Fall 2023 **Chemistry 2600 Midterm #1** ____/60 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam with (or in the presence of) any CHEM 2600 student who has yet to write it. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/60 on this exam.

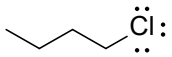
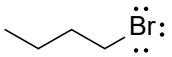
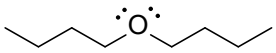
Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 60 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

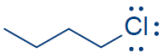
Q1	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**									**Total**
/ 8	/ 4	/ 12	/ 4	/ 10	/ 22									/ 60

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.

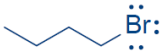
(a) Describe what you would expect to see in the molecular ion region of a mass spectrum for each of these three compounds. Be specific. Your answer should address two factors. *[5 marks]*



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

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

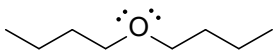


M^+ is the only significant peak in this region

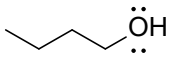
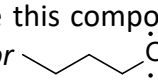
M^+ is at m/z 130

(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]*

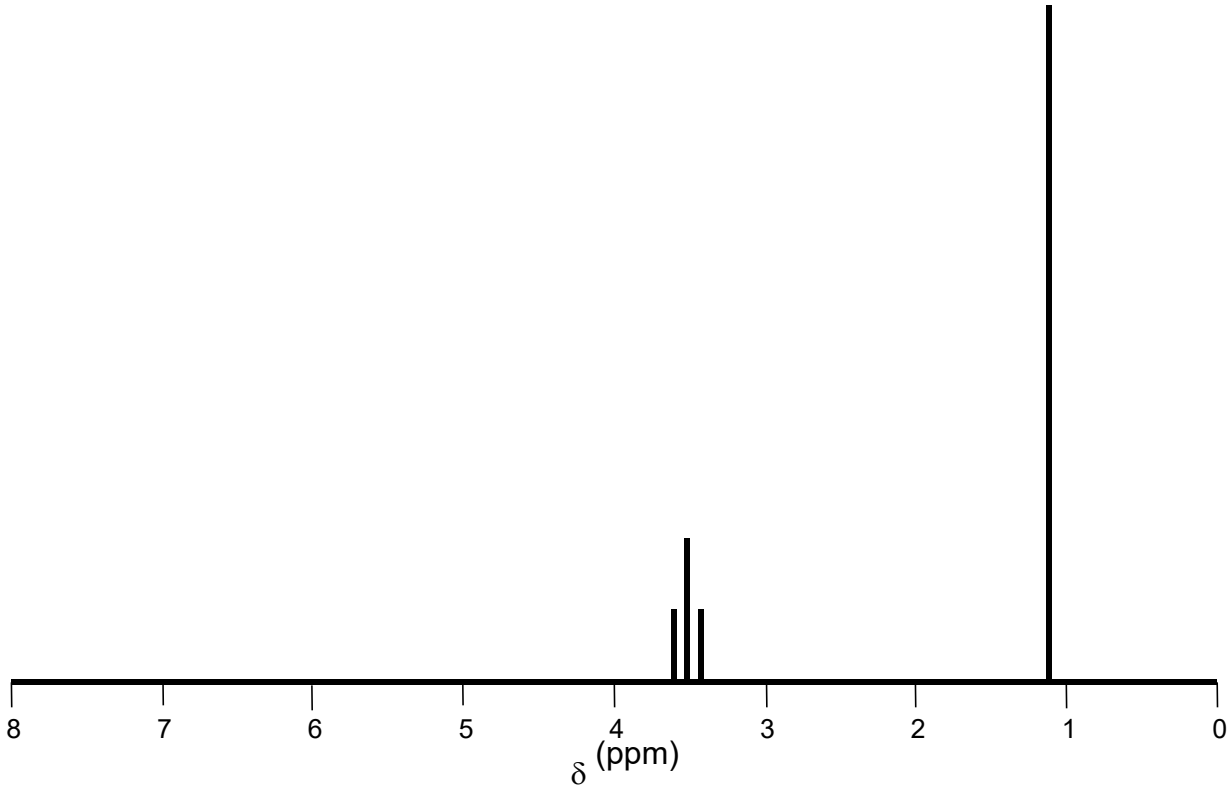
Integrals are **ratios**. All three compounds are expected to give four peaks with integral ratios of 2 : 2 : 2 : 3.

(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. I had to draw the ^{1}H NMR spectrum below myself because it can't possibly correspond to any real compound. Why not? What's wrong with it? Explain. **[4 marks]**

Since integrals are not provided, I will confirm that there are two peaks on this spectrum.



For clarity, I will refer to the triplet as X and the hydrogen atom(s) to which it corresponds as H_X.
If you do things like this in your answer, you must explicitly state what you're doing (as I did here).

Coupling must be mutual!!!

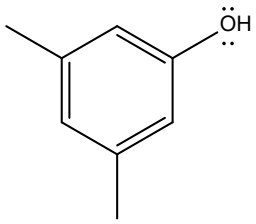
In order for X to be a triplet, H_X must have two "neighbouring" hydrogen atoms to which it couples. Those neighbouring hydrogen atoms must also couple to H_X. As such, it is IMPOSSIBLE for those neighbouring hydrogen atoms to give a singlet as their peak on the ^{1}H NMR spectrum.

It is impossible for any compound to generate a ^{1}H NMR spectrum containing only one non-singlet peak. That's why Susan had to draw the spectrum herself.

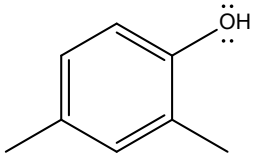
3. *I am listing many reasonable answers. You needed two (using different types of spectroscopy).*

[12 marks]

(a)

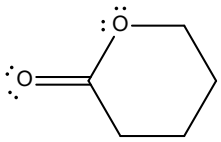


vs.

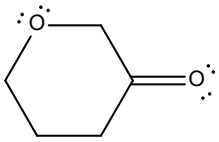


^{1}H NMR	4 signals in total	6 signals in total
	1 singlet integrating to 6H around 2.3 ppm (the methyl groups are equivalent)	2 singlets each integrating to 3H around 2.3 ppm (the methyl groups are not equivalent)
	2 signals at 6.5-8 ppm integrating to 1H and 2H (aromatic H)	3 signals at 6.5-8 ppm, each integrating to 1H (aromatic H)
^{13}C NMR	5 signals in total	8 signals in total
	4 signals at 110-160 ppm (aromatic C)	6 signals at 110 -160 ppm (aromatic C)

(b)

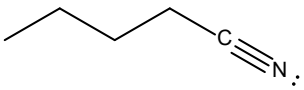


vs.

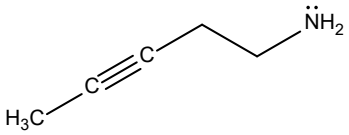


^{1}H NMR	Splitting patterns and integrations: • Triplet integrating to 2H • Pentet integrating to 2H • Pentet integrating to 2H • Triplet integrating to 2H	Splitting patterns and integrations: • Triplet integrating to 2H • Pentet integrating to 2H • Triplet integrating to 2H • Singlet integrating to 2H
	One peak downfield of 3ppm: • Triplet (2H) at ~4.1 ppm	Two peaks downfield of 3ppm: • Singlet (2H) at ~4 to 5 ppm • Triplet (2H) at ~3.4 ppm
^{13}C NMR	Carbonyl C for ester is expected to appear between 155 and 175 ppm, so if the carbonyl C appears upfield of 175 ppm, it is this isomer.	Carbonyl C for ketone is expected to appear between 175 and 220 ppm, so if the carbonyl C appears downfield of 175 ppm, it is this isomer.
IR	An unconjugated ester gives a C=O stretch between 1735 and 1750 cm^{-1}	An unconjugated ketone gives a C=O stretch between 1705 and 1725 cm^{-1}

(c)

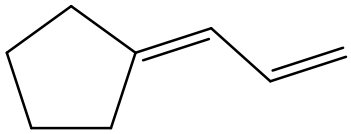


vs.



^{1}H NMR	Splitting patterns and integrations: • Triplet integrating to 3H • Sextet integrating to 2H • Pentet integrating to 2H • Triplet integrating to 2H	Splitting patterns and integrations: • Singlet integrating to 3H • Triplet integrating to 2H • Triplet integrating to 2H • Broad singlet integrating to 2H
^{13}C NMR	Expect to see **one** peak between 110 and 130 ppm for the C of the nitrile group (C≡N).	Expect two see **two** peaks between 70 and 100 ppm for the two C of the alkyne (C≡C).
IR	A nitrile gives a peak between 2100 and 2300 cm^{-1}	A primary amine gives two peaks between 3200 and 3500 cm^{-1}.

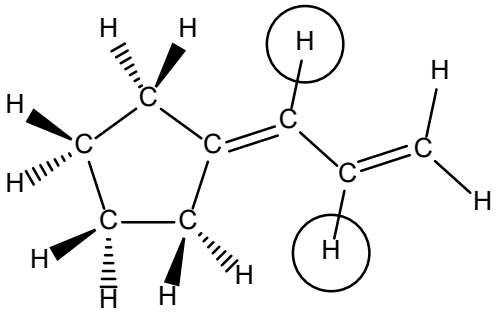
4. Consider the following molecule: **[4 marks]**



Below each drawing, write one of the following abbreviations (H, E, D or CD) to indicate the relationship between the circled hydrogen atoms:

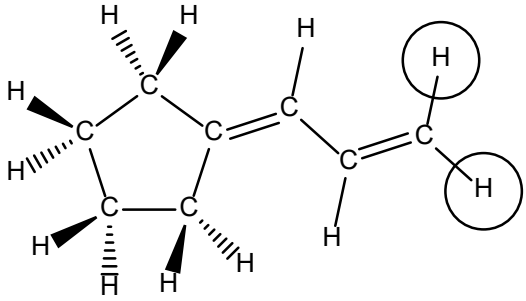
- Homotopic (H) *substitution test gives two copies of the same molecule*
- Enantiotopic (E) *substitution test gives a pair of enantiomers*
- Diastereotopic (D) *substitution test gives a pair of diastereomers*
- Constitutionally Different (CD) *substitution test gives a pair of constitutional isomers*

(a)



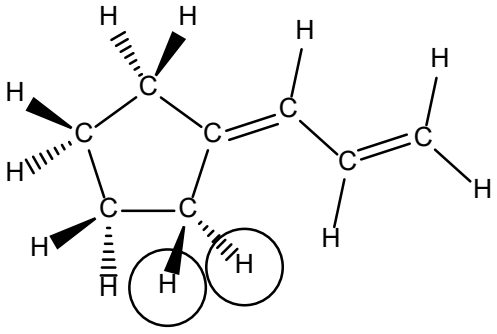
CD

(b)



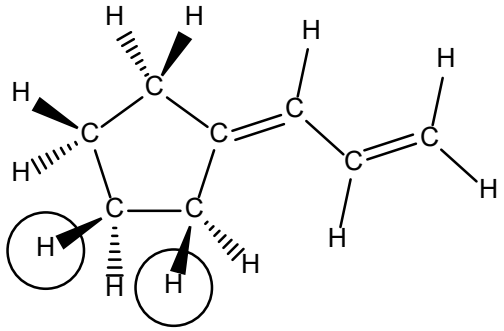
D

(c)



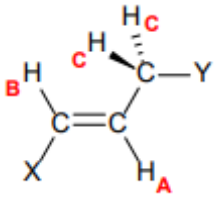
E

(d)



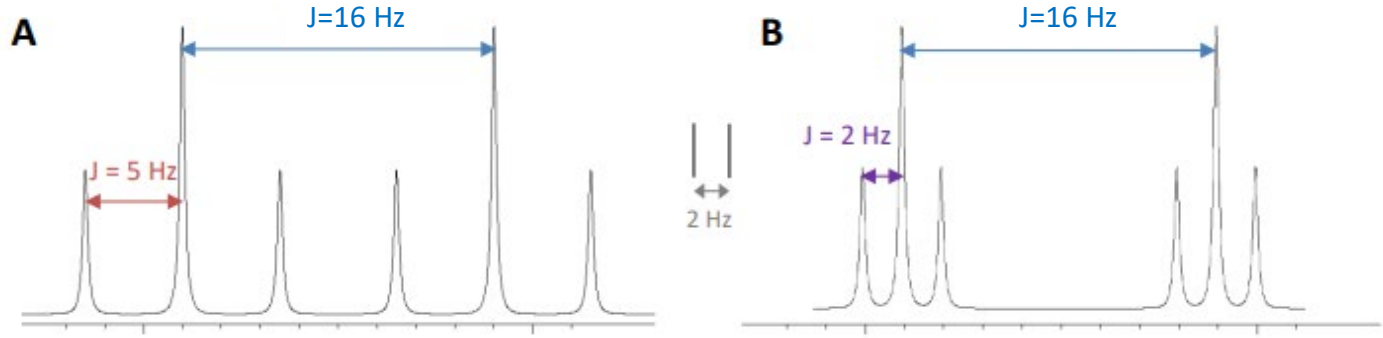
CD

5. 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) 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 15 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 ~16 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. Here, we measure 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 experiences 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".*

6. The following page contains spectra for Unknown X ($C_5H_{14}N_2$). **[22 marks]**

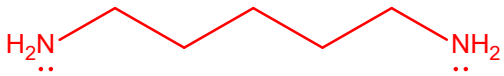
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(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
2 marks for calculating integrals for ^{1}H NMR
2 marks for IR peak assignment
4 marks for ^{1}H NMR assignment
(correct for correct answer; "reasonable" for incorrect answers)
3 marks for ^{13}C NMR assignments
(correct for correct answer; "reasonable" for incorrect answers)
10 marks for logic (this page plus legible rough work on spectra, etc.); verbal explanation is required for full credit; includes 1 mark for correct calculation of DU if your strategy required it

One Way to Arrive at the Answer

Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(5)+2+2-14}{2} = \frac{0}{2} = 0$
- Unknown X does not contain any double bonds, triple bonds or rings

Step 2: Calculate integral ratio for ^{1}H NMR

- Measuring the heights of the integral trails gives an integral ratio of 2 : 2 : 2 : 1; however, there are fourteen H in the molecular formula so double those numbers to 4 : 4 : 4 : 2. *Given the difficulty in resolving how high the integral trail climbs for each of the two pentets, I accepted integral ratios of 2 : 2 : 3 (therefore 4 : 4 : 6). The expansion does clearly show that the "6H" correspond to two pentets even if it's not as clear exactly how many H correspond to each individual pentet.*

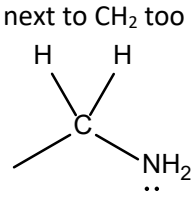
Step 3: Look at IR for relevant peaks

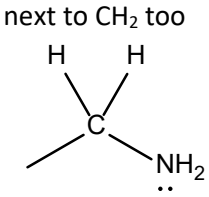
- There are two peaks at 3284 cm^{-1} and 3362 cm^{-1} , suggesting presence of an NH_2 group.
  - There is a broad singled on the ^{1}H NMR that exchanges with D_2O. Exchangeable peaks are for OH or NH – but there are no oxygen atoms in the molecular formula, so this must be for NH. It integrates to 4H, so that's consistent with two equivalent NH_2 groups.



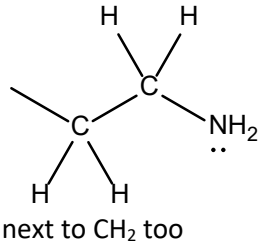
Step 4: Consider the peaks on ^{1}H NMR

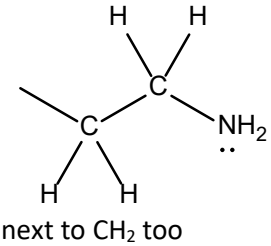
- There are four peaks on the ^{1}H NMR. The broad singlet at 1.4 ppm was discussed in Step 3.
- The remaining three peaks are:
  - a triplet at ~2.1 ppm (4H)
    - must be hydrogen atoms attached to the C that are attached to nitrogen atoms
    - integrates to 4H so two CH_2 groups
    - triplet so each CH_2 is next to another CH_2 (the NH_2 peak is a singlet, so it's not coupling to these H; that's because exchangeable H don't couple)



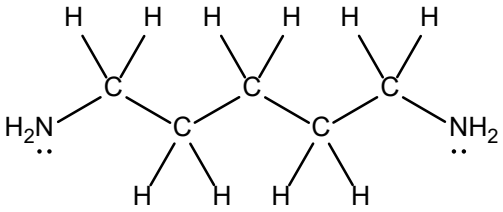


  - a pentet at ~0.9 ppm (4H)
    - must be the CH_2 groups next to each of the CH_2 groups drawn above (it's the only remaining peak that integrates to 4H)
    - pentet so each of these CH_2 has a CH_2 on either side (to give 4 "neighbours")





  - a pentet at ~0.9 ppm (2H)
    - at this point, we've used all atoms in the molecular formula except for one C and two H; so, this must be the last CH_2 group; it must therefore fit between the two pieces drawn above
    - pentet so it has 4 "neighbours" – consistent with being between two CH_2 groups



- This is consistent with the fact that there are three peaks on the ^{13}C NMR (which suggested that the final answer ought to have symmetry)

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

- IR
  - Two $N-H$ stretches are visible at 3284 cm^{-1} and 3362 cm^{-1}. These are the symmetric and asymmetric stretches of the NH_2 group.
  - We also see $C-H$ stretches below 3000 cm^{-1} for H attached to tetrahedral C. Most organic molecules give these stretches.
  - *For those interested, the peak at 1600 cm^{-1} is an $N-H$ bend; it was not peak picked so you were not required to assign it. It could not correspond to $C=C$ because there were no peaks on ^{13}C NMR above 110 ppm.*
- ^1H NMR
  - The triplet integrating to 4H at ~2.1 ppm on the ^1H NMR is consistent with two CH_2 groups, each attached to N. It's a triplet because each CH_2 is next to one other CH_2 group.
  - The broad singlet integrating to 4H at ~1.4 ppm on the ^1H NMR is consistent with two NH_2 groups. It exchanges with D_2O so does not participate in coupling.
  - The pentet integrating to 4H at ~0.9 ppm on the ^1H NMR is consistent with two CH_2 groups, each between two other CH_2 groups.
  - The pentet integrating to 2H at ~0.8 ppm on the ^1H NMR is consistent with a CH_2 group between two other CH_2 groups.
- ^{13}C NMR
  - The peak at ~40 ppm is consistent with $C-N$.
  - The peak at ~32 ppm will correspond to the CH_2 groups attached to CH_2NH_2 (labeled "2" on the diagram on the next page).
  - The peak at ~22 ppm will correspond to the CH_2 group in the middle of the molecule (farthest from the electron withdrawing nitrogen atoms).

6. *…continued*

$C_5H_{14}N_2$

