Chemistry 618B
Spring 2001

Midterm Exam I

Prof. Willson T-Th 12:30 – 2:00

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

Social Security Number_____

Signature_____

Here is some useful and some useless information

$F=Ma$, $y=mX+b$; $E=MC^2$, office = WEL5.240, C= $3x10^8$m sec^{-1}, h=$9.5x10^{-14}$ kcal sec mol^{-1}, TA = Trinque ; TA = Meiring, Meiring $\neq$ Trinque; spin states = $2I+1$, C_nH_{2n+2}; 95 = A, r =1.987 cal deg^{-1} mol^{-1}, 1m = 10^6μm; $v=(k/\mu)^{-1/2}$;. ¥ < $

Name _____

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1. _____   (   )

2. _____   (   )

3. _____   (   )

4. _____   (   )

5. _____   (   )

6. _____   (   )

7. _____   (   )

8. _____   (   )

9. _____   (   )

10. _____   (   )

11. _____   (   )

12. _____   (   )

13. _____   (   )

14. _____   (   )

Total   _____

T-Score   _____

**Grade**   _____

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1. (5 pts)   I have a new quartz cell that I would like to use for UV-vis spectroscopy. I cannot accurately measure the length of the cell with a ruler because the opening is too small. So…I fill it with a 1.50×10^{-4} molar solution of my favorite blue dye (it absorbs at 500nm) that has an extinction coefficient of 13,100 L $\text{mol}^{-1}\text{cm}^{-1}$. The absorbance of the cell was measured 4 times at 500nm and the average absorbance was. 1.30. What is the length of the cell in cm?   <u>Show your work.</u>

2. (5 pts)   The proton nmr spectrum of chloroform ($CHCl_3$) shows a single sharp peak at 7.3δ when measured on a 60MHz nmr spectrometer. How many Hz down field of TMS would one find this resonance if it were measured on a 360MHz spectrometer?

3. (5 pts)   The characteristic (C=O) infrared absorbance of acetone is 1710 cm^{-1}.
a)Please express this absorbance in units of Hz

b) Please calculate the wavelength of this absorbance in micrometers

4. (5 pts) Please consider cyclononatriene. Which would be the most stable, the radical, the anion or the cation? Please explain with MO diagrams. (This was supplemental homework)
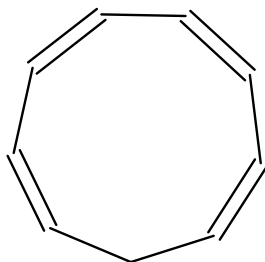
5. (10 pts) You believe your lab unknown to be $BrCH_2CH_2CH_2Br$.

    a) You run the mass spectrum to make a final judgment. What do you predict to be the ratio of the M peak to the M + 2 peak if your proposed structure is correct.

    b) Sketch the nmr spectrum you would predict for this compound. We do not seek the exact chemical shift, only the <u>approximate chemical shift</u>, the <u>splittings</u> and the <u>integral</u> for each peak in the spectrum. I have put in TMS for you just to be nice!

8.0

δ

0
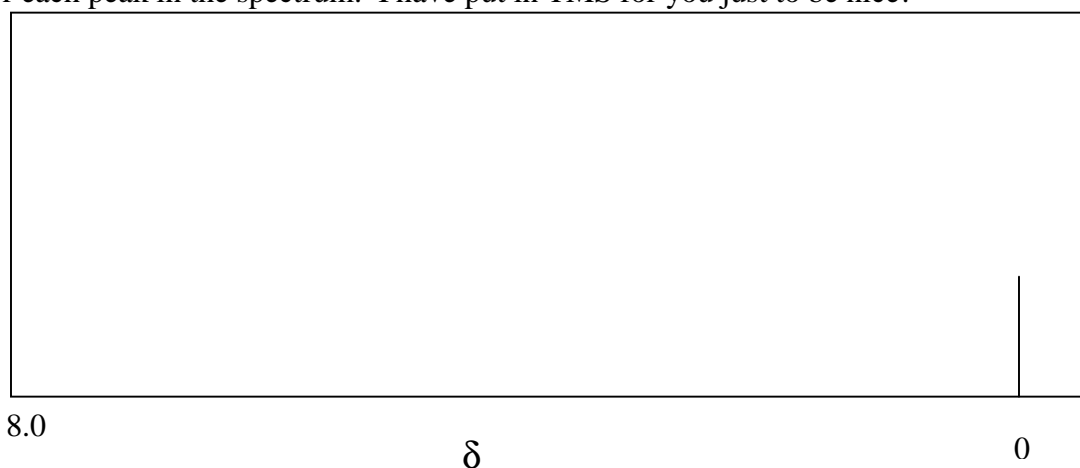
6. (5 pts) A figure depicting the "ring current" effect in benzene is shown below. Please draw an arrow that shows the direction of flow of <u>electrons</u> (not positive charge) that is induced by the applied field. The applied filed direction is indicated by the large arow.

Induced
circulation of
pi electrons
in the aromatic
ring

Applied field

Name _____

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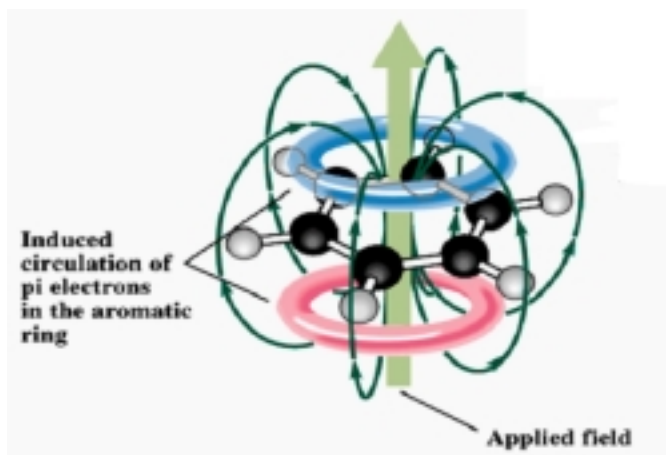
7. (10 pts) The carpet that was recently removed from the "West Wing" seems to be heavily stained and it is contaminated with an unknown toxin that has a powerful and deleterious effect on brain function. A secret service agent collected the mass spectrum of the toxin. It has a molecular ion at 102.13 and it clearly has two oxygen atoms in the empirical formula. Brian measured the infrared spectrum and found a strong sharp band at 1727 cm^{-1}.   Jason ran the ^{1}H-nmr spectrum and it is reproduced below together with an expansion of the high field area. I don't know what else to do with this stuff. I am afraid to smell this it for fear I will lose all sense of right and wrong. Can you suggest a structure that is consistent will all the spectral data?

Expansion Plot of Upfield Region
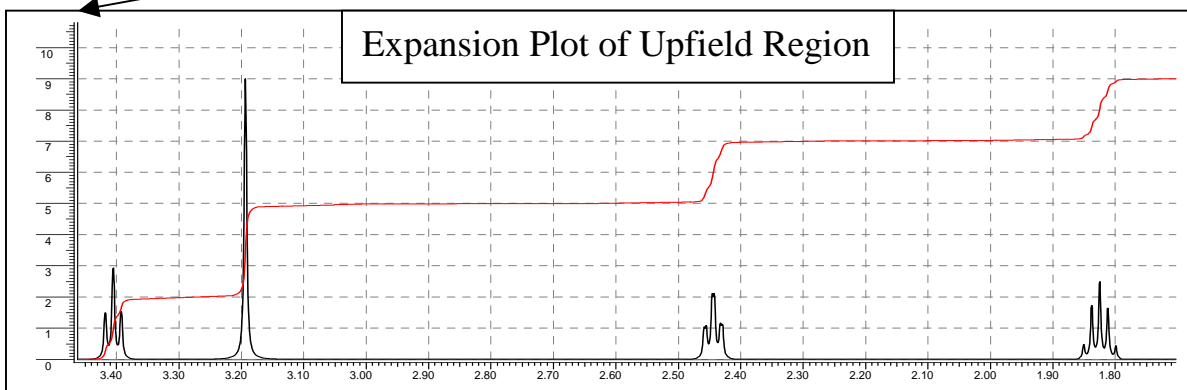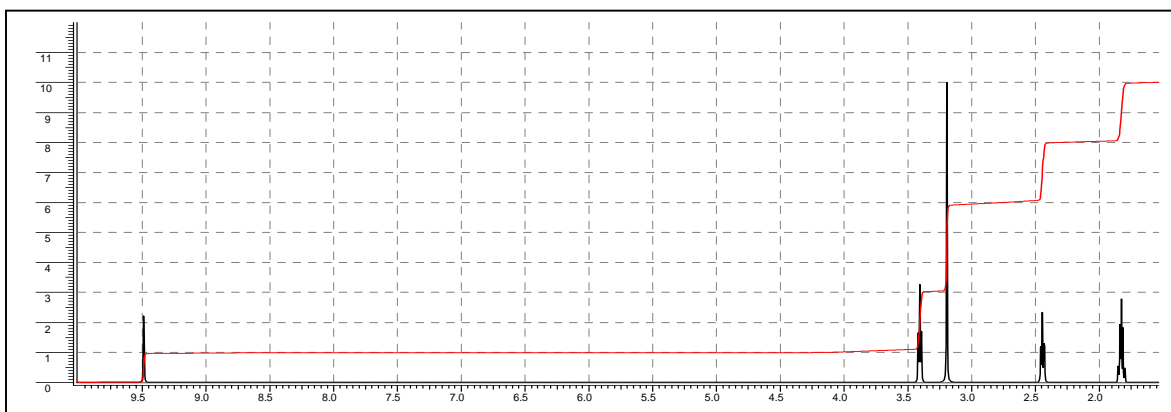
Structure of the toxin

If you can't figure out the structure, show below those aspects of the structure you can establish from the spectra.

Name _____

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8. (5 pts) The mass spectrum of an unknown compound shows a molecular ion at *m/z* 85, an M+1 peak at 86 of approximately 6% abundance relative to M, and an M+2 peak at 87 of less than 0.1% abundance relative to M. Propose a molecular formula for compound B. (propose a formula not a structure) (Homework 12.20a)

9. (5 pts) The nmr spectrum of an ethynyl ketone is shown below…isn't it pretty? Please calculate the ratio of the integral area of the peak marked in the multiplet to the area of **one** of the peaks in the doublet. Show your work.
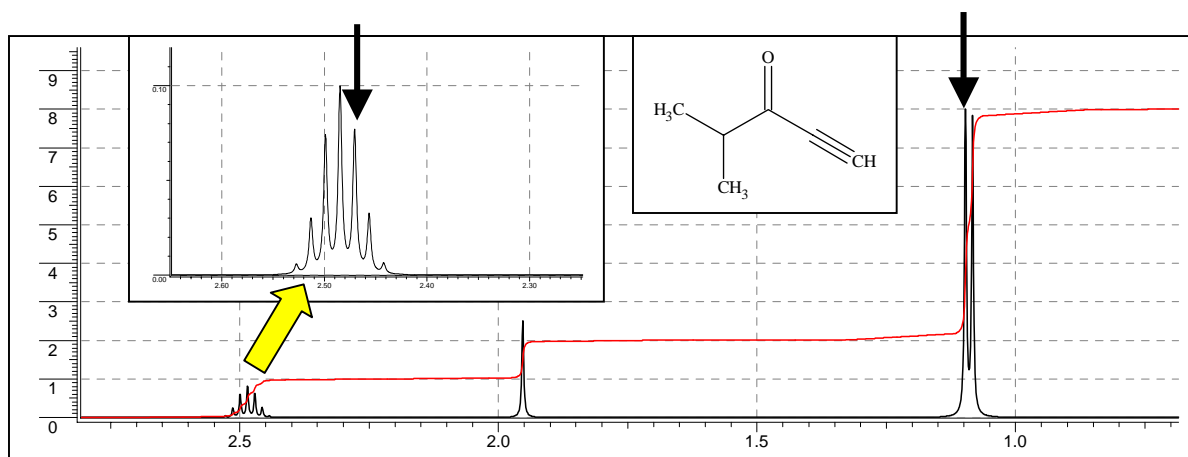
10. (5 pts) Explain (please keep it short…this isn't an essay exam) how to distinguish between the members of each pair of constitutional isomers based on the number of signals in the proton decoupled 13C-nmr spectrum of each member.
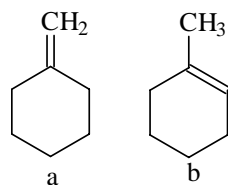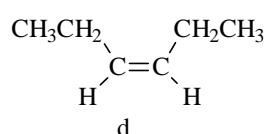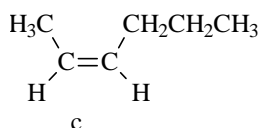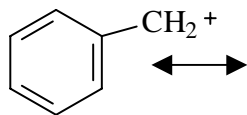

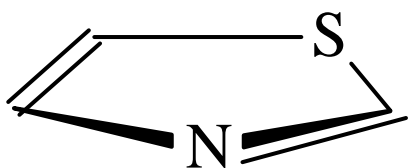Pair 1   Pair 2

11. (10 pts) Write all of the resonance structures for benzyl carbocation. Use the curved arrow convention to generate all of the resonance structures of benzyl carbocation.
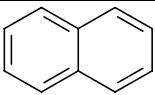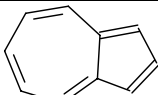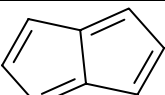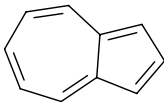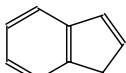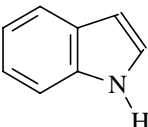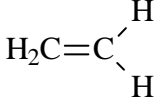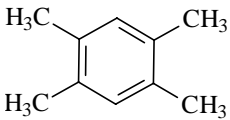

12. (10 pts) As you may know, the Grammy Awards are being presented while you are taking this test. The ceremony was interrupted when a toxic substance was found under the seat of M&M. Barry Manylough is being held as a suspect in this heinous act. Eltin Jonn recovered a sample of the substance and provided it to the Master Pee for analysis. He found that the material has a single peak in the nmr spectrum at δ 3.5 ppm in the proton nmr spectrum. It has two peaks in the ^{13}C-nmr spectrum and the DEPT analysis shows that the higher field peak appears as a positive peak and the lower field peak disappears completely. Mass spectroscopy reveals that the molecular weight of the compound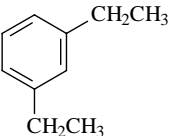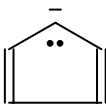 is 70.09. The combustion products of the compound are CO_2, H_2O and NO_2. What is the structure of this weird compound?? I will sell you the empirical of the compound for 3 points.

13. (5 pts) The structure of thiazole is provided below. Modify the structure to show exactly how the electrons on the nitrogen and the sulfur are incorporated into the pi system of the ring. Your modifications must be very clear to be counted. Do you think that this compound is aromatic? Justify your answer. (supplemental homework problem)

14. (15 @ 1pt each) Circle the one best answer.

Resonates at highest field	CH_3Cl	CH_3I	$(CH_3)_4Si$
Is not aromatic			
Most acidic Compound			
Absorbs IR at the lowest cm^{-1}	HCl	He	HF
Not a unit of frequency	Kyser	Hertz	Avis
Involves longest wavelength radiation	UV-spectroscopy	Nuclear Magnetic resonance	Infrared spectroscopy
Has largest down field shift from TMS in proton nmr	CCl_4	$CHCl_3$	CH_3Cl
Has the highest degree of unsaturation			
C-H stretching Absorbs at longest wavelength in the IR	$H_3C{-}H$	$H_2C{=}C{\scriptsize\begin{matrix}H\\ \\H\end{matrix}}$	$H{-}C{\equiv}C{-}H$
Best method to distinguish between nonane and octane	Infra red Spectroscopy	Mass Spectroscopy	Nmr Spectroscopy
DEPT means	Digital Electronic Polarization of Transitions	Differential Electronic Pulse Threshold	Distortionless enhancement of polarization transfer
Aromatic hydrocarbons	Have 2n+4 π electrons	Can not be charged	Have no non-bonding electrons
Strong acids have	A small Ka	A weak conjugate base	A large pKa
Has the largest number of peaks in 13C-nmr			
Has occupied nonbonding molecular orbitals			

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Average values of chemical shifts of representative types of hydrogens

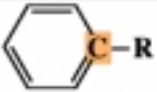| Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
$(CH_3)_4Si$	0 (by definition)	$\overset{\displaystyle O}{\overset{\|}{RC}}OCH_3$	3.7–3.9
RCH_3	0.9		
RCH_2R	1.2–1.4	$\overset{\displaystyle O}{\overset{\|}{RC}}OCH_2R$	4.1–4.7
R_3CH	1.4–1.7		
$R_2C{=}CRCHR_2$	1.6–2.6	RCH_2I	3.1–3.3
$RC{\equiv}CH$	2.0–3.0	RCH_2Br	3.4–3.6
$ArCH_3$	2.2–2.5		
$ArCH_2R$	2.3–2.8	RCH_2Cl	3.6–3.8
ROH	0.5–6.0	RCH_2F	4.4–4.5
RCH_2OH	3.4–4.0	$R_2C{=}CH_2$	4.6–5.0
RCH_2OR	3.3–4.0	$R_2C{=}CHR$	5.0–5.7
R_2NH	0.5–5.0	ArH	6.5–8.5
$\overset{\displaystyle O}{\overset{\|}{RC}}CH_3$	2.1–2.3	$\overset{\displaystyle O}{\overset{\|}{RC}}H$	9.5–10.1
$\overset{\displaystyle O}{\overset{\|}{RC}}CH_2R$	2.2–2.6	$\overset{\displaystyle O}{\overset{\|}{RC}}OH$	10–13

Here is some useful and some useless information

F=Ma, y=mX+b; E=MC^2, office = WEL5.240, C= 3x10^{8}m sec^{-1}, h=9.5x10^{-14} kcal sec mol^{-1}, TA = Trinque ; TA = Meiring Meiring = Trinque; spin states = 2I+1, C_nH_{2n+2}; 95 = A, r=1.987 cal deg^{-1} mol^{-1} 1m = 10^{6}μm; $v=(k/\mu)^{-1/2}$;. ¥ < $,

Precise masses and natural abundances of isotopes

Element	Atomic Weight	Isotope	Precise Mass (amu)	Relative Abundance
hydrogen	1.0079	^{1}H	1.00783	100
		^{2}H	2.01410	0.016
carbon	12.011	^{12}C	12.0000	100
		^{13}C	13.0034	1.11
nitrogen	14.007	^{14}N	14.0031	100
		^{15}N	15.0001	0.38
oxygen	15.999	^{16}O	15.9949	100
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
sulfur	32.066	^{32}S	31.9721	100
		^{33}S	32.9715	0.78
		^{34}S	33.9679	4.40
chlorine	35.453	^{35}Cl	34.9689	100
		^{37}Cl	36.9659	32.5
bromine	79.904	^{79}Br	78.9183	100
		^{81}Br	80.9163	98.0

^{13}C-NMR chemical shifts

Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
RCH$_3$	0–40	C–R (aromatic)	110–160
RCH$_2$R	15–55		
R$_3$CH	20–60		
RCH$_2$I	0–40	RCOR	160–180
RCH$_2$Br	25–65		
RCH$_2$Cl	35–80	RCNR$_2$	165–180
R$_3$COH	40–80		
R$_3$COR	40–80	RCOH	175–185
RC≡CR	65–85		
R$_2$C=CR$_2$	100–150	RCH, RCR	180–210