

## 6 Carbon-13 NMR

### A Rationale

Carbon-13 NMR has enough in common with proton NMR for it to be used to illustrate NMR in general. For example, its chemical scale is referenced to the same compound, tetramethylsilane; both nuclei have a spin quantum number of  $\frac{1}{2}$  and are ubiquitous in organic molecules; both techniques are routine in chemical laboratories. Carbon-13 NMR offers two distinct advantages over proton NMR:

- Spin-spin coupling is not observed in spectra. With a natural abundance of about 1%,  $^{13}\text{C}$ - $^{13}\text{C}$  coupling can go unnoticed in spectra.  $^{13}\text{C}$ - $^1\text{H}$  coupling is routinely eliminated from spectra by broadband proton decoupling. Note that a consequence of this decoupling is that peak intensities are not proportional to the number of nuclei in a given environment.
- The chemical shift scale with carbon-13 is more simple and intuitive than the proton scale. The general pattern of resonances shown in the chart on the next page is easily remembered.

An important point is that when a carbon atom has more than one of the features on the chart (e.g. it has a C-C bond and a C=O bond) then its resonance appears in the range with the highest chemical shift values.

The absence of spin-spin coupling means that carbon-13 spectra will be simpler in appearance than proton spectra. They therefore lend themselves to the study of larger and more complex molecules. With larger molecules there are more likely to be interesting symmetry considerations manifesting themselves in spectra. It is therefore an ideal context for considering molecular symmetry.

### Problem-solving exercises

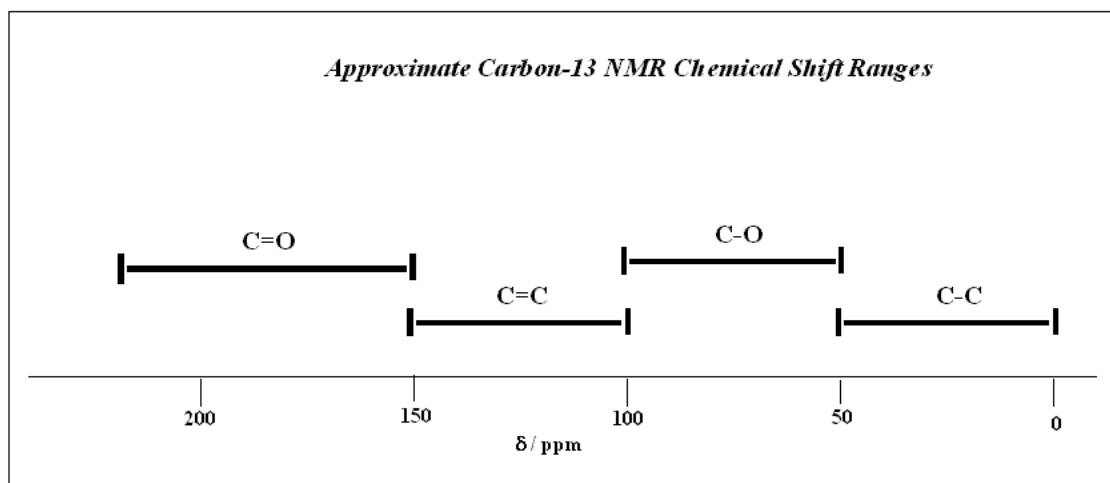
Spectral problem-solving is most easily mastered through practice, and to that end a series of spectra is provided. The first two are simply to illustrate a range of chemical shift values in molecules with no important symmetry. Examples 3 to 6 are of molecules with symmetry elements that make some of the carbon atoms chemically equivalent. The remaining examples are of pairs of isomers.

Candidates need to concentrate on two aspects of the spectra:

- The types of carbon atom in the molecule (following the chart on the next page).
- The number of different chemical environments of carbon in the molecule (and the region of the spectrum that pertains to each one). In order to appreciate when chemical environments are the same, candidates must be able to recognise symmetry relationships where they apply, and that rotation of carbon-carbon single bonds is fast on the nmr time scale.

Candidates should also be able to predict the number of peaks in each of the four regions of the spectrum for a given molecule.

Handout on approximate carbon-13 chemical shift ranges. (Figure produced by Mike Thompson, Winchester College.)



## B Sample exercises

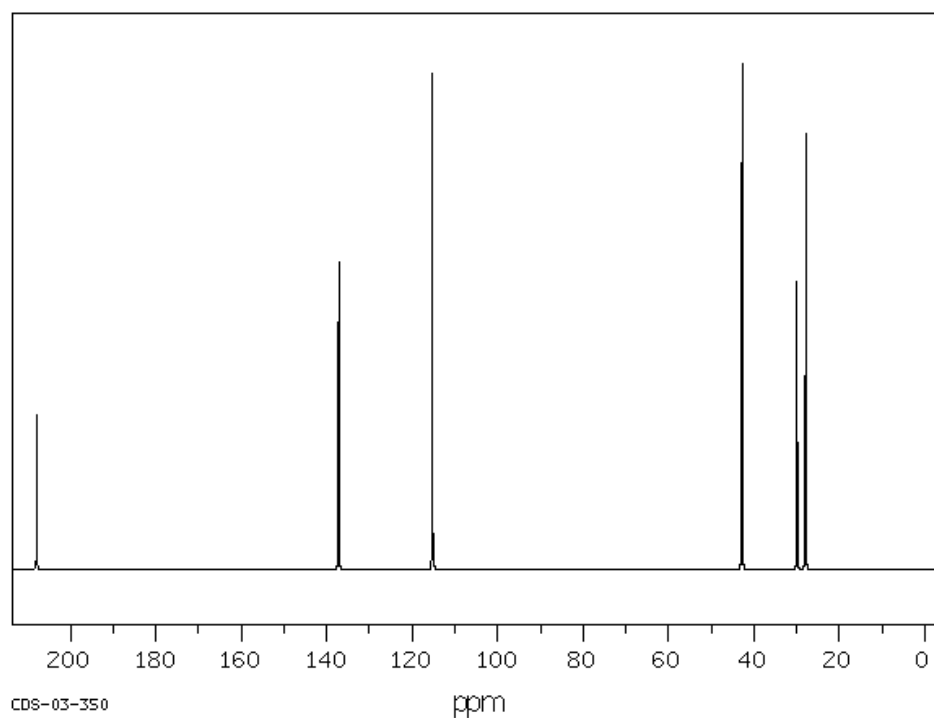
The following spectra were taken from the National Institute of Advanced Industrial Science and Technology of Japan at <http://riodb01.ibase.aist.go.jp/sdbs/>

Following each spectrum the assignment for each peak is given. There is also a brief commentary.

Candidates should, as far as possible, assign all the peaks in the spectra and explain how the number of peaks is consistent with the symmetry of the molecule.

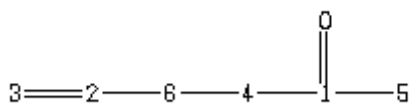
Initially candidates could be given the full assignment and asked to justify the assignment. Then candidates could be given the molecular structure and asked to assign as far as possible each of the carbons in the molecule to a peak in the spectrum. The most able could be given just the spectrum and asked to propose a molecule that is consistent with it.

## Example 1



## Assignment

Hex-5-en-2-one

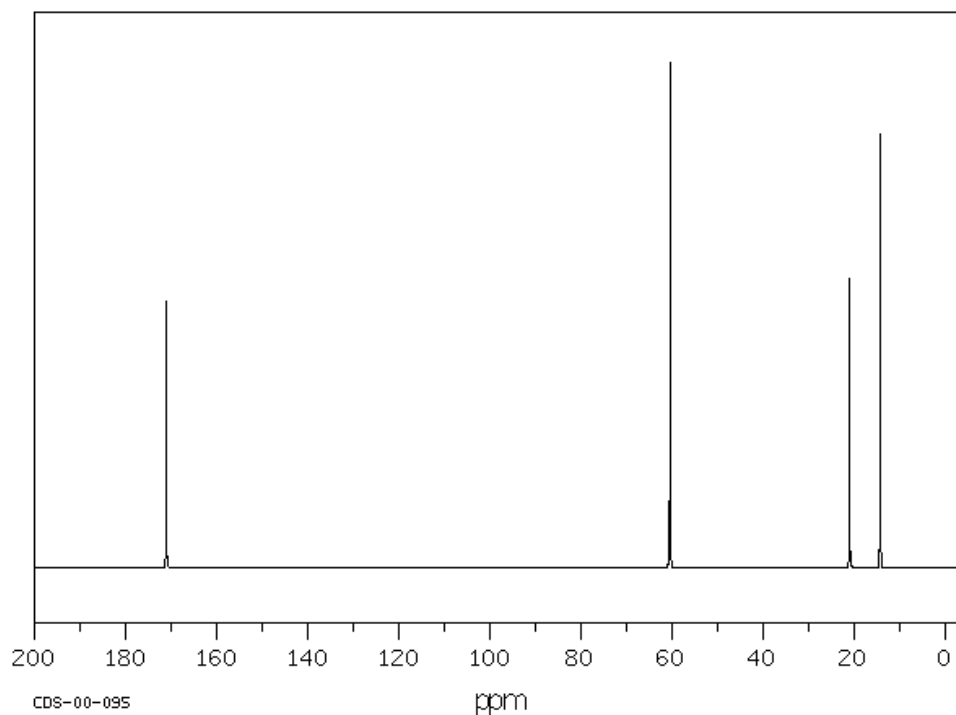


ppm	Int.	Assign.
207.87	305	1
137.19	605	2
115.24	981	3
42.75	1000	4
29.88	567	5
27.88	862	6

## Commentary

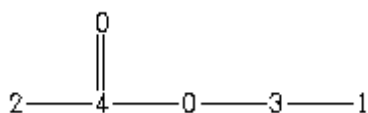
No equivalent carbons in this molecule. Chemical shifts conforming to the general principle, noting that the carbonyl carbon is a little beyond 200 ppm.

## Example 2



## Assignment

Ethyl ethanoate

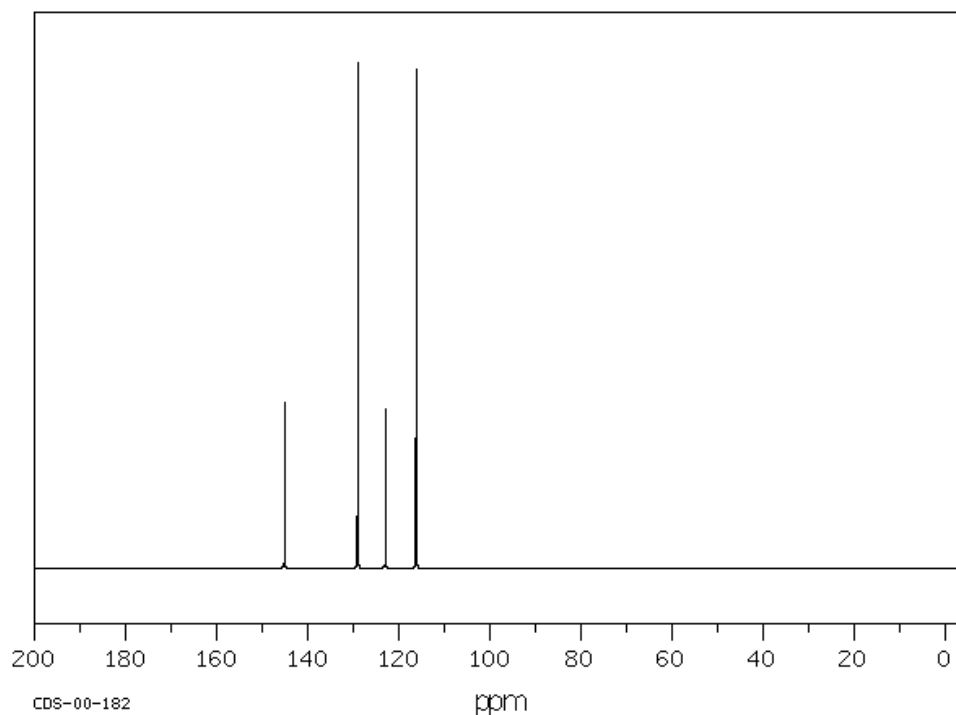


ppm	Int.	Assign.
171.08	527	4
60.44	1000	3
21.00	571	2
14.28	857	1

## Commentary

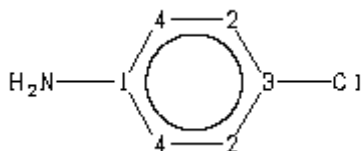
As in the previous example, all carbon environments are non-equivalent. Note that carbon 4 belongs in the C=O region even though it is also a C-O carbon.

## Example 3



## Assignment

4-chlorophenylamine

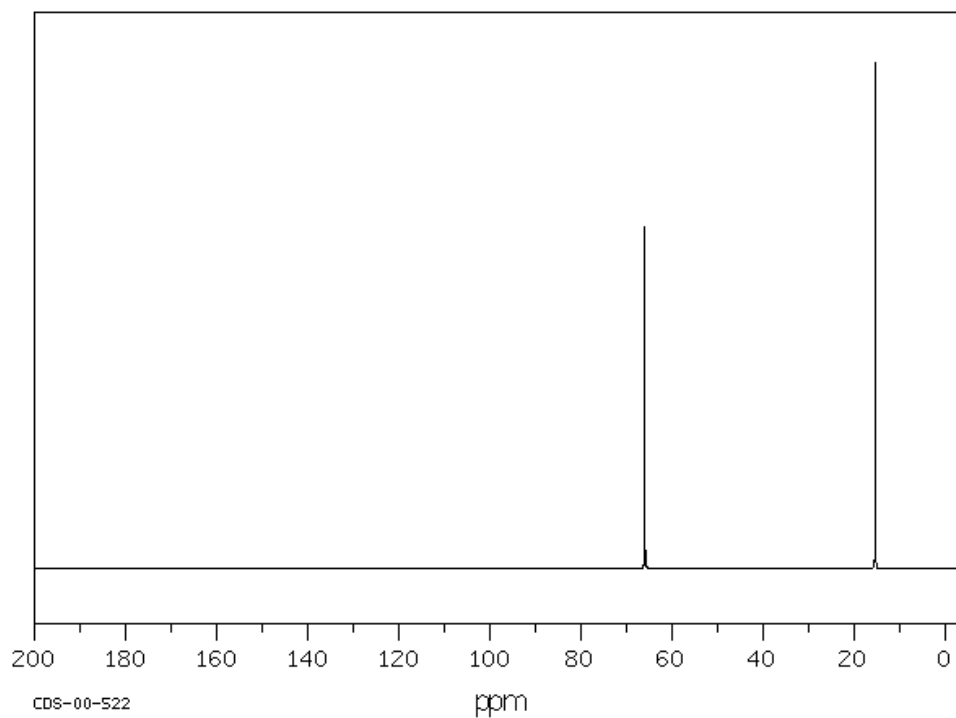


ppm	Int.	Assign.
145.06	328	1
129.05	1000	2
122.92	313	3
116.21	985	4

## Commentary

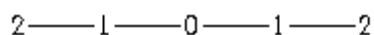
Mirror symmetry along the nitrogen to chlorine axis makes for two pairs of equivalent carbons, reducing the number of signals in the spectrum to four. Considering the benzene ring as alternating single and double bonds, we consider each carbon to be in the C=C region.

## Example 4



## Assignment

Ethoxyethane

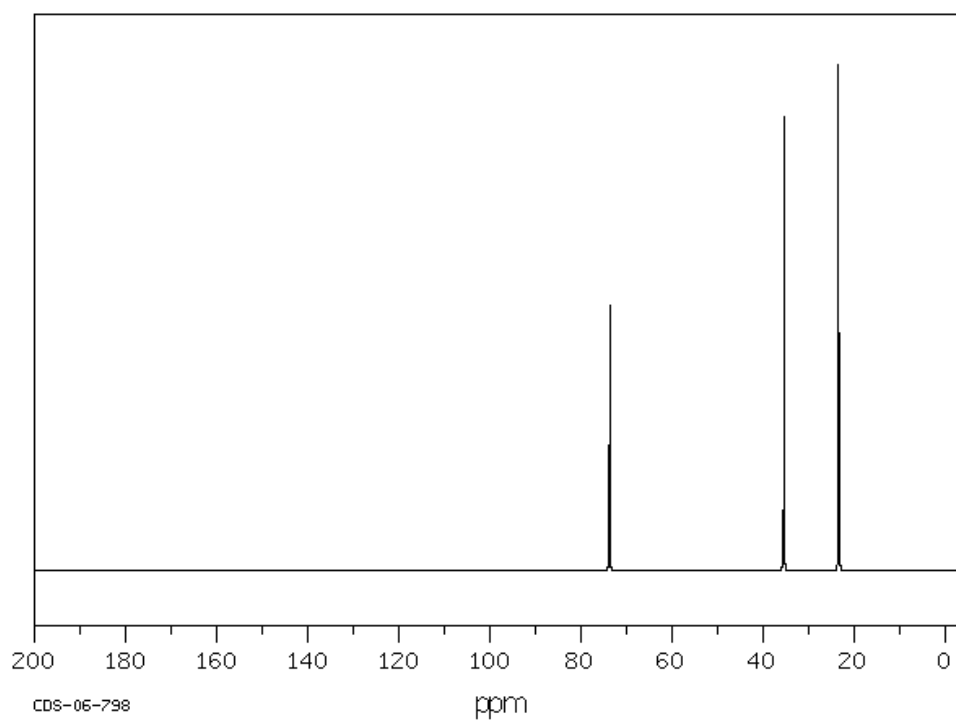


ppm	Int.	Assign.
65.97	675	1
15.35	1000	2

## Commentary

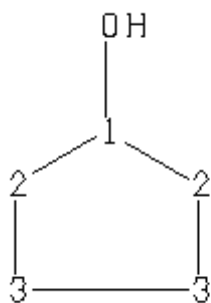
Due to mirror symmetry through the oxygen and half-way between the ethyl groups, there are two pairs of equivalent carbons and only two peaks in the spectrum. Note that the molecule isn't truly linear but that the rapid rotation of the single bonds means it can be treated as such.

## Example 5



## Assignment

Cyclopentanol

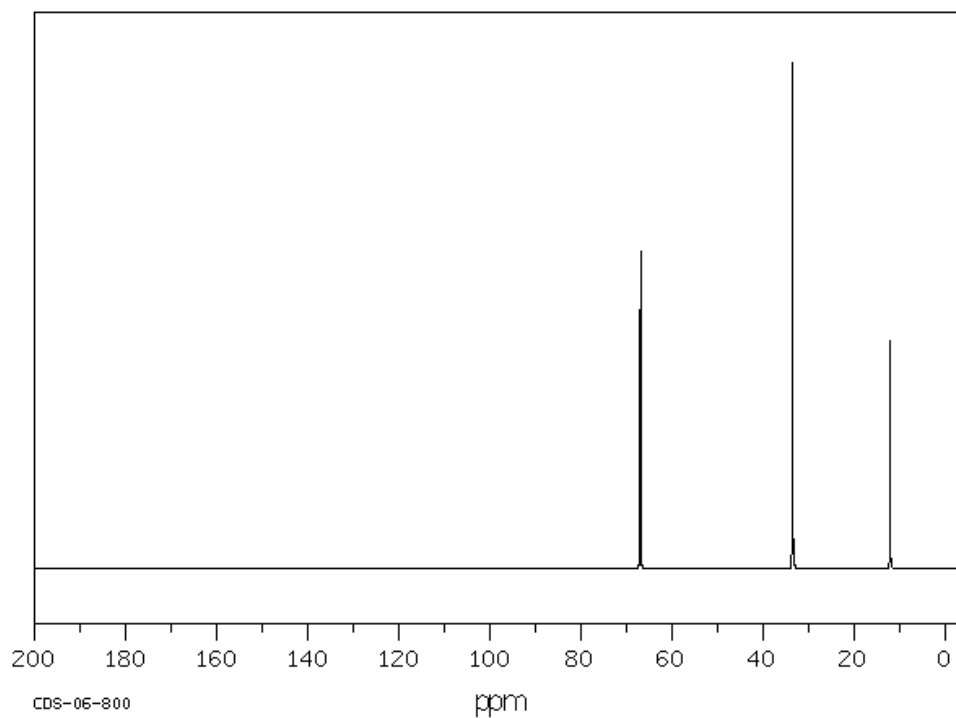


ppm	Int.	Assign.
73.72	522	1
35.44	897	2
23.40	1000	3

### Commentary

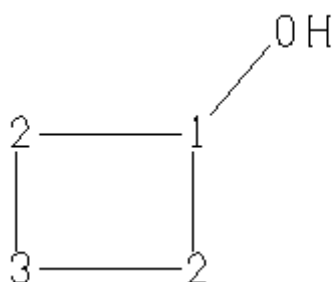
There is a mirror plane along the carbon 1 to oxygen axis, creating two pairs of equivalent nuclei, reducing the number of signals to three. The orientation of the O-H bond doesn't matter as the C(1)-O bond is rotating rapidly.

### Example 6



### Assignment

Cyclobutanol

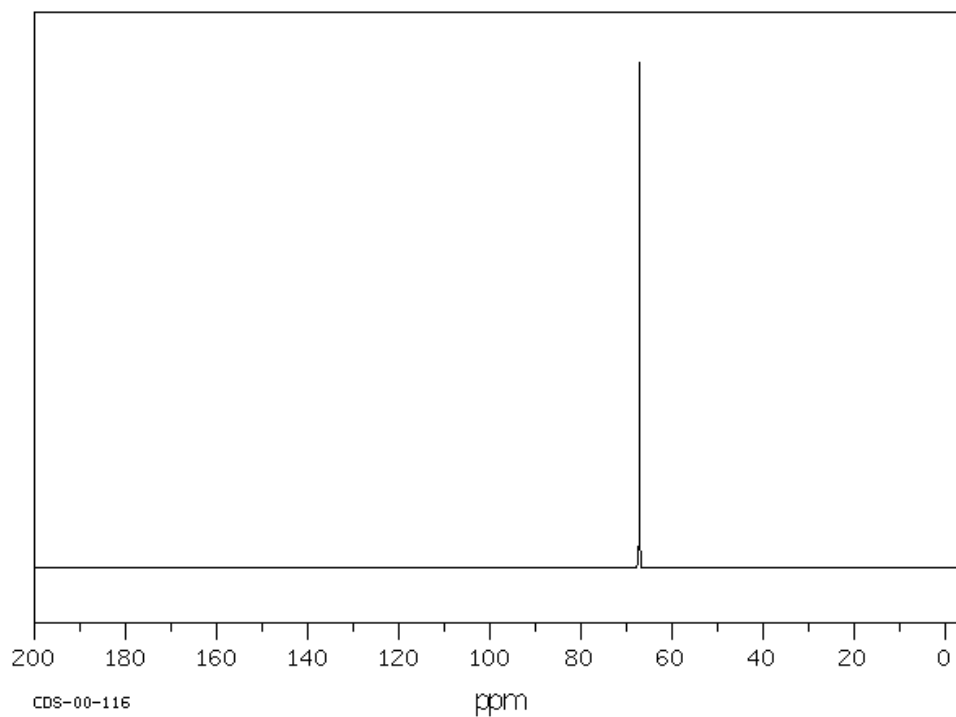


ppm	Int.	Assign.
66.95	626	1
33.52	1000	2
12.10	449	3

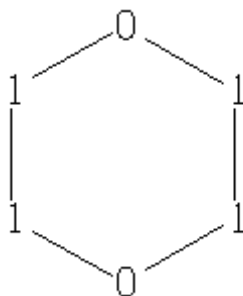


**Commentary**

Similar to the previous example except just one pair of carbons is made equivalent by the mirror plane, bringing the number of signals to three.

**Example 7****Assignment**

1,4-dioxane

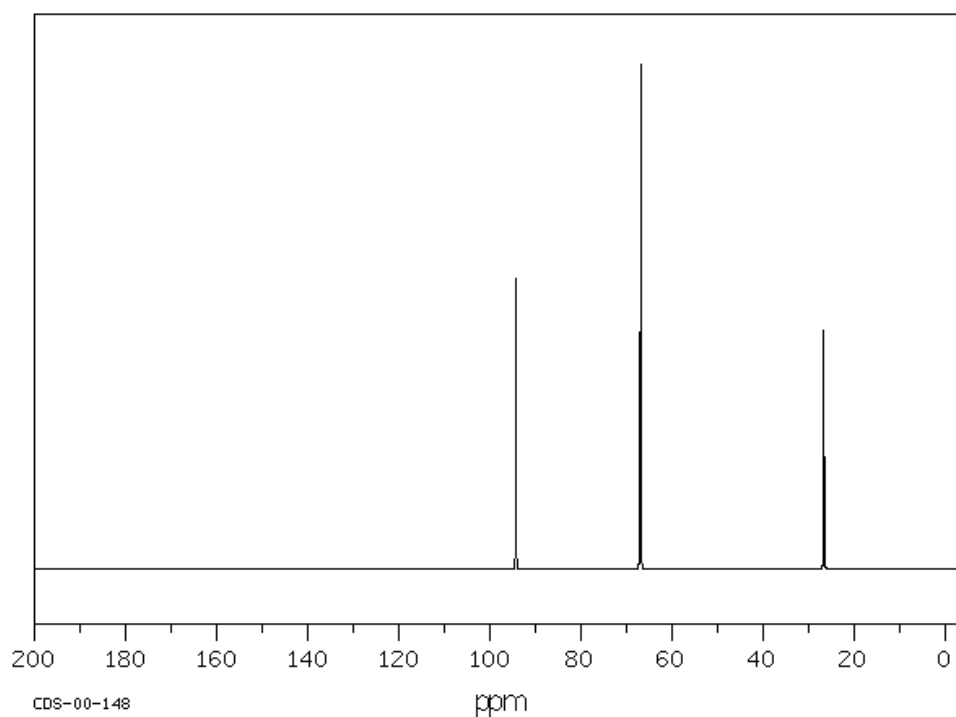


ppm	Int.	Assign.
67.15	1000	1

### Commentary

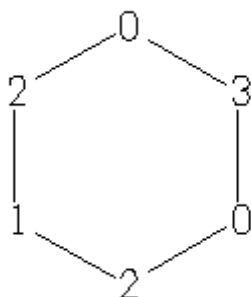
This molecule should be considered alongside the next example. The two perpendicular mirror planes – one through the oxygen atoms and the other bisecting the carbon-carbon bonds – make all of the carbon atoms equivalent. Note that the molecule isn't actually flat but that fast rotation of the single bonds means that it is on average and so can be treated here as if it were.

### Example 8



### Assignment

1,3-dioxane

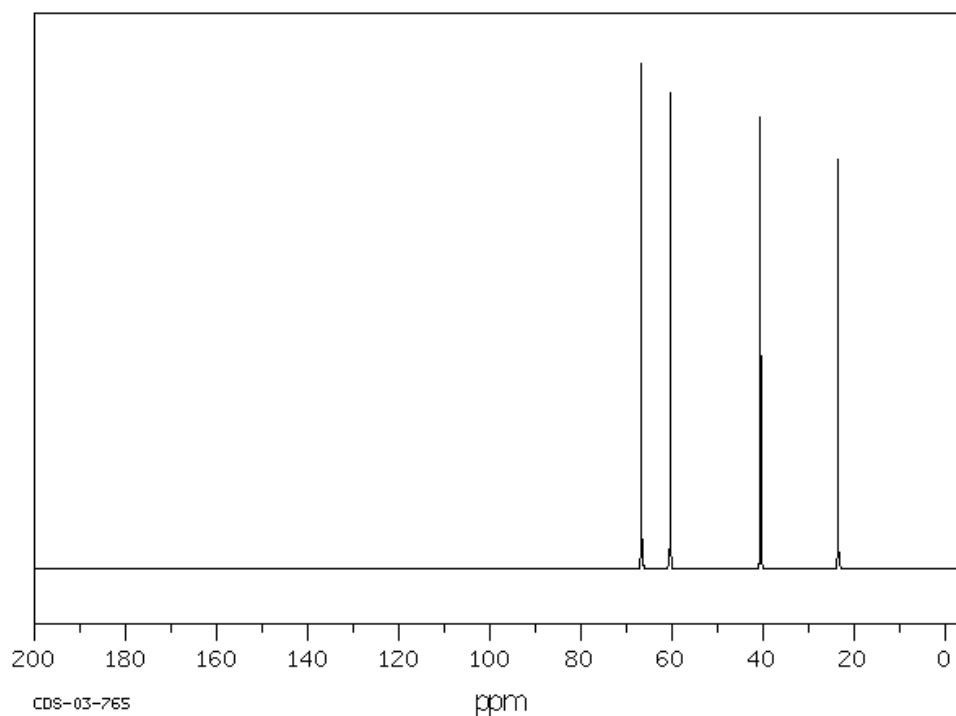


ppm	Int.	Assign.
94.28	575	3
66.94	1000	2
26.64	471	1

### Commentary

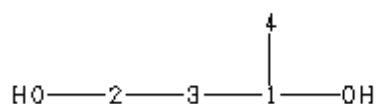
Similar to the previous example except just one mirror plane (through carbons 1 and 3), bringing the number of signals to three.

### Example 9



### Assignment

Butane-1,3-diol

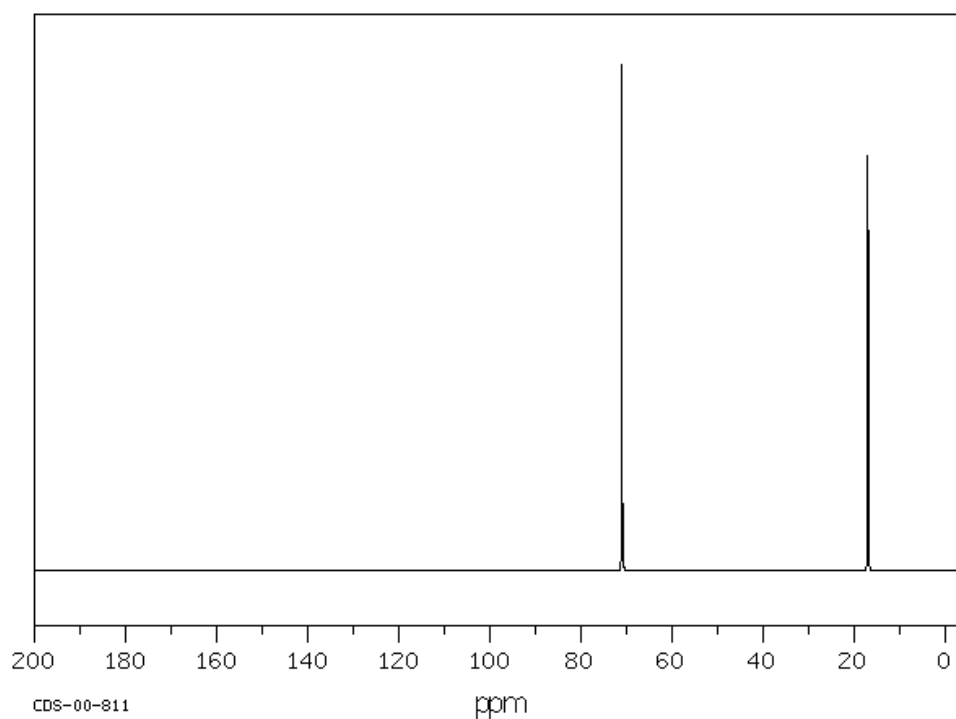


ppm	Int.	Assign.
66.72	1000	1
60.37	942	2
40.54	894	3
23.52	808	4

### Commentary

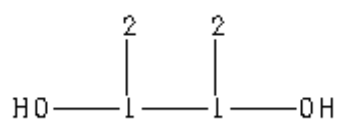
This molecule should be considered alongside the next example. In this case there is no symmetry in the molecule, and so there are four peaks in the spectrum in the predicted regions.

### Example 10



### Assignment

Butane-2,3-diol



ppm	Int.	Assign.
70.98	1000	1
16.96	820	2

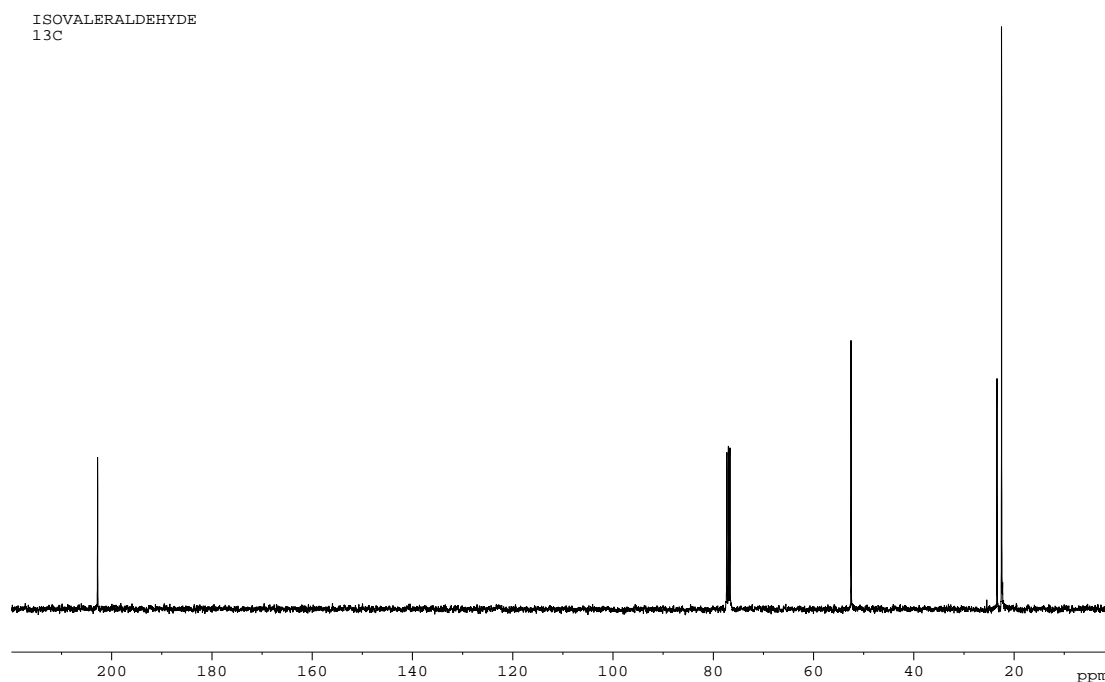
### Commentary

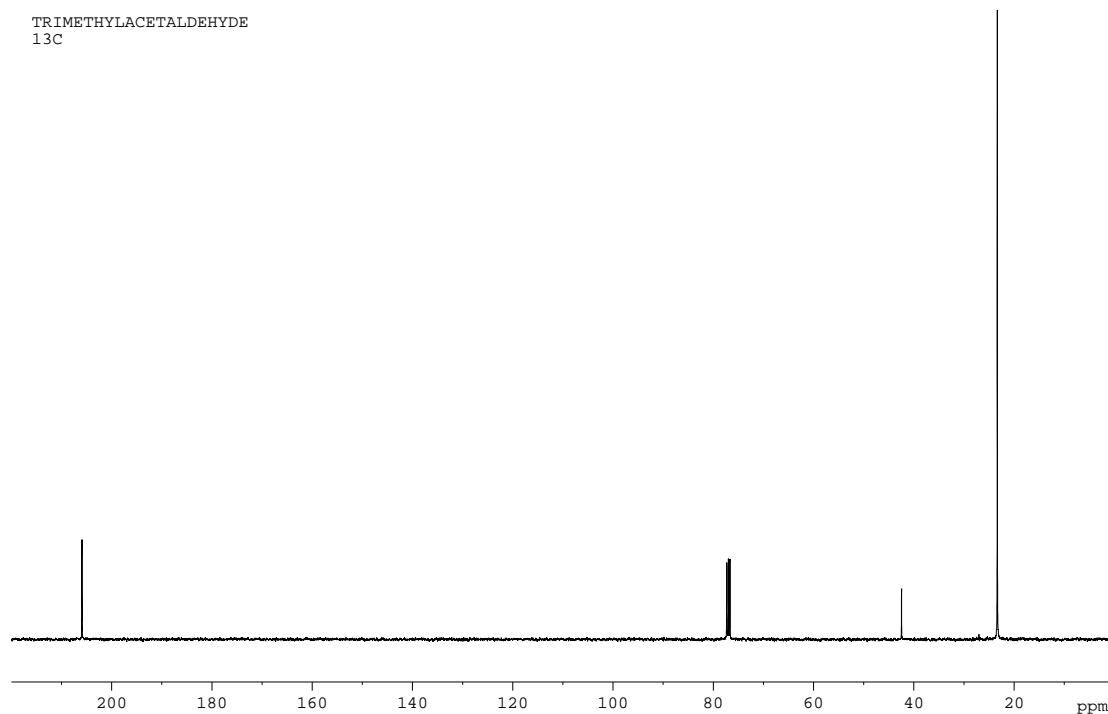
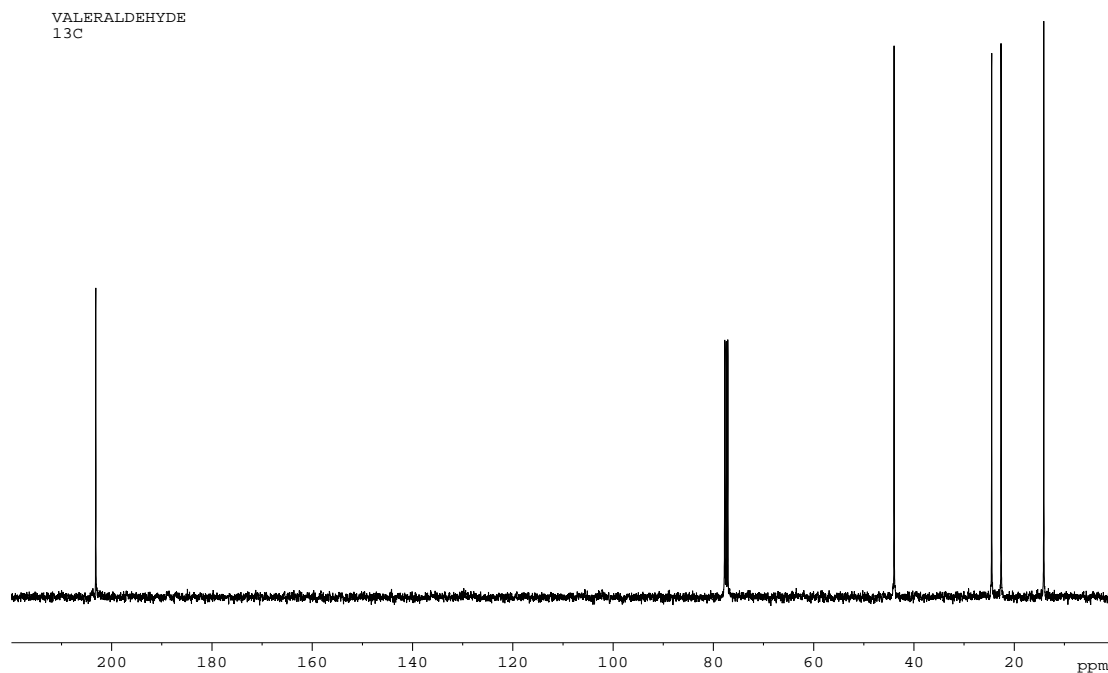
In this case there is mirror symmetry cutting the molecule into two equal halves. Since the carbons bonded to the hydroxyl groups are both asymmetric, then they are equivalent in the case of the meso compound by reflection symmetry. As for the (R,R) and (S,S) enantiomers the two chiral carbons in each case are equivalent to each other by rotational symmetry. This equivalence also relies upon the rapid rotation of the central carbon-carbon bond.

### C Isomerism problem

The carbon-13 spectra below are of isomers of  $C_5H_{10}O$ . The three molecules are:

- Pentan-2-one
- Dimethylpropanal
- 3-Methylbutanal





Assign each molecule to one of the spectra, explaining your reasoning. Note that in each of the spectra there is a peak at 78 ppm that corresponds to the solvent, chloroform.

### Answer

Top spectrum is 3-methylbutanal. The two methyl groups are equivalent, leaving four carbon signals. They are all in the 0-50 ppm region except the carbonyl carbon just past 200 ppm.

Middle spectrum is pentan-2-one. All five carbons are non-equivalent, so there are five peaks. Four are in the 0-50 ppm region except the carbonyl carbon just past 200 ppm.

Bottom spectrum is dimethylpropanal. The three methyl groups are equivalent, leaving three carbon signals. Again, the carbonyl carbon appears a little over 200 ppm and the remaining carbon signals are in the 0-50 ppm region.

### **Acknowledgement**

The spectra of  $C_5H_{10}O$  were provided by Peter Wothers of Cambridge University.