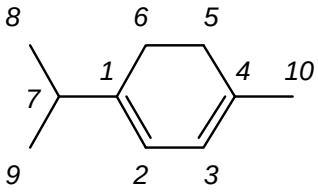
Chemistry 4361/8361 Wednesday, October 17

In-Class Exercise Solutions
Multiple-Bond Correlations in HMBC



α-*terpinene*

In this problem, some of the assignments were obvious from simple spectra, but a few were not. Looking at the 1-D ^{1}H NMR, assignments for the isopropyl and methyl group protons are pretty clear based on splitting patterms and intensity (3H singlet for the methyl group, 6H doublet and 1H multiplet for the isopropyl). It's also clear that H2 and H3 should be in the 5.6 ppm set of peaks, and that H5a/b and H6a/b should be in the 2.1 ppm group, but it's not clear in either case which is which. (Okay, for this molecule I'm not sure it's really important to know which is which. But for other molecules it might—maybe you want to be sure which proton to excite selectively in a subsequent experiment—so I hope you'll bear with me on this problem.) So, right off the bat, we can frame what we know and what we don't know in the chart:

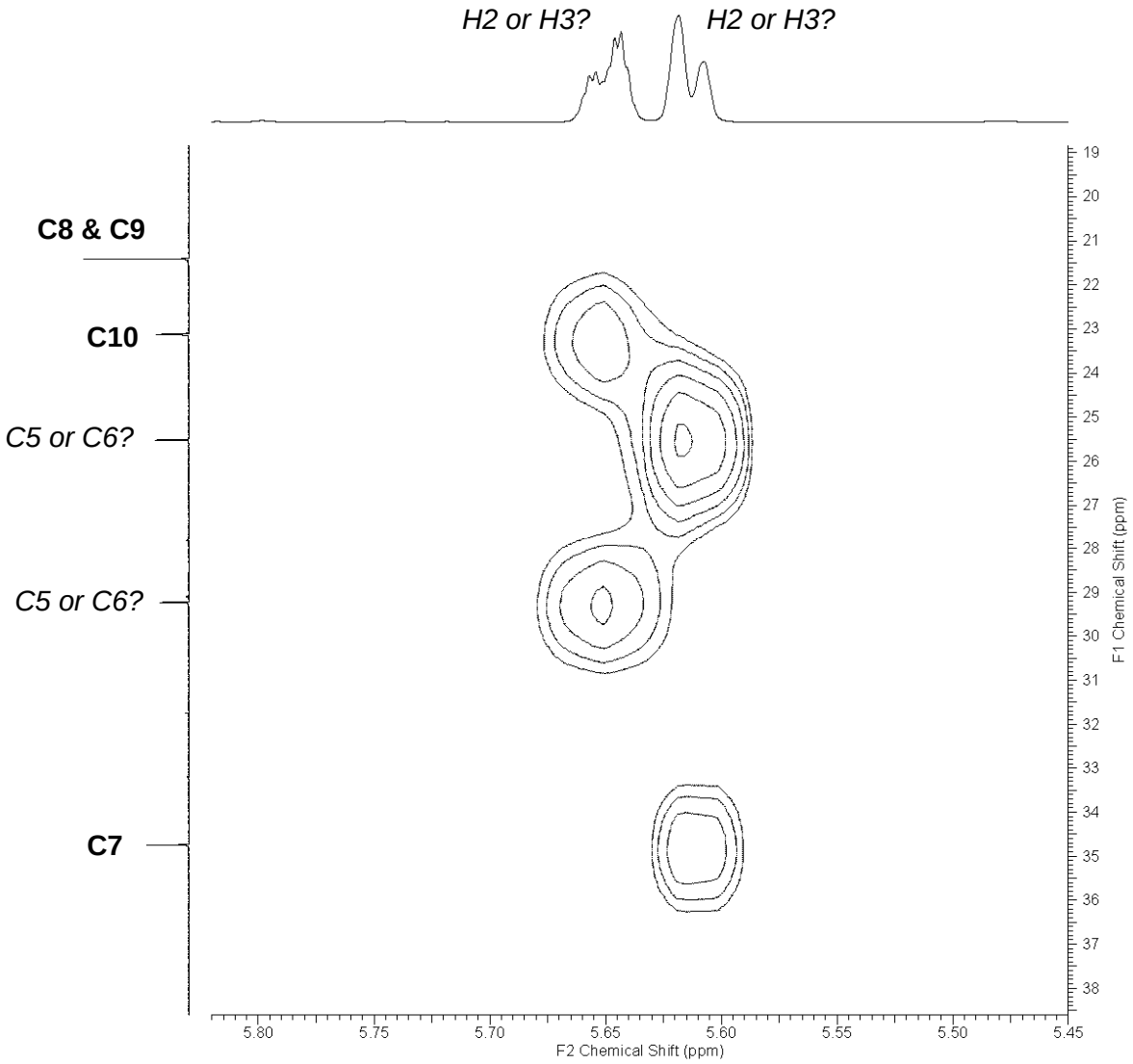
^{1}H resonances:

δ (ppm)	Name(s) of hydrogen(s)
5.65	*H2 or H3?*
5.61	*H2 or H3?*
2.31	**H7**
2.14	*H5 or H6?*
2.11	*H5 or H6?*
1.79	**H10**
1.05	**H8 & H9**

^{13}C resonances:

δ (ppm)	Name(s) of carbon(s)
142.3	*C1 or C4?*
132.9	*C1 or C4?*
119.5	*C2 or C3?*
116.4	*C2 or C3?*
34.4	**C7**
28.9	*C5 or C6?*
25.2	*C5 or C6?*
22.8	**C10**
21.1	**C8 & C9**

Unfortunately, there is no ^{1}H-^{1}H coupling across C1 or C4, so there is no way for us to "walk" from the exterior alkyl groups to the interior using COSY or coupling constants. But we can use the HMBC spectrum to cross this barrier. For example, looking at the first close-up spectrum of the HMBC, and marking it with the information we already know,



At the top, it looks like C10 shows a long-range coupling to one proton out of the H2/H3 set, and not to the other. We have to assume it's the closer one, H3. On the bottom, C7 shows a correlation with the other proton, which must be H3. This allows us to assign chemical shifts to H2 and H3. But wait! There's more! It looks like H2 and H3 each show coupling to another carbon in this region. H2 is closer to C6, and H3 is closer to C5, so I think we can also assign C5 and C6 from this data. The HMQC then allows us to associate these assignments to attached $^{1}H/^{13}C$ atoms. From this, we can update the chart:

^{1}H resonances:

δ (ppm)	Name(s) of hydrogen(s)
5.65	**H3**
5.61	**H2**
2.31	**H7**
2.14	**H6**
2.11	**H5**
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21.1	**C8 & C9**

The last thing we don't know is the assignment for C1 and C4. This information comes from closeup 2 of the HMBC, which shows correlations between H3 and C4 on the left, and between H2 and C1 on the right. So δ(C4) = 142.3 ppm, and δ(C1) = 132.9 ppm.