Basic Concepts of NMR: Distinguishing Between the Isomers of $C_4H_8O_2$ by ^1H NMR Spectroscopy
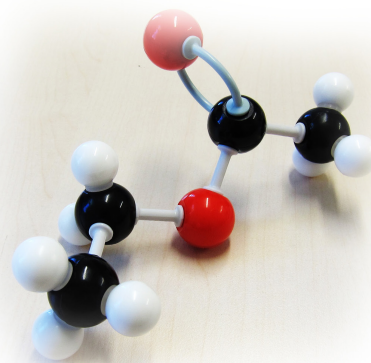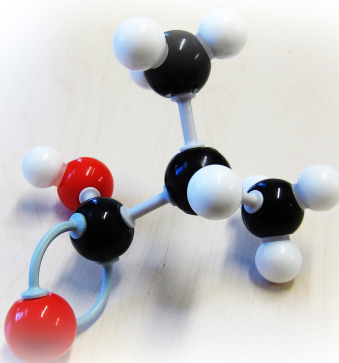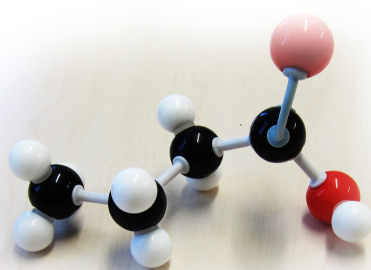
Objectives

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 distinguish between the structural isomers with the chemical formula $C_4H_8O_2$.

Student Instructions

The three isomers below 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 samples by pipetting approximately 700 μL of the liquid into a 5 mm NMR tube. Identify the 1D proton spectrum of each compound and assign the resonances in the spectrum to the structure.
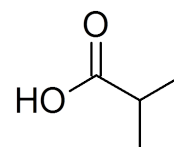
Tip:

It is useful first to consider the structure of the three possible isomers and think about how the 1D proton NMR spectrum will look. Aspects to consider are the number of environments, integration, multiplicity and chemical shift. Identify the number of proton environments you would expect to see and create a table with integration, splitting and chemical shift in order to predict what the spectrum will look like. You can then use these predictions to identify which spectrum belongs to each isomer.
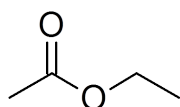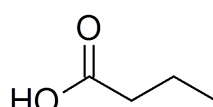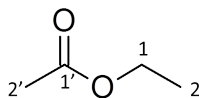
Ethyl Acetate   Butyric Acid   Isobutyric Acid

Example Discussion

Ethyl acetate

Number of environments observed in spectrum: 3 (1, 2, 2')

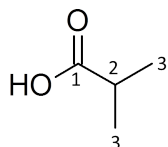| Position	Integration	Splitting	Chemical shift
1	2	Three nearest neighbours that are equivalent - quartet	Single bond to oxygen - deshielded
2	3	Two nearest neighbours that are equivalent - triplet	Saturated alkyl group far from ester group - shielded
2'	3	No nearest neighbours - singlet	Adjacent to the carbon of a carbonyl – slightly deshielded

Butyric acid
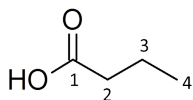
Number of environments observed in spectrum: 3 or 4 (2, 3, 4, possibly OH)

Exchangeable protons such as the OH of a carboxylic acid are sometimes absent from the proton NMR spectrum because they exchange on the timescale of the NMR experiment.

Position	Integration	Splitting	Chemical shift
2	2	Two nearest neighbours that are equivalent -triplet	Adjacent to the carbon of a carbonyl – slightly deshielded
3	2	Five nearest neighbours in two different environments – quartet of triplets or triplet of quartets (will be observed as a multiplet)	Saturated alkyl group far from carboxylic acid group - shielded
4	3	Two nearest neighbours - triplet	Saturated alkyl group far from carboxylic acid group - shielded
OH	1	Exchangeable proton - singlet	Proton directly bound to an oxygen – highly deshielded

Isobutyric acid

HO—C(=O)—CH(CH₃)(CH₃) *(structure: carboxylic acid carbon labeled 1, CH labeled 2, two methyl groups labeled 3)*

Number of environments observed in spectrum: 2 or 3 (2,3, possibly OH)

| Position	Integration	Splitting	Chemical shift
2	1	Six nearest neighbours that are equivalent - septet	Adjacent to the carbon of a carbonyl – slightly deshielded
3	6 – equivalent methyl groups	One nearest neighbour -doublet	Saturated alkyl group far from carboxylic acid group - shielded
OH	1	Exchangeable proton - singlet	Proton directly bound to an oxygen – highly deshielded

Spectrum 1
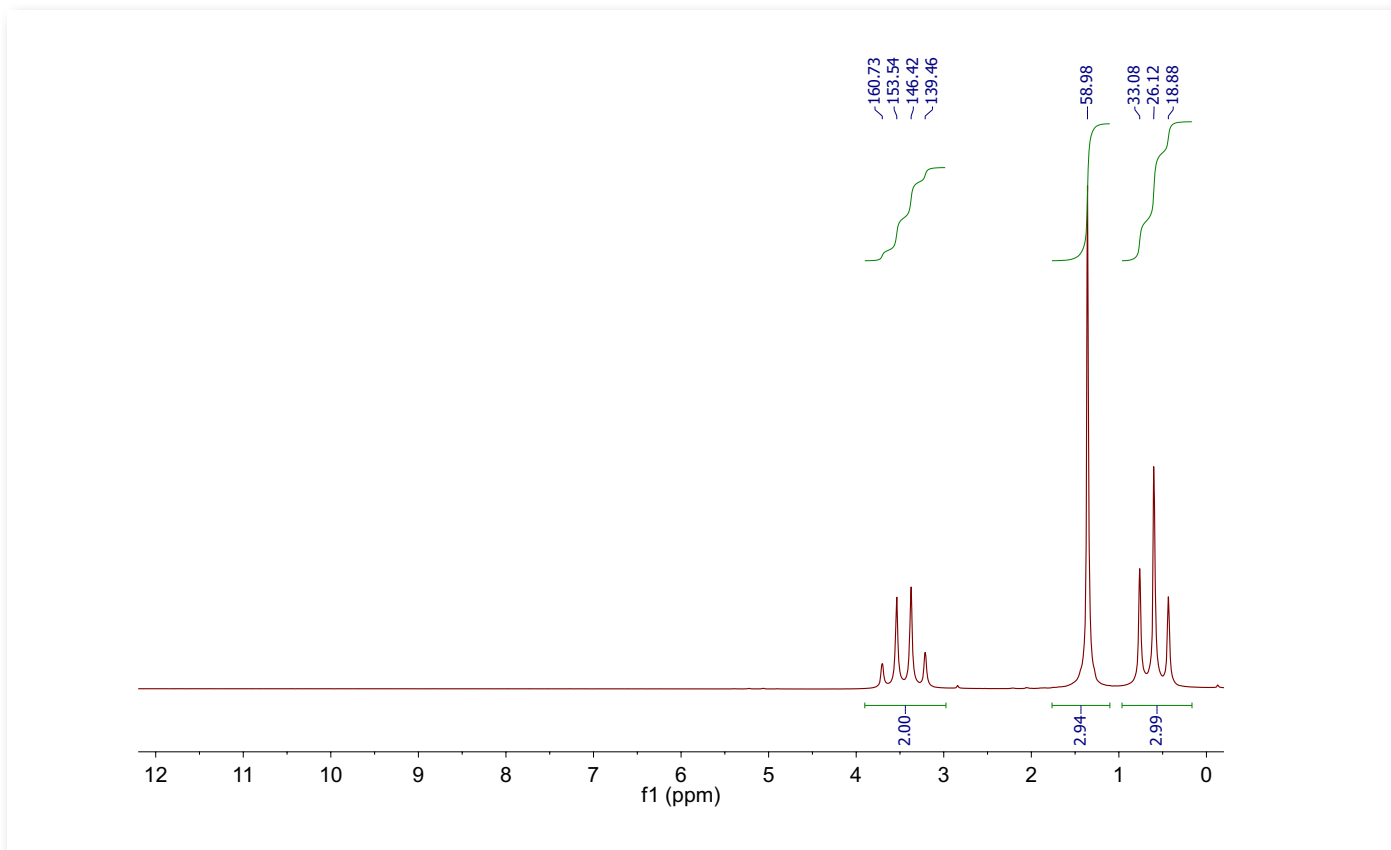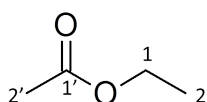
Spectrum 2
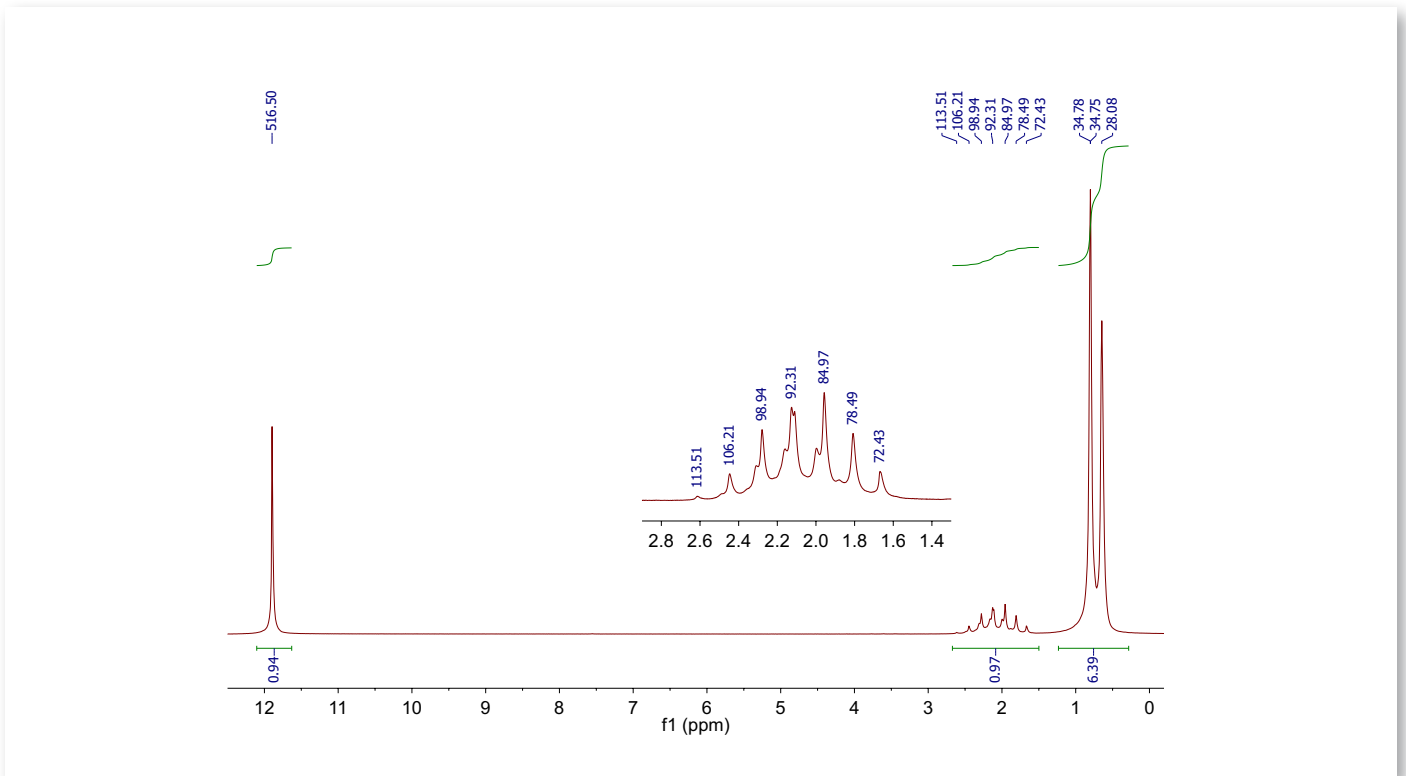
Spectrum 3
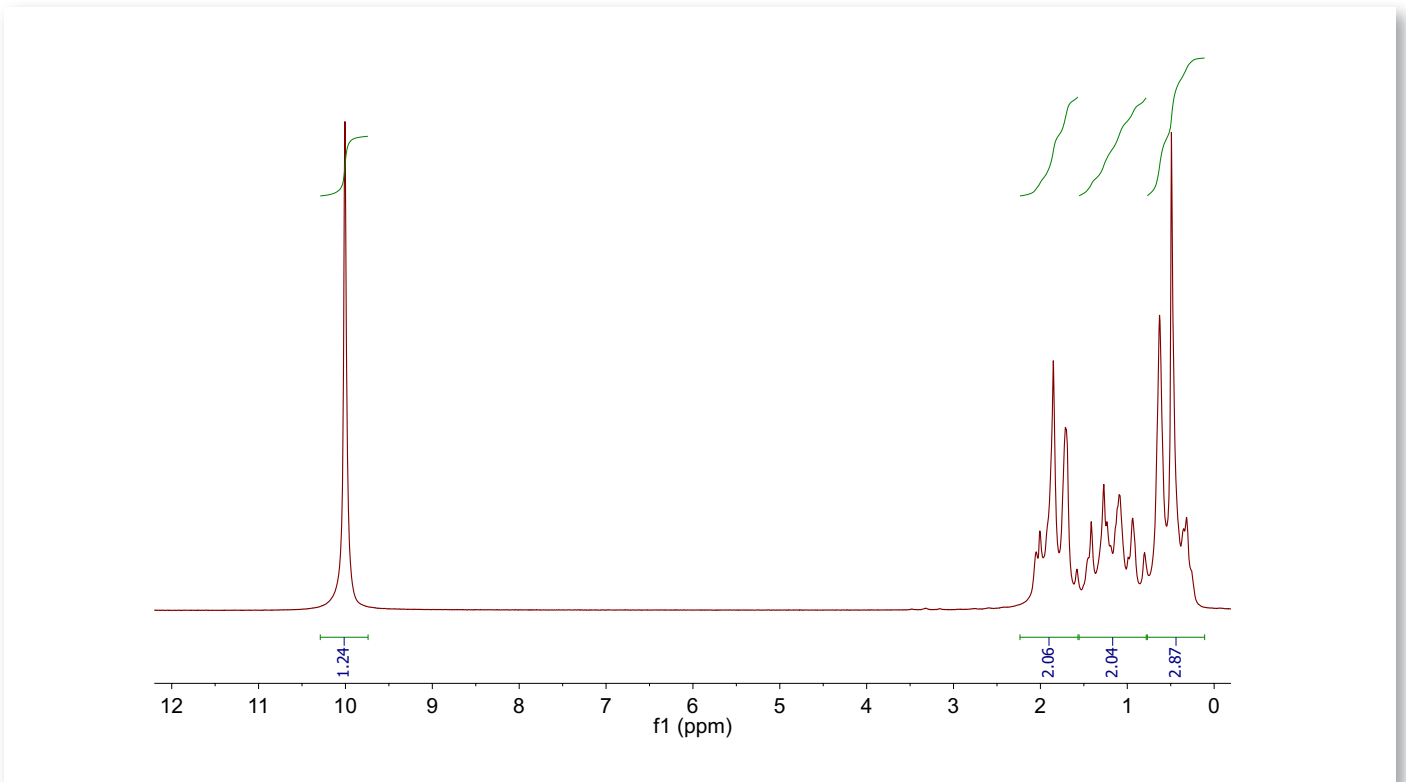
Spectrum 1 does not contain an OH peak, although that does not mean there is no OH. However, the integration values of the observed protons add to 8, so there is no OH in the molecule. There is one slightly downfield resonance that appears as a quartet, and two methyl groups that appear as a triplet and a singlet. These observations are consistent with the assignment of the molecule as ethyl acetate.

Spectrum 2 and 3 both contain the OH peaks of a carboxylic acid. Spectrum 2 has three chemical environments, the OH, a septet and a doublet. This is consistent with the predictions for isobutyric acid.

In Spectrum 3 there is the carboxylic acid OH peak and a complex cluster of peaks between 0 and 2 ppm, which is characteristic of an alkyl chain. Despite appearing complex, three slightly different environments can be observed. The upfield chemical shift of these three protons is consistent with the predictions made for butyric acid. Considering the predictions made for the multiplicity of these protons, it could be suggested that the cluster of peaks are two triplets and a multiplet.
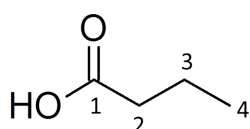
Ethyl acetate: Spectrum 1

^{1}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).

Isobutyric acid: Spectrum 2
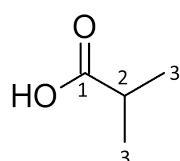
^{1}H NMR (42.5 MHz, neat) δ 11.90 (s, 1 H, OH), 2.13 (sept, J = 6.8, 1 H, H-2), 0.73 (d, J = 6.7, 6 H, H-3).

Butyric acid: Spectrum 3

^{1}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).

References

1)   Structural isomer identification via NMR: A nuclear magnetic resonance experiment for organic, analytical, or physical chemistry
      Zvi Szafran
      Journal of Chemical Education 1985 62 (3), 260

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