

¹³C -NMR: Cracking Those Carbons

A little background:

Protons, neutrons, and electrons all have something called “spin.” This doesn’t mean that they’re actually spinning around in tight circles like Olympian ice skaters, but they’re moving nonetheless and this movement creates a magnetic field around each particle. But for simplicity (and because Chem 14C doesn’t require anything more complicated) we’ll just picture these subatomic particles like miniature planets that are spinning in space around a central axis.

When nothing around the atom is generating an external magnetic field these axes point in random directions, but when an external magnetic field is applied, like it is in NMR, they will align with each other. This doesn’t mean that they will all point in the same direction, however. If we stick with the planet metaphor we can picture all the little planets of our molecule now having north and south poles that point along the same line, but some of them have the north pole facing up (in the same direction as the external field, B_0) and some have the north pole facing down (in the opposite direction of B_0). In chemistry terms, the particles that have axes pointing in the same direction are called *parallel*, and those with axes pointing in opposite directions are called *antiparallel*.

In NMR, energy from photons causes nuclei to change their spin. Generally they have a “ground state” spin of $+1/2$, and excitation causes the poles to swap and the spin changes to the higher energy state of $-1/2$. It is the amount of energy required for this spin flip (or alternatively the amount of energy released as a nucleus relaxes to its original state) that we measure in NMR.

What it is: ¹³C-NMR is a technique very similar to ¹H-NMR, in which we study the nuclear spin flips of various atoms and use a lot of math and brainpower to put the pieces together and try to figure out the structure of a molecule.

What does it do: ¹³C -NMR gives us the *carbon* backbone of a molecule, which is incredibly useful when we’re trying to figure out the structures of organic substances.

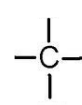
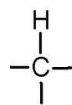
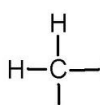
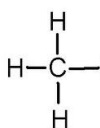
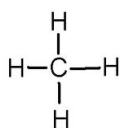
What do we use: NMR works for any atom whose nucleus has a spin quantum number that does NOT equal zero. Since $l \neq 0$ for any atom that has an odd number of protons and/or neutrons, we use the ¹³C isotope for ¹³C -NMR.

Now that we know why we’re putting ourselves through the hassle of understanding all of this, let’s get started with the analysis process.

First, we need to understand what the ¹³C -NMR spectrum is showing us.

1. The number of signals tells us if there are equivalent carbons.
 - a. If the number of signals is less than the total number of carbons in the molecule, there is at least one pair of equivalent carbons. This also means that there is some symmetry to the molecule; if you’re confused about this, build a model.

- The chemical shift tells us if there are highly electronegative atoms or pi electron clouds in the molecule. Both of these things influence chemical shift just like they do in ^1H -NMR, the only thing that's different is that the numerical value of the shifts is higher in ^{13}C -NMR. See table 1 below.
- Integration gives us the ratios of equivalent carbons. Remember that this is NOT always the exact number of carbons, it is a ratio!
- The coupling patterns tell us the number of neighbors each carbon has. A piece of good news: this is actually much more simple to figure out than in ^1H -NMR! Here's why:
 - Only nuclei with $I \neq 0$ can couple with each other, so ^{12}C isn't a valid coupling candidate.
 - When you look at a list of all the atoms ^{13}C could couple with (^1H , ^2H , ^{10}B , ^{13}C , ^{19}F , etc.), the most common one by far is ^1H . The relative abundance of ^{13}C is only 1.1%, so the likelihood of having two ^{13}C atoms right next to each other is only 0.012%. That's reallyyyy unlikely. In fact it's SO unlikely that for our purposes it's completely insignificant and we can just ignore it! So basically all we do is look at the hydrogen atoms bonded to each carbon.
 - ^{13}C -NMR splitting is limited to nuclei separated by just one **sigma** bond. This means that all we have to care about are hydrogens **directly** attached to carbons.
 - There are only 5 splitting patterns in ^{13}C -NMR:



4 H's = **pentet** 3 H's = **quartet** 2 H's = **triplet** 1 H = **doublet** 0 H's = **singlet**

Now that we know what elements we're looking for, let's discuss the process of finding them. The best way to do this is by walking through a practice problem. In general ^{13}C -NMR comes into play at the end of a spectroscopy problem as a way of checking our work, but I won't go through the initial parts of the problem because this tutorial focuses on the ^{13}C -NMR.

(Practice Problem #16)

Molecular formula: $\text{C}_{16}\text{H}_{18}\text{O}_2$

IR:

Alcohol O-H
Aryl/vinyl C-H
Alkyl C-H
Benzene C=C
Alkene C=C- maybe

^1H -NMR pieces:

2x phenyl C_6H_5
 CH_2CH_2
2x OH
 $\text{CH}_2\text{CH}_2\text{CH}_2$
 CH_2CH_2
 C

^{13}C -NMR:

142.3 (singlet), 128.4 (doublet), 128.3 (doublet), 125.8 (doublet), 78.5 (singlet),
62.0 (triplet), 39.5 (triplet), and 27.2 (triplet)


Remember those four things ^{13}C -NMR tells us? Here is where we find those things.

1) The first thing to do is look at the number of signals in ^{13}C -NMR. We have 16 carbons but only 8 signals, which means that there has to be some symmetry to our molecule.

2) Let's look at those chemical shifts!

Now the ^{13}C -NMR shift table comes in handy:

C-13 CHEMICAL SHIFTS

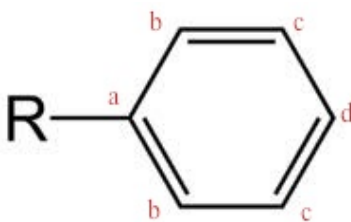
Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0	$\text{C}-\text{I}$	0-40
$\text{R}-\text{CH}_3$	8-35	$\text{C}-\text{Br}$	25-65
$\text{R}-\text{CH}_2-\text{R}$	15-50	$\text{C}-\text{Cl}$	35-80
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{CH}-\text{R} \end{array}$	20-60	$\text{C}-\text{N}$	40-60
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	30-40	$\text{C}-\text{O}$	50-80
$\equiv\text{C}$	65-85	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ -\text{N} \end{array}$	165-175
$=\text{C}$	100-150	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{RO} \end{array}$	165-175
	110-170	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array}$	175-185
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{array}$	190-200
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R} \end{array}$	205-220

Looking at the table, the only thing that fits our IR data and the ^{13}C -NMR shifts given in the problem is a benzene ring. Since we have 4 shifts in the 110-170 range, we have 4 non-equivalent sets of carbons that are part of benzene rings, and based on our ^1H -NMR data there are 2 such rings. This makes sense, because if there are two identical benzene

rings and the rest of the molecule is not symmetrical we will have a total of 8 ^{13}C -NMR signals, which is what we are given. We also know that there have to be some carbons attached to highly electronegative atoms, because carbons that are just attached to H or C won't give a shift of 78.5. More analysis below.

3) Integration. Well, we don't have the integral values given to us in this problem, so we're going to skip this part for now. It isn't hard to do without it, although knowing integrations can be helpful. You do ^{13}C -NMR integration analysis the EXACT same way as for ^1H -NMR, so if you need help with this find another tutorial that goes over it in more detail.

4) Splitting! Let's look at each of the benzene carbon signals individually, focusing on the splitting patterns to differentiate between them.



Carbon a: Has 0 hydrogens attached so must be a singlet. Is not equivalent to any other atom in this ring.

Carbon b: Has 1 hydrogen attached so must be a doublet. Is equivalent to one other atom in this ring.

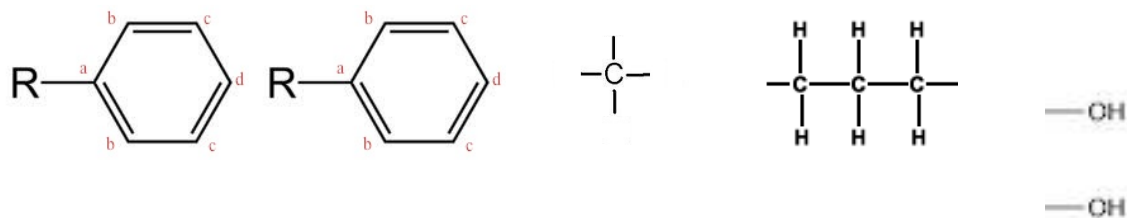
Carbon c: Has 1 hydrogen attached so must be a doublet. Is equivalent to one other atom in this ring.

Carbon d: Has 1 hydrogen attached so must be a doublet. Is not equivalent to any other atom in this ring.

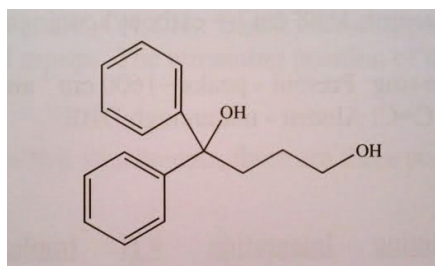
We can now easily assign the four benzene shifts to these carbons. Don't worry about whether b or c is the 128.4 vs. 128.3 shift; they are, for our purposes, completely interchangeable.

So now we have four more shifts to analyze and four unused carbons. Looking at our ^1H -NMR data, we have a $\text{CH}_2\text{CH}_2\text{CH}_2$ chain and a carbon with no hydrogens attached. We also have two OH groups.

Based on our ^{13}C -NMR table above, the carbons with the shifts of 78.5 and 62.0 ppm must each be bound to an oxygen atom. Aha, we've found where our alcohols go! The other two carbons have ordinary $\text{R-CH}_2\text{-R}$ shifts so they're not attached to any electronegative atoms or pi bonds (all DBEs are used in the 2 benzene rings). Now all we have to do is put our pieces together.

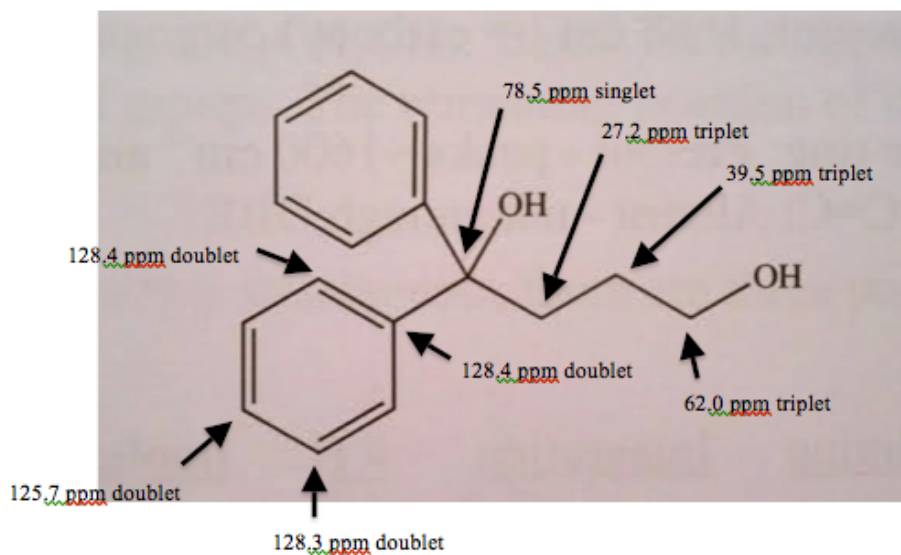


We know that there are two carbons bonded to the alcohols, and one of them must be the singlet carbon (if both of the CH_2 's were bonded to an OH, we would not be able to connect these pieces into one molecule) and the other must be one of the CH_2 's. So now the pieces fall together in a pretty logical way to make:



Ta da! Now all that's left is to check our work. For the sake of this tutorial, we're only going to check the carbons to see if they fit the ^{13}C -NMR spectrum, but don't forget to check the molecule matches all the other parts of the problem too!

Total signals: 8 ✓



So all of our ^{13}C -NMR signals are accounted for. Remember that the benzene rings are equivalent, and each one contains two sets of two equivalent carbons. Don't overcount your signals!

Works Cited

Images

<http://upload.wikimedia.org/wikipedia/commons/b/b2/Methane-2D-flat-small.png>

http://andromeda.rutgers.edu/~huskey/images/nmr_c_table.png

<http://www.proprofs.com/flashcards/upload/a4222257.png>

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<http://www.bbc.co.uk/scotland/learning/bitesize/standard/chemistry/images/6a.gif>

Dr. Hardinger's Thinkbook, C-NMR pp #16

Dr. Hardinger's Lecture Supplement, C-NMR slides