Proton Nuclear Magnetic Resonance ($^1$H-NMR) Spectroscopy: Eating up our jigsaw puzzle cake! :D

$^1$H-NMR spectroscopy tells us the molecular structure of the compound or the arrangement of the connectivity of the atoms.

Basics of $^1$H-NMR Spectroscopy:

1. Chemical shift: the position of the signals on the x-axis of the $^1$H-NMR graph.
   A higher chemical shift indicates a greater electronegativity of atoms near the hydrogen we are examining. In addition, a higher chemical shift indicates a more deshielded (lesser electron density around) hydrogens.

2. Splitting: results from the influences of hydrogen’s neighbors.
   If hydrogen has “n” amount of neighbors, a signal will be split into “n+1” peaks.
   Remember that the neighbors need to be nonequivalent to the hydrogen that you are analyzing.

3. Integral: relative intensity of peak.
   In other words, the area under the peaks. We can determine the number of hydrogens present per signal.

4. Implications formula: possible arrangements of atoms per signal.

5. Molecular structure: Basically a jigsaw puzzle. But in the end, with more practice, the jigsaw puzzle will be a piece of cake! Yum!!!

Tips of $^1$H-NMR Spectroscopy:

1. Double bond equivalence, DBE
   a. DBE ≥ 4, There exists a possible benzene ring.

2. (Chemical) Shift
   a. A chemical shift that is greater than 6.5 ppm generally indicates that we have a benzene ring or a benzene ring with attachments.
   b. Do not always assume that a range of chemical shift values indicate a specific atom, group of atoms, and functional groups.
   c. The closer the hydrogen is to an electronegative atom in the structure, the greater the chemical shift will be.

3. Splitting
   a. Multiplet generally indicates a ring of atoms (for example, benzene).

4. Integral
   a. Lowest integral is usually set as 1 in order to make calculations easier.
5. The Puzzle
   a. From the jigsaw pieces that we’ve created (the different derivations of the hydrogen attachments with respect to the neighboring atoms), you can generally assume the jigsaw piece with the least number of atoms.
   b. For the jigsaw pieces, do not violate the valence shell rules!
      i. For example, carbon can only have a maximum of 8 valence electrons (octet rule).
      ii. Keep note that we can have a double bond for atoms, such as oxygen and nitrogen. If we have at least one oxygen in the molecular formula, we can have functional groups, such as an ether, ketone, and aldehyde. If we have at least 2 oxygens, we can have an ester.

The Process:

1. Calculate DBE based on molecular formula, which is determined from mass spectroscopy:
   a. DBE = C – H/2 + N/2 + 1
2. Determine the ratio between the number of hydrogens and integral.
   a. For example, molecular formula: C₉H₁₀

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<table>
<thead>
<tr>
<th>Integral</th>
<th>Number of Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4 Integral (1 Hydrogen/Integral) = 4 Hydrogens</td>
</tr>
<tr>
<td>4</td>
<td>4 Integral (1 Hydrogen/Integral) = 4 Hydrogens</td>
</tr>
<tr>
<td>2</td>
<td>4 Integral (1 Hydrogen/Integral) = 2 Hydrogens</td>
</tr>
</tbody>
</table>
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3. Derive the possible arrangements of the hydrogen atoms with neighboring Hydrogen atoms.
   a. These arrangements vary depending on the splitting of the signals.
   b. For example, if we have a triplet, we know that we have $3 - 1 = 2$ Hydrogen neighbors.
      i. We will go into more detail in our problem.
4. Based on the jigsaw pieces (the possible arrangements of atoms per signal that we have determined from integral and splitting), we now put these pieces together to make one whole picture.
5. Check your jigsaw puzzle (the structure you made) with the molecular formula (from mass spectroscopy) and the functional groups (from infrared/IR spectroscopy). Also, by
looking at the DBE and counting the number of atoms of your created structure, check that the structure you made match the number of atoms from the pieces used.

Problem:

1. Molecular Formula (determined from mass spectroscopy): C$_9$H$_{10}$
   Alkane CH’s and benzene ring are present (determined from IR spectroscopy).
   DBE = 9 – 10/2 + 0/2 + 1 = 9 – 5 + 1 = 5

<table>
<thead>
<tr>
<th>Shift</th>
<th>Splitting</th>
<th>Integral</th>
<th>Hydrogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 ppm</td>
<td>Multiplet</td>
<td>4</td>
<td>4 (1 Hydrogen / 1 Integral) = 4 Hydrogens</td>
</tr>
<tr>
<td>2.9 ppm</td>
<td>Triplet</td>
<td>4</td>
<td>4 (1 Hydrogen / 1 Integral) = 4 Hydrogens</td>
</tr>
<tr>
<td>2.1 ppm</td>
<td>Pentet</td>
<td>2</td>
<td>2 (1 Hydrogen / 1 Integral) = 2 Hydrogens</td>
</tr>
</tbody>
</table>

Total Integral = 4 + 4 + 2 = 10 Integral
From molecular formula: Total Number of Hydrogens = 10
Ratio between number of hydrogens and integral = 10 Hydrogens / 10 Integral = 1 Hydrogen / 1 Integral

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<td>C$_6$H$_4$</td>
</tr>
<tr>
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<td>Triplet</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>2.1 ppm</td>
<td>Pentet</td>
<td>2</td>
<td></td>
</tr>
</tbody>
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7.1 ppm > 6.5 ppm and from IR Spectroscopy, benzene ring or a benzene ring with attachements is present.

C$_6$H$_4$

- H$_4$ because we have 4 Hydrogens (integral of 4)
- DBE: 5 – 4 = 1, because benzene ring is present, so 3 pi bonds plus another pi bond for the ring, so 4 DBE total is used up.

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<td>4</td>
<td>2x CH$_2$CH$_2$</td>
</tr>
<tr>
<td>2.1 ppm</td>
<td>Pentet</td>
<td>2</td>
<td>2x CHCH$_2$CH</td>
</tr>
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Possible jigsaw pieces/arrangements:
2x CH$_2$CH$_2$
- The underline indicates the hydrogen we are examining. Since integral is 4, we need to have a total of 4 hydrogens and therefore, we have 2x for 2xCH₂ => H₄ (4 hydrogens). Also, the 2x means that we have two of the CH₃CH₂ set.
- Triplet indicates 3 – 2 neighbors. The not underlined portion indicates the neighboring hydrogen atoms. In this jigsaw piece, CH₃CH₂, we have one CH₂ around CH₂. There are already 2 neighboring hydrogens (from CH₂) around the hydrogens that we are examining.

2x CHCH₂CH

- We do not have a combination of CH₄CH₂ or CHCH₂CH because we would be violating the valence shell (octet rule for carbon).

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<td></td>
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Possible jigsaw pieces/arrangements:
CH₂CH₂CH₂
CHCH₂CH₃
- We do not include CH₃CH₂CH because CHCH₂CH₃ and CH₃CH₂CH are the same.

2x CHCHCH₃
- We do not include 2x CH₃CHCH because 2x CHCHCH₃ and 2x CH₃CHCH are the same.

2x CH₂CHCH₂

Jigsaw puzzle time!!! – Eating up our pieces of cake

Taking the least number of atoms for the chemical shift 2.9 ppm, we pick 2x CH₂CH₂. 2x CH₂CH₂ means that we have a combination that has two CH₂ with two neighboring hydrogen atom of CH₂. CH₂ is the commonality between the two CH₂CH₂.

Now, looking at the possible jigsaw pieces for the chemical shift 2.1 ppm, we figure out which jigsaw piece contains CH₂CH₂. CH₂CH₂CH₂ contains CH₂CH₂ and then, we figure out a way to include CH₂CH₂CH₂ to match up with the benzene jigsaw piece, C₆H₄.

With the benzene ring, we only have one DBE left. This one DBE means that we can either have a ring or a double bond. We know that we do not have a double bond because the IR
spectroscopy did not indicate the presence of an alkene. However, it is possible to have a ring, so we need to figure out a way to make a ring that attached to the benzene ring.

So, now that we know that we need to have a benzene ring with attachments (C₆H₄), “two” (note: the quotation marks around two) attachments of CH₂CH₂CH₂ to the benzene ring, and a ring from the one DBE, we can start formulating a structure. The CH₂CH₂CH₂ can form a ring that can attach to the benzene ring. As such, we will have a structure such as the following:

![Structure](image)

We now check our structure to make sure that it follows the molecular formula.

We have 6 carbons and four hydrogens from the benzene ring. From the other ring, we have 3 carbons and 6 hydrogens. 6 + 3 carbons = 9 carbons. 4 + 6 hydrogens = 10 hydrogens. Our given molecular formula is C₉H₁₀ and our structure matches the number of carbons and hydrogens. Congratulations! We’ve determined the structure of for this problem.

Reference:

