Solving Spectroscopy Problems
Step by Step — Figuring out the implications in $^1$H-NMR

Is this how you feel when solving spectroscopy problems?
• I know how to get the formula from mass spectrometry ✔
• I know how to get the DBE from the formula ✔
• I know how to analyze the IR spectrum to see what functional groups are present and absent in each zone ✔
• I know how to start the $^1$H-NMR:
  • I copied the NMR data to the table:

<table>
<thead>
<tr>
<th>Chemical shift</th>
<th>Splitting</th>
<th>Integral</th>
<th># of H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>..... ppm</td>
<td>.....</td>
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<td>..... ppm</td>
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<td>..... ppm</td>
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</tr>
</tbody>
</table>

• I converted the integral to the # of hydrogens accordingly
• NOW WHAT?
  • How do I combine the splitting with the number of hydrogens to get the IMPLICATIONS, so I can finish the problem and actually get the structure for the formula?

Summary — Procedure in solving spectroscopy problems
✓ Formula (from mass spectrometry)
  • m/z: ... (M): Molecular weight (lowest mass isotopes)
  • m/z: ... (M+1): Carbon count
  • m/z: ... (M+2): Presence of S, Cl, or Br

✓ DBE (from formula)
  • C - H/2 - N/2 + 1
    • One DBE = 1 ring or 1 pi bond
    • Two DBE = 2 rings, 2 pi bonds, or 1 ring and 1 pi bond
    • Four DBE = maybe benzene ring

✓ IR analysis of functional groups (The Five Zones)
  • Formula and DBE
    • Zone 1 (3700-3200 cm$^{-1}$)
      • Alcohol O-H
      • Amide/amine N-H
      • Terminal alkyne ≡C-H
    • Zone 2 (3200-2700 cm$^{-1}$)
      • Aryl/vinyl $sp^2$ C-H
      • Alkyl $sp^3$ C-H
• Aldehyde C-H
• Carboxylic acid O-H
• Zone 3 (2300-2000 cm\(^{-1}\))
  • Alkyne C≡C
  • Nitrile C≡N
• Zone 4 (1850-1650 cm\(^{-1}\))
  • Carbonyl C=O (if present)...
    • Ketone
    • Ester
    • Aldehyde
    • Carboxylic acid
    • Amide
• Zone 5 (1680-1450 cm\(^{-1}\))
  • Benzene ring
  • Alkene C=C

C-H Skeleton from \(^1\)H-NMR
1. Copy the given NMR data to the table (shown above) ✔
2. Divide the hydrogens according to the integrals ✔
3. Combine the splitting with the number of hydrogens to get the implications ✔
4. Select the “best” implication (least # of atoms)
5. Check that all the atoms and DBE are used
6. Assemble all the pieces to obtain the structure
7. Check your work!

STEP BY STEP: (A closer look at the implications)

The information in the table tells us:
❖ Chemical shift- tells the position of signals (magnetic environment of protons)
❖ Splitting of signals- tells proton neighbors
  • The signal for a proton with \(n\) neighbors is split into \(n+1\) lines
  • For example:
    • Singlet- no neighbors
    • Doublet- one neighbor
    • Triplet- two neighbors
    • Quartet- three neighbors
    • Pentet- four neighbors
    • Sextet- five neighbors
❖ Use the integral to find the number of hydrogens
Correspond each signal to CH$_3$, CH$_2$, CH, OH, NH depending on the number of hydrogens

- For example:
  - 1 H - CH or OH (if oxygen present in formula) or NH (if nitrogen present in formula)
    - Consider the IR spectrum to determine whether it is likely for an OH or NH. Look at what functional groups are present in each zone.
  - 2 H - CH$_2$ or 2 x CH or 2 x OH (if there is enough oxygen in formula) or 2 x NH (if there is enough nitrogen in formula)
    - “Enough” in formula = the IR does not eliminate it or the $^1$H-NMR signal is not split
  - 3 H - CH$_3$ or 3 x CH or 3 x OH or 3 x NH (same applies from above-consider if there is “enough” in the formula or even if they are present)
  - 4 H - 2 x CH$_2$ or 4 x CH or 4 x OH or 4 x NH (same applies from above-consider if there is “enough” in the formula or even if they are present)

**To get the implications:**
1. Use the number of hydrogens to determine what the signal corresponds to:
   - CH$_3$, CH$_2$, CH, OH, NH, etc.
2. Use the n+1 rule and the splitting patterns in the table to find ALL the possible implications of the $^1$H-NMR signals.
   - For example:
     - From the table- 2H triplet → splitting: triplet and # of H: 2H
       - From the number of hydrogens, you know that the signals can either be CH$_2$ or 2 x CH
       - From the splitting pattern, you know that each signal must have 2 neighbors (triplet: n+1=3; n=2)
       - From this, you can tell that:
         - CH$_2$ can have two neighbors when it is:
           - Next to CH$_2$ → CH$_2$ in CH$_2$CH$_2$
           - Between two CH → CH$_2$ in CHCH$_2$CH
         - 2 x CH can have two neighbors when it is:
           - Next to CH$_2$ → 2 x CH in CHCH$_2$
           - Between two CH → 2 x CH in CHCHCH
       - Therefore, these are all the possibilities of the $^1$H-NMR signals:
         (The underlined hydrogens correspond to the given chemical shifts)
         CH$_2$ in CH$_2$CH$_2$
         CH$_2$ in CHCHCH
         2 x CH in CHCH$_2$
         2 x CH in CHCHCH
HELPFUL!
If you are still having trouble determining all the possibilities of the $^1$H-NMR signals, then think about using this small table for EACH NMR signal to come up with all the implications.

<table>
<thead>
<tr>
<th>Neighbors (splitting)</th>
<th>Number of hydrogens (integral)</th>
<th>CH$_2$</th>
<th>2 x CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$</td>
<td>CH$_2$ in CH$_2$CH$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH and CH</td>
<td>CH$_2$ in CHCH$_2$CH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

You can also draw the more expanded versions of all the possibilities to help you visualize it better:

3. After you have determined all the possibilities for the $^1$H-NMR signals, choose the simplest piece that gives the least number of atoms for each signal.
   - In the example above, the best guess is: CH$_2$ in CH$_2$CH$_2$
4. Now, that you know the steps in getting the implications, you can finally find ALL the pieces, and assemble them to make your final structure for the formula!
C-H Skeleton from $^1$H-NMR

1. Copy the given NMR data to the table (shown above) ✔
2. Divide the hydrogens according to the integrals ✔
3. **Combine the splitting with the number of hydrogens to get the implications** ✔
4. Select the “best” implication (least # of atoms) ✔
5. Check that all the atoms and DBE are used ✔
6. Assemble all the pieces to obtain the structure ✔
7. Check your work!!

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Practice: Dr. Hardinger’s Thinkbook Page 158 #2a

Write all possible implications for the following integral and splitting combination:

3H singlet

1. Use the number of hydrogens to determine what the signal corresponds to:
   • CH$_3$, CH$_2$, CH, OH, NH, etc.
   • 3 hydrogens $\to$ CH$_3$ or 3 x CH; also 3 x OH or 3 NH
2. Use the n+1 rule and the splitting patterns in the table to find ALL the possibilities of the $^1$H-NMR signals.
   • singlet $\to$ no neighbors

From this, all the possible implications for the following integral and splitting combinations are: **CH$_3$ or 3 x CH or 3 x OH or 3 NH**

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Works Cited

- Dr.Harding’s Chemistry 14C Lecture Supplement
  - Proton NMR Spectroscopy
  - Solving Spectroscopy Problems
- Dr.Harding’s Thinkbook (Practice problems)
- All images (modified from Thinkbook or google)
- http://www.chem.ucla.edu/harding/index.html