Fall 2021 **Chemistry 2600 Midterm #1** ____/50 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:30pm Mountain Time on Thursday, October 14th, 2021. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/50 on this exam.

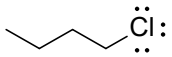
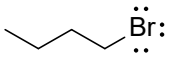
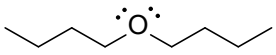
Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 5 pages of questions and a periodic table.
2) You have been given a 6-page Spectroscopy Data Package. **PLEASE DO NOT WRITE ON THE SPECTROSCOPY DATA PACKAGE**! If you need scrap paper, use the back of any page of the test. On questions with spectra, you may also do rough work directly on the spectra.
3) You may use a molecular model kit and ruler. You may not have written materials in your model kit.
4) You may use a calculator but only for calculation. No other electronic devices are allowed.
5) **DO NOT WRITE ON ANY QR CODE!!!** Work on pages without a QR code will not be graded.
6) If your work is not legible, it will be given a mark of zero. For full credit, explanations must be complete. In many cases, complete explanations include drawing relevant structures. If delocalization of electrons is invoked, the relevant resonance structures must be drawn.
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 2 hours to complete this test.

Question Breakdown

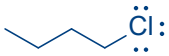
Q1	**Q2**	**Q3**	**Q4**	**Q5**									**Total**
/ 8	/ 4	/ 3	/ 10	/ 25									/ 50

1. You find an unlabeled bottle in the back of the chemical cabinet. In order to decide how best to dispose of it, you analyze it by ^{1}H NMR and ^{13}C NMR. That convinces you that it is one of the following three compounds: **[8 marks]**

The lab next door offers to let you use their mass spectrometer to analyze your mystery compound since that should let you choose definitively between these three options.

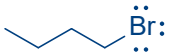
(a) Describe what you would expect to see in the molecular ion region of a mass spectrum for each of these three compounds. Be specific. Your answer should address two factors. *[5 marks]*



$M^+ : [M+2]^+ = 3:1$

M^+ is at m/z 92

$[M+2]^+$ is at m/z 94



$M^+ : [M+2]^+ = 1:1$

M^+ is at m/z 136

$[M+2]^+$ is at m/z 138

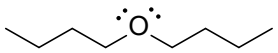


M^+ is the only significant peak in this region

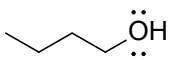
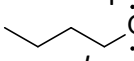
M^+ is at m/z 130

(There may also be a very short $[M+1]^+$ peak due to ^{13}C atoms.)

Labeled drawings of the molecular ion region were my favourite kind of answer for this question…

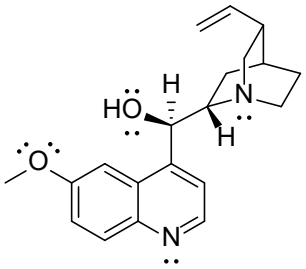
(b) Your friend points out that  contains a lot more hydrogen atoms than the other two options. Why can't you use the integrals on the ^{1}H NMR to distinguish between this option and the other two? *[1 mark]*

Integrals are **ratios**. All three compounds are expected to give four peaks with integral ratios of 2 : 2 : 2 : 3.

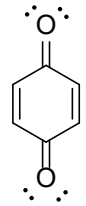
(c) Your friend also wonders why you haven't included  on your list of options. Which of the two types of NMR let you eliminate this compound as an option? How did it do that? *In other words, how would that spectrum for*  *be different from the spectrum for any of the three compounds in part (a). Describe any relevant peaks.* *[2 marks]*

The ^{1}H NMR spectrum for 1-butanol would have a fifth peak due to the OH hydrogen atom. This peak would be a broad singlet.

2. On another shelf of the cabinet, you find a small bottle whose label has been partially obscured. It must say either "quinine" or "quinone", but you can't tell which. **[4 marks]**



quinine



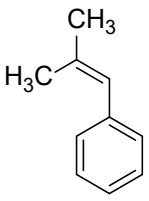
quinone

How could you use IR to quickly decide which compound was in the bottle? Your answer must include one peak that would be produced by quinine (but not quinone) and one peak that would be produced by quinone (but not quinine). For each peak, identify a wavenumber range where it would be expected and the bond responsible for that peak.

Quinine is expected to have an O-H stretch in the 3200-3500 cm^{-1} range.

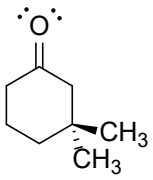
Quinone is expected to have a C=O stretch in the 1660-1700 cm^{-1} range.
*(This is the range for *conjugated* ketones. It turns out there's actually two stretches within this region. Like the NH_2 groups, this is not one for each C=O; it's one where they stretch symmetrically and one where they stretch asymmetrically.)*

3. On each molecule, two CH_3 groups have been explicitly drawn. Identify whether those two CH_3 groups are homotopic, enantiotopic, diastereotopic or constitutionally different. **[3 marks]**

(a) 

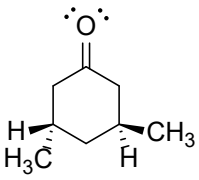
diastereotopic

groups are cis and trans to benzene ring

(b) 

enantiotopic

there is a mirror plane in the plane of the page

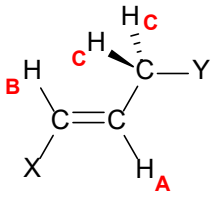
(c) 

homotopic

rotate the molecule 180° to exchange the groups

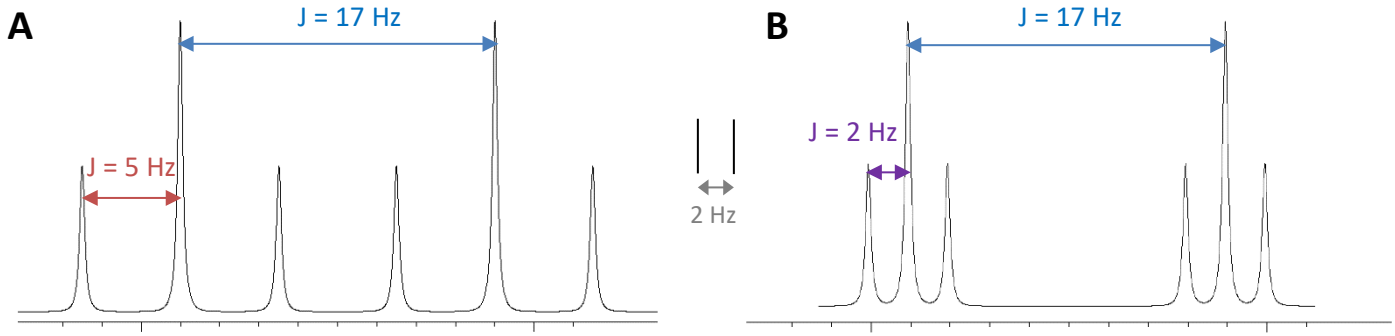
Your best approach to this type of question is always to build two copies of the molecule with your model kit and do a substitution test.

4. When the following molecule is analyzed by ^{1}H NMR, three signals are observed. **[10 marks]**



X and Y contain no hydrogen atoms.

Two of those signals are shown below (labeled "A" and "B"). The distance between adjacent "ticks" along the bottom of each spectrum is 2 Hz.



(a) Both signals have the same splitting pattern (with different coupling constants). *[2 marks]*
Name the splitting pattern.

doublet of triplets

(b) Measure or calculate the coupling constants for each signal. Label each diagram with the appropriate coupling constants, clearly indicating which lines were used to measure/calculate each coupling constant. *[4 marks]*

See drawings on spectra above. Anything within the 16 to 18 Hz range was acceptable for the larger coupling constant given the limitations of accurately measuring such small distances.

(c) Clearly identify which hydrogen atom(s) generated each of the two signals shown above. *[2 marks]*

See labels on structure above. The hydrogens labeled "C" give the third peak on the spectrum.

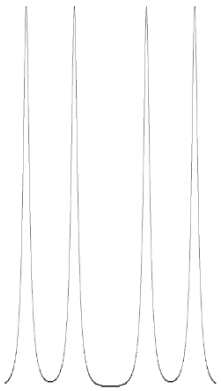
Rationale:

- *H_B experiences 3-bond coupling (trans double bond) with H_A. That's the ~17 Hz coupling.*
- *H_B also experiences 4-bond coupling with both H_C. As long-range coupling, that's expected to have a coupling constant between 0 and 2 Hz.*
- *H_A, on the other hand, experiences 3-bond coupling with both H_C. If the C to which H_A is attached were tetrahedral, we'd expect a coupling constant of ~7 Hz. Because it's trigonal planar, this coupling constant is a little smaller – around 5 Hz (see table in data package).*

(d) What does the third signal on the ^1H NMR look like? Sketch a picture and name the splitting pattern. *You are not expected to predict chemical shift since you do not know what "X" and "Y" are.* *[2 marks]*

Doublet of doublets:

(integrates to 2H)



Rationale:

- *Both H_C experience 3-bond coupling with H_A (a single atom). This was observed to have a coupling constant of 5 Hz (since H_C must couple to H_A with the same coupling constant as H_A couples to H_C).*
- *Both H_C experience 4-bond coupling with H_B (also a single atom). This was observed to have a coupling constant of 2 Hz (since H_C must couple to H_B with the same coupling constant as H_B couples to H_C).*
- Since there is coupling of one type to one hydrogen atom ("doublet") and coupling of another type to another hydrogen atom ("doublet"), the overall splitting pattern is a "doublet of doublets".

5. The following page contains spectra for Unknown X ($C_{14}H_{12}O_3$). **[25 marks]**

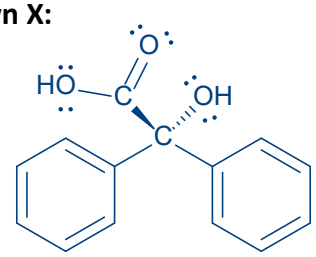
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your reasoning. **Calculation of integrals is required for full marks.**

(c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, drawing Unknown X in the box provided, and labeling each carbon or hydrogen atom with the appropriate peak number. For atoms that cannot be assigned with certainty, list the signals to which they might reasonably correspond.

(d) Label any important peaks on the IR, clearly identifying which bond(s) correspond(s) to each peak.

Unknown X:



General breakdown of marks:
1 mark for correct answer
3 marks for IR peak assignments
3 marks for ^{1}H NMR assignment (correct for correct answer; "reasonable" for incorrect answers)
4 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
1 mark for calculating DU
2 marks for calculating integrals
11 marks for logic/explanation (this page plus legible rough work on spectra, etc.)

One Way to Arrive at the Answer

Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

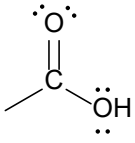
- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(14)+2-12}{2} = \frac{18}{2} = 9$
- Each degree of unsaturation corresponds to either a pi bond (double bond = 1 DU; triple bond = 2 DU) or a ring.
- Wow! That's a lot of degrees of unsaturation! There's probably at least one (maybe two) aromatic rings.

Step 2: Calculate integrals on ^{1}H NMR

- Measure the heights of the integral traces over each peak. Don't forget to include the one at 13.8 ppm! Integral ratio is 1 : 4 : 6 : 1 (or 1 : 10 : 1 if you weren't able to get clear definition between the two aromatic peaks/clusters).

Step 3: Look at IR for relevant peaks

- There's a strong peak at 1720 cm^{-1}. That's likely to be due to a carbonyl group.
  - There's a peak on the ^{13}C NMR at about 178 ppm. That's within the carbonyl range, supporting the idea of the unknown containing a carbonyl group.
  - There's a peak on the ^{1}H NMR at about 13.8 ppm. It exchanges with D_2O. That's almost certainly from a -CO_2H group. Exchangeable peaks are due to OH or NH groups, and our molecule doesn't contain any nitrogen atoms – and this is so far downfield that a carboxylic acid is the most likely explanation. This peak integrates to 1H, so there's only one -CO_2H group.
  - Looking back at the IR, we see a very broad peak stretching from about 3200 cm^{-1} down to about 2500 cm^{-1}. That looks a lot like the O-H stretch from a carboxylic acid. It's safe to predict that Unknown X contains a carboxylic acid:



- There's also a strong peak at 3400 cm^{-1}. It's sharper than we'd usually expect for an O-H but a bit far left for a ≡C-H peak. Keep both options in mind.

Step 4: Look at ^{1}H NMR for relevant peaks

- We've already addressed the peak at about 13.8 ppm. (from the -CO_2H group)
- There's a second peak on the ^{1}H NMR that exchanges with D_2O. That must have come from another OH group. It's at 6.5 ppm, so this one won't be from a carboxylic acid – just an alcohol of some sort. This peak integrates to 1H, so there's only one -OH group. (Also, this uses up our last oxygen atom.)

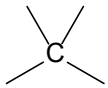


- The remaining peaks on the ^{1}H NMR are at 7.5-7.7 ppm, so within the aromatic region. These peaks integrate to a total of 10H, suggesting 10 hydrogen atoms attached to aromatic rings.
    - The two pieces drawn so far use up CH_2O_3 from the molecular formula, leaving $C_{13}H_{10}$ and 8 degrees of unsaturation. Two monosubstituted benzene rings would require $C_{12}H_{10}$ and use up all remaining degrees of unsaturation.
    - Looking at the ^{13}C NMR, there are four peaks in the aromatic region. *(You have to look at the expansion to see the fourth peak; there are two peaks at ~128 ppm.)* This suggests that the aromatic portion of our molecule must be highly symmetric if it has ten hydrogen atoms attached but only four unique carbon environments. That symmetry is also consistent with only seeing two peaks on ^{1}H NMR for those ten aromatic hydrogen atoms.
    - The most likely explanation is therefore two monosubstituted benzene rings attached to the same carbon atom:

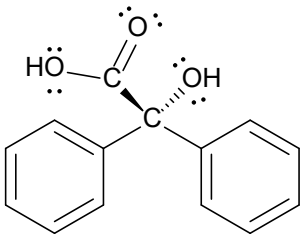


Step 5: Assemble the puzzle

- So far, we've drawn pieces corresponding $C_{13}H_{12}O_3$. That means we have one carbon atom left. It must correspond to the remaining peak on the ^{13}C NMR at about 82 ppm (which is the region you'd expect for a tetrahedral carbon atom bonded to an oxygen atom):



- There's only one way to connect the other four puzzle pieces to this central carbon atom. That gives:



Step 6: Check your answer against the spectra and assign the peaks.

- IR
  - The peak at 3400 cm^{-1} must have been from the alcohol O-H. It's sharper than usual – likely due to hydrogen bonding with the oxygen atom in the carbonyl group.
  - The broad peak from 3200 cm^{-1} to 2500 cm^{-1} is the carboxylic acid O-H.
  - The strong peak at 1720 cm^{-1} is the C=O stretch.
- ^{1}H NMR
  - The peak at 13.8 ppm that exchanges with D_2O corresponds to the carboxylic acid OH.
  - The peak at 6.5 ppm that exchanges with D_2O corresponds to the alcohol OH. This is further downfield than usual for an alcohol, but that's likely due to hydrogen bonding with the oxygen atom in the carbonyl group.
  - The peaks at 7.5 ppm and 7.6 ppm correspond to the ten aromatic H. Theoretically, we'd expect three peaks with a 4 : 4 : 2 integral ratio (ortho-to-central-C, meta-to-central-C, para-to-central-C) but two of the peaks must overlap and that's why we see a 4 : 6 ratio instead.
- ^{13}C NMR
  - The peak at 178 ppm must be the carbonyl carbon. That's well within the range for a carbon of a carboxylic acid.
  - The four peaks at 127 ppm, 128 ppm, 128 ppm and 142 ppm will correspond to the four carbon environments in the benzene rings (attached-to-central-C, ortho-to-central-C, meta-to-central-C, para-to-central-C). The peak at 142 ppm will be due to the carbon attached to the central C (the one that does NOT have a hydrogen atom attached).
  - The peak at 82 ppm will be for the central carbon atom. This carbon is tertiary and attached to an alcohol, and this chemical shift is well within the range for that type of carbon atom.

5. *…continued*

$C_{14}H_{12}O_3$

