Spin-Spin Coupling

Structure Evaluation

\[ J_{\text{trans}} > J_{\text{cis}} > J_{\text{gem}} \]

\[ J_{\text{trans}} = 15-18 \text{ Hz} \]
\[ J_{\text{cis}} = 9-12 \text{ Hz} \]
\[ J_{\text{gem}} = 1-3 \text{ Hz} \]

\[ J_{ab} = 4-10 \text{ Hz} \]
Spin-Spin Coupling

Structure Evaluation

vinyl acetate
Spin-Spin Coupling

Structure Evaluation

vinyl acetate

Hz

$H_c$: 2192.85 2186.60 2178.88 2172.63

$H_b$: 1472.57 1471.09 1458.59 1456.75

$H_a$: 1374.76 1373.29 1368.51 1367.04

Hz

$H_c$: 14.0 6.2

$H_b$: 14.0 1.5

$H_a$: 6.2 1.5

Structure of vinyl acetate with peaks and coupling constants.
Spin-Spin Coupling

Structure Evaluation

vinyl acetate

\[
\begin{align*}
J_{bc} &= 14.0 \text{ Hz} \\
J_{ac} &= 6.2 \text{ Hz} \\
J_{bc} &= 14.0 \text{ Hz} \\
J_{ba} &= 1.5 \text{ Hz} \\
J_{ac} &= 6.2 \text{ Hz} \\
J_{ab} &= 1.5 \text{ Hz}
\end{align*}
\]
Spin-Spin Coupling

Structure Evaluation

crotonic acid
**Spin-Spin Coupling**

Structure Evaluation

crotonic acid

\[
\begin{align*}
H_a & \quad Hz \\
7.0 & \quad 7.05, 580.98, 579.18, 573.93, 572.29 & \quad 1.80, 1.64, 1.7 \\
J & = 7.0, 1.7 \text{ Hz}
\end{align*}
\]

doublet of doublets (dd)

\[
\begin{align*}
J_{ac} & = 7.0 \text{ Hz} \\
J_{ab} & = 1.7 \text{ Hz}
\end{align*}
\]
Spin-Spin Coupling

Structure Evaluation

crotonic acid

\[ \text{H}_b \]

\( J = 15.5, 1.6 \text{ Hz} \)

\[
\begin{align*}
1767.89 \\
1766.25 \\
1764.61 \\
1762.96 \\
1752.46 \\
1750.82 \\
1749.02 \\
1747.38
\end{align*}
\]

doublet of quartets (dq)
Spin-Spin Coupling

Structure Evaluation

crotonic acid

\[ \text{H}_c \quad \text{Hz} \]
2150.34
2143.45
2136.39
2134.75
2129.50
2127.86
2120.97
2114.08

\[ J = 15.5, \, 6.9 \, \text{Hz} \]
Spin-Spin Coupling

Structure Evaluation

crotonic acid

\[ \text{C}_3\text{H}_5\text{CO}_2\text{H} \]

\[ \begin{align*}
\text{H} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{CO}_2\text{H}
\end{align*} \]

\[ \begin{align*}
\text{A} & \quad \text{B} \\
& \quad \text{C}
\end{align*} \]

\[ \begin{align*}
\text{H}_c \\
J = 15.5 \text{ Hz} \\
J = 6.9 \text{ Hz} \\
J = 6.9 \text{ Hz} \\
J = 6.9 \text{ Hz}
\end{align*} \]
Spin-Spin Coupling

Structure Evaluation

\[ J_{\text{trans}} > J_{\text{cis}} > J_{\text{gem}} \]

\[ J_{\text{trans}} = 15-18 \text{ Hz} \]
\[ J_{\text{cis}} = 9-12 \text{ Hz} \]
\[ J_{\text{gem}} = 1-3 \text{ Hz} \]
Spin-Spin Coupling

Structure Evaluation

crotonic acid

\[ J = 15.5, 6.9 \text{ Hz} \]
\[ J = 15.5, 1.6 \text{ Hz} \]
\[ J = 7.0, 1.7 \text{ Hz} \]

\[
\begin{align*}
\text{A} & : J_{\text{gem}} = 1-3 \text{ Hz} \\
\text{B} & : J_{\text{trans}} = 11-18 \\
\text{C} & : J_{\text{cis}} = 9-12, J_{\text{allyl}} = 1-3
\end{align*}
\]

crotonic acid: \[ J = 15.5, 7.0, 1.6 \text{ Hz} \]
Spin-Spin Coupling

Structure Evaluation

Analysis of Coupling Constants – First Order Spectra

Some helpful constraints:

• For every signal split into a multiplet, the component $J$-value(s) must match some other multiplet in the spectrum

• The distance (Hz) between the two outermost peaks in a multiplet is equal to the sum of each of the coupling constants

• The smallest $J$-value is typically given by the difference between the first and second peaks in the multiplet

• First order multiplets are symmetrically distributed about the center
**Spin-Spin Coupling**

**Structure Evaluation**

**Analysis of Coupling Constants – First Order Spectra**

Start with the simplest multiplet ($H_c$):

$H_c$ is an apparent doublet of doublets (dd)

**Step 1:**

- The distance between the first two lines always represents the smallest $J$ value
- If the ratio of these two lines (integral) is 1:1, this $J$ is unique; if it is 1:2, 1:3, etc. there are two or more identical smallest $J$s
  - 1:1 comes from coupling to one nucleus (e.g. doublet)
  - 1:2 first $J$ comes from coupling of 2 nuclei with same coupling constant → part of a 1:2:1 pattern
  - 1:3 first $J$ comes from coupling of 3 nuclei with same coupling constant → part of a 1:3:3:1 pattern
- Label this $J_{\text{small}}$

<table>
<thead>
<tr>
<th>$H_c$ (Hz)</th>
<th>580.98</th>
<th>579.18</th>
<th>573.93</th>
<th>572.29</th>
</tr>
</thead>
</table>

$580.98 - 579.18 = 1.80$ Hz
**Spin-Spin Coupling**

**Structure Evaluation**

**Analysis of Coupling Constants – First Order Spectra**

**Step 2:** (most difficult step for complex multiplets)
- Find the full set of pairs within the multiplet that are separated by \( J_{\text{small}} \)
- Each pair will have a reflected partner through the center of the multiplet
- For pairs where one of the lines has a relative intensity >1, that line will be part of more than one pair

\[
580.98 - 579.18 = 1.80 \text{ Hz}
\]
\[
579.18 - 573.93 = 5.25 \text{ Hz}
\]
\[
573.93 - 572.29 = 1.64 \text{ Hz}
\]

While these two may not seem equal, they must be matched if 1\textsuperscript{st} order
Spin-Spin Coupling

Structure Evaluation

Analysis of Coupling Constants – First Order Spectra

Step 3:

- Find the centers of each of the pairs generated in step 2 (average)
- These will collectively represent a new pattern (as if the $J_{\text{small}}$ was selectively decoupled)
- As with step 1, the spacing between the first two lines of this multiplet represent the next smallest $J$
- Label this $J$ as med-small, etc. as necessary

\[
\begin{align*}
H_c &:
\begin{array}{c}
580.98 \\
579.18 \\
573.93 \\
572.29 \\
\end{array}
\end{align*}
\]

\[
580.98 - 573.11 = 6.97
\]
Spin-Spin Coupling

Structure Evaluation

Analysis of Coupling Constants – First Order Spectra

Step 4:
• Find the midpoint(s) of this new pair(s), and repeat step 3

Step 5:
• Repeat steps 2 and 3 as necessary until all $J$-values have been found
• Remember, it must be internally consistent and all the $J$ values must add up to the difference between the outer peaks of the multiplet.

CHECK:
The two $J$s we determined are 1.80 (1.64) and 6.97

$$\frac{(1.80+1.64)}{2} + 6.97 = 8.69$$

The difference between the outermost peaks of the multiplet:

$$580.98 - 572.29 = 8.69$$
Spin-Spin Coupling

Structure Evaluation

Analysis of Coupling Constants – First Order Spectra

This process effectively generates a tree-diagram!

\[ H_c \]

\[ J_{\text{med}} = 7.0 \text{ Hz} \]

\[ J_{\text{small}} = 1.7 \text{ Hz} \] (average of 1.80 and 1.64)

This proton is coupled to two other protons, with coupling constants of 1.7 and 7.0; (1H, dd, J = 7.0, 1.7 Hz)
Spin-Spin Coupling

Structure Evaluation

Analysis of Coupling Constants – First Order Spectra

Repeat the analysis with the next most complex multiplet
Look for possible $J$-values of 1.72 and 6.97
Analyzing the $H_b$ proton; apparent doublet of quartets (dq):

Check:

$1.64 + 1.64 + 1.64 + 15.51 = 20.43$

$1767.89 - 1747.38 = 20.51$
Spin-Spin Coupling

Structure Evaluation

Analysis of Coupling Constants – First Order Spectra

Tree diagram for H_b:

\[ J_{\text{large}} = 15.5 \text{ Hz} \]
\[ J_{\text{small}} = 1.64 \text{ Hz} \]
\[ J_{\text{small}} = 1.64 \text{ Hz} \]
Spin-Spin Coupling

Structure Evaluation

Analysis of Coupling Constants – First Order Spectra

Tree diagram for $H_a$:

$J_{med} = 15.4$ Hz

$J_{small} = 6.9$ Hz
Spin-Spin Coupling

Structure Evaluation

4-allyloxyanisole

![Chemical structure of 4-allyloxyanisole](image)
Spin-Spin Coupling

Structure Evaluation

4-allyloxyanisole

expect (H_a)?
Spin-Spin Coupling

Tree Diagrams

Structure Evaluation

expect (H\textsubscript{a}):
\begin{align*}
J\text{ad} &= 4-10 \text{ Hz (7)} \\
J\text{ab} &= 0-3 \text{ Hz (2)} \\
J\text{ac} &= 0-3 \text{ Hz (2)}
\end{align*}
**Spin-Spin Coupling**

**Structure Evaluation**

**4-allyloxyanisole**

<table>
<thead>
<tr>
<th>Positions of peaks (Hz)</th>
<th>1.47</th>
<th>5.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1348.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1347.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1344.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1343.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1342.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Doublet of triplets**

\[ \delta 4.49 \ (1H, \text{dt}, J = 5.2, 1.5 \text{ Hz}) \]
Spin-Spin Coupling

Structure Evaluation

4-allyloxyanisole

expect (H_b)?
**Spin-Spin Coupling**

*Tree Diagrams*

**Structure Evaluation**

expect (H<sub>b</sub>):

- \( J_{bd} = 9-12 \text{ Hz} \) (10)
- \( J_{bc} = 1-3 \text{ Hz} \) (2)
- \( J_{ba} = 0-3 \text{ Hz} \) (2)
**Spin-Spin Coupling**

**Structure Evaluation**

**4-allyloxyanisole**

<table>
<thead>
<tr>
<th>Positions of peaks (Hz)</th>
<th>1589.12</th>
<th>1587.65</th>
<th>1586.18</th>
<th>1584.71</th>
<th>1578.46</th>
<th>1577.35</th>
<th>1575.88</th>
<th>1574.41</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.30</td>
<td>10.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**doublet of quartets**

$J = 10.3, 1.5$ Hz
Spin-Spin Coupling

Structure Evaluation

4-allyloxyanisole

expect \( \text{(H}_c \text{)} \)?
**Spin-Spin Coupling**

**Tree Diagrams**

**Structure Evaluation**

Expect ($H_c$):

- $J_{cd} = 12-18$ Hz (16)
- $J_{cb} = 0-3$ Hz (2)
- $J_{ca} = 1-3$ Hz (2)
Spin-Spin Coupling

Structure Evaluation

4-allyloxyanisole

Positions of peaks (Hz)

<table>
<thead>
<tr>
<th>Peaks</th>
<th>1.47</th>
<th>17.29</th>
</tr>
</thead>
<tbody>
<tr>
<td>1631.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1629.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1627.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1626.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1613.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1612.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1610.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1608.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

doublet of quartets

\[ J = 17.3, 1.5 \text{ Hz} \]
Spin-Spin Coupling

Structure Evaluation

4-allyloxyanisole

expect (H_d)?
Spin-Spin Coupling

Tree Diagrams

Structure Evaluation

expect (H_d):

\[ J_{da} = 4-10 \text{ Hz (5)} \quad - \quad 2H \]

\[ J_{db} = 9-12 \text{ Hz (10)} \]

\[ J_{dc} = 12-18 \text{ Hz (17)} \]
Spin-Spin Coupling

Structure Evaluation

4-allyloxyanisole
**Spin-Spin Coupling**

**Structure Evaluation**

*4-allyloxyanisole*

<table>
<thead>
<tr>
<th>Positions of peaks (Hz)</th>
<th>1834.73</th>
<th>5.15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1829.58</td>
<td>5.51</td>
</tr>
<tr>
<td></td>
<td>1824.07</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>1818.92</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>1817.45</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Positions of peaks (Hz)</th>
<th>1813.77</th>
<th>5.51</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1812.30</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>1806.79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1801.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1796.49</td>
<td></td>
</tr>
</tbody>
</table>

**doublet of doublet of triplets?**

\[ J = 17.3, 10.7, 5.2 \text{ Hz} \]
**Spin-Spin Coupling**

**Aromatic Systems**

*coupling constants*

- $J_{ab} = 7-10 \text{ Hz}$ (ortho)
- $J_{ab} = 2-3 \text{ Hz}$ (meta)
- $J_{ab} = 0-1 \text{ Hz}$ (para)
Spin-Spin Coupling

Aromatic Systems

substituent effects on chemical shift

CH$_2$CH$_3$

OCH$_3$

CHO
Spin-Spin Coupling

Aromatic Systems

\[
\begin{align*}
\text{NH}_2 & \quad \text{NO}_2 \\
\text{H}_a & \quad \text{H}_b \\
\text{H}_c & \quad \text{H}_d
\end{align*}
\]

\[
\begin{align*}
\text{NH}_2 & \quad \text{H}_d \\
\text{H}_a & \quad \text{H}_b \\
\text{H}_c & \quad \text{NO}_2
\end{align*}
\]

\[
\begin{align*}
\text{NH}_2 & \quad \text{H}_a \\
\text{H}_a & \quad \text{H}_b
\end{align*}
\]
**Spin-Spin Coupling**

Aromatic Systems

![Chemical Structure](image)

The diagram shows a spectrum with peaks labeled $H_a$, $H_c$, and $H_b$, with $H_c$ and $H_b$ close together and $H_a$ farther away. A line indicates the solvent position.
Spin-Spin Coupling

Other Resources for Coupling Constant Analysis

1st order multiplet evaluation:


pattern calculator:

http://www.colby.edu/chemistry/NMR/jmmset.html