Lectures 7 and 8 – Worked Problems
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Recap of Lecture 6

IR Spectroscopy

Useful for identifying functional groups present in organic molecules.

The X–H region ( > 2500 cm\(^{-1}\)) contains diagnostic absorptions from N–H and O–H stretches. On occasion C–H stretches may also be a useful diagnostic tool.

O–H stretches are broadened by H-bonding: intermolecular and intramolecular H-bonding are distinguished by taking spectra at different concentrations.

The triple bond region (2000–2500 cm\(^{-1}\)) contains diagnostic information from e.g. nitriles and alkynes.

The double bond region (1600–2000 cm\(^{-1}\)) contains absorptions from C=C (albeit weakly, around 1650) and from C=O (strongly, around 1700).

Carbonyls are strengthened by a neighbouring EWG and weakened by a neighbouring EDG.

Conjugation weakens carbonyls (approx. minus 30 cm\(^{-1}\)).

Ring strain stiffens carbonyls (approx. 40 cm\(^{-1}\) for successively smaller rings).
Solving Structures

*Double-bond equivalents (DBE)*:
If the molecular formula has been obtained from the mass spectrum, the number of *double-bond equivalents (DBE)* may be calculated. If the molecule contains only C, H, N and O atoms and is neutral, then:

\[
DBE = (2a + 2) - (b - c)
\]

The DBE is the number of double bonds and rings in the molecule (it is useful to remember that benzene has a total of four double-bond equivalents: three C=C double-bonds and one ring).

The above formula works since \((2a + 2)\) is the number of hydrogens in a saturated hydrocarbon and so subtracting \(b\), the actual number of hydrogens present and dividing by two gives the total number of double bonds and rings. The number of divalent atoms (e.g. O, S, etc) does not affect the DBE, but the number of mono- and trivalent atoms does. All monovalent atoms (e.g. F, Cl, Br, etc) count as hydrogens so should be added to \(b\), whilst all trivalent atoms (e.g. N, trivalent P, etc) count towards \(c\).
Solving Structures

Worked Problem: Determine the structures of seven isomers of $\text{C}_5\text{H}_{10}\text{O}$ using the following $^1\text{H}$, $^{13}\text{C}$ (broadband decoupled and DEPT-edited) NMR spectra:

Compound A: $^1\text{H}$ NMR

$\nu$ (ppm) 1.99 3.00 2.00 3.03

$\nu$ (ppm) 9 8 7 6 5 4 3 2 1 0

$\nu$ (ppm) 200 180 160 140 120 100 80 60 40 20 0

$\nu$ (ppm) 200
Solving Structures

Compound A: $\text{C}_5\text{H}_{10}\text{O}$

$^1\text{H}$ NMR data:

$\text{H}_a$ 2.38 2H  $t$
$\text{H}_b$ 2.1 3H  $s$
$\text{H}_c$ 1.58 2H  $sext$
$\text{H}_d$ 0.9 3H  $t$

Structural Fragments:

Structure of A: $^1\text{C}$ NMR Assignment:
Solving Structures

Compound B: $^1$H NMR

$^{13}$C NMR
Solving Structures

Compound B: C₅H₁₀O

\(^1\text{H} \text{NMR data:}\)

<table>
<thead>
<tr>
<th>H</th>
<th>δ</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hₐ</td>
<td>9.8</td>
<td>1H t</td>
</tr>
<tr>
<td>Hₖ</td>
<td>2.32</td>
<td>dd</td>
</tr>
<tr>
<td>Hₙ</td>
<td>2.23</td>
<td>m</td>
</tr>
<tr>
<td>Hₙ</td>
<td>1.0</td>
<td>6H d</td>
</tr>
</tbody>
</table>

Structural Fragments:

\(DBEs = 1\)

Structure of B: 

\(^{13}\text{C} \text{NMR Assignment:}\)
Solving Structures

Compound C: $^1$H NMR

$^1$C NMR
Solving Structures

Compound C: C₅H₁₀O

¹H NMR data:
Hₐ  9.78  1H    t
Hₐ  2.45  2H    td
Hₐ  1.64  2H    quin
Hₐ  1.38  2H    sext
Hₐ  0.95  3H    t

Structural Fragments:

Structure of C:

¹³C NMR Assignment:
Solving Structures

Compound D: \(^1H\) NMR

\(^{13}C\) NMR
Solving Structures

Compound D: C₅H₁₀O

¹H NMR data:
Hₐ  2.43  4H  q
Hₐ  1.05  6H  t

Structural Fragments:

Structure of D: ¹³C NMR Assignment:
Solving Structures

Compound E: $^1$H NMR

$^{13}$C NMR
Solving Structures

Compound E: C₅H₁₀O

¹H NMR data:

H₀  9.64  1H   d
H₁  2.29  1H   sext d
H₂  1.47  1H   complex multiplet
H₃  1.77  1H   complex multiplet
H₄  1.11  3H   d
H₅  0.97  3H   t

Structural Fragments:

Structure of E:

¹³C NMR Assignment:
Solving Structures

Compound F: $^1$H NMR

$^{13}$C NMR
Solving Structures

Compound F: C₅H₁₀O

¹H NMR data:
Hₐ  2.59  1H  sept
Hₖ  2.14  3H  s
Hₜ  1.1   6H  d

Structural Fragments:

Structure of F: 

¹³C NMR Assignment:
Solving Structures

Compound G: $^1$H NMR

$^{13}$C NMR
Solving Structures

Compound G: C₅H₁₀O

¹H NMR data:

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<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Hₐ</td>
<td>9.5</td>
<td>1H</td>
</tr>
<tr>
<td>Hₐ</td>
<td>1.1</td>
<td>9H</td>
</tr>
</tbody>
</table>

Structural Fragments:

Structure of G: 

¹³C NMR Assignment:
Solving Structures

Worked Problem: Determine the structure of $X$, $C_{13}H_{18}O_2$ given the following spectroscopic data:

DBEs:

IR spectrum:

Diagnostic absorptions:
### Solving Structures

\(^1\text{H} \text{ NMR spectrum (500 MHz):}\)

- d 0.86 (6H, d, J= 6.6 Hz), 1.34 (3H, d, J=7.1 Hz), 1.81 (1H, 9lines, J=6.6 Hz), 2.41 (2H, d, J=6.6 Hz),
- 3.63 (1H, q, J = 7.1 Hz), 7.10 (2H, d, 8.1 Hz), 7.19 (2H, d, J = 8.1 Hz) 12.25 (1H, broad s)

\(^1\text{H} \text{ NMR spectrum: (8 peaks, so 8 proton environments)}\)

<table>
<thead>
<tr>
<th>(H_a)</th>
<th>0.86</th>
<th>6H</th>
<th>d</th>
<th>(J = 6.6 \text{ Hz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_b)</td>
<td>1.34</td>
<td>3H</td>
<td>d</td>
<td>(J = 7.1 \text{ Hz})</td>
</tr>
<tr>
<td>(H_c)</td>
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<td>1H</td>
<td>9 lines</td>
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<td>2H</td>
<td>d</td>
<td>(J = 6.6 \text{ Hz})</td>
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<tr>
<td>(H_e)</td>
<td>3.63</td>
<td>1H</td>
<td>q</td>
<td>(J = 7.1 \text{ Hz})</td>
</tr>
<tr>
<td>(H_f)</td>
<td>7.10</td>
<td>2H</td>
<td>d</td>
<td>(J = 8.1 \text{ Hz})</td>
</tr>
<tr>
<td>(H_g)</td>
<td>7.19</td>
<td>2H</td>
<td>d</td>
<td>(J = 8.1 \text{ Hz})</td>
</tr>
<tr>
<td>(H_h)</td>
<td>12.25</td>
<td>1H</td>
<td>broad</td>
<td></td>
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</tbody>
</table>
Solving Structures

\(^{13}\)C NMR spectrum (125 MHz, proton decoupled)  \(^{13}\)C DEPT spectrum (125 MHz, proton decoupled):

Structural fragments:

Structure of X
Solving Structures

Worked Problem: Determine the structure of Y, C₈H₆O₃ given the following spectroscopic data:

DBEs:

IR spectrum:

Diagnostic absorptions:
### Solving Structures

$^1$H NMR spectrum (500 MHz): $\delta$ 6.04 (2H, s) 6.89 (1H, d, $J$=7.95 Hz), 7.28 (1H, d, $J$=1.6 Hz), 7.37 (1H, dd, $J$=7.95, 1.6 Hz), 9.77 (1H, s).

![NMR Spectrum Image]

$^1$H NMR spectrum: (5 peaks, so 5 proton environments)

<table>
<thead>
<tr>
<th>$H_a$</th>
<th>6.04</th>
<th>2H</th>
<th>s</th>
</tr>
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<tr>
<td>$H_b$</td>
<td>6.89</td>
<td>1H</td>
<td>d</td>
</tr>
<tr>
<td>$H_c$</td>
<td>7.28</td>
<td>1H</td>
<td>d</td>
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<td>1H</td>
<td>dd</td>
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<tr>
<td>$H_e$</td>
<td>9.77</td>
<td>1H</td>
<td>s</td>
</tr>
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</table>
Solving Structures

$^{13}$C NMR spectrum (125 MHz, proton decoupled):

$^{13}$C DEPT spectrum (125 MHz, proton decoupled):

Structural fragments:

Structure of Y
**Solving Structures**

**Worked Problem:** Determine the structure of Z, C₈H₁₄O given the following spectroscopic data:

DBEs:

IR spectrum:

![IR Spectrum](image)

Diagnostic absorptions:
Solving Structures

$^1$H NMR spectrum (300 MHz): δ 1.59 (3H, d, J=1.4 Hz) 1.67 (3H, d, J=1.4 Hz), 2.09 (3H, s), 2.24 (2H, q, J=7.2 Hz), 2.41 (2H, t, J=7.2 Hz), 5.05 (1H 3 x 7 lines, J=7.2, 1.4 Hz)

$^1$H NMR spectrum: (5 peaks, so 5 proton environments)

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<thead>
<tr>
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<tbody>
<tr>
<td>Ha</td>
<td>1.59</td>
<td>3H</td>
<td>d</td>
</tr>
<tr>
<td>Hb</td>
<td>1.67</td>
<td>3H</td>
<td>d</td>
</tr>
<tr>
<td>Hc</td>
<td>2.09</td>
<td>3H</td>
<td>s</td>
</tr>
<tr>
<td>Hd</td>
<td>2.24</td>
<td>2H</td>
<td>q</td>
</tr>
<tr>
<td>He</td>
<td>2.41</td>
<td>2H</td>
<td>t</td>
</tr>
<tr>
<td>Hf</td>
<td>5.05</td>
<td>1H</td>
<td>3x7 lines</td>
</tr>
</tbody>
</table>
Solving Structures

$^{13}$C NMR spectrum (75 MHz, proton decoupled):

$^{13}$C DEPT spectrum (125 MHz, proton decoupled):

Structural fragments:

Structure of Z