

INTRODUCTION TO STRUCTURE DETERMINATION

There are so many organic compounds in existence that it can be difficult to establish exactly what compounds, or what combinations of compounds, are present in a given sample. Chemical tests can be used to distinguish between different functional groups, and melting point and boiling point data can provide some further information as to the identity and purity of a compound, but they can generally only confirm suspected structures and can not usually be used to identify new compounds. Chemical techniques also require fairly large quantities of sample and are not always effective at distinguishing between similar compounds.

Chemists have developed a number of other, more precise, analytical techniques to determine the exact structure of organic compounds. These **include chromatography, mass spectrometry, infra-red spectroscopy and nuclear magnetic resonance (nmr) spectroscopy**. This topic is concerned with chromatography and nmr spectroscopy.

USING THE ANALYTICAL TECHNIQUES TOGETHER

If all the different spectra are available, then the most effective analytical strategy is to use them together. There are a number of useful steps to deducing the structure:

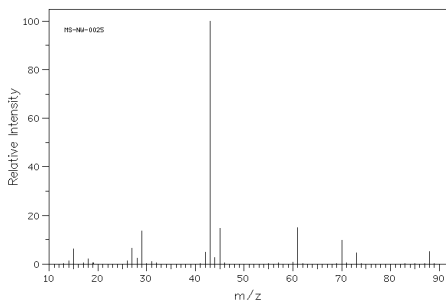
If composition data is available:

1. Use the composition data to work out the empirical formula.
2. Use the mass spectrum to deduce the relative molecular mass, and hence work out the molecular formula.
3. Use the infra-red spectrum to check for the presence of C=O and O-H bonds, and hence identify the functional group.
4. Using the integration factors and splitting patterns in the proton nmr spectra, identify pairs of hydrogen environments which are clearly linked to each other: Eg a 3H triplet and a 2H quartet means CH_3CH_2- , two 2H doublets means $-\text{CH}_2\text{CH}_2-$ and a 3H triplet and a 2H doublet means $\text{CH}_3\text{CH}-$.
5. Use the chemical shifts to attach the correct functional group to each hydrogen environment.

A worked example of combined analysis is given below (no composition data available):

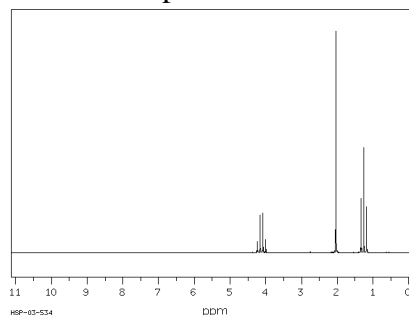
Use the following spectra to deduce the structure of A:

Mass spectrum:



Molecular ion peak = 88

Proton nmr spectrum:



three peaks:

$\delta = 1.3$, triplet, integration factor 3

$\delta = 2.0$, singlet, integration factor 3

$\delta = 4.1$, quartet, integration factor 2

Infra-red spectrum: sharp absorption at 1715 cm^{-1} , no broad absorptions between 1500 and 3500 cm^{-1}

ANSWER:

From mass spectrum, $r_{m/m} = 88$

From infra-red spectrum, C=O present

From proton nmr spectrum, sum of integration factors = 8

So 8, 16 or 24 hydrogen atoms present and at least one oxygen

If one O atom present, remaining mass = 62 and cannot make this using 8/16/24 H atoms

If two O atoms present, remaining mass = 56; can make this from 4 carbons and 8 hydrogens

So likely molecular formula = $C_4H_8O_2$.

From infra-red spectrum, no O-H is present, so it is not a carboxylic acid.

So is probably an ester.

Possible structures:

Methyl propanoate, ethyl ethanoate, propyl methanoate, methylethyl methanoate

From proton nmr spectrum:

There are 3 hydrogen environments so it cannot be propyl methanoate (which has 4).

The integration factors are 3:3:2 so cannot be methylethyl methanoate (which has the ratio 6:1:1).

The coupling (3H triplet, 2H quartet, 3H singlet) is consistent with both remaining possible structures.

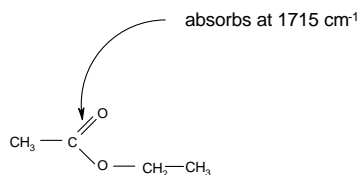
But the 3H singlet has a chemical shift of 2.0, which is consistent with CH_3CO and not CH_3O (for which the chemical shift would be 3.3 – 4.0)

The 2H quartet has a chemical shift of 4.1, which is consistent with CH_3CH_2O and not CH_3CH_2CO (for which the chemical shift would be 2.0 – 2.5)

So it cannot be methyl propanoate and therefore the structure is ethyl ethanoate.

Full explanation of spectra:

Infra-red spectrum:



Proton nmr spectrum:

