Lecture 18: $^{13}$C-NMR Spectroscopy  
Discussion Section Problems Solutions

1. (a) 
   ![Diagram](image1)
   A: Quartet, 0–40 ppm  
   B: Doublet, 20–60 ppm  
   C and D: Triplet, 15–55 ppm

   (b) 
   ![Diagram](image2)
   A: Quartet, 0–40 ppm  
   B: Singlet, 100–150 ppm  
   C–F: Triplet, 15–55 ppm  
   G: Doublet, 100–150 ppm

   (c) 
   ![Diagram](image3)
   A: Doublet, 180–220 ppm  
   B: Doublet, 20–60 ppm  
   C: Quartet, 0–40 ppm  
   D: Singlet, 160–180 ppm  
   E: Doublet, 40–80 ppm  
   F and G: Triplet, 15–55 ppm

   (d) 
   ![Diagram](image4)
   A: Doublet, 65–85 ppm  
   B: Singlet, 65–85 ppm  
   C and F: Singlet, 110–160 ppm  
   D and E: Doublet, 110–160 ppm  
   G: quartet, ? ppm

   The chemical shift for carbon G is not included in the characteristic $^{13}$C-NMR chemical shifts table, but we can estimate it. Sulfur has about the same electronegativity as carbon, so we expect the $^{13}$C-NMR chemical shift of S–CH$_3$ to be about the same as C–CH$_3$ (i.e., 0–40 ppm). The actual $^{13}$C-NMR chemical shift for SCH$_3$ is ~15–20 ppm.

2. A $^{13}$C-NMR signal at 176.4 ppm corresponds to the carbonyl carbon of an ester, amide, carboxylic acid, or less probably to an aldehyde or ketone. All of these give singlets except an aldehyde, so structure A is eliminated. An IR stretching frequency of 1737 cm$^{-1}$ is more consistent with an ester than an amide, so structure C is the best fit.

3. The presence of three $^{13}$C-NMR signals reveals that the molecule has three nonequivalent carbon atoms. DMF has only three carbons, so all of its carbons must be nonequivalent. A barrier to rotation around an amide C–N bond slows the bond rotation, allowing the NMR to differentiate the methyl groups. (In most other cases bond rotation faster due to a lower barrier to rotation. If the rotation is fast enough nuclei appear equivalent.) See the diagram below.
4. **DBE** = 10 - (14/2) + (0/2) + 1 = 4 *Possible benzene ring; confirmed by $^{13}$C-NMR.*

$^{1}$H-NMR:

<table>
<thead>
<tr>
<th>Chemical shift</th>
<th>Splitting</th>
<th>Integral</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.12–6.82 ppm</td>
<td>multiplet</td>
<td>4</td>
<td>4 H</td>
<td>Disubstituted benzene ring $\text{C}_6\text{H}_4$</td>
</tr>
<tr>
<td>3.74 ppm</td>
<td>singlet</td>
<td>3</td>
<td>3 H</td>
<td>$\text{CH}_3$ or 3 x CH</td>
</tr>
<tr>
<td>2.84 ppm</td>
<td>septet</td>
<td>1</td>
<td>1 H</td>
<td>$\text{CH}$ in $\text{CH(CH}_3)_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\text{CH}$ in $\text{CH(CH}_2)_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\text{CH}$ in $\text{CHCH(CH}_2)_3$</td>
</tr>
<tr>
<td>1.21 ppm</td>
<td>doublet</td>
<td>6</td>
<td>6 H</td>
<td>$2 \times \text{CH}_3$ in $\text{CH}_2\text{CH}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$3 \times \text{CH}_2$ in $\text{CH}_2\text{CH}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$6 \times \text{CH}$ in $\text{CHCH}$</td>
</tr>
</tbody>
</table>

**Totals** 14 14 H C$_6$H$_4$ + CH$_3$ + CH + (2 x CH$_3$) = C$_{10}$H$_{14}$

$^{13}$C-NMR: The formula has ten carbons whereas the $^{13}$C-NMR has seven signals, so molecule has some equivalent carbons (i.e., the molecule has some symmetry). The symmetry lies in the benzene ring, and in the methyl groups of the isopropyl group.

**Atom check:** C$_{10}$H$_{14}$O (given formula) - C$_{10}$H$_{14}$ ($^1$H-NMR) = one oxygen atom.

**DBE check:** Four DBE calculated from C$_{10}$H$_{14}$O are used by benzene ring.

**Pieces:** Disubstituted benzene ring (C$_6$H$_4$) 2 x CH$_3$ in (CH$_3$)$_2$CH

CH in CH(CH$_3$)$_2$

**Assembly:** The CH and 2 x CH$_3$ pieces become an isopropyl group, CH(CH$_3$)$_2$. The $^1$H-NMR chemical shift of the other CH$_3$ group is more consistent with OCH$_3$ than with benzene–CH$_3$. There is only one way to assemble the pieces which is consistent with all of the given data:
5. **Mass spectrum:** \( m/z = 250 \) (M): *Even number of nitrogen atoms*
   \( m/z = 251 \) (M+1): 15.74%/1.1% = 14.3 *Molecule has \( C_{14} \)*
   \( m/z = 252 \) (M+2): < 4% so no sulfur, chlorine or bromine

Formula: 250 - (14 x 12) = 82 amu for oxygen, nitrogen and hydrogen. IR shows obvious carbonyl (1727 cm\(^{-1}\)), so the molecule has at least one oxygen atom. For brevity, formulas that violate the Hydrogen Rule are not included in the table below.

<table>
<thead>
<tr>
<th>Oxygens</th>
<th>Nitrogens</th>
<th>( 82 - \text{O-N-H} )</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>82 - 64 - 0 = 18</td>
<td>( \text{C}<em>{14}\text{H}</em>{18}\text{O}_4 )</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>82 - 80 - 0 = 2</td>
<td>( \text{C}<em>{14}\text{H}</em>{2}\text{O}_5 )</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>82 - 32 - 28 = 22</td>
<td>( \text{C}<em>{14}\text{H}</em>{22}\text{N}_2\text{O}_2 )</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>82 - 48 - 28 = 6</td>
<td>( \text{C}_{14}\text{H}_6\text{N}_2\text{O}_3 )</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>82 - 16 - 56 = 10</td>
<td>( \text{C}<em>{14}\text{H}</em>{10}\text{N}_4\text{O} )</td>
</tr>
</tbody>
</table>

**DBE:** 14 - (18/2) - (0/2) + 1 = 6 DBE. *Possible benzene ring; confirmed by IR, \(^1\text{H-NMR and }^{13}\text{C-NMR.}*

**IR:**

Zone 1  Alcohol O–H: Absent; no peak.
         A/amide N–H: Absent; no peak.
         Terminal alkyne \( \equiv \text{C–H} \): Absent; no peak.

Zone 2  Aryl/vinyl C–H: Present; peaks > 3000 cm\(^{-1}\).
         Alkyl C–H: Present; peaks < 3000 cm\(^{-1}\).
         Aldehyde C–H: Absent; no peak ~2700 cm\(^{-1}\).
         Carboxylic acid O–H: Absent; not broad enough.

Zone 3  Alkyne C≡C and nitrile C≡N: Absent; no peaks.

Zone 4  C=O: Present at 1727 cm\(^{-1}\); could be conjugated ester, ketone, or conjugated ketone.

Zone 5  Benzene ring: Present; peaks ~1600 cm\(^{-1}\) and ~1500 cm\(^{-1}\).
         Alkene C≡C: Uncertain, but \(^{13}\text{C-NMR does not provide strong evidence for benzene ring plus alkene.} \)
**$^1$H-NMR:**

<table>
<thead>
<tr>
<th>Chemical shift</th>
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<th>Integral</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.68–7.53 ppm</td>
<td>multiplet</td>
<td>4</td>
<td>4 H</td>
<td>Disubstituted benzene ring $C_6H_4$</td>
</tr>
<tr>
<td>4.26 ppm</td>
<td>triplet</td>
<td>4</td>
<td>4 H</td>
<td>$2 \times CH_2$ in $CH_2CH_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$2 \times CH_2$ in $CHCH_2CH$</td>
</tr>
<tr>
<td>1.75 ppm</td>
<td>sextet</td>
<td>4</td>
<td>4 H</td>
<td>$2 \times CH_2$ in $CH_2CHCH_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$4 \times CH$ in $CH_3(CH)(CH)_2$</td>
</tr>
<tr>
<td>1.00 ppm</td>
<td>triplet</td>
<td>6</td>
<td>6 H</td>
<td>$2 \times CH_3$ in $CH_3CH_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$3 \times CH_2$ in $CH_2CH_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$3 \times CH_2$ in $CHCH_2CH$</td>
</tr>
</tbody>
</table>

**Totals** 18 18 H  $C_6H_4 + (2 \times CH_2) + (2 \times CH_2) + (2 \times CH_3) = C_{12}H_{18}$

**$^{13}$C-NMR:** The formula contains 14 carbons whereas the $^{13}$C-NMR includes 8 signals, so some of the carbons are equivalent. The $^{13}$C-NMR and $^1$H-NMR suggest this symmetry lies in the benzene ring and the propyl groups. However, one benzene ring plus two propyl groups account for 12 of the 14 carbons in the molecule, and seven of the eight $^{13}$C-NMR signals. Therefore the molecule must have two equivalent ester C=O groups to account for the additional carbons.

**Atom check:** $C_{14}H_{18}O_4$ (from mass spectrum) - $C_{12}H_{18}$ (from $^1$H-NMR) - 2 x CO$_2$ (two esters from $^{13}$C-NMR) = all atoms accounted for.

**DBE check:** One benzene ring + two esters = 6 DBE.

**Pieces:**

$C_6H_4$

$2 \times CH_3$ in $CH_2CH_2$

$2 \times CH_2$ in $CH_2CH_2$

$2 \times CH_2$ in $CH_2CH_2CH_3$

$2 \times CO_2$ (ester)

**Assembly:** The $2 \times CH_2$, $2 \times CH_2$, and $2 \times CH_3$ pieces form two propyl groups.

$C_6H_4$

$2 \times CO_2$ (ester)

$2 \times CH_2$ in $CH_2CH_2CH_3$

The propyl groups cannot be directly attached to the benzene ring, because this leaves no place for the ester groups. Therefore the propyl groups must be attached to the ester groups, but is the propyl $CH_2$ attached to the $O$ or the $C=O$ of the ester? Chemical shifts provide the answer. The observed $^1$H-NMR chemical shift for the terminal $CH_2$ of the propyl group is 4.26 ppm, which is more consistent with $CH_2-O$ (typically 3.3–4.1 ppm) than $CH_2-C=O$ (typically 2.2–3.0 ppm).
Therefore the molecule consists of a benzene ring with two COOCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3} groups. What is the position of these esters on the benzene ring? There are three possible isomers:

- **Ortho isomer**
- **Meta isomer**
- **Para isomer**

The \textsuperscript{13}C-NMR reveals the molecule has four nonequivalent benzene ring carbons. Labeling sets of equivalent benzene ring carbons reveals that only the meta isomer has the benzene ring carbon equivalency suggested by the \textsuperscript{13}C-NMR spectrum.