14.6

$C_{16}H_{20}O_2$

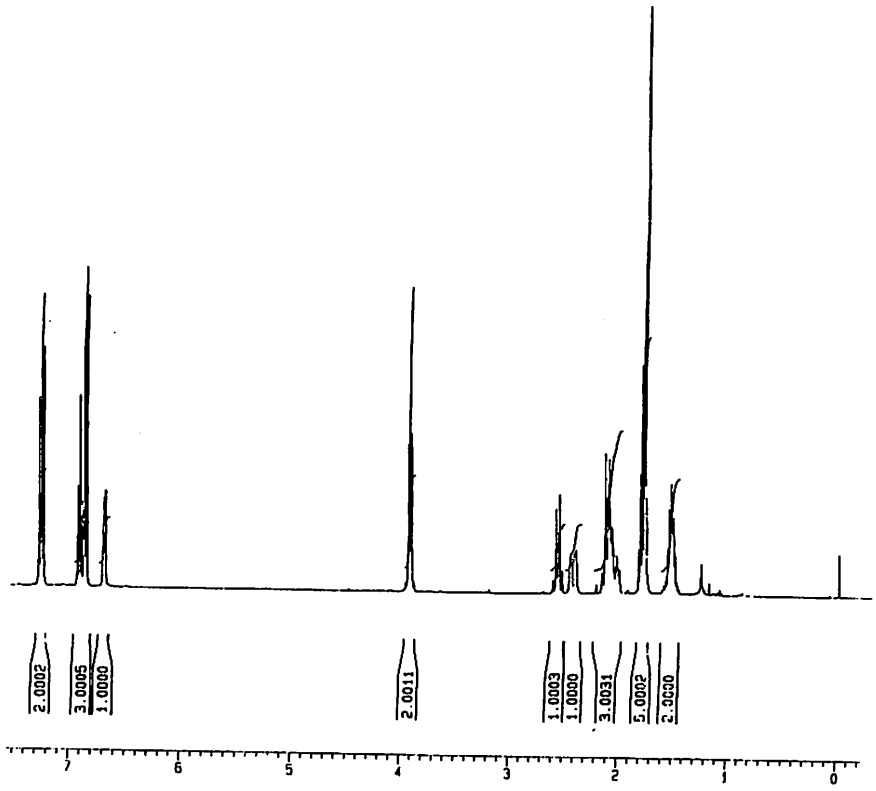
IR: 2922, 1673, 1245, 755, 692 cm^{-1}
MS: 244 (M^+, 43), 151 (42), 121 (16), 109 (100)

^{13}C NMR

199.8, s
158.7, s
144.6, d
135.4, s
129.3, d (2)
120.5, d
114.2, d (2)
67.4, t
44.4, t
35.3, d
32.3, t
32.1, t
26.2, t
15.6, q

^1H NMR

7.24–7.29, 2H, m
6.86–6.94, 3H, m
6.70, 1H, t, J = 4.5 Hz
3.93, 2H, t, J = 6.2 Hz
2.55, 1H, dd, J = 11.4, 8.2 Hz
2.44, 1H, m
2.10, 3H, m
1.80, 2H, m
1.77, 3H, s
1.52, 2H, m



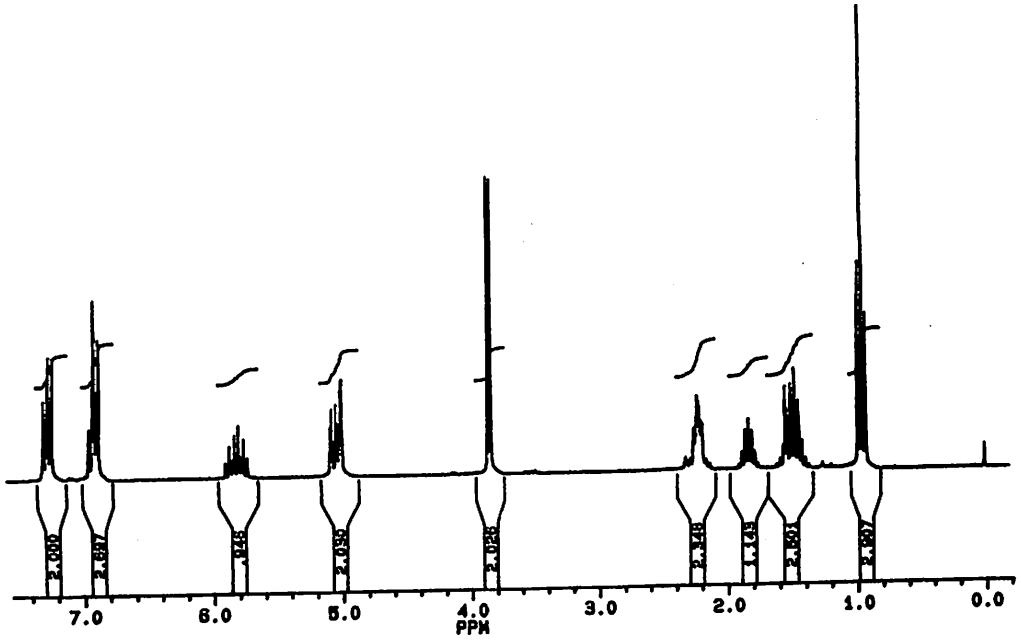
PROBLEM 14.7

$C_{13}H_{18}O$

IR: 3075, 2963, 1640, 1600 cm^{-1}
MS: 190 (M^+, 24), 94 (100), 81 (24)

^{13}C NMR
159.0, s
136.6, d
129.4, d (2)
120.4, d
116.4, t
114.5, d (2)
69.7, t
39.4, d
35.2, t
23.5, t
11.2, q

^1H NMR
7.27, 2H, m
6.91, 3H, m
5.80, 1H, ddt, J = 16.2, 10.4, 6.8 Hz
5.10, 1H, d, J = 16.2 Hz
4.98, 1H, d, J = 10.4 Hz
3.84, 2H, d, J = 5.8 Hz
2.23, 2H, m
1.82, 1H, m
1.48, 2H, m
0.95, 3H, t, J = 7.4 Hz



PROBLEM 14.8

$C_{17}H_{22}O_4$

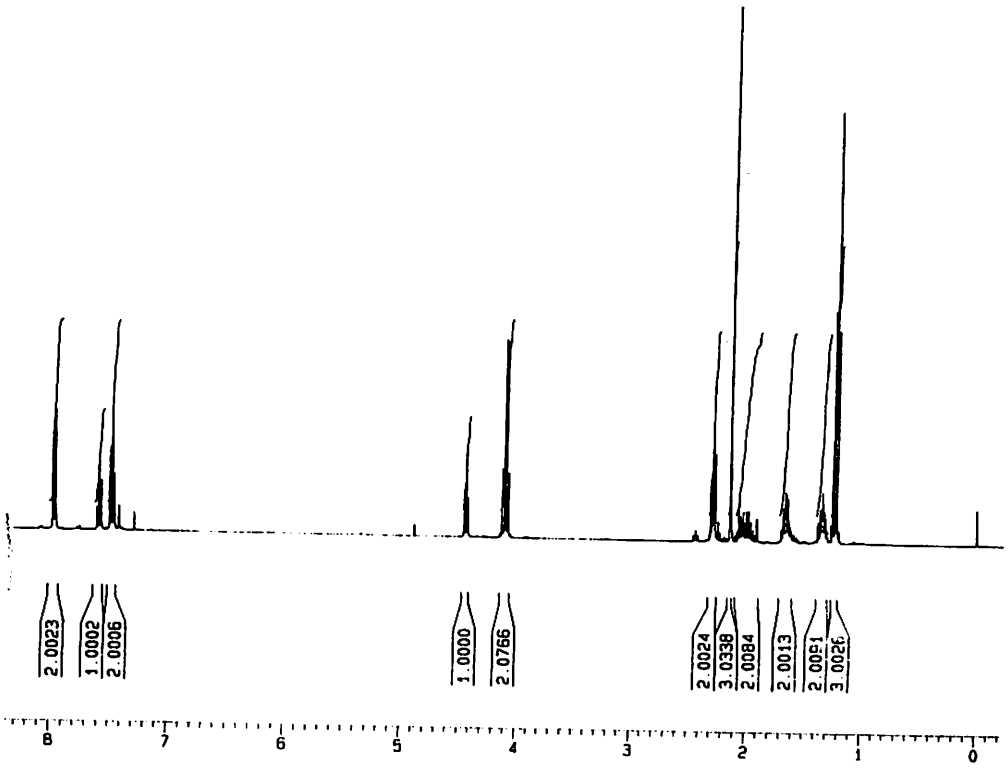
IR: 2938, 1731, 1681, 1596, 1448, 1359, 1182, 1096, 1031, 972, 773, 695 cm^{-1}
MS: 291 (M^+ +1, 100), 275 (33), 249 (39), 204 (11), 187 (26), 163 (15), 157 (11), 141 (12), 105 (41)

^{13}C NMR

204.1, s
196.2, s
173.3, s
136.3, s
133.7, d (2)
128.8, d
128.6, d (2)
63.1, d
60.2, t
33.8, t
28.5, t
27.8, q
27.0, t
24.6, t
14.1, q

^1H NMR

8.00, 2H, d, J = 8.5 Hz
7.61, 1H, m
7.45, 2H, m
4.44, 1H, t, J = 7.0 Hz
4.10, 2H, q, J = 7.1 Hz
2.29, 2H, t, J = 7.4 Hz
2.13, 3H, s
2.05, 2H, m
1.78, 2H, m
1.40, 2H, m
1.23, 3H, t, J = 7.1 Hz



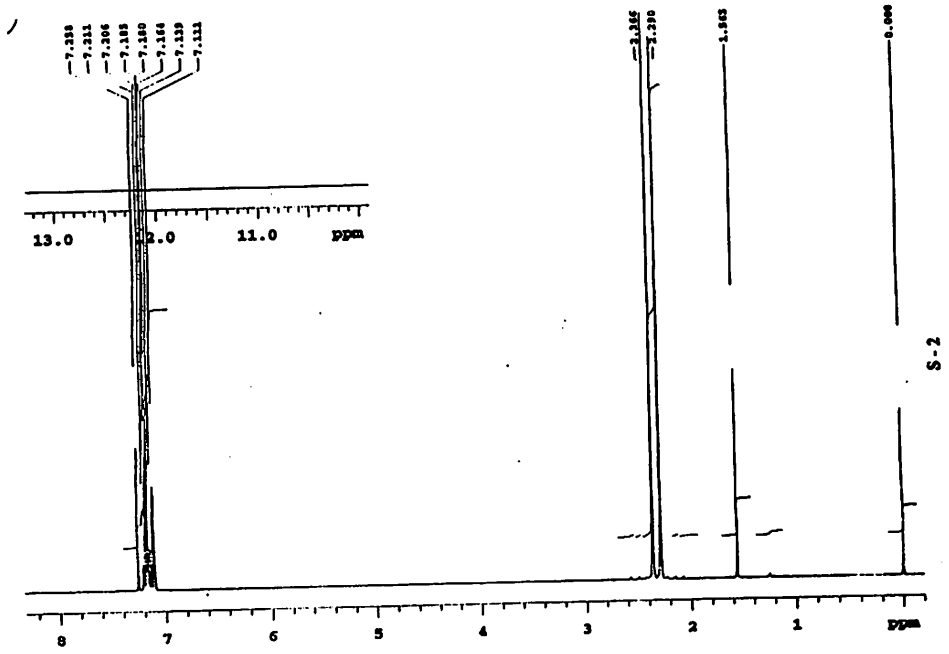
PROBLEM 14.9

$C_{17}H_{18}O$

IR: 1665 cm^{-1}
MS: 258 (M^+), 143, 115

^{13}C NMR
199.7, s
137.6, s (2)
133.5, s (2)
133.4, s (2)
130.3, d (2)
129.4, d (2)
129.1, d (2)
19.7, q (2)
18.5, q (2)

^1H NMR
7.2, 6H, m
2.37, 6H, s
2.29, 6H, s



PROBLEM 14.10

$C_{15}H_{13}BrO_2$

IR: 1666 cm^{-1}

MS: 306 (M^+), 304 (M^+), 185, 183, 157, 155, 149, 121

^{13}C NMR

194.1, s
153.8, s
135.3, s
131.2, d
130.0, d (2)
129.7, d (2)
128.6, s
128.5, d
126.5, s
126.4, s
110.0, d
54.2, q
18.8, q

^1H NMR

7.67, 2H, d, J = 8.6 Hz
7.57, 2H, d, J = 8.6 Hz
7.25, 1H, dd, J = 2.06, 8.44 Hz
7.17, 1H, d, J = 2.06 Hz
6.89, 1H, d, J = 8.44 Hz
3.68, 3H, s
2.33, 3H, s

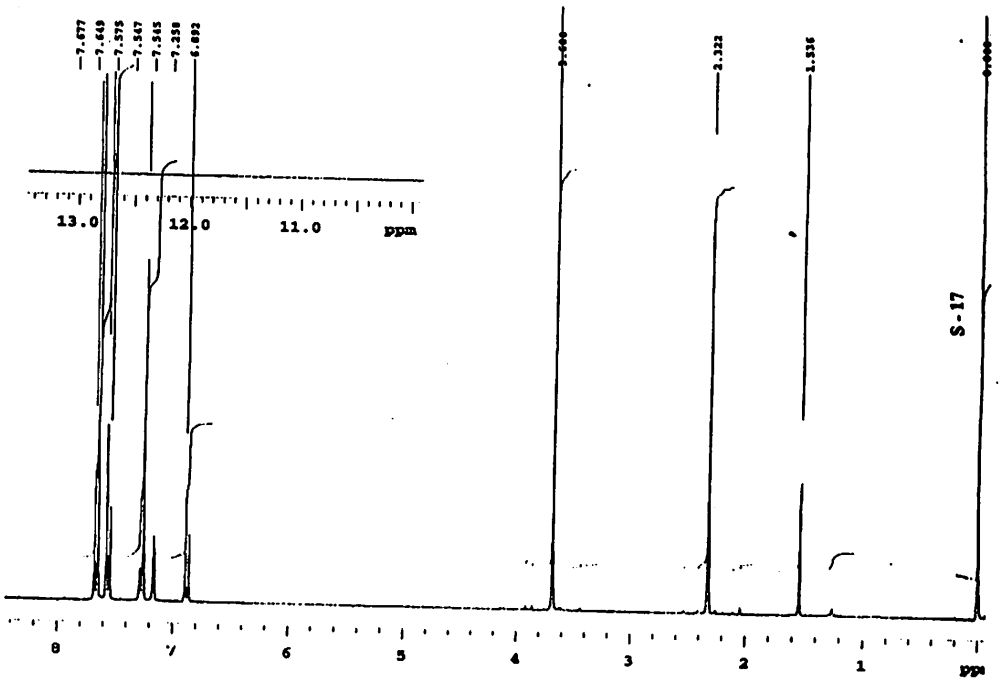
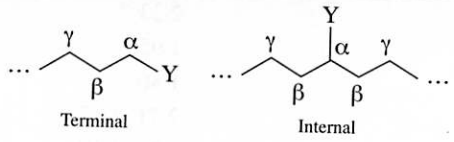


Table 14.1 The ^{13}C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

COMPOUND	C-1	C-2	C-3	C-4	C-5
Methane	−2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)	

From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. p. 236.

Table 14.2 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal[a] (+ downfield, − upfield)



Y	□ TERMINAL	□ INTERNAL	□ TERMINAL	□ INTERNAL	
CH_3	+ 9	+ 9	+ 6	+ 6	−2
$CH=CH_2$	+20		+ 6		−0.5
C CH	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+3	+ 2	−2
COO^-	+25	+20	+5	+ 3	−2
COOR	+20	+17	+3	+ 2	−2
COCl	+33	28		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+ 9	+ 7	−2
OH	+48	+41	+10	+ 8	−5
OR	+58	+51	+ 8	+ 5	−4
OCOR	+51	+45	+ 6	+ 5	−3
NH_2	+29	+24	+11	+10	−5
NH_3	+26	+24	+ 8	+ 6	−5
NHR	+37	+31	+ 8	+ 6	−4
NR_2	+42		+ 6		−3
NR_3	+31		+ 5		−7
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+ 7		−3
F	+68	+63	+ 9	+ 6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	− 6	+ 4	+11	+12	−1

[a]Add these increments to the shift values of the appropriate carbon atom in Table 12.1.

Source: F. W. Wehrli, A. P. Marchand, and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra.* 2nd ed., London: Heyden, 1983.

From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.3, p. 236.

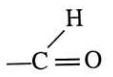
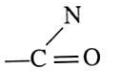
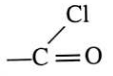
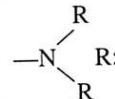
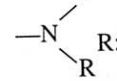
Table 14.3 Chemical Shifts of Alkyne Protons

HC≡CR	1.73–1.88
HC≡C—COH	2.23
HC≡C—C≡CR	1.95
HC≡CH	1.80
HC≡CAR	2.71–3.37
HC≡C—C≡CR	2.60–3.10

From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table D.3, p. 217.

Table 14.4 Calculation of ^{1}H NMR Chemical Shifts for Alkenes

See Figure 14.12 for more information.

	Z				Z		
SUBSTITUENT R	GEM	CIS	TRANS	SUBSTITUENT R	GEM	CIS	TRANS
—H	0	0	0		1.03	0.97	1.21
—Alkyl	0.44	−0.26	−0.29				
—Alkyl-ring[a]	0.71	−0.33	−0.30				
—CH_20, —CH_2I	0.67	−0.02	−0.07		1.37	0.93	0.35
—CH_2S	0.53	−0.15	−0.15				
—CH_2Cl, —CH_2Br	0.72	0.12	0.07		1.10	1.41	0.99
—CH_2N	0.66	−0.05	−0.23	—OR, R:aliph	1.18	−1.06	−1.28
—C≡C	0.50	0.35	0.10	—OR, R:conj[b]	1.14	−0.65	−1.05
—C N	0.23	0.78	0.58	—OCOR	2.09	−0.40	−0.67
—C=C	0.98	−0.04	−0.21	—Aromatic	1.35	0.37	−0.10
—C=C conj[b]	1.26	0.08	−0.01	—Cl	1.00	0.19	0.03
—C=O	1.10	1.13	0.81	—Br	1.04	0.40	0.55
—C=O conj[b]	1.06	1.01	0.95	 R: aliph	0.69	−1.19	−1.31
—COOH	1.00	1.35	0.74				
—COOH conj[b]	0.69	0.97	0.39	 R:conj[b]	2.30	−0.73	−0.81
—COOR	0.84	1.15	0.56				
—COOR conj[b]	0.68	1.02	0.33				
				—SR	1.00	−0.24	−0.04
				—SO_2	1.58	1.15	0.95

[a]Alkyl ring indicates that the double bond is part of the ring 

[b]The *Z* factor for the conjugated substituent is used when either the substituent or the double bond is further conjugated with other groups.

From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991; and C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta,* 49, 164 (1966). Reprinted with permission of John Wiley and Sons, Inc. Appendix D, p. 215.

Table 14.5 Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm, + downfield, − upfield). Carbon Atom of Substituents in parts per million from TMS[a]

SUBSTITUENT	C-1 (ATTACHMENT)	C-2	C-3	C-4	C OF SUBSTITUENT (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	9.3	+0.7	−0.1	−2.9	21.3
CH_2CH_3	+15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	+22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH_3)
$CH{=}CH_2$	+9.1	−2.4	+0.2	−0.5	137.1 (CH), 113.3 (CH_2)
$C{\equiv}CH$	−5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C_6H_5	+12.1	−1.8	−0.1	−1.6	
CH_2OH	+13.3	−0.8	−0.6	−0.4	64.5
CH_2OCCH_3 (O)	+7.7	~0.0	~0.0	~0.0	20.7 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	+26.6	−12.7	+1.6	−7.3	
OCH_3	+31.4	−14.4	+1.0	−7.7	54.1
OC_6H_5	+29.0	−9.4	+1.6	−5.3	
$OCCH_3$ (O)	+22.4	−7.1	−0.4	−3.2	23.9 (CH_3), 169.7 (C=O)
CH (O)	+8.2	+1.2	+0.6	+5.8	192.0
CCH_3 (O)	+7.8	−0.4	−0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
CC_6H_5 (O)	+9.1	+1.5	−0.2	+3.8	196.4 (C=O)
CCF_3 (O)	−5.6	+1.8	+0.7	+6.7	
COH (O)	+2.9	+1.3	+0.4	+4.3	168.0
$COCH_3$ (O)	+2.0	+1.2	−0.1	+4.8	51.0 (CH_3), 166.8 (C=O)
CCl (O)	+4.6	+2.9	+0.6	+7.0	168.5
$C{\equiv}N$	−16.0	+3.6	+0.6	+4.3	119.5
NH_2	+19.2	−12.4	+1.3	−9.5	
$N(CH_3)_2$	+22.4	−15.7	+0.8	−11.8	40.3
$NHCCH_3$ (O)	+11.1	−9.9	+0.2	−5.6	

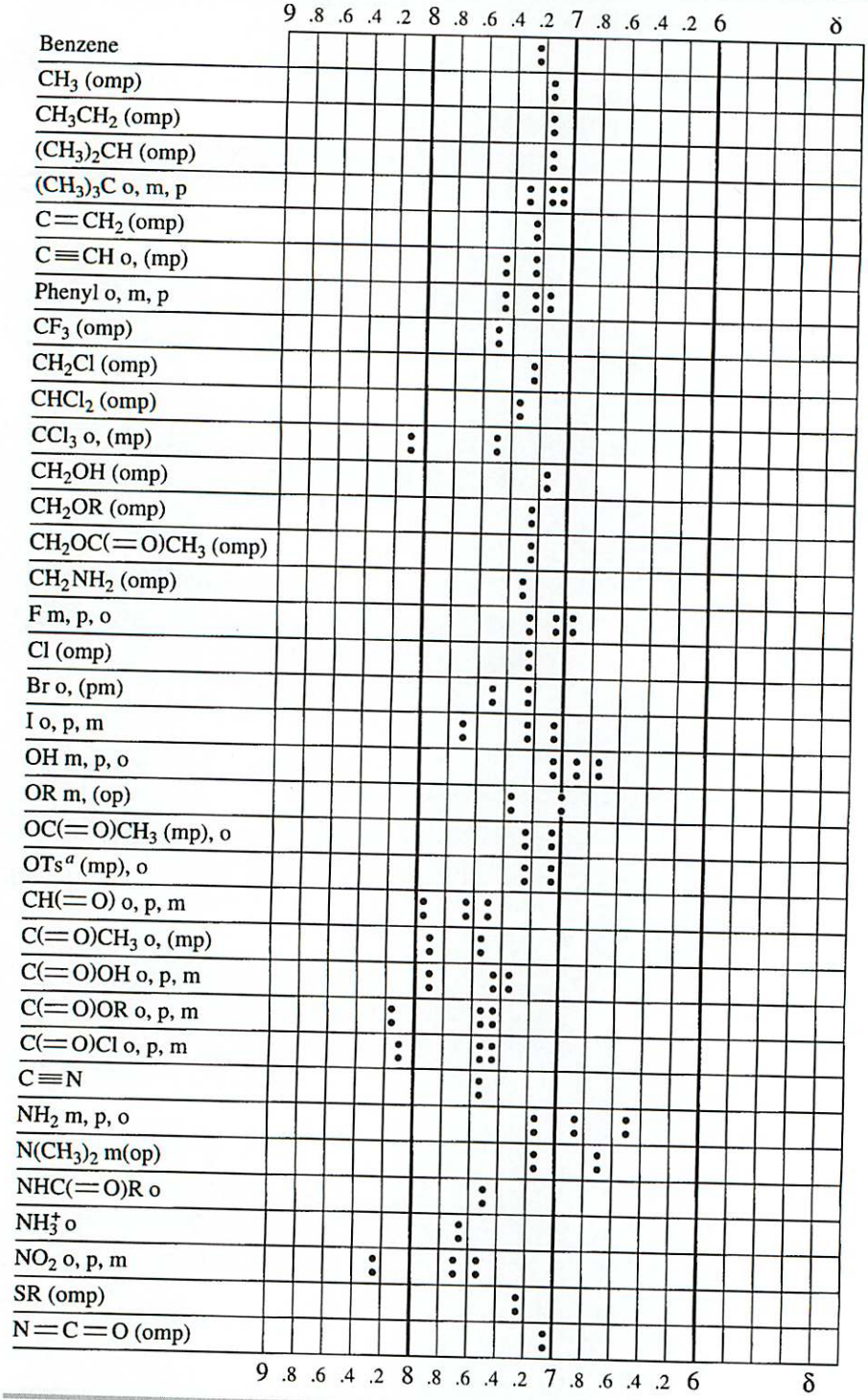
Table 14.5 (Continued)

SUBSTITUENT	C-1 (ATTACHMENT)	C-2	C-3	C-4	C OF SUBSTITUENT (ppm from TMS)
NO_2	+19.6	−5.3	+0.9	+6.0	
N═C═O	+5.7	−3.6	+1.2	−2.8	129.5
F	+35.1	−14.3	+0.9	−4.5	
Cl	+6.4	+0.2	+1.0	−2.0	
Br	−5.4	+3.4	+2.2	−1.0	
I	−32.2	+9.9	+2.6	−7.3	
CF_3	+2.6	−3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	−3.3	
SCH_3	+10.2	−1.8	+0.4	−3.6	15.9
SO_2NH_2	+15.3	−2.9	+0.4	+3.3	
$Si(CH_3)_3$	+13.4	+4.4	−1.1	−1.1	

[a]See D. E. Ewing, *Org. Magn. Reson.*, 12, 499 (1979) for chemical shifts of 709 monosubstituted benzenes.

From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Table 5.9, p. 240.

Table 14.6 Chemical Shifts of Protons on Monosubstituted Benzene Rings



[a] OTs = *p*-Toluenesulfonyloxy group.

From R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th ed., New York: John Wiley and Sons, Inc., 1991. Reprinted with permission of John Wiley and Sons, Inc. Chart D.1, p. 218.