Massachusetts Institute of Technology
Organic Chemistry 5.13

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Notes for Lecture #6
¹H NMR Spectroscopy – Spin-Spin Coupling and Connectivity
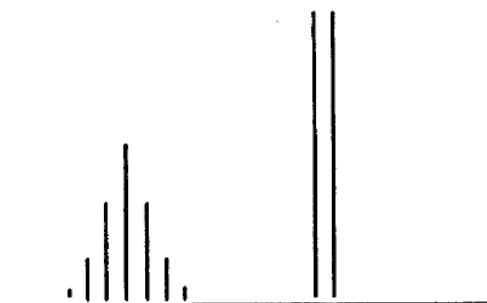
Signature "Splitting" Patterns in ¹H NMR Spectra

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

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

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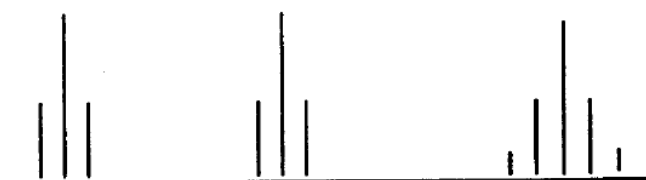Z = non H-bearing atom,
typically O, N, C of Ar, etc.

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

¹H NMR Coupling Constants (Expanded)

H—CH₂—CH₂—H   vicinal   6-8 Hz
(averaged by free rotation)
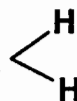
```
   H
    \
     C
    /
   H
```
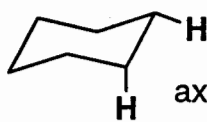geminal   12-15 Hz
 acyclic
can be 0-25 Hz in
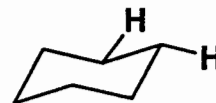*cyclic systems*

In rigid systems, vicinal coupling can range from 0 to15 Hz. For example:
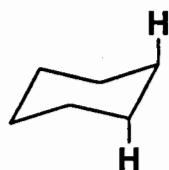
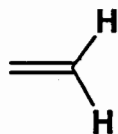ax-ax   6-14 Hz   ax-eq   0-5 Hz   eq-eq   0-5 Hz
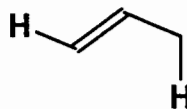
Spin-spin coupling in **alkenes**:

geminal   0-3 Hz   cis   6-12 Hz
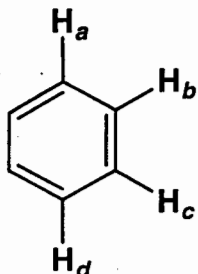
trans   12-18 Hz   allylic 0-3 Hz
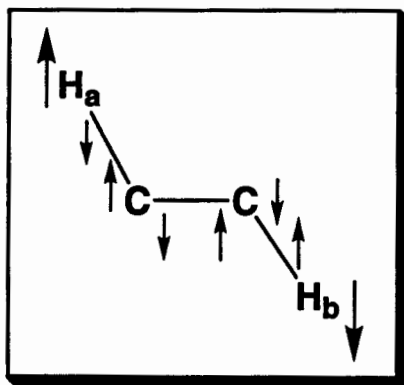
Spin-spin coupling in **arenes**:

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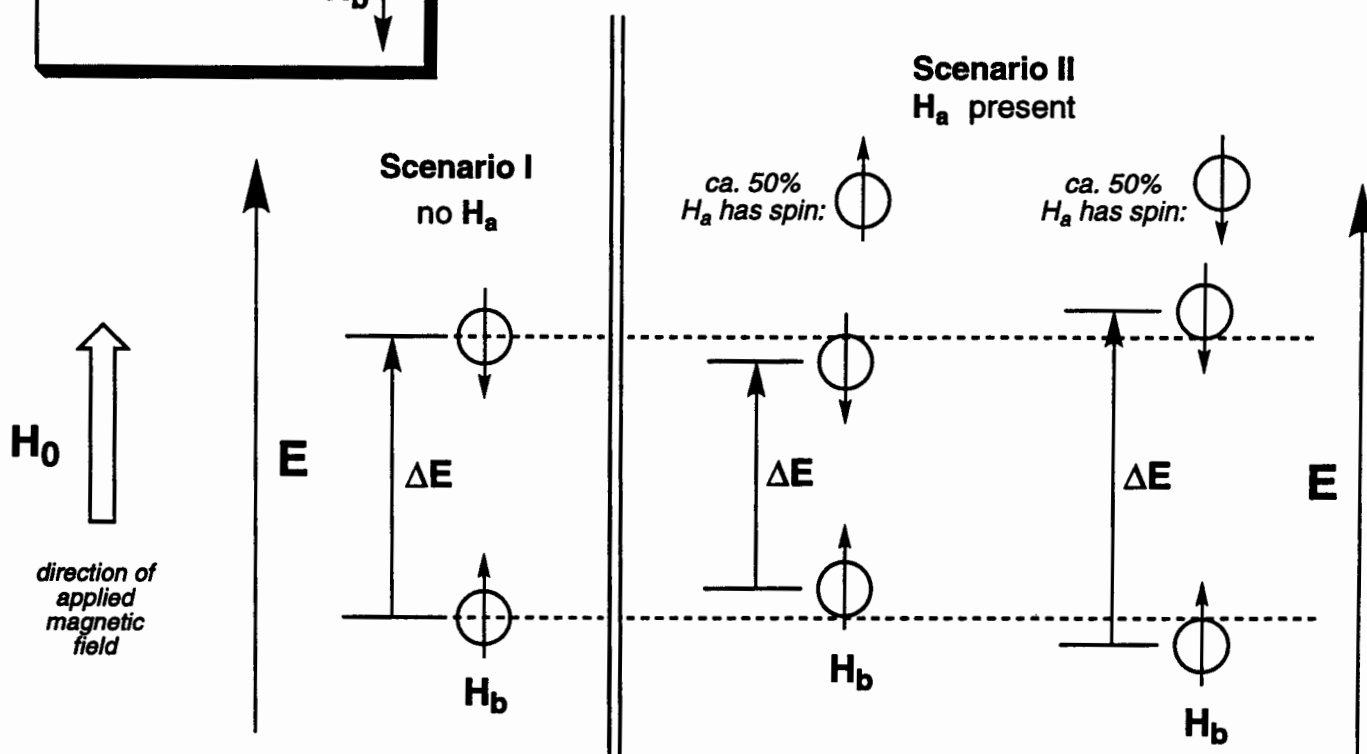J_{ac} (meta)   1-3 Hz
J_{ad} (para)   0-1 Hz

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).

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.

Scenario II
H_a present

Scenario I
no H_a

ca. 50% H_a has spin:

ca. 50% H_a has spin:

H_0

direction of applied magnetic field

E

ΔE

H_b

ΔE

H_b

ΔE

E

H_b

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 the number and type of intervening bonds, but is not affected by the strength of the applied field.

5. **"First-order spectra"** are obtained only if $(\nu_a - \nu_b)/J_{ab} > $ ca. 7 Hz.

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