IV. Chemical Shifts - δ unit

Each H nucleus in a molecule has a different degree of electron surrounding it. Higher the electron density is found surrounding the ¹H nucleus, more the external magnetic energy is needed for the excitation of that ¹H nucleus as the electron *shields* the nucleus. Where each ¹H peak appears in the ¹H NMR spectrum is the reflection of *what kind of a chemical environment* each ¹H nucleus is in,* thus the name “chemical shift.”

*This is manifested in the electron density surrounding each ¹H nucleus.

NMR spectra are obtained usually in CDCl₃ (99.8% D and 0.2% ¹H) with (CH₃)₂Si [tetramethylsilane or TMS] as internal reference in a certain operating magnetic field such as 200 MHz, 400 MHz, etc.

\[
\text{H}_3\text{C} = \text{CH}_3 \quad \text{in CDCl}_3 \text{ on a 200 MHz magnet NMR spectrometer:}
\]

- residual CHCl₃ in CDCl₃
- lower field or down-field
- acetone
- TMS
- higher field or up-field

"The peak of acetone ¹H's appears as one peak at 440 Hz down-field from TMS on a 200 MHz NMR spectrometer"

\[
\text{H}_2\text{C} = \text{CH}_3 \quad \text{in CDCl}_3 \text{ on a 400 MHz magnet NMR spectrometer:}
\]

- residual CHCl₃ in CDCl₃
- lower field or down-field
- acetone
- TMS
- higher field or up-field

"The peak of acetone ¹H's appears as one peak at 880 Hz down-field from TMS on a 200 MHz NMR spectrometer"

Note: MHz = \(10^6\) Hz
MHz (mega Hertz); Hz = cps

Since these are too lengthy descriptions of ¹H NMR data and the acetone peak appears at a down field position from TMS proportionally to the strength of an operating magnetic field, the following dimension less ppm unit has been introduced.

\[
\begin{align*}
\text{(H}_3\text{C)}_2\text{C}=\text{O} \text{ on a 200 MHz NMR spectrometer: } 440 \text{ Hz} / 200 \times 10^6 \text{ Hz} &= 2.2 \times 10^{-6} = 2.2 \text{ ppm} \\
\text{(H}_3\text{C)}_2\text{C}=\text{O} \text{ on a 400 MHz NMR spectrometer: } 880 \text{ Hz} / 400 \times 10^6 \text{ Hz} &= 2.2 \times 10^{-6} = 2.2 \text{ ppm}
\end{align*}
\]

Now, these are independent of the strength of an operating magnetic field.
Conversely, 1 ppm on a 200 MHz NMR spectrometer corresponds to: $1 \times 10^6 \times 200 \times 10^6 \text{Hz} = 200 \text{ Hz}$ and 1 ppm on a 400 MHz NMR spectrometer corresponds to: $1 \times 10^6 \times 400 \times 10^6 \text{Hz} = 400 \text{ Hz}$

This ppm scale relative to TMS and the increasing value to the lower magnetic field (i.e., to the left from TMS) is called “the δ-scale.” The $^1\text{H}$ peaks of most of the organic compounds fall in between $\delta = 0 \sim 10 \text{ ppm}$ (see Table 10.3 on p. 361 of Ege’s book).

### The Factors That Affect Chemical Shifts

1. **Hybridization**
   - $\text{sp}^3$: typically $\delta = 0.5 \sim 1.5 \text{ ppm}$
   - $\text{sp}^2$: typically $\delta = 5 \sim 6 \text{ ppm}$
   - $\text{sp}$: typically $\delta = 7 \sim 8 \text{ ppm}$

   ![Note: aromatic H's](image)

   However, $\text{-C = C} + \text{H} \delta = \sim 2.2 \text{ ppm}$

2. **Electron Density on each $^1\text{H}$**

   $$H_{\text{effective}} = H_0 (1 - \sigma)$$

   - $H_0$: applied magnetic field
   - $\sigma$: shielding constant, $10^2 \sim 10^5$ (reflects chemical environments of a specific $^1\text{H}$)

   - Increasing electron density on a $^1\text{H}$ → more shielding (larger $\sigma$)
   - → more external $H_0$ to reach $H_{\text{effective}}$ → $^1\text{H}$ peak at a higher field → a smaller $\delta$ value for the peak.

   **Examples:**
   - (i) tetramethylsilane (TMS):
     
     ![Electronegativity: 2.1](image)

     - Electronegativity: 2.1
     - e.n.: 1.8
     - Consequently, the electron density of the $^1\text{H}$'s of the CH$_3$ increases
     - $\rightarrow$ $^1\text{H}$'s of the CH become highly shielded $\rightarrow$ requires more external magnetic field energy.

     Therefore, (H,C)$_3$Si $^1\text{H}$’s appear at a significantly higher field than $^1\text{H}$’s in most of the organic compounds; one of the reasons why TMS is used as the internal reference compound.

   - (ii) Halomethanes [H$_3$C-X]
     
     ![Electronegativity: 4.0](image)

     - $\delta$: 4.30 $\rightarrow$ $^1\text{H}$'s least shielded; most deshielded
     - e.n.: 2.5
     - Electronegativity: 4.0

     ![Electronegativity: 3.0](image)

     - $\delta$: 3.05 $\rightarrow$ $^1\text{H}$'s more shielded
     - e.n.: 2.5
     - Electronegativity: 3.0

     ![Electronegativity: 2.70](image)

     - $\delta$: 2.70 $\rightarrow$ $^1\text{H}$'s more shielded
     - e.n.: 2.5
     - Electronegativity: 2.70

     ![Electronegativity: 2.10](image)

     - $\delta$: 2.10 $\rightarrow$ $^1\text{H}$'s more shielded
     - e.n.: 2.5
     - Electronegativity: 2.10

     Therefore, $^1\text{H}$'s of $\text{H}_3\text{C-X}$ appear at higher fields than $^1\text{H}$'s of $\text{H}_2\text{C-X}$, indicating an increase in electron density and shielding.
(iii) $H_2C\text{---OR}$ e.n.: 3.5 \hspace{1cm} $H_2C\text{---NR}_2$ e.n.: 3.0 \hspace{1cm} $H_2C\text{---SR}$ e.n.: 2.5

(iv) alkenes vs $\alpha,\beta$-unsaturated ketones

(3) Magnetic Anisotropy ----- A through-space effect

(i) Aromatic Ring-Current Effect


These aromatic delocalized 6 $\pi$ electrons start circulating into one direction in an external magnetic field ($H_0$). This circulation of the 6 $\pi$-electrons results in the induction of a secondary magnetic field following the Fleming's rule.

Date: January 9, 2013
(3) (i) Aromatic Ring-Current Effect (continued)

H's located inside this imaginary cone requires more external magnetic field power for their excitation → high-field shifted; smaller δ values

Example:

Strongly shielded by the ring current effect of the benzene 6π-electrons

Strongly deshielded

H's located outside the cone, including the H's on the benzene ring, requires less external magnetic field power (i.e., energy) for their excitation → down-field shift; larger δ values

The closer the H is to the center of the benzene ring, the stronger the extent of the ring current effect is.

(ii) Acetylene groups.

\[ R - C \equiv C - H \delta 2.2 \]

In a magnetic field, these π-electrons induce a secondary magnetic field

As this H is quite close to the center of the C ≡ C bond, an extremely strong shielding effect is observed for this H.

V. Integration

The peak intensity is proportional to the number of H’s belonging to each peak in the case of \(^1\)H NMR.

These 12 and 36 represent the integrated areas of each peak and their ratios correspond to the ratios of the number of H’s belonging to each peak, i.e., \(12 : 36 = 1 : 3\). This could mean 1 H and 3 H’s, 2H’s and 6 H’s, or 3 H’s and 9 H’s, etc.
Integration (continued).

- If there is a 1 : 1 mixture (on a molar basis) of acetone and chloroform [CHCl₃], the integrated ratio of each of the two peaks should be 1 : 6.

Conversely, if the ¹H NMR spectrum of a mixture of acetone and chloroform shows a 1 : 1 intensity by integration, what is the molar ratio of these two solvents in the solution?

**VI. Spin-Spin Couplings [Nuclear Spin-Nuclear Spin Interactions]-Through-Bond Interactions**

**Acyclic Systems**

The two spin states of H₁ interact, through bonds, with the two spin states of H₂, called "coupling," resulting in the formation of the spectral pattern consisting of a pair of doublets.

These H's are called a 3-bond neighbor to each other.
V. Spin-Spin Coupling (continued)

3-Bond Neighbor Analysis:

\[
\text{has 2 3-bond neighbors (i.e., neighboring H's)}
\]

\[
\text{have 2 3-bond neighbors}
\]

\[
\text{have 4 3-bond neighbors}
\]

---

\text{ethyl acetate [H}_3\text{C-CH}_2\text{-O-C(=O)-CH}_3\text{ ]}

\text{3 chemically equivalent H's; have 2 3-bond neighbors}

\text{2 chemically equiv. H's; have 3 3-bond neighbors}

\text{singlet}

\text{1H NMR spectrum of ethyl acetate}

\text{integration values}

\text{integration or intensity ratio}

\text{For the CH}_3\text{ H's: there are two 3-bond neighbors.}

After the interaction with the first 3-bond neighbor (assuming } J = 6 \text{ Hz) }

After the interaction with the second 3-bond neighbor - each of the above doublet peaks splits to a doublet

\text{peak intensity ratio}

\text{1 : 2 : 1}
V. Spin-Spin Coupling (continued)

For the CH₂ H's: there are three 3-bond neighbors.

After the interaction with the first 3-bond neighbor (assuming $J = 6$ Hz)

After the interaction with the second 3-bond neighbor - each of the above doublet peaks splits to a doublet

Thus, becoming a triplet with a 1 : 2 : 1 intensity ratio.

Now, the interaction with the third 3-bond neighbor - each of the 1 : 2 : 1 triplet peaks splits to a doublet

Overall, the CH₂ peaks show up as a 1 : 3 : 3 : 1 quartet.

In general, in an sp³ acyclic system:

If an H has an $n$-number of 3-bond neighbor H’s, the NMR signal of the former splits into an $(n + 1)$-number of peaks. This is due to the fact that all of the vicinal couplings (i.e., $^3J$) are virtually identical in a freely rotating acyclic system.

For example,

- have 1 3-bond neighbor $\rightarrow (1 + 1) = 2$ peaks: doublet
- has 6 3-bond neighbors $\rightarrow (6 + 1) = 7$ peaks: septet
- have no 3-bond neighbors $\rightarrow (0 + 1) = 1$ peak: singlet
V. Spin-Spin Coupling (continued)

“A $^1$H-$^1$H spin-spin coupling exists between any 2- and 3-bond neighboring H’s. However, the only couplings that can be observed in the spectrum are those between chemically non-equivalent H’s.”

1. singlet
   These 3H’s are homotopic.

2. singlet
   These 3H’s are homotopic.

3. $^2J$ is not observed in the $^1$H NMR spectrum. These 2H’s are chemically equivalent (i.e., enantiotopic) and appear as a quartet due to $^3J$ with the methyl H’s (three 3-bond neighbors).

4. singlet (no $^2J$ can be observed in the $^1$H NMR spectrum).
   These 2H’s are homotopic.

5. Alkenic H’s
   $^3J_{trans} = 12 - 20$ Hz
   $^3J_{cis} = 6 - 12$ Hz

For a pair of alkene stereoisomers:

$^3J_{trans} > ^3J_{cis}$
V. Spin-Spin Coupling (continued)

(6) vinyl acetate

\[ \delta 2.15 \text{ (singlet)} \]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\]

4.88 (doublet of doublets)

4.57 (doublet of doublets)

down-field shifted due to the strong inductive effect by the oxygen atom

7.27 (doublet of doublets)

These are high-field shifted due to the following resonance contribution:

The coupling constants among these three H's are:

\[ ^3J_{AX} = 14.2 \text{ Hz (trans-vicinal); } ^3J_{BX} = 6.5 \text{ Hz (cis-vicinal); } ^2J_{AB} = 1.2 \text{ Hz (geminal)} \]

For H_X:

Upon interaction with H_A

Then, upon interaction with H_B, each of the doublet splits into a doublet

\[ ^3J_{AX} \neq ^3J_{BX} \]

Unlike those in an acyclic system, these middle two peaks do not overlap, thus not producing a 1 : 2 : 1 triplet pattern.

The situation is the same for both H_A and H_B. Therefore, H_A and H_B each shows a doublet of doublets.
V. Spin-Spin Coupling (continued)

(7) Aromatic Hydrogens: typically $^3J \sim 8 \text{Hz (ortho)}$; $^4J \sim <1 \text{Hz (meta)}$; $^5J \sim 0 \text{Hz (para)}$

(a) *para*-Disubstituted Benzene

![Chemical structure]

- triplet (2 3-bond neighbors) at 1.2 ppm
- quartet (3 3-bond neighbors) at 2.8 ppm

Two groups of chemically equivalent aromatic H's:
each shows up as a doublet as a result of $^3J_{AB} \sim 8 \text{Hz}$
with a 2 H-intensity.

(b) Three isomers of nitroaniline

<table>
<thead>
<tr>
<th></th>
<th>ortho</th>
<th>meta</th>
<th>para</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6.82 \text{ ppm}$ (d)</td>
<td>6.95 (d)</td>
<td>7.48 (s)</td>
<td>6.61 (d)</td>
</tr>
<tr>
<td>$7.34 \text{ ppm}$ (t)</td>
<td>7.36 (t)</td>
<td>7.55 (d)</td>
<td>7.93 (d)</td>
</tr>
<tr>
<td>$8.08 \text{ ppm}$ (d)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$6.67 \text{ ppm}$ (t)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chemical shifts of each of these aromatic H's are explainable in terms of resonance
contributions of the NH$_2$ and NO$_2$ groups.

![Diagram]

(c) Long-range couplings

- doublet at 7.40 ppm
- singlet at 2.5 ppm
- a doublet of doublets at 8.04 ppm

$^3J$ (ortho coupling) $8.6 \text{Hz}$

$^4J$ (meta coupling) $2.2 \text{Hz}$

$^5J$ (para coupling) $\sim 0 \text{Hz}$