Problem Set 3 **^{1}H NMR Spectroscopy**

CHEM 393

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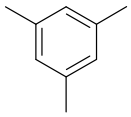
1. The following ^{1}H NMR spectrum was recorded on a 60 MHz spectrometer. It shows three signals. The molar mass of the hydrocarbon is 120 g/mol. **120/13 = 9 + 3/13, C_9H_{12}; U = 4**

   a) (1 point) What causes the unidentified, unintegrated signal? **TMS**

   b) (1 point) What are the chemical shifts of signals a and b in ppm? **-0.3 ppm => a 6.7 ppm, b 2.2 ppm**

   c) (4 points) Label signals a and b with all necessary information. Which compound is it? **pay close attention to the TMS position**



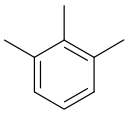
if you do not provide all labels, you will lose out on 3 points!

   d) (3 points) Calculate and evaluate the chemical shift for all non-equivalent protons. **evaluation in this question is versus the experimental values**

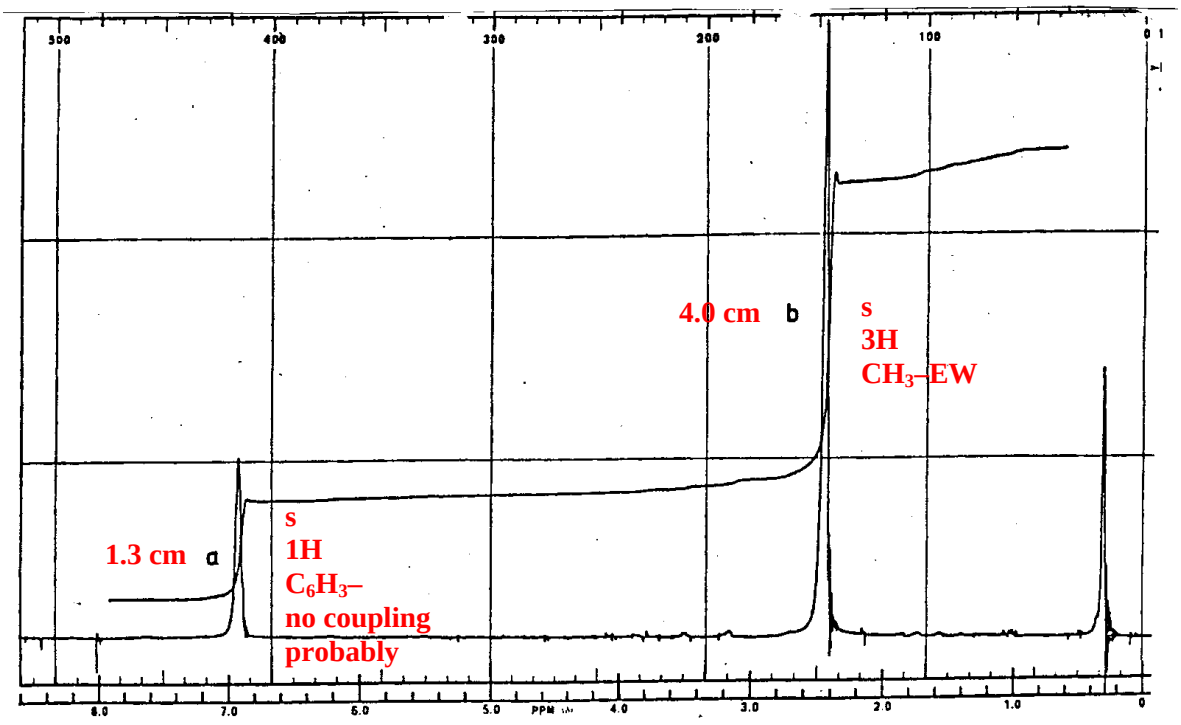
   a: δ^1H = 7.27 – 2·0.14 – 0.17 = 6.82 ppm (6.7 ppm) ok

   b: δ^1H = 0.23 + 1.85 + 0 = 2.08 ppm (2.2 ppm) ok

   e) (2 points) Give a closely related isomeric compound and reason why it is not a proper solution.

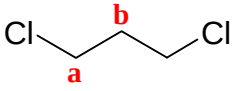


there would be 2 methyl signals in 2:1 ratio, the aromatic protons would probably show their different δ and coupling, the chemical shifts would be different

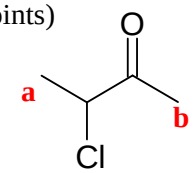


2. Predict the ^{1}H NMR spectra for the following compounds. Include chemical shift (with evaluation), integration and multiplicity. Give proper drawings that consider the intensity of the lines within a multiplet.

a) (4 points)



b) (5 points)

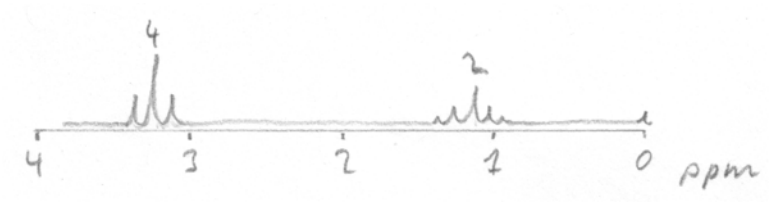


a: CH_2 (a): t, 4 H, δ^1H = 0.23 + 2.53 + 0.47 = 3.23 ppm ok

Cl R

CH_2 (b): quint, 2 H, δ^1H = 0.23 + 0.47 + 0.47$^?$ = 1.17 ppm (will be too low)

R R



evaluation in this question is versus the available increments

b: CH_3 (a): d, 3 H, δ^1H = 0.23 + 0.47$^?$ = 0.70 ppm (will be too low)

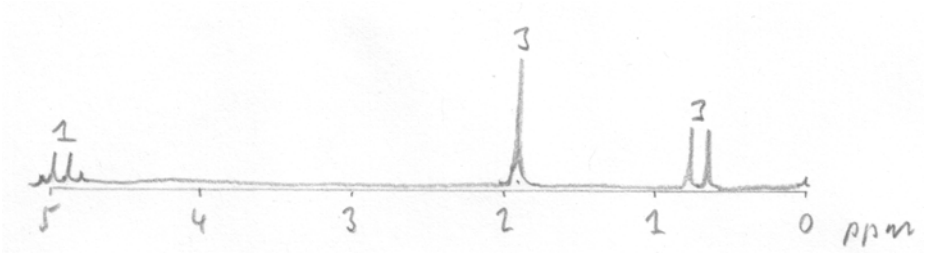
R

CH: q, 1 H, δ^1H = 0.23 + 0.47 + 2.53 + 1.70 = 4.93 ppm (cannot evaluate)

R Cl COR

CH_3 (b): s, 3 H, δ^1H = 0.23 + 1.70 = 1.93 ppm ok

COR



you do not have rules for methine (CH) protons, so you have to make do with simply adding three increments; this is not particularly predictive!

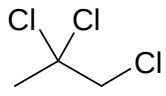
integration here is provided as area under the peak; you can also draw a steptrace

3. For each set of ^{1}H NMR data, suggest a structure that is consistent with the data.

a) (2 points) $C_3H_5Cl_3$: 2.20 ppm, 3H; 4.02 ppm, 2H

CH_3-EW -CH_2-EW

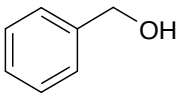
U = 0



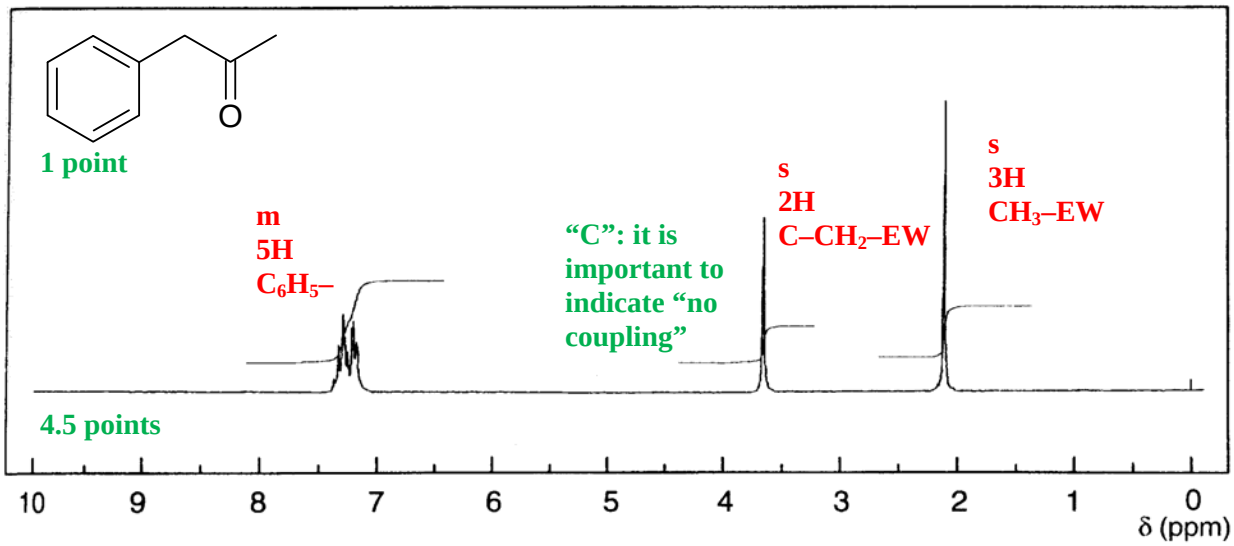
b) (2 points) C_7H_8O: 2.43 ppm, 1H; 4.58 ppm, 2H; 7.28 ppm, 5H

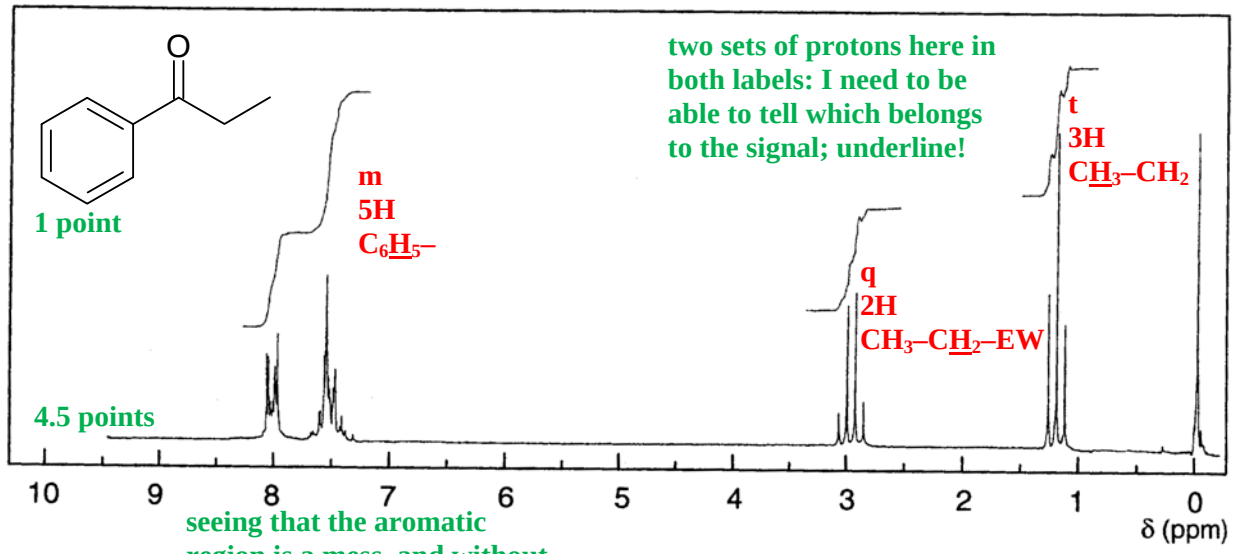
-OH -CH_2-O C_6H_5-

U = 4



4. (11 points) Two isomeric ketones show the following ^{1}H NMR spectra. Identify the compounds.



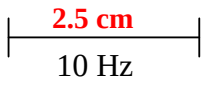


seeing that the aromatic region is a mess, and without more explicit instructions, you can treat both sets of signals as one, just like in the spectrum above

if you do not provide all labels, you will lose out on 9 points!

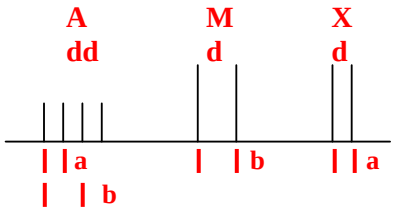
1/2 point for every piece of information

5. (10 points) The following multiplets are due to protons A, M, and X. Determine the signal multiplicity, the coupling constants J_{AM}, J_{AX} and J_{MX} as well as the number of protons in each group (take the sum of the height of the lines as an integral). Classify the systems as AMX or AM_2X.



remember that an integration records the total area under a signal (for example, under the three peaks of a triplet); therefore, in line spectra you need to sum up the heights of all lines that belong to a signal

a)

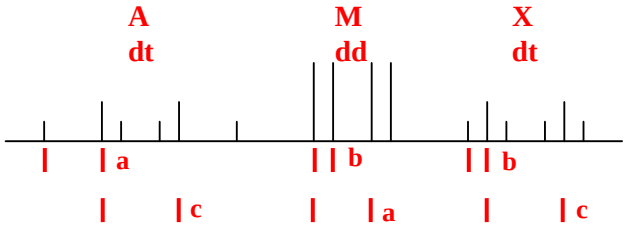


int.: 2:2:2 or 1:1:1 => AMX

b 0.5 cm J_{AM} = 2 Hz
a 0.25 cm J_{AX} = 1 Hz
J_{MX} = 0 Hz

the red lines indicate which distances you have taken for your analysis and need to be provided!

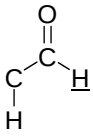
b)

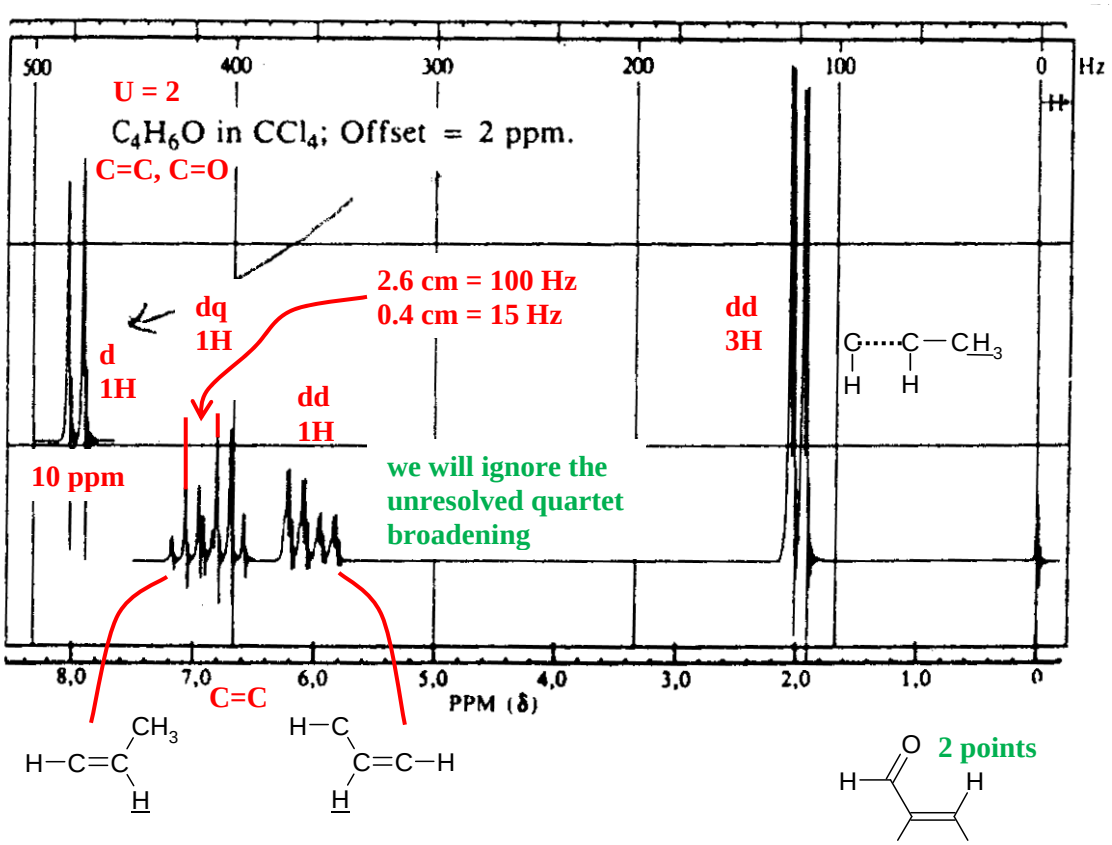


int.: 2:4:2 or 1:2:1 => AM_2X

a 0.75 cm J_{AM} = 3 Hz
c 1.0 cm J_{AX} = 4 Hz
b 0.25 cm J_{MX} = 1 Hz

6. (10 points) Identify the compound that shows the following ^{1}H NMR spectrum. Provide full labels for all signals.





2 points

H trans
^{3}J 11 - 18 Hz

the distances in cm given here might be a bit off due to the pdf conversion