1H NMR

• Use the following illustration to determine the approximate chemical shift for the methylene protons attached to C₄. Insert your response here: 8 1.5

<table>
<thead>
<tr>
<th>ppm, δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

• Provide a splitting tree for the resonant signal that can be described as a doublet of doublets, dd, with coupling constants of 2 and 6 Hz. Be sure the intensities are accurate.

• Illustrate the coupling patterns that would be observed for the protons that are highlighted in the following structure.

(CH₃)₃C-CH=CH-CHO

Would be a dd and would appear like

---
[a] Determine whether the highlighted H's are enantiotopic, diastereotopic, or homotopic.
[b] Which are non-equivalent in an achiral environment?

<table>
<thead>
<tr>
<th>classification</th>
<th>reasoning</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>enantiotopic</td>
</tr>
<tr>
<td></td>
<td>diastereotopic</td>
</tr>
</tbody>
</table>

- Describe the appearance of the \(^1\)H NMR spectrum for the **methine proton** in 1 under conditions of

- [a] rapid exchange
- [b] slow exchange
- [c] What would it look like after the addition of 2 drops of D\(_2\)O?
Your name: __________________________  Chem 6a
Your perm number: __________________

- The circled H's will appear [underline the correct response] upfield/downfield of all others and should be [underline the correct response] easy/difficult to pick out.

- What chemical shift does one anticipate for this proton?
  [a] upfield of 2.0 ppm
  [b] around 7.7 ppm
  [c] somewhere between 3 and 4 ppm downfield from TMS
  [d] approximately 5.2 ppm

- True/false – if false, indicate why.
  [a] Structure A should exist as one of two rapidly equilibrating structures.
    F True, t-Bu group provides a conformational lock.

  [b] [For structure A] The axial H's at C-2 and C-6 will couple with equal coupling constant to H-1.
    That is, J (2-axial, 1) = J (6-axial, 1)
    T

  [c] [For structure A] The equatorial H's at C-2 and C-6 will couple with equal coupling constant to H-1.
    That is, J (2-equatorial, 1) = J (6-equatorial, 1)
    T

  [d] [For structure A] J (6-equatorial, 1) will be larger than J (6-axial, 1)
    F. From the Karplus eqn., $J_{180} > J_{60}$

  [e] In structure B, H-1 will be split into a doublet of doublets (dd), and each of the coupling constants will be equal.
    F

Chem 6a, final exam, spring 2002
\(^1\)C NMR

- How could APT spectra be used to differentiate between the pair of \(C_7H_{11}\) isomers shown below?

[a] How many lines would one expect to see in the \(^1\)C NMR spectrum of each structure?

[b] Describe the overall appearance of the APT spectrum for each structure.

- The C-13 NMR spectrum of ethyl methyl ketone is shown below. Draw an arrow to the signal corresponding to each of the numbered carbons. [Ignore the signals between 70 and 80].

Chem 6a, final exam, spring 2002
• The proton-proton 2-D COSY spectrum for ethyl methyl ketone (abbreviated below as “MEK”) is illustrated below. Refer to the following structure and the numbering system shown when responding to the questions.

\[ \text{MEK} \]

[a] Determine the approximate chemical shift for the H’s appended to C-1. Write your response here.

[b] Determine the approximate chemical shift for the methylene protons. Write your response here.

[c] Determine the approximate chemical shift for the H’s appended to C-4. Write your response here.

EXTRA CREDIT: Draw correlation lines to indicate how the 2-D spectrum can be used to confirm the structure of “MEK”.

Chem 6a, final exam, spring 2002
IR
[a correlation chart is appended]

• Why does one not see an absorption corresponding to the C-C triple bond stretch in 2-butyne?

\[
\text{H}_2\text{C} \equiv \text{C} \equiv \text{CH}_3
\]

\[\text{No change in dipole moment.}\]

• Provide the energy range, in kcal/mol, for infrared spectroscopy.

\[2 - 12\]

• Which of the following processes are studied using infrared spectroscopy? Circle the correct response(s).

[a] molecular rotations
[b] molecular vibrations
[c] the relative orientations of nuclear spins

• A compound displays an intense and relatively sharp IR absorption band at 1710, and a broad band centered at 3500 cm\(^{-1}\). There is no absorption in the region between 3000 and 3100 wavenumbers. What can one conclude regarding the structure of this substance?

(E means "there exists")

\[\begin{align*}
\text{\(E\)} & \Rightarrow \text{\(\#\) C=O} \\
\text{\(E\)} & \Rightarrow \text{\(\#\) C-H} \\
\text{\(E\)} & \Rightarrow \text{\(\text{O-H}\)}
\end{align*}\]

• How could infrared spectroscopy be used to distinguish between the pair of \(\text{C}_4\text{H}_8\text{O}\) isomers illustrated below? Indicate the characteristic absorption frequencies for each functional group.

\[
\text{\(\text{C=C}\)} \quad \approx 1650 \quad \approx 3500 \text{ cm}^{-1} \\
\text{\(\text{C-O}\)} \quad \approx 3000 - 3100
\]
• Examine the following infrared spectrum. Then, respond to the following statements, indicating that they are either **true** (mark with a "T") or **false** (mark with an "F"). **If true**, then **draw an arrow** to the absorption in the spectrum that corresponds to the indicated vibration. **If false**, then **indicate where you would have expected to have seen the absorption** (use the wavenumber scale).

![Infrared Spectrum Diagram]

[a] There is a carbon-carbon triple bond stretch.

F 2160/2250

[b] There is a C-H stretch where the H is appended to an sp-hybridized carbon.

F ~ 3200

[c] There is a carbonyl stretch.

T

[d] There is an OH stretch.

F ~ 3550

[e] One sees a C-H stretch, one where the H is attached to an sp³-hybridized carbon.

T