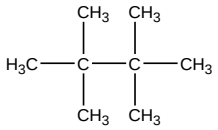
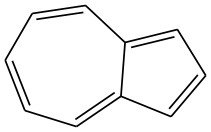


Chemistry 318N



Spring 2012
Dr. Willson

First Midterm Exam

This evening you will take two tests, one in chemistry and one in integrity. I want you to get A's on both of these tests but if you are to fail one, let it be the one on organic chemistry. GW

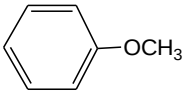
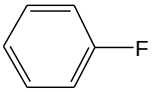
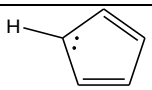
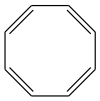
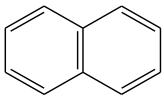
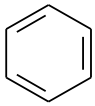
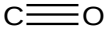
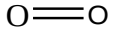
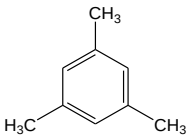
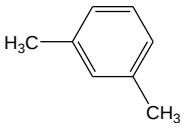
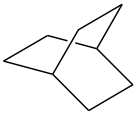
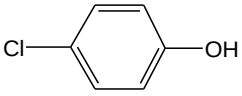
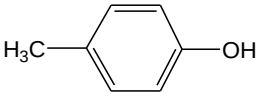
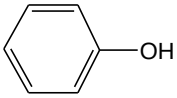
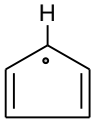
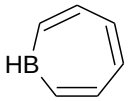
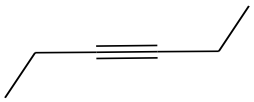
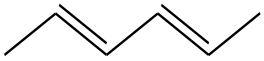
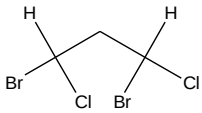
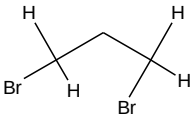
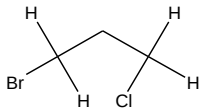
Name (Print as it appears on the Class Roster)_____

Signature_____

Here is some useful and some useless information

F=Ma, y=mx+b; $E=MC^2$, Office = WEL 5.240, C= $3x10^8$m sec^{-1}, $\upsilon = \gamma B$, h=$9.5x10^{-14}$ kcal sec mol^{-1} = 4.0 x 10^{-13}kJ; TA^3 = (Greg x Michael x Andrew) , Willson ≠ Wilson C_nH_{2n+2}; 95 = A, r =1.987 cal deg^{-1} mol^{-1}, 1m = 10^6μm; $\nu=(k/\mu)^{-1/2}$;. ¥ < $; V = $4/3\pi r^3$, $\nu\lambda$ = C, 85 = B, γ_{1H} = 42.576 MHz/T, γ_{13C} = 10.705 MHz/T, D=VT, $A=\varepsilon CL = \log I_0/I$, 12:31 = tardy %T = I/I_0 x 100, micrometer = μm = 10^{-6} m, 1nm = 10^{-9}m, log 3 = 0.477, log 2 = 0.301, a+b = b+a, $a^x a^y = a^{x+y}$, $A=4\pi r^2$, OPEN=cool, $R = 8.314\ J\cdot mol^{-1}\cdot K^{-1}$. V=IR

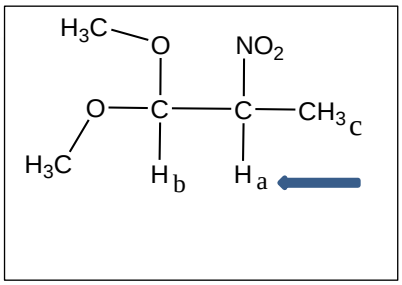
1. (15 points) Circle the one best answer in each row.

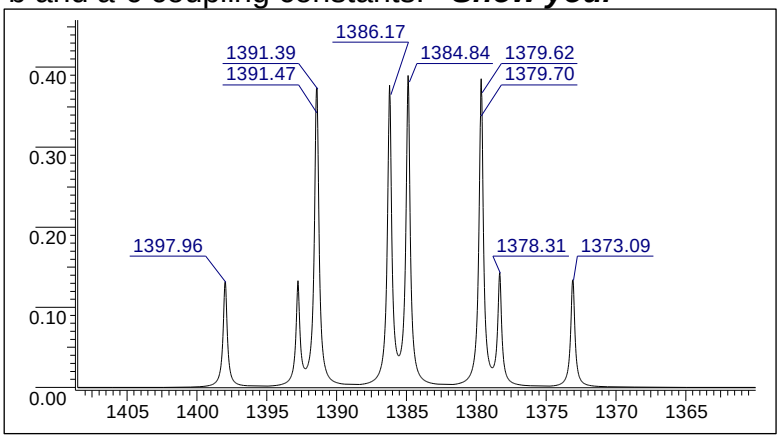
Has highest field proton resonance			
Has non-bonding molecular orbitals			
Has the shortest carbon–carbon bond			
Absorbs IR at the shortest wavelength			
Compound with exactly 3 peaks in its ^{13}C-nmr spectrum			
Has the most stable conjugate base			
Is in the infra red spectral region	10 cm^{-1}	10 micrometers	10 MHz
Not a unit of frequency	Hertz	Tesla	Kayser
Has 6 pi electrons			
Resonates at highest frequency (same B)	^{13}C	^{12}C	^{1}H
Has a base peak at m/z=55			
Aromatic compounds	Have electrons in non-bonding orbitals	Have 2n+4 π electrons in a planar, cyclic structure	Have no electrons in anti-bonding orbitals
Strongest acid	Has the smallest pKa	Smallest Ka	Highest pH
Has a pentet splitting pattern in the ^{1}H nmr spectrum			
Has the highest degree of unsaturation	C_5H_9N	$C_9H_{13}Br$	$C_9H_{12}NCl$

2. (12 pts) The ^{1}H nmr spectrum of the nitro compound below includes a multiplet that is assigned to the proton designated with an arrow and the label "a" in the drawing. The spectrum was well resolved because it was measured using a spectrometer with an 8.0 Tesla magnet.

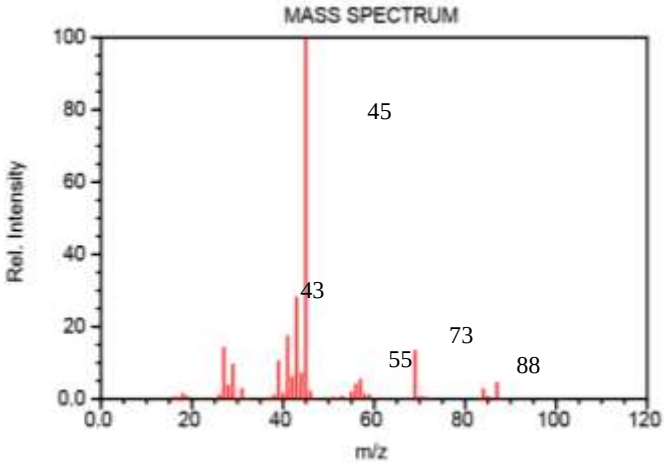
a) Please calculate the chemical shift of proton a in ppm and

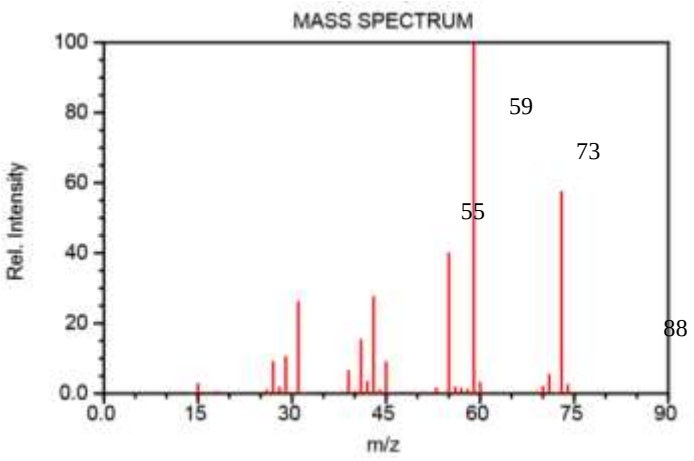
b) Please calculate the a-b and a-c coupling constants. ***Show your work***.





3. (10 pts) Below are mass spectra for the isomers 2-pentanol and 2-methyl-2-butanol. Assign each isomer to its correct spectrum and <u>*explain the basis for*</u>

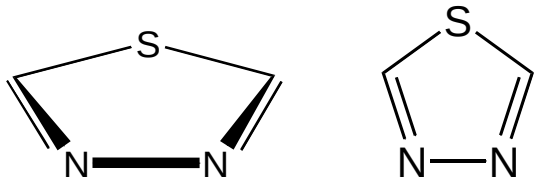




4. (8 pts) The line of integration of the two signals in the ^{1}H-nmr spectrum of a ketone with the molecular formula $C_7H_{14}O$ rises 62 and 10 chart divisions respectfully. Calculate the number of hydrogens that give rise to each signal and propose a structural formula for this compound. Please show your work. (homework problem 13.4)

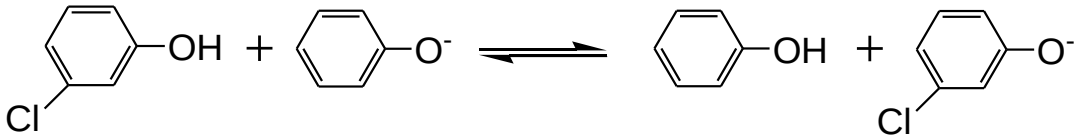
5. (10 pts) The biggest magnets currently available enable a 1000 MHz proton nmr spectrometer. What is the spectrometer frequency for ^{13}C using this magnet? Show your work.

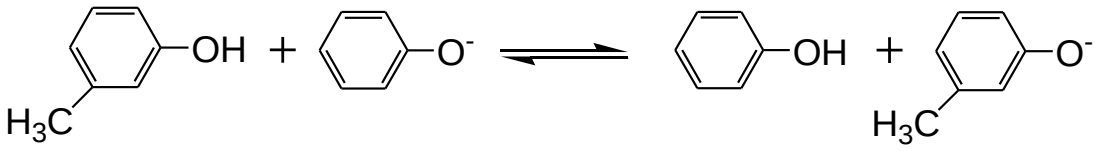
6. (10 pts) The structure of the heterocycle 1,3,4-thiadiazole is shown below in two ways. One provides some perspective and one is flat. Please modify the perspective structure to show exactly how the electrons on the nitrogen atoms and the sulfur atom are incorporated into the pi system of the ring. Your modifications must be very clear to be counted. Is this compound aromatic? Justify your answer.

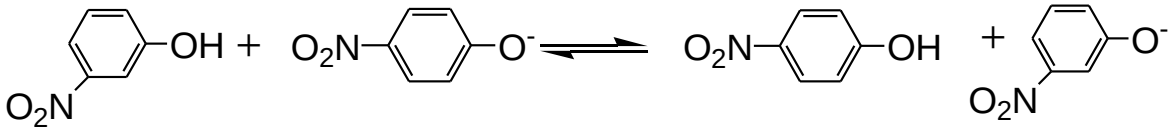


7. (10 pts) Below are depicted 5 equilibrium equations. Assuming equimolar concentrations of the substances on the left of the arrow were mixed, in which direction would the equilibrium lie? Please circle the most stable conjugate base in each equation and then draw a bold arrow over the equilibrium arrow that shows which way the equilibrium would lie.

a) pKa= 4.0 pKa=7.5

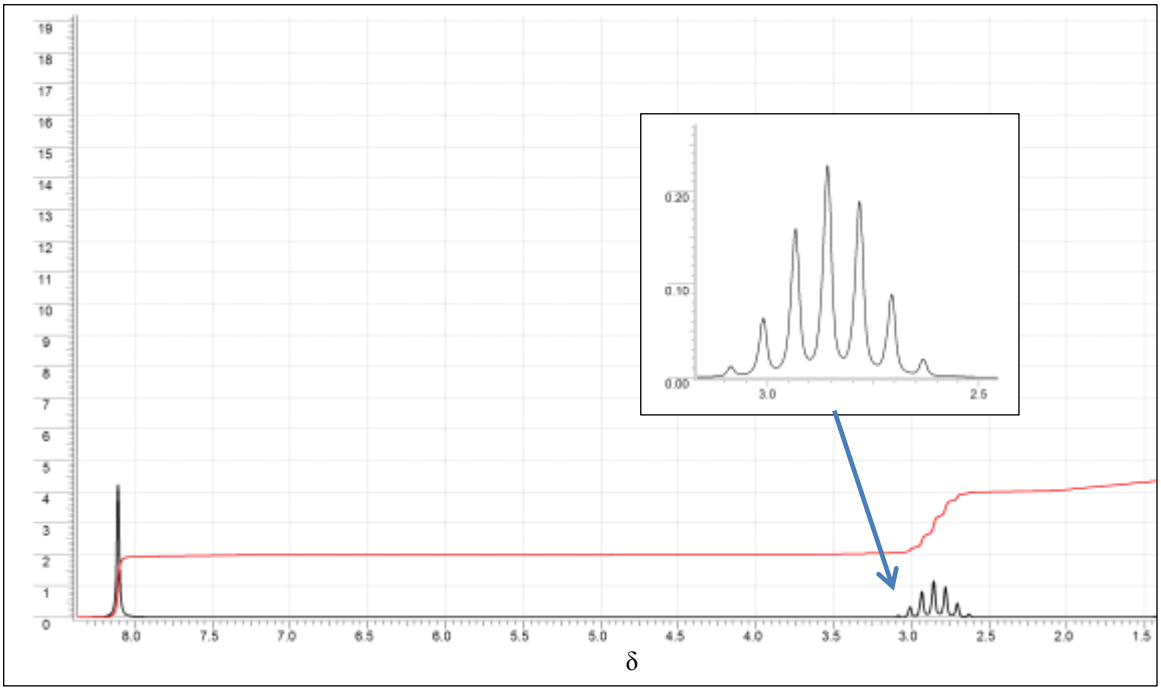




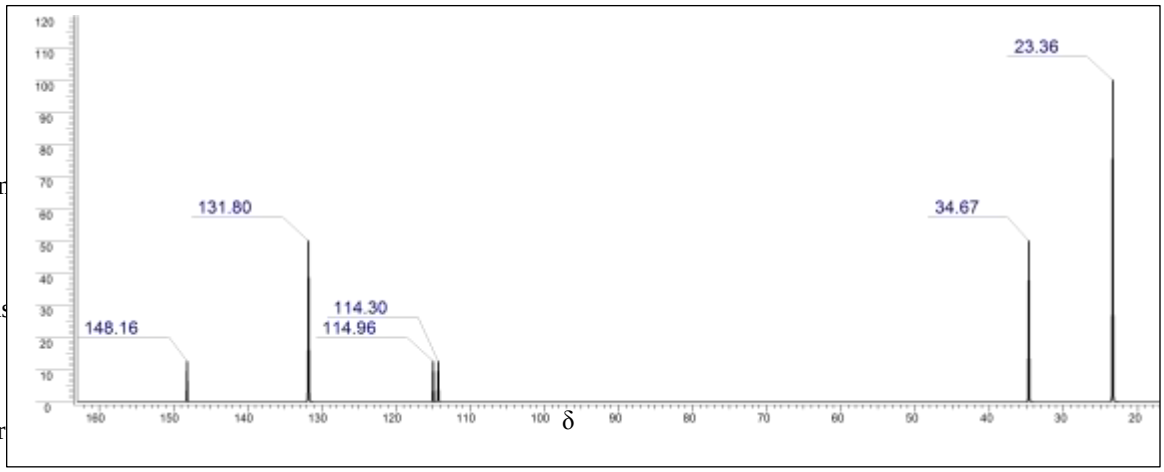


8. (5 pts) An interesting hydrocarbon with an empirical formula of C_7H_{12} was isolated from the product stream of an experimental cracking tower. The substance has only one singlet in the proton nmr at 1.65δ. The ^{13}C-nmr is more interesting. It shows 3 well resolved peaks, two of which disappear in the DEPT experiment. Please write the structure of this hydrocarbon in the small box below. The box is small to limit transmission of your answer to those with exceptional visual acuity. Please keep it covered.

9. (20 pts) Here it is, the unknown! A small sample of a strange substance was isolated from white powdery residues that were found in the bottom of Demi's hand bag. The powder smells a bit like rosemary. Combustion analysis revealed an empirical formula of C_7H_8N. The ^{1}H-nmr spectrum and the ^{13}C-nmr spectrum are provided below. In the DEPT spectrum of this residue, the three peaks at 114.30, 114.96 and 148.16 disappear, but all of the other peaks are unchanged. The infrared spectrum shows a medium strength band at 3027 cm^{-1}, strong bands between 2860 and 2920 cm^{-1} and a sharp, medium strength band at 2243 cm^{-1}. There are medium bands in the region of 1600 to 1690 cm^{-1}, strong bands in the region of 720 – 810 cm^{-1} and multiple peaks in the fingerprint region. The mass spectrum of the substance shows a strong molecular ion at m/z = 212. On the next page, please list all that you can discern/learn/interpret about the structure from each of the pieces of data supplied and then propose a structure for the compound.



Cor



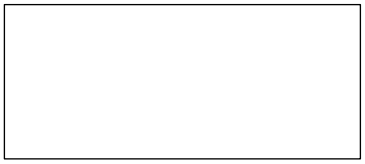
Mas

Infr

^{1}H-nmr spectrum:

^{13}C-nmr spectrum:

DEPT experiment:



KEEP IT COVERED!!