NMR
CHAP 13

NMR- nuclear magnetic resonance

Advantages-

1. small sample.
2. Non-destructive (sometimes slightly acidic)
3. Detailed structural information

Used to study nuclei with odd atomic spin numbers (1/2) which means odd mass numbers and odd atomic numbers.

Ex. $^1$H, $^{13}$C (isotope), $^{15}$N (isotope), $^{19}$F, $^{31}$P

Treat a proton as a rotating sphere, movement of charge generates a magnetic field.

Like a canoe in a river, the magnetic field is equivalent to the current.
\[ E = \frac{\hbar H_o}{2} \]  
\( H_o \) = strength of magnet  
\( \hbar \) = gyromagnetic rotation depends on nucleus

\[ E = 1 \times 10^{-5} \text{ kcal/mol} \]

Resonance occurs when the proton flips its spin, goes from alpha to beta spin state by being irradiated with radio frequency photons.

Resonance frequency is equal to  
\[ \frac{\gamma}{2 \pi} = \frac{1}{2} \hbar H_o \]

Dependent on magnetic field.

Old days used CW (continous wave) NMR

Now use FT-NMR- uses short microsecond rf pulses applied along the x-axis and provides the entire frequency range, hits all protons simultaneously.
Pulses are measured by the angle of the pulse.

Pulse hits all protons simultaneously, central frequency I the pulse is slightly off-resonance for all nuclei, each nucleus shows a free induction decay (FID). Fourier transformation converts it to a spectra.

1. Chemical shift- If all protons were the same all protons would absorb at the same frequency and magnetic field.

However, \( H_{\text{effective}} = H_{\text{external}} - H_{\text{shielding}} \)

Density of \( e' \) gives a magnetic field, which corresponds to shielding. \( E' \) field opposes external field of proton magnetic field.

Shielded protons require a stronger magnetic field.

Chemical shifts- difference (in ppm) between the resonance frequency and tetramethyilsilane (TMS). Now use deuterated solvents as internal lock.

TMS is the most shielded used as a reference, is less electronegative than C.

\[
\text{chemical shift (ppm)} = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}
\]
ppm = fraction of applied field.

TMS = 0

*Overhead t-butyl ether.

Effects can be additive, table of chloroethane, each chlorine is additive about 2.3 ppm but gets less and is not exact.

*Overhead of chemical shifts.

Aromatic protons- very deshielded. e’ circulate and add to external field at edges of benzene, \[7\] to \[8\]

Vinyl protons- also deshielded, less localized \[5\] to \[6\]

2. Number of signals-
   In identical chemical environments, have the same chemical shift.

   \[
   \begin{array}{c}
   \text{H}_4 \\
   \text{O} \\
   \text{C} \text{-} \text{H}_2 \\
   \text{H}_3 \\
   \end{array}
   \]

   H\text{1-3} are chemically and agnetically equivalent.

   Same chemical shift.

3. Area of peaks- area underneath the peak is proportional to the number of hydrogens contributing to that peak.
Can be equal areas, need to integrate the peaks, area of the peaks are ratios

Can be 1:3  2:6  3:9 can’t tell without molecular formula.

4. Spin-spin splitting

Ocurs because two different types of protons are close enough so that their magnetic field influences each other.

\(2I + 1 = \text{number of peaks} \quad 1/2 = \text{spin number}\)

\[
\begin{array}{c}
\text{proton A} \\
(\text{H} \text{H})
\end{array}
\begin{array}{c}
\text{proton B} \\
\text{B}
\end{array}
\]

Total possibilities for A sees B:

- Less energy (more downfield)
- Even energy
- More energy (more upfield)

Add together.

See a triplet

Use N + 1 rule

See H get a doublet, see 2H get a triplet. All protons must have equivalent chemical equivalency. See 2 or 3 bond coupling.

Area is equal to Pascal’s triangle.
*Ethyl benzene overhead.

![Chemical Structure of Ethyl Benzene](image)

Appears as a quartet only.

Can also see gem coupling.

*methyl isopropyl ketone overhead.

5. Coupling constants (J) - distance between the peaks in Hz in a splitting pattern. Depends on dihedral angle between protons.

![Chemical Structure of Methyl Isopropyl Ketone](image)

\[ \text{J}_{ab} = 7 \text{ Hz} \]

Calculated by the \( J = \frac{\text{differences in chemical shift}}{\text{MHz NMR}} \)

Can have non-first order coupling - coupling constant is larger than the chemical shift separation. Seen on benzene rings. Can be resolved by using a bigger NMR.

*overhead of styrene

![Chemical Structure of Styrene](image)
non-equivalent protons. Ha sees cis Hc and trans Hb. Double doublet.