PROTON (1H) NMR

From 1H NMR we can determine:

- the electronic environment of different protons
- the number of different types of protons present in the molecule
- the relative number of different types of protons
- the number of hydrogen ‘neighbors’ that a proton has

CHEMICAL SHIFT

The chemical shift of a proton is dependent upon its electronic environment.

A shielded proton (near an electron donating group) will absorb at lower ppm (upfield). Because of the increased electron density surrounding the proton nucleus, the external magnetic field must be made larger by the spectrometer in order to compensate.

A deshielded proton (near an electron withdrawing group) will absorb higher ppm (downfield). Because of the decreased electron density surrounding the proton nucleus, the external magnetic field strength required to achieve resonance is less.

NUMBER OF UNIQUE SIGNALS

Protons in the same environment (chemically equivalent protons) will have identical chemical shifts in 1H NMR.

- To determine if protons are chemically equivalent, substitute another atom (Z) for each of the protons in question.
  - If the same product is formed, regardless of which proton is substituted, the protons are chemically equivalent (homotopic).
  - If a different product is formed (cis or trans-isomers, diastereomers), the protons are not chemically equivalent (diastereotopic).
- Most of the time, protons on the same carbon have an identical chemical shift—unless they have a locked conformation, in which case they are diastereotopic.
- If there is another stereocenter in the molecule, CH2’s in the molecule are often diastereotopic.
How many unique signals would each of the following molecules give in the $^1$H NMR spectrum?

- $\text{H}_3\text{C}-\text{CH}_3$
- $\text{O}$
- $\text{H}_3\text{C}$
- $\text{CH}_3$
- $\text{Br}$

**INTEGRATION**

The area under the NMR resonance is proportional to the number of protons which that resonance represents. Experimentally, the integrals appear as a line over the NMR spectrum.

**SIGNAL SPLITTING**

Splitting of a chemical signal arises from the magnetic influence of protons on atoms adjacent to those bearing the hydrogen atoms causing the signal being considered. In general the signal for a proton or equivalent protons will be split into $n+1$ peaks, where $n =$ # of protons on the adjacent atom or atoms.

Spin-spin coupling occurs when two different types of protons are close enough that their magnetic fields influence each other. Spin-spin coupling does not occur between protons that have identical chemical shifts. When the protons attached to a single carbon have the same chemical shift, the n+1 rule ($n =$ number of H neighbors) successfully predicts the splitting patterns. The n+1 rule is strictly obeyed if the coupling constants are the same for every successive pair of carbons.

The distance between the two peaks in the $^1$H NMR spectrum is known as the coupling constant ($J_{ab}$, coupling constant between $H_a$ and $H_b$), usually given in Hertz (Hz). The coupling constant between freely rotating alkyl groups (as described above) is usually 7 Hz.
When analyzing coupling constants, we look for doublets, triplets, quartets, etc. that have the same coupling constant and chances are that these multiplets are coupled to each other because they arise from same spin-spin couplings.

In a regular $^1$H NMR experiment, what splitting pattern and approximate chemical shift would be observed for unique signal in CH$_3$CH$_2$OCH$_3$?

<table>
<thead>
<tr>
<th>Spin-spin splitting pattern</th>
<th>Approx. chemical shift</th>
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<tbody>
<tr>
<td>CH$_3$CH$_2$OCH$_3$</td>
<td></td>
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<tr>
<td>CH$_3$CHOCH$_3$</td>
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</tr>
<tr>
<td>CH$_3$CH$_2$OCH$_3$</td>
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**COUPLING CONSTANTS ARE USEFUL FOR DETERMINING THE SUBSTITUTION PATTERN ON AN AROMATIC RING.**

a. Protons that are ortho- (1,2-disubstituted) to one another show a ($J_{1,2} =$) 6-9 Hz coupling constant.
b. Protons that are meta- (1,3-disubstituted) to one another show a ($J_{1,32} =$) 1-3 Hz coupling constant.
c. Protons that are para- (1,4-disubstituted) to one another show a ($J_{1,4} =$) 0-1 Hz coupling constant.

Consider the following disubstituted aromatic rings:

Of the possible substitution patterns on a benzene ring, the para-disubstituted benzene ring is most easily recognized. Because of the plane of symmetry, $H_a$ and $H_a'$ (and $H_b$ and $H_b'$) have the same chemical shift. When $H_a$ and $H_b$ have similar chemical shifts, a singlet may also be observed (integrating to 4 protons).

**COUPLING CONSTANTS ALSO HELP TO DISTINGUISH BETWEEN ALKENE ISOMERS.**

$$J_{ab} = 7-12 \text{ Hz} \quad J_{ab} = 13-18 \text{ Hz} \quad J_{ab} = 0.5-3 \text{ Hz} \quad J_{ab} = 0.5-3 \text{ Hz} \quad J_{ab} = 0-3 \text{ Hz (cis or trans)}$$
SOMETIMES THE N+1 RULE FAILS. This can happen when protons on the same carbon are chemically non-equivalent. This phenomenon is observed mostly in a “locked” conformation such as with rings and double bonds.

HOW TO CALCULATE COUPLING CONSTANTS: Sometimes the hertz values are listed in the $^1$H NMR spectrum. For a spectrum obtained at X MHz, 1.00 ppm corresponds to X Hz. For example, for a spectrum obtained at 400 MHz, 1.00 ppm in the $^1$H NMR spectrum corresponds to 400 Hz. This information can be used to determine coupling constants using a ruler or the chemical shifts of each signal in a multiplet.

CARBON ($^{13}$C) NMR
From $^{13}$C NMR we can determine the number of unique carbon atoms in an organic molecule.

Using $^1$H decoupled $^{13}$C spectrum ($^1$H coupling suppressed) - most common
The number of unique carbon atoms in a molecule (number of peaks) - each unique carbon produces one peak.

Using $^{13}$C spectra with $^1$H coupling – less common
The $^{13}$C signal is split into n+1 peaks where n = # of protons attached to the carbon.

$CH_3$ = quartet         $CH_2$ = triplet         $CH$ = doublet         $C$ = singlet