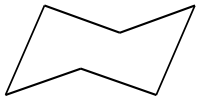
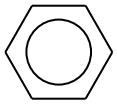


Chemistry 318N



Spring 2005

Dr. Willson

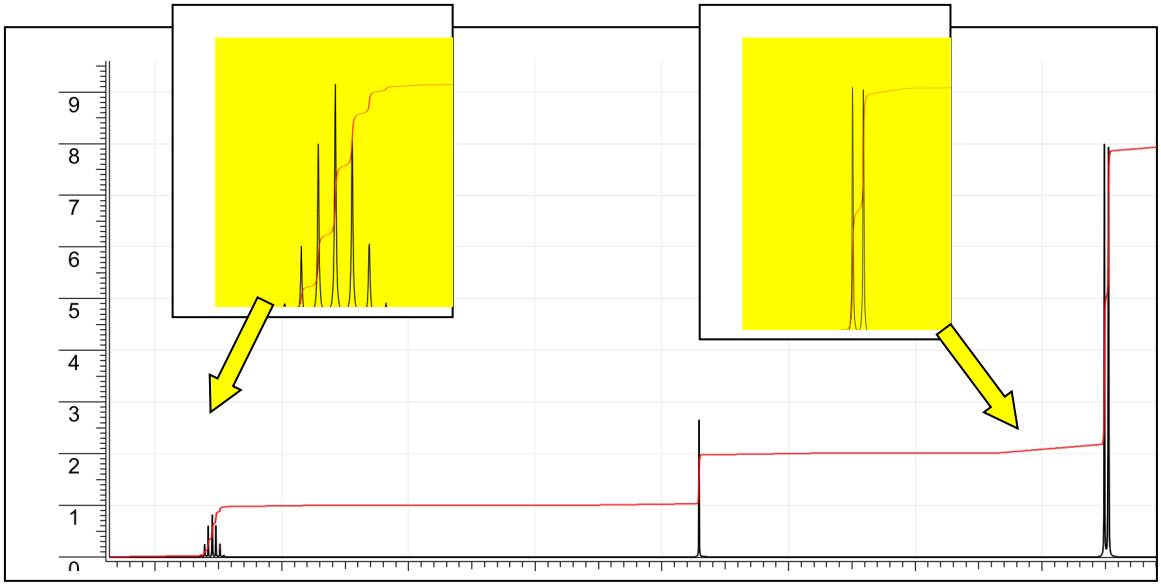
First Midterm Exam

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

Signature_____

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.

1. (15 Pts) An unknown organic compound is being produced as a minor impurity in your product stream. The substance has an empirical formula of C_3H_4O. There are strong, sharp peaks in the infrared at 3297, 2974 1742 and 1180 cm^{-1} and no other strong bands. The mass spectrum of the molecule shows a molecular ion at 112 amu . The proton nmr spectrum of the molecule is reproduced below. Please list those pieces of structural information that can be extracted from the mass spectrum, from the infrared and from the nmr and suggest a structure for the unknown. Please label the hydrogens in your structure and show which peaks in the nmr spectrum are correlated with hydrogen atoms in your structure. You will NOT get full credit for only listing the correct structure. You must list the information that can be gleaned from the spectral data.



Structure and assignments

Infrared spectrum teaches:

nmr spectrum teaches:

Other information:

2. (15 pts) A seemingly simple compound with a strong IR peak at 1740 cm^{-1} was isolated and carefully recrystallized to constant melting point. The compound has an empirical formula of C_3H_60 and displays a molecular ion at 174. The ^{13}C nmr spectrum of the compound has three resonances, 194.72, 59.57 and 27.59. In the DEPT experiment, the two lower field resonances disappear but the high field resonance is unchanged. The proton nmr spectrum is boring. It displays only a single strong resonance at 1.88 ppm. Please show all of the structural information that can be derived from the information provided and propose a structure for the molecule that is consistent with these data.

3. (10pts) You have just purchased a new proton nmr spectrometer on e-Bay. It was so expensive that it broke your Pay-Pal account but the seller did not know the strength of the magnet. You measured the "spectrometer frequency" and found it to be 400MHz. What is the strength of the field in Tesla? Show your work.

4. (10 pts) We have lost the labels from some valuable samples. Fortunately, using your spectroscopic analysis skills, you have managed to identify all but two of the compounds. We know that they are 3-pentanone ($C_5H_{10}O$) and 3-methylpentane (C_6H_{14}). You labeled the bottles A and B. The high resolution mass spectrum of A gives a molecular ion at 86.1096. *Calculate the precise mass of both substances. What is the name of A and what is the name of B?* Show your work. *If you could do one more spectroscopic measurement to confirm your identification, what would it be and why?*

5. (10 Pts) Each compound below gives only one signal in its 1H-NMR spectrum. Propose a structural formula for each. a) $C_3H_6Cl_2$, b) C_4H_6. (Homework 13.3)

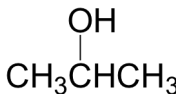
6. (10 Pts) Calculate the energy of red light (680 nm) in kilojoules per mole. Which form or radiation carries more energy, infrared radiation of wavelength 2.50μm or red light of wavelength 680nm? (Homework problem 12.1)

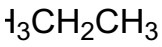
7. (10 Pts) The undergraduate intern in your plant has broken the cells for the uv-visible spectrophotometer. She purchased new cells that are reported to have exactly a 1cm path length. In order to test the claim of the vendor, you ask her to measure the path length by recording the spectrum of a very carefully prepared and calibrated solution of a dye standard that has log e = 4.000 at λmax = 480nm and a concentration of 3.20×10^{-5} M. The undergraduate recorded the spectrum of this standard solution and found the transmission at 480nm to be 50.00%. What is the length of the new cell? Show all work neatly.

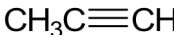
8. (10 Pts) State the number of p-orbital electrons in each of the following structures and circle those you predict to be aromatic:

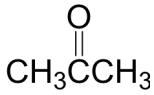
_____ _____ _____ _____ _____

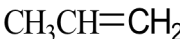
10.) (3 pts) Below are three IR spectra and a list of structures. From the list of structures, pick the structure that would produce each spectrum? Write the number of the correct structure over the corresponding spectrum.

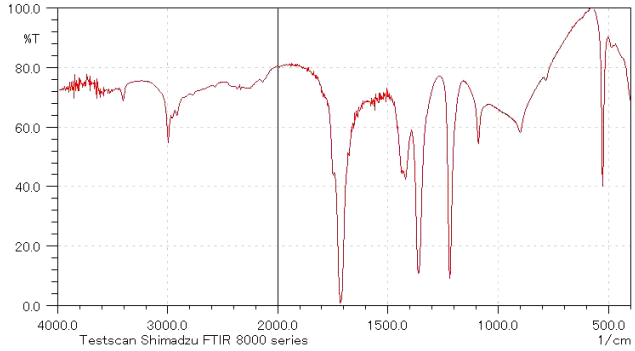
1. 

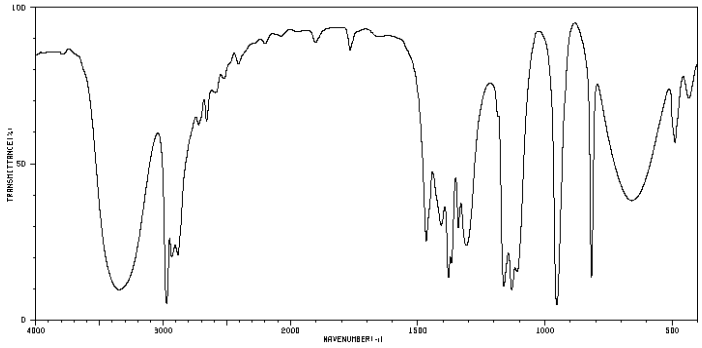
2. 

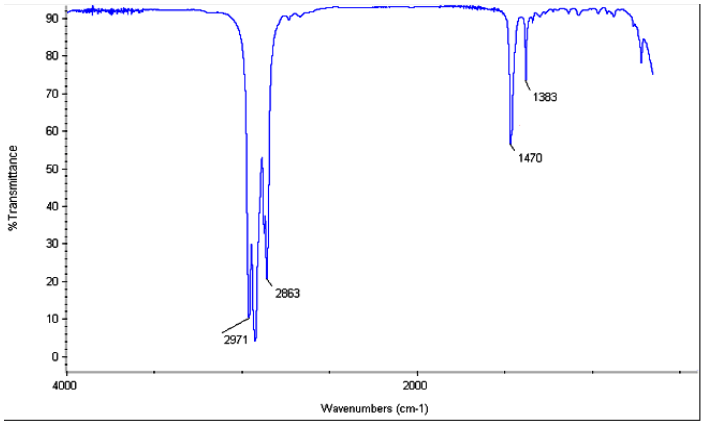
3. 

4. 

5. 

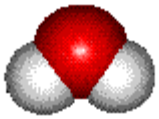






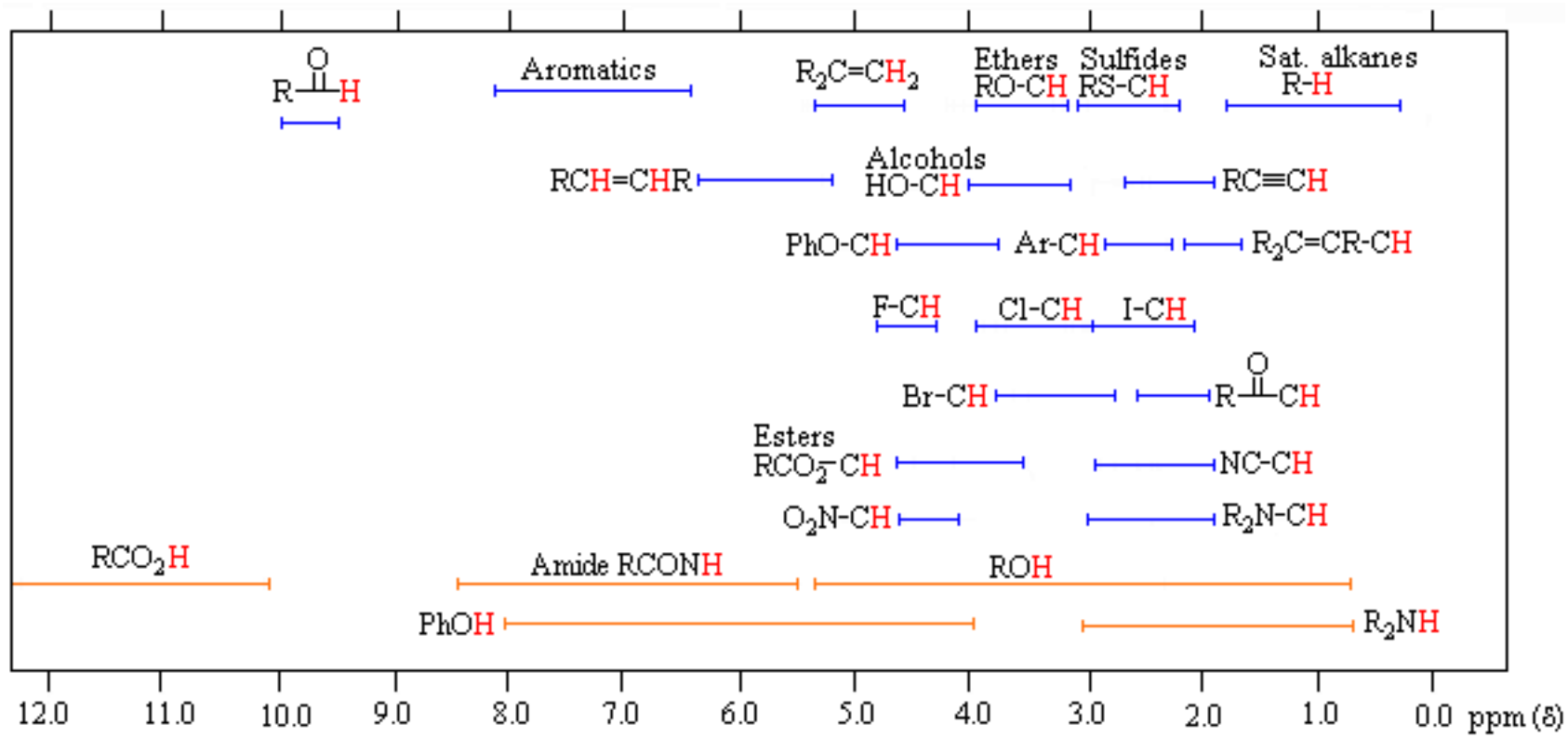
Average values of chemical shifts of representative types of hydrogens

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)	$RCOCH_3$	3.7–3.9
RCH_3	0.9	$RCOCH_2R$	4.1–4.7
RCH_2R	1.2–1.4	RCH_2I	3.1–3.3
R_3CH	1.4–1.7	RCH_2Br	3.4–3.6
$R_2C{=}CRCHR_2$	1.6–2.6	RCH_2Cl	3.6–3.8
$RC{\equiv}CH$	2.0–3.0	RCH_2F	4.4–4.5
$ArCH_3$	2.2–2.5	$R_2C{=}CH_2$	4.6–5.0
$ArCH_2R$	2.3–2.8	$R_2C{=}CHR$	5.0–5.7
ROH	0.5–6.0	ArH	6.5–8.5
RCH_2OH	3.4–4.0	RCH	9.5–10.1
RCH_2OR	3.3–4.0	$RCOH$	10–13
R_2NH	0.5–5.0		
$RCCH_3$	2.1–2.3		
$RCCH_2R$	2.2–2.6		

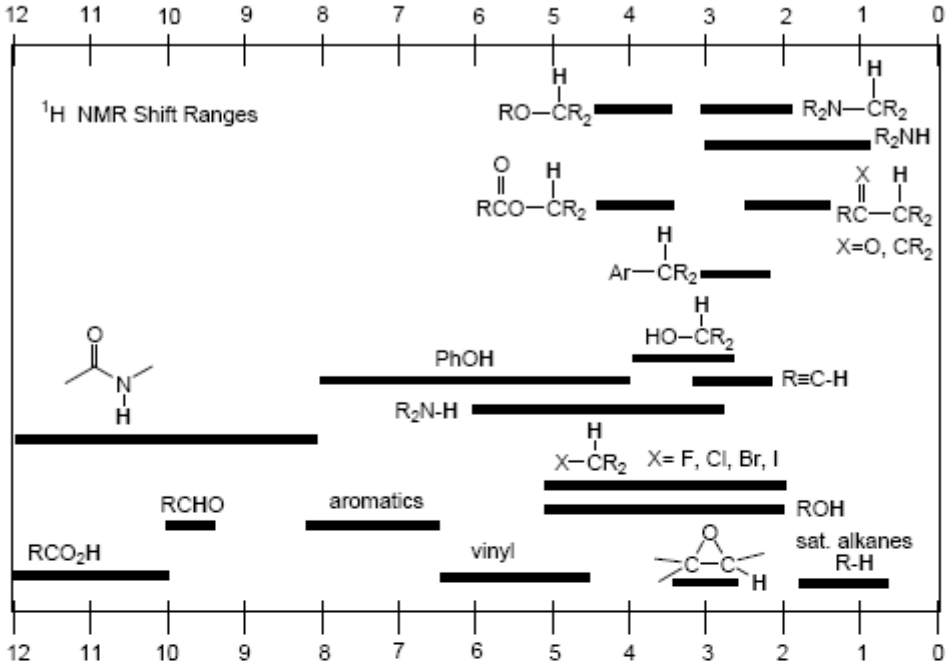


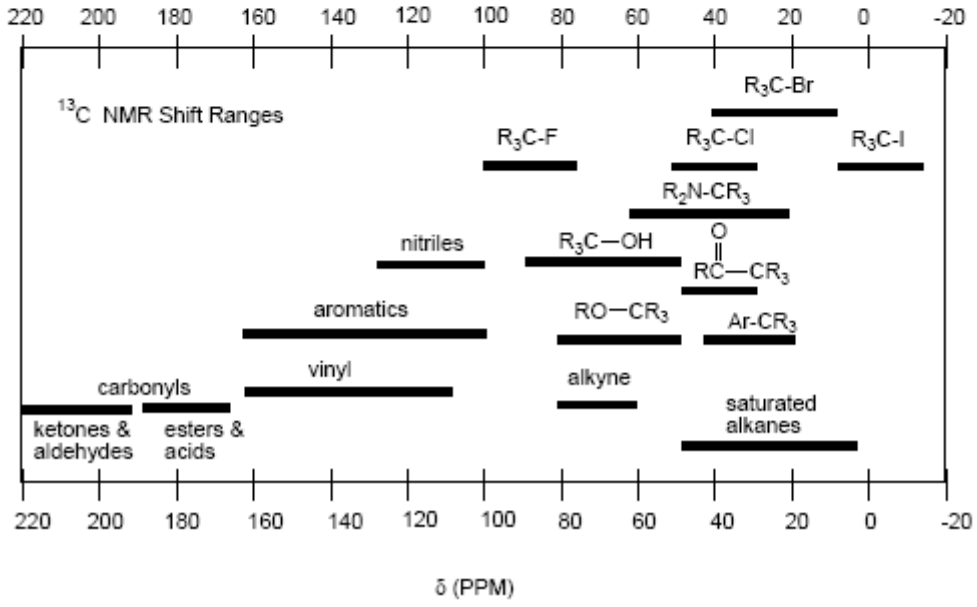
CHEMISTRY 318N

CHARACTERISTIC PROTON CHEMICAL SHIFTS		
Type of Proton	**Structure**	**Chemical Shift, ppm**
Cyclopropane	C_3H_6	0.2
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	3.3-4
Esters	RCOO-C-**H**	3.7-4.8
Esters	**H**-C-COOR	2-2.2
Acids	**H**-C-COOH	2-2.6
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


R-CHO
Aromatics
R2C=CH2
Ethers RO-CH
Sulfides RS-CH
Sat. alkanes R-H
RCH=CHR
Alcohols HO-CH
RC≡CH
PhO-CH
Ar-CH
R2C=CR-CH
F-CH
Cl-CH
I-CH
Br-CH
R-CO-CH
Esters RCO2-CH
NC-CH
O2N-CH
R2N-CH
RCO2H
Amide RCONH
ROH
PhOH
R2NH
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (δ)

Approximate NMR Shift Ranges





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(v) 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