Spectroscopy: ^{1}H NMR

Note Title 3/20/2014

Announcements:

(1) Go to Discussion Section!

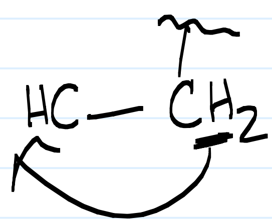
(2) Regrade Requests

(3) Check website for notes + links to practice problems tonight.

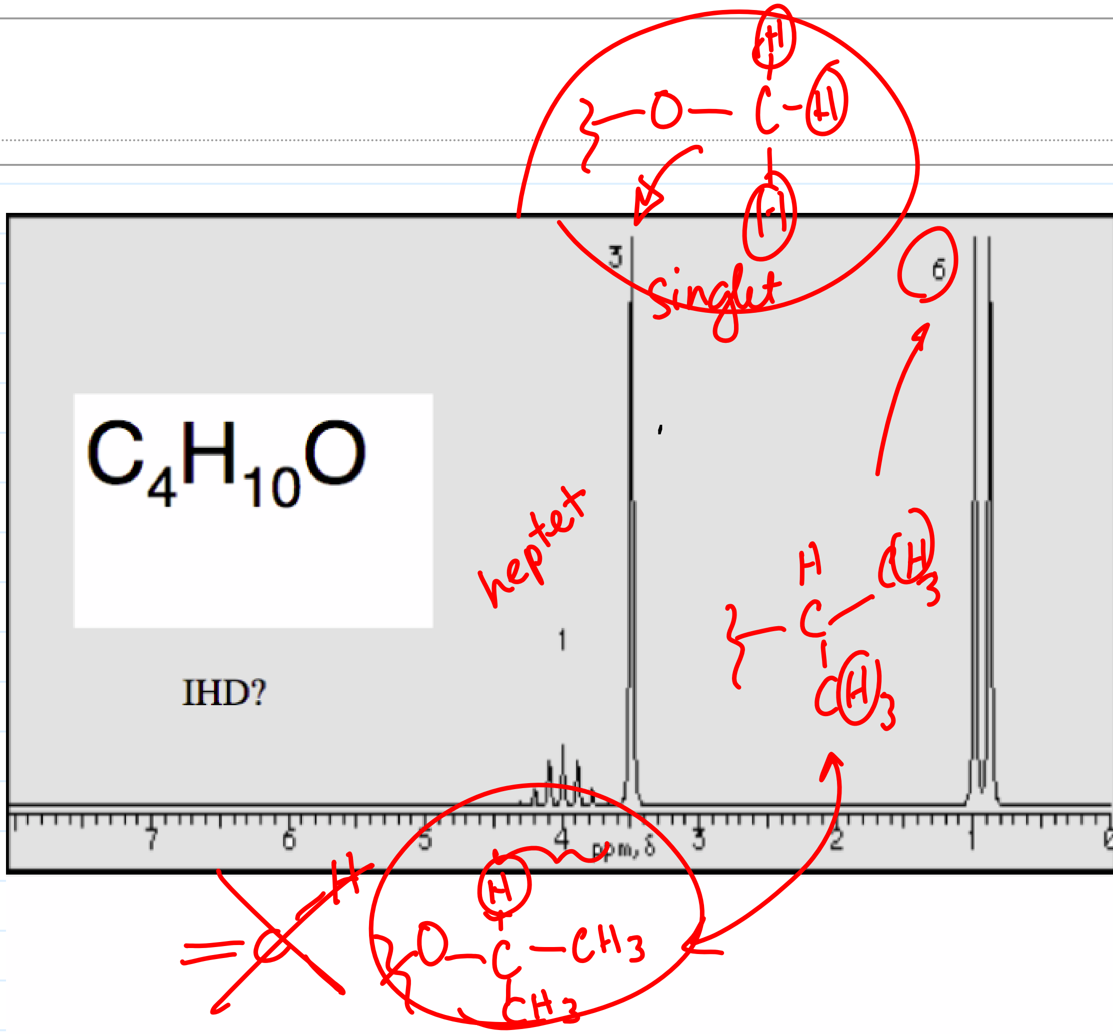
^1H NMR:

(1) How many <u>types</u> of H's are in molecule
↳ Chemical shift → electronic environment.

(2) Coupling : (n+1) rule



(3) Integration : Relative # of H's in each peak.



$C_4H_{10}O \rightarrow C_4H_{10}$ (HCF)

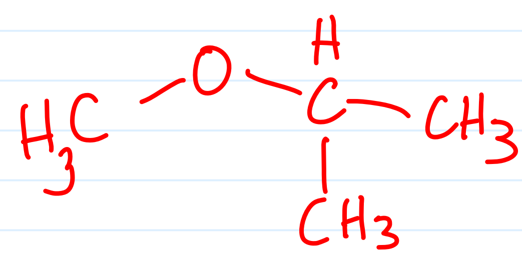
$C_nH_{(2n+2)}$ $n=4$

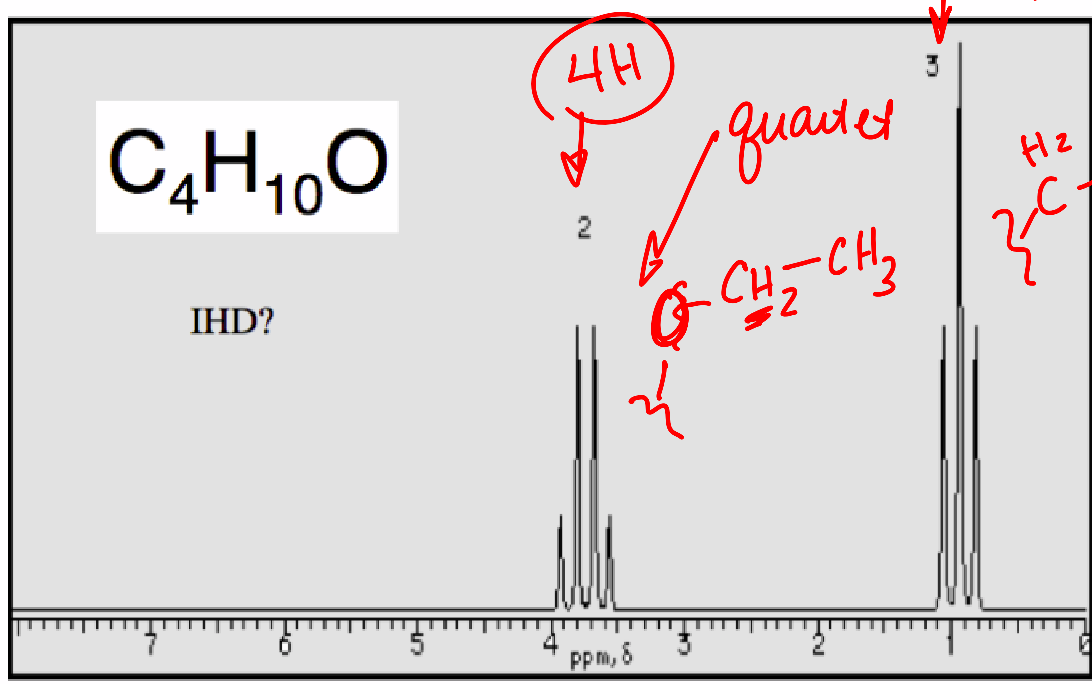
$2n+2=10$

$\downarrow$

C_4H_{10}

Ø degrees of unsat.





6H triplet

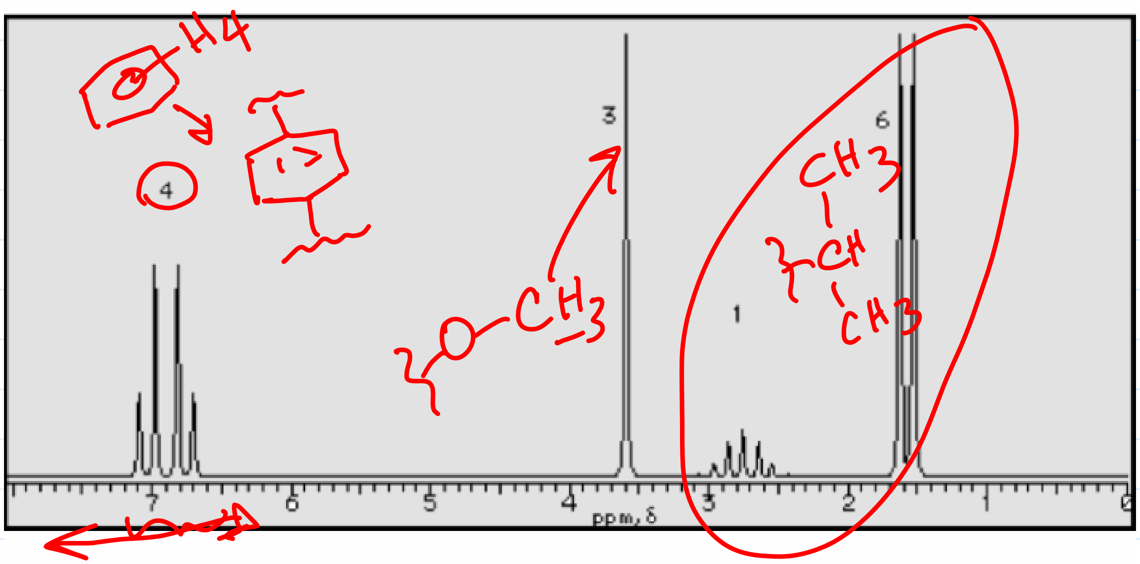
Symmetry

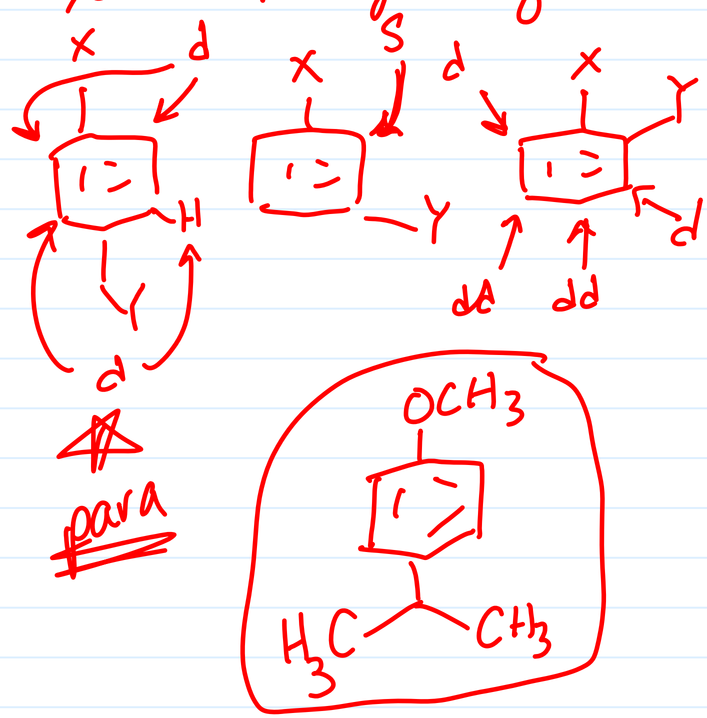
$H_3C-H_2C-O-CH_2-CH_3$

$C_{10}H_{14}O$ → HCF $C_{10}H_{14}$ sat alkane $C_{10}H_{22}$

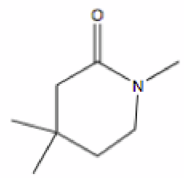
$22 - 14 = 8$

$8/2$ → 4 degrees of unsat.





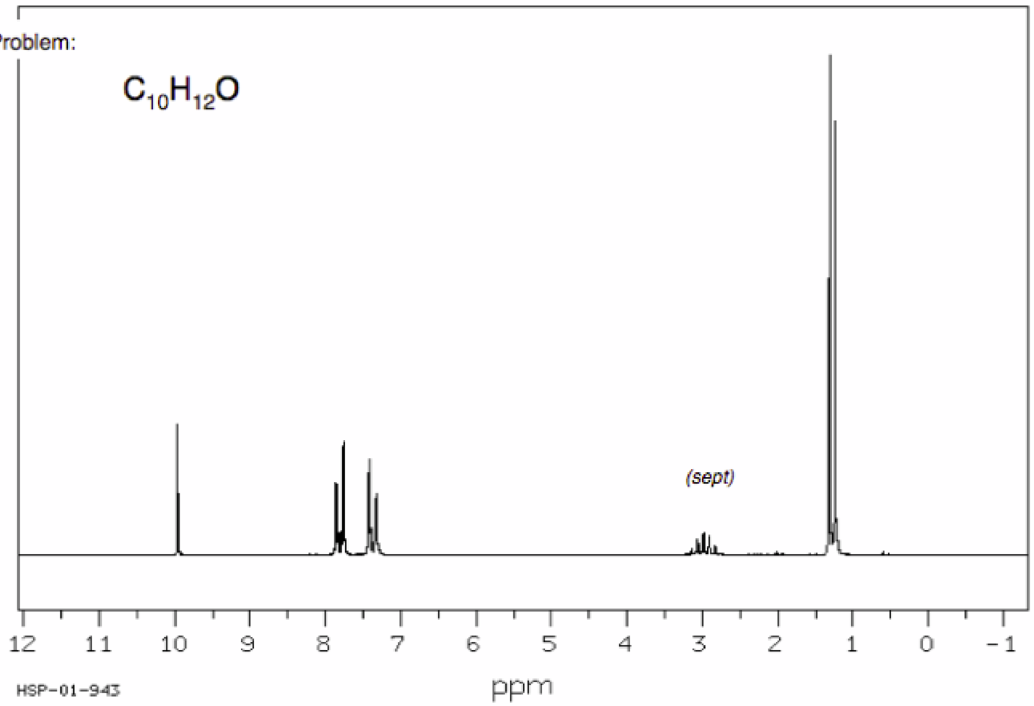
$C_8H_{15}NO$



C-13			**H-1**		
173.2	s		2.90	s	3H
46.9	t		3.2	t	2H
46.5	t		2.10	s	2H
44.2	t		1.47	t	2H
32.6	q		1.11	s	6H
27.4	s				
25.9	q (2)				

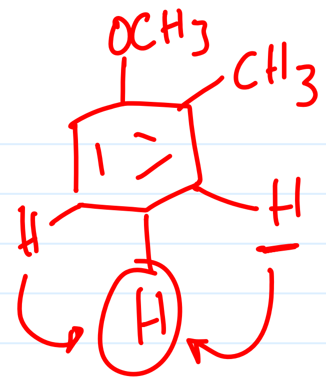
Problem:

$C_{10}H_{12}O$



from: structural database for organic compounds

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

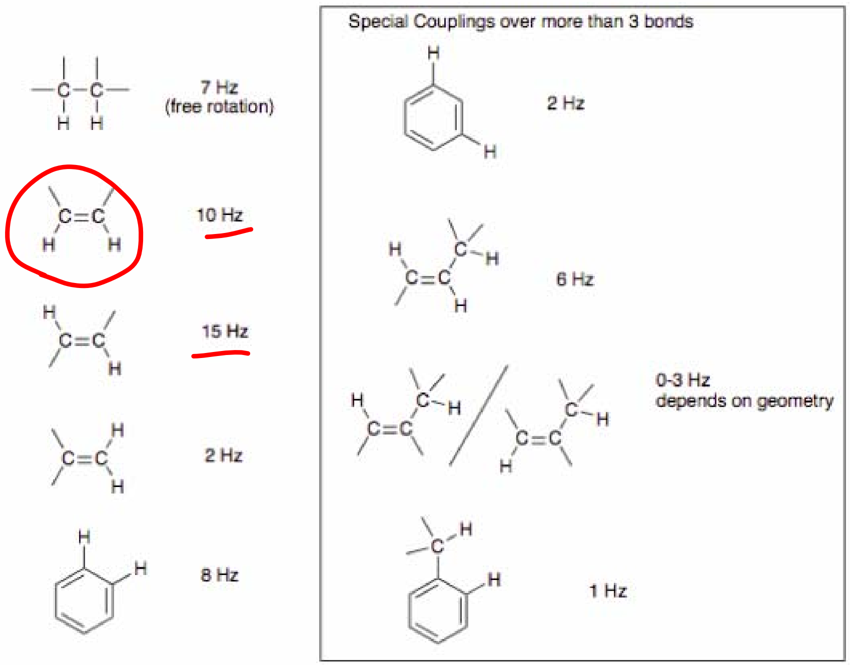


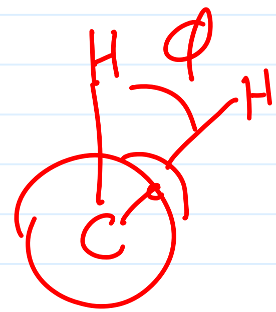
•Bad News: Life gets more complicated

•Good News: Splitting tells us more about the chemical structure.

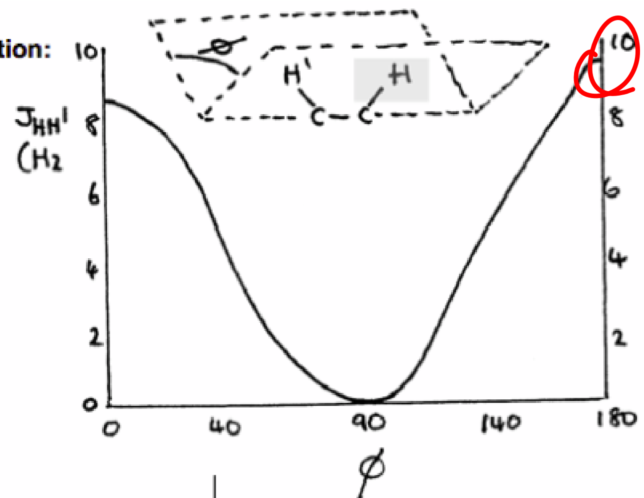
Coupling Constants Depends on Structure and Geometry

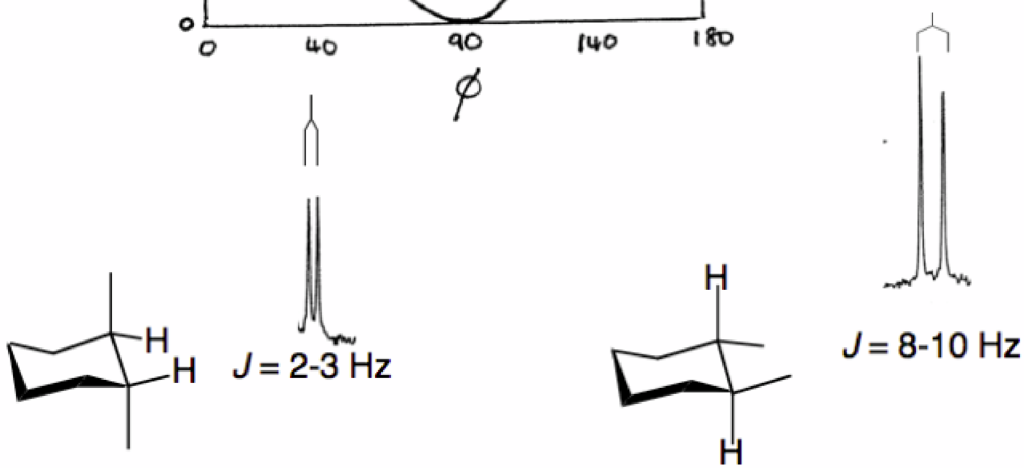
Approximate Coupling Constants.



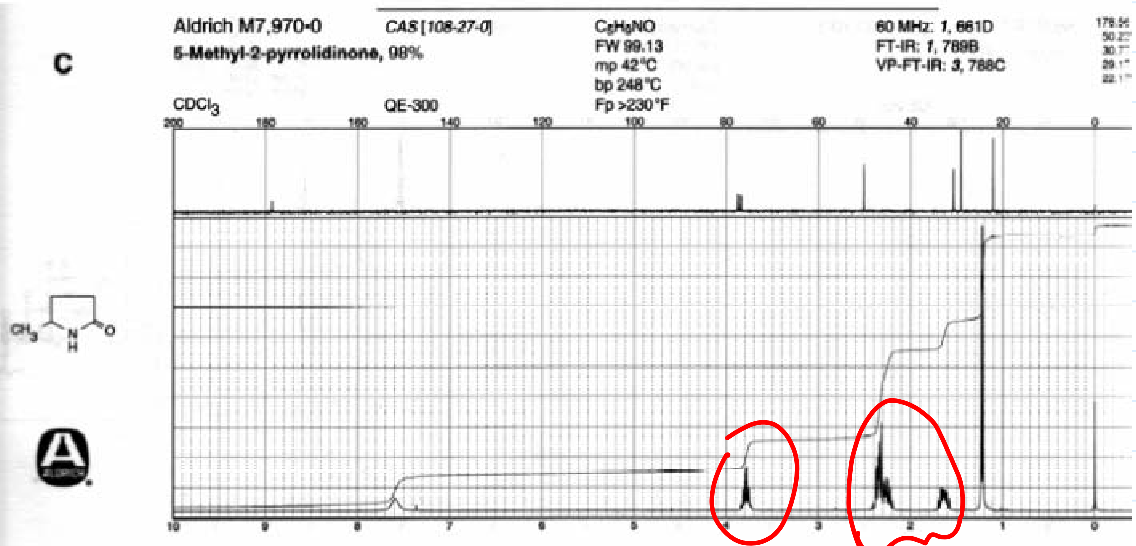


Karplus Equation:

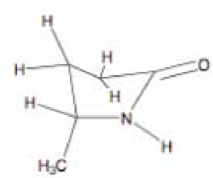




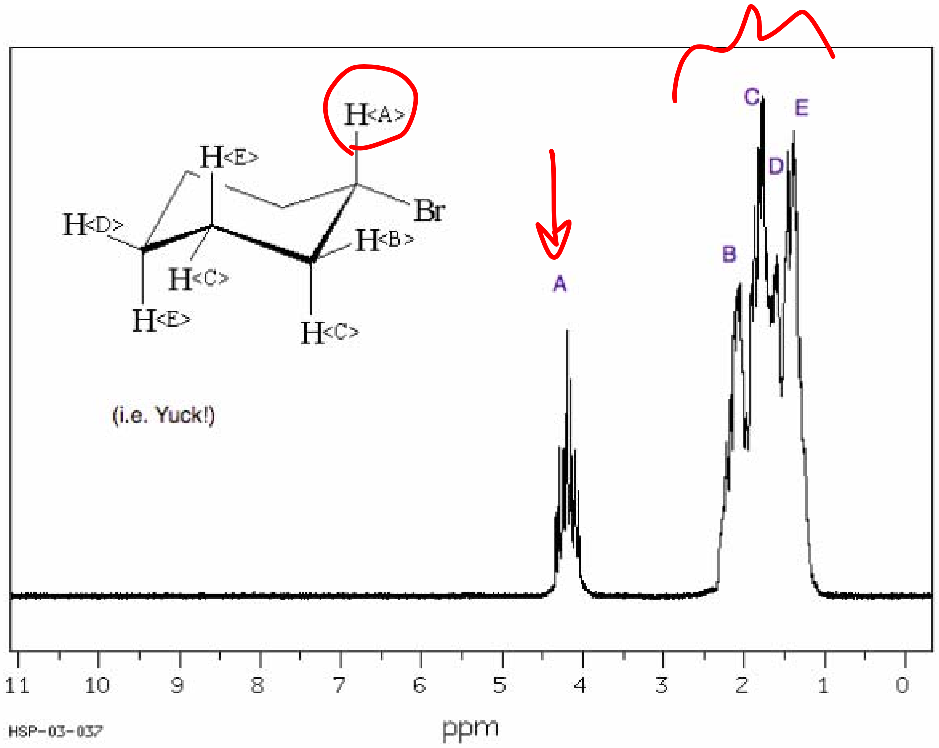
C

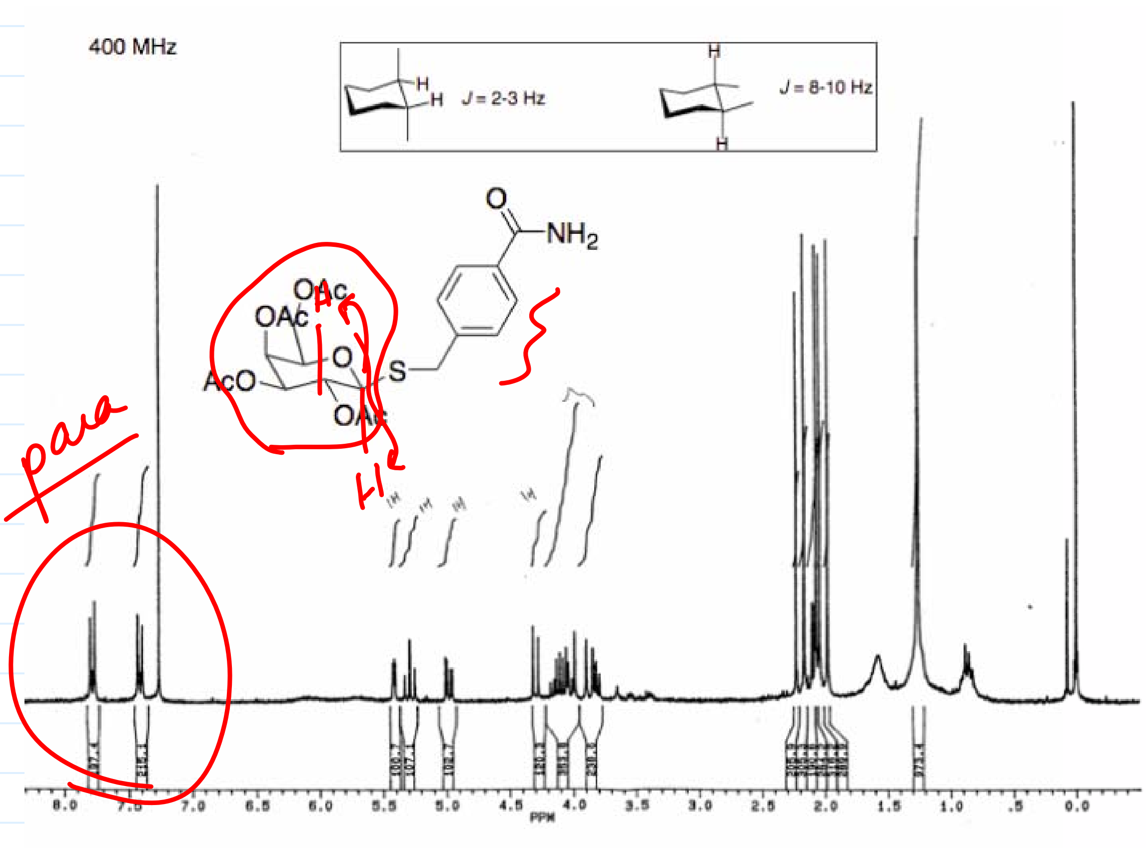


Aldrich M7,970-0
5-Methyl-2-pyrrolidinone, 98%
CAS [108-27-0]
C5H9NO
FW 99.13
mp 42°C
bp 248°C
Fp >230°F
60 MHz: 1, 661D
FT-IR: 1, 789B
VP-FT-IR: 3, 788C
CDCl3
QE-300

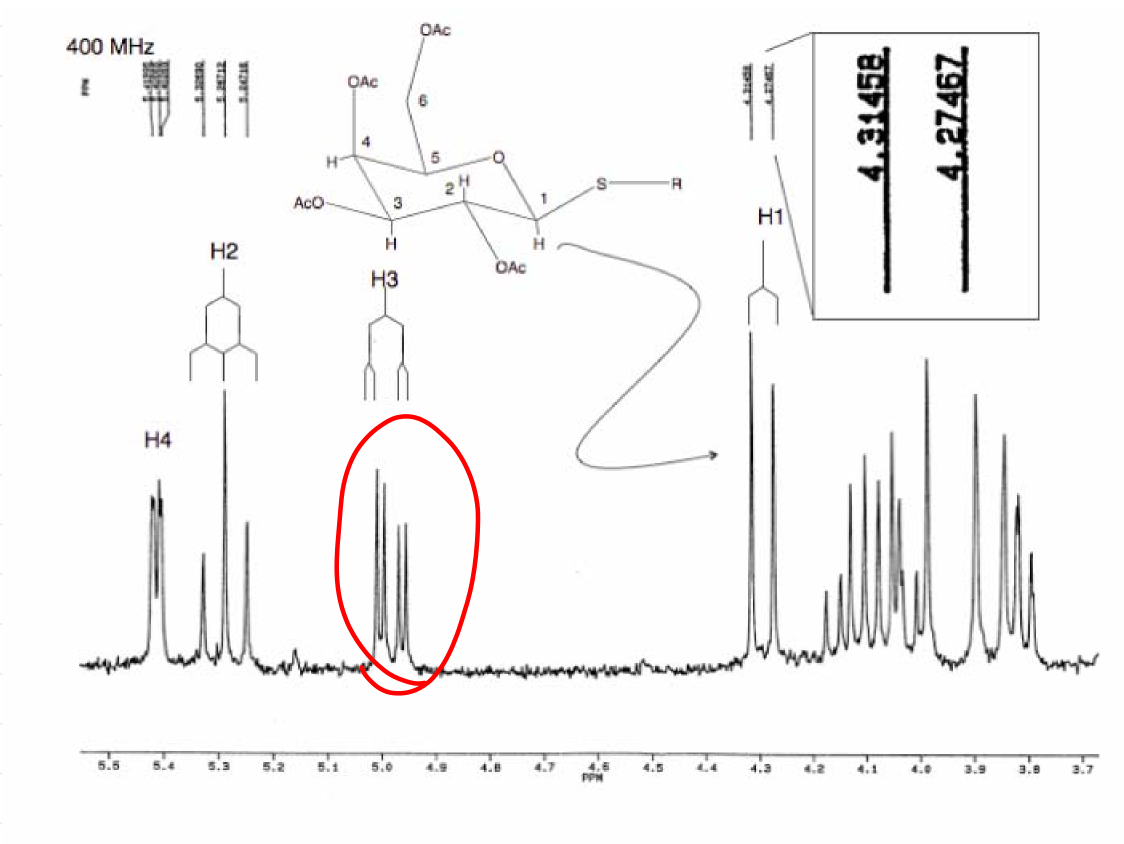


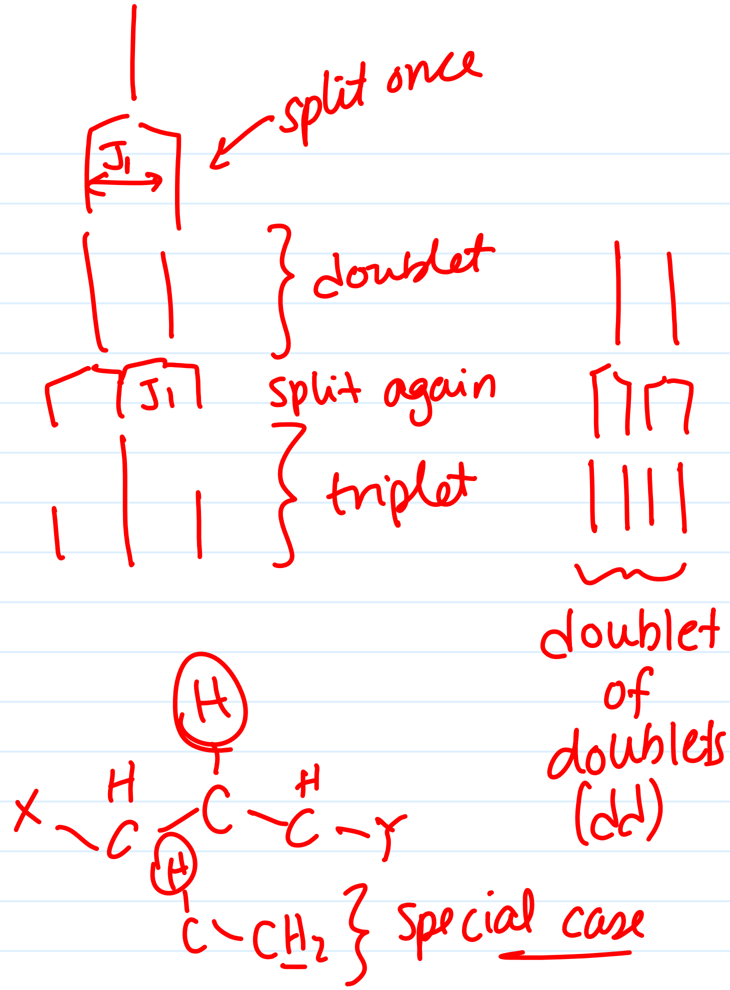
H
H
H
H
H
O
N
H
H3C


H<A>
H<E>
Br
H<D>
H<B>
H<C>
H<E>
H<C>
(i.e. Yuck!)
A
B
C
D
E
11 10 9 8 7 6 5 4 3 2 1 0
ppm
HSP-03-037

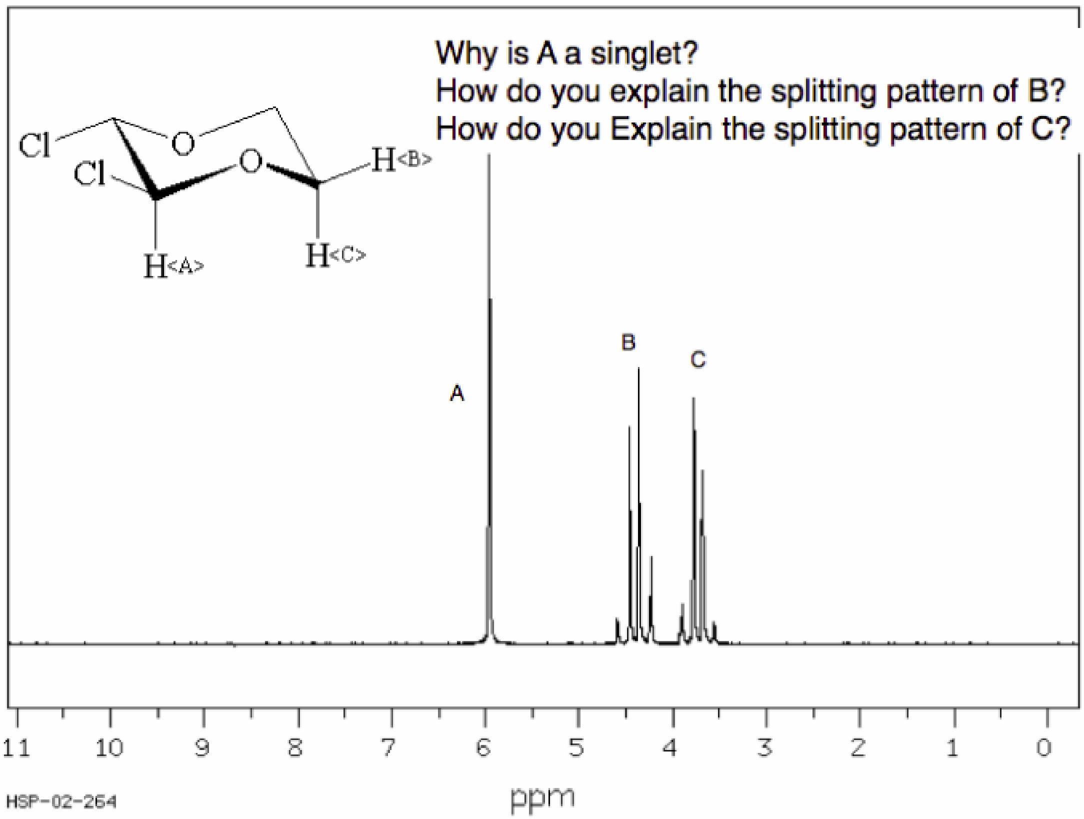


400 MHz
J = 2-3 Hz
J = 8-10 Hz
O
NH2
OAc
OAc
AcO
O
S
OAc
para
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM

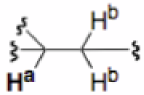

400 MHz
OAc
OAc
AcO
OAc
S
R
H1
H2
H3
H4
4.31458
4.27467
PPM

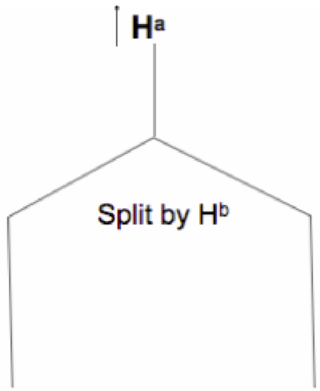

split once
J_1
doublet
split again
J_1
triplet
doublet of doublets (dd)
X
Y
H
C
CH_2
special case

Why is A a singlet?
How do you explain the splitting pattern of B?
How do you Explain the splitting pattern of C?

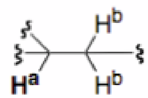


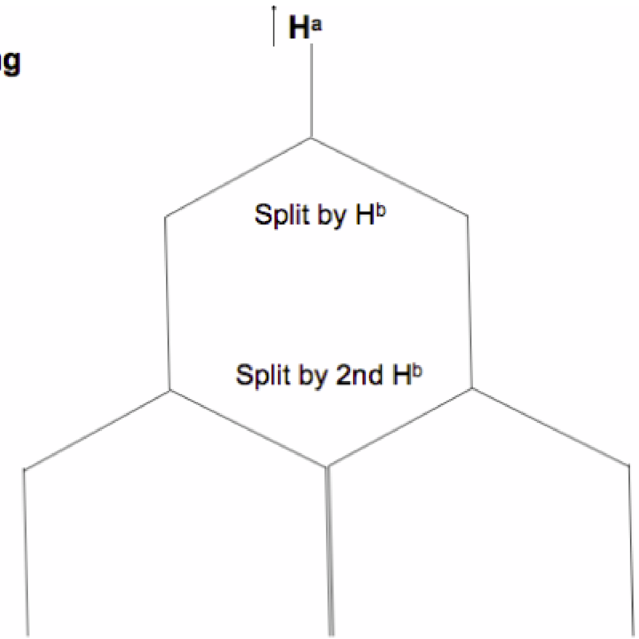
Spin splitting diagrams



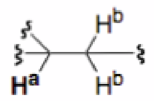


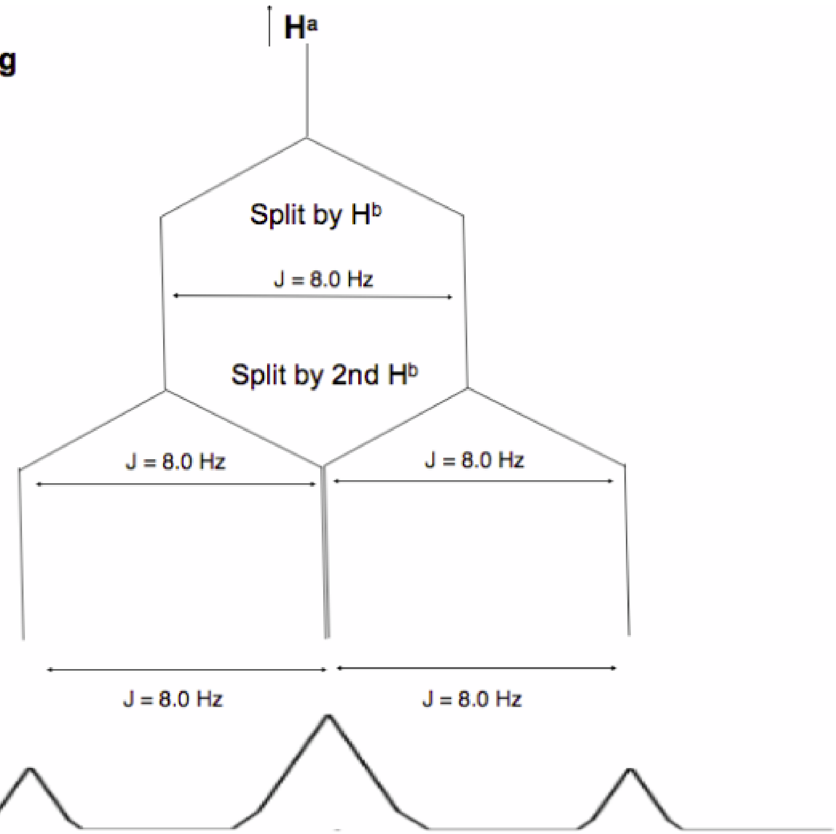
Spin splitting diagrams



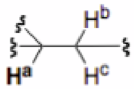


Spin splitting diagrams

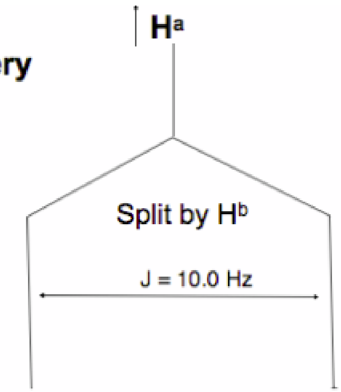




What if the H's are different, and have very different coupling constants??!



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



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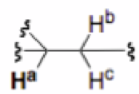

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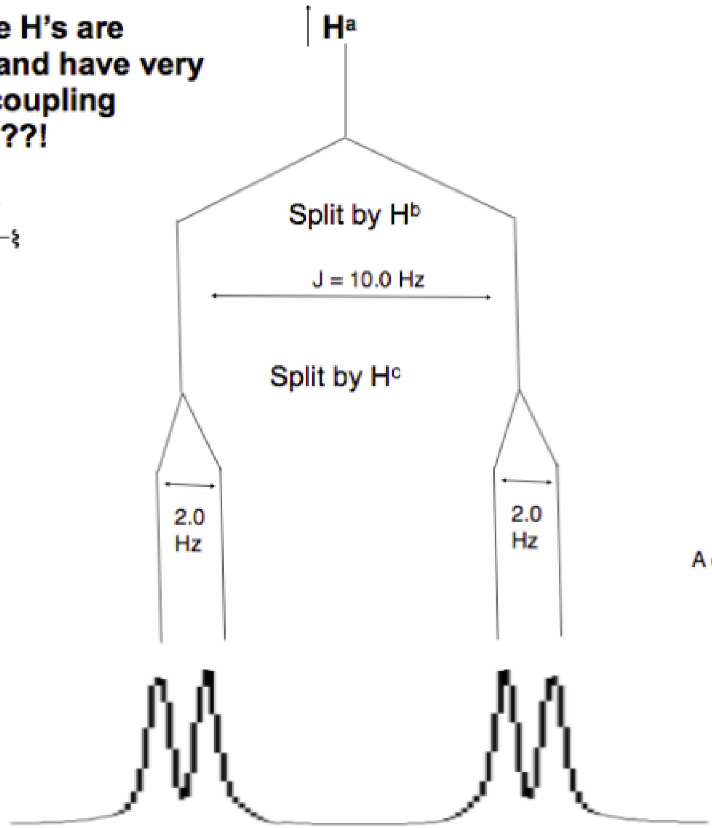
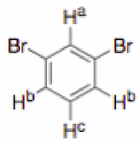


A doublet of doublets

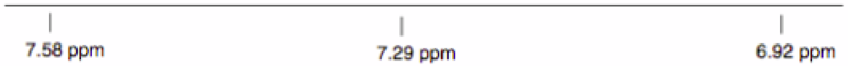
Aromatic (o,m,p) coupling constants

H^a 7.58 ppm
H^b 7.29 ppm
H^c 6.92 ppm



$J(H_{ab})$ 1.9 Hz
$J(H_{bc})$ 8.0 Hz
$J(H_{ac})$ 0.3 Hz

3 doublets of doublets



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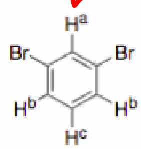

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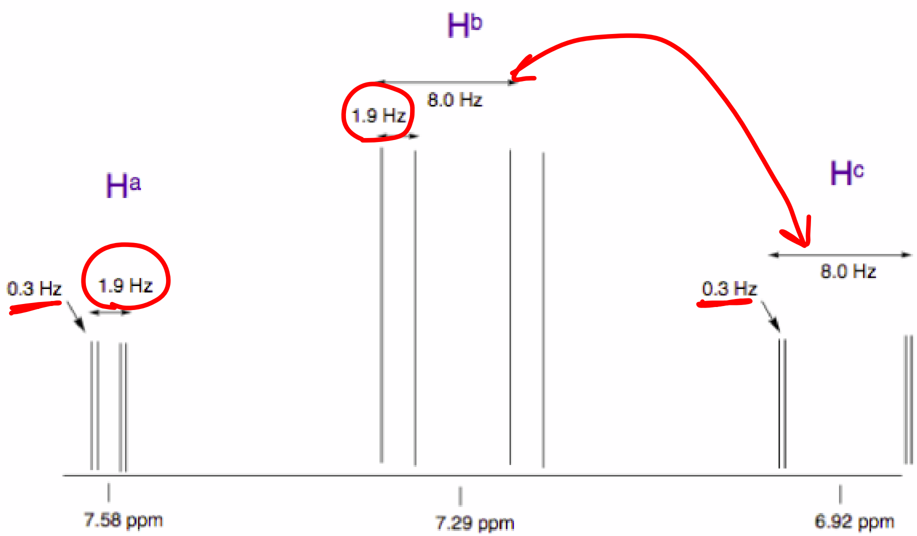
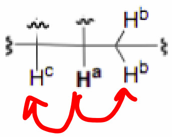
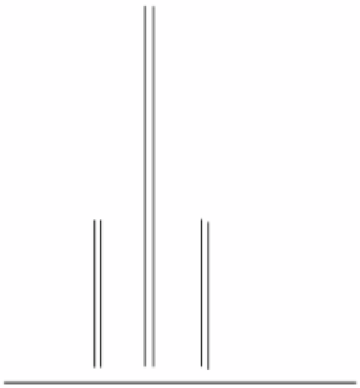


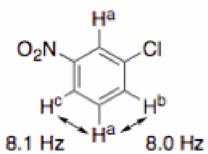
‘Doublets of triplets’ and ‘doublets of quartets’

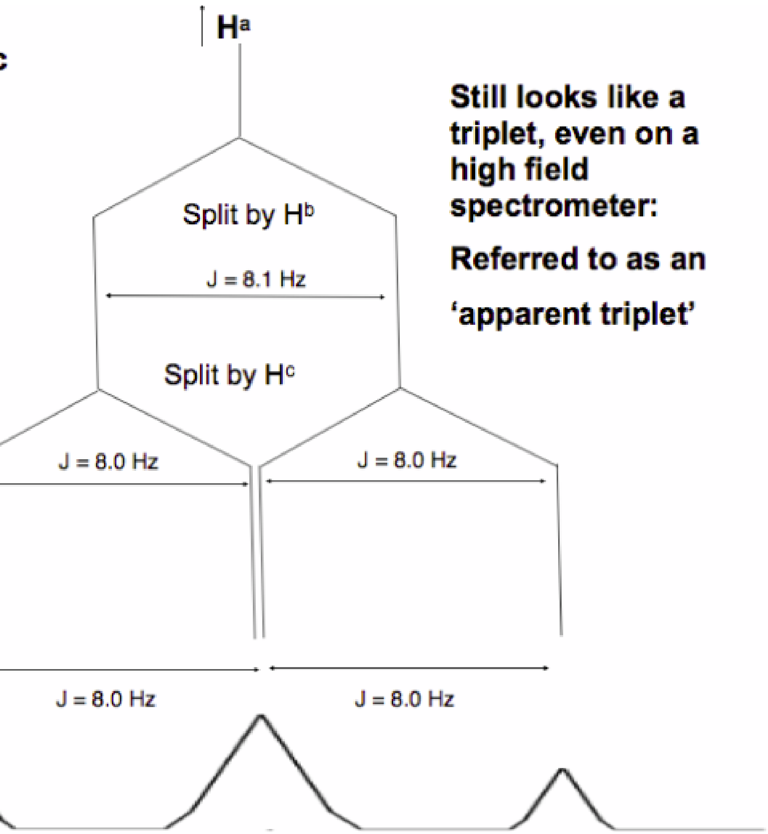
where $J_{ab} \neq J_{ac}$





What if Jab ~ Jac



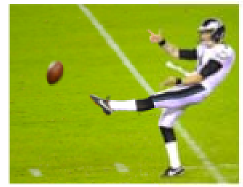


Still looks like a triplet, even on a high field spectrometer:

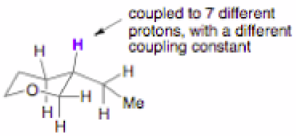
Referred to as an 'apparent triplet'

When the going gets really tough...

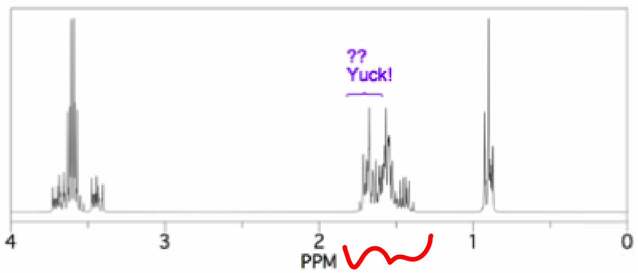
... we call things a **multiplet (m)**



situation 1: coupling pattern is very complex



described as: 1.5–1.3 (**m**, 1H)



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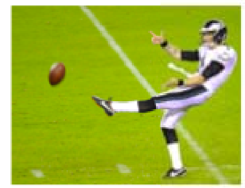
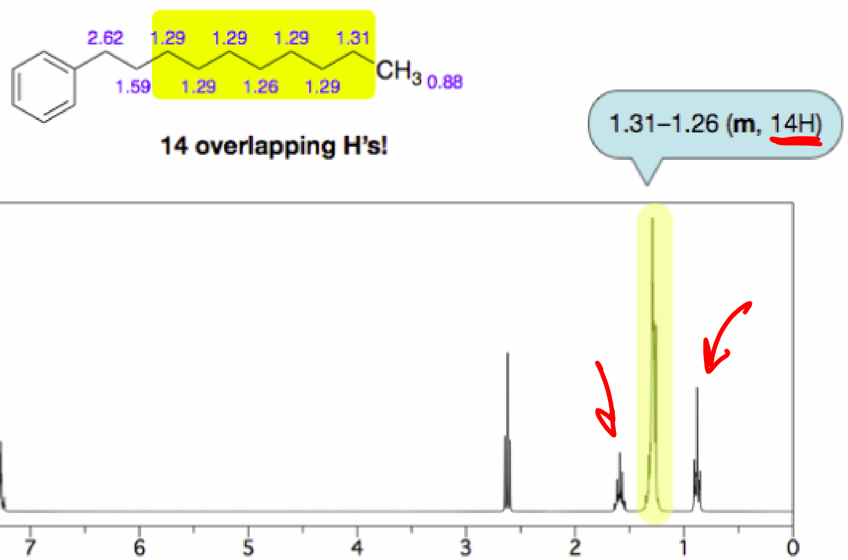
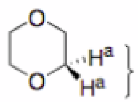


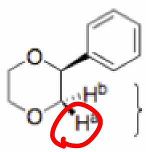
situation 2: your peak overlaps with other resonances



Diastereotopic Protons



Same chemical shift
No coupling

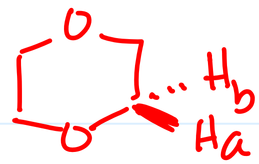


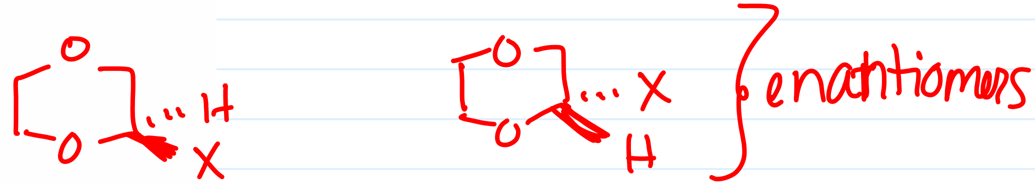
Different! "diastereotopic" protons

Diastereotopic protons:

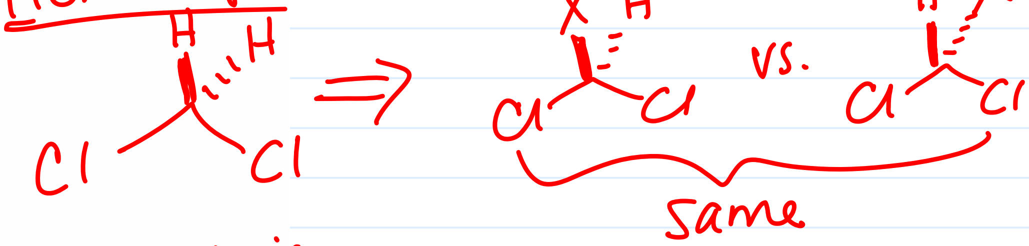
- CH_2 nearby a chiral center
- Chemical shifts differ (but may overlap in some cases)
- Coupling can often be observed

Enantiotopic

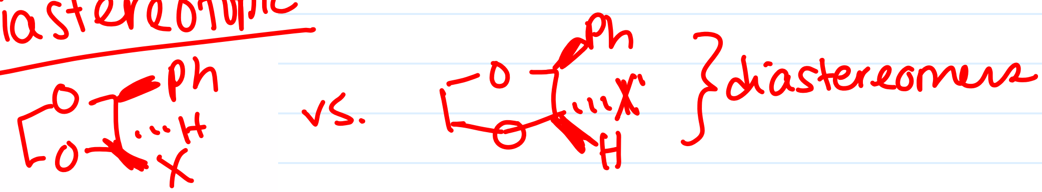




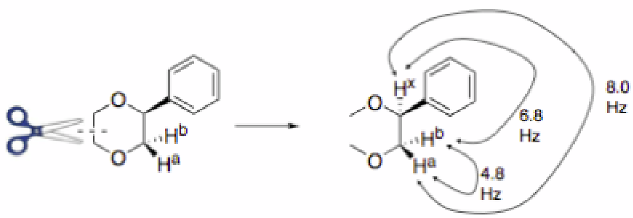
Homotopic



Diastereotopic



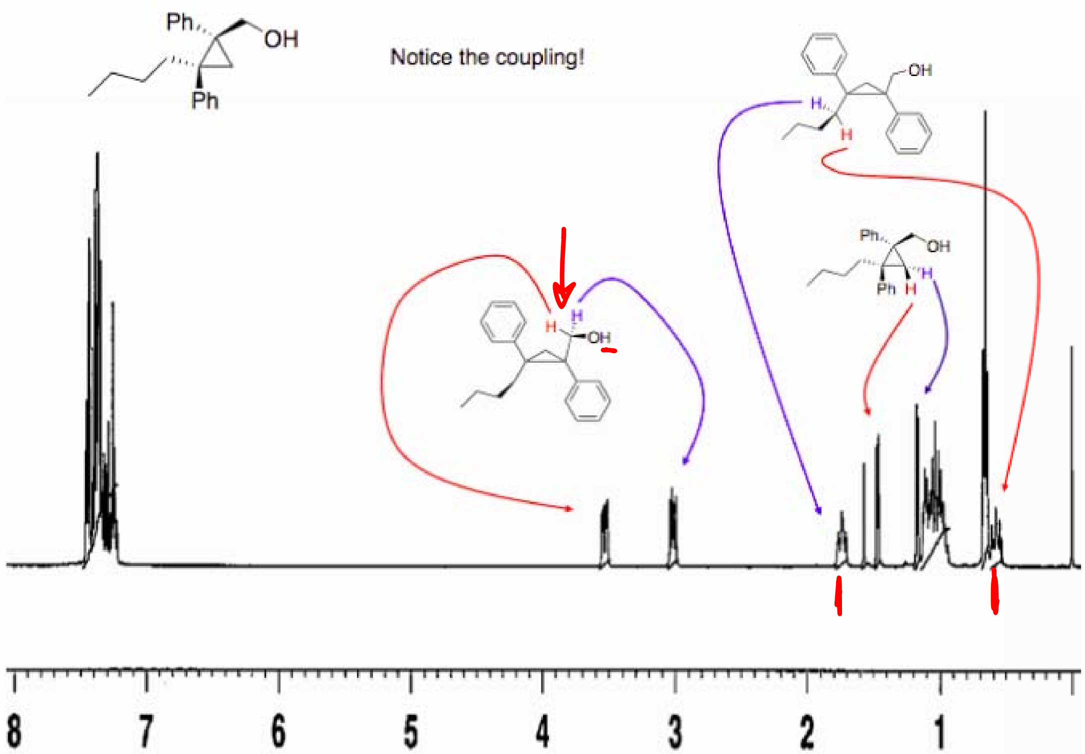
Diastereotopic Protons: not just in cyclic systems



Still diastereotopic

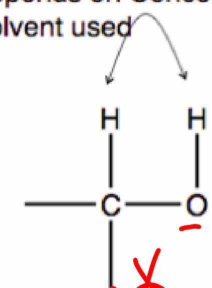
H^a: 3.6 ppm,dd, J = 8.0 Hz, 4.8 Hz
H^b: 3.9 ppm, dd, J = 6.8, 4.8 Hz
H^x: 4.5 ppm, dd, J= 6.8, 8.0 Hz

3 diastereotopic methylenes

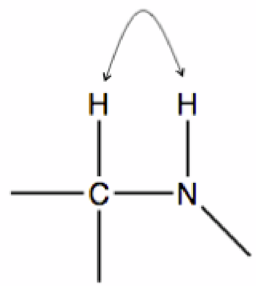


Coupling to Hetero Atoms

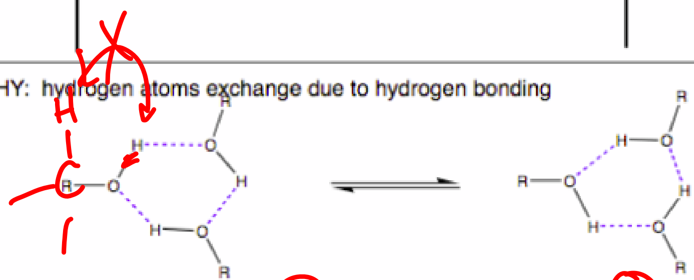
Observed Only Sometimes
Depends on Concentration
Solvent used



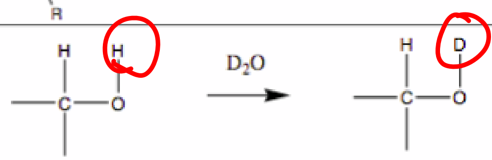
Rarely Observed



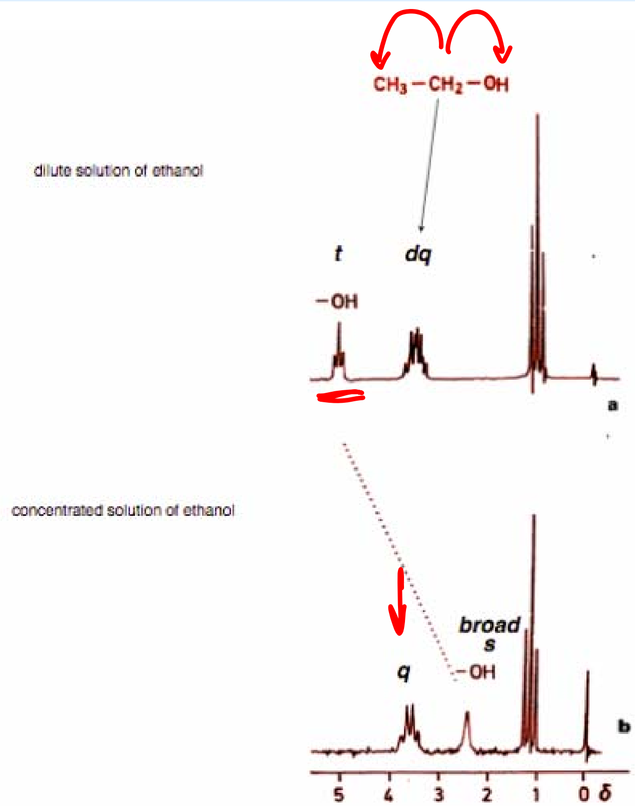
WHY: hydrogen atoms exchange due to hydrogen bonding



Easy Test



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



from M. Denk http://131.104.156.23/Lectures/CHEM_207/CHM_207_NMR.htm