We have a compound with a molecular formula of $C_8H_{12}O$. We have the following spectra: IR, ^1H NMR, ^{13}C NMR, and DEPT. What is the structure?

Step 1: Calculate the IHD.
C_8 means our reference alkane is C_8H_{18}.
IHD = (18-12)/2 = 6/2 = 3

Step 2: Look at spectra.
IR: Good looking OH.
        3307 cm^{-1} looks like a C-H stretch, so if we look at a correlation table, we see that an alkyne C-H stretch comes around 3300 and should be pretty sharp. So this is probably an alkyne C-H. There doesn't seem to be an C-C stretch for an alkyne, these are often really weak. So we'll wait to see if this is consistent with the other data....

^1H NMR: Wow! What a mess. There seem to be at least 6 signals, but it is hard to tell.

^{13}C NMR: Ok, this is more reasonable. We have 6 signals. We need to account for 8 carbons, so there is some symmetry element that is making some of the carbons equivalent (ring?)

Step 4: Chemical shift
^1H NMR: We have two peaks between 2.5 and 2.8 ppm. Looking at a correlation table, these could be protons on an O-H or NH group (but we don't have any nitrogens in the MF) or on a carbon that is a) allylic, b) next to a carbonyl group, c) next to an aromatic group, or d) part of an alkyne. The IR says we have an -OH group, and suggests we have an alkyne C-H. so the observations we made about the IR spectrum are consistent with the ^1H NMR.

We have a whole bunch of plain old alkyl group protons (1.2 ppm - 2.0 ppm). So many that it is kind of hard to get much information from these peaks.

Note that we do not have any signal between 3.4 - 4.0 ppm but that we have an alcohol (by IR). This means that the carbon attached to the alcohol oxygen does not have any protons attached to it (i.e. it is a quaternary carbon).

^{13}C NMR: we have 3 carbon signals that are in the normal alkane region (18.4, 20.4, 35.1 ppm). We have 3 signals that could be from a) a carbon attached to a heteroatom like oxygen or nitrogen, or b) alkyne carbons. We think we have an alkyne, so that accounts for 2 carbons, and we think we have an alcohol. So that's the third carbon. No alkenes or carbonyls. He have two really short carbons, so these might be quaternary carbons.

Step 5: Splitting patterns.

Here's where we run into problems. The signals between 2.5 and 2.8 ppm are both singlets (consistent with an alkyne and an alcohol), but the mess between 1.0 and 2.0 ppm is almost indecipherable. We need more help. So lets look at the DEPT spectrum.

The DEPT 45 experiment (lowest spectrum on the page) tells us how many carbons have protons attached. So we do indeed have 2 quaternary carbons. But one of them is the tall peak at 67. **SHORT PEAKS ARE NOT ALWAYS QUATERNARY - BE CAREFULL! We only use that as an estimation of which might be quaternary.** The other one is at 64 ppm. Although difficult to see in the stacked spectral plot, the signal at 83 is still there. Analysis: 2 quaternary carbons.

the DEPT 90 experiment (middle spectrum) shows us only carbons that have 1 proton attached (CH groups). We have 1: the peak at 83 ppm. The blips in the alkyl region do not count because it is obvious that the computer tried to subtract them out, but didn't quite get it all. Analysis: 1 CH group.

the DEPT 135 experiment (top spectrum) show all protonated carbons (like the DEPT 45) but the phase of CH_2 signals are inverted. CH and CH_3 are normal phase (up) and CH_2 is inverted (down). So, we see our CH group at 83 ppm (easily identified as CH rather than CH_3 because it was in the DEPT 90 also), and we see 3 CH_2 group signals - but no CH_3 signals (Not signals of normal phase that were not present in the DEPT 90 spectrum). Analysis: 3 CH_2 groups.
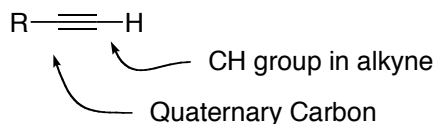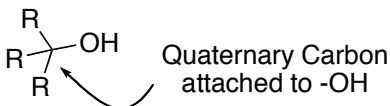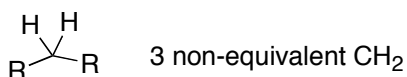
Final analysis:
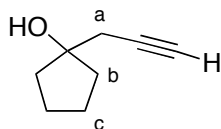2 quaternary carbons
1 CH carbon
3 CH_2 carbons.

We also know we have 1 -OH group and 1 -CCH (terminal alkyne)

We know we have 1 quaternary carbon attached to the alcohol oxygen (remember that we had no proton signals between 3.4 and 4 ppm in the ^1H NMR). The alkyne also contains 1 quaternary carbon and 1 CH group. So, we know we have these pieces:

H H
R — R   3 non-equivalent CH_2

R
R — OH   Quaternary Carbon
R   attached to -OH

R ≡ H
               CH group in alkyne
               Quaternary Carbon

We also know that we have 2 carbon that must be accounted for (6 signals in the ^{13}C but 8 carbons in the molecular formula). We have 2 units of hydrogen deficiency accounted for by the alkyne, but we need one more. There are no carbonyls and there are no alkenes (based on the spectra), so the third IHD unit must come from a ring (symmetry makes two of the carbons identical)!

So lets just put the pieces together (using the CH_2 groups in a ring) and see if it fits:

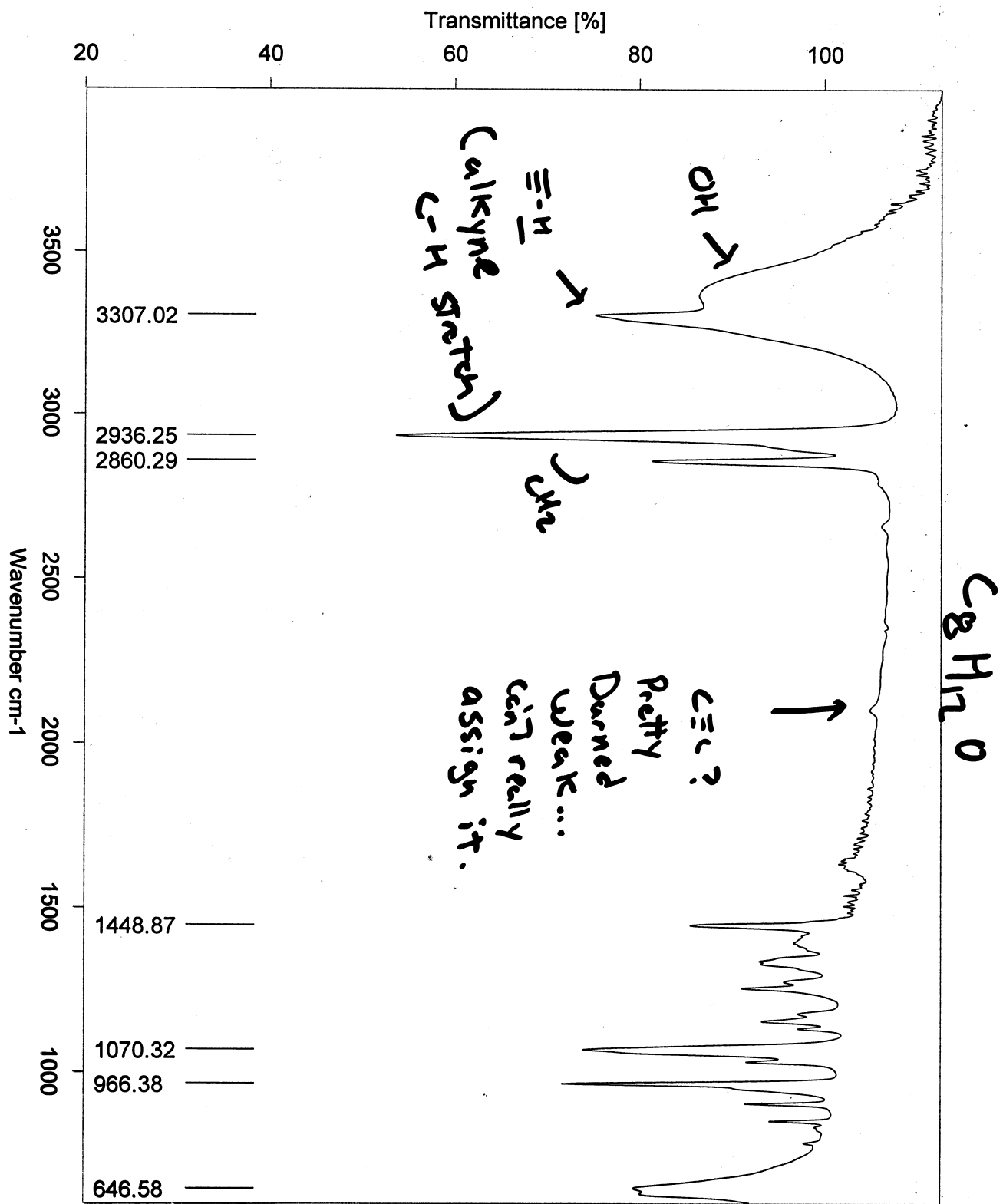We have an alkyne (with CH), an alcohol attached to a quaternary carbon, and three distinct CH_2 groups. This seems to fit (and I would give full credit for this answer). Problem: the CH_2 group labeled a is next to an electron withdrawing alkyne, and has no neighbors to give a splitting pattern. We should see a singlet that integrates to 2 H somewhere near 2.0 ppm in the ^{1}H NMR. Given the mess in the alkyl portion of the ^{1}H NMR spectrum, it could be hard to pick out.

Another option that still gives us 2 quaternary carbons is:
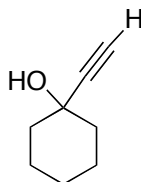
This fits the data better...but without having seen the spectrum for the cyclopentane derivative shown above, it would be hard to tell. So, either answer would be correct!

Final comments: As you can see from the last example, sometimes you can come up with two answers that both seem correct. For the purposes of this class, that's OK. As long as the structures you come up with are consistent with the data provided, I will give full credit. The most important part of this is learning how to apply the problem solving strategy. If you can do that, you're doing alright.

Transmittance [%]

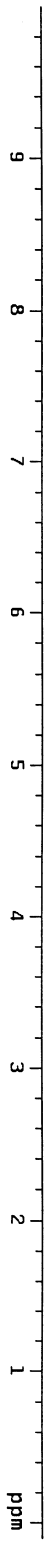Wavenumber cm-1

$C_8H_{12}O$

OH

≡-H
(alkyne
C-H stretch)

CH_2

C≡C?
Pretty
Darned
Weak...
can't really
assign it.

3307.02
2936.25
2860.29
1448.87
1070.32
966.38
646.58

$C_8H_{12}O$

6+ Signals

Could be:
a) Next to $C=O$
b) $O-H$
c) $-C\equiv-H$

Argh!!!! what a mess!!

H_2O?

(1)

(2)

(3)

(4)

(5)

(6)

Alkane (lots of them)

more than 1 signal?

Normalized integration: 1:1   2:7:1

2.00   1.84   4.17   15.34   2.82

C_8H_nO

INDEX	FREQUENCY	PPM	HEIGHT
1	6278.957	83.210	5.0
2	5584.806	72.951	4.8
3	5472.740	72.526	4.7
4	5440.675	72.101	5.2
5	5098.261	67.563	39.5
6	4823.415	63.921	5.7
7	2645.254	35.056	133.2
8	1538.996	20.395	85.0
9	1390.121	18.422	90.1

6 Signals ... Need 8.
ring?

These 3 sigs.
could be
a) C~O-R
b) C-N-R₂
c) -≡-H

Short Qut? →

← Short Qut?

Alkane

DEPT

$C_8H_{12}O$

135

No Methyl
1 C-H
3 CH$_2$
2 Quat.

CH

CH$_2$

CH$_2$

90

CH

CH$_2$

1CH group

4 Protonated carbons

45

This is rei'?

Gone

Quat?