H-NMR Implications

Hello fellow O-Chem students! When practicing spectroscopy problems do you struggle to understand the H-NMR implications? Have no fear, after reading this tutorial and dedicating some time to practice problems you will soon be an expert!

All H-NMR problems will be given in a format similar to this:
4.0 ppm (triplet; integral = 1), 3.9 ppm (singlet; integral = 1.5), 3.0 ppm (singlet, integral =1), 1.3 (sextet; integral = 1), .9 ppm (triplet; integral = 1.5)

-Calculated Formula from Mass Spectroscopy: C₆H₁₂O₃

**Step 1: Move all data into a table.**

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Splitting</th>
<th>Integration</th>
<th># of Hydrogens</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>Triplet</td>
<td>1</td>
<td>1 x 2 = 2</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>Singlet</td>
<td>1.5</td>
<td>1.5 x 2 = 3</td>
<td></td>
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<td>3.0</td>
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<td>1 x 2 = 2</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>Sextet</td>
<td>1</td>
<td>1 x 2 = 2</td>
<td></td>
</tr>
<tr>
<td>.9</td>
<td>Triplet</td>
<td>1.5</td>
<td>1.5 x 2 = 3</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>6</td>
<td>12 H</td>
<td></td>
</tr>
</tbody>
</table>

Before moving trying to list out all of the implications it’s important to remember the following about H-NMR.

1. **Chemical Shift:** Deshielding by electronegative atoms leads to a higher chemical shift.

2. **Splitting:** The signal of a proton with n neighbors is split n+1 lines (first order coupling). This means CH₃ is a singlet because it has n=0 neighbors (no H neighbors). CH₃CH is a doublet because it has n=1 neighbors (1 H neighbor). CH₃CH₂ is a triplet because it has n=2 neighbors (2 H neighbors). The rule follows as the number of H neighbors increases (ie. quartet, pentet. sextet…)

3. **Integration:** Add up the numbers in the integration to find the number of hydrogens → 1+1.5+1+1.5 = 6 Since there are 12 H’s in the formula (given by Mass Spectroscopy), there is a 1:2 ratio. Thus, multiply the integration number by 2 to find the # of H’s for your implications.

Now that have some solid background knowledge we can find the implications.

**Step 2: Use information from 1) splitting and 2) # of H’s to start finding implications.**

The first chemical shift has a triplet splitting pattern, meaning it has 2 H neighbors and 2 H in the actual implication based of integration.
Step 3: Determine what combinations of C\(_x\)H\(_y\) (number of H’s) you can have and the number of C\(_x\)H\(_y\) (number of H neighbors).

There can only be 2 H’s for each underlined portion (corresponding to the number of H’s) for the first chemical shift and for the non-underlined portion as well. Thus, you start with these two possibilities: CH in 2 x CH and CH\(_2\) in CH\(_2\).

Step 4: Combine the underlined portion with the various possibilities for the non-underlined portion number of C\(_x\)H\(_y\) (number of H neighbors).

CH in 2 x CH\(_2\)CH\(_2\)
CH in 2 x CHCHCH\(_3\)
CH\(_2\) in CH\(_2\)CH\(_2\)
CH\(_2\) in CH\(_2\)CH\(_2\)CH

I filled in subsequent shifts by following the same 4 steps.

**Hint:** Start by finding the simplest combinations (ie. CH, then CH\(_2\) and finally (if it has 3 H’s) CH\(_3\).

<table>
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<th>Integration</th>
<th># of Hydrogens</th>
<th>Implications</th>
</tr>
</thead>
</table>
| 4.0                  | Triplet   | 1           | 1 x 2 = 2      | CH in 2 x CHCH\(_2\)
|                      |           |             |                | CH in 2 x CHCHCH\(_3\)
|                      |           |             |                | CH\(_2\) in CH\(_2\)CH\(_2\)
|                      |           |             |                | CH\(_2\) in CH\(_2\)CH\(_2\)CH\(_2\)                                        |
| 3.9                  | Singlet   | 1.5         | 1.5 x 2 =3     | CH\(_3\) in CH\(_3\)
|                      |           |             |                | CH in 3 x CH                                                               |
| 3.0                  | Singlet   | 1           | 1 x 2 =2       | CH\(_2\) in CH\(_2\)
|                      |           |             |                | CH in 2 x CH                                                               |
| 1.3                  | Sextet    | 1           | 1 x 2 =2       | CH\(_2\) in CH\(_3\)CH\(_2\)
|                      |           |             |                | CH in 2xCH\(_3\)CH\(_2\)CH\(_2\)                                          |
|                      |           |             |                | CH in 2xCH\(_3\)CH(CH\(_2\))                                            |
| .9                   | Triplet   | 1.5         | 1.5 x 2 = 3    | CH\(_3\) in CH\(_3\)CH\(_2\)
|                      |           |             |                | CH in 3xCH\(_2\)CH\(_2\)                                                 |
|                      |           |             |                | CH in 3xCHCH\(_2\)CH                                                       |
| **Total**            |           | 6           | 12 H           |                                                                            |
**Hint:** The most likely implications are those with the LEAST number of atoms, in **bold**.
However, on the test Dr. H may give us something tricky and this may not always hold true. That is why we write all the implications!!

- Add up the **bold** implications to find your total from H-NMR:
  \[ \text{CH}_2 + \text{CH}_3 + \text{CH}_2 + \text{CH}_2 + \text{CH}_3 = \text{C}_5\text{H}_{12} \]
- Use this calculated formula and subtract it from the formula you got from Mass Spectroscopy to determine what atoms you have leftover.

**Practice Problems:**
1) 3.19 ppm (triplet; integral=1), 3.12 (singlet; integral=1), 1.84 ppm (triplet; integral=1), 1.12 ppm (singlet; integral=3) with formula C_6H_{12}Cl
2) 3.1 ppm (triplet; integral=1), 1.7 ppm (sextet; integral=1), 1.0 ppm (triplet; integral=1.5) with formula C_3H_7Br

**Solutions:**
1) Implications:
   - **Triplet-CH**\textsubscript{2} in CH\textsubscript{2}CH\textsubscript{2}
   - CH\textsubscript{2} in CHCH\textsubscript{2}CH
   - 2x CH in CH\textsubscript{2}CH
   - 2x CH in CHCHCH
   - **Singlet-CH**\textsubscript{2}
   - 2x CH

   - **Triplet-CH**\textsubscript{2} in CH\textsubscript{2}CH\textsubscript{2}
   - CH\textsubscript{2} in CHCH\textsubscript{2}CH
   - 2x CH in CH\textsubscript{2}CH
   - 2x CH in CHCHCH
   - **Singlet-2x CH**\textsubscript{3}
   - 3x CH

2) **Triplet- CH**\textsubscript{2} in CH\textsubscript{2}CH\textsubscript{2}
   - CH\textsubscript{2} in CH\textsubscript{2}CHCH
   - 2x CH in CH\textsubscript{2}CH
   - 2x CH in CHCHCH
   - **Sextet-CH**\textsubscript{2} in CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}
   - 2x CH in CH\textsubscript{2}CHCH\textsubscript{3}
   - 2x CH in (CH)\textsubscript{2}CHCH\textsubscript{3}
   - 2x CH in (CH\textsubscript{2})\textsubscript{2}CHCH

   - **Triplet-CH**\textsubscript{3} CH\textsubscript{3}CH\textsubscript{2}
   - 3x CH in CH\textsubscript{2}CH
   - 3 x CH in CHCHCH
Good luck on the test everyone! Study hard. 😊

Reference:
