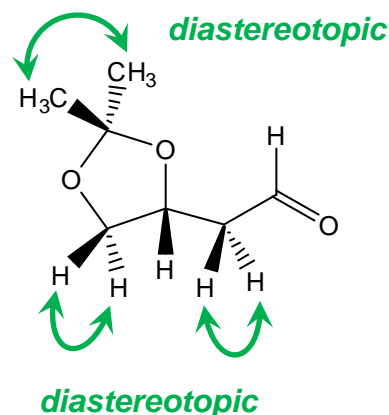


In-Class Exercise Solutions: Resonances With Multiple Coupling Constants

The acetonide in this problem is a racemic mixture of enantiomers, with a chiral center at the tertiary carbon. The two enantiomers have the same NMR spectrum—remember, the NMR instrument can't tell them apart—so we can just consider one of the two. When we do that, we see that protons on different methyl groups, and the two protons on each $-\text{CH}_2-$ group, are diastereotopic, and thus inequivalent. That means this molecule has 8 chemically inequivalent types of protons: two sets of 3, and six singles, for a total of eight resonances in the ^1H NMR spectrum. That is in fact what we've got in the ^1H NMR—two methyl group singlets at $\delta = 1.37$ & 1.43 ppm, and then six multiplets with intensity 1. So we're on the right track.



It will help us to determine splitting patterns and coupling constants for each multiplet before trying to assign the resonances. The triplet and quintet on the left side are super easy to read J values from, because you can calculate J from the shift difference between any adjacent peak in the multiplet.

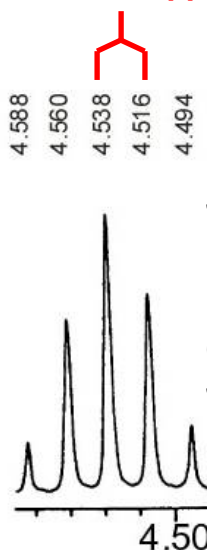
$\Delta\delta = 0.006$ ppm



$$\begin{aligned}
 J &= (\Delta\delta)(\nu_{\text{Larmor}}) \\
 &= (0.006 \text{ ppm})(270 \text{ MHz}) \\
 &= \mathbf{1.6 \text{ Hz}}
 \end{aligned}$$

(or, you could also say
 $J_1 = J_2 = 1.6 \text{ Hz}$)

$\Delta\delta = 0.022$ ppm



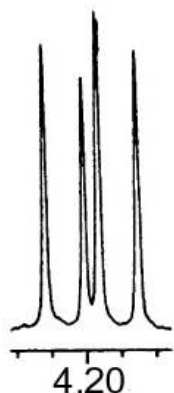
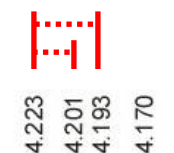
$$\begin{aligned}
 J &= (\Delta\delta)(\nu_{\text{Larmor}}) \\
 &= (0.022 \text{ ppm})(270 \text{ MHz}) \\
 &= \mathbf{5.9 \text{ Hz}}
 \end{aligned}$$

(or, you could also say
 $J_1 = J_2 = J_3 = J_4 = 5.9 \text{ Hz}$)

J values from doublets of doublets (dd's) can be read by looking at the shift differences between peaks 1 and 2 and between peaks 1 and 3. I actually find it a little more reliable to measure a couple of differences (1-2, 3-4) and average them.

$\Delta\delta_{1,2} = 0.022 \text{ ppm}$

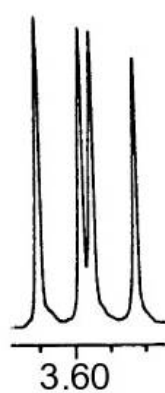
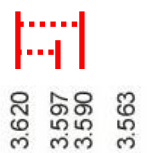
$\Delta\delta_{1,3} = 0.030 \text{ ppm}$



$J_{1,2} = 5.9 \text{ Hz}$
 $J_{1,3} = 8.1 \text{ Hz}$

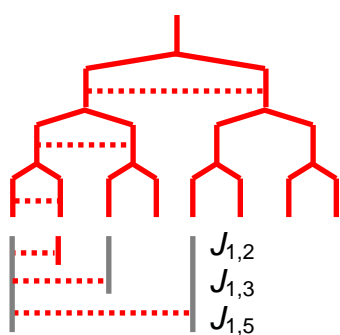
$\Delta\delta_{1,2} = 0.025 \text{ ppm}$

$\Delta\delta_{1,3} = 0.032 \text{ ppm}$

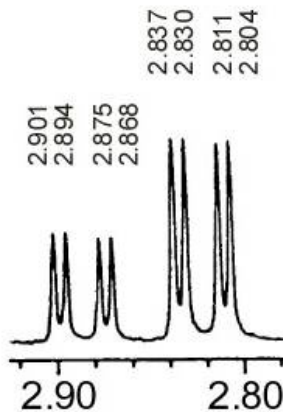


$J_{1,2} = 6.8 \text{ Hz}$
 $J_{1,3} = 8.6 \text{ Hz}$

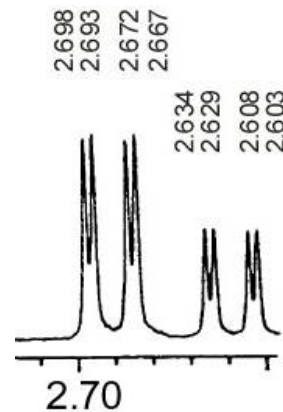
The last two resonances are actually doublets of doublets of doublets (ddd's). We can actually read coupling constants off of these too, by thinking about how the coupling tree relates to the peaks.



$J_{1,2} = 1.9 \text{ Hz}$
 $J_{1,3} = 7.0 \text{ Hz}$
 $J_{1,5} = 17.3 \text{ Hz}$

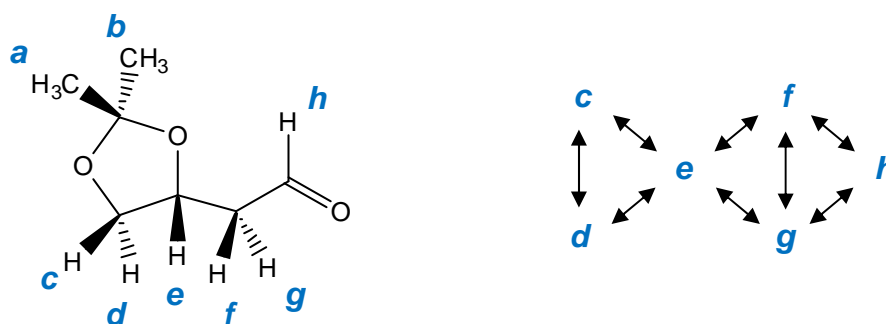


$J_{1,2} = 1.4 \text{ Hz}$
 $J_{1,3} = 7.0 \text{ Hz}$
 $J_{1,5} = 17.3 \text{ Hz}$

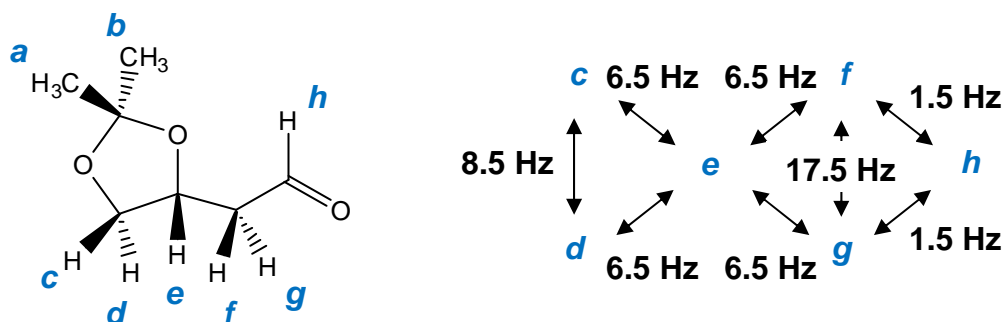


In these ddd's, the intensities look a little distorted, with peaks on one side taller than the other. This is caused by the fact that the multiplets are coupled to each other, and that the difference in chemical shift between the multiplets is on the order of the coupling constant inside the multiplet. (More on this later.) For now, ignore this effect.

Many of the measured J values match up perfectly, but a few do not; this can happen in NMR, where imperfections in the spectrum can lead to differences in measured J values. We'll just try to work with it. We can draw a map of expected coupling in the molecule, assuming that only geminal and vicinal coupling is observed:



The aldehyde proton **h** must be the triplet at $\delta = 9.8$ ppm, based on chemical shift. It shows a very small coupling constant (1.6 Hz), that is shared only by the ddd's. So the ddd's must correspond to protons **f** and **g**. Those two multiplets are the only ones that have the very large J (17.3 Hz), so that must be the coupling constant between them. Proton **e** is the only proton in the molecule with four coupling partners, and the only multiplet with four J 's—the quintet at $\delta = 4.7$ ppm—must correspond to it. I think that means that the 7.0 Hz coupling constant measured for the ddd's must be too high; for now we'll guess that it's closer to 6.5 Hz, and that this is also the coupling constant between **c** and **e** and between **d** and **e**. Redrawing our map with coupling constants (rounded to the nearest 0.5 Hz), that means:



I don't think there will be any way to know which chemical shift corresponds to which proton within a geminal pair, but I do think we can build a chart:

proton	chemical shift (δ , ppm)	coupling constants
H _a and H _b	1.37 and 1.43	<i>none</i>
H _c and H _d	3.60 and 4.20	$J_{c,d} = 8.5$ Hz $J_{c,e} = 6.5$ Hz $J_{d,e} = 6.5$ Hz
H _e	4.54	<i>see above and below</i>
H _f and H _g	2.65 and 2.85	$J_{e,f} = 6.5$ Hz $J_{e,g} = 6.5$ Hz $J_{f,g} = 17.5$ Hz $J_{f,h} = 1.5$ Hz $J_{g,h} = 1.5$ Hz
H _h	9.61	<i>see above</i>

I think the chemical shifts of all of these protons match chemical shift tables pretty well; all -CH₂-OR protons are in the $\delta = 3 - 4.5$ range, the protons α to the carbonyl are in the $\delta = 2 - 2.5$ range, and the methyl groups are in the alkyl region. (As well as the aldehyde being far downfield, which we already talked about.)