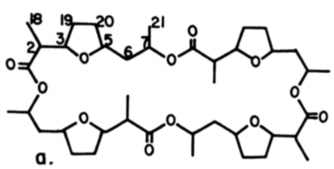
BCMB/CHEM 8190
ANSWERS TO PROBLEM SET 3

1) Assuming adenine H2s have the six-membered ring of other adenines 3 Å above and below, each would shift the H2 upfield by 0.75 ppm. (one can find this number on the "Shielding From a Benzene Ring" slide/plot near the end of lecture notes on chemical shifts). Hence, a flipped out base would have an H2 resonance downfield by 1.5 ppm.

2) According to Spera and Bax the alpha carbon resonance of an amino acid in an alpha helix would be approximately 5 ppm downfield of its corresponding position in a beta sheet.

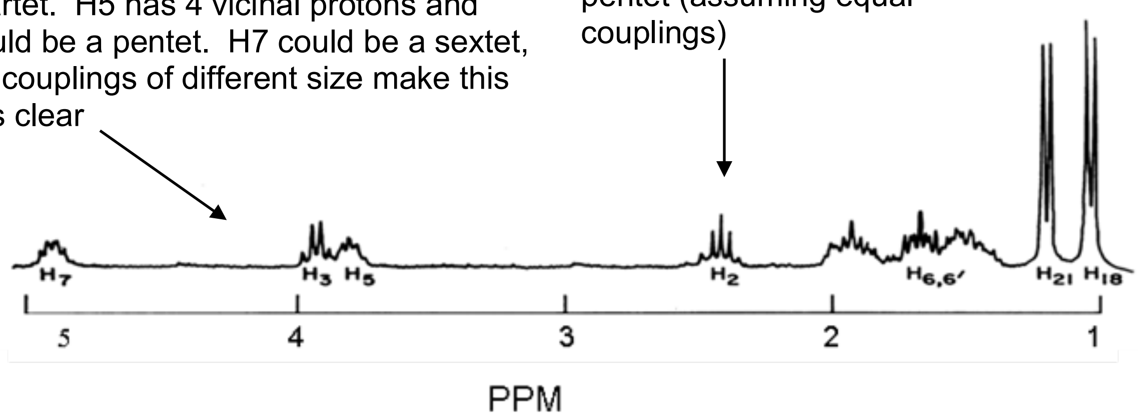
3)



High field, intensity 3, coupled to one vicinal proton – must be methyls 18 and 21. 21 is only one bond away from O – further down field

H3, H5, and H7 are all methines next to a carbon with an oxygen and would be down field. H3 has only 3 vicinal protons and, assuming equal couplings, would be a quartet. H5 has 4 vicinal protons and would be a pentet. H7 could be a sextet, but couplings of different size make this less clear

H2 would be further upfield than H5 (O is 3 bonds removed), has 4 vicinal protons and would be a pentet (assuming equal couplings)



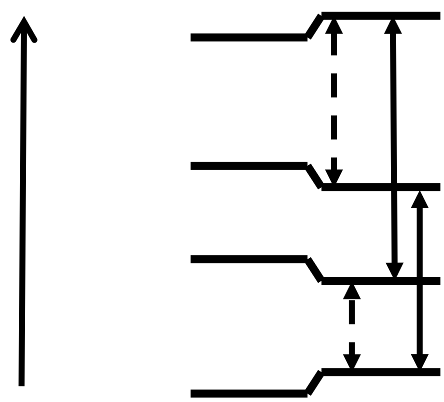
4) We worked out in detail the energy for the $\alpha\alpha$ state in class. Here is one more example – for the $\beta\alpha$ state:

$$\mathbf{H}|\beta\alpha> = -h\nu_1 \mathbf{I}_{\mathbf{1z}}|\beta\alpha> -h\nu_2 \mathbf{I}_{\mathbf{2z}}|\beta\alpha> + hJ_{A12}\, \mathbf{I}_{\mathbf{1z}} \mathbf{I}_{\mathbf{2z}}|\beta\alpha>$$

$$\mathbf{H}|\beta\alpha> = -h\nu_1(-½)\, \beta\alpha -h\nu_2 ½\, \beta\alpha + hJ_{12}(-½)½\, \beta\alpha$$

$$E = <\beta\alpha|\, \mathbf{H}\, |\beta\alpha> = +h\nu_1 ½ -h\nu_2 ½ -hJ_{12} ¼ = ½h(\nu_1-\nu_2) - ¼hJ_{12}$$

We worked out the energy differences in class. The energy level diagram would look as follows, assuming $\nu_1<\nu_2$ and that *J* is positive. (chemical shift effects are greatly exaggerated)



Note decrease in energy of $\beta\alpha$ by –h*J*/4

The spectrum with labeled transitions would look as follows: