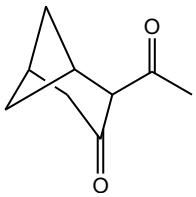

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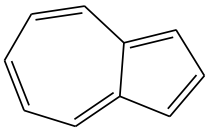


Spring 2008
Dr. Willson

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 = Xinyu&Brandon, 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=εCL = log I_0/I, %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, $R = 8.314\ J \cdot mol^{-1} \cdot K^{-1}$, 12:31 = tardy V=IR

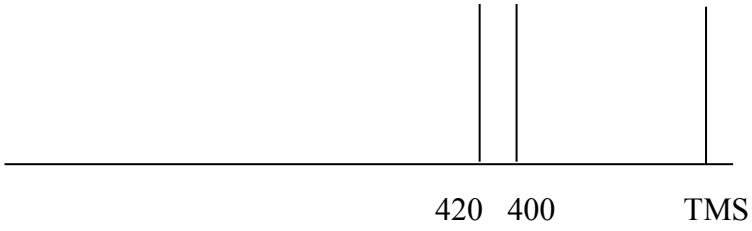
CH 318N Spring 2008 Name_____

1. (5 Pts) After hours of detailed analytical studies, we have narrowed down the structure of our unknown to one of two isomers of pentene. We are sure that we have either 1-pentene or 2-pentene. The mass spectrum shows a molecular ion at M/e = 70 amu and a base peak at 55 amu. Which isomer do we have? You must explain your answer to receive credit!

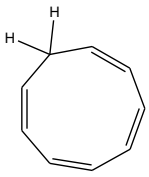
2. (10 pts) The easy way to tell the difference between cyclohexanone ($C_6H_{10}O$) and methyl cyclohexane (C_7H_{14}) is by comparison of their IR spectra. Unfortunately, our spectrometer is broken, and I have a sample that is either one of these compounds or the other. The molecular ion of my sample has a mass of 98.10962. *Calculate the precise mass of both substances* and by so doing, identify the unknown. Please show your work.

3. (10 pts) The resonance of peak one and peak two on our old 200 MHz proton nmr spectrometer was 400Hz and 420Hz respectfully as shown below.
   a) At what frequency will these protons resonate on our new spectrometer with the gigantic, 18.0 Tesla Magnet?

   b) Calculate the chemical shift of the low field proton on both spectrometers.



4. (10 pts) Cyclononatetraene, shown below, is a molecule that has no special stability. It can form a radical, an anion or a cation. Do any of these structures have special stability and if so, why? Write a molecular orbital energy level diagram for this molecule and support your answer based on molecular orbital arguments.



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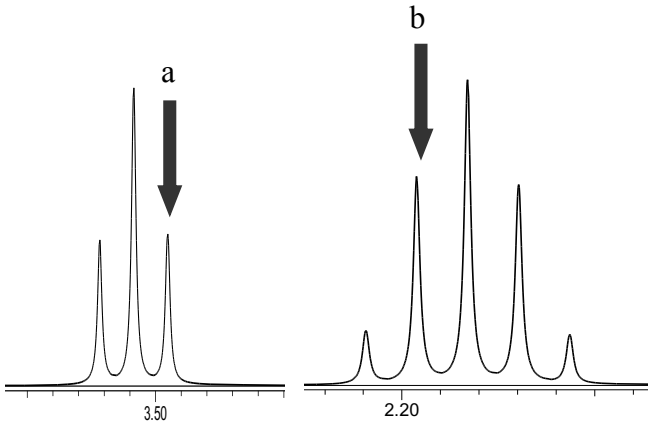
5. (5 pts) List the number of p orbital electrons in each molecule or ion and state which are aromatic according to the Hückel Criteria. (homework 21.15 & 21.16)

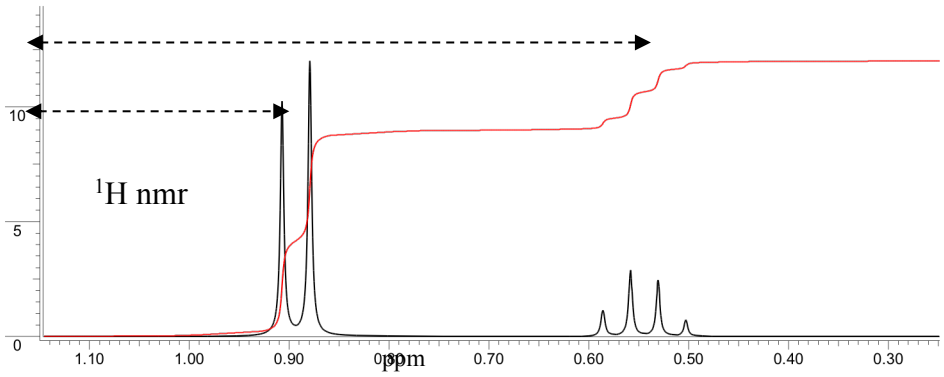
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____

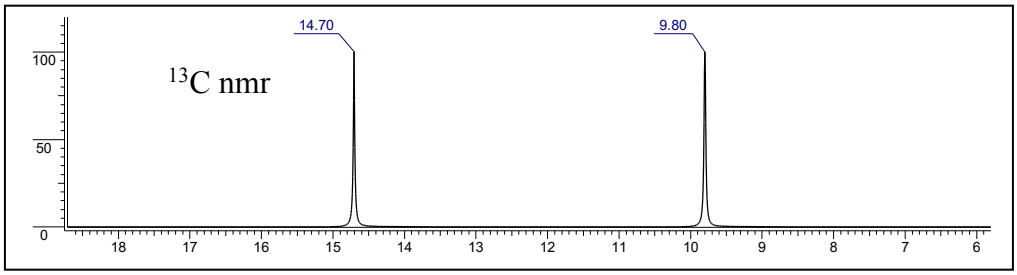
6. (10 pts) The proton nmr spectrum of 1,3-dichloropropane shows a triplet and a pentet as shown below. Please calculate there relative areas (a/b) of the peaks marked explicitly in the multiples. Show your work.



$ClCH_2\ CH_2\ CH_2Cl$

7. (20 Pts) A very pure sample of an interesting new compound was isolated as a distillation fraction. The mass spectrum of the compound shows a molecular ion at 84 daltons and combustion analysis gave an empirical formula of CH_2. The infrared spectrum of the compound shows strong peaks in the region of 2800-2950 cm^{-1} and 1400 cm^{-1}, there are no peaks above 3000cm^{-1} and no other strong peaks. The proton and carbon nmr spectra are provided below. The DEPT spectrum shows only two positive peaks, it looks just like the proton decoupled spectrum. Please interpret these spectral data and provide a structure that matches the data.





8. (5 Pts) Calculate the index of hydrogen deficiency of these compounds (homework problem 13.10)

a) Aspirin $C_9H_8O_4$ b) Pyridine C_5H_5N

c) Urea CH_4N_2O d) p-Chloromethylstyrene C_9H_9Cl

9. (10 pts) The visible spectrum of β-carotene ($C_{40}H_{56}$, MW 536.89) dissolved in hexane shows intense absorbance maxima at 463nm ($\log \varepsilon = 5.10$) and 494nm ($\log \varepsilon = 4.77$), both in the blue green region. Because light is absorbed in this region by β-carotene, we perceive the color of the pigment as the compliment, namely burnt orange. Calculate the concentration in milligrams per milliliter of solution of β-carotene that gives an absorbance of 1.8 at 463nm in a standard, 1cm cell. (Home work problem 20.5)

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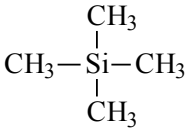
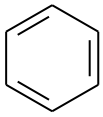
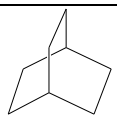
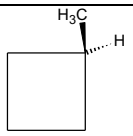
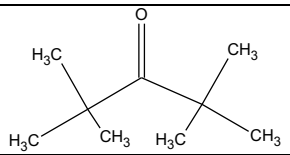
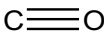
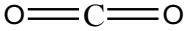
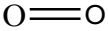
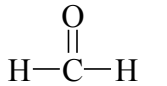
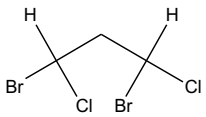
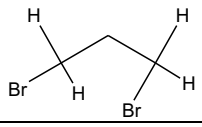
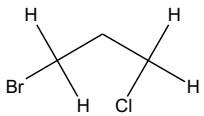
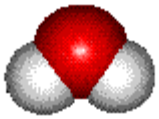
10. (15 points) Circle the one best answer in each row.

Has lowest field proton resonance		CCl_4	
Is not aromatic			
Has exactly 3 different ^{13}C resonances			
absorbs IR at the shortest wavelength			
Attometer	10^{-16} cm	10^{-21}m	10^{-23} cm
strongest acid			
Is in the infra red spectral region	10 cm^{-1}	1000 cm^{-1}	5000 cm^{-1}
Has more bonding than antibonding molecular orbitals			
Has 6 pi electons			
Resonates at highest frequency (same B)	^{13}C	^{12}C	^{1}H
Has the largest M+2 peak	$CH_3SCH_2CH_2F$	$CH_3OCH_2CH_2F$	$CH_3CH_2CHF_2$
Aromatic compounds			
Resonates at lowest field in ^{13}C-nmr			$(CH_3)_4Si$
Has a pentet splitting pattern in the ^{1}H nmr spectrum			
Has no nonbonding molecular orbitals			



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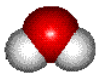
CHARACTERISTIC PROTON CHEMICAL SHIFTS		
Type of Proton	**Structure**	**Chemical Shift, ppm**
Cyclopropane	C_3H_6	0.6
Primary	R-C**H**$_3$	0.9
Secondary	R_2-C**H**$_2$	1.3
Tertiary	R_3-C-**H**	1.5
Vinylic	C=C-**H**	4.6-5.9
Acetylenic	C≡C-**H**	2-3
Aromatic	Ar-**H**	6-8.5
Benzylic	Ar-C-**H**	2.2-3
Allylic	C=C-C**H**$_3$	1.7
Fluorides	**H**-C-F	4-4.5
Chlorides	**H**-C-Cl	3-4
Bromides	**H**-C-Br	2.5-4
Iodides	**H**-C-I	2-4
Alcohols	**H**-C-OH	3.4-4
Ethers	**H**-C-OR	2.8-3.8
Nitriles	**H**-C-C≡N	2.1-2.4
Esters	**H**-C-COOR	2.0-2.2
Carbonyl Compounds	**H**-C-C=O	2-2.7
Aldehydic	R-(**H**-)C=O	9-10
Hydroxylic	R-C-O**H**	1-5.5
Phenolic	Ar-O**H**	4-12
Enolic	C=C-O**H**	15-17
Carboxylic	RCOO**H**	10.5-12
Amino	RN**H**$_2$	1-5



CHEMISTRY 318N

CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES		
Bond	**Compound Type**	**Frequency range, cm^{-1}**
C-H	Alkanes	2960-2850(s) stretch
		1470-1350(v) scissoring and bending
	CH_3 Umbrella Deformation	1380(m-w) - Doublet - isopropyl, *t*-butyl
C-H	Alkenes	3080-3020(m) stretch
		1000-675(s) bend
C-H	Aromatic Rings	3100-3000(m) stretch
	Phenyl Ring Substitution Bands	870-675(s) bend
	Phenyl Ring Substitution Overtones	2000-1600(w) - fingerprint region
C-H	Alkynes	3333-3267(s) stretch
		700-610(b) bend
C=C	Alkenes	1680-1640(m,w)) stretch
C≡C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric -- Alcohols, Phenols	3640-3160(s,br) stretch
	Hydrogen-bonded -- Alcohols, Phenols	3600-3200(b) stretch
	Carboxylic acids	3000-2500(b) stretch
N-H	Amines	3500-3300(m) stretch
		1650-1580 (m) bend
C-N	Amines	1340-1020(m) stretch
C≡N	Nitriles	2260-2220(m) stretch
NO_2	Nitro Compounds	1660-1500(s) asymmetrical stretch
		1390-1260(s) symmetrical stretch

v - variable, m - medium, s - strong, br - broad, w - weak

Precise Masses and Natural Abundances

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