

¹H NMR

Protons (nucleus of a hydrogen atom) also have a net spin and can be observed in the NMR.

•Hydrogen atoms are more than 99% ¹H.

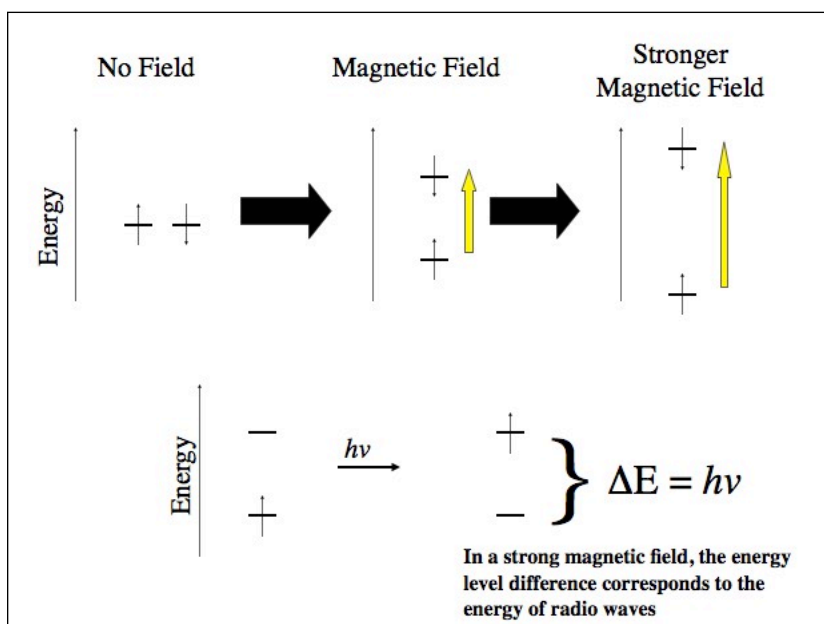
Other isotopes have special names

²H = deuterium

³H = Tritium (radioactive)

•Remember ¹³C is only 1% of carbon; ¹H NMR is much more sensitive.

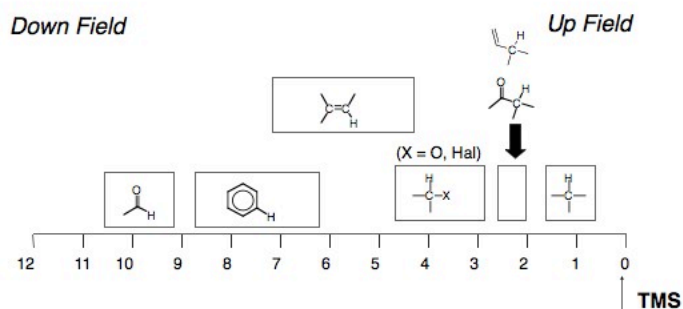
–Practically speaking for a typical lab molecule, you can obtain a ¹H-NMR with 1-2 mg of compound in a matter of minutes but the same sample may require a few hours to obtain a ¹³C spectrum.



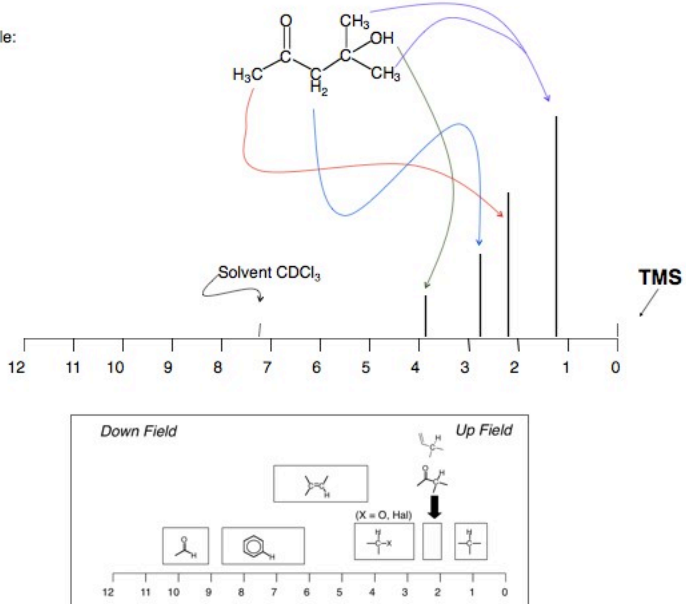
Protons resonate at a different frequency than ¹³C's. Typical compounds lie within a smaller range of frequencies than ¹³C.

PROTONS ON TYPICAL ORGANIC COMPOUNDS **1-12 ppm**

Typical locations of ¹H-NMR resonances.



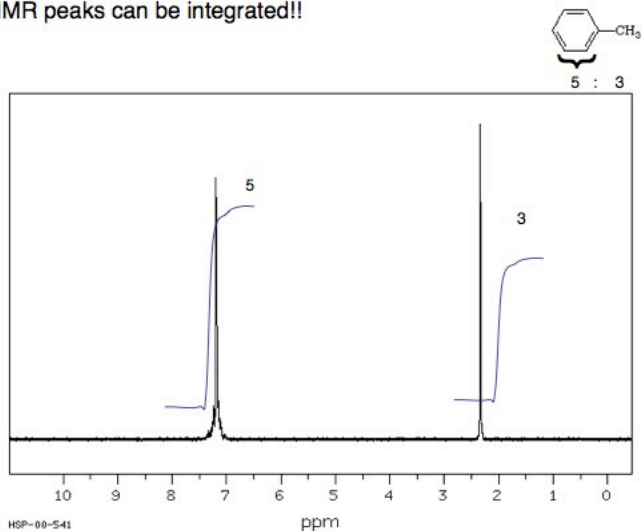
Example:



WHAT IS SO SPECIAL ABOUT PROTON NMR?

- You can accurately integrate your spectra to know how many of each proton type you have.
- Through bond coupling tells us about what is adjacent to the protons of a particular resonance.

$^1\text{H-NMR}$ peaks can be integrated!!

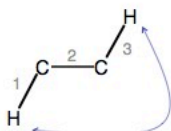


Tells you the ratio of the number of protons that compose each resonance. This is particularly helpful when you have symmetry.

Protons can split other protons by through bond J-coupling.

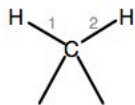
Coupling can be observed between two protons.

The coupling originates because in a magnetic field, the nuclear spin will perturb the local distribution of electrons.



Protons on adjacent carbons are said to be **Vicinal** protons

Are coupled over three bonds.



Splitting over two bonds is usually not observed.

Geminal coupling is only observed when the two protons are in different "chemical environments",

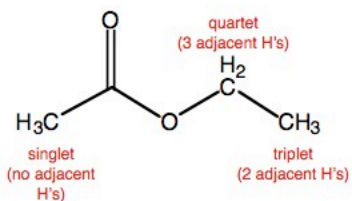
Note: there are exceptions when the protons are diastereotopic (more on this later).

Protons on the same carbons are said to be **geminal** protons

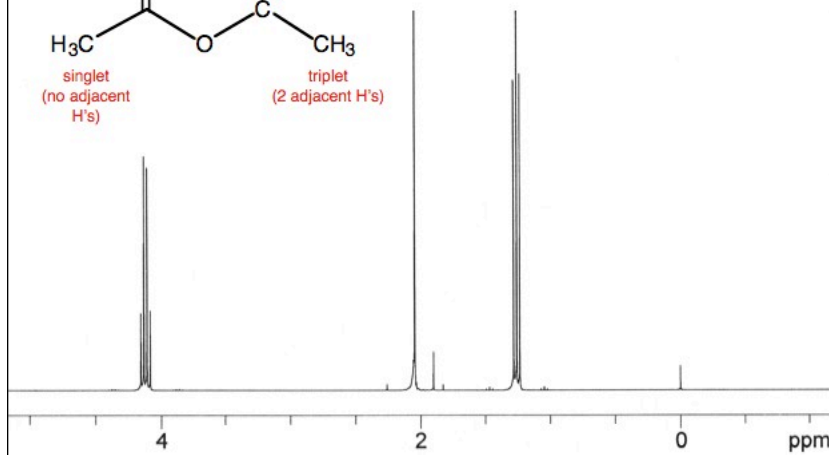


Proton NMR signals are split following the N+1 rule

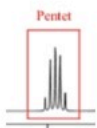
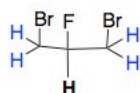
for proton NMR, *N* typically represents the number of adjacent protons.



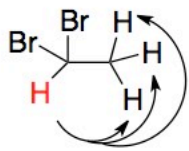
N+1 RULE APPLIES
(note: it can get more complicated)



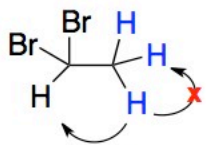
N+1 rule extends beyond quartets



clickers



- a. singlet
- b. doublet
- c. triplet
- d. quartet ←

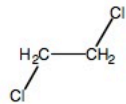


- a. singlet
- b. doublet ←
- c. triplet
- d. quartet

Rules for J-coupling

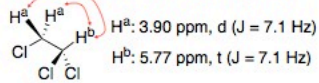
•Nuclei must be chemical shift NON-EQUIVALENT to show (obvious) coupling to each other:

•1,2-dichloroethane is a singlet



•The coupling is mutual: A splits B the same amount as B splits A

$$J_{AB} = J_{BA}$$

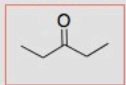


•Coupling constants are reported in Hz and will have the same value on different instruments.

$C_5H_{10}O$

CLICKERS

Which is it?



A

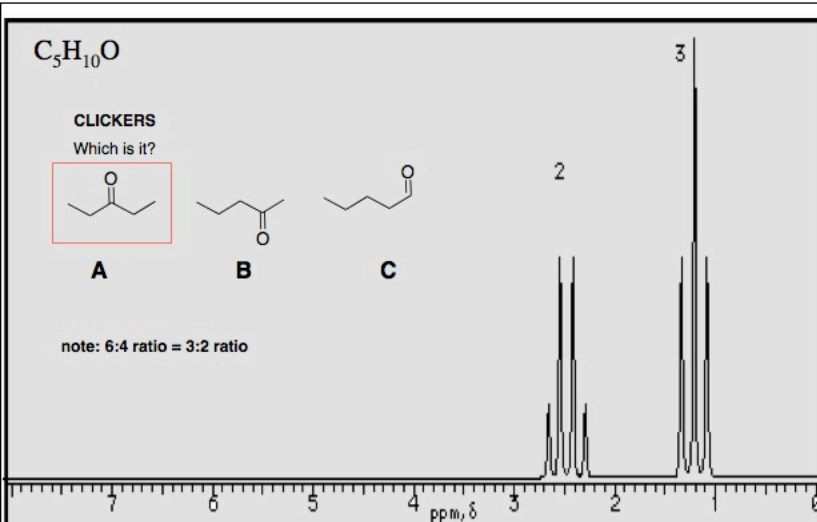


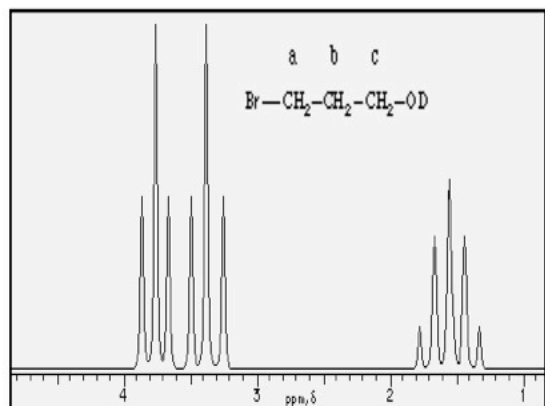
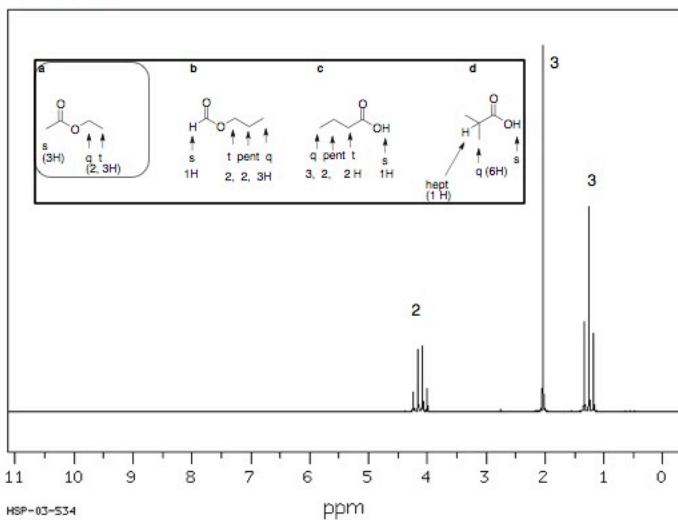
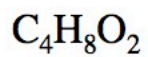
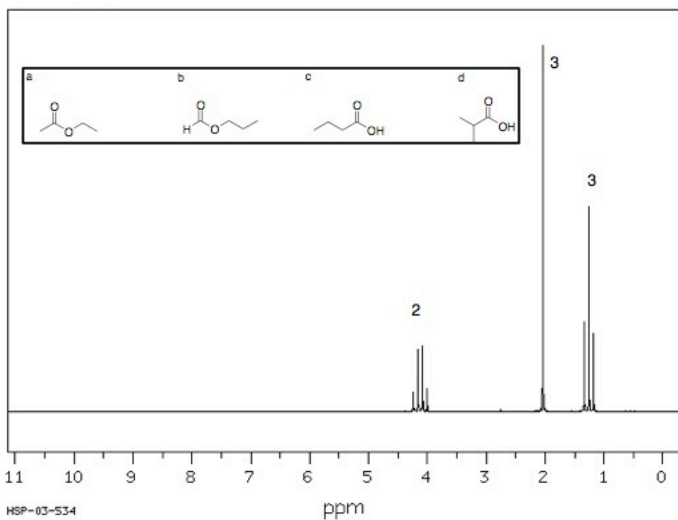
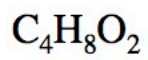
B

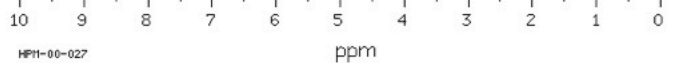
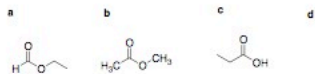


C

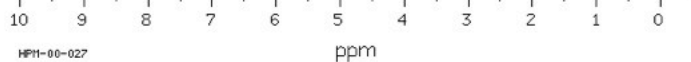
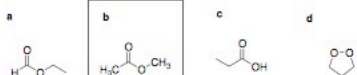
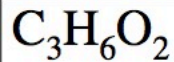
note: 6:4 ratio = 3:2 ratio



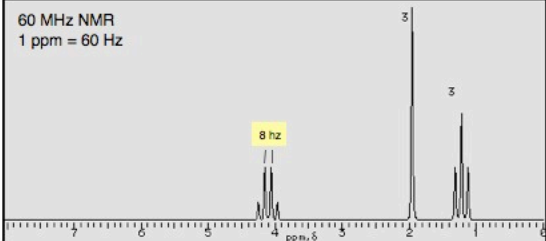




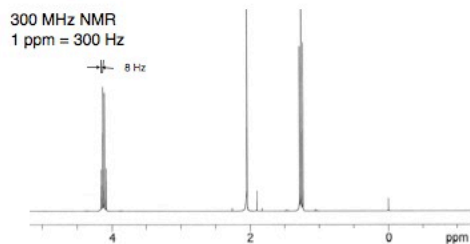
HP11-00-027



HP11-00-027

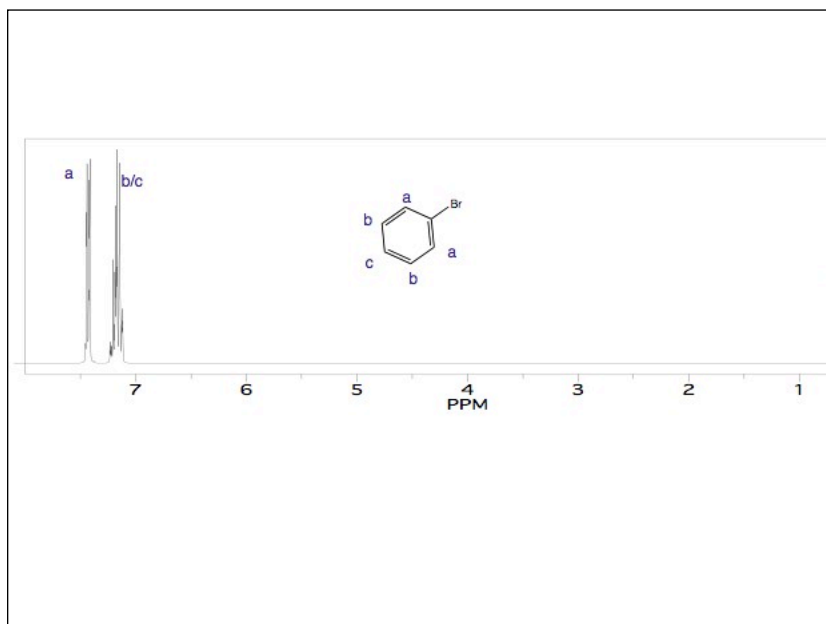
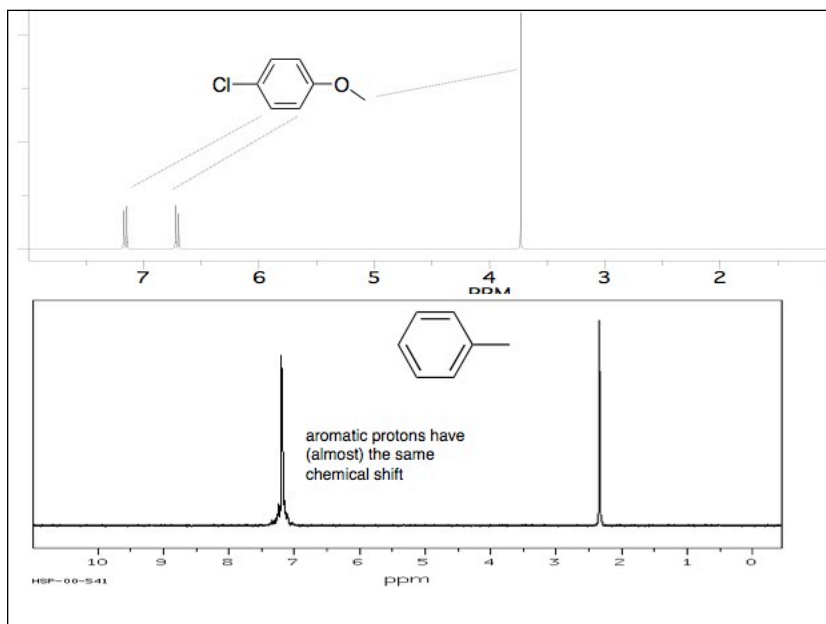
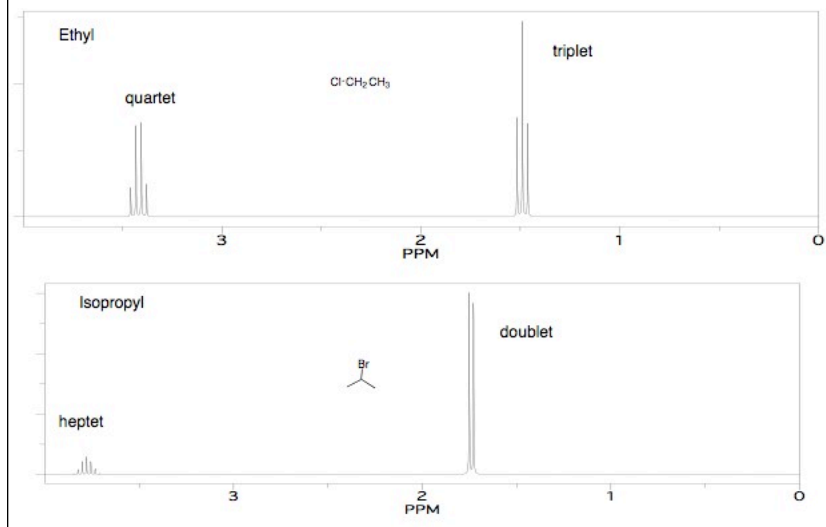


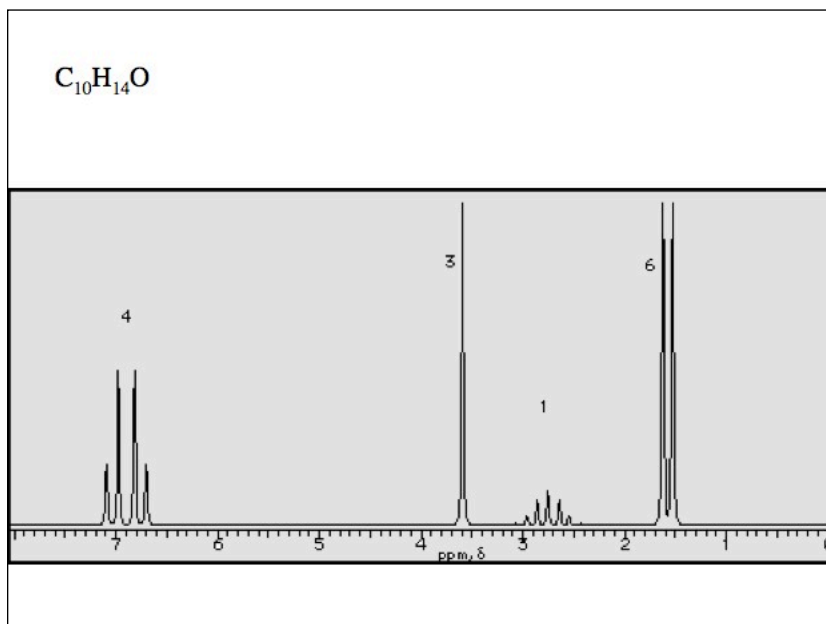
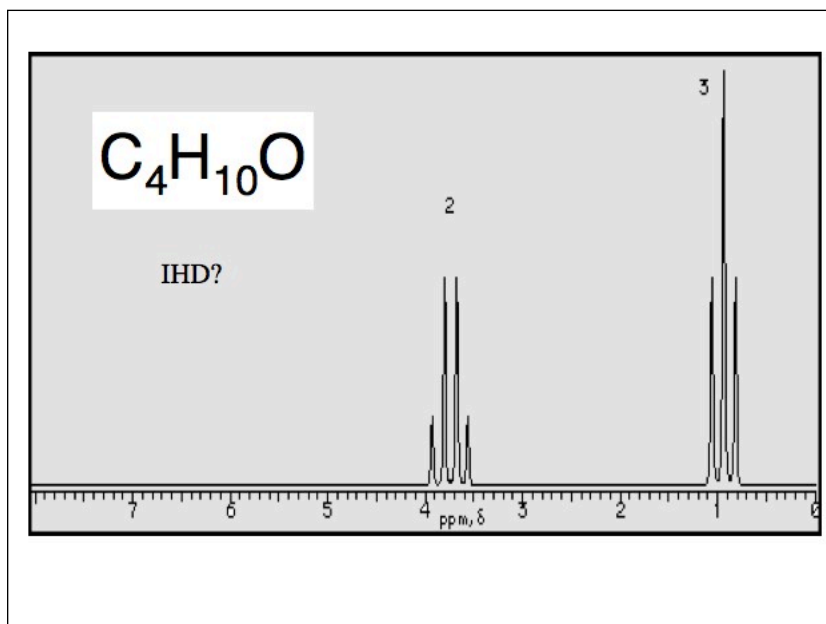
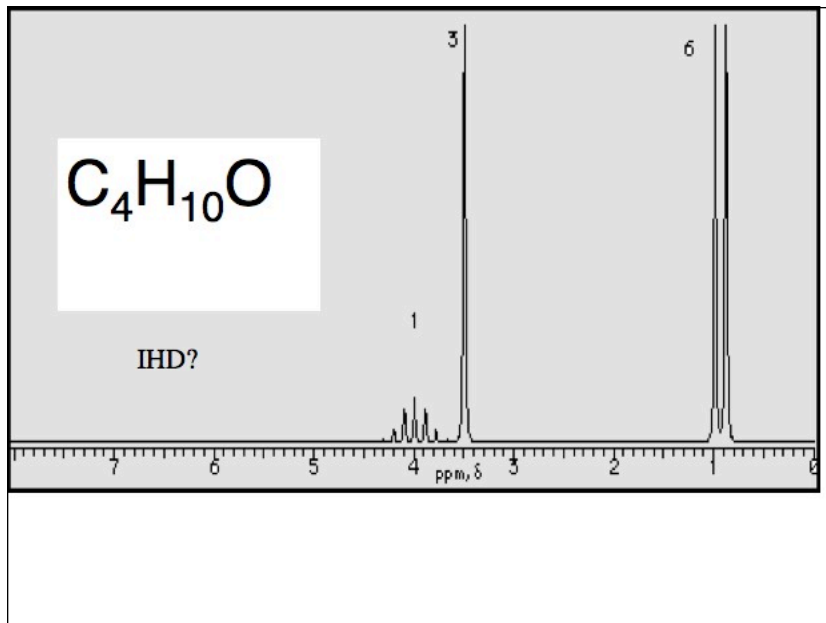
Same compound run on a 60 MHz and a 300 MHz spectrum



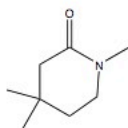
Coupling constant is measured by taking the difference between peaks (in ppm) within a multiplet and multiplying by the field strength in Hz.

Common Splitting Patterns





$C_8H_{15}NO$

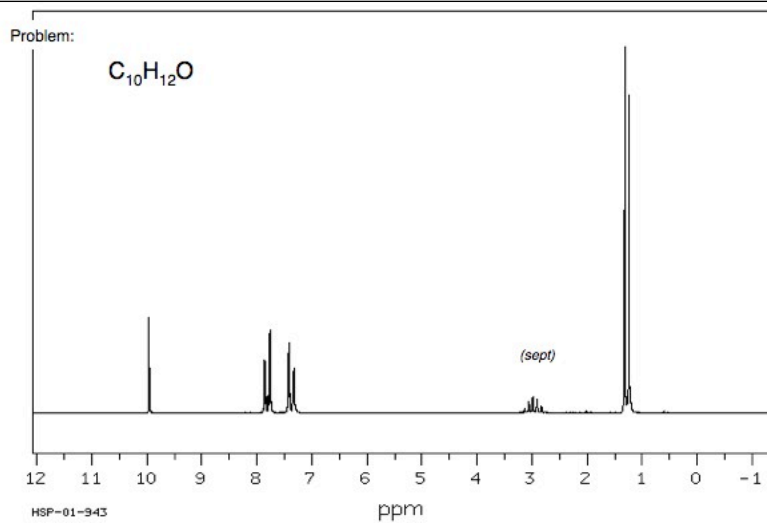


C-13

173.2 s
46.9 t
46.5 t
44.2 t
32.6 q
27.4 s
25.9 q (2)

H-1

2.90 s 3H
3.2 t 2H
2.10 s 2H
1.47 t 2H
1.11 s 6H



from: structural database for organic compounds

Protons in different chemical structures have different amounts of splitting or “coupling constants”.

- Bad News: Life gets more complicated
- Good News: Splitting tells us more about the chemical structure.

Coupling Constants Depends on Structure and Geometry

Approximate Coupling Constants.

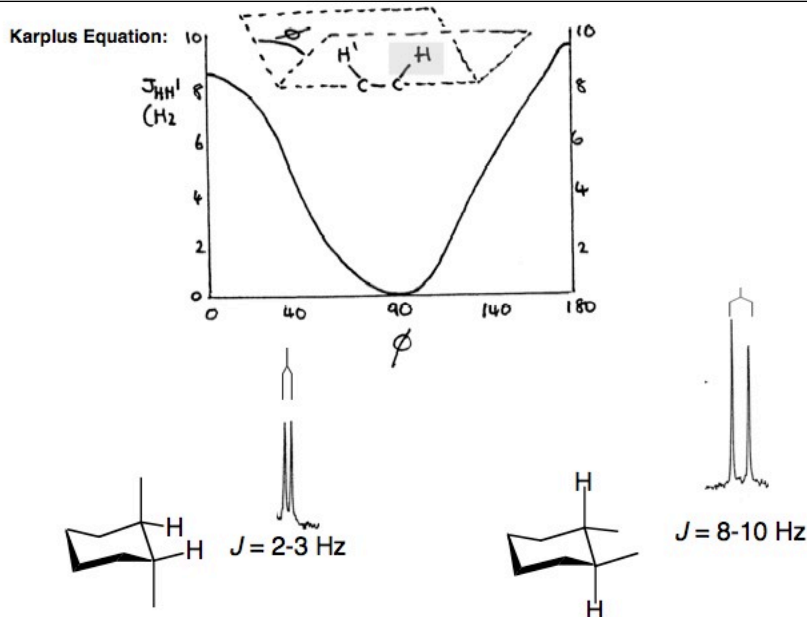
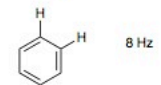
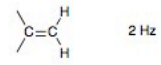
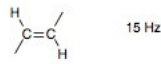
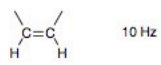
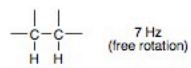
Special Couplings over more than 3 bonds

1,3-diene: 2 Hz

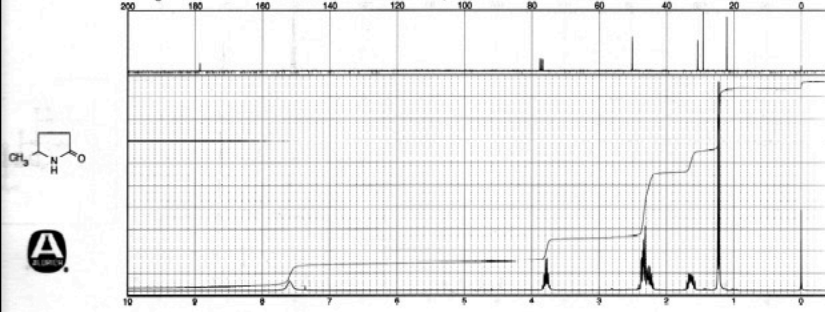
1,4-diene: 6 Hz

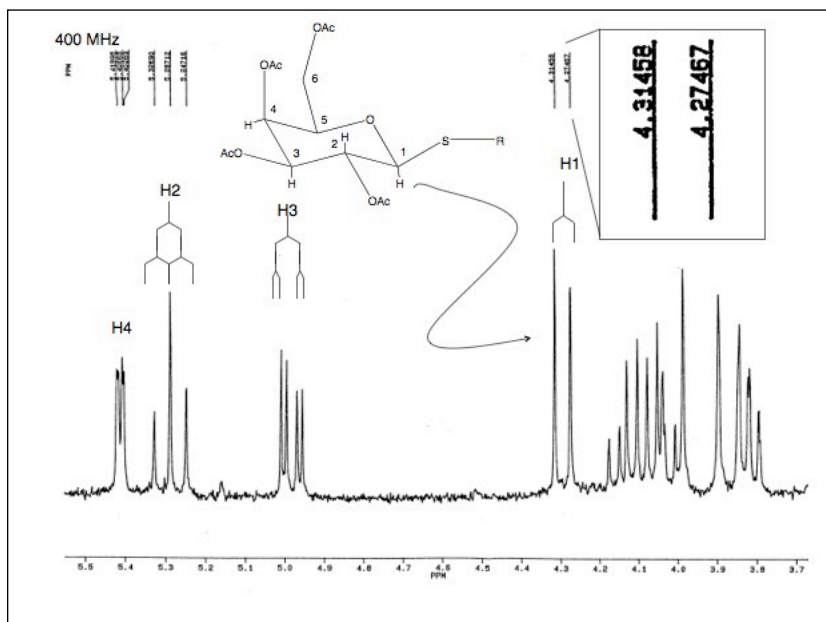
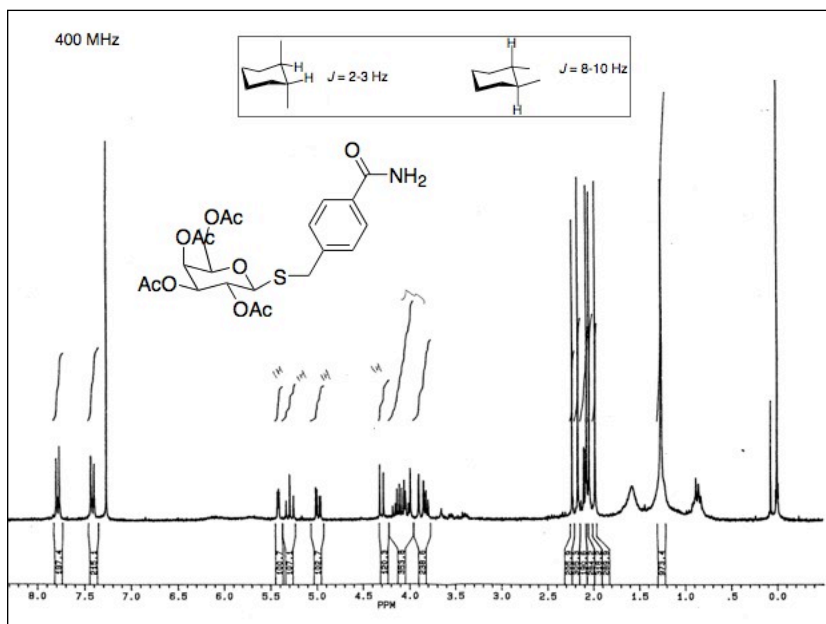
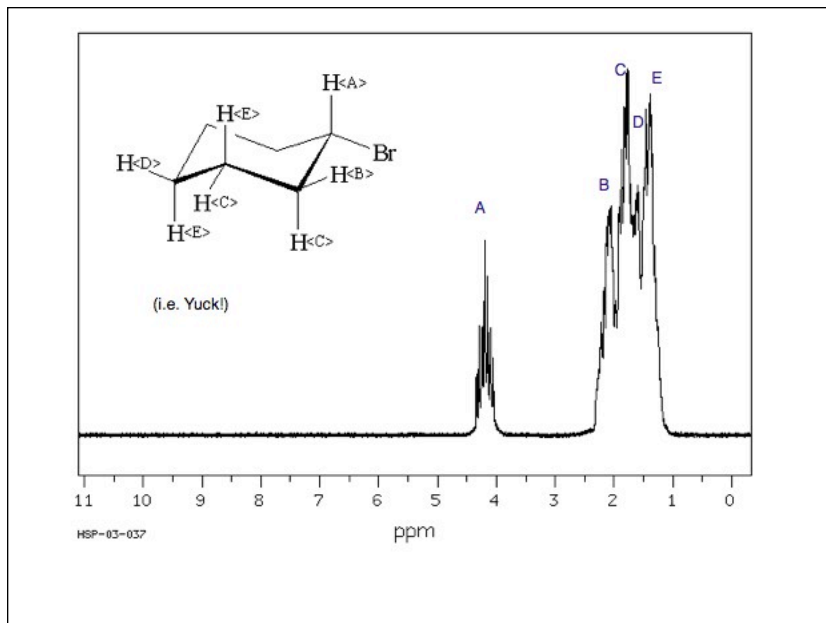
1,5-diene: 0-3 Hz depends on geometry

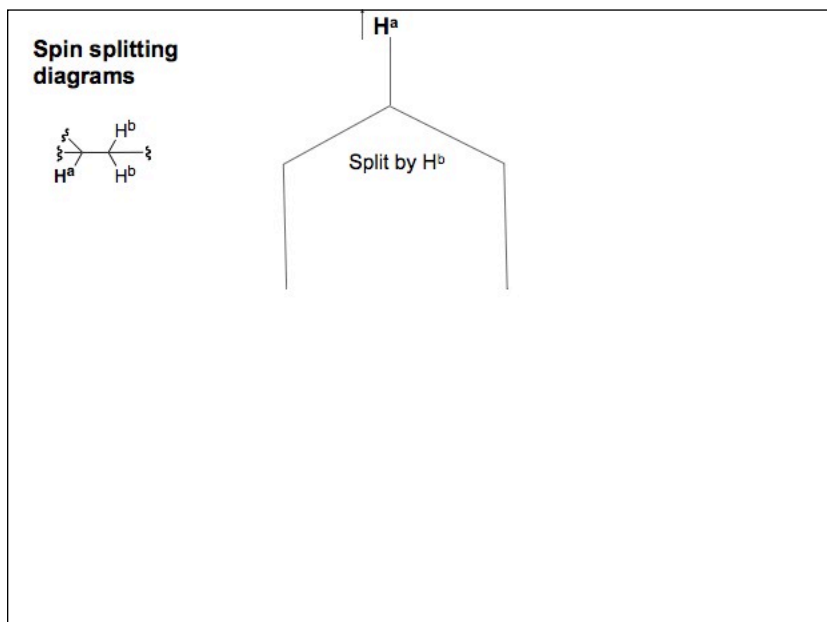
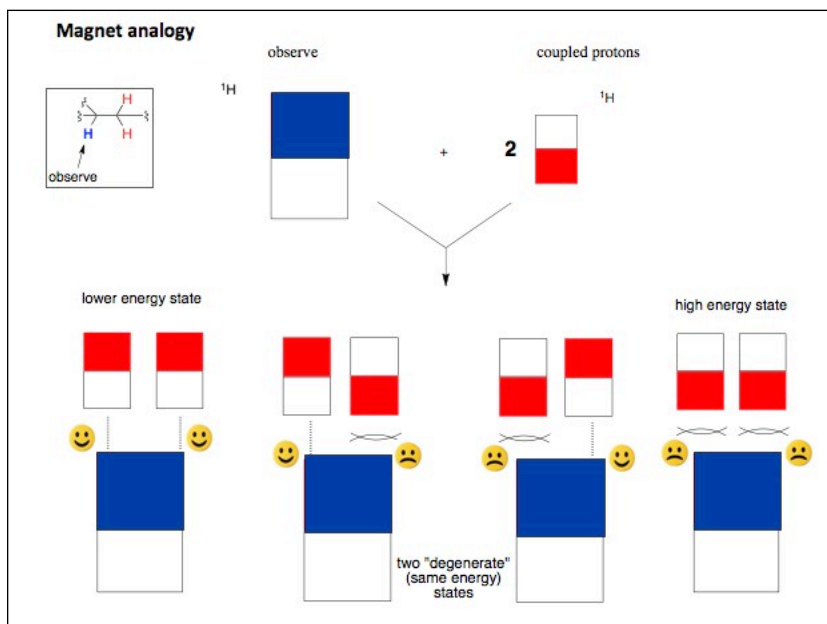
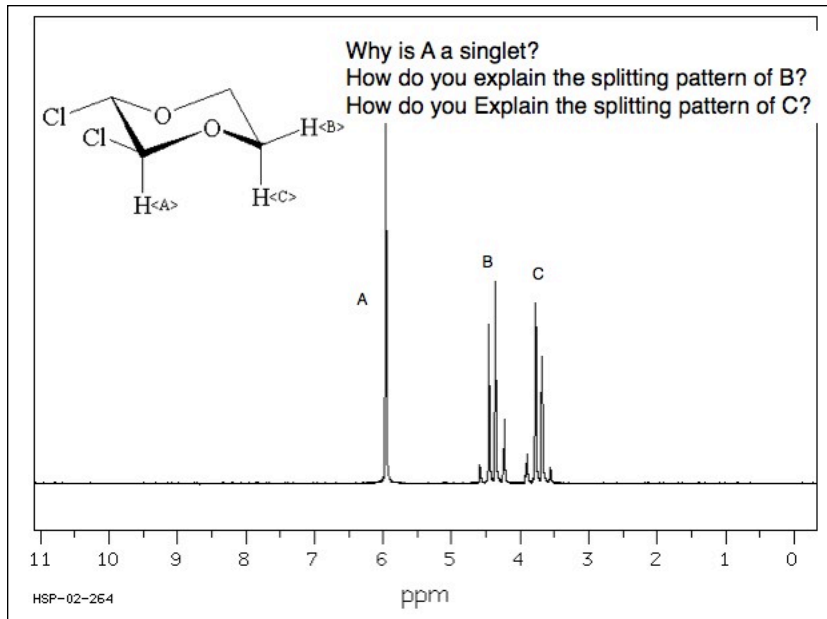
ortho-substituted benzene: 1 Hz



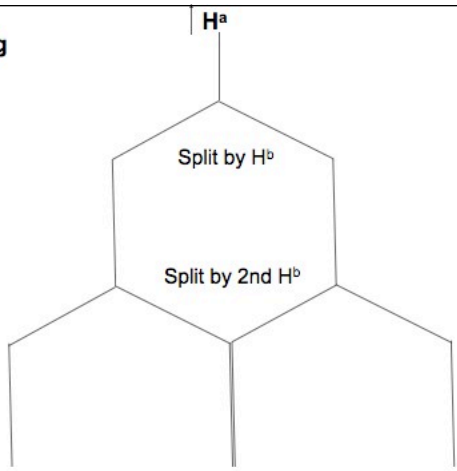
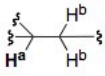
Aldrich M7,970-0 CAS [108-27-0] C_5H_9NO 60 MHz: 1,661D 178.95
 5-Methyl-2-pyrrolidinone, 98% FW 99.13 FT-IR: 1,789B 50.2
 mp 42°C VP-FT-IR: 3,788C 30.7
 bp 248°C Fp >230°F 28.1
 22.1



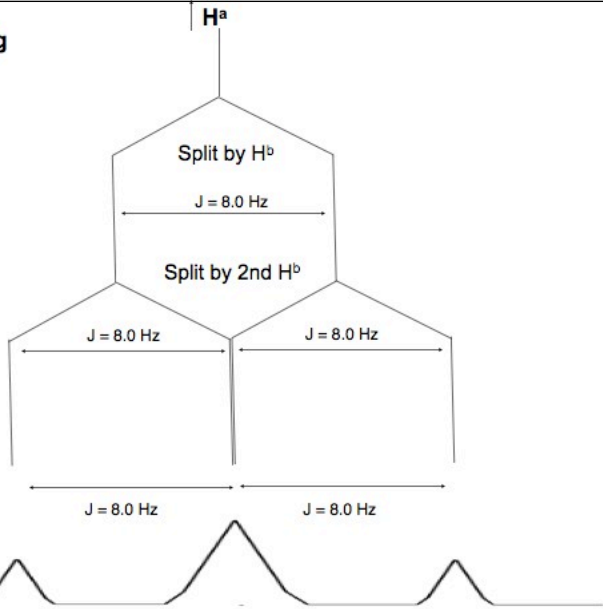
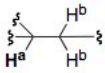




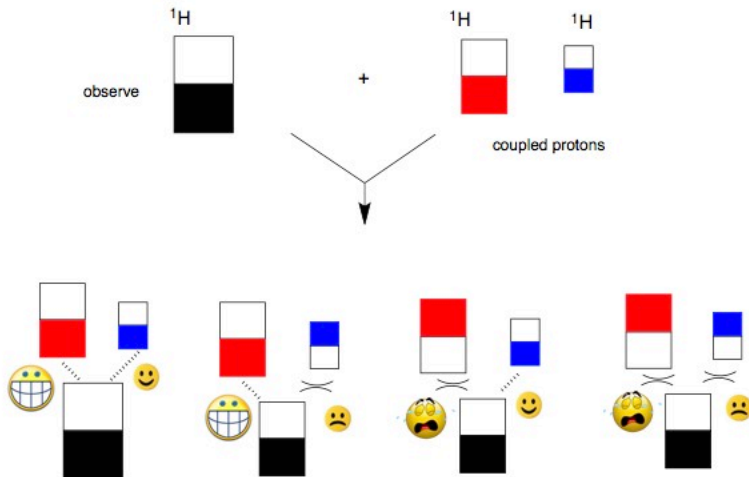
Spin splitting diagrams



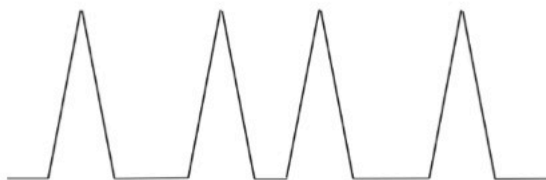
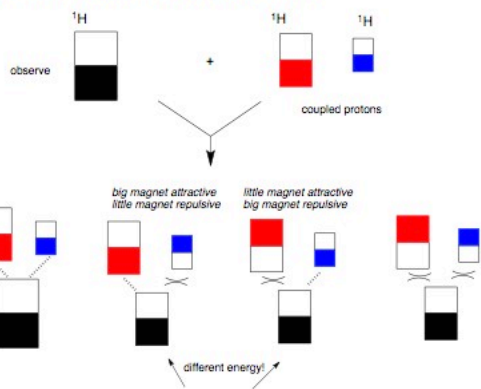
Spin splitting diagrams



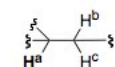
What if we have a strong and weak magnet?



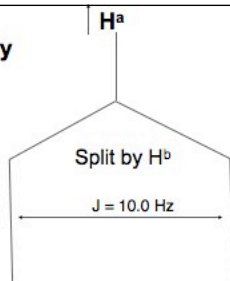
What if we have a strong and weak magnet?



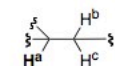
What if the H's are different, and have very different coupling constants??!



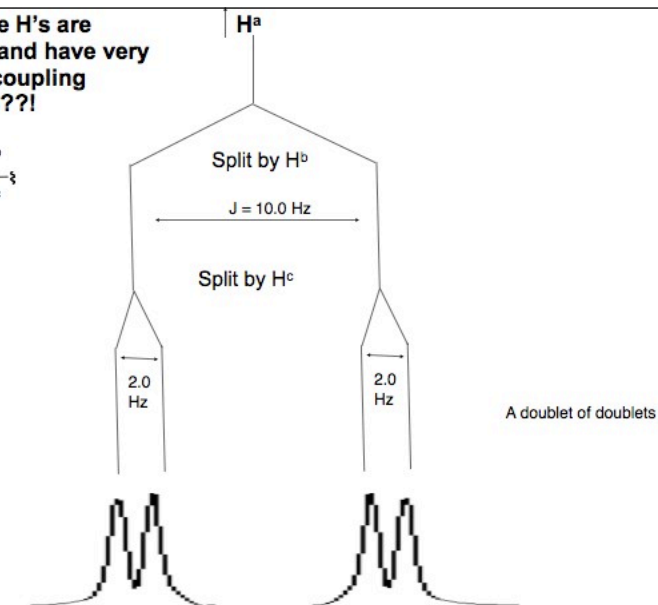
J_{AB} 10 Hz
 J_{AC} 2 Hz



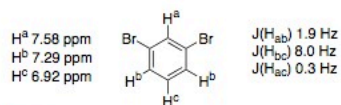
What if the H's are different, and have very different coupling constants??!



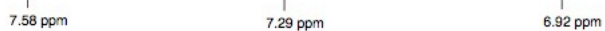
J_{AB} 10 Hz
 J_{AC} 2 Hz



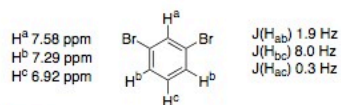
Aromatic (o,m,p) coupling constants



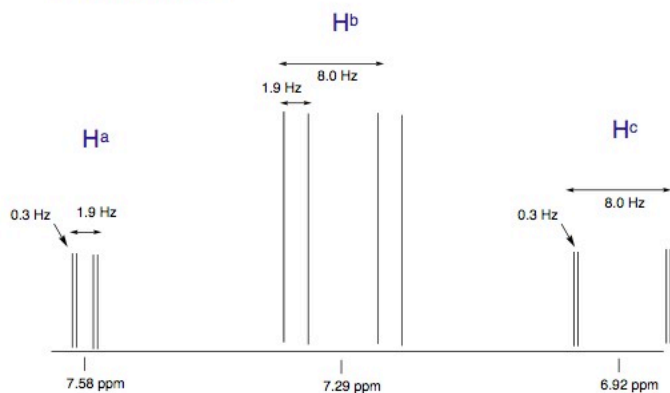
3 doublets of doublets



Aromatic (o,m,p) coupling constants

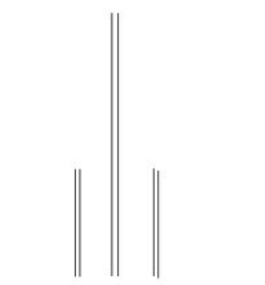
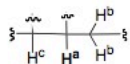


3 doublets of doublets

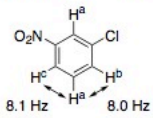


'Doublets of triplets' and 'doublets of quartets'

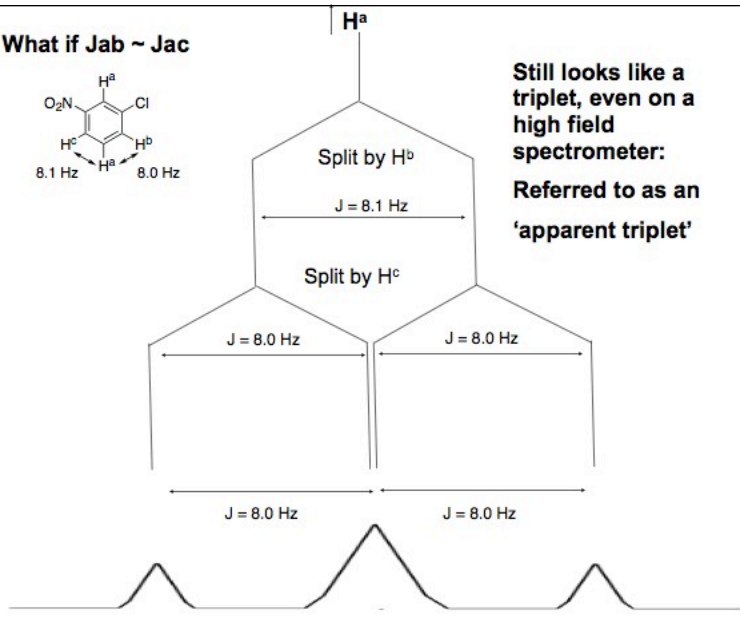
where $J_{ab} \neq J_{ac}$



What if Jab ~ Jac



Still looks like a triplet, even on a high field spectrometer:
Referred to as an 'apparent triplet'

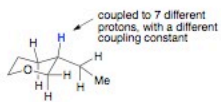


When the going gets really tough...

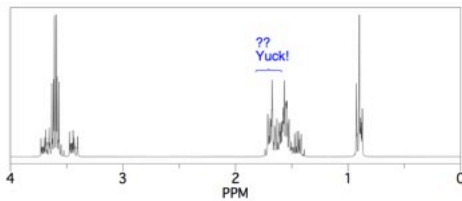
... we call things a **multiplet (m)**



situation 1: coupling pattern is very complex



described as: 1.5–1.3 (m, 1H)

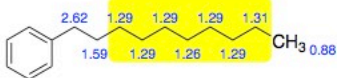


When the going gets really tough...

... we call things a **multiplet (m)**

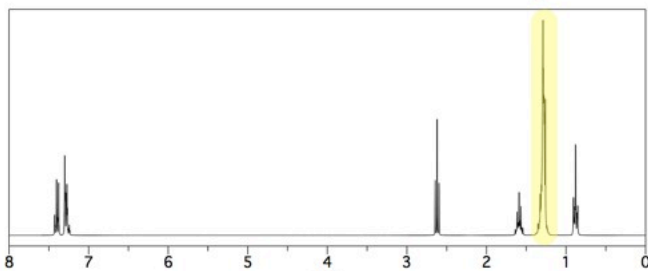


situation 2: your peak overlaps with other resonances



14 overlapping H's!

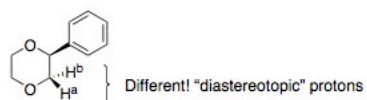
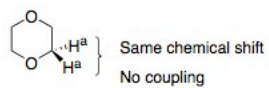
1.31–1.26 (m, 14H)



skip to slide 70

49

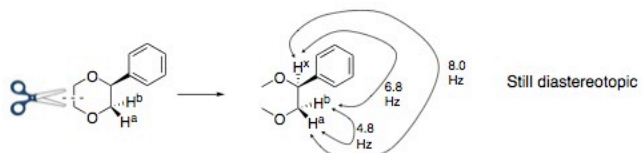
Diastereotopic Protons



Diastereotopic protons:

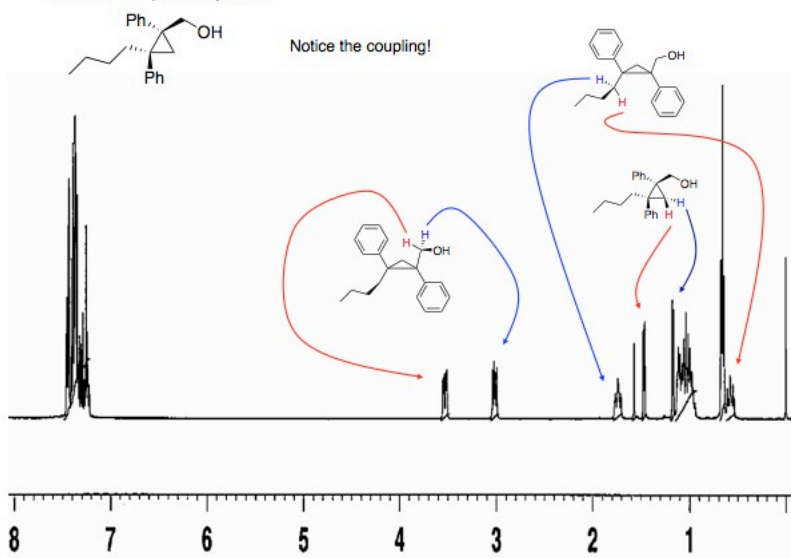
- CH_2 nearby a chiral center
- Chemical shifts differ (but may overlap in some cases)
- Coupling can often be observed

Diastereotopic Protons: not just in cyclic systems



H^a : 3.6 ppm, dd, $J = 8.0 \text{ Hz}, 4.8 \text{ Hz}$
 H^b : 3.9 ppm, dd, $J = 6.8, 4.8 \text{ Hz}$
 H^x : 4.5 ppm, dd, $J = 6.8, 8.0 \text{ Hz}$

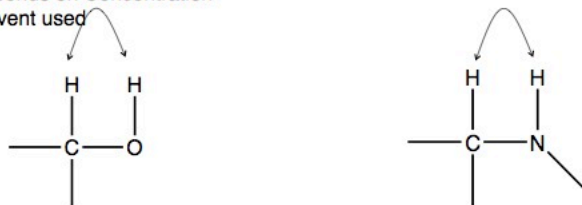
3 diastereotopic methylenes



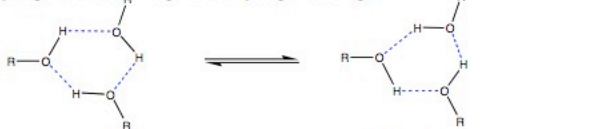
Coupling to Hetero Atoms

Observed Only Sometimes
Depends on Concentration
Solvent used

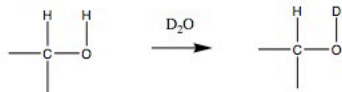
Rarely Observed



WHY: hydrogen atoms exchange due to hydrogen bonding

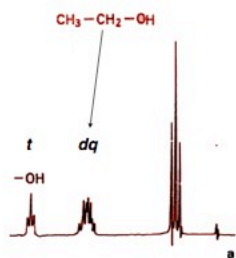


Easy Test



The hydrogen isotope deuterium (^2H) has no spin and cannot couple

dilute solution of ethanol



concentrated solution of ethanol

