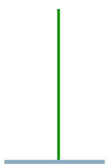
Massachusetts Institute of Technology
Organic Chemistry 5.13

September 18 and 20, 2006
Prof. Timothy F. Jamison

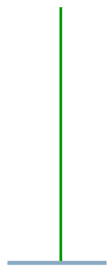
Notes for Lectures #6 and #7

^{1}H NMR Spectroscopy – Spin-Spin Coupling and Connectivity

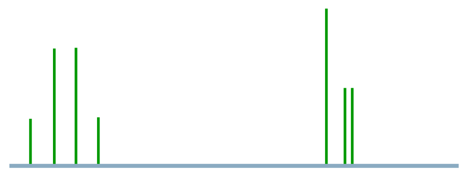
Signature "Splitting" Patterns in ^{1}H NMR Spectra



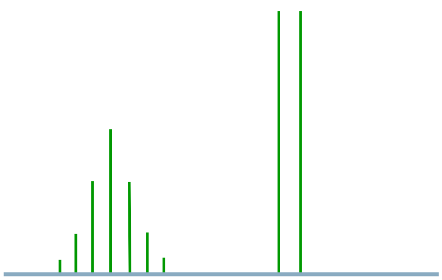
Singlet, 3H Methyl group
CH_3-Z
Z= non H-bearing atom;
typically O, N, C of Ar, etc.



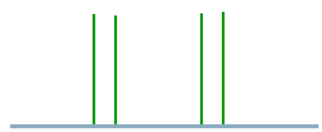
Singlet, 9H at ca. 1ppm
t-Butyl group $(CH_3)_3C$-



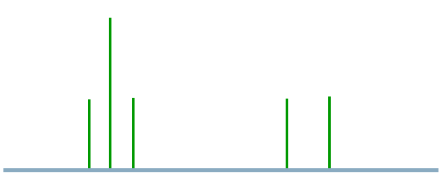
Quartet (2H) and Triplet (3H) Ethyl group
CH_3CH_2-Z
Z= non H-bearing atom, typically
O, N, C of Ar, etc.



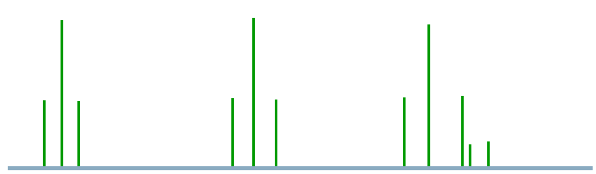
Septet (1H) and Doublet (6H) Isopropyl group
$(CH_3)_2CH$-Z
Z = non H-bearing atom,typically O, N, C of Ar, etc.



Doublet of Doublets (1H) Proton coupled
to two non-equivalent protons which are
attached to the same or different atoms



Two Triplets (each 2H) Adjacent methylene groups
Z^1-CH_2CH_2 -Z^2
Z^1, Z^2 = very different non H-bearing atoms

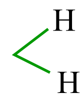


Two Triplets (each 2H) and Quintet (2H) Three adjacent
methylene groups Z^1-$CH_2CH_2CH_2$-Z^2
Z^1, Z^2 = very different non H-bearing atoms

Figure by MIT OCW.

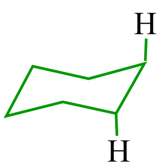
^{1}H NMR Coupling Constants (Expanded)

vicinal 6-8 Hz
(averaged by free rotation)

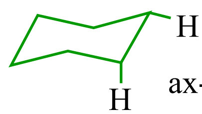


geminal 12-15 Hz
acyclic
can be 0-25 Hz in
cyclic system

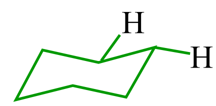
In rigid systems, vicinal coupling can range from 0 to 15 Hz. For example:



ax-ax 6-14 Hz

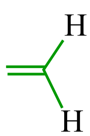


ax-eq 0-5 Hz

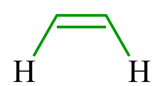


eq-eq 0-5 Hz

Spin-spin coupling in ***alkenes***:

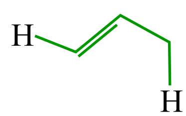


geminal 0-3-Hz



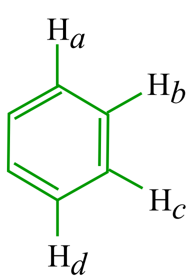
cis 6-12 Hz

trans 12-18 Hz



allylic 0-3 Hz

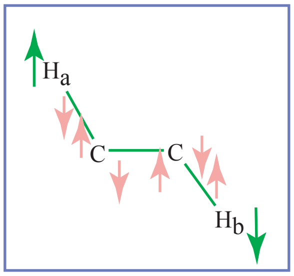
Spin- spin coupling in ***arenes***:



J_{ab} (ortho) 6-10 Hz
J_{ac} (meta) 1-3 Hz
J_{ad} (para) 0-1 Hz

Note: Structures shown above represent generic coupling situations and not the specific molecules depicted (in which the labeled protons would be chemically equivalent and would not couple).

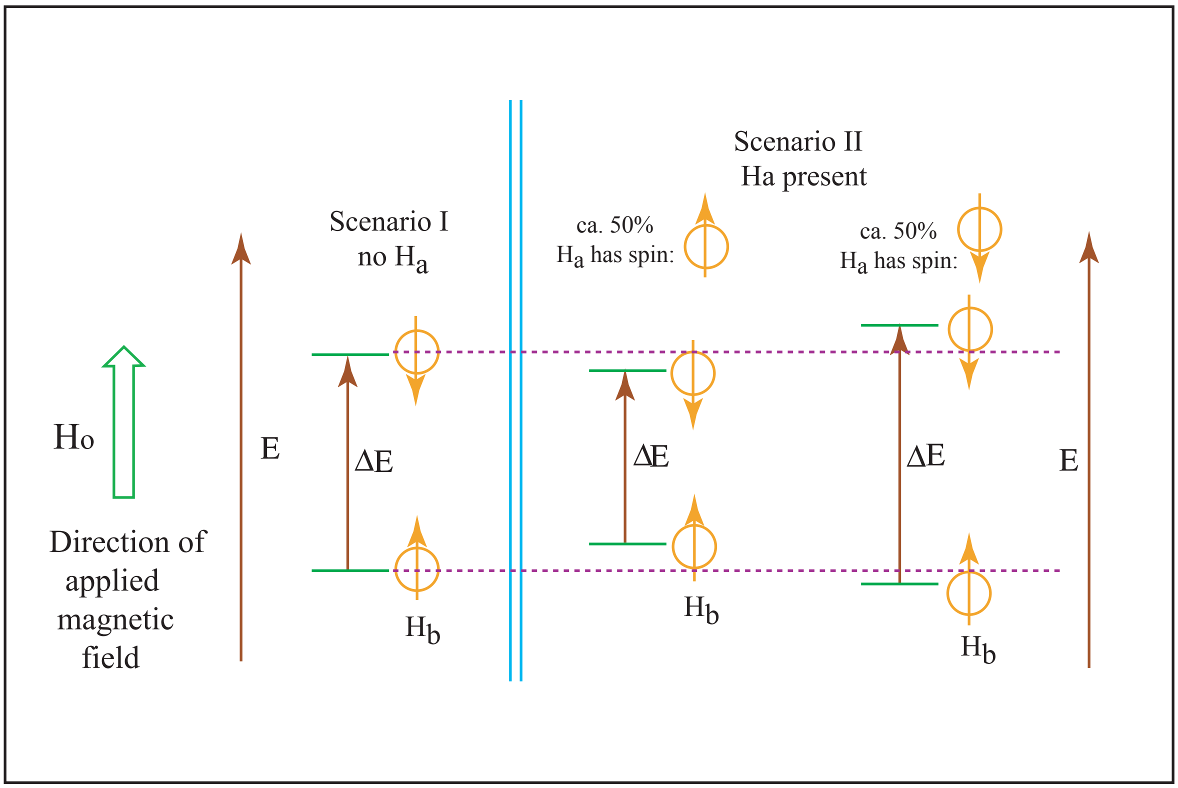
Figure by MIT OCW.



Spin-Spin Coupling for "Vicinal" Protons

The spin of proton H_a influences the energy of the two spin states of proton H_b. This "coupling" is transmitted by the electrons in the bonds linking H_a and H_b. The lowest energy state for proton H_b occurs when the spins of the two protons are antiparallel. Note that this effect does not require that the molecule be in an external magnetic field.

Figure by MIT OCW.



Key Features of Spin-Spin Splitting

1. No coupling occurs among chemically (and magnetically) equivalent atoms.

2. A nucleus coupled to *n* equivalent nuclei with spin *I* is split into $2nI + 1$ lines.

3. Nuclei coupled to each other have the same coupling constant ("**J**").

4. The magnitude of the coupling constant **J** depends on the dihedral angle and type of intervening bonds, but is not affected by the strength of the applied field.

5. "**First-order spectra**" are obtained only if $(v_a - v_b)/\mathbf{J}_{ab}$ > ca. 7 Hz.

6. The splitting pattern for nuclei coupled to two or more **nonequivalent** atoms can be predicted using "tree diagrams".