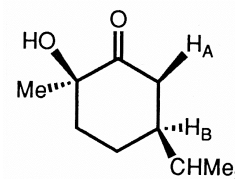


Exam 2: CHEM/BCMB 4190/6190/8189 (133 points) Thursday, 1 October, 2020

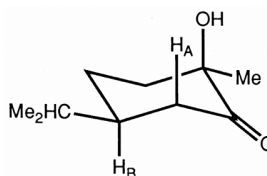
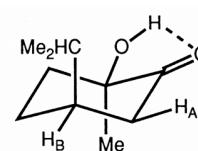
1). For a sample of CHCl_3 , you apply a very long (seconds), low power pulse at the ^1H frequency of the single ^1H nucleus in the molecule. Immediately after this pulse, you apply a normal, high power 90 degree pulse at the same frequency and then record the FID. Sketch what you would expect the FID to look like. Also, sketch the spectrum you would expect to observe following Fourier transformation of the FID. You must thoroughly explain your answers for credit. (6 points).

A long pulse leads to equilibration of the α and β spin populations of the nucleus. In such an instance, there is no net, bulk (macroscopic) magnetization in either the longitudinal direction or transverse plane. If some longitudinal component were present, the 90 degree pulse would rotate that component into the transverse plane and it could then be detected. Because there is no such component, the 90 degree pulse does nothing, and there is no detectable signal. So, the FID will just be noise, and there will be no observable signals in the transformed spectrum.

2). When the cyclohexanone shown (right) is dissolved in methanol, the three-bond scalar coupling constant between H_A and H_B ($^3J_{\text{HAHB}}$) is 11 Hz. However, when it is dissolved in benzene, this coupling is 3 Hz. Please explain in detail why the couplings are different and the origins of the difference. For credit, your answer must include the word “Karplus” used in a contextually correct way. (6 points)

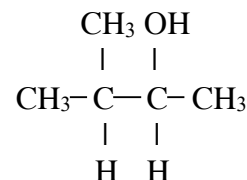


These observations suggest that the conformation of the molecule in methanol is different than the conformation in benzene. For a three bond ^1H - ^1H coupling, the Karplus relationship suggests that the dihedral angle between H_A and H_B is near 0° or 180° for the molecule in methanol, but that this angle is perhaps 60° in benzene. This cyclohexanone most likely exists in one of two stable chair conformations, in which case the hydrogens H_A and H_B can both be axial (dihedral angle $\sim 180^\circ$), both equatorial (dihedral angle $\sim 60^\circ$), or one axial and the other equatorial (dihedral angle also $\sim 180^\circ$). Structure ‘a’ (below) shows the most likely conformation in methanol (dihedral angle $\sim 180^\circ$, $^3J_{\text{HAHB}} \sim 11$ Hz), whereas structure ‘b’ (below) shows the most likely conformation in benzene (dihedral angle $\sim 0^\circ$, $^3J_{\text{HAHB}} \sim 3$ Hz). Incidentally, whereas the hydroxyl group is hydrogen bonded to the solvent in methanol, and the isopropyl group is in the more stable equatorial position, in benzene, where hydroxyl group hydrogen bonding with solvent is not possible, intramolecular hydrogen bonding of the hydroxyl with the carbonyl oxygen stabilizes this conformation greatly and is the reason this conformation predominates in benzene.

**a****b**

3). Consider the isomerically pure compound (S)-(+)-3-methyl-2-butanol (right).

a. Indicate how many signals will be in the ^1H NMR spectrum (ignore the hydroxyl hydrogen). You will have to explain/justify your answer for credit. (4 points)



There will be five signals. For each of the methyl groups, the three hydrogens are equivalent due to fast rotational averaging. The two methyl groups at the 3 position are NOT equivalent to one another (they are diastereomeric), so each will give a separate signal. The hydrogens at positions 2 and 3 are not equivalent to one another, so will each give a signal, as will the methyl group at the 2 position.

b. State what the multiplicity is for each signal (i.e. doublet, triplet, triplet of doublets, etc.). Then, provide a detailed but concise explanation of your answer. Assume that 4-bond, 5-bond, or longer range couplings are NOT observed. Also, assume that there are no observable couplings to the hydroxyl hydrogen. (15 points)

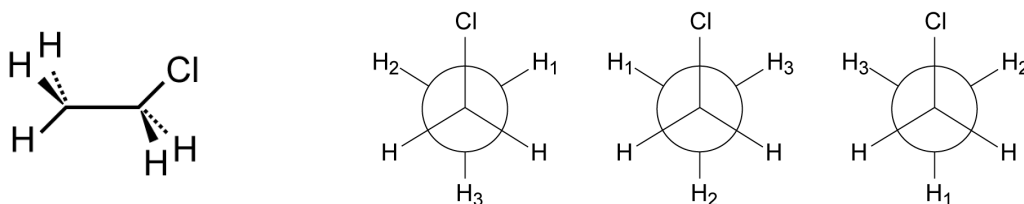
The signal from the hydrogens of the methyl carbon at the 2 position will be split by the hydrogen at the 2 position (3 bond coupling) to give a doublet. There are no other couplings (2 or 3-bond) so there are no additional splittings. Thus, this signal will be a doublet.

The signal from the hydrogen at position 2 will be split into a quartet by the hydrogens on the methyl group at position 2, and each of these quartets will be split into a doublet by the hydrogen at position 3. There are no additional couplings (2 or 3-bond), so there will be no additional splittings. Thus, this signal will be a doublet of quartets.

The signals from each of the two methyl groups at position 3 will be split by the hydrogen at position 3 into a doublet. For each of these methyl groups, there are no additional couplings (2 or 3-bond), so there will be no additional splittings. Thus, each of these signals will be a doublet.

The signal from the hydrogen at position 3 will be split into a quartet by the hydrogens of one of the methyl groups at position 3. Each of the peaks in this quartet will be split into a quartet by the hydrogens of the other methyl group at position 3 to give a quartet of quartets. Finally, each of these peaks will be split by the hydrogen at position 2 into a doublet. There are no additional couplings (2 or 3-bond), so there will be no additional splittings. Thus, this signal will be a quartet of quartet of doublets.

4). Consider chemical and magnetic equivalence in ethyl chloride



For each of the following questions, you will need to provide a detailed explanation in order to receive credit!

a. Are the two methylene hydrogens chemically equivalent? Why? **(4 points)**

No. These enantiotopic hydrogens are not in identical chemical environments. They are in mirror image chemical environments. However, the hydrogens themselves feel identical chemical environments, and there is a plane of symmetry (plane defined by C-C-Cl) relating them, so they have identical chemical shifts. In chiral environments, the chemistry of these hydrogens are different, and their chemical shifts can be different.

b. Are the three methyl hydrogens chemically equivalent? Why? **(4 points)**

Yes. Because of rapid rotation about the C-C bond, the hydrogens of the methyl group are chemically equivalent by averaging, and show identical chemical shifts.

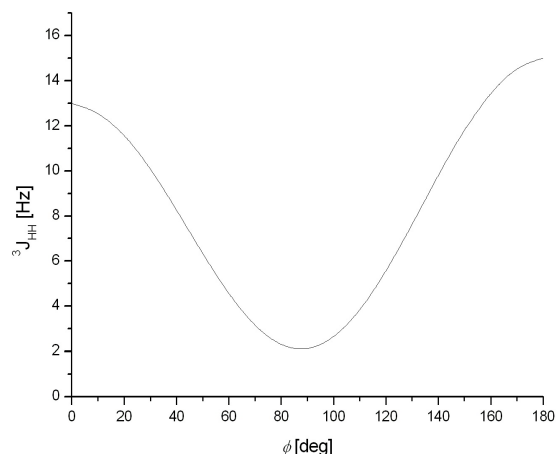
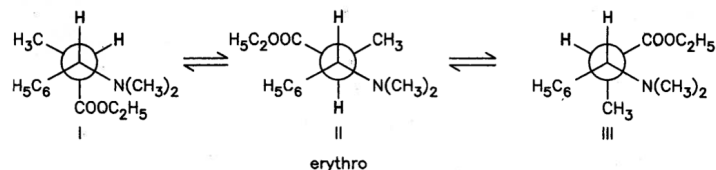
c. Are the methylene hydrogens magnetically equivalent? Why? **(4 points)**

Yes. Because these are enantiotopic they have identical chemical shifts. Because of the plane of symmetry, they show identical couplings to both carbon atoms and also to the chlorine atom (the splitting by the chlorine is normally not observable). Because of rapid rotation about the C-C bond, the couplings to each of the methyl hydrogens are also identical.

d. Are the methyl hydrogens magnetically equivalent? Why? **(4 points)**

Yes. Because of rotational averaging about the C-C bond, these hydrogens, besides having identical chemical shifts, have identical couplings to each of the other nuclei in the molecule (both carbons, the chlorine, and the methylene hydrogens).

5). The Karplus curve for ethylene derivatives is shown (right). The three rotamers of the *erythro* isomer 2-methyl-3-dimethylamino-3-phenylpropionic acid ethyl ester are shown below.



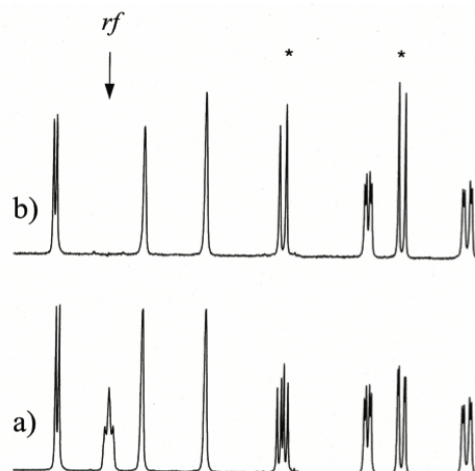
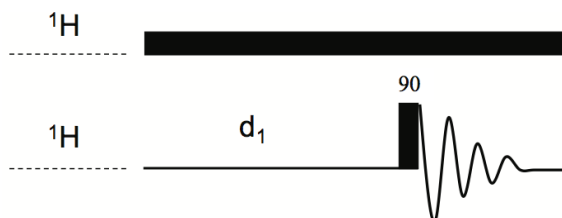
a. If you measured the magnitude of the 3-bond (vicinal) coupling constant between the two methine hydrogens of 2-methyl-3-dimethylamino-3-phenylpropionic acid ethyl ester, and found it to be equal to 4 Hz ($^3J_{HH} = 4$ Hz), what might you conclude regarding the relative populations of conformers I, II, and III? Please explain. **(4 points)**

For conformers I and III the dihedral angle between the methine hydrogens is about 60° , which, according to the Karplus curve, corresponds to a coupling constant of about 4 Hz. The 180° dihedral angle in conformer II corresponds to a coupling constant of about 15 Hz. Therefore, we would conclude that the mixture consists of conformers I and III with little or no conformer II.

b. If you measured the same coupling constant as a function of increasing temperature, and found that the value increased to about 7.5 Hz ($^3J_{HH} = 7.5$ Hz) and then leveled off and did not further increase as the temperature was increased, what would you conclude regarding the relative populations of conformers I, II, and III? Please explain. **(4 points)**

We would conclude that an increase in temperature promotes free rotation around the central C-C bond, such that at high temperature all three conformers are present in essentially equal concentrations ($^3J_{\text{observed}} = F_1 ^3J_1 + F_2 ^3J_2 + F_3 ^3J_3 = 1/3 \times 4 + 1/3 \times 15 + 1/3 \times 4 \approx 7.5$)

6). For a particular molecule, the homonuclear (^1H - ^1H) selective decoupling experiment was performed using the pulse sequence diagrammed below, with the results shown (right), where the result in 'a' is without decoupling, and the result in 'b' is with decoupling. In 'b', the arrow indicated by "rf" points the frequency at which the decoupling field is applied.



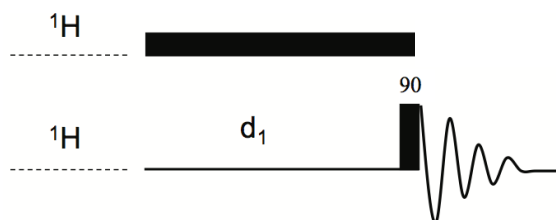
a. In general, for a pair of coupled hydrogens in a molecule, explain the mechanism by which application of a long pulse at the Larmor frequency of one of them leads to decoupling and loss of splitting in NMR spectra? Please use complete sentences and no diagrams or equations. (4 points)

Application of an applied field at the Larmor frequency, i.e. the resonance condition, causes both absorption and emission of energy to occur with equal probability, i.e. nuclei in the α spin state are converted to the β state and vice versa. If the pulse is applied for a long time, the average lifetime for nuclei in any given spin state will be short, as it will undergo continuous interconversion between spin states. Coupling of nuclei requires that the lifetimes of the spin states of the coupled nuclei are long compared to the inverse of their coupling constant. Thus, when the lifetime is shortened by the long pulse, the nuclei become decoupled and the splitting is not observed.

b. Explain why the decoupling experiment (pulse sequence) shown above results in the spectra shown in 'b'. Your explanation should address all changes to signals in 'b' compared to 'a' and the mechanisms by which these result from using the decoupling pulse sequence. (4 points)

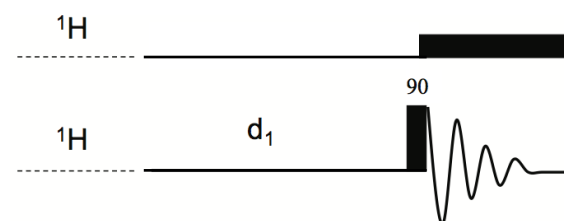
The signal at the frequency indicated by 'rf' is gone in 'b'. This is because application of the rf field at the Larmor frequency of the nucleus during d_1 that gives rise to the signal saturates the spin populations (equalizes the populations of α and β spins), so that no net/bulk magnetization is present before the 90° pulse, and, thus, no transverse magnetization is created for this signal. The signals indicated by the asterisks are from hydrogens that are coupled to the signal at whose Larmor frequency the decoupling field is applied. Splittings in these signals are therefore removed by application of the decoupling field during acquisition, as is shown in 'b'.

c. Describe the result you would expect to observe if, instead of using the pulse sequence shown above, the experiment was performed with the pulse sequence shown here (right). You will have to explain or otherwise justify your answer for credit. **(4 points)**



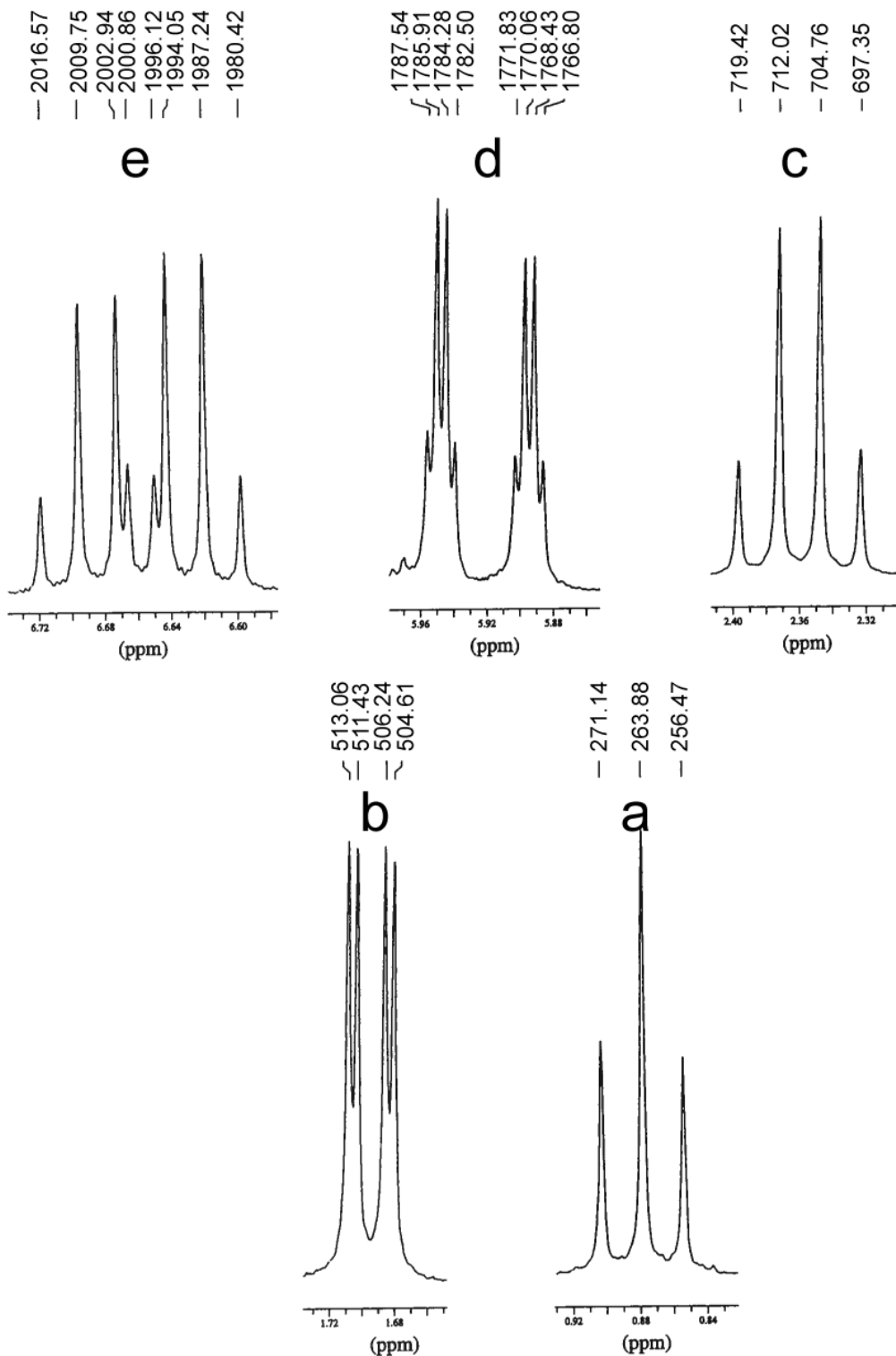
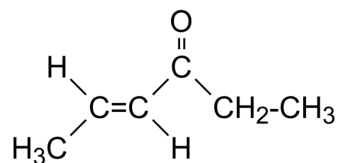
In this case, the decoupling field is still on during d_1 but turned off just before acquisition begins. Because the decoupling field is still on during d_1 , the resonance at whose Larmor frequency it is applied will be saturated, and this signal should be missing in the spectrum, as it is in 'b'. Once the decoupling field is turned off, the peak splittings return instantaneously. So, the splittings observed in the signals in 'a' indicated by asterisks would still be observed.

d. Describe the result you would expect to observe if, instead of using the pulse sequence shown above, the experiment was performed with the pulse sequence shown here (right). You will have to explain or otherwise justify your answer for credit. **(4 points)**



In this case, the decoupling field is off during d_1 but on during acquisition. Because the decoupling field is off during d_1 , the resonance at whose Larmor frequency it is applied will not be saturated before the 90° pulse is applied, so the signal will not disappear from the spectrum as in spectrum 'b'. However, the signal will be attenuated due to the decoupling field applied during acquisition. Because the decoupling field is turned on during acquisition, the splittings to signals from coupled nuclei will be removed, as shown in spectrum 'b'.

7). The signals from the ^1H NMR spectrum of *trans*-4-hexen-3-one (right) are shown below. The frequencies of the individual peaks in the signals are indicated (in Hz).



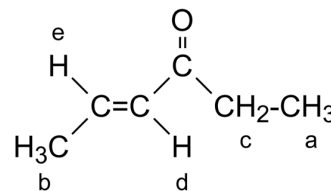
a. Calculate the field strength (in Tesla) of the magnet used to acquire these spectra? (6 points)

Pick any two peaks. Determine the chemical shift difference (ppm) and frequency difference (Hz), and use the equations below. For instance, the chemical shift and frequency differences between the signals at 2.32 ppm (697.35 Hz) and 6.60 ppm (1980.42 Hz) are 4.28 ppm and 1282.97 Hz, respectively. Then:

$$\Delta\delta = \frac{\Delta\nu}{\text{observe frequency}} \times 10^6 \quad \text{observe frequency} = \frac{\Delta\nu}{\Delta\delta} \times 10^6 = \frac{1282.97}{4.28} \times 10^6 \approx 300 \text{ MHz}$$

$$\nu_L = \frac{\gamma B_0}{2\pi} \quad B_0 = \frac{\nu_L \times 2\pi}{\gamma} = \frac{300,000,000 \text{ Hz} \times 2\pi}{26.7519 \times 10^7 \text{ rad T}^{-1}\text{s}^{-1}} = 7.05 \text{ T}$$

b. Label the hydrogens on the molecule (right) a-e, corresponding to the signals shown above. Below, justify each assignment. Your justifications should include explanations as to why the chemical shift, signal splitting, and coupling constant information available in the spectra support your assignments. Coupling constants should be reported using standard nomenclature. (20 points)



Signal a. Signal 'a' is from the hydrogens of the methyl group bound to the methylene ($\delta = 0.88$ ppm). The signal resulting from the equivalent hydrogens of this methyl will be split into a triplet by a 3-bond coupling to the two equivalent hydrogens of the methylene ($^3J_{ac} = 7.4$ Hz), which is the only observable coupling to these hydrogens. The hydrogens of this methyl group would be expected to be the most shielded of all the hydrogens in the molecule, as this methyl carbon is bound to the methylene and not bound to an electron withdrawing center (methyl 'b' would be expected to be further downfield because it is bound to the ethylenic carbon).

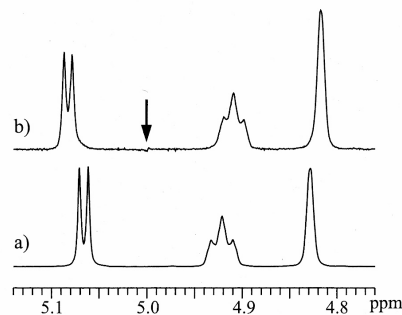
Signal b. Signal 'b' is from the three equivalent hydrogens of the methyl group bound to the ethylenic carbon ($\delta = 1.695$ ppm). The signal resulting from these hydrogens will be split into a doublet by a large, 3-bond coupling to hydrogen 'e' ($^3J_{be} = 6.8$ Hz). The peaks in this doublet are also split into doublets (doublet of doublets) by a small coupling, which is the 4-bond coupling to hydrogen 'd' ($^4J_{bd} = 1.6$ Hz). This methyl group would be deshielded relative to methyl group 'a' because it is bound to the electron-withdrawing ethylenic carbon.

Signal c. Signal 'c' is from the methylene hydrogens ($\delta = 2.36$ ppm). The signal resulting from the two equivalent hydrogens of this methylene will be split into a quartet by coupling to the three equivalent hydrogens of the methyl group ('a') it is bound to ($^3J_{ac} = 7.4$ Hz), which is the only observable coupling to the methylene hydrogens. The hydrogens of this methylene group would be expected to be deshielded relative to the methyl group it is bound to because the methyleneic carbon is bound to an electron withdrawing carbonyl group.

Signal d. Signal 'd' is from the ethylenic hydrogen germinal to the carboxyl group ($\delta = 5.92$ ppm). This signal will be split into a doublet by a very large, 3-bond trans ethylenic coupling to hydrogen 'd' ($^3J_{de} = 15.7$ Hz). The peaks in this doublet are also split into quartets (doublet of quartets) by a small coupling, which is the 4-bond coupling to the three hydrogens of the methyl group 'b' ($^4J_{db} = 1.6$ Hz). This ethylenic hydrogen is expected to be relatively deshielded, and appears relatively far downfield, but not as far downfield as the ethylenic hydrogen 'e' for the reasons noted below.

Signal e. Signal 'e' is from the ethylenic hydrogen germinal to the ethylenic methyl group ($\delta = 6.66$ ppm). This signal will be split into a quartet by a large, 3-bond coupling to the three equivalent hydrogens of the methyl group ($^3J_{eb} = 6.8$ Hz). The peaks of these quartets will be split again into a doublet (doublet of quartets) by a very large, 3-bond trans ethylenic coupling to hydrogen 'd' ($^3J_{ed} = 15.7$ Hz). The ethylenic hydrogen 'e' is expected to be relatively deshielded, however, due to resonance with the carbonyl, the ethylenic carbon that 'e' is bound to bears a partial positive charge. This further deshields this hydrogen. Also, proximity with the carbonyl oxygen further deshields this hydrogen. As a result, the signal from hydrogen 'e' is the most downfield in the spectrum.

8). When performing selective homonuclear decoupling experiments, if the decoupling field is applied during the acquisition of the FID, signals in the spectrum ('b') can move relative to their positions in the control spectrum ('a') where no decoupling field is applied. This is demonstrated in the spectra shown (right), where the arrow indicates the frequency at which the decoupling field was applied for spectrum 'b'. This effect is known as the Bloch-Siegert effect. This effect is not observed if the decoupling field is turned off prior to acquisition. Provide a plausible explanation for the Bloch-Siegert effect. (8 points)



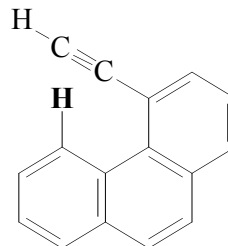
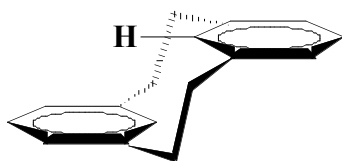
Resonance frequency is dependent on the magnetic field strength experienced by the nuclei. Because the signals change frequency slightly due to the Bloch-Siegert effect, the effect must be due to a change in magnetic field strength experienced by the nuclei when the decoupling field is turned on. This is the case. Even the relatively weak electromagnetic field generated by the decoupling field can produce this effect. This effect is dependent on the frequency difference (in Hz) between the frequency of the applied decoupling field and the Larmor frequency of the nucleus, and, thus, has the effect of moving the signals away from the decoupler frequency.

9). Circle the word in each pair of parentheses that makes the following statement true: As the value for the shielding constant, σ , increases, this indicates (decreased / increased) shielding of a nucleus, a/an (decrease / increase) in the effective magnetic field experienced by the nucleus, a/an (downfield / upfield) shift in the chemical shift, and a (lower / higher) resonance frequency for the nucleus. (4 points)

10). Why is the term σ_{para} necessary to describe the shielding constant, σ ? (4 points)

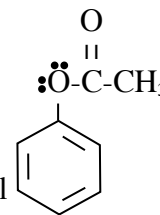
The σ_{dia} term accounts for the spherically symmetric charge distribution about a nucleus. However, the electron distribution about nuclei in molecules is normally not spherically symmetric. The term σ_{para} is used to describe and account for non-spherical charge distribution.

11). For benzene, the ^1H chemical shift of the hydrogens is 7.27 ppm. For ethane, ethylene, and acetylene, the ^1H chemical shifts of the hydrogens are 1.96, 5.84, and 2.88 ppm, respectively. Estimate the chemical shift of the shown (bolded) hydrogen atom in each of the two molecules shown below. You will need to thoroughly explain and justify your answers. (6 points)



The chemical shift of the hydrogen in the molecule on the left is approximately -3 ppm. The chemical shift for a hydrogen in a benzene ring is normally about 7.27. However, this hydrogen is placed directly above the plane of a second benzene ring. The magnetic anisotropy of the benzene ring is such that above the plane is the shielding region. Thus, this hydrogen will have a substantially reduced chemical shift. The chemical shift of the hydrogen in the molecule on the right is approximately 10. In the absence of the acetylene group, its chemical shift would be about 7.27. However, this hydrogen is placed in the deshielding region of the acetylene group. Thus, the chemical shift is dramatically increased.

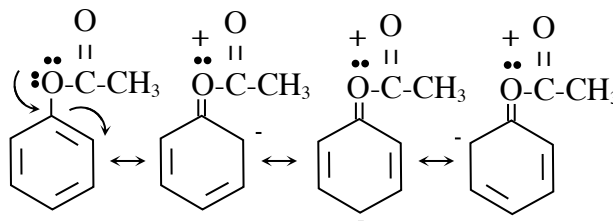
12). The ^1H and ^{13}C NMR spectra of phenyl ethanoate (right) were recorded. The ^1H signals for the protons in the benzene ring (ignoring coupling) were, from largest to smallest, found to be 7.25, 7.15, and 7.06 ppm. The ^{13}C signals for the carbon atoms in the benzene ring (ignoring coupling) were, from largest to smallest and not including the ^{13}C chemical shift of the carbon bound to the oxygen, found to be 128.9, 125.3, and 121.4. You also know that for unsubstituted benzene, the chemical shift of the protons is 7.27 ppm and the chemical shift of the ^{13}C atoms is 128.5 ppm.



a. Indicate in the table below which of the ^1H and ^{13}C shifts correspond to the ortho, meta, and para positions by placing the correct chemical shift in the correct position in the table. (6 points)

	Chemical Shifts		
	δ_{ortho}	δ_{meta}	δ_{para}
^1H	7.06	7.25	7.15
^{13}C	121.4	128.9	125.3

b. Justify your answer to part 'a'. In order to receive credit for parts 'a' and 'b' you will have to 1). draw appropriate resonance structures to justify your table entries, and 2). discuss why each position is more/less shielded relative to the others. (8 points)



Resonance structures show that ortho and para positions will be shielded, thus the chemical shifts will be smaller (more upfield) at these positions. The chemical shift will be smallest at ortho due to proximity to the electron donating substituent.

Name _____

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You may find some of the information below useful:

Table 1-1.

Properties of some nuclides of importance in NMR spectroscopy.

Nuclide	Spin I	Electric quadrupole moment ^{a)} [eQ] [10^{-28} m^2]	Natural abundance) [%]	Relative sensitivity ^{b)}	Gyromagnetic ratio $\gamma^a)$ [$10^7 \text{ rad T}^{-1} \text{ s}^{-1}$]	NMR frequency [MHz] ^{b)} ($B_0 = 2.3488 \text{ T}$)
^1H	1/2	–	99.985	1.00	26.7519	100.0
^2H	1	2.87×10^{-3}	0.015	9.65×10^3	4.1066	15.351
$^3\text{H}^c)$	1/2	–	–	1.21	28.5350	106.664
^6Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
^{10}B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
^{11}B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
^{12}C	0	–	98.9	–	–	–
^{13}C	1/2	–	1.108	1.59×10^{-2}	6.7283	25.144
^{14}N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
^{15}N	1/2	–	0.37	1.04×10^{-3}	-2.7126	10.133
^{16}O	0	–	99.96	–	–	–
^{17}O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	-3.6280	13.557
^{19}F	1/2	–	100	0.83	25.1815	94.077
^{23}Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
^{25}Mg	5/2	0.22	10.13	2.67×10^{-3}	-1.6389	6.1195
^{29}Si	1/2	–	4.70	7.84×10^{-3}	-5.3190	19.865
^{31}P	1/2	–	100	6.63×10^{-2}	10.8394	40.481
^{39}K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
^{43}Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	-1.8028	6.728
^{57}Fe	1/2	–	2.19	3.37×10^{-5}	0.8687	3.231
^{59}Co	7/2	0.42	100	0.28	6.3015	23.614
^{119}Sn	1/2	–	8.58	5.18×10^{-2}	-10.0318	37.272
^{133}Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
^{195}Pt	1/2	–	33.8	9.94×10^{-3}	5.8383	21.499

B_0 (Tesla, T)	Resonance frequencies (MHz)	
	^1H	^{13}C
9.4	400	100.6
11.74	500	125.7
14.09	600	150.9
18.79	800	201.2

$$\gamma_{^1\text{H}} = 26.7519 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{10}\text{B}} = 2.8747 \times 10^7 \text{ rad/T/s}, I = 3$$

$$\gamma_{^{11}\text{B}} = 8.5847 \times 10^7 \text{ rad/T/s}, I = 3/2$$

$$\gamma_{^{13}\text{C}} = 6.7283 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{15}\text{N}} = -2.7126 \times 10^7 \text{ rad/T/s}, I = 1/2$$

$$\gamma_{^{17}\text{O}} = -3.6280 \times 10^7 \text{ rad/T/s}, I = 5/2$$

You may find some of the following information or equations useful:

$$k_B = 1.381 \times 10^{-23} \text{ J/K}$$

$$\text{Avagadro's number} = 6.02214179 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\hbar = h/(2\pi)$$

$$P = \hbar \sqrt{I(I+1)}$$

$$P_z = m\hbar$$

$$\mu = \gamma P = \hbar \gamma \sqrt{I(I+1)}$$

$$\text{for } m = \frac{1}{2}, \cos(\theta) = \frac{m\hbar}{\hbar \sqrt{I(I+1)}} = \frac{m}{\sqrt{I(I+1)}}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$M_0 = \frac{N\gamma^2 \hbar^2 B_0 I(I+1)}{3k_B T}$$

$$B_2 = \frac{\Delta \nu \sqrt{J^2 - J_r^2}}{J_r} = \frac{J \Delta \nu}{J_r}$$

$$\varepsilon \propto dM/dt = \gamma M_0 B = \frac{N\gamma^3 \hbar^2 B_0^2 I(I+1)}{3k_B T}$$

$$\Delta \nu = \nu_{BS} - \nu_0 = \frac{B_2^2}{2(\Delta B)} = \frac{B_2^2}{2(\nu_0 - \nu_i)}$$

$$S/N \propto NS^{1/2} \text{ (signal-to-noise improves with (number of scans)}^{1/2})$$

$$m = (-I, -I+1, \dots, I-1, I)$$

$$\Theta = \gamma B_1 \tau_p$$

$$E = -\mu_z B_0 = -m\gamma \hbar B_0$$

$$\frac{N_\beta}{N_\alpha} \approx 1 - \left(\frac{\gamma \hbar B_0}{k_B T} \right)$$

$$\Delta E = \mu_z B_0 = \gamma \hbar B_0 = h\nu_L = h\nu_1$$

$$B_{eff} = B_0(1 - \sigma)$$

$$\nu_L = |\gamma/(2\pi)| B_0 = \omega_0/(2\pi)$$

$$\nu_L = \frac{\gamma}{2\pi} (1 - \sigma) B_0$$

$$\omega_0 = \gamma B_0$$

$$\Delta \delta = \frac{\Delta \nu}{\text{observe frequency}} \times 10^6$$

$$M_y = M_0 e^{-t/T_2^*}$$

$$M_z = M_0(1 - e^{-t/T_1})$$

$$M_z = M_0(1 - 2e^{-t/T_1})$$

$$\Delta \nu_{1/2} = \frac{1}{\pi T_2^*}$$

$$\frac{1}{T_2^*} = \frac{\gamma \Delta B_0}{2} + \frac{1}{T_2} \quad \frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2(B_0)}$$

$$t_{\text{zero}} = T_1 \ln(2)$$

$$\eta = \gamma_a / (2\gamma_x)$$

$$I = (1 + \eta) I_0$$

$$I \propto 1/r^6$$

$$SW = 1/(2DW) = \text{Nyquist frequency } (\nu_{NQ})/2$$

$$AQ = DW * TD$$

$$DR = 2SW/TD = 1/AQ$$

$$(TD \equiv NP)$$

$$\cos \alpha_{\text{Ernst}} = e^{-((d_1 + AQ)/T_1)}$$

$$\pi/2 \text{ radians} = 90^\circ$$

$$1 + \gamma_A/\gamma_X \quad 1 - \gamma_A/\gamma_X$$

$$\text{multiplicity} = 2nI + 1$$

$$\Theta = 2\pi J \tau$$