Solving Spectroscopy Problems: Putting it All Together

Once you've analyzed the mass spectrometry, infrared spectrometry, ^{1}H-NMR, and ^{13}C-NMR data, there is no one way to put them together. It's all about trial and error, but here are a few helpful tips and tricks to help you get on the right track.

First, here's an overview of the information you should have obtained based on your analyses of the data from the 4 methods of spectrometry.

Mass Spectrometry- molecular formula, DBE
Infrared Spectrometry- present functional groups
^{1}H-NMR- backbone structure (C-H)
^{13}C-NMR- hydrogens attached to the carbons, confirms functional groups found in IR and implications determined by H-NMR

Key things to remember as you proceed with the puzzle:

1) Keep track of the number atoms in your molecule. Make sure the sum of the atoms in your ^{1}H-NMR implications + functional groups from IR spectrum matches the molecular formula obtained from the mass spectrum.
2) Keep track of the DBE count, especially when doing IR analysis.
3) Check that your implications and your final molecule match ^{1}H-NMR and ^{13}C-NMR chemical shifts.
4) Check that your final molecule matches the number of signals, splitting pattern, and number of hydrogen atoms as the ^{1}H-NMR and ^{13}C-NMR data

The information from the mass spectrum is pretty straight forward. Use it to keep track of the number of each atom as you proceed with the IR analysis and the ^{1}H-NMR spectrum (number of carbons and hydrogens).

Here's a handy table that will help you out with determining the functional group associated with the given carbonyl group:

Functional Group	IR	^{1}H-NMR	^{13}C-NMR
Aldehyde	2 C-H peaks: ~2900 and ~2700 cm^{-1} C=O stretch 1740-1720 cm^{-1}	Aldehyde proton 9.5-11 ppm	C=O carbon doublet 180-220 ppm
Ketone	C=O stretch 1750-1705 cm^{-1}	No characteristic ^{1}H chemical shift	C=O carbon singlet 180-220 ppm
Ester	C=O stretch 1750-1735 cm^{-1}	No characteristic ^{1}H chemical shift	C=O carbon singlet 160-180 ppm
Carboxylic acid	Broad O-H stretch 3000-2500 cm^{-1} C=O stretch 1725-1700 cm^{-1}	COOH proton 10-13 ppm	C=O carbon singlet 175-185 ppm

Amide	N-H stretch 3500-3300 cm^{-1} (2 peaks if 1°, 1 peak if 2°, none if 3°) C=O stretch 1690-1650 cm^{-1}	N-H proton 5-9 ppm	C=O carbon singlet 160-180 ppm

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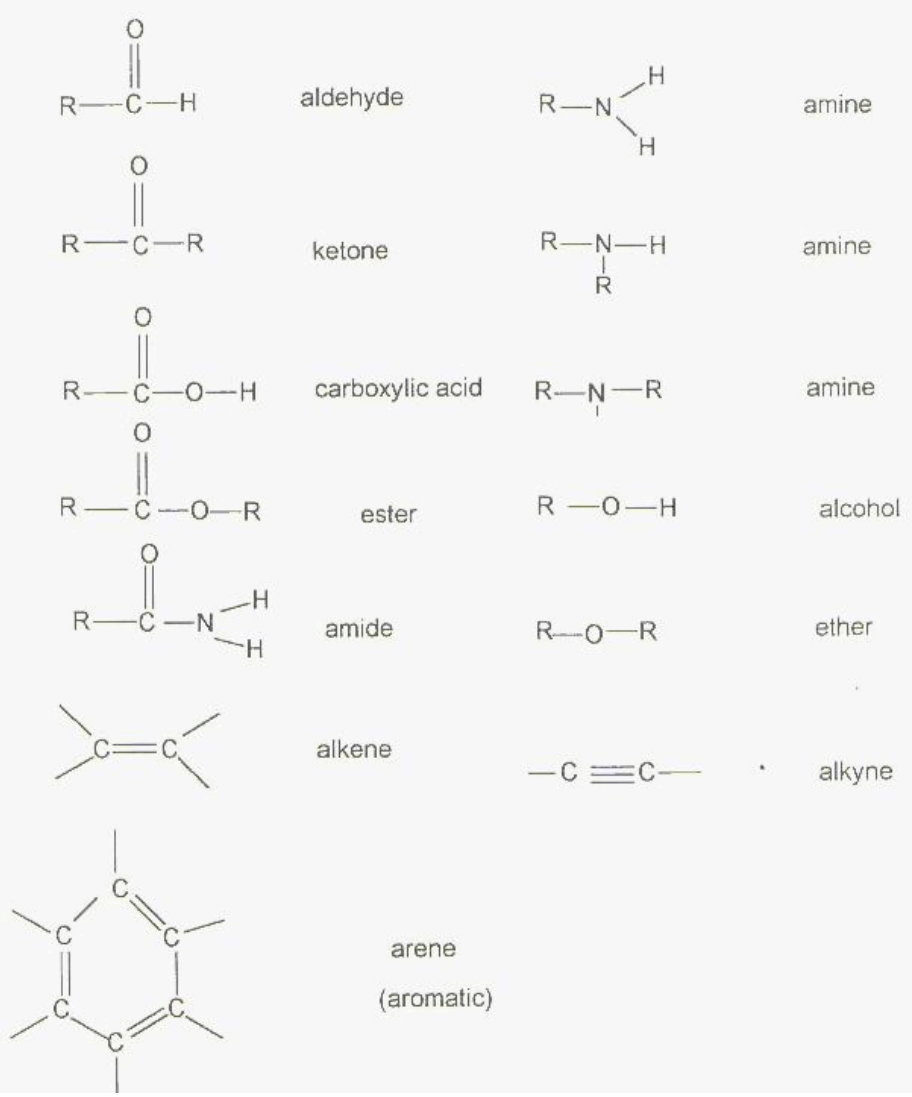
First, list out all implications, functional groups, and remaining atoms that you have found from the IR, ^{1}H-NMR, and ^{13}C-NMR data. Consolidate as many ^{1}H-NMR implications from different signals as possible (will be discussed shortly).

Once that's settled, a good starting place is to draw out the functional groups found in the IR spectrum such as:



Then, use trial and error to attach the remaining pieces (^{1}H-NMR and IR functional groups).

For ^{1}H-NMR, here are some hints and patterns that occur frequently (but not always):

But first, here's a table of the more common implications and the ones that are most likely to make up part of the final molecule (i.e. one that show up in the Thinkbook and practice exams). It does **not** show all possible implications.

these are often overlooked, but keep these implications in mind when there are oxygens (alcohols more specifically) and nitrogens in the molecular formula and when alcohols, amines, carbonyls, carboxylic acids, and aldehydes are present it the IR spectrum

these atoms represent the carbons with the correct number of hydrogens indicated by the integration

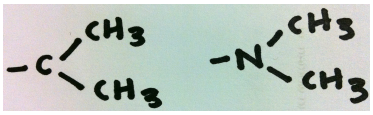
Shift	Signal	Integration	Number of Hydrogens	Implications
	singlet	1	1	CH, OH, NH, C=O, CHO, COOH
		2	2	CH_2, CH x 2
		3	3	CH_3 CH x 3
		4	4	CH_2 x 2, CH x 4
		6	6	CH_3 x 2, CH_2 x 3, CH x 6
		9	9	CH_3 x 3, CH x 9
	Doublet	1	1	CHCH
		2	2	$CHCH_2$
		3	3	$CHCH_3$
		4	4	$CHCH_2$,
		6	6	$CHCH_3$ x 2
		9	9	$CHCH_3$ x 3
	Triplet	1	1	CH_2CH, CHCHCH
		2	2	CH_2CH_2,, $CHCH_2CH$
		3	3	CH_2CH_3, $CHCH_3CH$
		4	4	CH_2CH_2 x 2, $CHCH_2CH$ x 2
		6	6	CH_2CH_3 x 2, $CHCH_3CH$ x 2
		9	9	CH_2CH_3 x 3, $CHCH_3CH$ x 3
	Quartet	1	1	CH_3CH, CH_2CHCH
		2	2	CH_3CH_2,, CH_2CH_2CH
		3	3	CH_3CH_3, CH_2CH_3CH
		4	4	CH_3CH_2 x 2, CH_2CH_2CH x 2
		6	6	CH_3CH_3 x 2, CH_2CH_3CH x 2
		9	9	CH_3CH_3 x 3, CH_2CH_3CH x 3
	Pentet	1	1	CH_3CHCH, CH_2CHCH_2
		2	2	CH_3CH_2CH,, $CH_2CH_2CH_2$
		3	3	CH_3CH_3CH, $CH_2CH_3CH_2$
		4	4	CH_3CH_2CH x 2, $CH_2CH_2CH_2$ x 2
		6	6	CH_3CH_3CH x 2, $CH_2CH_3CH_2$ x 2
		9	9	CH_3CH_3CH x 3, $CH_2CH_3CH_2$ x 3
	Sextet	1	1	CH_3CHCH_2, CH_2CHCH_2

		3	3	$CH_3CH_3CH_2$, $CH_2CH_3CH_3$
		4	4	$CH_3CH_2CH_2$ x 2
		6	6	$CH_3CH_3CH_2$ x 2
		9	9	$CH_3CH_3CH_2$ x 3
	Septet	1	1	CH_3CHCH_3
		2	2	$CH_3CH_2CH_3$
		3	3	$CH_3CH_3CH_3$
		4	4	$CH_3CH_2CH_3$ x 2
		6	6	$CH_3CH_3CH_3$ x 2
		9	9	$CH_3CH_3CH_3$ x 3
	Multiplet	5	5	C_6H_5 monosubstituted benzene ring
	2 Doublets	4	4	C_6H_4 disubstituted benzene ring

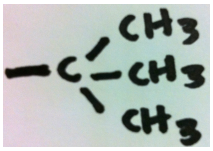
Multiplets and "doublets of doublets" are usually benzene rings for our purposes.

Implications of the form CH_3 x 2 or 3 are often present in molecules with 2 or 3 CH_3 groups attached to the same atom or show symmetry in other ways across the molecule.

i.e. CH_3 x 2 :



CH_3 x 3 :



Often times you can couple together implications for several signals if they coincide with each other.

i.e. a triplet CH_2CH_3 and a quartet CH_3CH_2 can be put together into one single piece: CH_2CH_3

When you need to separate implications for different signals so that they don't couple, try inserting these atoms/molecules in between them:

O C=O N

i.e. $CH_3CH_2CH_2CH_2CH_2$

Gives: 2 triplets, 2 pentets, 1 sextet

whereas

$CH_3CH_2OCH_2CH_2CH_2$

Gives: 3 triplets, 1 quartet, and 1 pentet

Now let's put it all together with some practice problems!

^{13}C-NMR, 2D-NMR, and MRI OWL #4. Suggest the structure for a molecule of formula $C_{10}H_{14}O$ with the following NMR data.

Formula: $C_{10}H_{14}O$

DBE = 10 – (14/2) + (1/0) + 1 = 4 (probably benzene ring)

^{1}H-NMR: 7.12 ppm (doublet of doublets; integral= 2), 6.82 ppm (doublet of doublets; integral = 2), 3.74 ppm (singlet; integral = 3), 2.84 ppm (septet; integral = 1), and 1.21 ppm (doublet; integral = 6).

^{13}C-NMR: 157.9 ppm (singlet), 141.1 ppm (singlet), 127.3 ppm (doublet), 113.9 ppm (doublet), 55.2 ppm (quartet), 33.4 ppm (doublet), and 24.2 ppm (quartet)

After completion of the IR and NMR analyses, you should have the following pieces:

^{1}H-NMR:

C_6H_4 disubstituted benzene ring

CH_3 singlet

CH$(CH_3)2$

CH_3CH x 2 } $CH(CH_3)_2$

^{13}C-NMR:

157.9 ppm singlet –benzene ring C

141.1 ppm singlet – benzene ring C

127.3 ppm, 113.9 ppm –2 CH on benzene ring

55.2 ppm quartet – CH_3 (probably directly attached to benzene ring)

33.4 ppm doublet – CH (probably directly attached to benzene ring)

24.2 ppm quartet – CH_3

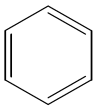
Here I've matched the proton and carbon NMR implications by highlighting them with the same color. You can see that ^{13}C-NMR confirms the ^{1}H-NMR implications

KEEP TRACK of the number of atoms in your molecule!

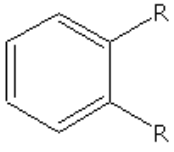
C_6H_4+ $CH(CH_3)_2$ + CH_3 = $C_{10}H_{14}$

What's left: O

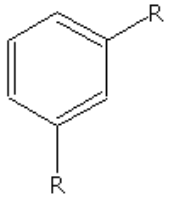
1) start by drawing the benzene ring:



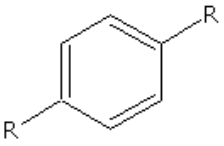
2) Since the benzene ring is isubstiuted there are 2 carbons on it that can connect to the 2 remaining pieces of the puzzle. These 2 pieces can be arranged in 3 possible ways:



ortho



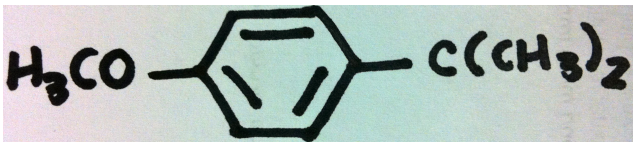
meta



para

Since there are 4 ^{13}C-NMR signals attached to the benzene ring. Only the para isomer gives this arrangement fits our structure.

3) Since we still have an oxygen left, it can attach to either the CH or the CH_3 singlet. Look at the ^{1}H-NMR chemical shift and you will see that the CH_3 singlet has the higher chemical shift, so it is probably attached to the oxygen. So, attach the $CH(CH_3)_2$ on one position on the benzene ring and the CH_3O you just made on the other position.



Make sure to check you have all the required atoms and check for the correct number of NMR signals and the correct chemical shifts.

And there you have it!

Let's try a harder one:

^{13}C-NMR, 2D-NMR, and MRI Practice Problem #16: Deduce the structure that corresponds to the spectral data.

Mass Spectrum: m/z 242 (M: 100%), m/z 243 (17.87%), and m/z 132 (0.50%)

Solve for formula: $C_{16}H_{18}O_2$

DBE = 8

IR: alcohol O-H, aryl/vinyl sp_2 C-H, alkyl sp^3 C-H, benzene ring

^{1}H-NMR: 7.24-7.14 ppm (multiplet; integral = 5), 3.62 ppm (triplet; integral = 1), 2.50 ppm (singlet; integral = 1) 1.68 ppm (pentet; integral = 1), and 1.51 ppm (triplet; integral = 1)

^{13}C-NMR: 142.3 ppm (singlet), 128.4 ppm (doublet), 128.3 ppm (doublet), 125.7 ppm (doublet), 78.5 ppm (singlet), 62.0 ppm (triplet), 39.5 ppm (triplet), and 27.2 ppm (triplet)

Pieces:

2 x C_6H_5 monosubstituted benzene ring

2 x OH

leftovers: O, C

Put these 3 together $CH_2CH_2CH_2$

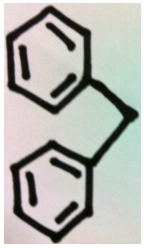
~~CH_3~~~~CH_2~~~~CH~~ or $CH_2CH_2CH_2$ ← (this one fits better with the other implications- CH_2CH_2)

CH_2CH_2

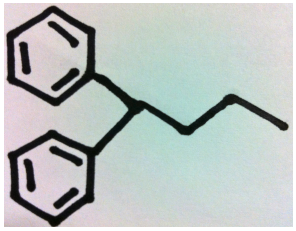
CH_2CH_2

1) Since the 2 benzene rings are equivalent (same signal), draw out the benzene rings next to each other so they can somehow be equivalent.

2) It seems you can't attach them with the remaining pieces in between them, linking them together as the $CH_2CH_2CH_2$, C, and O cannot form a symmetric chain on its own. The leftover C must attach the two rings.

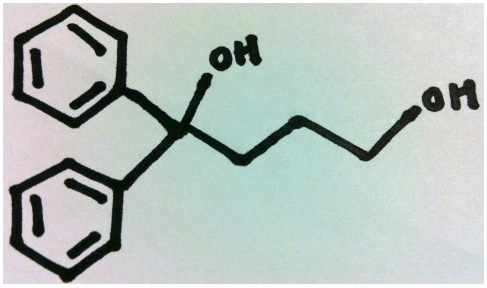


3) The leftover C has 2 benzene rings attached, so it has 2 more bonds to form. One can be the $CH_2CH_2CH_2$ chain.



4) The other must be an OH as that is all we have left.

5) The other OH must cap off the end of the $CH_2CH_2CH_2$ chain to complete the molecule.
And since "The two ends of this $CH_2CH_2CH_2$ piece are not equivalent" the molecule must be constructed this way. (Dr. Hardinger's Chemistry 14C Thinkbook , Ninth Edition)



Remember again to check your work- molecular formula, IR functional groups, NMR signals, integrals, and chemical shifts.

References:

Dr. Hardinger's Chemistry 14C Thinkbook , Ninth Edition (pgs. 217, 221-222, 229, 233-235)

http://www.google.com/imgres?q=functional+groups+with+carbonyl+group&um=1&hl=en&client=safari&rls=en&biw=1139&bih=680&tbm=isch&tbnid=aOKDVE2NLZKKqM:&imgrefurl=http://chemcases.com/nutra/nutra1b.htm&docid=1MbiE9tMRQOpmM&imgurl=http://chemcases.com/nutra/images/fig1-06.jpg&w=602&h=721&ei=VgbAT8GgLcWTiQKJuPWZCA&zoom=1

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