

Chapter 13 – Structure Determination: Nuclear Magnetic Resonance Spectroscopy

Chapter Outline

I. Principles of Nuclear Magnetic Resonance Spectroscopy (Sections 13.1 – 13.3).

A. Theory of NMR Spectroscopy (Section 13.1).

1. Many nuclei behave as if they were spinning about an axis.
 - a. The positively charged nuclei produce a magnetic field that can interact with an externally applied magnetic field.
 - b. The ^{13}C nucleus and the ^1H nucleus behave in this manner.
 - c. In the absence of an external magnetic field the spins of magnetic nuclei are randomly oriented.
2. When a sample containing these nuclei is placed between the poles of a strong magnet, the nuclei align themselves either with the applied field or against the applied field.

The parallel orientation is slightly lower in energy and is slightly favored.
3. If the sample is irradiated with radiofrequency energy of the correct frequency, the nuclei of lower energy absorb energy and "spin-flip" to the higher energy state.
 - a. The magnetic nuclei are in resonance with the applied radiation.
 - b. The frequency of the rf radiation needed for resonance depends on the magnetic field strength and on the identity of the magnetic nuclei.
 - i. In a strong magnetic field, higher frequency rf energy is needed.
 - ii. At a magnetic field strength of 4.7 T, rf energy of 200 MHz is needed to bring a ^1H nucleus into resonance, and energy of 50 MHz for ^{13}C .
4. Nuclei with an odd number of protons and nuclei with an odd number of neutrons show magnetic properties.

B. The nature of NMR absorptions (Section 13.2).

1. Not all ^{13}C nuclei and not all ^1H nuclei absorb at the same frequency.
 - a. Each magnetic nucleus is surrounded by electrons that set up their own magnetic fields.
 - b. These small fields oppose the applied field and shield the magnetic nuclei.
 - i. $B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}}$
 - ii. This expression shows that the magnetic field felt by a nucleus is less than the applied field.
 - c. These shielded nuclei absorb at slightly different values of magnetic field strength.
 - d. A sensitive NMR spectrometer can detect these small differences.
 - e. Thus, NMR spectra can be used to map the carbon–hydrogen framework of a molecule.
2. NMR spectra.
 - a. The horizontal axis shows effective field strength, and the vertical axis shows intensity of absorption.
 - b. Each peak corresponds to a chemically distinct nucleus.
 - c. Zero absorption is at the bottom.
 - d. Absorptions due to both ^{13}C and ^1H can't both be observed at the same time.
3. Operation of an NMR spectrometer
 - a. A solution of a sample is placed in a thin glass tube between the poles of a magnet.
 - b. The strong magnetic field causes the nuclei to align in either of the two possible orientations.

- c. The strength of the applied magnetic field is varied, holding the rf frequency constant.
- d. Chemically distinct nuclei come into resonance at slightly different values of B .
- e. A detector monitors the absorption of rf energy.
- f. The signal is amplified and recorded.
4. Time scale of NMR absorptions.
 - a. The time scale (10^{-3} s) of NMR spectra is much slower than that of most other spectra.
 - b. If a process occurs faster than the time scale of NMR, absorptions are observed as "time-averaged" processes.
NMR records only a single spectrum.
 - c. NMR can be used to measure rates and activation energies of fast processes.
 - i. Because cyclohexane ring-flips are very fast at room temperature, only a single peak is observed for equatorial and axial hydrogens at room temperature.
 - ii. At -90° , both axial and equatorial hydrogens can be identified.
- C. Chemical Shifts (Section 13.3).
 1. Field strength increases from left (downfield) to right (upfield).
 - a. Nuclei that absorb downfield require a lower field strength for resonance and are deshielded.
 - b. Nuclei that absorb upfield require a higher field strength and are shielded.
 2. TMS is used as a reference point in both ^{13}C NMR and ^1H NMR.
The TMS absorption occurs upfield of other absorptions, and is set as the zero point.
 3. The chemical shift is the position on the chart where a nucleus absorbs energy.
 4. NMR charts are calibrated by using an arbitrary scale – the delta scale.
 - a. One δ equals 1 ppm of the spectrometer operating frequency.
 - b. By using this system, all chemical shifts occur at the same value of δ , regardless of the spectrometer operating frequency.
 5. NMR absorptions occur over a narrow range.
 - a. ^1H absorptions occur 0–10 δ downfield from TMS.
 - b. ^{13}C absorptions occur 1–220 δ downfield from TMS.
 - c. The chances of accidental overlap can be reduced by using an instrument with a higher field strength.
- II. ^{13}C NMR spectroscopy (Sections 13.4 – 13.7).
 - A. Signal averaging and FT-NMR (Section 13.4).
 1. The low natural abundance of ^{13}C (1.1%) makes it difficult to observe ^{13}C peaks because of background noise.
 2. If hundreds of individual runs are averaged, the background noise cancels.
This technique takes a long time.
 3. In FT-NMR, all signals are recorded simultaneously.
 - a. The sample is irradiated with a pulse of rf energy that covers all useful frequencies.
 - b. The resulting complex signal must be mathematically manipulated before display.
 - c. FT-NMR takes only a few seconds per spectrum.
 4. FT-NMR and signal averaging provide increased speed and sensitivity.
 - a. Only a few mg of sample are needed for ^{13}C NMR spectra.
 - b. Only a few μg of sample are needed for ^1H NMR spectra.
 - B. Characteristics of ^{13}C NMR spectroscopy (Section 13.5).
 1. Each distinct carbon shows a single line.
 2. The chemical shift depends on the electronic environment within a molecule.
 - a. Carbons bonded to electronegative atoms absorb downfield.

- b. Carbons with sp^3 hybridization absorb in the range 0–90 δ .
 - c. Carbons with sp^2 hybridization absorb in the range 110–220 δ .
Carbonyl carbons absorb in the range 160–220 δ .
 - 3. Symmetry reduces the number of absorptions.
 - 4. Peaks aren't uniform in size.
 - C. DEPT ^{13}C NMR spectra (Section 13.6).
 - 1. With DEPT experiments, the number of hydrogens bonded to each carbon can be determined.
 - 2. DEPT experiments are run in three stages.
 - a. A broadband decoupled spectrum gives the chemical shifts of all carbons.
 - b. A DEPT-90 spectrum shows signals due only to CH carbons.
 - c. A DEPT-135 spectrum shows CH_3 and CH resonances as positive signals, and CH_2 resonances as negative signals.
 - 3. Interpretation of DEPT spectra.
 - a. Subtract all peaks in the DEPT-135 spectrum from the broadband-decoupled spectrum to find C.
 - b. Use DEPT-90 spectrum to identify CH.
 - c. Use negative DEPT-135 peaks to identify CH_2 .
 - d. Subtract DEPT-90 peaks from positive DEPT-135 peaks to identify CH_3 .
 - D. Uses of ^{13}C NMR spectroscopy (Section 13.7).
 ^{13}C NMR spectroscopy can show the number of nonequivalent carbons in a molecule and can identify symmetry in a molecule.
- III. ^1H NMR Spectroscopy (Sections 13.8 – 13.13).
- A. Proton equivalence (Section 13.8).
 - 1. ^1H NMR can be used to determine the number of nonequivalent protons in a molecule.
 - 2. If it is not possible to decide quickly if two protons are equivalent, replace each proton by $-\text{X}$.
 - a. If the protons are unrelated, the products formed by replacement are constitutional isomers.
 - b. If the protons are chemically identical, the same product will form, regardless of which proton is replaced, and the protons are homotopic.
 - c. If the replacement products are enantiomers, the protons are enantiotopic.
 - d. If the molecule contains a chirality center, the replacement products are diastereomers, and the protons are diastereotopic.
 - B. Chemical shifts in ^1H NMR spectroscopy (Section 13.9).
 - 1. Chemical shifts are determined by the local magnetic fields surrounding magnetic nuclei.
 - a. More strongly shielded nuclei absorb upfield.
 - b. Less shielded nuclei absorb downfield.
 - 2. Most ^1H NMR chemical shifts are in the range 0–10 δ .
 - a. Protons that are sp^3 -hybridized absorb at higher field strength.
 - b. Protons that are sp^2 -hybridized absorb at lower field strength.
 - c. Protons on carbons that are bonded to electronegative atoms absorb at lower field strength.
 - 3. The ^1H NMR spectrum can be divided into 5 regions:
 - a. Saturated (0–1.5 δ).
 - b. Allylic (1.5–2.5 δ).
 - c. H bonded to C next to an electronegative atom (2.5–4.5 δ).
 - d. Vinylic (4.5–6.5 δ).
 - e. Aromatic (6.5–8.0).
 - f. Aldehyde and carboxylic acid protons absorb even farther downfield.

- C. Integration of ^1H NMR signals: proton counting (Section 13.10).
1. The area of a peak is proportional to the number of protons causing the peak.
 2. Integrated peak areas are superimposed over a spectrum as a stair-step line.
 3. To compare two peaks, measure their relative heights.
- D. Spin-spin splitting (Section 13.11).
1. The tiny magnetic field produced by one nucleus can affect the magnetic field felt by other nuclei.
 2. Protons that have n equivalent neighboring protons show a peak in their ^1H NMR spectrum that is split into $n + 1$ smaller peaks (a multiplet).
 3. This splitting is caused by the coupling of spins of neighboring nuclei.
 4. The distance between peaks in a multiplet is called the coupling constant (J).
 - a. The value of J is usually 0–18 Hz.
 - b. The value of J is determined by the geometry of the molecule and is independent of the spectrometer operating frequency.
 - c. The value of J is shared between both groups of hydrogens whose spins are coupled.
 - d. By comparing values of J , it is possible to know the atoms whose spins are coupled.
 5. Three rules for spin-spin splitting in ^1H NMR:
 - a. Chemically identical protons don't show spin-spin splitting.
 - b. The signal of a proton with n equivalent neighboring protons is split into a multiplet of $n + 1$ peaks with coupling constant J .
 - c. Two groups of coupled protons have the same value of J .
 6. Spin-spin splitting isn't seen in ^{13}C NMR.
 - a. Although spin-spin splitting can occur between carbon and other magnetic nuclei, the spectrometer operating conditions suppress it.
 - b. Coupling between the spins of two ^{13}C nuclei isn't seen because of the low probability that two ^{13}C nuclei would be adjacent.
- E. Complex spin-spin splitting (Section 13.12).
1. At times the signals in a ^1H NMR absorption overlap accidentally.
 2. Also, signals may be split by two or more nonequivalent kinds of protons.
 - a. To understand the effect of multiple coupling, it helps to draw a tree diagram.
 - b. In this type of multiplet, the peaks on one side of the multiplet may be larger than those on the other side.
 - i. The larger peaks are on the side nearer to the coupled partner.
 - ii. This helps identify the nuclei whose spins are coupled.
- F. ^1H NMR can be used to identify the products of reactions. (Section 13.13).

Solutions to Problems

13.1

$$E = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{\lambda \text{ (in m)}}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ m/s}}{\nu}; \quad \nu = 187 \text{ MHz} = 1.87 \times 10^8 \text{ Hz}$$

$$\lambda = \frac{3.0 \times 10^8 \text{ m/s}}{1.87 \times 10^8 \text{ Hz}} = 1.60 \text{ m}$$

$$E = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{1.60} = 7.5 \times 10^{-5} \text{ kJ/mol}$$

Compare this value with $E = 8.0 \times 10^{-5} \text{ kJ/mol}$ for ^1H . It takes slightly less energy to spin-flip a ^{19}F nucleus than to spin-flip a ^1H nucleus.

13.2

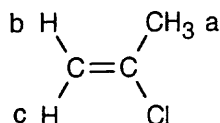
$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ m/s}}{\nu}; \nu = 300 \text{ MHz} = 3.0 \times 10^8 \text{ Hz}$$

$$\lambda = \frac{3.0 \times 10^8 \text{ m/s}}{3.0 \times 10^8 \text{ Hz}} = 1.0 \text{ m}$$

$$E = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{1.0} = 1.20 \times 10^{-4} \text{ kJ/mol}$$

Increasing the spectrometer frequency increases the amount of energy needed for resonance.

13.3



2-Chloropropene has three kinds of protons. Protons b and c differ because one is cis to the chlorine and the other is trans.

13.4

$$\delta = \frac{\text{Observed chemical shift (in Hz)}}{200 \text{ MHz}}$$

$$(a) \delta = \frac{1454 \text{ Hz}}{200 \text{ MHz}} = 7.27 \delta \text{ for } \text{CHCl}_3 \quad (b) \delta = \frac{610 \text{ Hz}}{200 \text{ MHz}} = 3.05 \delta \text{ for } \text{CH}_3\text{Cl}$$

$$(c) \delta = \frac{693 \text{ Hz}}{200 \text{ MHz}} = 3.46 \delta \text{ for } \text{CH}_3\text{OH} \quad (d) \delta = \frac{1060 \text{ Hz}}{200 \text{ MHz}} = 5.30 \delta \text{ for } \text{CH}_2\text{Cl}_2$$

13.5

$$(a) \delta = \frac{\text{Observed chemical shift (\# Hz away from TMS)}}{\text{Spectrometer frequency in MHz}}$$

Units of δ are parts per million. In this problem, $\delta = 2.1 \text{ ppm}$

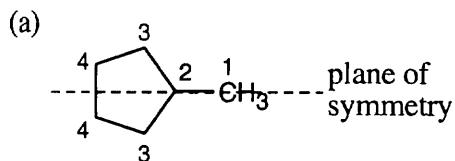
$$2.1 \text{ ppm} = \frac{\text{Observed chemical shift}}{200 \text{ (MHz)}}$$

$$420 \text{ Hz} = \text{Observed chemical shift}$$

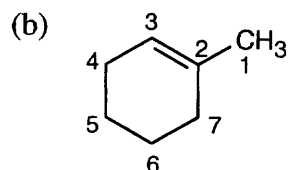
(b) If the ^1H NMR spectrum of acetone were recorded at 500 MHz, the position of absorption would still be 2.1 δ because measurements given in ppm or δ units are independent of the operating frequency of the NMR spectrometer.

$$(c) 2.1 \delta = \frac{\text{Observed chemical shift}}{500 \text{ (MHz)}}; \text{Observed chemical shift} = 1050 \text{ Hz}$$

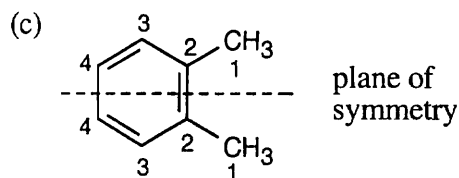
13.6

**Methylcyclopentane**

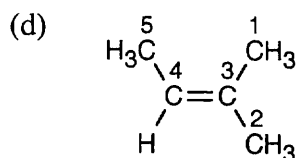
Four resonance lines are observed because of symmetry.

**1-Methylcyclohexene**

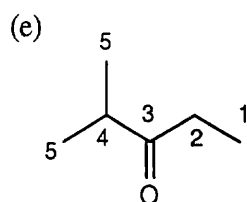
Seven lines are seen because no two carbons are equivalent

**1,2-Dimethylbenzene**

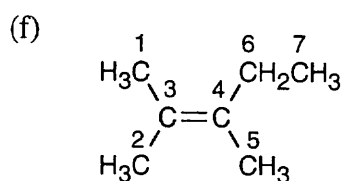
Four resonance lines are seen.

**2-Methyl-2-butene**

Five resonance lines are observed. Carbons 1 and 2 are nonequivalent because of the double bond stereochemistry.

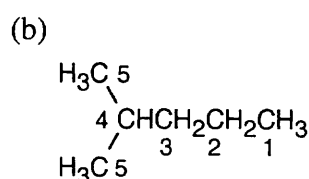
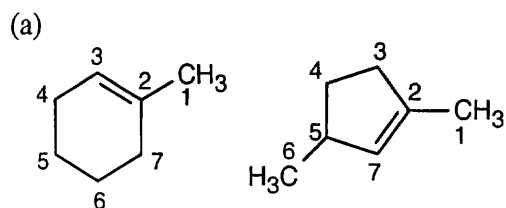


Five resonance lines are seen.

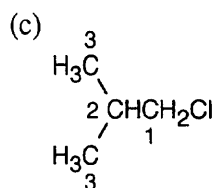


Seven resonance lines are seen.

13.7

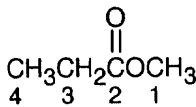


Two of the 6 carbons are equivalent.



Two of the 4 carbons are equivalent.

- 13.8** Methyl propanoate has 4 unique carbons, and each one absorbs in a specific region of the ^{13}C spectrum. The absorption (4) has the lowest value of δ and occurs in the $-\text{CH}_3$ region of the ^{13}C spectrum. Absorption (3) occurs in the $-\text{CH}_2-$ region. The methyl group (1) is next to an electronegative atom and absorbs downfield from the other two absorptions. The carbonyl carbon (2) absorbs far downfield.

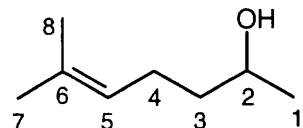
	δ (ppm)	Assignment
	9.3	4
	27.6	3
	51.4	1
	174.6	2

- 13.9 Strategy:** The top spectrum shows all eight ^{13}C NMR peaks. The middle spectrum (DEPT-90) shows only peaks due to CH carbons. From the DEPT-90 spectrum, the absorption at 124 δ can be assigned to the vinyl carbon (5), and the absorption at 68 δ can be assigned to the $-\text{OH}$ carbon (2).

The DEPT-135 spectrum shows all but the quaternary carbon (6), which appears in the top spectrum at 132 δ . The top half of the DEPT-135 spectrum shows absorptions due to CH_3 carbons and CH carbons (which we have already identified). The 3 remaining peaks on the top of the DEPT-135 spectrum are due to methyl groups. Although we haven't learned enough to identify these peaks, the peak at 23 δ is due to carbon (1). The other two peaks arise from carbons (7) and (8) (18 δ , 26 δ).

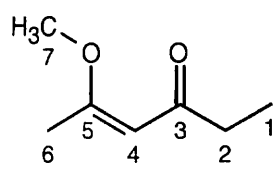
The bottom half of the DEPT-135 shows the two CH_2 carbons. Carbon (3) absorbs at 39 δ (negative), and carbon (4) absorbs at 24 δ (negative).

Solution:

	Carbon	Chemical Shift (δ)
	1	23
	2	68
	3	39 (negative)
	4	24 (negative)
	5	124
	6	132
	7, 8	18, 26

- 13.10 Strategy:** Identify the carbons as CH_3 , CH_2 , CH or quaternary, and use Figure 13.7 to find approximate values for chemical shifts. (When an actual spectrum is given, it is easier to assign the carbons to the chemical shifts.) Remember: DEPT-90 spectra identify CH carbons, and DEPT-135 spectra identify CH_3 carbons (positive peaks), CH carbons (positive peaks already identified), and CH_2 carbons (negative peaks). Quaternary carbons are identified in the broadband-decoupled spectrum, in which all peaks appear.

Solution:

	Carbon	Chemical Shift (δ)	DEPT-90?	DEPT-135?
	1	10–30	no	yes (positive)
	2	30–50	no	yes (negative)
	3	160–220	no	no
	4	110–150	yes	yes (positive)
	5	110–150	no	no
	6	10–30	no	yes (positive)
	7	50–90	no	yes (positive)

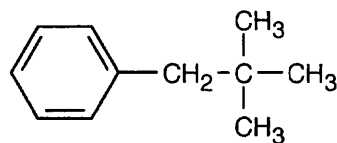
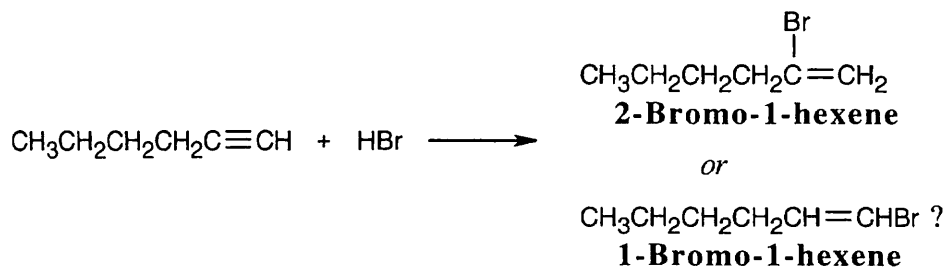
13.11 Strategy: Always start this type of problem by calculating the degree of unsaturation of the unknown compound. $C_{11}H_{16}$ has 4 degrees of unsaturation. Since the unknown hydrocarbon is aromatic, a benzene ring accounts for all four degrees of unsaturation.

Next, look for elements of symmetry. Although the molecular formula indicates 11 carbons, only 7 peaks appear in the ^{13}C NMR spectrum, indicating a plane of symmetry. Four of the 7 peaks are due to aromatic carbons, indicating a benzene ring that is probably monosubstituted. (Prove to yourself that a monosubstituted benzene ring has 4 different kinds of carbons).

Solution: The DEPT-90 spectrum shows that 3 of the kinds of carbons in the aromatic ring are CH carbons. The positive peaks in the DEPT-135 spectrum include these three peaks, along with the peak at 29.5 δ , which is due to a CH_3 carbon. The negative peak in the DEPT-135 spectrum is due to a CH_2 carbon.

Two peaks remain unidentified and are thus quaternary carbons; one of them is aromatic.

At this point, the unknown structure is a monosubstituted benzene ring with a substituent that contains CH_2 , C, and CH_3 carbons. A structure for the unknown compound that satisfies all data:

**13.12**

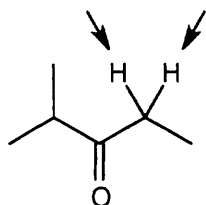
The two possible products are easy to distinguish by using ^{13}C NMR. 2-Bromo-1-hexene, the actual product formed, shows no peaks in its DEPT-90 ^{13}C NMR spectrum because it has no CH carbons. The other possible product, 1-bromo-1-hexene, shows 2 peaks in its DEPT-90 spectrum.

13.13 Strategy: First, check for protons that are unrelated (none appear in this problem). Next, look for molecules that already have chirality centers. Replacement of a $-\text{CH}_2-$ proton by X in (d) and (e) produces a second chirality center, and the two possible replacement products are diastereomers. Thus, the indicated protons in (d) and (e) are diastereotopic.

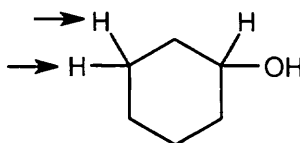
Finally, for the other molecules, mentally replace each of the two hydrogens in the indicated set with X, a different group. In (a), the resulting products are enantiomers, and the protons are enantiotopic. Replacement of the protons in (b) produces two chirality centers (the carbon bearing the hydroxyl group is now chiral) and the indicated protons are diastereotopic. Replacement of one of the methyl protons in each of the groups in (c) produces a pair of double-bond isomers that are diastereomers; these protons are diastereotopic. The protons in (f) are homotopic.

Solution:

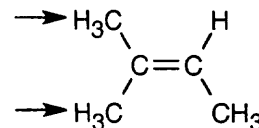
(a) enantiotopic



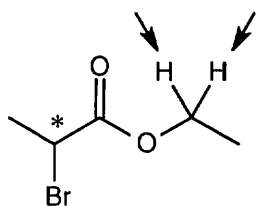
(b) diastereotopic



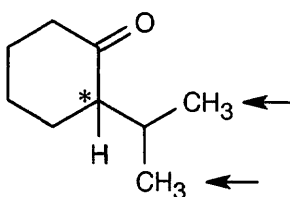
(c) diastereotopic



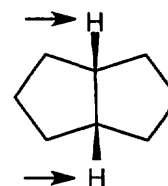
(d) diastereotopic



(e) diastereotopic

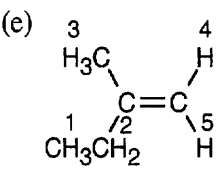
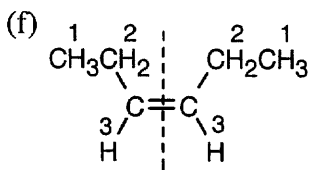


(f) homotopic

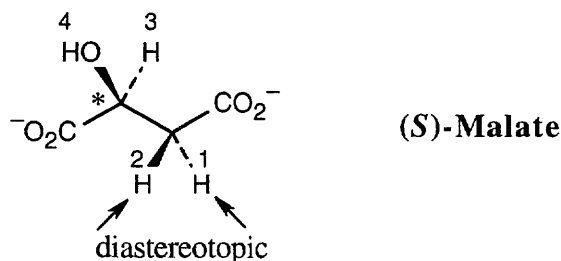


13.14

Compound	Kinds of non-equivalent protons	Compound	Kinds of non-equivalent protons
(a) $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\text{Br}$	2	(b) $\overset{1}{\text{CH}_3}\overset{2}{\text{OCH}_2}\overset{3}{\text{CH}}\overset{4}{\text{CH}_3}$	4
(c) $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\text{NO}_2$	3	(d)	4

Compound	Kinds of non-equivalent protons	Compound	Kinds of non-equivalent protons
(e) 	5	(f) 	3
The two vinylic protons are nonequivalent.		plane of symmetry	

13.15

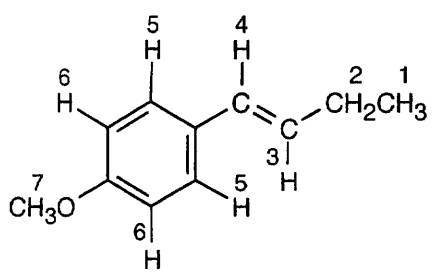


Because (*S*)-malate already has a chirality center (starred), the two protons next to it are diastereotopic and absorb at different values. The ^1H NMR spectrum of (*S*)-malate has four absorptions.

13.16

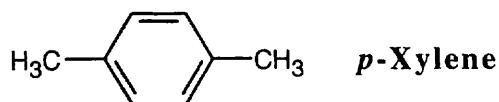
Compound	δ	Kind of proton
(a) C_6H_{12}	1.43	secondary alkyl
(b) CH_3COCH_3	2.17	methyl ketone
(c) C_6H_6	7.37	aromatic
(d) CH_2Cl_2	5.30	protons adjacent to two halogens
(e) OHCCHO	9.70	aldehyde
(f) $(\text{CH}_3)_3\text{N}$	2.12	methyl protons adjacent to nitrogen

13.17

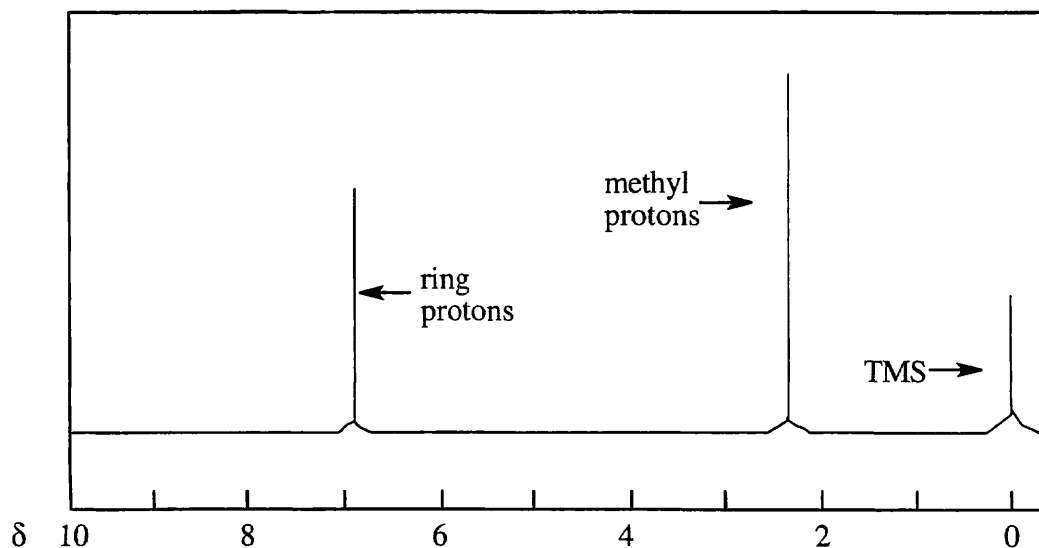
	Proton	δ	Kind of proton
	1	1.0	primary alkyl
	2	1.8	allylic
	3	6.1	vinylic
	4	6.3	vinylic (different from proton 3)
	5	7.2	aromatic
	6	6.8	aromatic
	7	3.8	ether

This compound has seven different kinds of protons. Notice that the two protons labeled 5 are equivalent, as are the two protons labeled 6 because of rotation around the bond joining the aromatic ring and the alkenyl side chain.

13.18

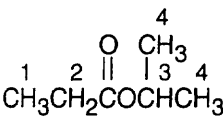
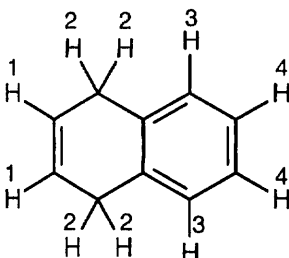


There are two absorptions in the ^1H NMR spectrum of *p*-xylene. The four ring protons absorb at 7.0 δ , and the six methyl-group protons absorb at 2.3 δ . The peak ratio of methyl protons:ring protons is 3:2.



13.19

Compound	Proton	Number of Adjacent Protons	Splitting
(a) $\overset{1}{\text{CH}}\text{Br}_2\overset{2}{\text{CH}}_3$	1	3	quartet
	2	1	doublet
(b) $\overset{1}{\text{CH}}_3\text{OCH}_2\overset{2}{\text{CH}}_2\overset{3}{\text{CH}}_2\text{Br}$	1	0	singlet
	2	2	triplet
	3	2	triplet
(c) $\overset{1}{\text{Cl}}\text{CH}_2\overset{2}{\text{CH}}_2\overset{1}{\text{CH}}_2\text{Cl}$	1	2	triplet
	2	4	quintet
(d) $\begin{array}{ccccccc} & 1 & & & & & \\ & \text{H}_3\text{C} & \text{O} & & & & \\ & & & & & & \\ 1 & \text{CH}_3 & \text{CH} & \text{CO} & \text{CH}_2 & \text{CH}_3 & \\ & 1 & 2 & 3 & 4 & & \end{array}$	1	1	doublet
	2	6	septet
	3	3	quartet
	4	2	triplet

Compound	Proton	Number of Adjacent Protons	Splitting
(e) 	1	2	triplet
	2	3	quartet
	3	6	septet
	4	1	doublet
(f) 	1	2	triplet
	2	1	doublet
	3	1	multiplet
	4	1	multiplet

The splitting patterns for protons 3 and 4 are complex and are not explained in the text.

13.20 Strategy: Calculate the degree of unsaturation, and note the number of peaks to see if symmetry is present.

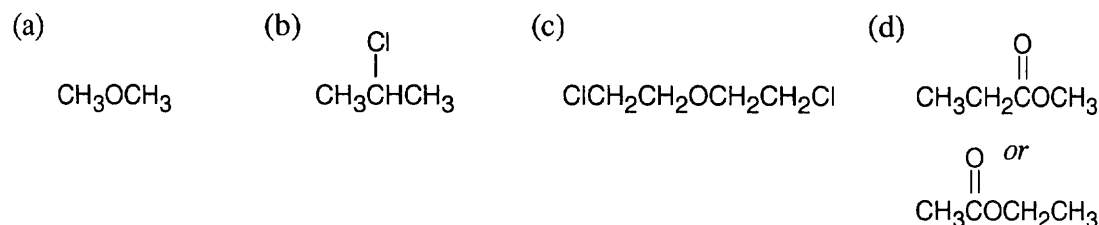
(a) This compound has no degrees of unsaturation and only one kind of hydrogen. The only possible structure is CH_3OCH_3 .

(b) Again, this compound has no degrees of unsaturation and has two kinds of hydrogens. The compound is 2-chloropropane.

(c) This compound, with no degrees of unsaturation, has two different kinds of hydrogen, each of which has two neighboring hydrogens.

(d) $\text{C}_4\text{H}_8\text{O}_2$; one degree of unsaturation and 3 different kinds of hydrogen.

Solution:

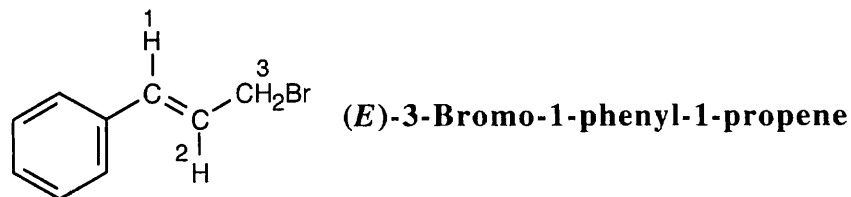


13.21 The molecular formula ($\text{C}_4\text{H}_{10}\text{O}$) indicates that the compound has no multiple bonds or rings. The ^1H NMR spectrum shows two signals, corresponding to two types of hydrogens in the ratio 33:50, or 2:3. Since the unknown contains 10 hydrogens, four protons are of one type and six are of the other type.

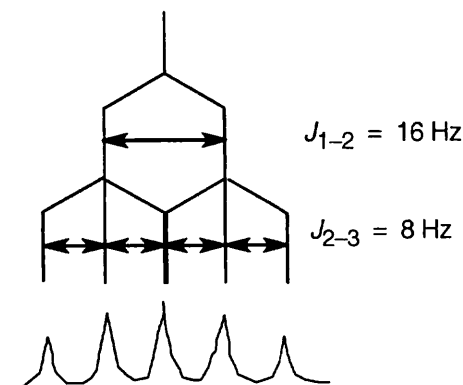
The upfield signal at 1.2 δ is due to saturated primary protons. The downfield signal at 3.5 δ is due to protons on carbon adjacent to an electronegative atom – in this case, oxygen.

The signal at 1.2 δ is a triplet, indicating two neighboring protons. The signal at 3.5 δ is a quartet, indicating three neighboring protons. The compound is diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$.

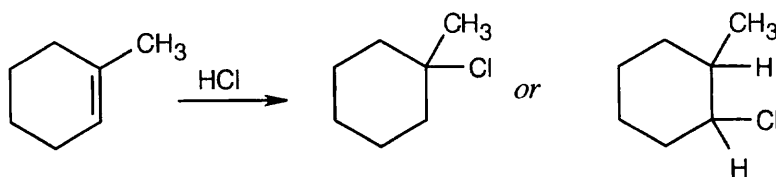
13.22



Coupling of the C2 proton to the C1 vinylic proton occurs with $J = 16$ Hz and causes the signal of the C2 proton to be split into a doublet. The C2 proton is also coupled to the two C3 protons with $J = 8$ Hz. This splitting causes each leg of the C2 proton doublet to be split into a triplet, producing six lines in all. Because of the size of the coupling constants, two of the lines coincide, and a five-line multiplet is observed.



13.23

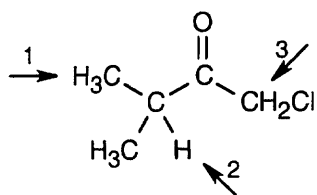


Focus on the ^1H NMR methyl group absorption. In the first product, the methyl group signal is unsplit; in the other product, it appears as a doublet. In addition, the second product shows a downfield absorption in the $2.5\delta - 4.0\delta$ region due to the proton bonded to a carbon that is also bonded to an electronegative atom. If you were to take the ^1H NMR spectrum of the reaction product, you would find an unsplit methyl group, and you could conclude that the product was 1-chloro-1-methylcyclohexane.

Visualizing Chemistry

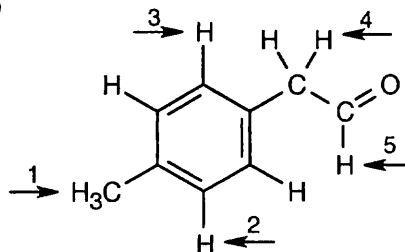
13.24

(a)



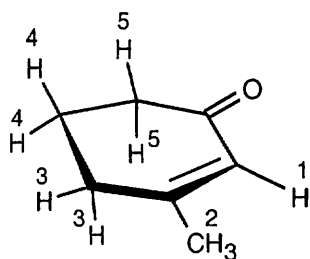
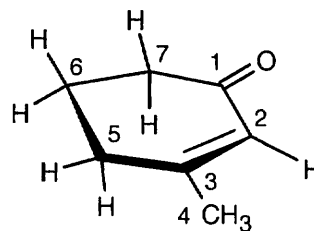
1. doublet
2. septet
3. singlet

(b)

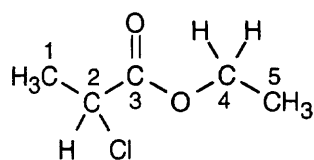
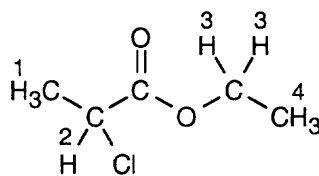


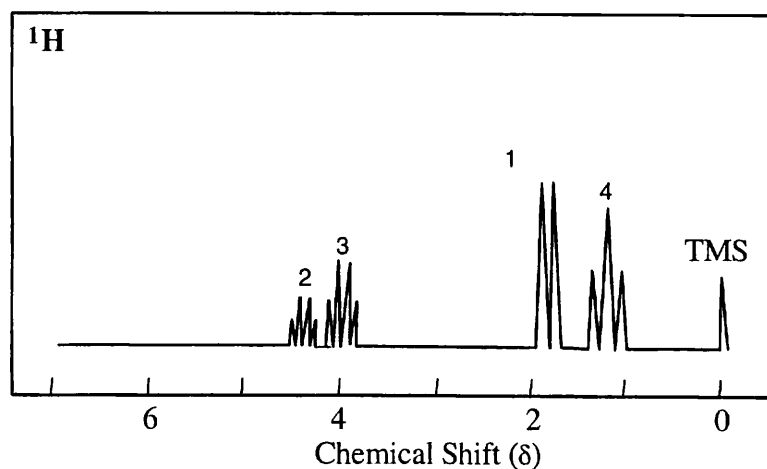
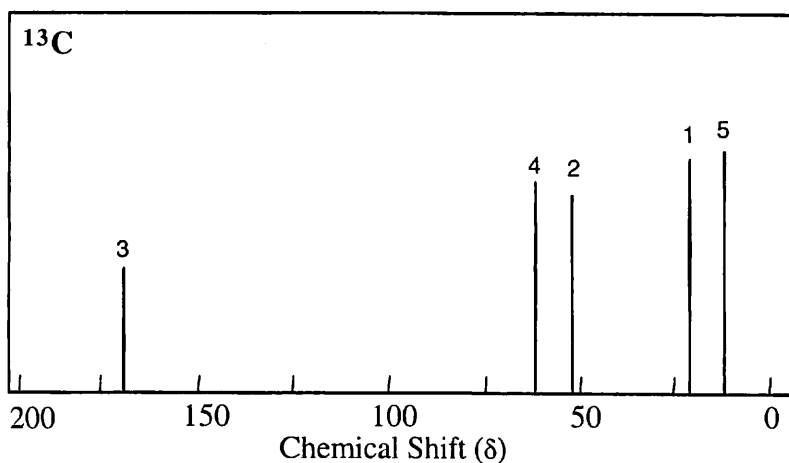
1. singlet
2. doublet
3. doublet
4. doublet
5. triplet

13.25

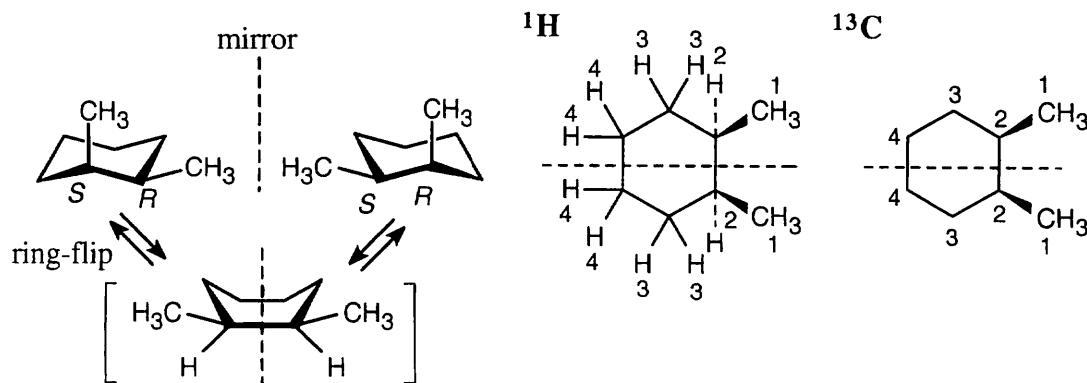
 ^1H NMR: 5 signals ^{13}C NMR: 7 signals

13.26 The compound has 5 different types of carbons and 4 different types of hydrogens.

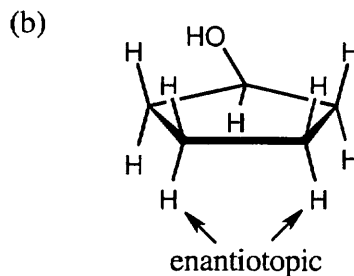
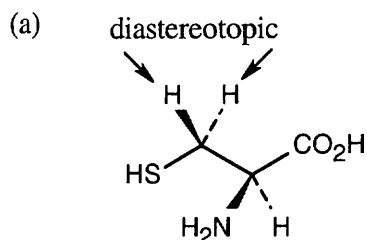
 ^{13}C  ^1H 



13.27 If you assign *R,S* configurations to the two carbons bonded to the methyl group, it is apparent that *cis*-1,2-dimethylcyclohexane is a meso compound. When the cyclohexane ring undergoes a ring-flip, the ring passes through an intermediate that has a plane of symmetry. Both the ^{13}C NMR spectrum and the ^1H NMR spectrum show 4 peaks.



- 13.28** (a) Because cysteine has a chirality center, the indicated protons are diastereotopic.
 (b) Imagine replacing first one, then the other, of the indicated protons with a substituent X. The two resulting compounds would be enantiomers.



Additional Problems

13.29

$$\delta = \frac{\text{Observed chemical shift (in Hz)}}{200 \text{ MHz}}$$

- (a) 2.18 δ (b) 4.78 δ (c) 7.52 δ

13.30 $\delta \times 300 \text{ MHz} = \text{Observed chemical shift (in Hz)}$

- (a) 630 Hz (b) 1035 Hz (c) 1890 Hz (d) 2310 Hz

13.31 (a) Since the symbol " δ " indicates ppm downfield from TMS, chloroform absorbs at 7.3 ppm.

(b)

$$\delta = \frac{\text{Observed chemical shift (in Hz)}}{\text{Spectrometer frequency in MHz}}$$

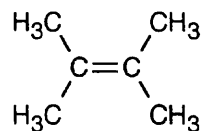
$$7.3 \text{ ppm} = \frac{\text{chemical shift}}{360 \text{ MHz}}; 7.3 \text{ ppm} \times 360 \text{ MHz} = \text{chemical shift}$$

$$2600 \text{ Hz} = \text{chemical shift}$$

- (c) The value of δ is still 7.3 because the chemical shift measured in δ is independent of the operating frequency of the spectrometer.

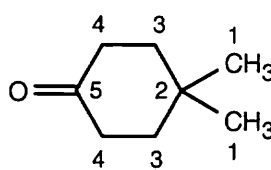
13.32

(a)

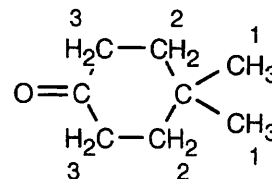


^{13}C : 2 absorptions
 ^1H : 1 absorption

(b)

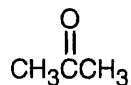


^{13}C : 5 absorptions
 (at room temperature)



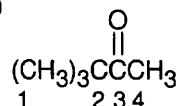
^1H : 3 absorptions
 (at room temperature)

(c)

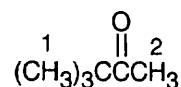


^{13}C : 2 absorptions
 ^1H : 1 absorption

(d)

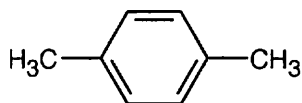


^{13}C : 4 absorptions



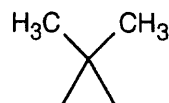
^1H : 2 absorptions

(e)



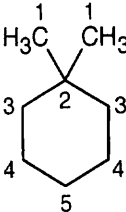
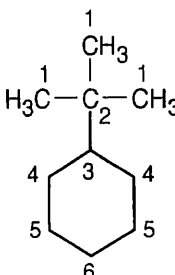
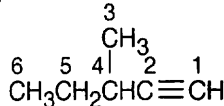
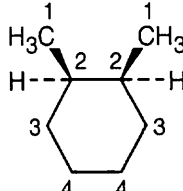
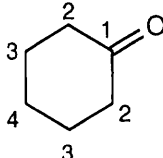
^{13}C : 3 absorptions
 ^1H : 2 absorptions

(f)



^{13}C : 3 absorptions
 ^1H : 2 absorptions

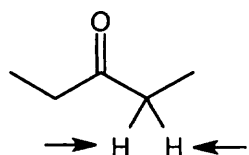
13.33–13.34

Compound	Number of ^{13}C Absorptions	Carbons Showing Peaks in DEPT-135 ^{13}C NMR Spectrum		
		Positive Peaks	Negative Peaks	No Peaks
(a) 	5	carbon 1	carbons 3,4,5	carbon 2
(b) $\text{CH}_3\text{CH}_2\text{OCH}_3$	3	carbons 1,3	carbon 2	
(c) 	6	carbons 1,3	carbons 4,5,6	carbon 2
(d) 	6	carbons 1,3,4,6	carbon 5	carbon 2
(e) 	4	carbons 1,2	carbons 3,4	
(f) 	4		carbons 2,3,4	carbon 1

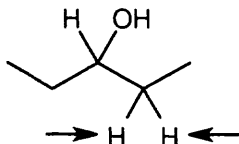
13.35 ^{13}C NMR absorptions occur over a range of 250 ppm, while ^1H NMR absorptions generally occur over a range of only 10 ppm. The spread of peaks in ^{13}C NMR is therefore much greater, so accidental overlap is less likely. In addition, normal ^{13}C NMR spectra are uncomplicated by spin–spin splitting, and the total number of lines is smaller.

13.36 A nucleus that absorbs at 6.50 δ is less shielded than a nucleus that absorbs at 3.20 δ and thus requires a weaker applied field to come into resonance. A shielded nucleus feels a smaller effective field, and a stronger applied field is needed to bring it into resonance.

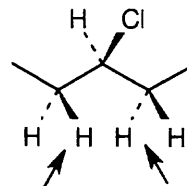
13.37 (a) enantiotopic



(b) diastereotopic



(c) diastereotopic

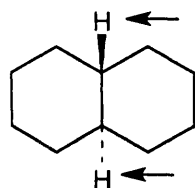


Refer to Problem 13.13 for help. The protons in (c) are diastereotopic because the molecules that result from replacement of the indicated hydrogens are diastereomers (prove it to yourself with models).

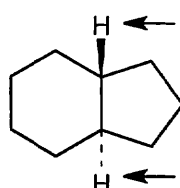
13.38

Compound	Kinds of non-equivalent protons	Compound	Kinds of non-equivalent protons
(a)	4	(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$	4
(c)	2	(d)	6
(e)	5		

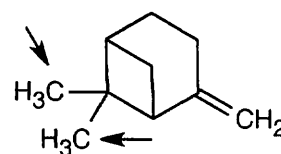
13.39 (a) homotopic



(b) enantiotopic



(c) diastereotopic



13.40

Lowest Chemical Shift \longrightarrow Highest Chemical Shift

CH_4 < Cyclohexane < CH_3COCH_3 < CH_2Cl_2 , $\text{H}_2\text{C}=\text{CH}_2$ < Benzene
 0.23 1.43 2.17 5.30 5.33 7.37

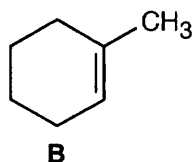
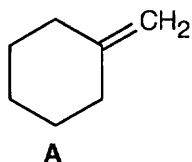
13.41

Compound	Number of peaks	Peak Assignment	Splitting Pattern	
(a) $\begin{array}{cc} 1 & 2 \\ (\text{CH}_3)_3\text{CH} \end{array}$	2	1 2	doublet multiplet (dectet)	(9H) (1H)
(b) $\begin{array}{ccccc} & & \text{O} & & \\ & & & & \\ 1 & 2 & & 3 & \\ \text{CH}_3 & \text{CH}_2 & & \text{COCH}_3 & \end{array}$	3	1 2 3	triplet quartet singlet	(3H) (2H) (3H)
(c) $\begin{array}{ccc} & 2 & 1 \\ & \text{H} & \text{CH}_3 \\ & \diagdown & / \\ & \text{C} = \text{C} & \\ / & & \diagdown \\ 1 & & 2 \\ \text{H}_3\text{C} & & \text{H} \end{array}$	2	1 2	doublet quartet	(6H) (2H)

13.42

	Peak Assignment	Splitting Pattern	
$\begin{array}{ccccccc} & & \text{O} & & & & \\ & & & & & & \\ 1 & 2 & & 3 & 4 & & \\ \text{CH}_3 & \text{CH}_2 & & \text{COCH} & (\text{CH}_3)_2 & & \end{array}$	1 2 3 4	triplet quartet septet doublet	(3H) (2H) (1H) (6H)

13.43 Use of ^{13}C NMR to distinguish between the two isomers has been described in the text in Section 13.7. ^1H NMR can also be useful.

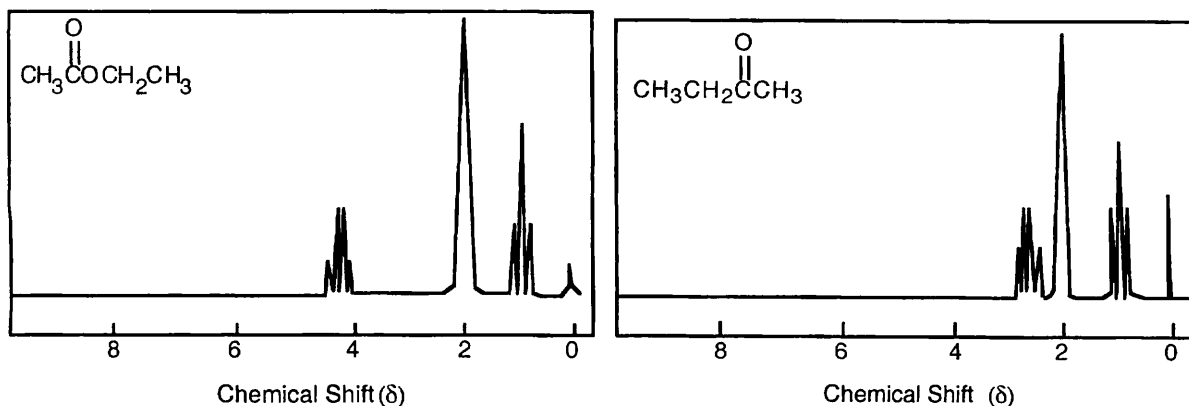


Isomer **A** has only four kinds of protons because of symmetry. Its vinylic proton absorption (4.5–6.5 δ) represents two hydrogens. Isomer **B** contains six different kinds of protons. Its ^1H NMR shows an unsplit methyl group signal and one vinylic proton signal of relative area 1. These differences make it possible to distinguish between **A** and **B**.

13.44 First, check each isomer for structural differences that are obviously recognizable in the ^1H NMR spectrum. If it is not possible to pick out distinguishing features immediately, it may be necessary to sketch an approximate spectrum of each isomer for comparison.

- (a) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$ has two vinylic protons with chemical shifts at 5.4–5.5 δ . Because ethylcyclopropane shows no signal in this region, it should be easy to distinguish one isomer from the other.
- (b) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ has two kinds of protons, and its ^1H NMR spectrum consists of two peaks — a triplet and a quartet. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$ has four different types of protons, and its spectrum is more complex. In particular, the methyl group bonded to oxygen shows an unsplit singlet absorption.

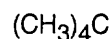
- (c) Each compound shows three peaks in its ^1H NMR spectrum. The ester, however, shows a downfield absorption due to the $-\text{CH}_2-$ hydrogens next to oxygen. No comparable peak shows in the spectrum of the ketone.



- d) Each isomer contains four different kinds of protons — two kinds of methyl protons and two kinds of vinylic protons. For the first isomer, the methyl peaks are both singlets, whereas for the second isomer, one peak is a singlet and one is a doublet.

13.45

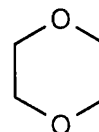
(a)



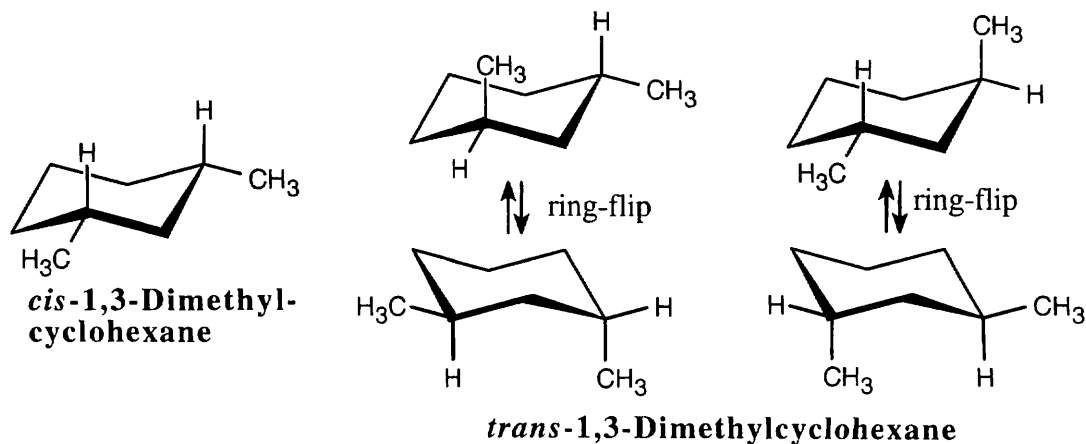
(b)



(c)

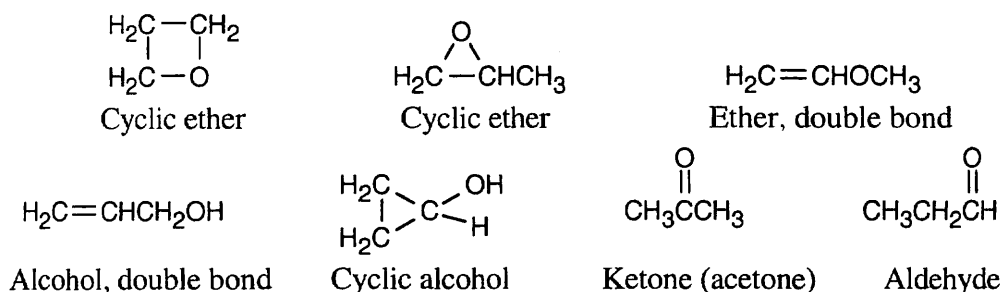


13.46



cis-1,3-Dimethylcyclohexane is a meso compound. Because of symmetry, it shows 5 absorptions in its ^{13}C NMR spectrum. *trans*-1,3-Dimethylcyclohexane exists as a pair of enantiomers, which, at room temperature, undergo ring-flips that average the absorptions due to nonequivalent carbons. Like the *cis* isomer, the racemic mixture of *trans* enantiomers shows 5 absorptions in its ^{13}C spectrum.

13.47 (a),(b) C_3H_6O contains one double bond or ring. Possible structures for C_3H_6O include:



(c) Saturated ketones absorb at 1715 cm^{-1} in the infrared. Only the last two compounds above show an infrared absorption in this region.

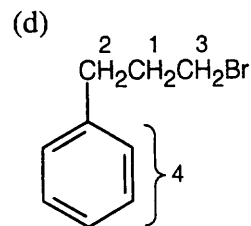
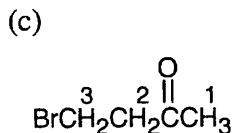
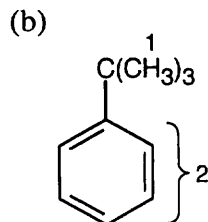
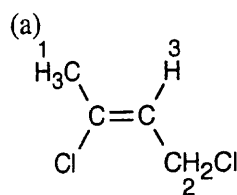
(d) Because the aldehyde from part (b) has three different kinds of protons, its 1H NMR spectrum shows three peaks. The ketone, however, shows only one peak. Since the unknown compound of this problem shows only one 1H NMR absorption (in the methyl ketone region), it must be acetone.

13.48 Either 1H NMR or ^{13}C NMR can be used to distinguish among these isomers. In either case, it is first necessary to find the number of different kinds of protons or carbon atoms.

Compound	Kinds of Protons	Kinds of Carbon atoms	Number of 1H NMR peaks	Number of ^{13}C NMR peaks
$\begin{array}{c} H_2C-CH_2 \\ \quad \\ H_2C-CH_2 \end{array}$	1	1	1	1
$H_2C=CHCH_2CH_3$	5	4	5	4
$CH_3CH=CHCH_3$	2	2	2	2
$(CH_3)_2C=CH_2$	2	3	2	3

^{13}C NMR is the simplest method for identifying these compounds because each isomer differs in the number of absorptions in its ^{13}C NMR spectrum. 1H NMR can also be used to distinguish among the isomers because the two isomers that show two 1H NMR peaks differ in their splitting patterns.

13.53

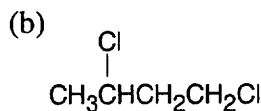
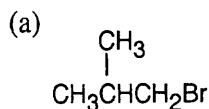


1 = 2.18 δ (allylic) 1 = 1.30 δ (saturated) 1 = 2.11 δ (next to C=O) 1 = 2.15 δ
 2 = 4.16 δ (H,Cl bonded to same C) 2 = 7.30 δ (aromatic) 2 = 3.52 δ (next to C=O, Br) 2 = 2.75 δ (benzylic)
 3 = 5.71 δ (vinylic) 3 = 4.40 δ (H,Br bonded to same C) 3 = 3.38 δ (H,Br bonded to same C)
 4 = 7.22 δ (aromatic)

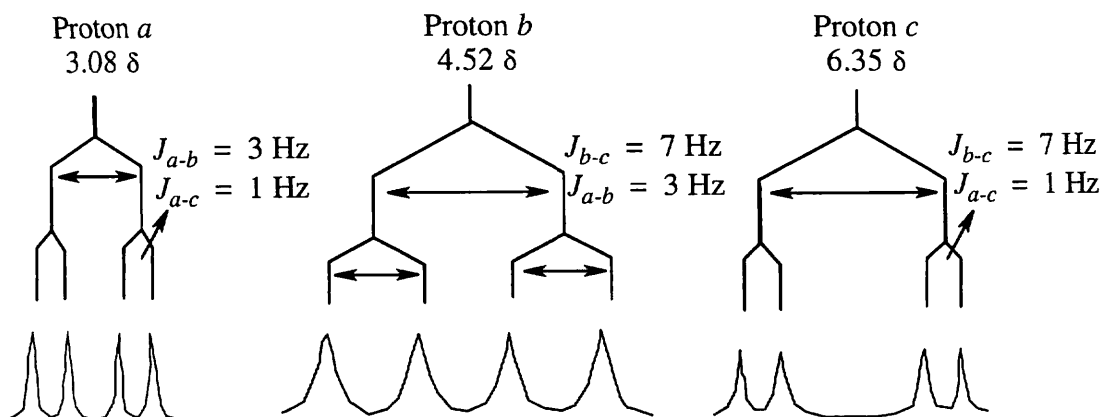
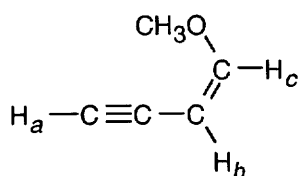
The *E* isomer is also a satisfactory answer

In (b) and (d), the aromatic ring hydrogens accidentally have the same chemical shift.

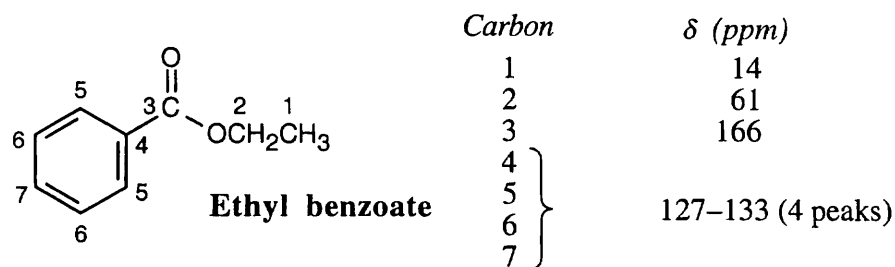
13.54



13.55

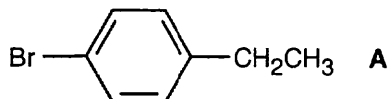


13.56



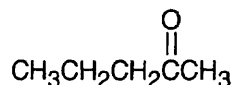
13.57 Compound A (4 multiple bonds and/or rings) must be symmetrical because it exhibits only six peaks in its ^{13}C NMR spectrum. Saturated carbons account for two of these peaks ($\delta = 15, 28$ ppm), and unsaturated carbons account for the other four ($\delta = 119, 129, 131, 143$ ppm).

^1H NMR shows a triplet (3 H at 1.1 δ), and a quartet (2 H at 2.5 δ), indicating the presence of an ethyl group. The other signals (4 H at 6.9–7.3 δ are due to aromatic protons.

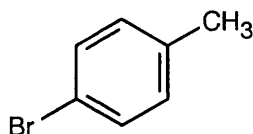


13.58

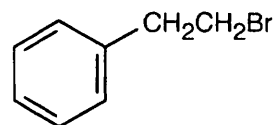
(a)



(b)

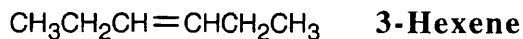


(c)



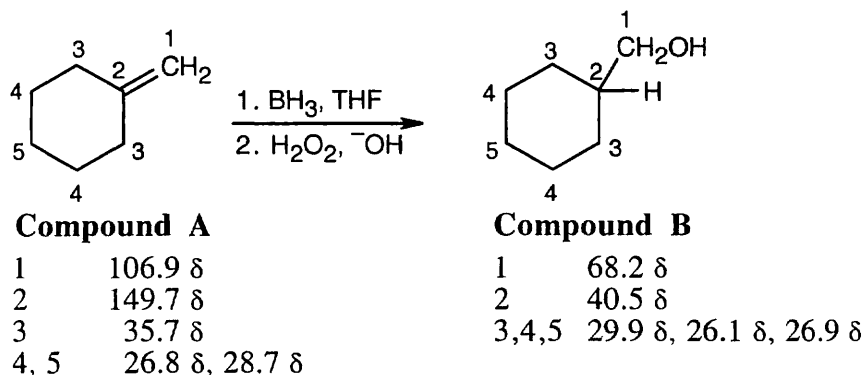
13.59 The peak in the mass spectrum at $m/z = 84$ is probably the molecular ion of the unknown compound and corresponds to a formula of C_6H_{12} – one double bond or ring. The base peak, at $m/z = 55$, corresponds to the loss of an ethyl group.

^{13}C NMR shows three different kinds of carbons and indicates a symmetrical hydrocarbon. The absorption at 132 δ is due to a vinylic carbon atom. A reasonable structure for the unknown is 3-hexene. The data do not distinguish between cis and trans isomers.



- 13.60** Compound **A**, a hydrocarbon having $M^+ = 96$, has the formula C_7H_{12} , indicating two degrees of unsaturation. Because it reacts with BH_3 , Compound **A** contains a double bond. From the broadband decoupled ^{13}C NMR spectrum, we can see that C_7H_{12} is symmetrical, since it shows only five peaks.

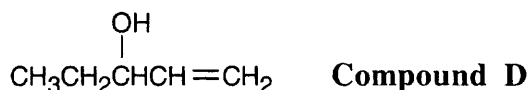
The DEPT-135 spectrum of Compound **A** indicates three different CH_2 carbons, one $=CH_2$ carbon and one $-C=$ carbon; the last two carbons are shown to be sp^2 -hybridized by their chemical shifts. In the DEPT-135 spectrum of Compound **B**, the absorptions due to double bond carbons have been replaced by a CH carbon and a CH_2 carbon bonded to an electronegative group.



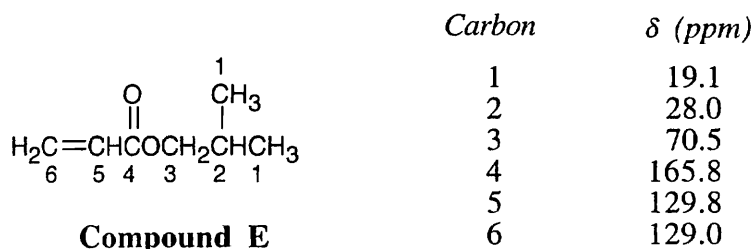
- 13.61** The IR absorption indicates that **C** is an alcohol. From M^+ , we can arrive at a molecular formula of $C_5H_{10}O$, which indicates one degree of unsaturation. The broadband-decoupled spectrum shows five peaks; two are due to a double bond, and one is due to a carbon bonded to an electronegative atom (O).

The DEPT spectra show that **C** contains 4 CH_2 carbons and one CH carbon, and that **C** has a monosubstituted double bond. $HOCH_2CH_2CH_2CH=CH_2$ is a likely structure for **C**.

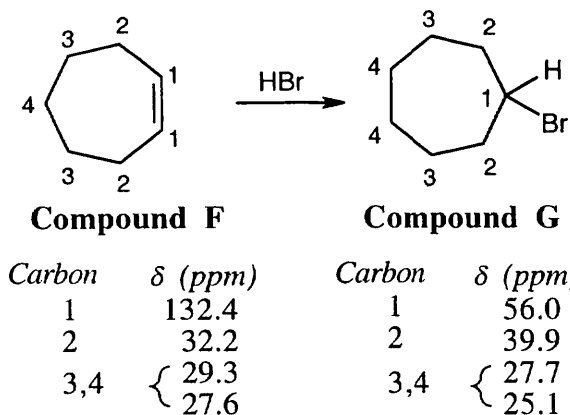
- 13.62** Compound **D** is very similar to Compound **C**. The DEPT spectra make it possible to distinguish between the isomers. **D** has 2 CH carbons, one CH_3 carbon, and 2 CH_2 carbons, and, like **C**, has a monosubstituted double bond. The peak at 74.4 δ is due to a secondary alcohol.



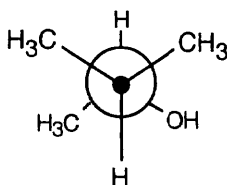
- 13.63** Compound **E**, $C_7H_{12}O_2$, has two degrees of unsaturation and has two equivalent carbons because its broadband-decoupled spectrum shows only 6 peaks. Two carbons absorb in the vinylic region of the spectrum; because one is a CH carbon and the other is a CH_2 carbon, **E** contains a monosubstituted double bond. The peak at 165.8 δ (not seen in the DEPT spectra) is due to a carbonyl group.



13.64



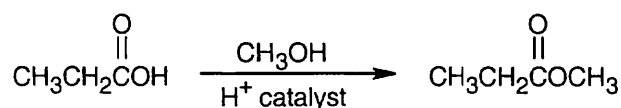
13.65 Make a model of one enantiomer of 3-methyl-2-butanol and orient it as a staggered Newman projection along the C2-C3 bond. The *S* enantiomer is pictured.



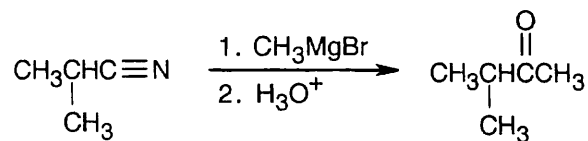
Because of the chirality center at C2, the two methyl groups at the front of the projection are diastereotopic. Since the methyl groups aren't equivalent, their carbons show slightly different signals in the ^{13}C NMR.

13.66 Commercial 2,4-pentanediol is a mixture of three stereoisomers: (*R,R*), (*S,S*), and (*R,S*). The meso isomer shows three signals in its ^{13}C NMR spectrum. Its diastereomers, the *R,R* and *S,S* enantiomeric pair, also show three signals, but two of these signals occur at different δ values from the meso isomer. This is expected, because diastereomers differ in physical and chemical properties. One resonance from the meso compound accidentally overlaps with one signal from the enantiomeric pair.

13.67 The product ($M^+ = 88$) has the formula $\text{C}_4\text{H}_8\text{O}_2$. The IR absorption indicates that the product is an ester. The ^1H NMR shows an ethyl group and an $-\text{OCH}_3$ group.



13.68 The product is a methyl ketone.



Review Unit 5: Spectroscopy

Major Topics Covered (with vocabulary):

Mass Spectrometry:

cation radical mass spectrum base peak double-focusing mass spectrometer molecular ion
alpha cleavage McLafferty rearrangement dehydration MALDI ESI TOF mass analyzer

The Electromagnetic Spectrum:

electromagnetic radiation wavelength frequency hertz amplitude quanta absorption spectrum

Infrared Spectroscopy:

wavenumber fingerprint region

Nuclear Magnetic Resonance Spectroscopy:

nuclear magnetic resonance rf energy effective magnetic field shielding downfield upfield
chemical shift delta scale FT-NMR DEPT ^{13}C NMR homotopic enantiotopic diastereotopic
integration multiplet spin-spin splitting coupling $n + 1$ rule coupling constant tree diagram

Types of Problems:

After studying these chapters, you should be able to:

- Write molecular formulas corresponding to a given molecular ion.
- Use mass spectra to determine molecular weights and base peaks, to distinguish between hydrocarbons, and to identify selected functional groups by their fragmentation patterns.
- Calculate the energy of electromagnetic radiation, and convert from wavelength to wavenumber and *vice versa*.
- Identify functional groups by their infrared absorptions.
- Use IR and MS to monitor reaction progress.
- Calculate the relationship between delta value, chemical shift, and spectrometer operating frequency.
- Identify nonequivalent carbons and hydrogens, and predict the number of signals appearing in the ^1H NMR and ^{13}C NMR spectra of compounds.
- Assign resonances to specific carbons or hydrogens of a given structure.
- Propose structures for compounds, given their NMR spectra.
- Predict splitting patterns, using tree diagrams if necessary.
- Use NMR to distinguish between isomers and to identify reaction products.

Points to Remember:

- * In mass spectrometry, the molecular ion is a cation radical. Further fragmentations of the molecular ion can be of two types – those that produce a cation plus a radical, and those that produce a different cation radical plus a neutral atom. In all cases, the fragment bearing the charge – whether cation or cation radical – is the one that is detected.
- * Although mass spectrometry has many uses in research, we are interested in it for only a limited amount of data. The most important piece of information it provides for us is the molecular weight of an unknown. A mass spectrum can also show if an unknown is branched

or straight-chain (branched hydrocarbons have more complex spectra than their straight-chain isomers). Finally, if we know if certain groups are present, we can obtain structural information about an unknown compound. For example if we know that a ketone is present, we can look for peaks that correspond to alpha cleavage and/or McLafferty rearrangement fragments.

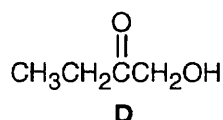
- * The position of an IR absorption is related to both the strength of the bond and to the nature of the two atoms that form the bond. For example, a carbon-carbon triple bond absorbs at a higher frequency than a carbon-carbon double bond, which absorbs at a higher frequency than a carbon-carbon single bond. Bonds between two atoms of significantly different mass absorb at higher frequencies than bonds between two atoms of similar mass.
- * Not all IR absorptions are due to bond stretches. Many of the absorptions in the fingerprint region of an IR spectrum are due to bending and out-of-plane motions.
- * It is confusing, but true, that larger δ values in an NMR spectrum are associated with nuclei that are less shielded, and that these nuclei require a lower field strength for resonance. Nuclei with small values of δ are more shielded and require a higher field strength for resonance.
- * Both ^{13}C NMR and ^1H NMR are indispensable for establishing the structure of an organic compound. ^{13}C NMR indicates if a molecule is symmetrical and shows the types of carbons in a molecule (by DEPT NMR). ^1H NMR shows how the carbons are connected (by spin-spin splitting) and how many protons are in the molecule (by integration). Both types of spectra show (by chemical shift) the electronic environment of the magnetic nuclei.

Self-Test:

Compound **A** is a hydrocarbon with $M^+ = 78$. What is its molecular formula? What is its degree of unsaturation? Draw three possible formulas for **A**. The ^{13}C NMR spectrum of **A** shows 3 peaks – at 18.5 δ , 69.4 δ and 82.4 δ , and the ^1H NMR spectrum shows two peaks. What is the structure of **A**? What significant absorptions would you see in the IR spectrum of **A**?

Compound **B** has the molecular formula C_8H_{14} , and shows 3 peaks in its ^1H NMR spectrum – at 1.7 δ (6H), 2.1 δ (4H) and 4.7 δ (4H). All 3 peaks are singlets. **B** also shows an IR absorption at 890 cm^{-1} . What is a possible structure for **B**? If you're still not sure, the following peaks were observed in the ^{13}C NMR spectrum of **B**: 22 δ , 36 δ , 110 δ , 146 δ . The peaks at 36 δ and 110 δ were negative signals in the DEPT-135 spectrum, and the peak at 22 δ was a positive signal.

Compound **C** is a hydrocarbon with $M^+ = 112$. What are possible molecular formulas for **C**? The five peaks in the ^1H NMR spectrum of **C** are all singlets and occur at the following δ values: 0.9 δ (9 H), 1.8 δ (3 H), 1.9 δ (2 H), 4.6 δ (1 H) and 4.8 δ (1 H). An IR absorption at 890 cm^{-1} is also present. What is the structure of **C**?



Describe the ^{13}C NMR and ^1H NMR spectra of **D**. For the ^1H NMR spectrum, include the spin-spin splitting patterns, peak areas, and positions of the chemical shifts. Give two significant absorptions that you might see in the IR spectrum. Would you expect to see products of McLafferty rearrangement in the mass spectrum of **D**? Of alpha cleavage?

Multiple choice:

- Which of the following formulas could not arise from a compound with $M^+ = 142$ that contains C, H, and possibly O?
(a) $C_{11}H_{10}$ (b) $C_{10}H_8O$ (c) $C_9H_{18}O$ (d) $C_8H_{14}O_2$
- Which of the following mass spectrum fragments is a cation, rather than a cation radical?
(a) molecular ion (b) product of alpha cleavage (c) product of McLafferty rearrangement (d) product of dehydration of an alcohol
- Which element contributes significantly to $(M+1)^+$?
(a) N (b) H (c) C (d) O
- In which type of spectroscopy is the wavelength of absorption the longest?
(a) NMR spectroscopy (b) infrared spectroscopy (c) ultraviolet spectroscopy (d) X-ray spectroscopy
- Which functional group is hard to detect in an IR spectrum?
(a) aldehyde (b) $-C\equiv C-$ (c) alcohol (d) ether
- IR spectroscopy is especially useful for:
(a) determining if an alkyne triple bond is at the end of a carbon chain or is in the middle
(b) predicting the type of carbonyl group that is present in a compound
(c) deciding if a double bond is monosubstituted or disubstituted
(d) all of these situations
- If a nucleus is strongly shielded:
(a) The effective field is smaller than the applied field, and the absorption is shifted downfield. (b) The effective field is larger than the applied field, and the absorption is shifted upfield. (c) The effective field is smaller than the applied field, and the absorption is shifted upfield. (d) The effective field is larger than the applied field, and the absorption is shifted downfield.
- When the operating frequency of an 1H NMR spectrometer is changed:
(a) The value of chemical shift in δ and of the coupling constant remain the same. (b) The values of chemical shift in Hz and of the coupling constant change. (c) The value of chemical shift in Hz remains the same, but the coupling constant changes. (d) The values of chemical shift in δ and of the coupling constant change.
- ^{13}C NMR can provide all of the following data except:
(a) the presence or absence of symmetry in a molecule (b) the connectivity of the carbons in a molecule (c) the chemical environment of a carbon (d) the number of hydrogens bonded to a carbon
- Which kind of carbon is detected in DEPT-90 ^{13}C NMR spectroscopy?
(a) primary carbon (b) secondary carbon (c) tertiary carbon (d) quaternary carbon
- The protons on carbon 3 of (*R*)-2-bromobutane are:
(a) homotopic (b) enantiotopic (c) diastereotopic (d) unrelated