

13.12: USES OF ^{13}C NMR SPECTROSCOPY

OBJECTIVES

After completing this section, you should be able to use data from ^{13}C NMR spectra to distinguish between two (or more) possible structures for an unknown organic compound.

FEATURES OF A ^{13}C NMR SPECTRUM

Butane shows two different peaks in the ^{13}C NMR spectrum, below. Note that: the chemical shifts of these peaks are not very different from methane. The carbons in butane are in a similar environment to the one in methane.

- there are two distinct carbons in butane: the methyl, or CH_3 , carbon, and the methylene, or CH_2 , carbon.
- the methyl carbon absorbs slightly upfield, or at lower shift, around 10 ppm.
- the methylene carbon absorbs at slightly downfield, or at higher shift, around 20 ppm.
- other factors being equal, methylene carbons show up at slightly higher shift than methyl carbons.

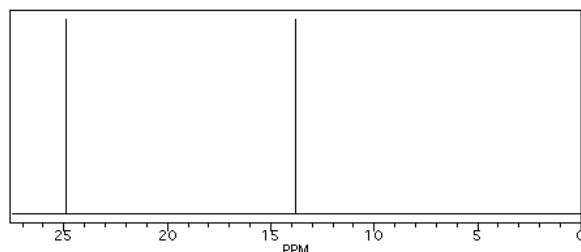


Figure 13.12.1 Simulated ^{13}C NMR spectrum of butane (showing only the upfield portion of the spectrum).

In the ^{13}C NMR spectrum of pentane (below), you can see three different peaks, even though pentane just contains methyl carbons and methylene carbons like butane. As far as the NMR spectrometer is concerned, pentane contains three different kinds of carbon, in three different environments. That result comes from symmetry.

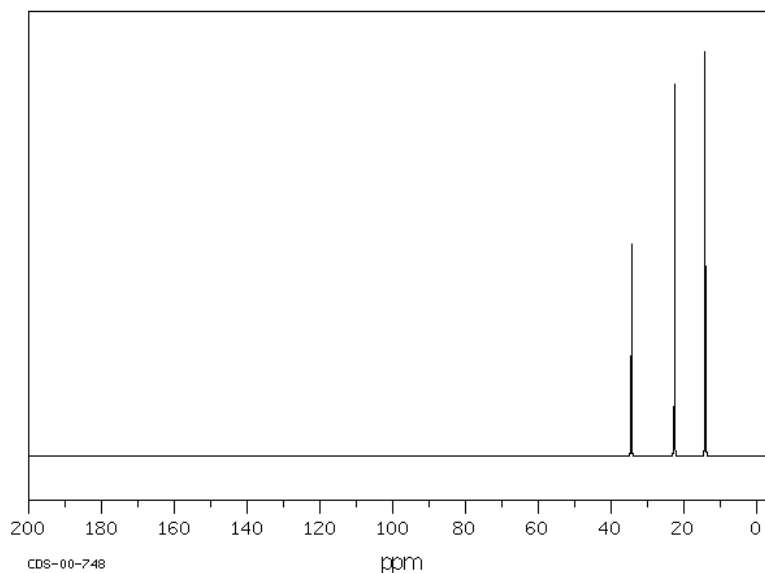


Figure 13.12.2 ^{13}C NMR spectrum of pentane. Source: SDBSWeb : <http://riodb01.ibase.aist.go.jp/sdbs/> (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

Symmetry is an important factor in spectroscopy. Nature says:

- atoms that are symmetry-inequivalent can absorb at different shifts.
- atoms that are symmetry-equivalent must absorb at the same shift.

To learn about symmetry, take a model of pentane and do the following:

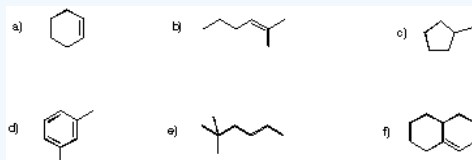
- make sure the model is twisted into the most symmetric shape possible: a nice "W".

- choose one of the methyl carbons to focus on.
- rotate the model 180 degrees so that you are looking at the same "W" but from the other side.
- note that the methyl you were focusing on has simply switched places with the other methyl group. These two carbons are symmetry-equivalent via two-fold rotation.

By the same process, you can see that the second and fourth carbons along the chain are also symmetry-equivalent. However, the middle carbon is not; it never switches places with the other carbons if you rotate the model. There are three different sets of inequivalent carbons; these three groups are not the same as each other according to symmetry.

✓ EXAMPLE 13.12.1

Determine how many inequivalent carbons there are in each of the following compounds. How many peaks do you expect in each ^{13}C NMR spectrum?



Practically speaking, there is only so much room in the spectrum from one end to the other. At some point, peaks can get so crowded together that you can't distinguish one from another. You might expect to see ten different peaks in eicosane, a twenty-carbon alkane chain, but when you look at the spectrum you can only see seven different peaks. That may be frustrating, because the experiment does not seem to agree with your expectation. However, you will be using a number of methods together to minimize the problem of misleading data.

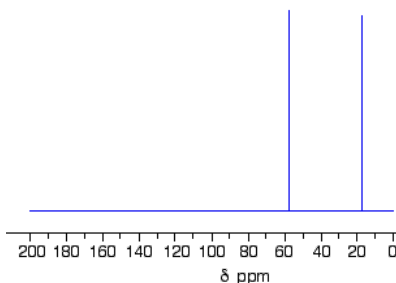
Solution

- Three inequivalent carbons/three peaks. There is a plane of symmetry that bisects the cyclohexene horizontally. The three different carbons are one of the alkene (C1), the CH_2 next to alkene (C3) and C4.
- Six inequivalent carbons/six peaks. The two methyl groups attached to the alkene are identical.
- Four inequivalent carbons/four peaks. This molecule has a plane of symmetry through the molecule, including the methyl group. The two carbons adjacent to the methyl group are equivalent (C2 and C5). C3 and C4 are also equivalent.
- Five inequivalent carbons/five peaks. This molecule has a plane of symmetry that passes through the ring carbon between the two methyl groups. The two methyl carbons are identical. The two ring carbons with the methyl groups attached are identical (C1 and C3). C4 and C6 are also equivalent.
- Six inequivalent carbons/six peaks. The three methyl groups at the end of the molecule are equivalent.
- Ten inequivalent carbons/ten peaks. There is no symmetry for the carbons in this molecule.

THE ^{13}C NMR SPECTRUM FOR ETHANOL

This is a simple example of a ^{13}C NMR spectrum. Don't worry about the scale for now - we'll look at that in a minute.

C-13 nmr spectrum for ethanol, $\text{CH}_3\text{CH}_2\text{OH}$



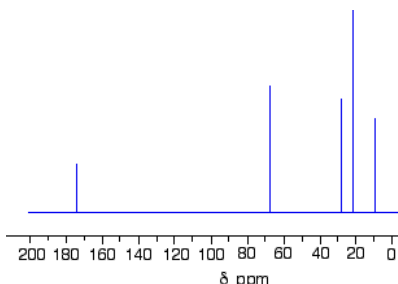
NOTE

Note: The NMR spectra on this page have been produced from graphs taken from the Spectral Data Base System for Organic Compounds (SDBS) at the National Institute of Materials and Chemical Research in Japan.

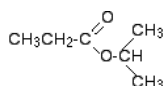
There are two peaks because there are two different environments for the carbons. The carbon in the CH_3 group is attached to 3 hydrogens and a carbon. The carbon in the CH_2 group is attached to 2 hydrogens, a carbon and an oxygen. The two lines are in different places in the NMR spectrum because they need different external magnetic fields to bring them in to resonance at a particular radio frequency.

THE ^{13}C NMR SPECTRUM FOR A MORE COMPLICATED COMPOUND

This is the ^{13}C NMR spectrum for 1-methylethyl propanoate (also known as isopropyl propanoate or isopropyl propionate).



This time there are 5 lines in the spectrum. That means that there must be 5 different environments for the carbon atoms in the compound. Is that reasonable from the structure?



If you count the carbon atoms, there are 6 of them. So why only 5 lines? In this case, two of the carbons are in exactly the same environment. They are attached to exactly the same things. Look at the two CH_3 groups on the right-hand side of the molecule.

You might reasonably ask why the carbon in the CH_3 on the left is not also in the same environment. Just like the ones on the right, the carbon is attached to 3 hydrogens and another carbon. But the similarity is not exact - you have to chase the similarity along the rest of the molecule as well to be sure.

The carbon in the left-hand CH_3 group is attached to a carbon atom which in turn is attached to a carbon with two oxygens on it - and so on down the molecule. That's not exactly the same environment as the carbons in the right-hand CH_3 groups. They are attached to a carbon which is attached to a single oxygen - and so on down the molecule. We'll look at this spectrum again in detail on the next page - and look at some more similar examples as well. This all gets easier the more examples you look at.

For now, all you need to realize is that each line in a ^{13}C NMR spectrum recognizes a carbon atom in one particular environment in the compound. If two (or more) carbon atoms in a compound have exactly the same environment, they will be represented by a single line.

NOTE

You might wonder why all this works, since only about 1% of carbon atoms are ^{13}C . These are the only ones picked up by this form of NMR. If you had a single molecule of ethanol, then the chances are only about 1 in 50 of there being one ^{13}C atom in it, and only about 1 in 10,000 of both being ^{13}C .

But you have got to remember that you will be working with a sample containing huge numbers of molecules. The instrument can pick up the magnetic effect of the ^{13}C nuclei in the carbon of the CH_3 group and the carbon of the CH_2 group even if they are in separate molecules. There's no need for them to be in the same one.

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