



Using Nuclear Magnetic Resonance Spectroscopy to Identify an Unknown Compound

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PURPOSE OF THE EXPERIMENT Prepare an unknown sample for nuclear magnetic resonance (NMR) analysis. Obtain and interpret the proton (^1H) NMR spectrum of the unknown compound. Obtain and interpret the carbon-13 (^{13}C) and DEPT spectra of the unknown compound (optional). Identify the unknown compound from its molecular formula and NMR spectrum. Interpret the ^1H , ^{13}C , and DEPT spectra of 4-propoxybenzaldehyde.

EXPERIMENTAL OPTIONS Using a Continuous-Wave (CW) NMR Spectrometer 11
Using a Fourier-Transform (FT) NMR Spectrometer 12

BACKGROUND REQUIRED You should be familiar with NMR spectroscopy, including theory and interpretation, and with determining the unsaturation number of an organic compound as calculated from its molecular formula.

BACKGROUND INFORMATION Chemists use nuclear magnetic resonance (NMR) spectroscopy to confirm the structures of known compounds and to elucidate the structures of new ones. Spectrometers provide a wealth of structural information using a few milligrams of a compound.

The fact that certain isotopic nuclei such as ^1H (proton) or ^{13}C have a nuclear spin that results in a magnetic moment provides the basis for NMR. The nuclear spin quantum number is $\frac{1}{2}$ for ^1H and ^{13}C nuclei. Two spin states, $+\frac{1}{2}$ and $-\frac{1}{2}$, are allowed. When these nuclei are placed in an applied magnetic field (B_0), the two spin states separate. The $+\frac{1}{2}$ spin state, which is aligned with B_0 , is at a slightly lower energy than the $-\frac{1}{2}$ spin state, which is aligned against B_0 .

A small excess of spins exists in the $+\frac{1}{2}$ spin state at equilibrium. The NMR phenomenon, called **magnetic resonance**, occurs when the protons in the $+\frac{1}{2}$ spin state absorb energy of a specific frequency and change their spin states to $-\frac{1}{2}$. The spectrometer records the NMR spectrum as these nuclei return to equilibrium in a process called **relaxation**.

Interpreting a ^1H NMR Spectrum The 60-MHz ^1H NMR spectrum of *N*-methylbenzylamine is shown in Figure 1.

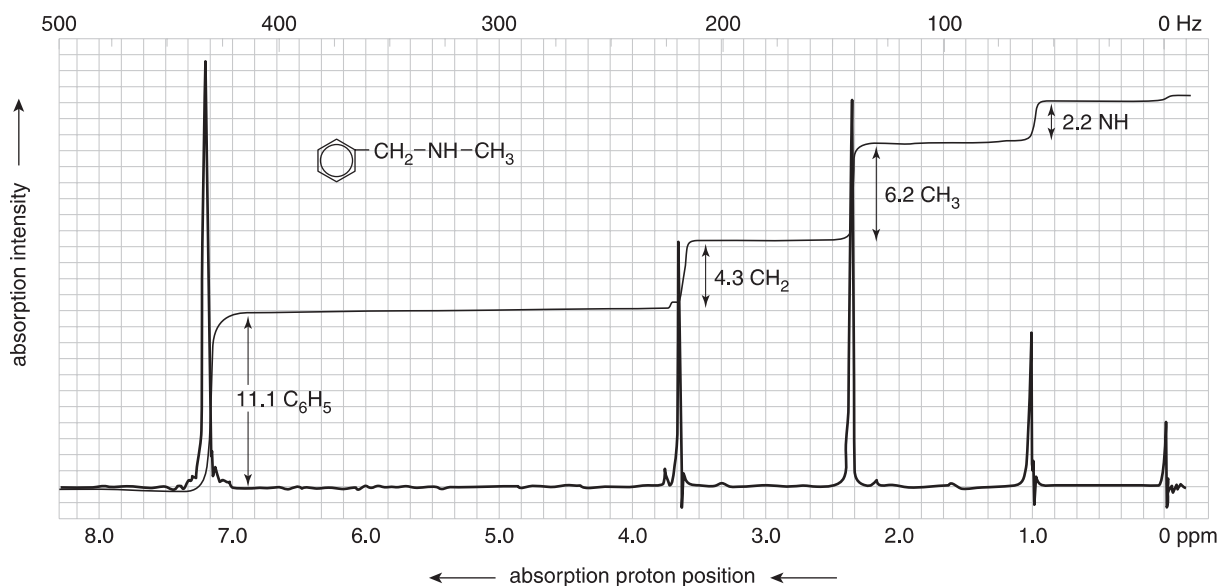


Figure 1 60-MHz ^1H NMR spectrum of *N*-methylbenzylamine

The absorption intensity is shown on the vertical axis and the absorption positions of various protons are indicated on the horizontal axis. Various protons absorb energy at slightly different frequencies because some protons are located in areas of different electron density than others. These differential absorptions are manifested as different **chemical shifts**, the difference between the absorption position of an observed proton and the absorption of the protons of a reference standard such as tetramethylsilane (TMS), $\text{Si}(\text{CH}_3)_4$.

Because the differences in chemical shifts between protons are very small compared to the magnetic field strength, chemical shifts are expressed in units of parts per million (ppm) on a delta (δ) scale, as shown in Equation 1.

$$\delta = \frac{\text{chemical shift, Hz}}{\text{instrument operating frequency, MHz}} \quad (\text{Eq. 1})$$

The spectrum of *N*-methylbenzylamine in Figure 1 reveals four different peaks, signifying four different proton signals. The fifth peak, at 0 ppm, is due to TMS. The number of proton signals and their individual chemical shifts are the first important pieces of information that can be derived from the spectrum. Typical chemical shifts of various proton signals appear in Table 1.

Certain protons, such as those attached to carbons bearing a nitrogen, oxygen, or halogen atom, resonate at higher ppm values than those of primary (RCH_3), secondary (RCH_2R), or tertiary (R_3CH) alkyl groups. A higher ppm value corresponds to a slight decrease in the magnetic field strength needed to bring that proton into resonance. For example, the methylene protons of an alkyl chloride, RCH_2Cl , resonate from 3.6–3.8 ppm, compared to 0.8–1.0 ppm for the protons of a RCH_3 group. The alkyl chloride protons are said to resonate *downfield* from the methyl group, and the methyl group resonates *upfield* from the alkyl chloride protons. This effect arises from the fact that an electron cloud

Table 1 Approximate chemical shifts in ^1H NMR spectroscopy

<i>proton</i>	<i>chemical shift (ppm)</i>
RCH_3	0.8–1.2
RCH_2R	1.2–1.4
R_3CH	1.4–1.7
$\text{R}_2\text{C}=\text{CRCH}_3$	1.6–1.9
$\text{R}_2\text{N}(\text{C}=\text{O})\text{CH}_3$	1.6–1.8
$\text{R}(\text{C}=\text{O})\text{CH}_3$	2.0–2.6
R_2NCH_3	2.1–3.1
ArCH_2R	2.2–2.6
$\text{R}_2\text{NCH}_2\text{R}$	2.3–3.7
$\text{RC}\equiv\text{CH}$	2.5–3.1
RCH_2X (X=Cl, Br, I)	3.1–3.8
ROCH_2R , $\text{R}(\text{C}=\text{O})\text{OCH}_2\text{R}$	3.3–3.9
ArOCH_2R , HOCH_2R	3.3–4.0
$\text{R}_2\text{C}=\text{CH}_2$	4.6–6.1
$\text{R}_2\text{C}=\text{CHR}$	5.2–5.7
ArH	6.0–9.5
$\text{R}(\text{C}=\text{O})\text{H}$, $\text{Ar}(\text{C}=\text{O})\text{H}$	9.5–10.0
$\text{RCO}_2\text{H}^{\text{a}}$	10–13
RNH_2^{a} , ArNH_2^{a}	1–5
$\text{R}(\text{C}=\text{O})\text{NHR}^{\text{a}}$	5–9
$\text{R}-\text{OH}^{\text{a}}$	0.5–6.0
ArOH^{a}	4.5–7.7

^aThe chemical shifts of these protons vary with concentration, temperature and type of solvent.

surrounds a given proton and shields it. When placed in an applied magnetic field, B_0 , the electron cloud generates a small local magnetic field that *opposes* B_0 . This effect is called **diamagnetic shielding**. An electronegative atom such as chlorine withdraws electron density, thus decreasing the magnitude of the local magnetic field. The chlorine atom is said to *deshield* the proton from B_0 . As a result, the proton experiences a slightly weaker magnetic field and resonance occurs at a higher ppm value.

Table 1 shows that aldehyde, alkene, and aromatic protons resonate even farther downfield than an alkyl chloride. The pi electrons of double bonds and aromatic rings circulate when placed in a magnetic field, producing a ring current. The ring current generates a small local magnetic field, which deshields the proton from the external magnetic field.

The second important piece of information gained from an NMR spectrum is the relative numbers of each kind of proton present. The area under each peak is proportional to the number of protons generating the peak. The spectrometer measures the area under each peak using a process called **integration**. Measuring the distance between the horizontal integration lines for each peak and comparing these measurements determines the relative numbers of protons for each peak. Figure 1 shows that measuring the integration lines of the peaks at 1.00, 2.36, 3.63, and 7.19 ppm gives 2.2, 6.2, 4.3, and 11.1 squares, respectively. [NOTE 1] If each

NOTE 1: Alternatively, the distance between horizontal integration lines can be measured in millimeters using a ruler.

value is divided by 2.2, the smallest number, the following results are obtained: $2.2/2.2 = 1.0$; $6.2/2.2 = 2.8$; $4.3/2.2 = 2.0$; $11.1/2.2 = 5.0$. Rounding these numbers to the nearest whole number gives the relative numbers of protons for each chemical shift, as shown in Table 2.

Table 2 Relative numbers of protons in *N*-methylbenzylamine

<i>ppm</i>	<i>number of protons</i>
1.00	1
2.36	3
3.63	2
7.19	5

Assignments are made by comparing these numbers to the structure of *N*-methylbenzylamine. The single NH proton resonates at 1.00 ppm, the *N*-CH₃ group at 2.36 ppm, the benzylic CH₂ group at 3.63 ppm, and the five aromatic protons at 7.19 ppm.

The third important piece of information available in an NMR spectrum arises from a phenomenon called **spin-spin coupling**, in which a given proton is affected by the spin states of protons on adjacent carbon atoms. As a result, the signal of the observed proton splits into $n + 1$ peaks, where n is the number of protons on directly adjacent carbon atoms. This pattern is called the **$n + 1$ rule**.

An example of spin-spin coupling can be observed in the spectrum of ethyl acetate shown in Figure 2. The CH₃ group (a) appears as a triplet because its neighbor (c) has two protons; the CH₂ group (c) appears as a quartet because its neighbor (a) has three protons. The CH₃ group (b) appears as a singlet because its neighbor has no protons. The type of splitting (doublet, triplet, quartet, etc.) is referred to as **multiplicity**.

The distance between the adjacent peaks in a multiplet undergoing spin-spin coupling is known as the **coupling constant, J** , expressed in units of Hz. In the 60-MHz spectrum of ethyl acetate, the average distance between the peaks in the quartet is approximately 7 Hz. Because 1 ppm = 60 Hz, 7 Hz corresponds to approximately 0.12 ppm. The

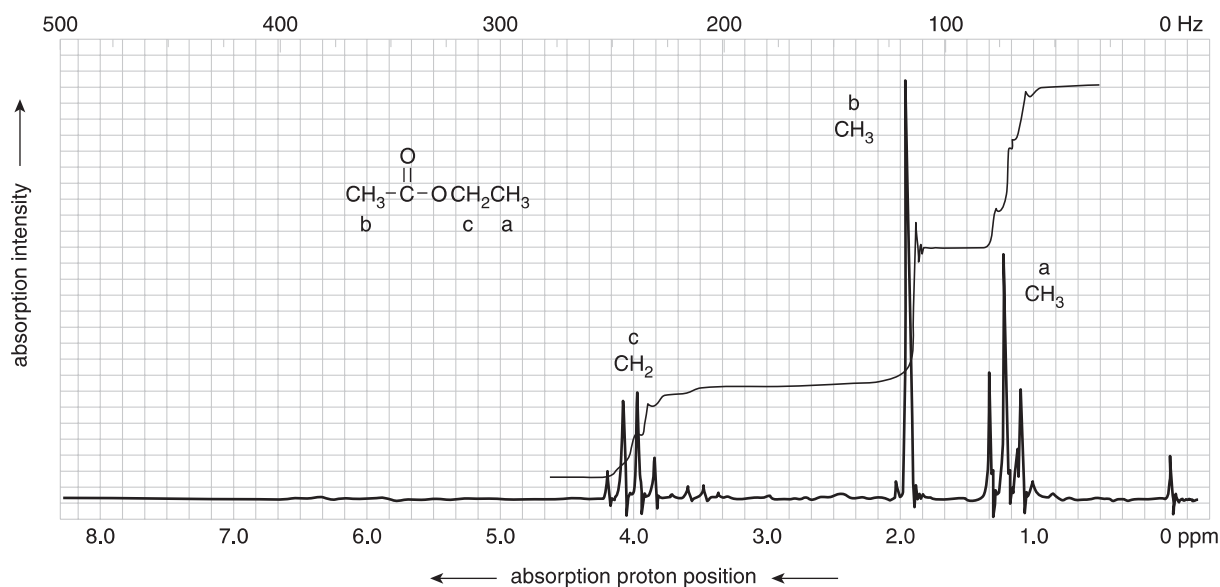


Figure 2 60-MHz ¹H NMR spectrum of ethyl acetate

J value for the triplet of ethyl acetate is also 7 Hz. Peaks that are coupled via spin–spin coupling always show the same J values. This information can often provide structural clues in spectra involving several multiplets. Values of J vary from < 1 to 18 Hz, depending upon what kinds of protons are present. Typical coupling constants for various proton systems appear in Table 3.

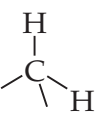
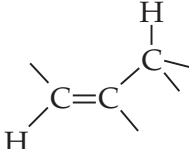
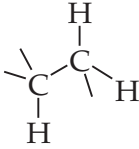
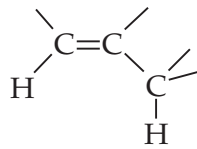
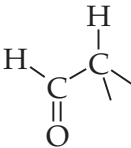
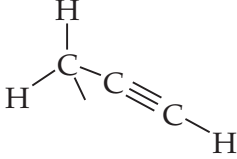
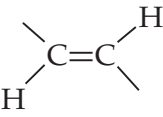
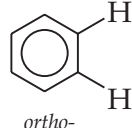
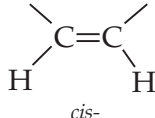
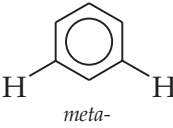
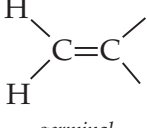
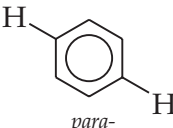
	J , Hz		J , Hz
 geminal-	12–15	 trans-allylic	0–3
 vicinal-	5–8	 cis-allylic	0–3
	2–3		2–3
 trans-	12–18	 ortho-	6–10
 cis-	6–12	 meta-	1–3
 geminal-	0–2	 para-	0–1

Table 3 Some coupling constants found in ^1H NMR spectroscopy

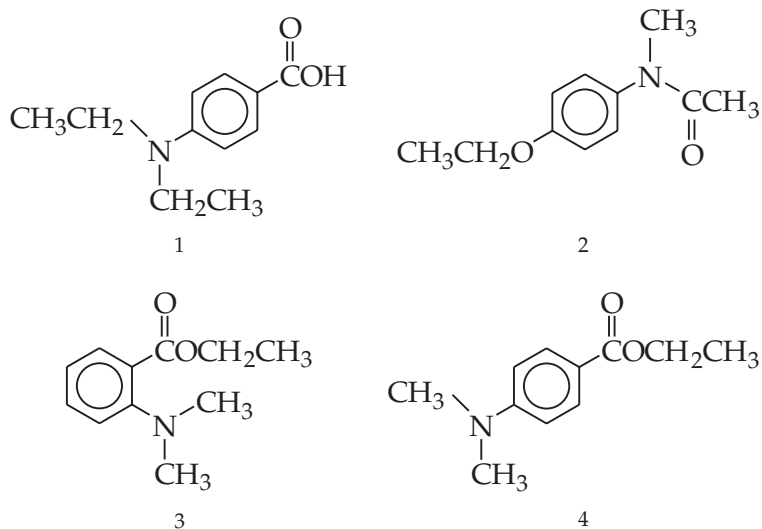
Using the Unsaturation Number in Conjunction with NMR Data

The molecular formula reveals the unsaturation number, which gives clues to the structure of an organic compound. Consider, for example, a compound with the molecular formula $\text{C}_{11}\text{H}_{15}\text{NO}_2$. This compound has an unsaturation number of 5. There are many different structural possibilities. Using the unsaturation number, along with the NMR data shown in Table 4 on the next page, quickly narrows the choices.

Table 4 NMR data for $C_{11}H_{15}NO_2$

ppm	number of hydrogens	multiplicity	J (Hz)
1.30	3	triplet	7
3.00	6	singlet	—
4.25	2	quartet	7
6.65	2	doublet	8
7.80	2	doublet	8

The two signals at 6.65 and 7.80 ppm, each of which integrates for two protons, are typical of a disubstituted benzene ring. These two signals account for four aromatic protons and four of the five sources of unsaturation because an aromatic ring consists of one ring and contains the equivalent of three double bonds. The presence of a triplet and a quartet is indicative of an ethyl group. At this point structures 1–4 can be proposed, as shown in Figure 3.

Figure 3 Proposed structures for $C_{11}H_{15}NO_2$ 

Structure 1 can be eliminated because it contains *two* chemically equivalent ethyl groups. This structure is inconsistent with the multiplets at 1.30 and 4.25 ppm, which arise from a *single* ethyl group. Structure 2 shows two different methyl singlets because one is attached to a nitrogen atom and the other to a carbonyl carbon atom. This structure is inconsistent with the data, which show a six-proton singlet at 3.00 ppm due to two chemically equivalent methyl groups. Structures 3 and 4 appear to be consistent with all of the data. However, closer examination of the aromatic protons shows that the two-proton doublets ($J = 8$ Hz) are supportive of a *para*-disubstituted benzene ring. This fact eliminates structure 3, which, because it is *ortho*-disubstituted, would show a more complicated pattern for the aromatic protons. So would *meta*-disubstituted benzene rings. Only structure 4 is completely consistent with all of the data. The CH_2 quartet appears downfield at 4.25 ppm because it is directly bonded to the strongly deshielding oxygen atom. Finally, the fifth source of unsaturation is accounted for by the ester carbonyl group. You will use a similar strategy in determining the structure of your unknown.

Using ^{13}C NMR Spectroscopy

The most abundant isotope of carbon is ^{12}C , with a natural abundance of 98.9%. However, because these nuclei have no magnetic spin, they cannot give rise to an NMR signal. ^{13}C nuclei, on the other hand, do have a magnetic spin and, like protons, can assume spin states of $+\frac{1}{2}$ or $-\frac{1}{2}$. Because ^{13}C has a natural abundance of only 1.1%, especially sensitive FT-NMR spectrometers are used to acquire ^{13}C spectra.

^{13}C NMR spectra are normally acquired under conditions where the protons are decoupled from their respective carbon atoms. That is, the carbon signals are not split by the protons directly attached to them. Thus, all of the signals appear as singlets. Carbon atoms that are directly bonded do not split each other because of the extremely low probability that two adjacent carbons will *both* be ^{13}C . ^{13}C NMR spectra are normally not integrated because the areas under the signals are not exactly proportional to the number of carbon atoms giving rise to the signal.

^{13}C NMR also offers an advantage in that it includes a much larger range of chemical shifts when compared to ^1H NMR spectroscopy. Whereas proton chemical shifts usually cover a range of 0–13 ppm, ^{13}C chemical shifts extend to over 200 ppm. Overlapping of peaks is sometimes a problem in ^1H NMR spectroscopy because of the limited range of chemical shifts. Such overlapping rarely occurs in ^{13}C NMR. Some approximate ^{13}C chemical shifts are listed in Table 5.

Table 5 ^{13}C NMR chemical shift ranges

<i>carbon group</i>	<i>chemical shift (ppm)</i>
alkyl	0–50
alkyl halide or amine	10–65
alcohol or ester	50–90
alkyne	60–90
alkene	100–170
aryl (phenyl)	100–170
nitrile	120–130
amide carbonyl	150–180
carboxylic acid or ester carbonyl	160–185
aldehyde or ketone carbonyl	180–215

Each chemically distinct carbon atom gives rise to a single peak in its normal ^{13}C NMR spectrum. However, this spectrum gives us no information as to what *types* of carbon atoms are present. The four possible types are methyl (CH_3), methylene (CH_2), methine (CH), and quaternary (C), depending upon the number of hydrogens directly attached to a particular carbon atom. A technique called Distortionless Enhancement by Polarization Transfer (DEPT) is used to distinguish carbon types. This method generates three different spectra. In the first spectrum, called DEPT-45, all carbons with attached protons appear as positive peaks. In the second spectrum, called DEPT-90, only CH carbons appear as positive signals. In the third spectrum, called DEPT-135, CHs and CH_3 s produce positive peaks and CH_2 s produce negative peaks. Quaternary carbons do not appear in DEPT spectra. Quaternary carbons can be identified by comparing the DEPT-45 spectrum, which shows all carbon resonances with attached protons, with the normal ^{13}C spectrum, which shows *all* carbon resonances. Any extra peaks found in the normal ^{13}C spectrum are due to quaternary carbons.

Figure 4 shows the normal ^{13}C spectrum of benzocaine ($\text{C}_9\text{H}_{11}\text{NO}_2$). The three-line pattern centered at 77 ppm is due to the solvent CDCl_3 and may be ignored. Notice that even though the molecule contains nine carbon atoms, only seven resonances appear in the ^{13}C spectrum. This pattern is due to the fact that the molecule contains a symmetrical *para*-disubstituted aromatic ring. The chemically equivalent carbons labeled 2 give rise to a single peak, as do the carbons labeled 3.

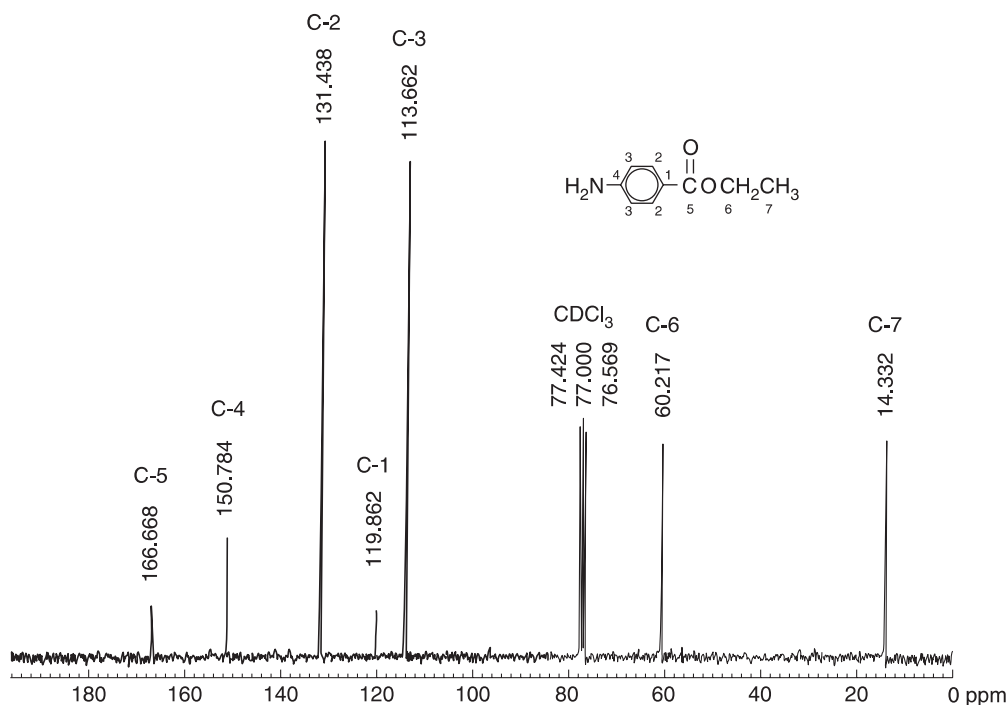


Figure 4 ^{13}C NMR spectrum of benzocaine

The DEPT spectra of benzocaine appear in Figure 5. All protonated carbons appear as positive signals in the DEPT-45 spectrum in Figure 5(a). Notice that only four peaks appear. When this spectrum is compared with the normal ^{13}C spectrum, it is obvious that the peaks at 119.86, 150.78, and 166.67 ppm are due to quaternary carbons. The DEPT-90 spectrum in Figure 5(b) identifies the two CH resonances at 113.66 and 131.44 ppm. In the normal ^{13}C spectrum, these two peaks are larger than the others because they each represent two carbon atoms, while each of the other peaks represents only one carbon atom. The DEPT-135 spectrum in Figure 5(c) identifies the CH_2 resonance as a negative peak at 60.22 ppm. Because this spectrum shows both CH_3 s and CHs as positive peaks, the CH_3 at 14.33 ppm can quickly be identified by comparison to Figure 5(b), which shows only CHs as positive peaks.

DEPT spectroscopy is able to identify carbon types, but it is not able to distinguish between specific resonances *within* each carbon type. In benzocaine, for example, there are two different CH resonances and three different quaternary carbon resonances. In order to assign each one, chemical shift arguments and resonance theory are often helpful. For example, from Table 5, ester carbonyl groups fall in the range of 160–185 ppm. Therefore, the resonance at 166.67 can be assigned to the C-5 carbonyl group. This assignment leaves quaternary carbons 1 and 4. Carbon 4 is attached to an electronegative nitrogen

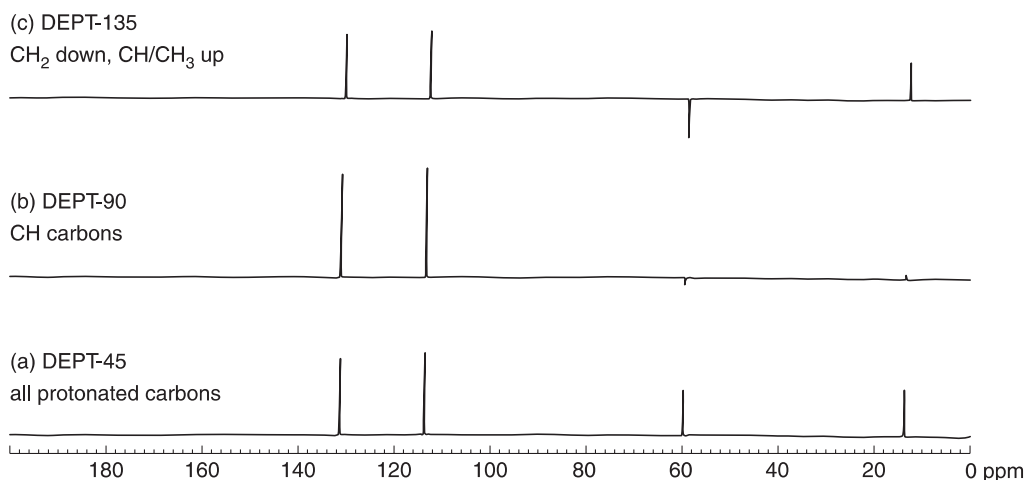


Figure 5 ¹³C DEPT spectra of benzocaine: (a) DEPT-45; (b) DEPT-90; and (c) DEPT-135

atom, while C-1 is attached to a less electronegative carbon atom. Therefore, C-4 is deshielded relative to C-1 and resonates farther downfield (at 150.78 ppm) than C-1 (at 119.86 ppm). To distinguish between the two CH resonances, consider the resonance structures shown in Figure 6.

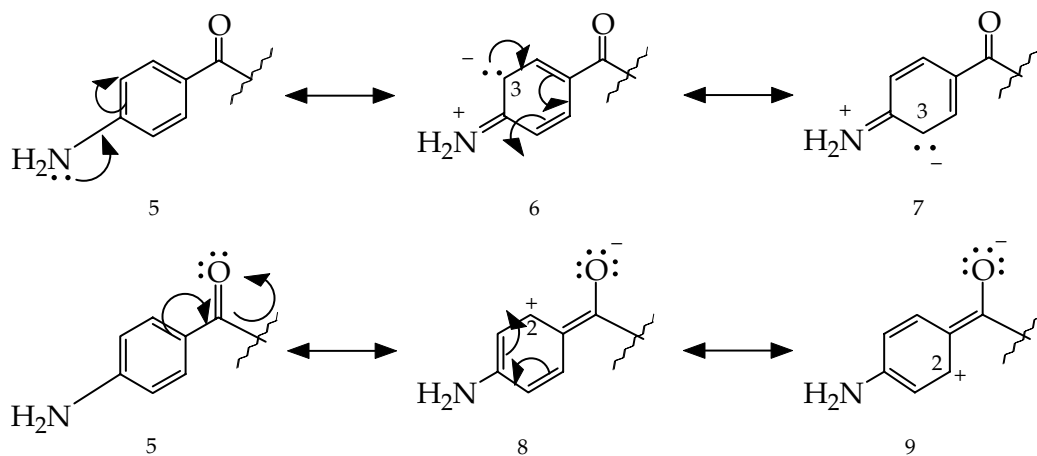


Figure 6 Resonance structures for benzocaine

Shifting the unshared pair of electrons on nitrogen in structure 5 generates resonance forms 6 and 7. In these structures, additional electron density is placed on the carbons labeled 3. This electron density shields these carbons from the external magnetic field and causes them to resonate *upfield* at a lower ppm value of 113.66 ppm. Additional resonance forms 8 and 9 can be drawn. Because of a positive charge, there is a decrease in the electron density at the carbons labeled 2. This decrease in electron density has a deshielding effect that causes these carbons to resonate farther *downfield* at 131.44 ppm.

These resonance arguments can also be used to assign the two kinds of aromatic protons that appear as separate two-proton doublets at 7.8 and 6.6 ppm in the ¹H NMR spectrum. The protons attached to C-2 are deshielded and resonate at 7.8 ppm, while the protons attached to C-3

are shielded and resonate at 6.6 ppm. Taken together, the ^{13}C and ^1H NMR spectra are powerful tools for verifying the structures of organic molecules.

A Strategy for Using NMR Spectroscopy in Structure Determination

1. If you know the molecular formula of the compound, determine its unsaturation number.
2. Obtain a ^1H spectrum. If the unsaturation number is 1 or more, look for alkene protons in the 4.6–6.1 ppm range. If the unsaturation number is 2 or more, look for alkene protons or an alkyne proton in the 2.5–3.1 ppm range. If the unsaturation number is 4 or more, look for phenyl protons in the 6–9.5 ppm range.
3. Integrate the spectrum to obtain the relative numbers of each kind of proton. Find the signal with the smallest area and assign this area a value of 1. All other areas that contain more than one hydrogen should be approximate multiples of 1. The smallest area that you chose could be due to two or more hydrogens. Comparison with the molecular formula can provide additional information.
4. Look at the chemical shifts of the various kinds of protons. Deshielding effects caused by electronegative atoms and pi electrons of multiple bonds cause protons to resonate at higher ppm values. Typical values appear in Table 1.
5. Look at the spin–spin coupling patterns (the $n + 1$ rule applies) to get an idea of what neighboring protons are present. Analysis of coupling constants (J values) may reveal which spins are coupled. Beware of overlapping signals that can complicate the interpretation.
6. Obtain a proton-decoupled ^{13}C spectrum. You will see a single line for each chemically distinct carbon atom in the molecule. If you see fewer lines than the number of carbons in the molecular formula, then two or more carbons are chemically equivalent.
7. Examine the chemical shifts of the various carbons to get a preliminary idea of the kinds of carbons present, as shown in Table 5.
8. Examine the DEPT spectra to distinguish between CH_3s , CH_2s and CHs . Quaternary carbons do not appear in DEPT. To assign quaternary carbons, compare the DEPT-45 spectrum, which shows all protonated carbons, to the proton-decoupled ^{13}C spectrum, which shows all carbons.
9. Propose a structure consistent with all of the available data.

You will interpret and assign the ^1H , ^{13}C , and DEPT spectra of 4-propoxybenzaldehyde provided by your laboratory instructor. You will prepare an unknown sample, acquire its ^1H NMR spectrum, and interpret it. Using its molecular formula and the ^1H spectrum, you will assign a structure to the unknown. If you are using a FT-NMR spectrometer, you may also acquire and interpret the ^{13}C and DEPT spectra of the unknown and propose a structure consistent with all of the data.

Using A Continuous-Wave NMR Spectrometer

Equipment

10-mL beaker	microspatula
glass wool	5-mm i.d. NMR tube
gloves	2 Pasteur pipets, with latex bulb
lint-free tissues	1-dram vial, with cap
micropipet, 100–1000 μL	

Reagents and Properties

<i>substance</i>	<i>quantity</i>
<i>d</i> -chloroform containing 2–5% tetramethylsilane	0.7 mL
unknown	100 mg

Preview

- Interpret the ^1H , ^{13}C , and DEPT spectra of 4-propoxybenzaldehyde
- Prepare a sample of the unknown
- Obtain and interpret a ^1H NMR spectrum of the unknown
- Propose a structure for the unknown

PROCEDURE **Caution:** Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

Always use caution in the laboratory. Many chemicals are potentially harmful. Consider the unknown compounds used in this experiment to be flammable, toxic, corrosive, and irritating. Keep away from flames or other heat sources. If you spill any unknown, notify your laboratory instructor immediately. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

1. **Interpreting ^1H , ^{13}C , and DEPT Spectra** Interpret the ^1H , ^{13}C , and DEPT spectra of 4-propoxybenzaldehyde provided by your laboratory instructor while waiting your turn on the NMR spectrometer.

2. **Preparing a Sample of the Unknown** **Caution:** *d*-Chloroform (CDCl_3) with 2–5% tetramethylsilane (TMS) is toxic, a suspected carcinogen, and hygroscopic. Use gloves and a *fume hood* when handling this reagent.

Obtain an unknown compound and its molecular formula from your laboratory instructor. Record its identification code and formula.

Wearing gloves, prepare all samples in a *fume hood*. Keep the container capped except for the brief time necessary to remove a sample.

Place a 1-dram vial into a 10-mL beaker for support. Transfer approximately 100 mg of your unknown into the vial.

Under a *fume hood*, use a micropipet to add 600–700 μL of CDCl_3 containing 2–5% TMS to the sample. [NOTE 2] Cap the vial. Thoroughly mix to dissolve.

NOTE 2: Deuterated solvents do not give ^1H NMR signals in the region of proton absorption. However, a small peak at 7.24 ppm will probably be visible due to residual traces of CHCl_3 .

Pack a small piece of glass wool firmly into the neck of a Pasteur pipet. Place the pipet into a clean, dry NMR tube.

Use a second Pasteur pipet to carefully transfer the sample to the glass wool-packed pipet. Cap the NMR tube when all the sample has filtered into it. Check with your laboratory instructor to make certain the liquid level is correct.

3. Obtaining the ^1H NMR Spectrum of the Unknown

Caution: If you have a pacemaker or metal implant, do not go inside the 5-Gauss line that encircles the magnet. Keep away from the magnet items with magnetic components, such as credit cards, computer disks, and audio- or videotapes.

Use the instructions provided by your laboratory instructor to operate the spectrometer. Place your prepared NMR tube into the sample chamber. Plot and integrate a spectrum. Check with your laboratory instructor to make sure that the spectrum you recorded is acceptable. If not, obtain another spectrum.

4. Cleaning Up

Remove the unknown from the NMR tube and place the unknown into your original vial. Return the vial to your laboratory instructor. Clean your NMR tube as directed by your laboratory instructor. Place other recovered materials in the appropriate labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

Using A Fourier-Transform NMR Spectrometer

Equipment

10-mL beaker	microspatula
glass wool	5-mm i.d. NMR tube
gloves	2 Pasteur pipets, with latex bulb
lint-free tissues	1-dram vial, with cap
micropipet, 100–1000 μL	

Reagents and Properties

<i>substance</i>	<i>quantity</i>
<i>d</i> -chloroform containing 0.05% tetramethylsilane (TMS)	0.7 mL
unknown	100 mg

Preview

- Interpret the ^1H , ^{13}C , and DEPT spectra of 4-propoxybenzaldehyde
- Prepare a sample of the unknown
- Obtain ^1H NMR spectrum of the unknown
- Obtain ^{13}C and DEPT NMR spectra of the unknown (optional)
- Propose a structure for the unknown

PROCEDURE **Caution:** Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

Always use caution in the laboratory. Many chemicals are potentially harmful. Consider the unknown compounds used in this experiment to be flammable, toxic, corrosive, and irritating. Keep away from flames or other heat sources. If you spill any unknown, notify your laboratory instructor immediately. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

1. Interpreting ^1H , ^{13}C , and DEPT Spectra

Interpret the ^1H , ^{13}C , and DEPT spectra of 4-propoxybenzaldehyde provided by your laboratory instructor while waiting your turn on the NMR spectrometer.

2. Preparing a Sample of the Unknown

Caution: *d*-Chloroform (CDCl_3) with 0.05% tetramethylsilane (TMS) is toxic, a suspected carcinogen, and hygroscopic. Use gloves and a *fume hood* while handling this reagent.

Obtain an unknown compound and its molecular formula from your laboratory instructor. Record its identification code and formula.

Wearing gloves, prepare all samples in a *fume hood*. Keep the container capped except for the brief time necessary to remove a sample.

Place a 1-dram vial into a 10-mL beaker for support. Put approximately 100 mg of your unknown into the vial.

Under a *fume hood*, use a micropipet to add 600–700 μL of CDCl_3 containing 0.05% TMS to the sample. [NOTE 2] Cap the vial. Thoroughly mix to dissolve.

NOTE 2: Deuterated solvents do not give ^1H NMR signals in the region of proton absorption. However, a small peak at 7.24 ppm will probably be visible due to residual traces of CHCl_3 .

Pack a small piece of glass wool firmly into the neck of a Pasteur pipet. Place the pipet into a clean, dry NMR tube.

Use a second Pasteur pipet to carefully transfer the sample to the glass wool-packed pipet. Cap the NMR tube when all the sample has filtered into it. Check with your laboratory instructor to make certain the liquid level is correct.

3. Obtaining the ^1H NMR Spectrum of the Unknown

Caution: If you have a pacemaker or metal implant, do not go inside the 5-Gauss line that encircles the magnet. Keep away from the magnet items with magnetic components, such as credit cards, computer disks, and audio- or videotapes.

Use the instructions provided by your laboratory instructor to operate the spectrometer. Place the NMR tube containing the unknown sample in a spinner. Adjust the sample height in the spinner, as demonstrated by your laboratory instructor. Lock and shim your sample.

Obtain an integrated ^1H NMR spectrum of the unknown. Check with your laboratory instructor to make sure the spectrum is acceptable. If not, obtain another spectrum.

4. Obtaining the ^{13}C Spectrum of the Unknown (optional)

Obtain and plot the proton-decoupled ^{13}C NMR spectrum of your unknown, along with the chemical shift of each peak. Check with your laboratory instructor to make sure the spectrum is acceptable. If not, obtain another spectrum.

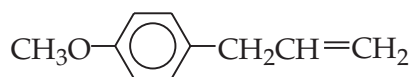
5. **Obtaining the DEPT Spectra of the Unknown (optional)** Obtain and plot the DEPT-45, 90, and 135 spectra. Check with your laboratory instructor to make sure that the spectra are acceptable. If they are not, obtain other spectra.

6. **Cleaning Up** Remove the unknown from the NMR tube and place the unknown into your original vial. Return the vial to your laboratory instructor. Clean your NMR tube as directed by your laboratory instructor. Place other recovered materials in the appropriate labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

Post-Laboratory Questions If you acquired only an ^1H NMR spectrum, answer questions 1, 3, and 4. If you acquired ^1H , ^{13}C , and DEPT NMR spectra, answer questions 2, 3, and 4.

- Propose a structure consistent with the molecular formula and ^1H NMR spectrum of your unknown compound. Briefly explain your answer.
- Propose a structure consistent with the molecular formula, ^1H , ^{13}C , and DEPT spectra of your unknown compound. Briefly explain your answer.
- Using the ^1H , ^{13}C , and DEPT spectra, along with chemical shift arguments and resonance theory, assign all of the peaks in the ^1H and ^{13}C NMR spectra of 4-propoxybenzaldehyde. Briefly explain your reasoning.
- Use the following ^{13}C NMR data, along with chemical shift arguments and resonance theory, to assign the ^{13}C spectrum of 4-allylanisole, whose structure appears below. Place the correct peak number next to the corresponding carbon atom in the structure.



<i>peak #</i>	<i>ppm</i>	<i>carbon type*</i>
1	39.25	CH ₂
2	55.13	CH ₃
3	113.75	CH (2 carbons)
4	115.32	CH ₂
5	129.41	CH (2 carbons)
6	131.98	C
7	137.81	CH
8	157.90	C

*determined from DEPT spectroscopy

NAME _____

SECTION _____

DATE _____

*TECH 711/Using Nuclear Magnetic Resonance Spectroscopy
to Identify an Unknown Compound*

Pre-Laboratory Assignment

1. Briefly define the following terms:

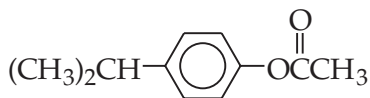
- (a) chemical shift
- (b) spin-spin coupling
- (c) coupling constant

2. Using an appropriate reference, draw the structure of 4-propoxybenzaldehyde.

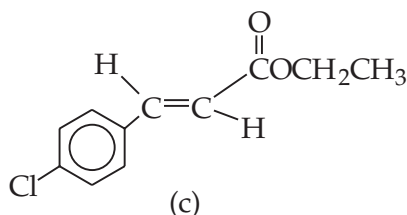
3. Predict the splitting pattern for each kind of proton in the ^1H NMR spectra of the following molecules:



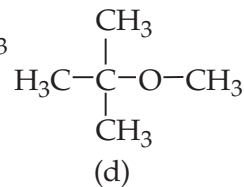
(a)



(b)



(c)



(d)

4. Predict the number of signals that would appear in the ^{13}C NMR spectrum of each of the molecules in Pre-Laboratory Assignment 3.

5. Propose a structure for a molecule with a molecular formula $\text{C}_{10}\text{H}_{13}\text{NO}$ and the following ^1H NMR data. Briefly explain your answer.

<i>ppm</i>	<i>number of Hs</i>	<i>multiplicity</i>
1.05	3	triplet
1.75	3	singlet
3.70	2	quartet
7–7.6	5	complex multiplet