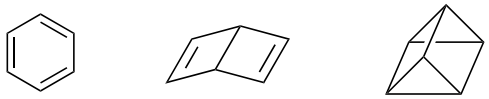
CHEMISTRY 744

Organic Spectroscopy, Spring 2019

Homework #1
due Wed, Jan 23

1. During the process of discovering the correct representation for benzene, three structures were considered at different times. These include (a) delocalized cyclohexatriene **1**; (b) Dewar benzene **2**; and (c) Ladenberg benzene **3** (prismane). The table below summarizes the properties expected for each ot these structures. Correlate each structure with the appropriate properties and explain your assignment.

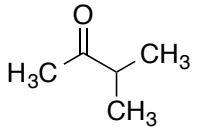


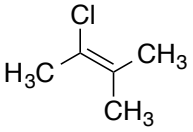
1 **2** **3**

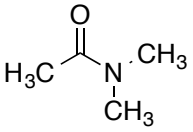
method	**A**	**B**	**C**
^{13}C NMR	one peak (sp^2)	two peaks	one peak (sp^3)
MS - MF	C_6H_6	C_6H_6	C_6H_6
IR	many peaks	many peaks	many peaks
UV-VIS	broad peak	no peaks	no peaks

2. Combustion analysis on pure limonene shows the following elemental analysis; C=88.2%, H=11.7%. By mass spectrometry it is found to have a MW of 136. What is the molecular formula?

3. Explain the different number of methyl NMR signals observed for each of the following compounds.







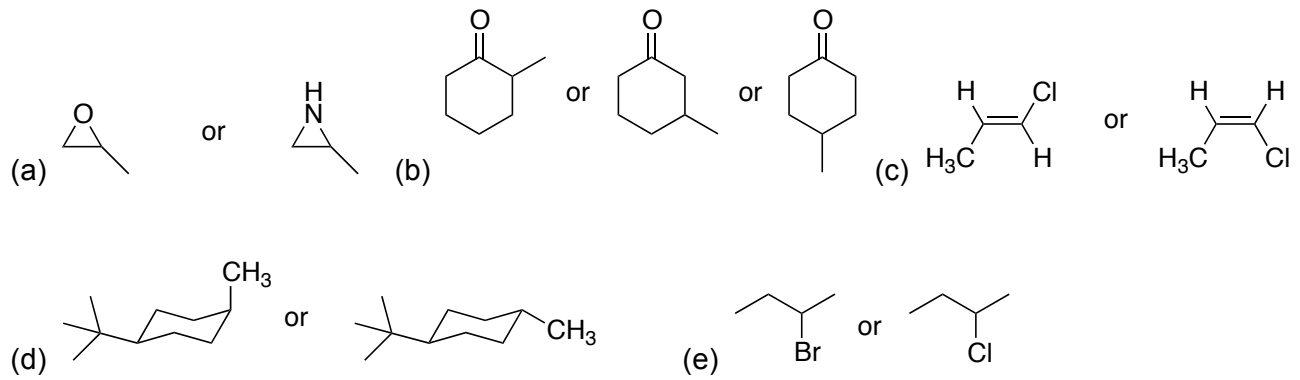
# of methyl signals (ratio) 2 (1:2) 3 (1:1:1) 3 (1:1:1)

4. Calculate the chemical shift in ppm (δ) for the following:
   (a) Cyclohexane protons observed at 414 Hz relative to TMS at 300 MHz.
   (b) Cyclohexane carbons observed at 660 Hz relative to TMS at 25 MHz.

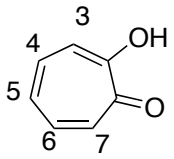
5. Why are very broad NMR peaks observed for a sample of ethyl chloride dissolved in benzene-d_6 that is saturated with oxygen?

6. A compound's combustion analysis shows 100% carbon. It has a MW of 720 and shows a single peak in the ^{13}C NMR at 126 ppm. Propose a structure for this molecule.

7. For each of the following sets of molecules, describe how you could use NMR spectroscopy to distinguish between them.

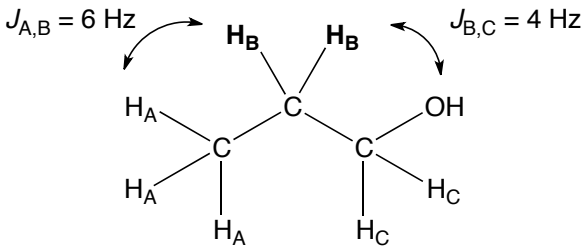


8. The chemical shifts for the vinylic protons of hydroxytropolone are listed below. Provide an explanation for why protons 3,7 and 4,6 are equivalent?

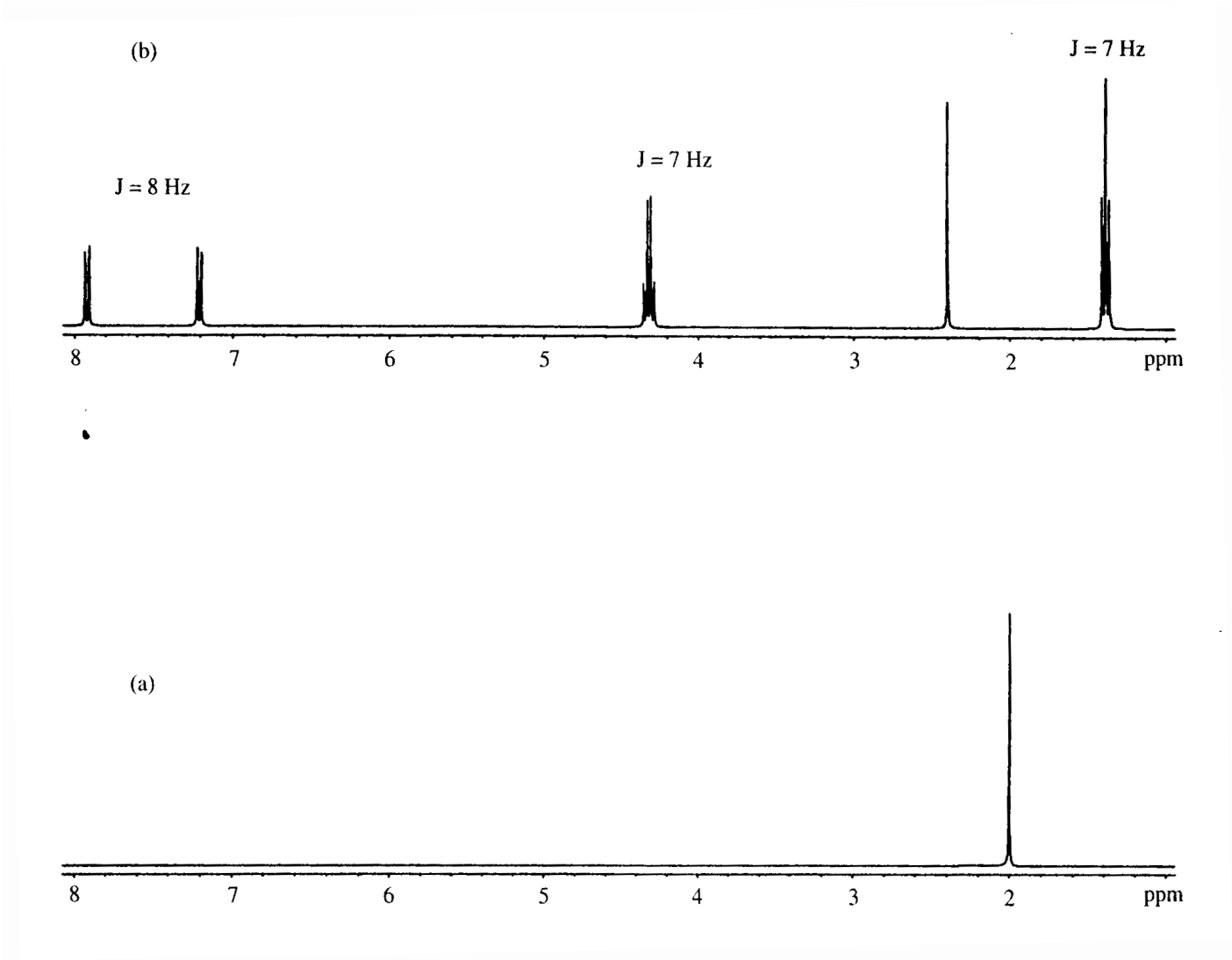


proton	ppm
3	7.23
4	7.35
5	6.99
6	7.35
7	7.23

9. The proton NMR of 1-propanol shows a resonance for the methylene (H_B) at 1.80 ppm and it is split by the methyl group (H_A) with a coupling constant of 6 Hz, and by the methylene adjacent to the alcohol (H_C) with a coupling constant of 3 Hz. How would this molecule be described using spin system notation? Show what the peak pattern for H_B would look like on a 100MHz NMR and a 500MHz NMR.



10. The following ^1H spectra represent two isomers (a and b) with a molecular formula of $C_{10}H_{12}O_2$. Identify their structures and correlate them with the spectra. Explain.



11. The following spectra obtained on a 400 MHz instrument represent a compound with a molecular formula of $C_{22}H_{20}O$. Identify the structure and offer an explanation for any anomalous splitting observed.