CHEM 344 Summer 2016 Spectroscopy and WebMO Exam (75 pts)

Name:

TA Name:

Exam Length = 120 min
DO NOT REMOVE ANY PAGES FROM THIS EXAM PACKET.

Directions for drawing molecules, reactions, and electron-pushing mechanisms:

Draw all lone pairs, bonds, arrows, formal charges, and stereochemistry explicitly in all molecular structures.

Directions for all calculations:

Explicitly show all work on all calculations and include all important labels.

Directions for analyzing graded spectra:

- Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. Assign each **^{1}H-NMR** signal and write your assignments directly onto the spectrum. Use the empirical chemical shift parameters (Curphy-Morrison parameters) or chemical shift tables found at the end of the exam to ***assist*** your ^{1}H-NMR analysis and signal assignments.

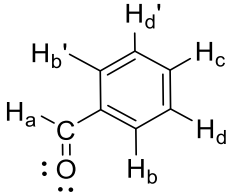
- Assign the hybridization of the ^{13}C-atoms responsible for each **^{13}C-NMR** signal. Identify specific functional group signals; you do not need to assign individual carbon atoms to each signal.

- Assign each key **IR** absorption band >1500 cm^{-1} to a specific functional group. Draw a part structure responsible for the vibration next to each band.

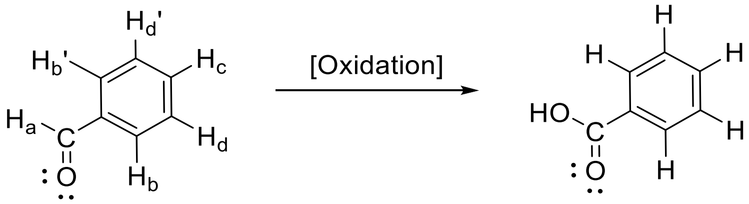
- Draw fragments for all labeled peaks in the **EI-MS** directly onto the spectrum (you do not need to show the fragmentation mechanism unless directed to do so).

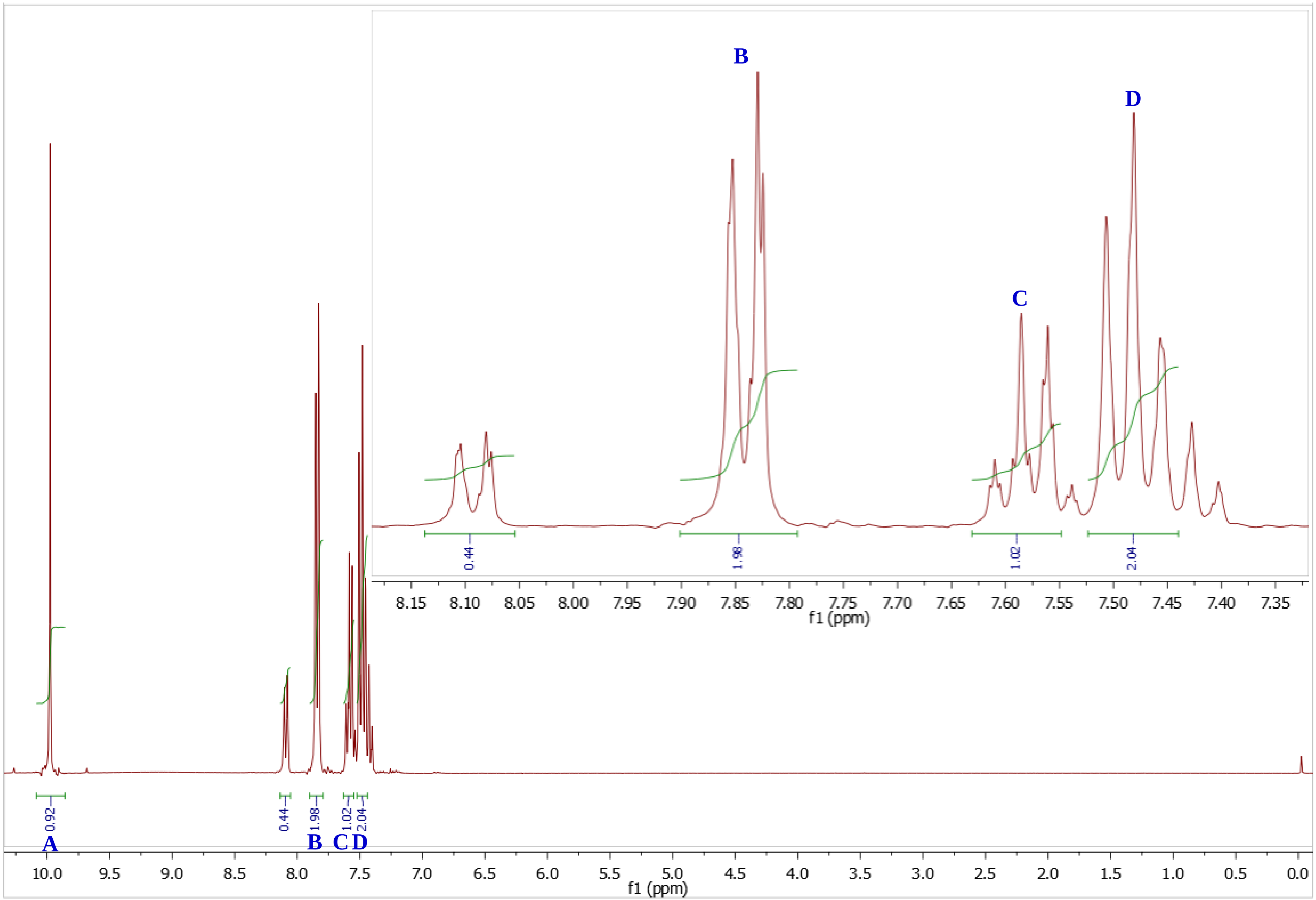
1) Benzaldeyde (shown below) is a common organic reagent, but is prone to oxidation to benzoic acid. The ^{1}H-NMR spectrum is shown for a sample of benzaldehyde which has partially oxidized to benzoic acid. **(8 pts total)**

a) Draw a series of resonance structures of benzaldehyde that justify the ^{1}H-NMR assignments shown on the subsequent page. Explicitly show all bonds, formal charges, lone pairs, etc. **(4 pts)**



b) Use the ^{1}H-NMR spectrum of the mixture to determine the ratio of benzaldehyde to benzoic acid. You do not need to fully assign the spectrum of benzoic acid. Express the ratio in the form x:y where y = 1. Show all work in the space below. **(4 pts)**



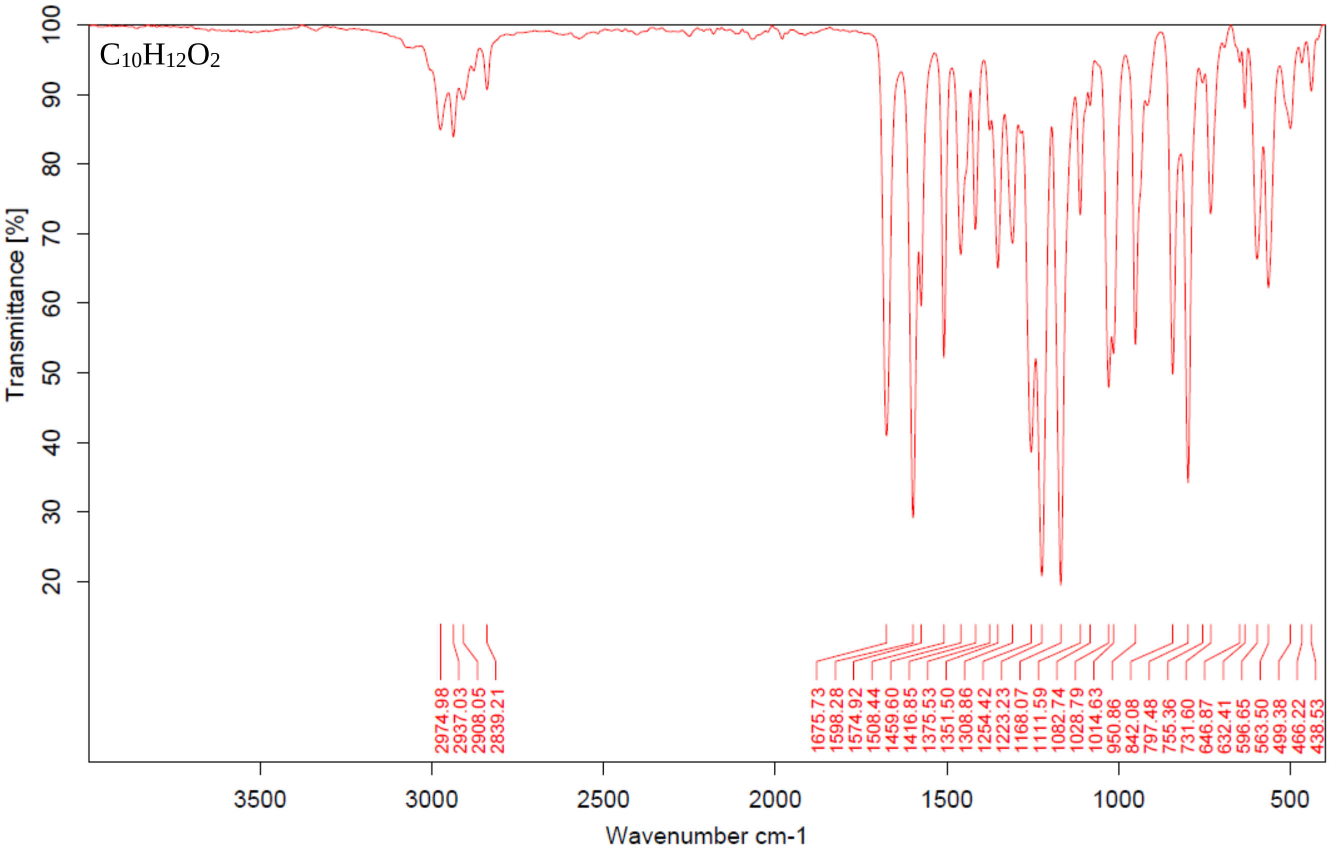

B
D
C
0.44
1.98
1.02
2.04
8.15
8.10
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
f1 (ppm)
0.92
0.44
1.98
1.02
2.04
A
B
C
D
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2) The spectra below were obtained from an organic molecule ($C_{10}H_{12}O_2$). Determine the structure of the molecule using the spectra provided and by answering the questions below. **(25 pts total)**

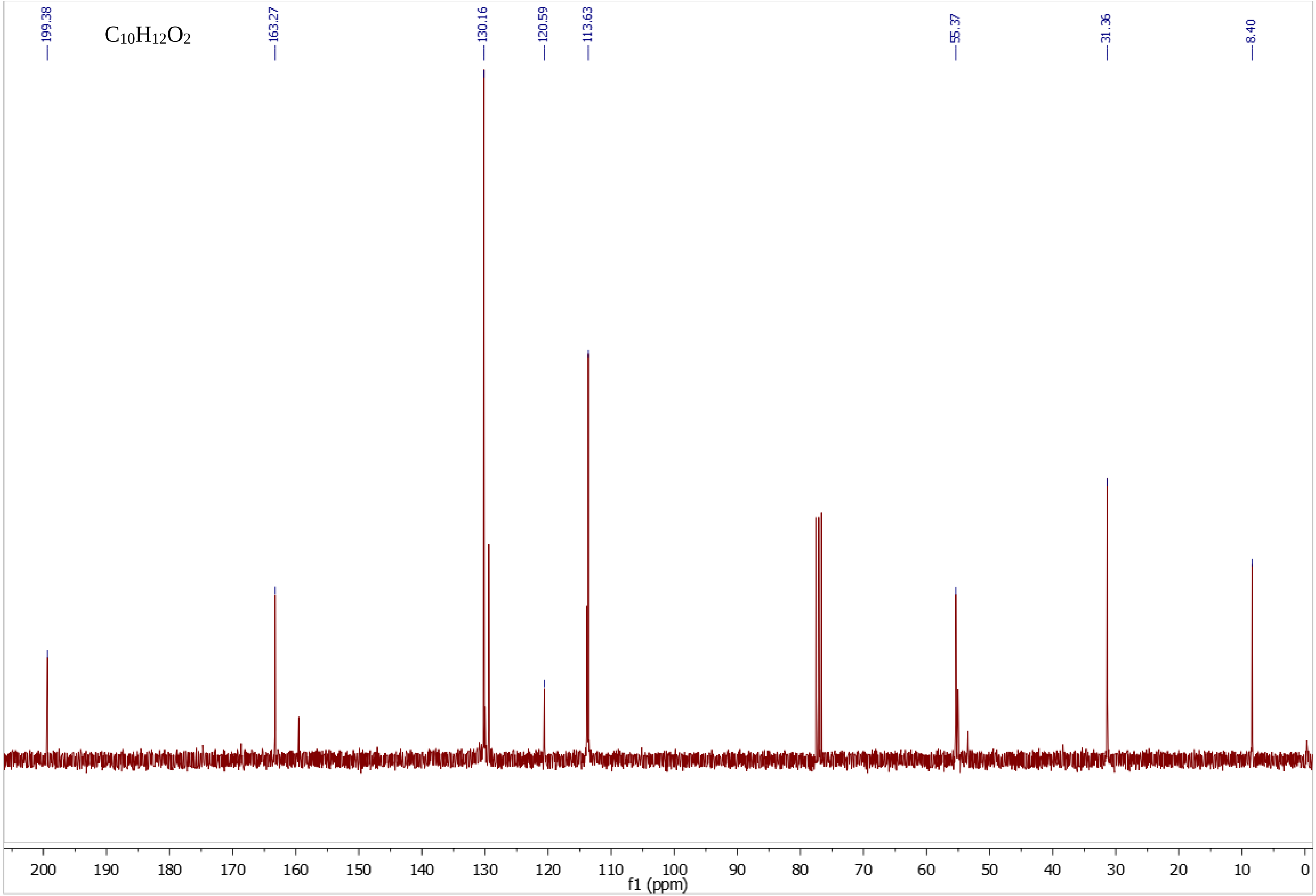
a) Calculate the number of double bond equivalencies, unsaturation number, or the index of hydrogen deficiency for this molecule using the equation provided. **(2 pts)**

$$IHD = \frac{2C + N - H - X + 2}{2}$$

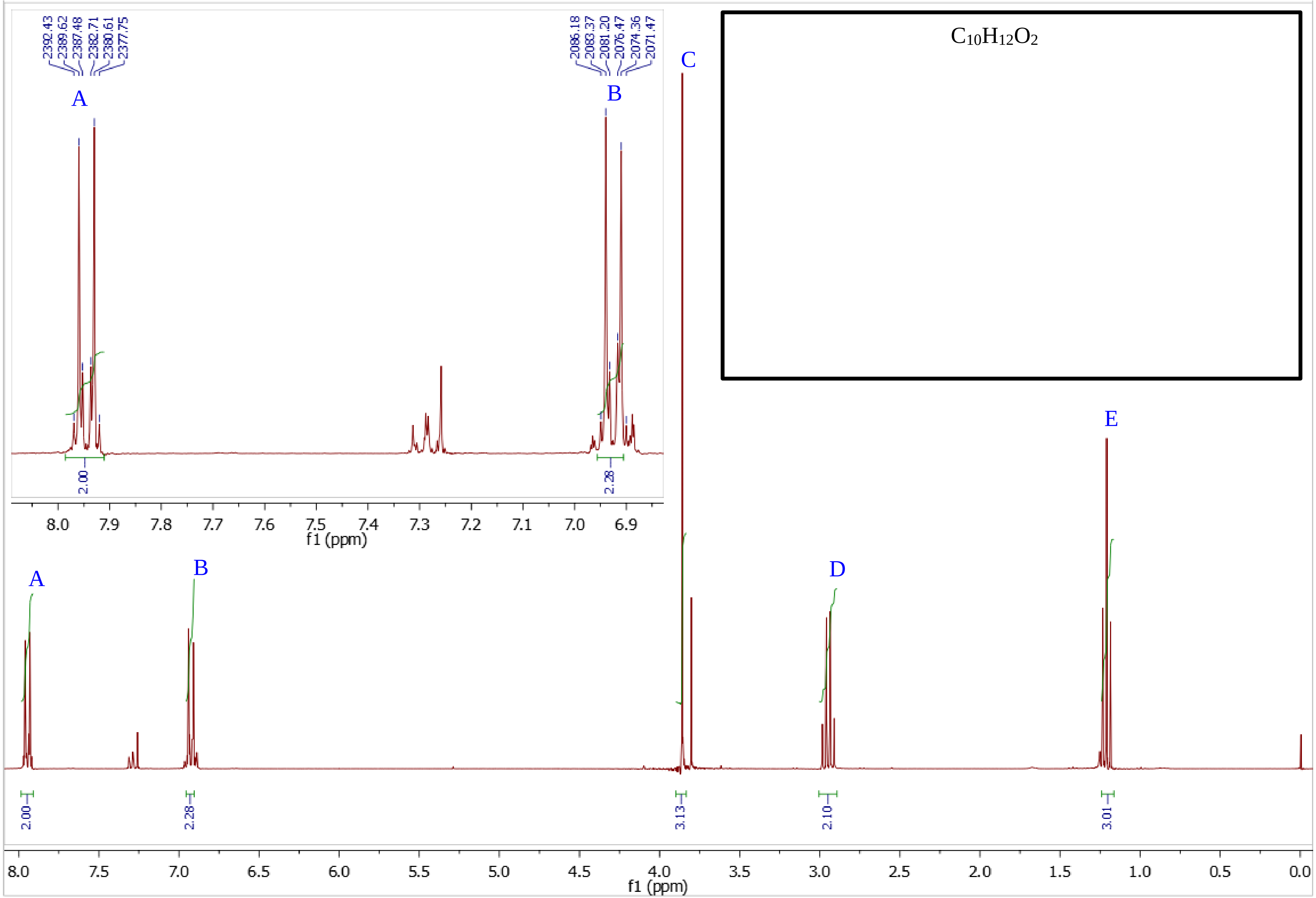
b) Based upon the chemical formula, index of hydrogen deficiency, and the IR spectrum below, suggest which organic functional groups are possible/likely in this molecule. Label the signal from each suggested functional group. **(3 pts)**



c) Use the ^{13}C-NMR spectrum below, collected in $CDCl_3$, to identify the hybridization of each ^{13}C-atom and identify any key functional group signals. Only the peak-picked signals are from the desired molecule, $C_{10}H_{12}O_2$. **(3 pts)**

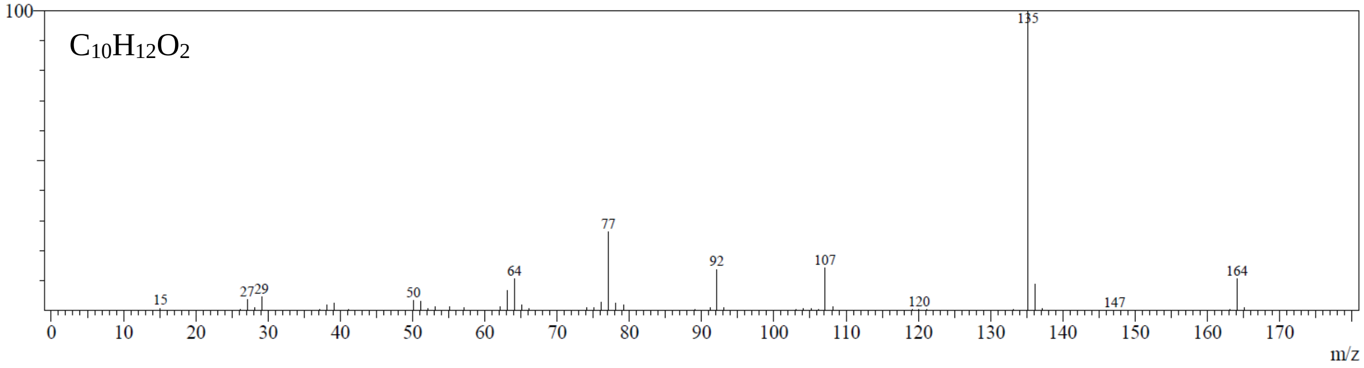


d) Use the information from parts a – c and the ^{1}H-NMR spectrum (collected in $CDCl_3$) below to determine the structure of the molecule and assign each ^{1}H-atom. Label each set of equivalent protons using the *H*$_a$, *H*$_b$, *H*$_c$, *etc.* labeling system. Draw your answer in the box on this page. **(10 pts)**

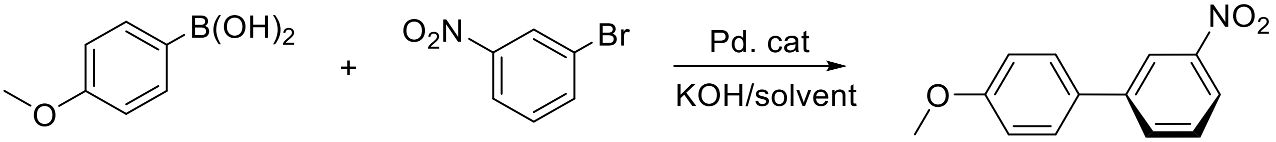


$C_{10}H_{12}O_2$

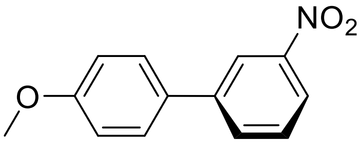
e) Confirm your structure determination by use of the EI-Mass spectrum provided below. Provide an electron pushing mechanism that accounts for the appearance of signals with *m/z* = 164, 135, and 107. Show all lone pairs and formal charges. **(7 pts)**



3) Suzuki-Miyaura coupling reaction are effective methods for forming C(sp^2)–C(sp^2) bonds between an arylboronic acid and aryl halide. The coupling reaction below involves forming a biaryl from 1-bromo-3-nitrobenzene and 4-methoxyphenylboronic acid. **(17 pts total)**

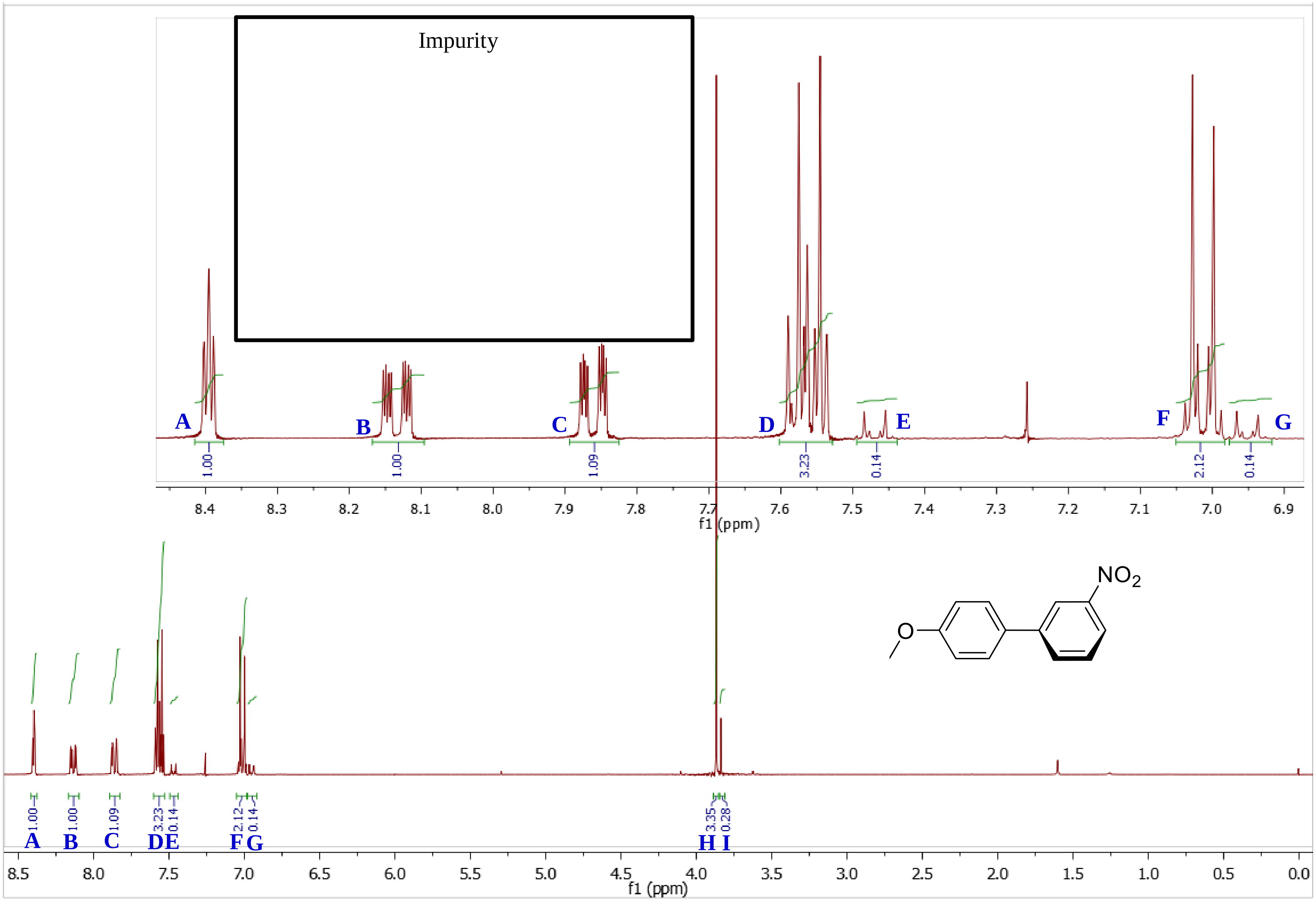


a) Estimate the ^{1}H-NMR chemical shifts of each ^{1}H-atom in the product below using empirical (Curphy-Morrison) parameters. Clearly label which values you have chosen in each case. **(5 pts)**

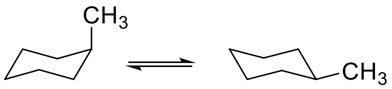


b) On the subsequent page, assign all ^{1}H-NMR signals to their corresponding ^{1}H-atoms in the product using the *H$_a$, H$_b$, H$_c$, etc*. labeling system given. Write all assignments on the product structure provided on the ^{1}H-NMR spectrum. In cases of overlapping signals, non-equivalent ^{1}H-atoms can be given the same label. **(7 pts)**

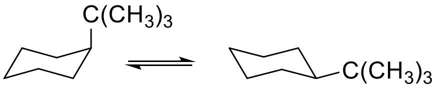
c) There is an impurity present in this spectrum. Identify the impurity, draw its structure in the box provided, and assign all ^{1}H-NMR signals to their corresponding ^{1}H-atoms using the *H$_a$, H$_b$, H$_c$, etc*. labeling system given. **(5 pts)**


Impurity
A
B
C
D
E
F
G
1.00
1.00
1.09
3.23
0.14
2.12
0.14
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
NO2
O
1.00
1.00
1.09
3.23
0.14
2.12
0.14
3.35
0.28
A
B
C
D
E
F
G
H
I
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

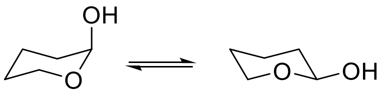
4) Mono-substituted cyclohexanes and their derivatives exist in an equilibrium in which their substituents can occupy *axial* or *equatorial* positions. The exact ratio of products to reactants is determined by their relative energies, which can be estimated *via* computational chemistry. Use the B3LYP/6-31G(d) optimized structures and associated energies of the *axial* and *equatorial* conformations of methylcyclohexane, tert-butylcyclohexane, and 2-hydroxytetrahydropyran to explore each equilibrium.



methylcyclohexane



tert-butylcyclohexane

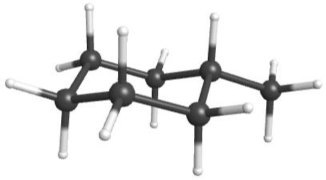


2-hydroxytetrahydropyran

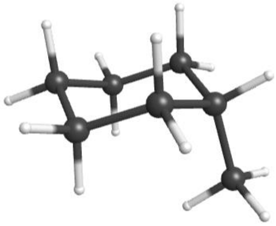
a) For each pair of conformers determine the relative energy difference, ΔE_{rxn}, as written above with the axial conformation on the reactant side and the equatorial conformation on the product side of the equilibrium. Used the optimized structures and their associated energy values on the subsequent page. (1 Hartree/particle = 627.509 kcal/mol) **(9 pts)**

$$\Delta E_{rxn} = E_{products} - E_{reactants}$$

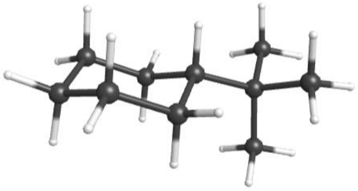
Molecule Name	**Energy B3LYP/6-31G(d) (kcal/mol)**	**ΔE_{rxn} B3LYP/6-31G(d) (kcal/mol)**
axial methylcyclohexane		
equatorial methylcyclohexane		
axial tert-butylcyclohexane		
equatorial tert-butylcyclohexane		
axial 2-hydroxytetrahydropyran		
equatorial 2-hydroxytetrahydropyran		



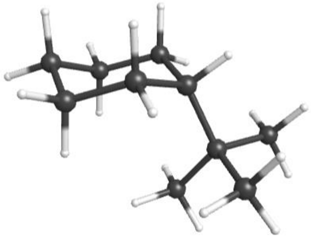
-275.19560



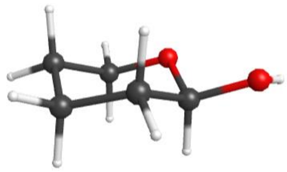
-275.19209



-393.12937



-393.12086

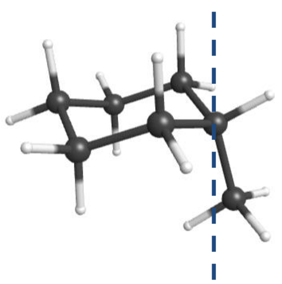


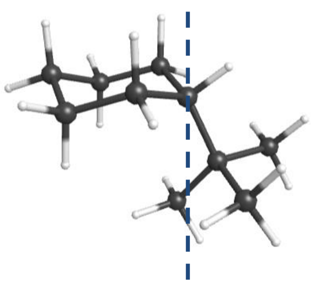
-346.99040

-346.99233

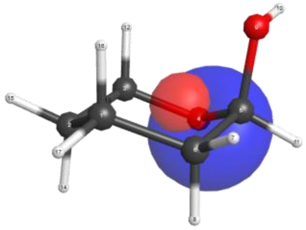
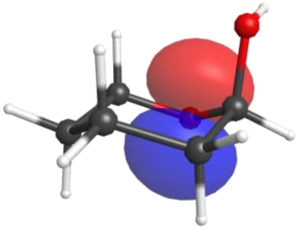
b) Based upon the ΔE_{rxn}, identify which of the conformational isomers will be favored in each of the conformational equilibrium and circle the most stable conformational isomer in each equilibrium. **(6 pts)**

c) The angle of deviation from vertical in the *axial* conformations is not the same for *tert*-butylcyclohexane and methylcyclohexane. Rationalize the difference in the angles. **(5 pts)**

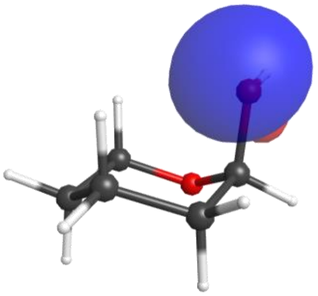
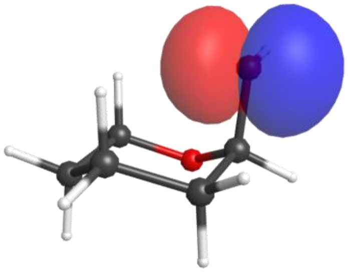




d) In axial 2-hydroxypyran, identify the B3LYP/6-31G(d) NBO-predicted hybridization of each O-atom lone pair in the sp^x notation. Compare these lone pair hybridizations to those that would be predicted from a VSEPR-predicted tetrahedral electron geometry. **(5 pts)**

	LP(1)O4 s(43.16%)p1.32(56.77%)d0.00(0.07%)	LP(2)O4 s(0.17%)p99.99(99.73%)d0.55(0.09%)
NBO-predicted hybridization		
VSEPR-predicted hybridization		

	LP(1)O9 s(48.24%)p1.07(51.69%)d0.00(0.07%)	LP(2)O9 s(1.05%)p94.23(98.84%)d0.10(0.11%)
NBO-predicted hybridization		
VSEPR-predicted hybridization		

CHEM 344 Summer 2016 Spectroscopy & WebMO Exam (75 pts)

Name:

TA Name:

Problem 1	**Problem 2**	**Problem 3**	**Problem 4**
a) ______ /4	**a) ______ /3**	**a) ______ /6**	**a) ______ /6**
b) ______ /4	**b) ______ /2**	**b) ______ /3**	**b) ______ /3**
c) ______ /5	**c) ______ /3**	**c) ______ /6**	**c) ______ /6**
d) ______ /6	**d) ______ /1**	**d) ______ /4**	**d) ______ /4**
e) ______ /9	**e) ______ /8**	**e) ______ /4**	**e) ______ /4**
	f) ______ /3		
Total______ /28	**Total______ /24**	**Total______ /23**	**Total______ /25**

Total = ______ /75

Double check = ______ /75