Learning Guide for Chapter 5 - NMR Spectroscopy

I. Introduction to NMR spectroscopy

To introduce you to NMR spectroscopy, we will first compare it to IR spectroscopy.

IR spectroscopy	NMR spectroscopy
type of light: infrared	type of light: radio waves
what causes light to be absorbed: vibration of a bond with a dipole at the same frequency as the light	what causes light to be absorbed: transistions in energy state of nuclei of atoms (complicated - we won't worry about how it works)
what bands represent: bonds	what peaks represent: atoms
x-axis: frequency in cm^{-1}	x-axis: ratio of magnetic field strength in ppm
what we learn about a compound: functional group	what we learn about a compound: structure of the compound

Which kind of spectroscopy can distinguish each pair of compounds?

IR			no
	functional group	yes C=O vs O-H, C-O	both have O-H, C-O (different fingerprints)
NMR	structure	yes	yes

Which type of spectroscopy is more powerful?

NMR - more powerful, more complication, more expensive!

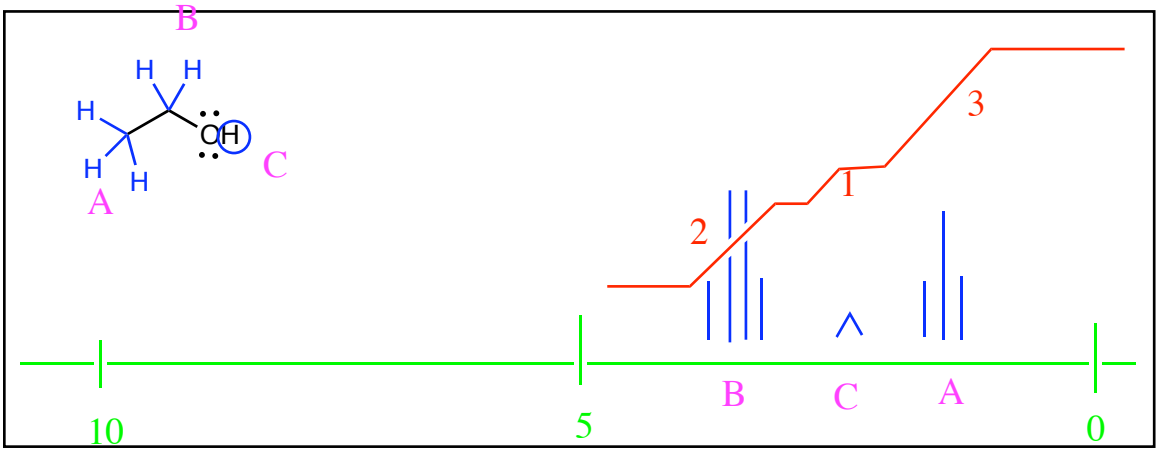
What characteristic allows an atom to be detected by NMR?

atomic weight is an odd number

What elements are commonly found in organic molecules? Which are suitable for NMR?

element:	isotopes:	NMR?
carbon	^{12}C	no
	^{13}C	yes - not as useful, only 1% of C's
hydrogen	^{1}H	yes - most common kind of NMR (also called proton NMR)
oxygen	^{16}O	no
nitrogen	^{14}N	no

A typical proton NMR spectrum looks like this:



Each cluster of spikes is called a: peak

Where can you find each of the following, and what does it tell you about the peak?

chemical shift:	where it is on the x-axis	what other atoms are nearby
integration:	area under the peak	how many H's are in that peak
splitting:	how many spikes	how many neighbors

What should you be able to do?

1. Assign peaks on a compound to a spectrum.
2. Sketch the spectrum of a compound.
3. Deduce the structure of an unknown compound from its spectrum.

II. Distinguishing Equivalent Hydrogens

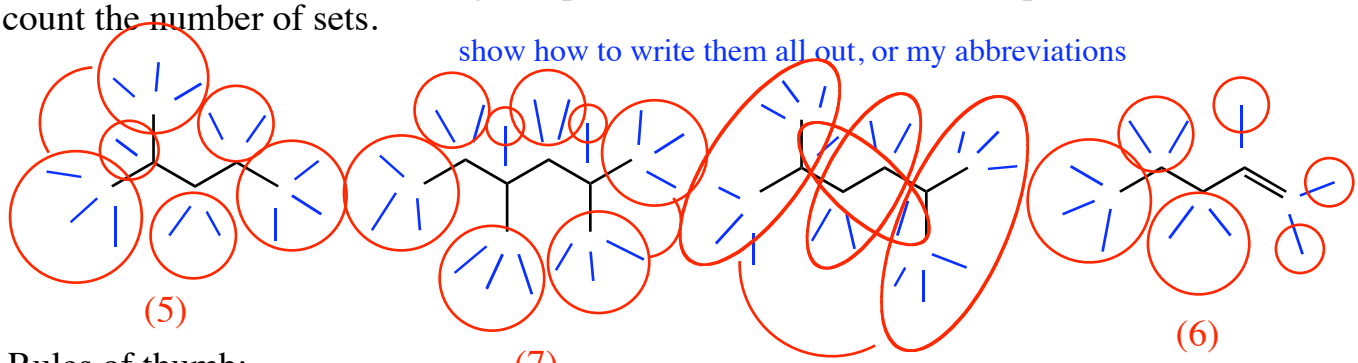
When do we say that two H's are equivalent? same nearby atoms, same # of neighbors

What happens on a spectrum when two H's are equivalent?

both part of the same peak, gets more area (draw two peaks on top of each other, then show the integration getting larger)

Draw in all H's for the following compounds. Circle those that are equivalent, and then count the number of sets.

show how to write them all out, or my abbreviations



(5) (7) (3) (6)

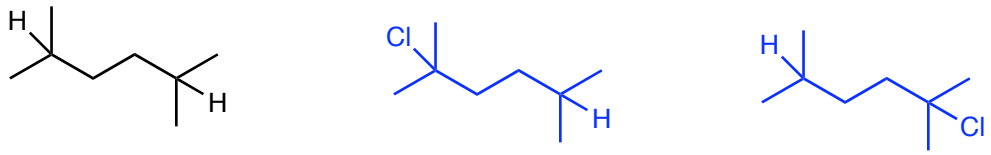
Rules of thumb:

1 - H's on the same carbon are equivalent (except on C=C)

2 - H's on different carbons are not equivalent (except on identical groups)

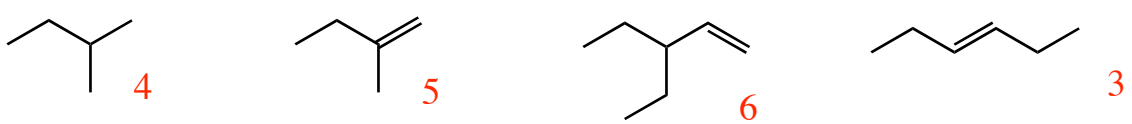
More exact rule:

If you can separately replace two H's with a Cl, and the same compound results, they are equivalent.

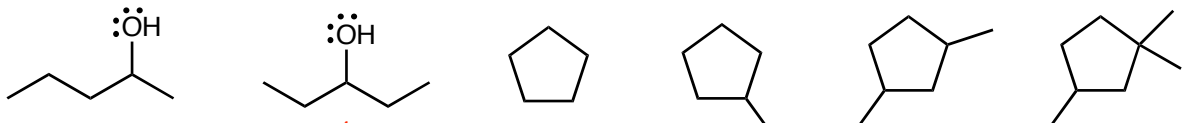


same compound - H's are equivalent

How many sets of equivalent H's are present in each of the following molecules?



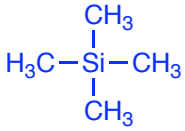
4 5 6 3



6 4 1 4 4 6

III. Chemical Shift

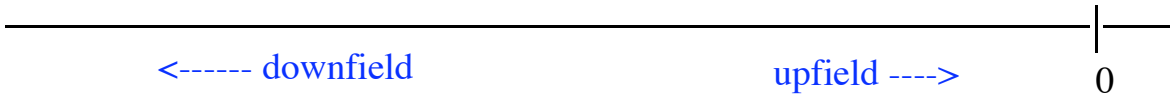
What compound is used to establish "0" on the chemical shift axis? Why do you think this would make a good reference compound?

tetramethylsilane (TMS) 

12 equivalent H's - strong signal with small amount of compound

H's near Si are to the right of nearly all other compounds

Draw arrows showing the direction of upfield and downfield:



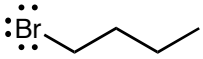
Predict which set of hydrogens will be farthest downfield. When will this rule be useful?

1) CH > CH_2 > CH_3

1.4 1.3 0.9

fewer H's - farther downfield

CH_3's - farthest upfield
can tell CH and CH_2 apart

2) 

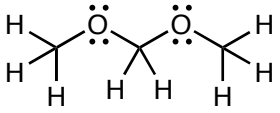
3.4 1.7 1.3 0.9

closer to EN atom
farther downfield

CH_3F CH_3Cl

4.26 ppm 3.05 ppm

more EN atom
farther down



3.23 ppm 4.42 ppm

two EN groups
farther downfield
(effect is additive)

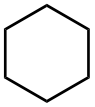
good for detecting H's next to alcohols, amines, alkyl halides

3) $H_2C{=}CH_2$ $HC{\equiv}CH$ $H_3C{-}CH_3$

4.5 - 6.5 ppm 2.5 - 3.0 ppm 0.5 - 1.5 ppm

sp^2 downfield sp sp^3 upfield

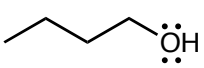
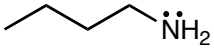
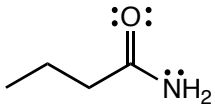
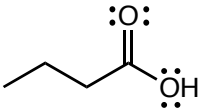
makes H's attached to C=C easy to spot

4)  

huge effect - easy to identify H's on benzene rings

7.2 ppm 1.3 ppm

aromatic - way downfield

5)    

1-5 ppm 1-5 ppm 7.5-9.5 ppm 10-13 ppm

hydrogen bonding - wide range possible

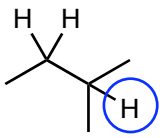
affects alcohols, amines, amides, and carboxylic acids

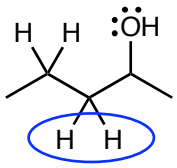
affected by concentration of sample - same compound may have different values under different conditions

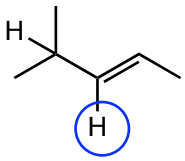
also affects width of band - may be so wide you can't see (except in integration line)

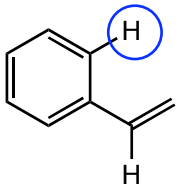
skinny peak broadened peak very broad peak

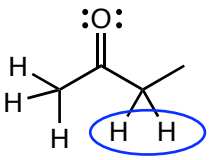
Which of the set of H's shown on each compounds will appear furthest downfield?

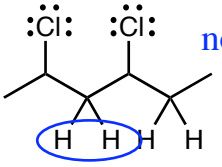
 $CH > CH_2$

 closer to O

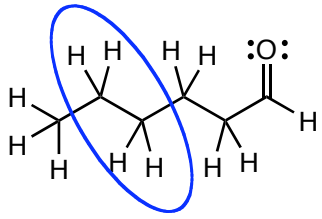
 $sp^2 > sp^3$

 aromatic

 $CH_2 > CH_3$

 next to 2 Cl's

How many peaks should the following compound have? Which two would be most likely to overlap?



should be 6

only 5 actually show up

two sets are too close to separate

What are some useful ranges to remember?

H's on C next to C=O 2.0-2.5 ppm

H's on C with N 2.5-3.0 ppm

H's on C with O or X 3-4 ppm

OH or NH in alcohols or amines 1-5 ppm

H's on C=C 4.5-6.5 ppm

H's on aromatic ring 6.5-8.5 ppm

H's on amides 7-9 ppm

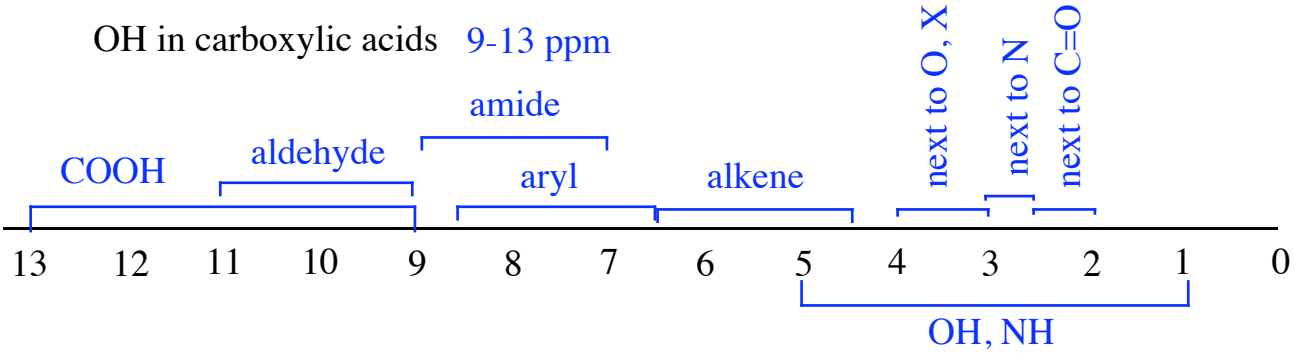
H's on C=O 9-11 ppm

OH in carboxylic acids 9-13 ppm

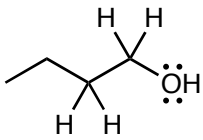
these are not rules, only guidelines

not all H's are covered here

if more than one thing affects an H, both will pull it downfield



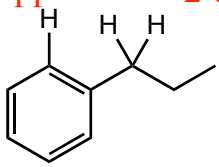
Give the range at which you would expect to find the following H's:



3-4 ppm

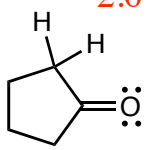
1-5 ppm

less than 3 ppm

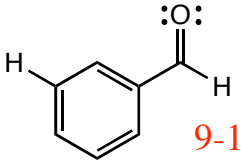


~ 7 ppm

2-3 ppm

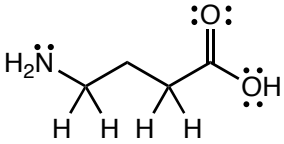


2.0-2.5 ppm



~ 7 ppm

9-11 ppm

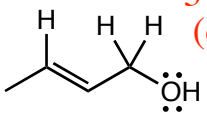


1-5

9-13

2.5-3

2-2.5

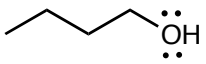


4.5-6.5

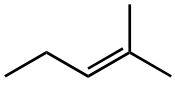
3-4 (closer to 4)

1-5 ppm

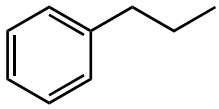
What H's should stand out on the following compounds?



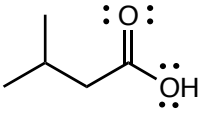
3-4 ppm
1-5 ppm (broad)



4-6 ppm



~7 ppm



9-13 ppm (broad)

IV. Integration

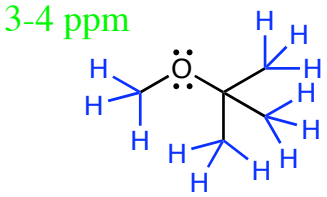
What does integration mean, mathematically? the area under a curve

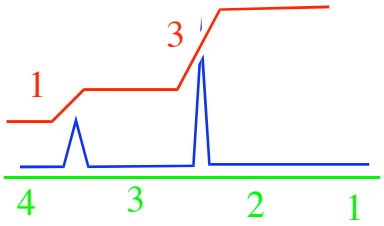
What does the integration tell us on an NMR spectrum? how many H's are in that peak

Why does the area under a curve increase when there are more H's in a peak?

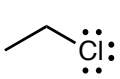
the peaks exactly overlap, so that they just get bigger (more area)

Identify the sets of equivalent H's in the following compound. Which is furthest downfield? Which will have a greater integration?

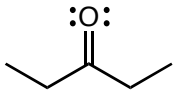




Compare the integration ratios for the following compounds. Can you tell them apart?

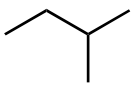


2:3

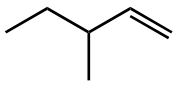


4:6 = 2:3 integration would look the same

Predict the integration ratio for each of the following compounds.



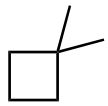
3:2:1:6



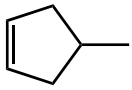
3:2:1:3:1:1:1

1

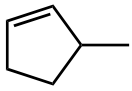
2:4:1:3



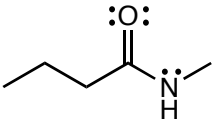
2:4:6
(1:2:3)



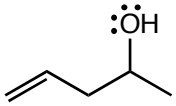
2:4:1:3



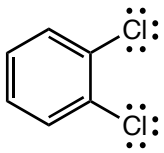
1:1:2:2:1:2



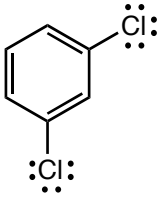
3:2:2:1:3



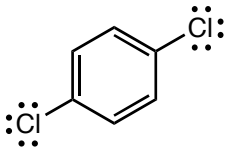
1:1:1:2:1:1:3



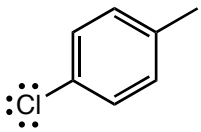
2:2



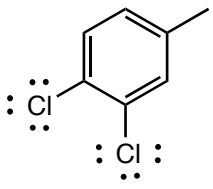
1:2:1



1



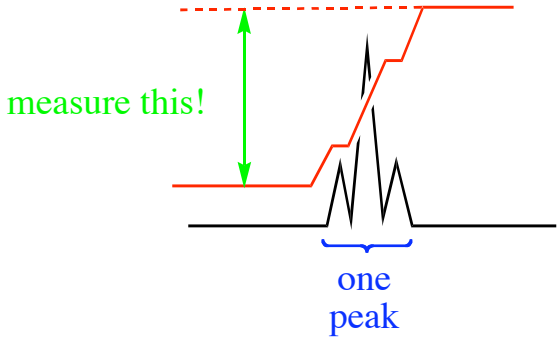
2:2:3



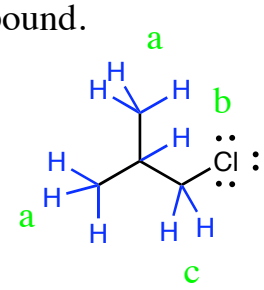
1:1:1:3

How do we measure the integration?

measure how far up the integration line goes
from the beginning of the peak to the end



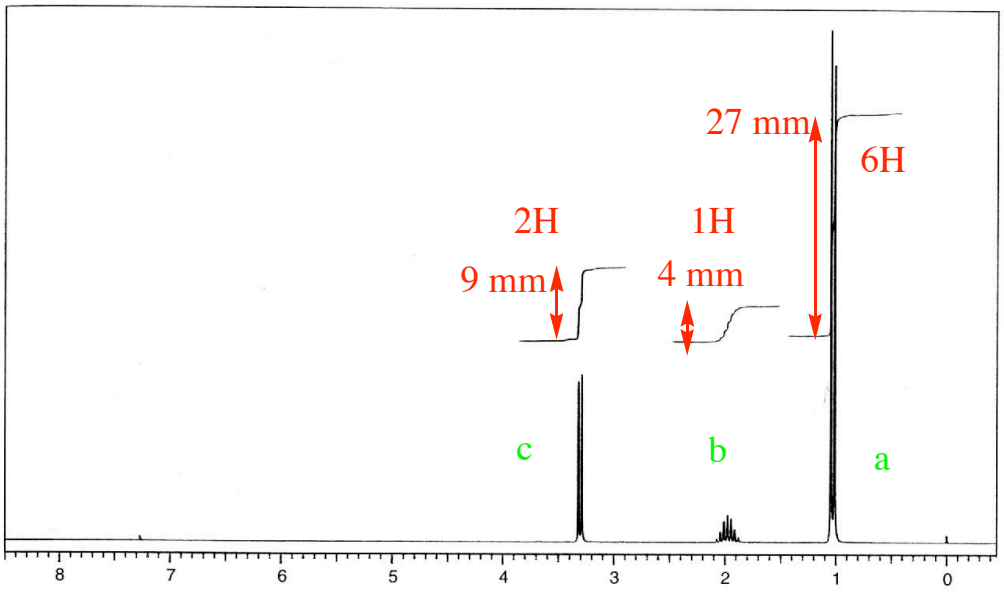
Identify each set of equivalent H's in the following compound.
Give the chemical shifts you would expect.
Give the integration.
Match up the H's with the peaks in the spectrum.



c - 3-4 ppm

c > b > a

2:1:6



What does the height of a peak tell you? nothing! only the area matters

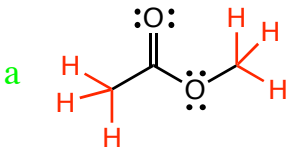
short, broad peak tall, narrow peak

same area!
same # of H's

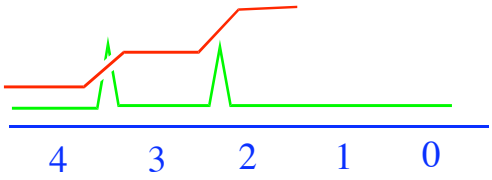
V. Spin-spin splitting

What does splitting mean? the number of spikes in a peak

What happens when H's are separated by more than one atom? they are both singlets



a - 2-2.5 ppm
b - 3-4 ppm
3:3



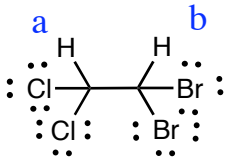
What happens when a set of equivalent H's has one or more neighboring H's?

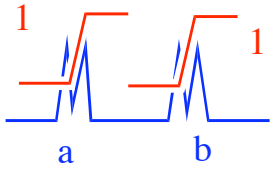
the peak is split into cluster of spikes

How can you tell what splitting a peak will have?

original spike + one for every neighbor

Sketch the spectra of the following compounds:



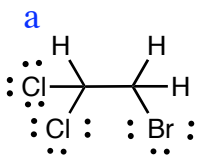


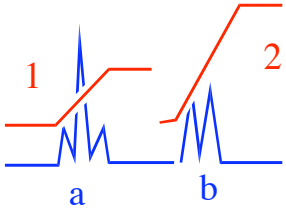
1 neighbor = doublet (equal height)

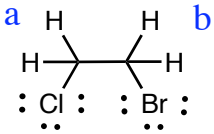
sometimes lean toward each other

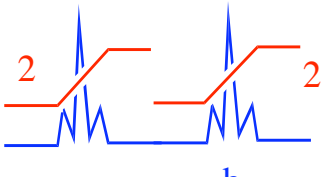
H's that split each other are said to be "coupled"

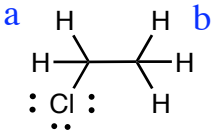
2 neighbors = triplet (1:2:1)

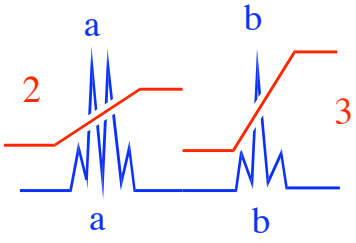




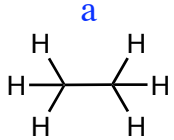


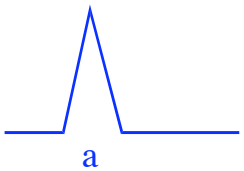




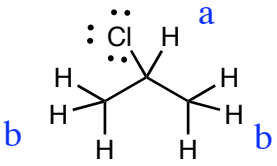


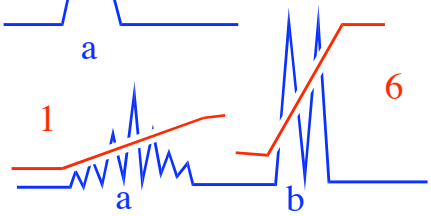
3 neighbors = quartet (1:3:3:1)





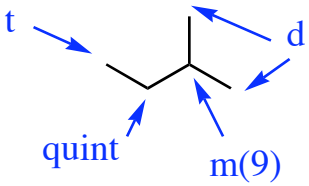
if they are equivalent,
they don't count as neighbors

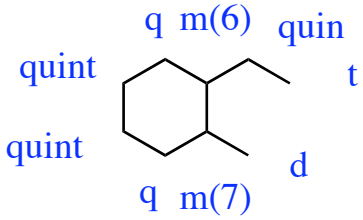




4 neigbors = quintet
5 neighbors = multiplet(6)
6 neighbors = multiplet(7) etc

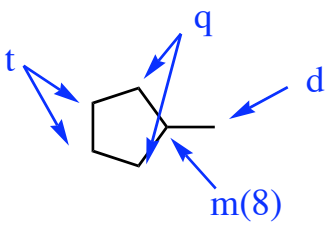
Assign splitting to each set of equivalent H's in the following compounds.

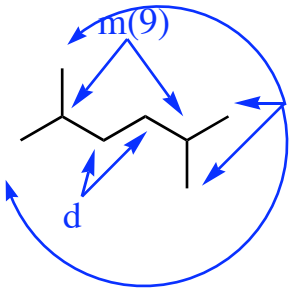




doublet = d
triplet = t
quartet = q
quintet = quin
multiplet(6) = m(6)
etc

H's on either side count



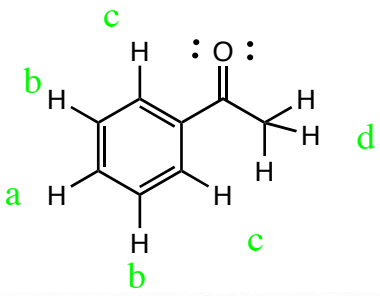


12:2:9
d, m(9), d

H's in the same set can't split each other
H's can only see their own neigbors (not equivalent's neighbors)

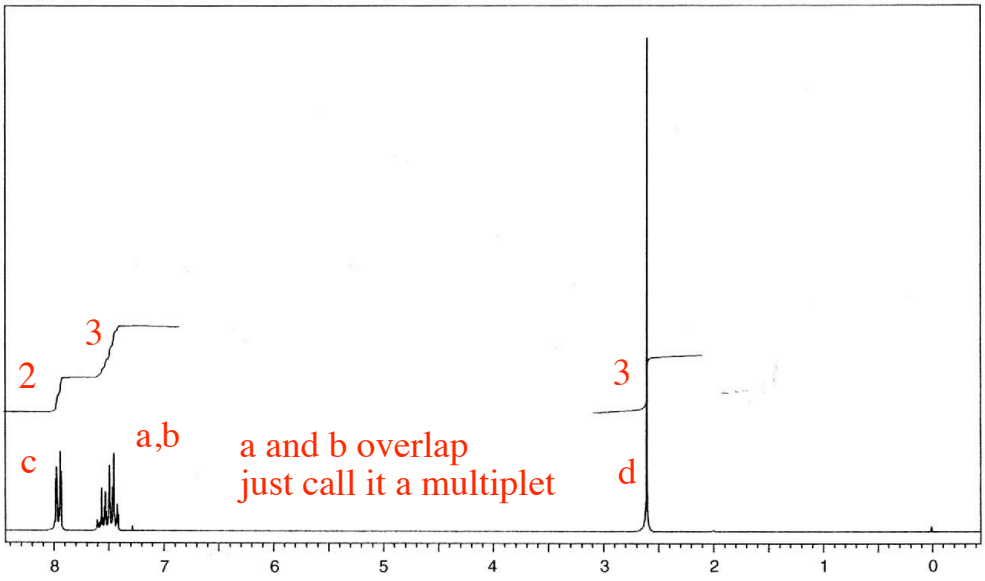
What happens when the chemical shifts of two separate peaks are so similar that they overlap?

it forms a multiplet



a - 1 H, t
b - 2H, t
c - 2H, d
d - 3 H, s

c > b > a > d

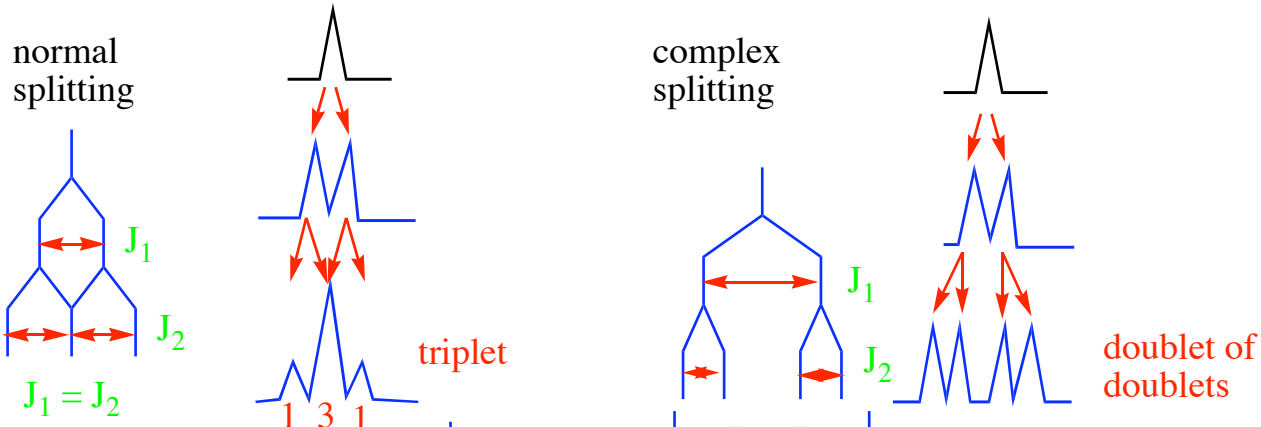


When is this common? H's on benzene rings, lots of CH_2's in a row

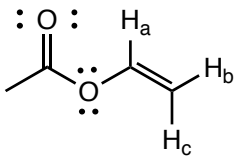
What is complex splitting? neighbor + 1 rule doesn't work

What kind of H's commonly show this? H's on C=C

What causes it? coupling constants are not the same, so splitting doesn't overlap

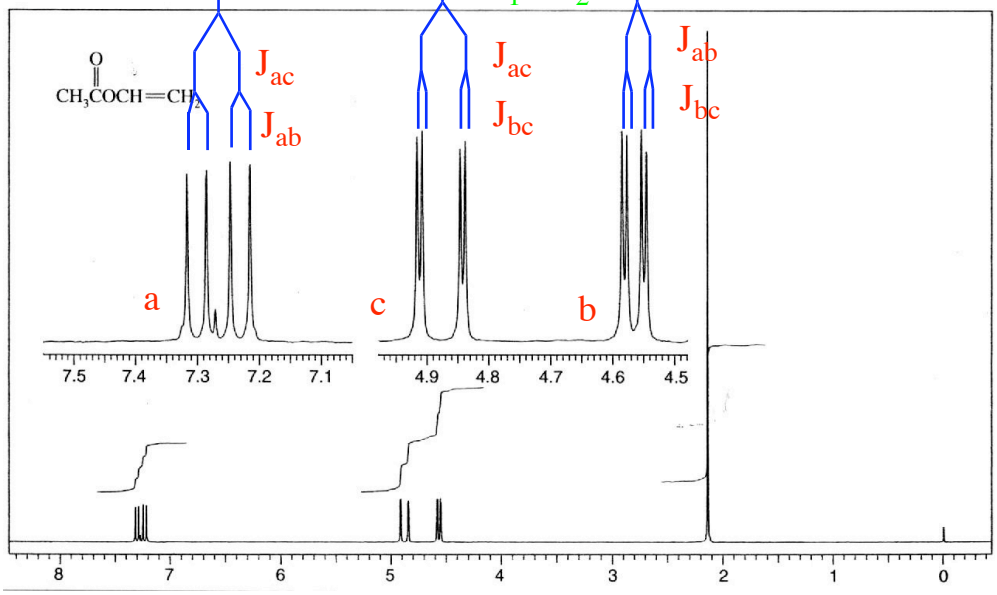


Example:



trans > cis

smallest J on same C

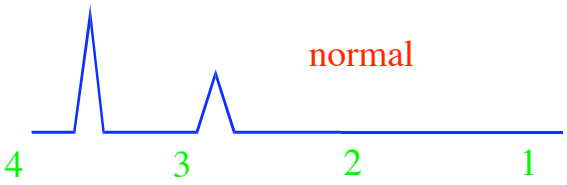


Do H's on alcohols and amines usually participate in splitting? no - H-bonding causes splitting to average out

CH_3OH (regular sample)

a: 3-4, 3H, s

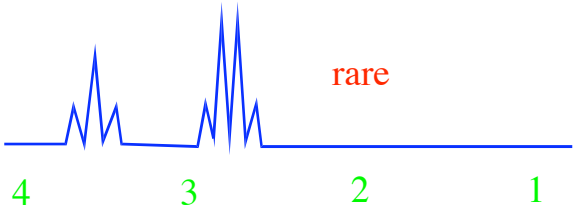
b: 1-5, 1H, s



CH_3OH (dilute, no water)

a: 4-6, 3H, d

b: 1-5, 1H, q



VI. Deuterium in NMR

What is deuterium?

isotope of hydrogen — ^1H regular hydrogen H; ^2H deuterium D — same chemical behavior

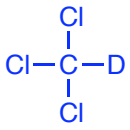
Why is it useful in NMR? doesn't show up on an NMR spectrum - it is invisible!

Why are deuterated solvents needed in NMR?

to take a spectrum, the sample must be dissolved in a solvent

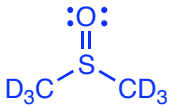
we don't want the solvent to show up, only the sample compound

What are the most common NMR solvents?

$CDCl_3$ 

nonpolar, moderately polar compounds

most common

DMSO-d_6 

polar compounds

more expensive, absorbs water

Do deuterated solvents show up on an NMR spectrum? no

Is there a peak that shows up because of the solvent? Why?

contamination with regular H

$CHCl_3$ 7.25 ppm

DMSO 2.5 ppm

If water is present in the compound or the solvent, where will it appear on the spectrum?

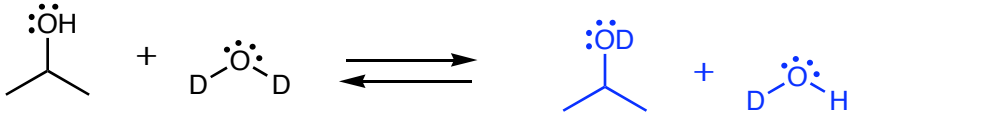
depends on the solvent

water in $CDCl_3$ - 1.5 ppm

water in DMSO-d_6 - 3.35 ppm

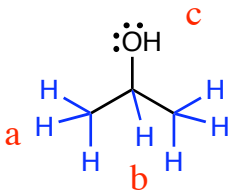
What will happen if D_2O is added to a sample containing an alcohol?

H will be replaced with a D - won't show up on the spectrum



OH peak — no peak — no OH peak — H shows up

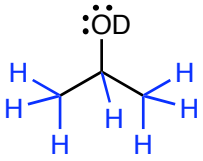
spectrum before adding D_2O:



a

a - 6H, d
b - 1H, m(7)
c - 1H, s

spectrum after adding D_2O:



a - 6H, d
b - 1H, m
c - nothing!

What functional groups will have H's that disappear when shaken with D_2O?

anything with OH or NH amine amide carboxylic acid alcohol (not aldehyde)

VII. Carbon-13 NMR

Why isn't ^{13}C NMR as useful as ^{1}H NMR?

^{13}C isn't as common - only 1% of all C atoms

takes longer, need more concentrated samples, more noise

Why isn't integration used? interference from H atoms

How is the peak affected by the number of H's attached to the carbon?

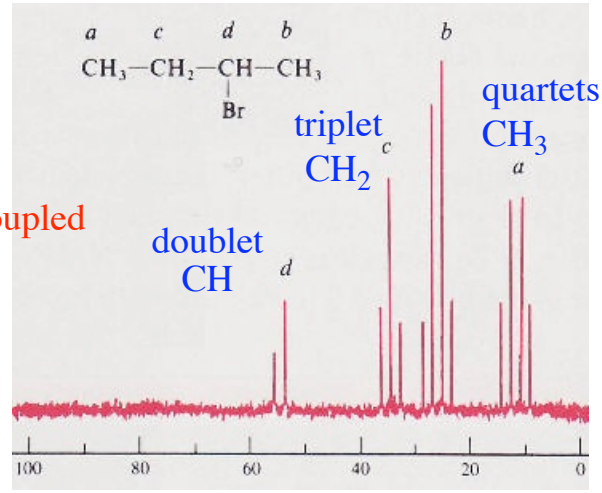
CH_3 taller than CH_2, then CH, then C w/ no H's

Why won't you see any carbon-carbon splitting? no ^{13}C's next to each other

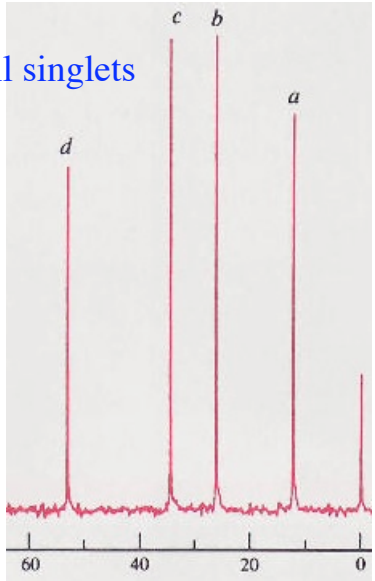
Why is carbon-hydrogen splitting usually eliminated? usually makes the spectrum too hard to read

What do you call a spectrum with no C-H splitting? proton-decoupled

proton coupled



all singlets



What is the most useful information you can get from a ^{13}C NMR spectrum?

the number of non-equivalent C's

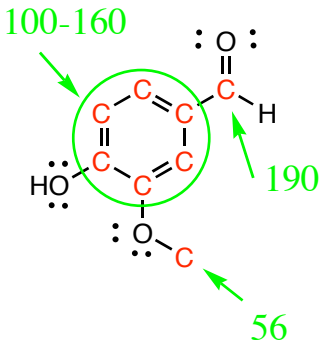
What are some common chemical shift ranges?

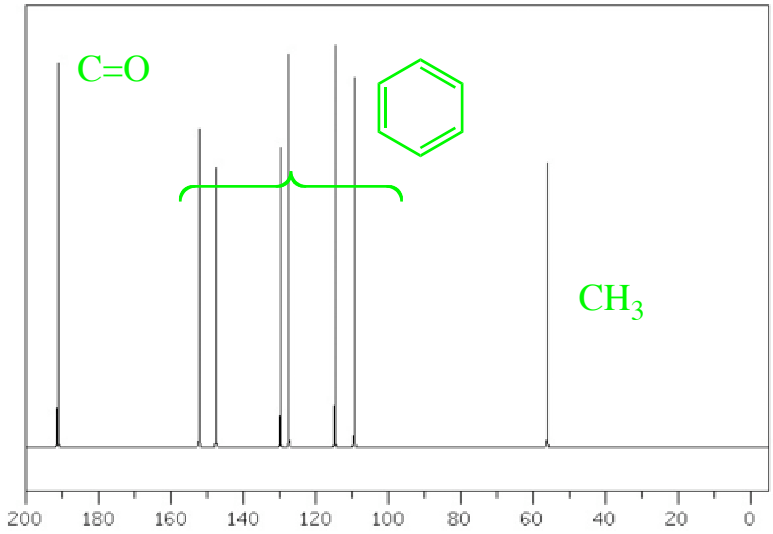
sp3 carbon atoms 0-80 ppm

C=C in alkenes and aromatic rings 100-160 ppm

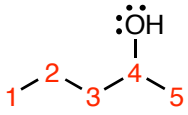
C=O 160-220 ppm

In the following spectrum of vanillin, assign the carbon atoms to the peaks where possible.



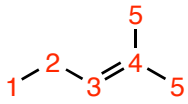


How many peaks would you expect each of the following compounds to have? What chemical shift ranges would they fall in?



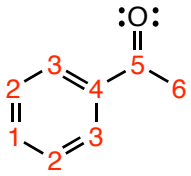
5 peaks

all 0-80 ppm



5 peaks

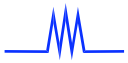
3 0-80 ppm
2 100-160 ppm



6 peaks

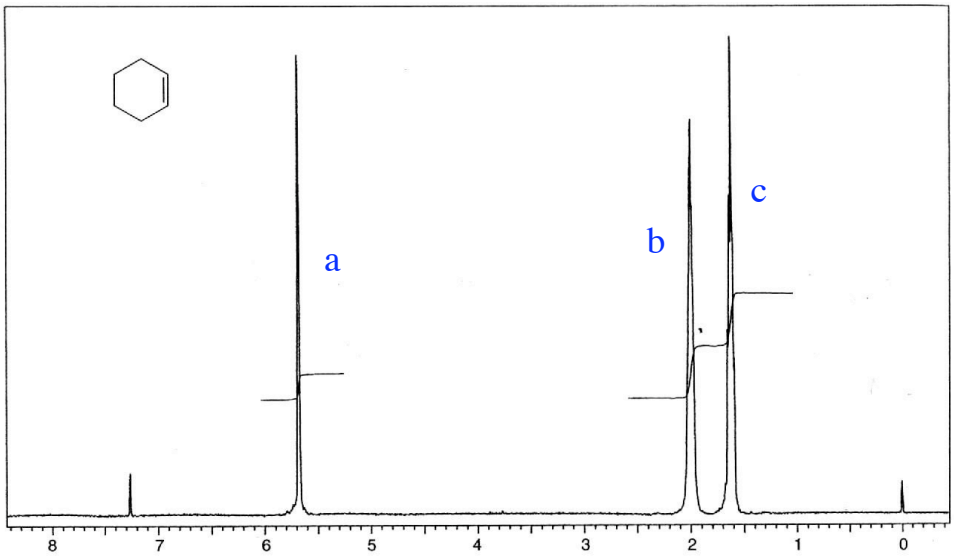
1 0-80 ppm
4 100-160 ppm
1 160-220 ppm

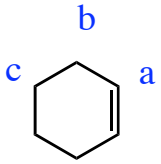
Where does the solvent peak appear for $CDCl_3$?

78 ppm - small triplet 

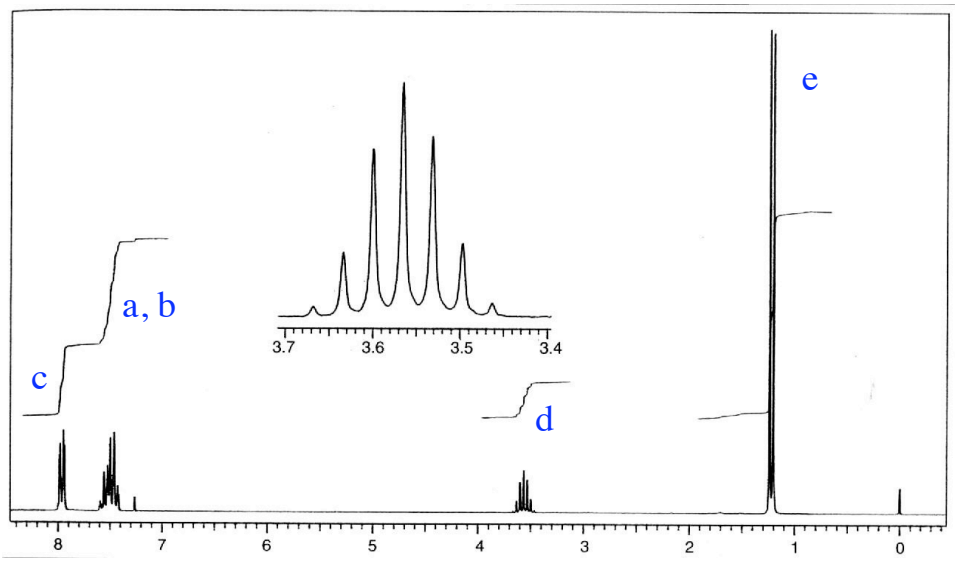
VIII. Practice with NMR spectra

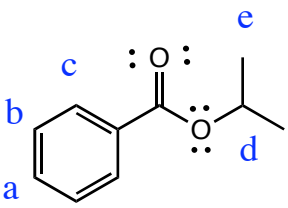
Match the peaks in the following compounds with the H's in the structures shown.



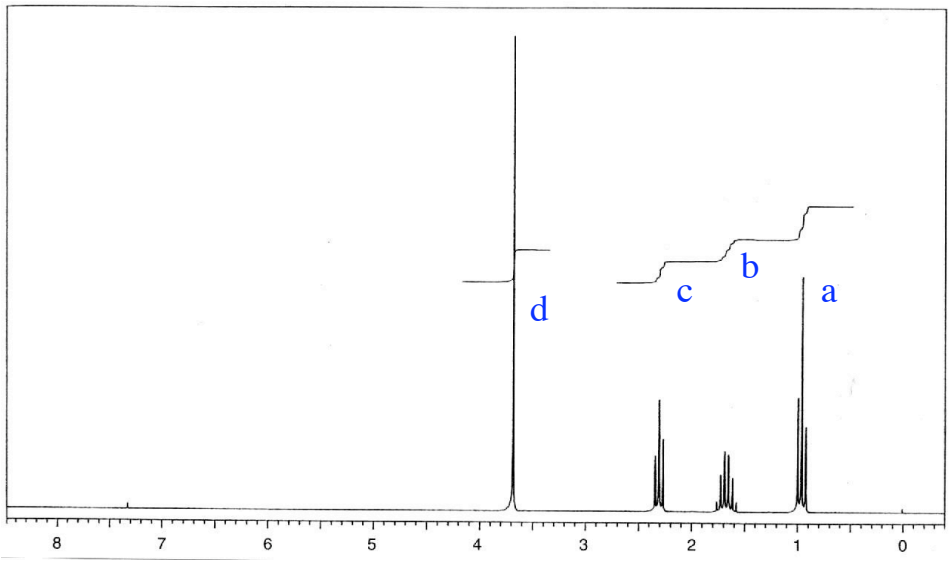


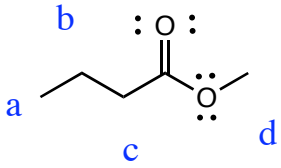
a: 2H, t (4-6)
b: 4H, q
c: 4H, t





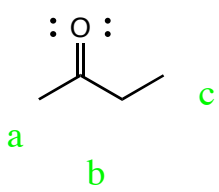
a: 1H, t ~7
b: 2H, t ~7
c: 2H, d~7
d: 1H, m(7) 3-4
e: 6H, d





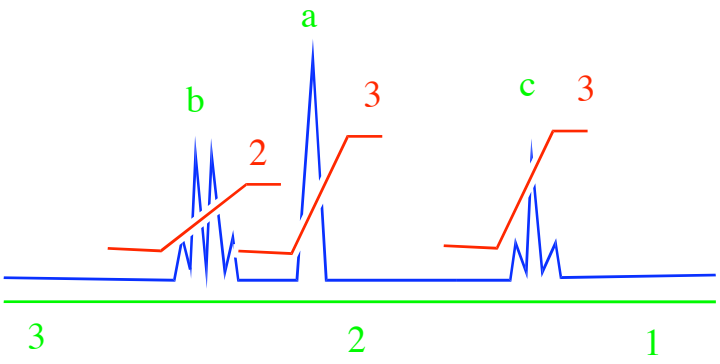
a: 3H, t
b: 2H, m(6)
c: 2H, t 2-2.5
d: 3H, s 3-4

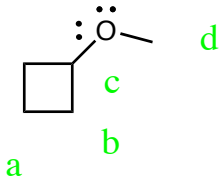
Sketch the spectrum of the following compounds.



a: 3H, s 2-2.5
b: 2H, q 2-2.5
c: 3H, t

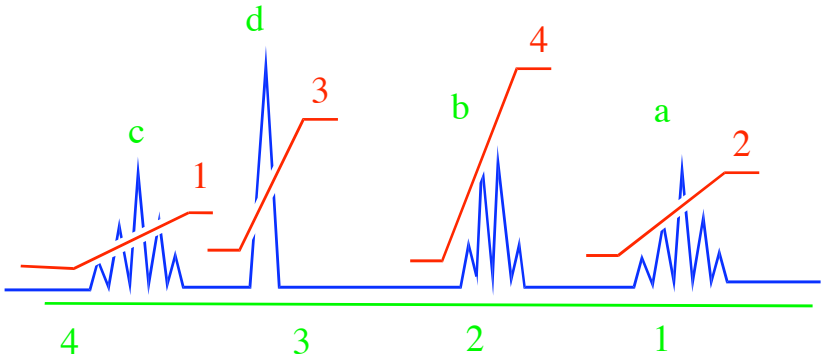
b > a > c



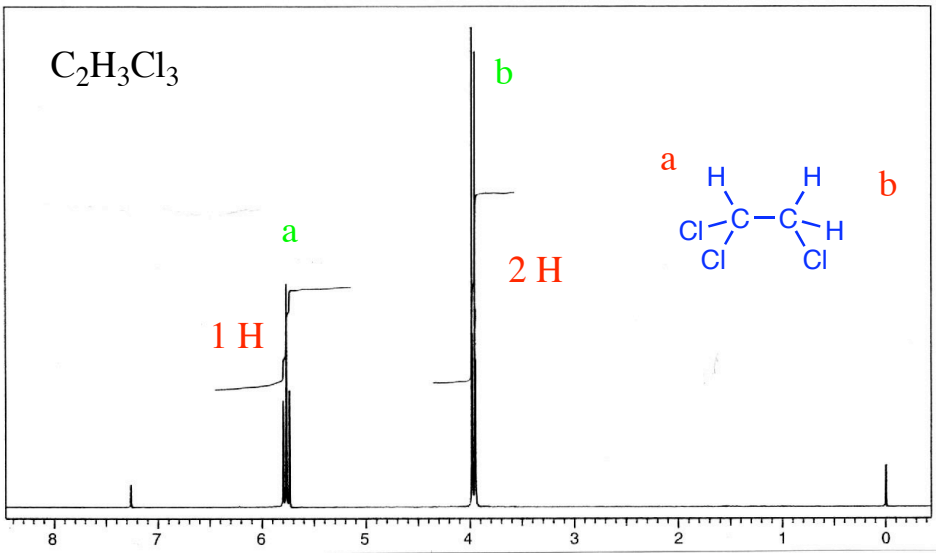


a: 2H, quint
b: 4H, q
c: 1H, quint 3-4
d: 3H, s 3-4

c > d > b > a



Deduce the structure of the following compounds.



integration:

only 3 H's - integrations must add to 3

so, 1:2

splitting:

triplet - 2 neighbors

doublet - 1 neighbor

chemical shifts:

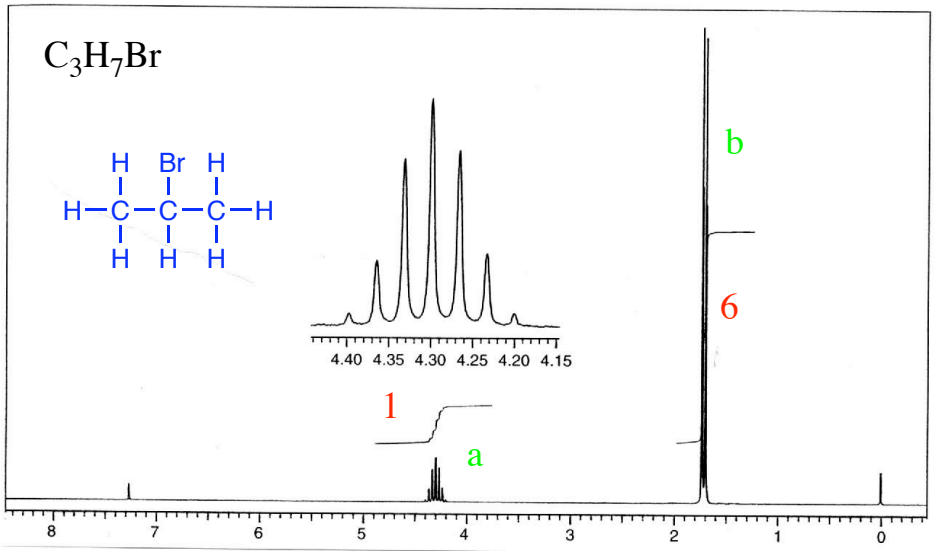
a is at 5.7 - next to 2 Cl's

b is at 3.9 - next to one Cl, two more nearby

a - 1H, t, 5.7 ppm

b - 2H, d, 3.9 ppm

(there are only 2 options with this formula - evidence points to 2 Cl's on one C, 1 Cl on the other rather than all 3 Cl's on one C)



integration:
7 H's - 1:6

splitting:

a - multiplet(7): 6 neighbors

b - doublet: 1 neighbor

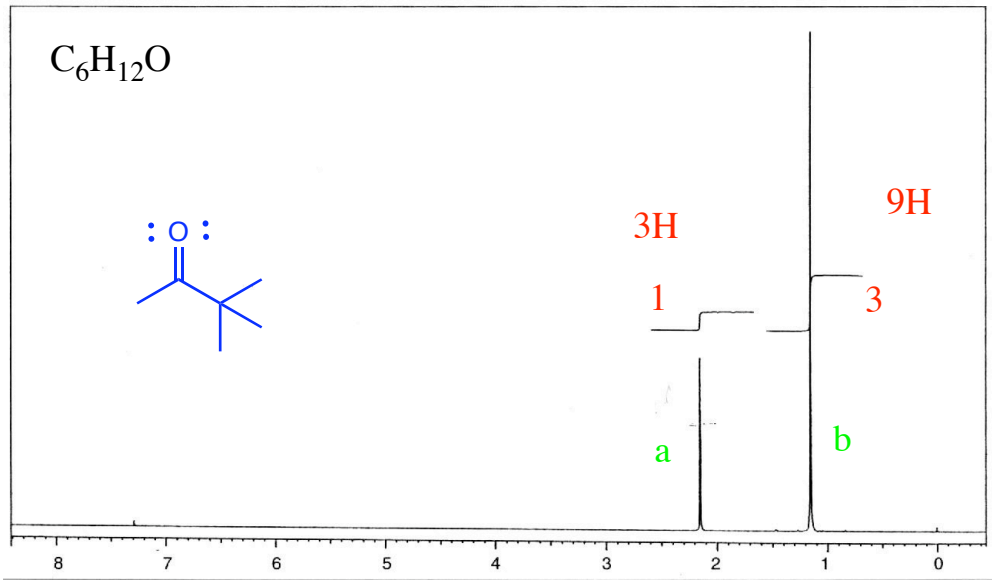
chemical shifts:

a is at 4.2 ppm

b is at 1.7 ppm

a is next to Br

(there are only 2 options with this formula as well;
all evidence points to Br in the middle instead of on the end)



integration:
12 H's, but only
two peaks

1:3 = 3:9

splitting:

both singlets
no neighbors!

chemical shifts:

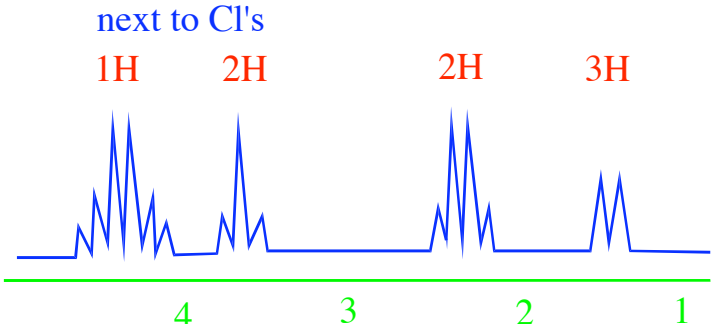
a is at 2.1 ppm

b is at 1.2 ppm

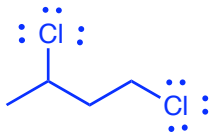
not an alcohol, ester, COOH, aldehyde, ether, or anhydride
must be a ketone

$C_4H_8Cl_2$

1.60 ppm (3H, d)
2.15 ppm (2H, q)
3.75 ppm (2H, t)
4.27 ppm (1H, m(6))



CH_3-CH-CH_2-CH_2



4 C's, 4 peaks - each C has one set of H's
only one 3H - an end;
it has only one neighbor - a CH

CH has 5 neighbors - 3 + 2
must be 2 CH_2's
add Cl's