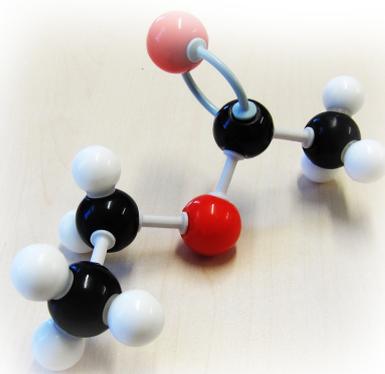
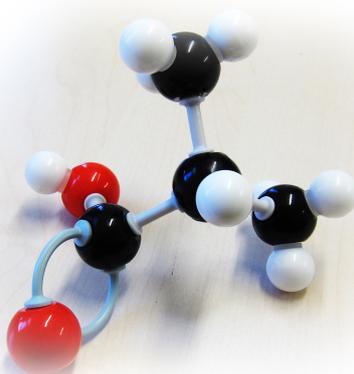
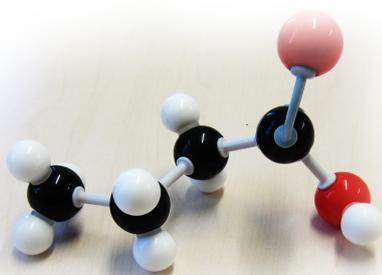


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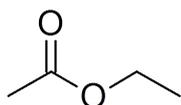
**Basic Concepts of NMR:
Identification of the Isomers
of C₄H₈O₂ by ¹H NMR
Spectroscopy**



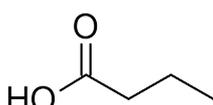
Objectives

NMR spectroscopy is a powerful tool in determining the structure of compounds. Not only is it able to give you information regarding which functional groups are present, but NMR spectra are also capable of giving information about the

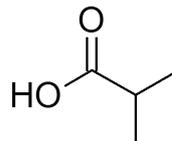
positions of atoms in the molecule. Here is an example where NMR can be used to identify the structure of different compounds which all have the chemical formula $C_4H_8O_2$.



Ethyl Acetate



Butyric Acid



Isobutyric Acid

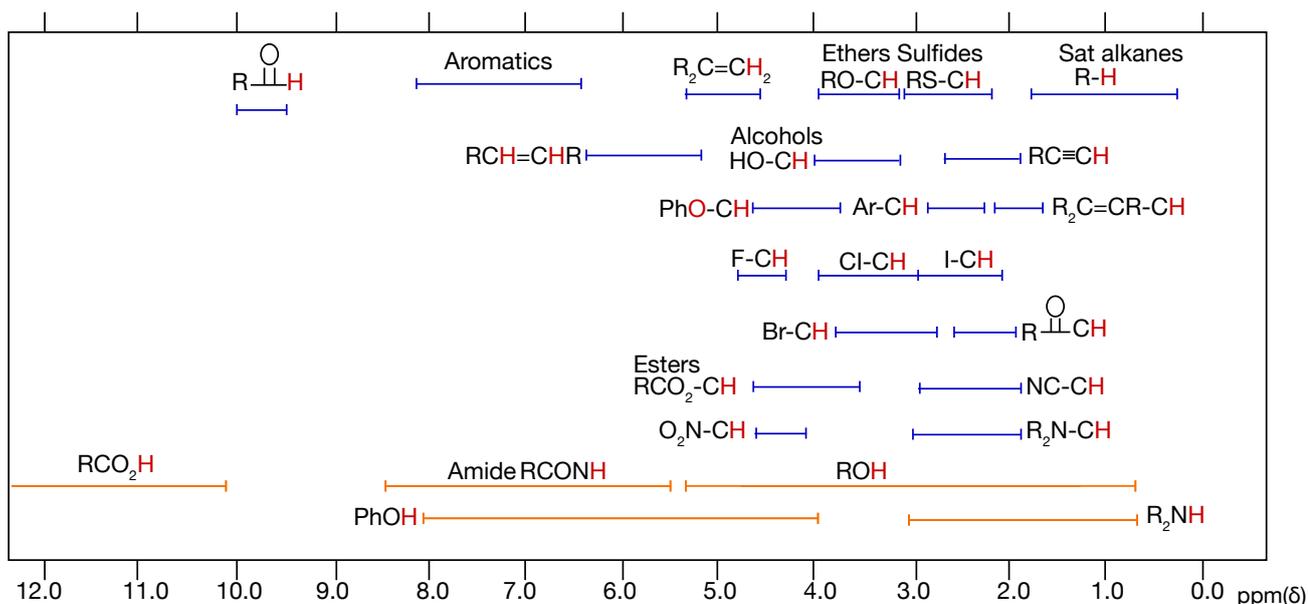
Student Instructions

The three isomers with the molecular formula $C_4H_8O_2$ contain different functional groups and carbon skeletons.

All three compounds are liquids at room temperature. Measure the 1D proton spectra of neat samples on the Spinsolve[®] Proton NMR spectrometer. Prepare your sample by pipetting approximately 700 μ L of the liquid into a 5 mm NMR tube. Identify the compound for each 1D proton spectrum and assign the resonances in the

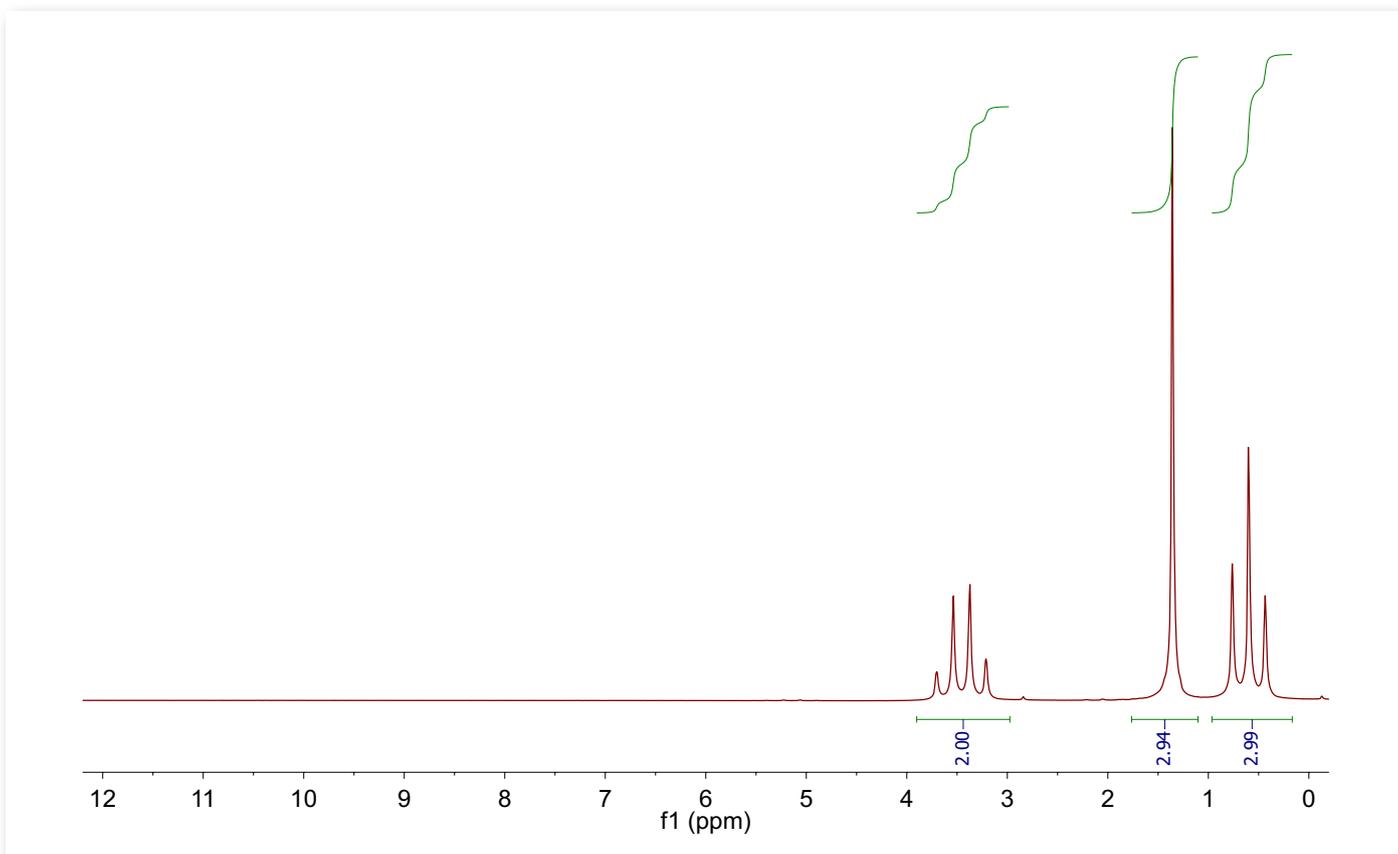
spectrum to the structure.

Create a table for each unknown with five columns: chemical shift, integration value, multiplicity (splitting pattern of the peak), coupling constant and possible environment. Chemical shift tables such as that below show the typical range for the chemical shifts of common functional groups in organic compounds. When used in combination with the splitting pattern and integration values, chemical shift can be used to identify the structure of a compound.



Worked Example

Compound 1



δ ^1H	Integration	Multiplicity	Coupling Constant	Environment
3.45	2	Quartet	7.1 Hz	ROH, RCO ₂ CHR, PhOCHR ₂ , R ₂ CHOH
1.36	3	Singlet	-	ROH, R(CO)CHR ₂ , R ₂ C=CRCHR ₂ , RC≡CH
0.60	3	Triplet	7.1 Hz	ROH, R ₃ CH

Note that some of these chemical shifts overlap with functional groups that contain atoms other than carbon, hydrogen and oxygen. It is useful to exclude these because the chemical formula is known and does not contain any of those other atoms.

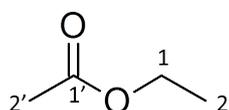
This compound contains three different proton environments, but from the molecular formula we know that there are four carbons. This means one of the carbons is nonprotonated or two of the carbons are equivalent.

The number of protons in the 1D proton spectrum adds to 8, accounting for all of the hydrogen atoms in the molecule.¹ The chemical shift of the resonance at δ_{H} 3.45 is very downfield, thus deshielded. This suggests that the carbon at this position has a single bond to an oxygen atom. The resonance at δ_{H} 1.36 is slightly downfield, and its chemical shift suggests that it may be near a carbonyl or carbon-carbon multiple bond. Since none of the compounds contain carbon-carbon multiple bonds, there must be a carbonyl in Compound 1. δ_{H} 0.60 is at the chemical shift expected for a 'regular' carbon in a saturated environment.

Analysis of the coupling pattern of the peaks in the spectrum allows building blocks to be assembled in order to elucidate the structure. The proton at δ_{H} 3.45 is a quartet, so it couples to three equivalent protons on the neighbouring carbon. Therefore the adjacent group is a methyl. This resonance accounts for a CH_2 because it

integrates for 2 protons. The carbon is therefore attached to two hydrogens and a methyl group (accounts for three bonds). The lack of additional coupling means that the fourth bond is to a nonprotonated atom. The chemical shift suggests that it is an oxygen atom. Both of the remaining resonances are methyl groups as they integrate for three protons. The proton δ_{H} 0.60 appears in the spectrum as a triplet, which means it is adjacent to a carbon with two equivalent protons. Thus δ_{H} 0.60 couples to the protons at δ_{H} 3.45, therefore they are connected. The chemical shift of δ_{H} 0.60 is consistent with this position (shielded, saturated carbon). The methyl group at δ_{H} 1.36 is a singlet, so it does not have any nearest neighbours. This means it is not adjacent to a protonated atom, and from the chemical shift it is next to the carbonyl.

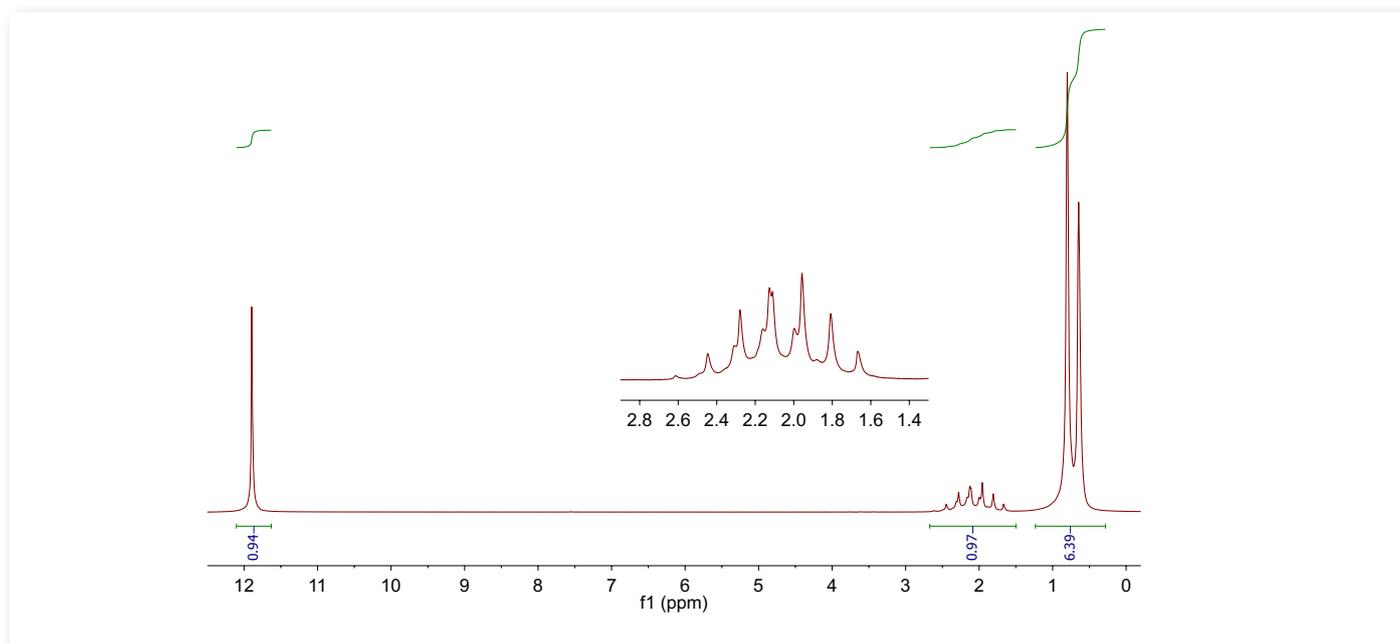
Putting together the building blocks and considering the functionality suggested by the chemical shifts and molecular formula, Compound 1 can be identified as ethyl acetate.



$^1\text{H NMR}$ (42.5 MHz, neat) δ 3.45 (q, $J = 7.1$, 2 H, H-1), 1.36 (s, 3 H, H-2'), 0.60 (t, $J = 7.1$, 3 H, H-2).

1. Exchangeable protons often appear as broad peaks, sometimes such that they cannot be observed.

Compound 2



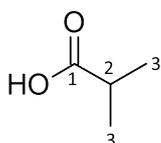
δ ^1H	Integration	Multiplicity	Coupling Constant	Environment
11.90	1	Singlet	-	RC(O)OH
2.13	1	Septet	6.8 Hz	ROH, R(CO)CH ₃ , R ₂ C=CRCHR ₂ , RC≡CH
0.73	6	Doublet	6.7 Hz	ROH, R ₃ CH

There are three different proton environments and from the molecular formula there are four carbon atoms, therefore one of the carbons is nonprotonated or there are two equivalent carbon atoms.

The chemical shift of the resonance at δ_{H} 11.90 is shifted downfield such that it must be the hydroxyl proton of a carboxylic acid. This accounts for both oxygen atoms and a hydrogen atom. The resonance at δ_{H} 2.13 integrates for one proton, therefore it is a CH group. The slight downfield shift of this resonance from the regular aliphatic protons at δ_{H} 0.73 suggests that it is near the carboxylic acid functional group. The splitting of

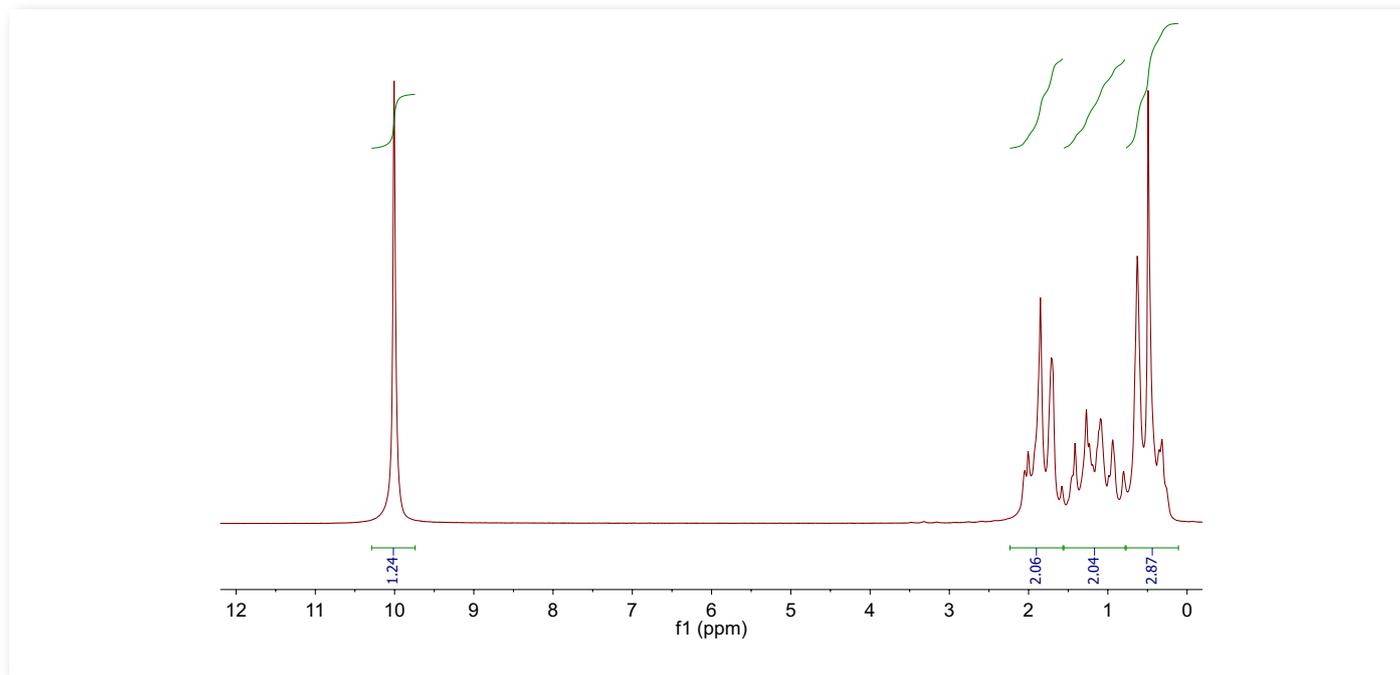
the resonance at δ_{H} 2.13 is observed as a septet, which means it couples to 6 equivalent protons, those at δ_{H} 0.73. The peak at δ_{H} 0.73 integrates for 6 protons and appears as a doublet, meaning it couples to the proton at δ_{H} 2.13. With the carboxylic acid functional group and a CH group accounted for, we are left with 2 carbons and 6 hydrogens. Therefore the 6 protons at δ_{H} 0.73 are equivalent methyl groups.

Putting together the building blocks and considering the functionality suggested by the chemical shifts and molecular formula, Compound 2 can be identified as isobutyric acid.



^1H NMR (42.5 MHz, neat) δ 11.90 (s, 1 H, OH), 2.13 (sept, $J = 6.8$, 1 H, H-2), 0.73 (d, $J = 6.7$, 6 H, H-3).

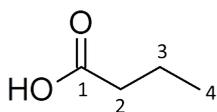
Compound 3



δ ^1H	Integration	Multiplicity	Coupling Constant	Environment
10.02	1	Singlet	-	RC(O)OH
2.1-1.6	2	Multiplet	-	$\text{ROH, R(CO)CH}_3, \text{R}_2\text{C=CRCHR}_2, \text{RC}\equiv\text{CH, R}_3\text{CH}$
1.6-0.8	2	Multiplet	-	$\text{ROH, R}_2\text{C=CRCHR}_2, \text{RC}\equiv\text{CH, R}_3\text{CH}$
0.8-0.2	3	Multiplet	-	R_3CH

The spectrum contains four different proton environments. The chemical shift of the resonance at δ_{H} 10.02 is highly shifted downfield and therefore falls in the chemical shift range for the hydroxyl proton of a carboxylic acid. The three remaining proton environments are not well resolved and it is therefore difficult to determine their chemical shift and multiplicity. However this does give information about the structure, in that these protons are in a similar chemical

environment, which is characteristic for alkyl chains. The position of the peaks can be estimated and integrated and from these integration values we see CH_2 , CH_2 , CH_3 . It can also be determined from the chemical shift range the distance from the carbonyl group, with the CH_2 group at δ_{H} 2.1-1.6 being the closest and the CH_3 group at δ_{H} 0.8-0.2 being the furthest. A carboxylic acid with a 3-carbon alkyl leads to the assignment of Compound 3 as butyric acid.



$^1\text{H NMR}$ (42.5 MHz, neat) δ 10.02 (s, 1 H, OH), 2.1-1.6 (m, 2 H, H-2), 1.6-0.8 (m, 2 H, H-3), 0.8-0.2 (m, 3 H, H-4).



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Journal of Chemical Education 1985 62 (3), 26

Manuscript prepared by Sarah Moore.

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