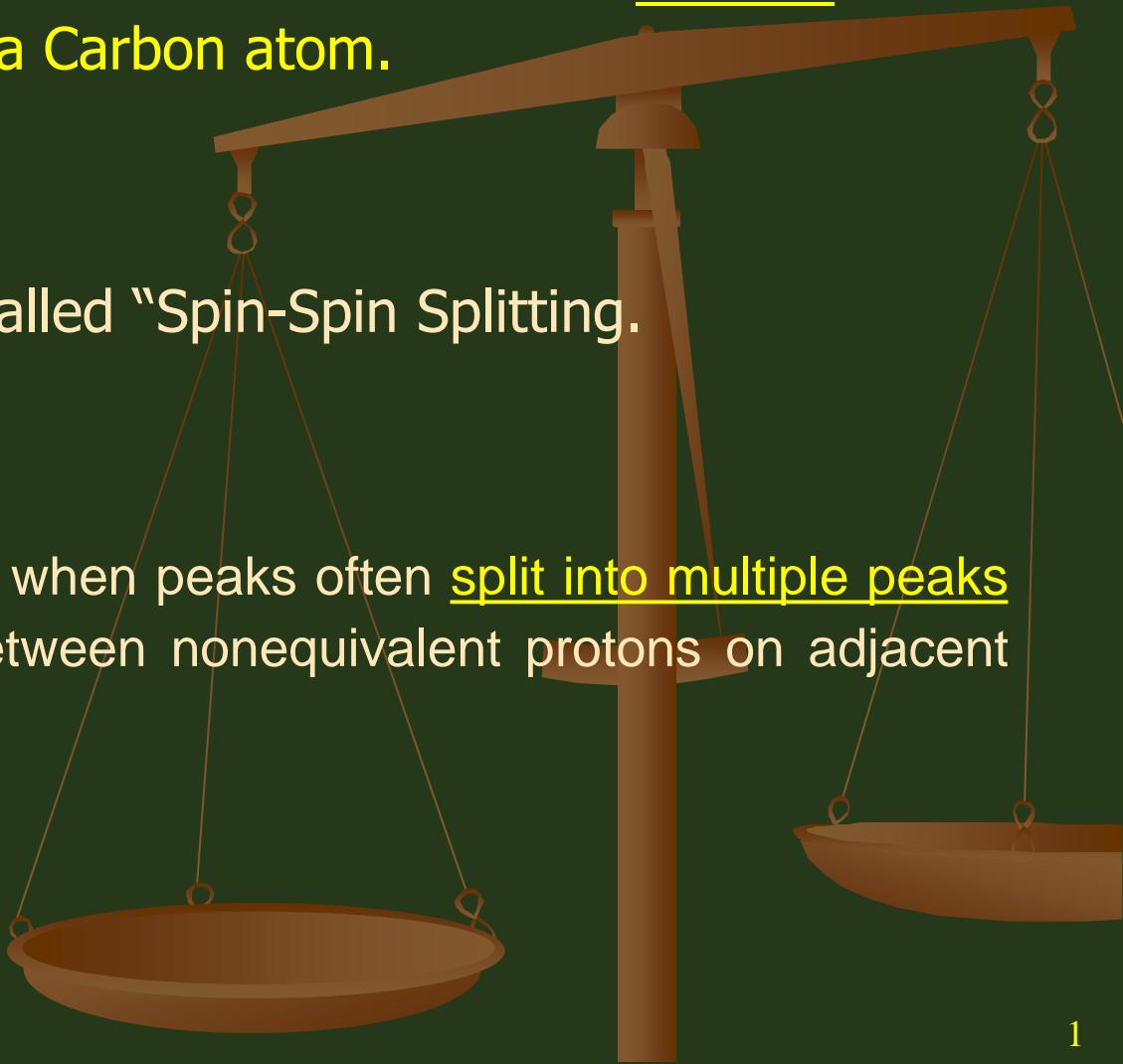


Spin – Spin Splitting

- In addition to the Chemical Shift and Signal Area, the NMR spectrum can provide information about the number of the protons attached to a Carbon atom.
- Through a process called “Spin-Spin Splitting.
- **Spin-spin splitting** is when peaks often split into multiple peaks due to interactions between nonequivalent protons on adjacent carbons.

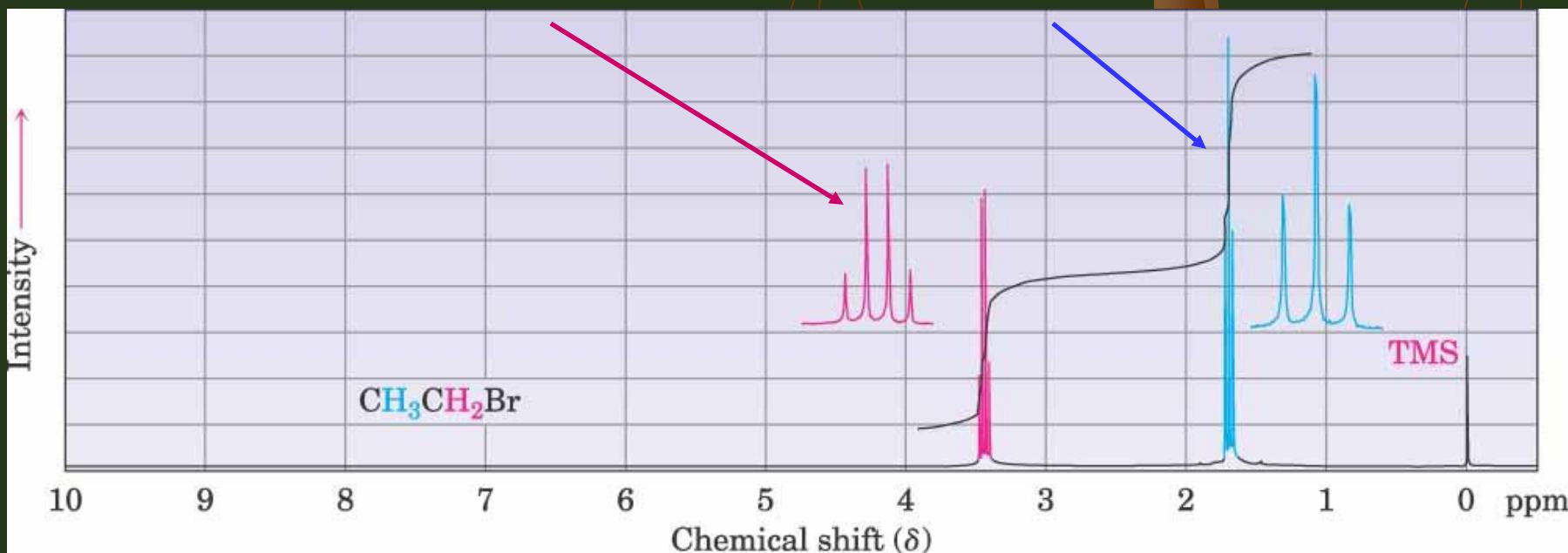


The number of lines (multiplicity) observed in the NMR signal for a group of protons is not related to the number of protons in that group; the multiplicity of lines is related to the number of protons in neighboring groups.

- Example: Bromoethane ($\text{CH}_3\text{CH}_2\text{Br}$)

The $-\text{CH}_2\text{Br}$ protons have four peaks (quartet) at 3.42δ

The $-\text{CH}_3$ protons have three peaks (triplet) at 1.68δ



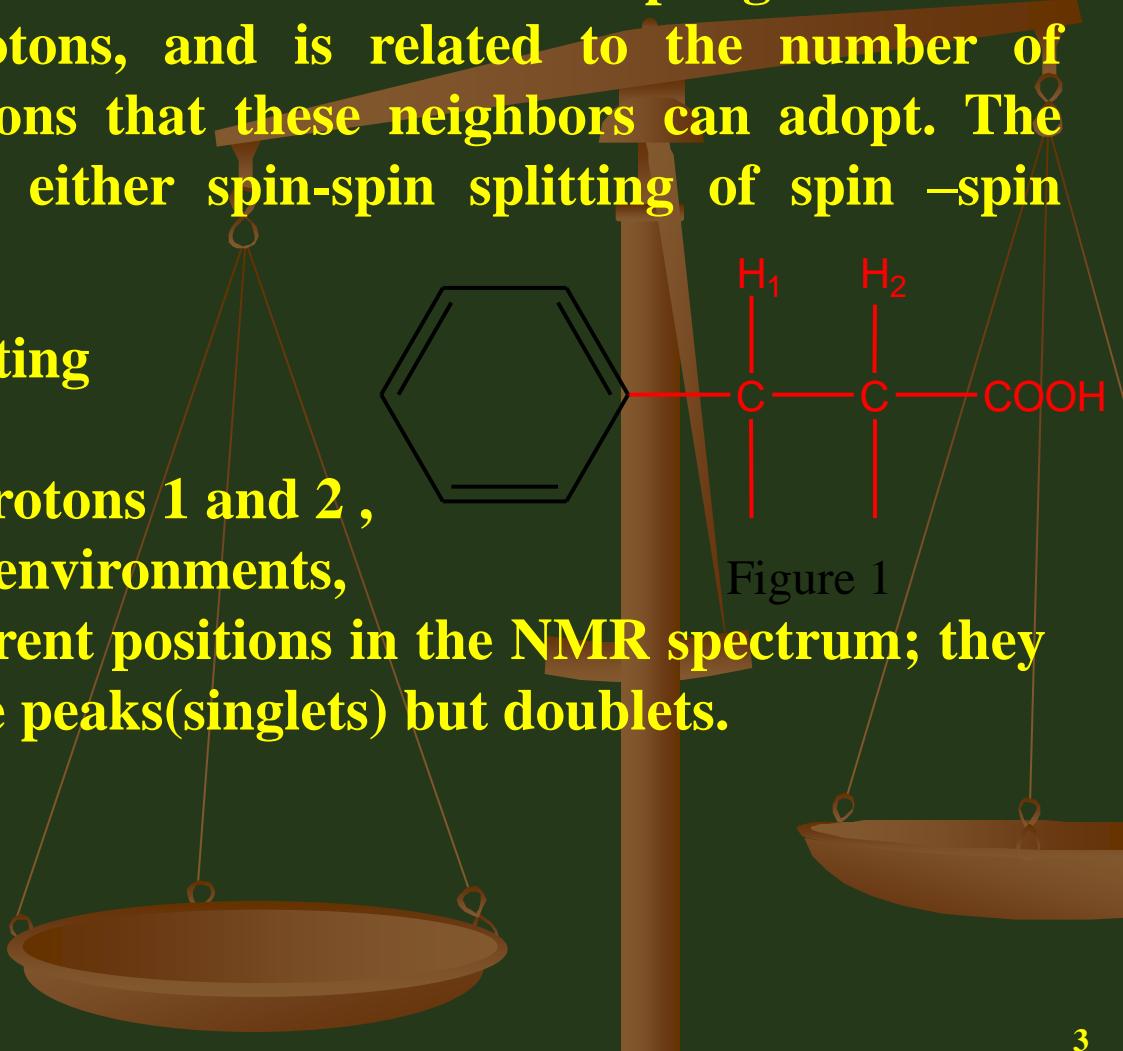
(n+1) rule:

The simplest rule is: to find the multiplicity of the signal from a group of protons , count the number neighbors(n) and add 1.

Splitting of the spectral lines arise because of a coupling interaction between neighbor protons, and is related to the number of possible spin orientations that these neighbors can adopt. The phenomenon is called either spin-spin splitting or spin –spin coupling.

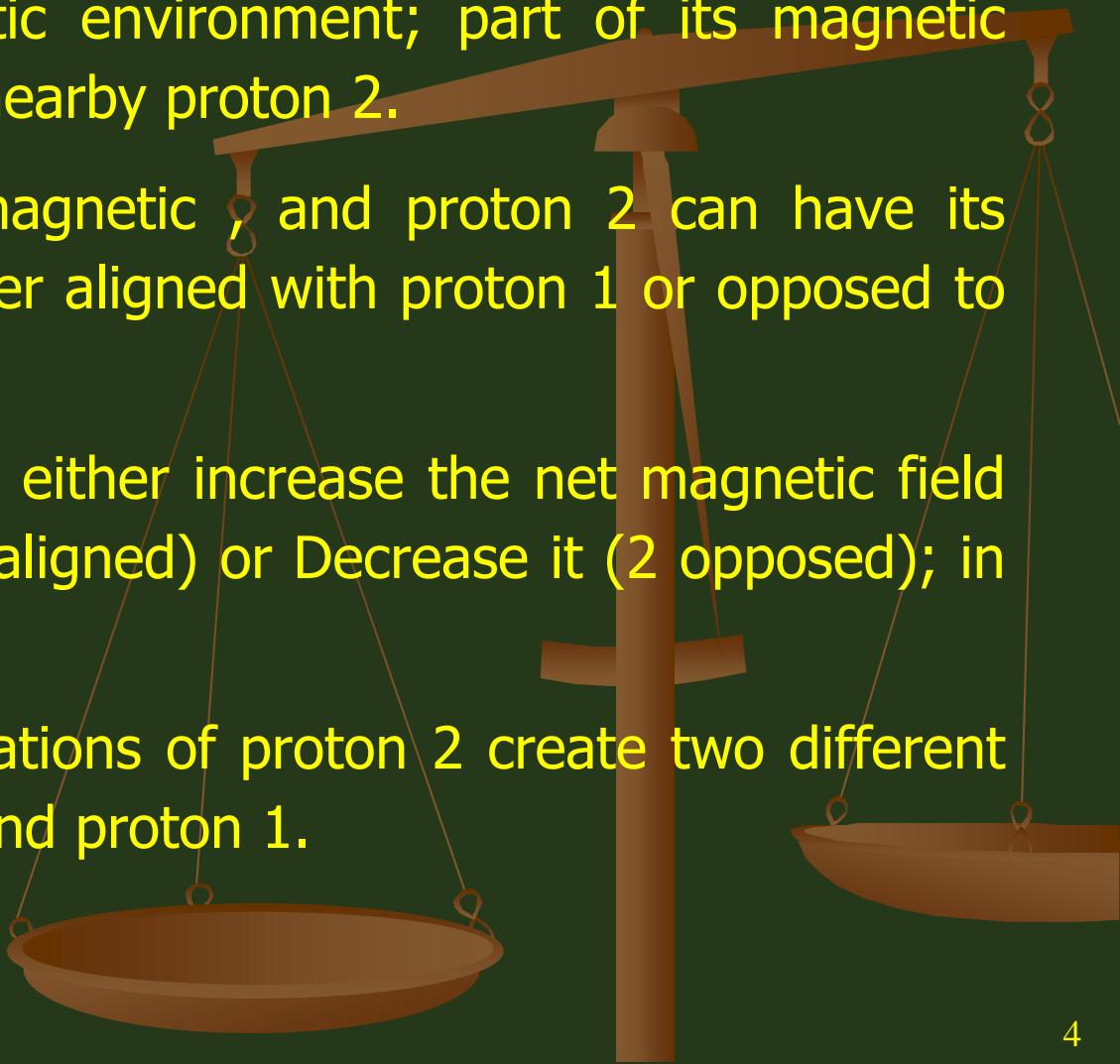
Theory of spin – spin Splitting

For example fig 1 ,these protons 1 and 2 , having different magnetic environments, come to resonance at different positions in the NMR spectrum; they do not give rise to single peaks(singlets) but doublets.



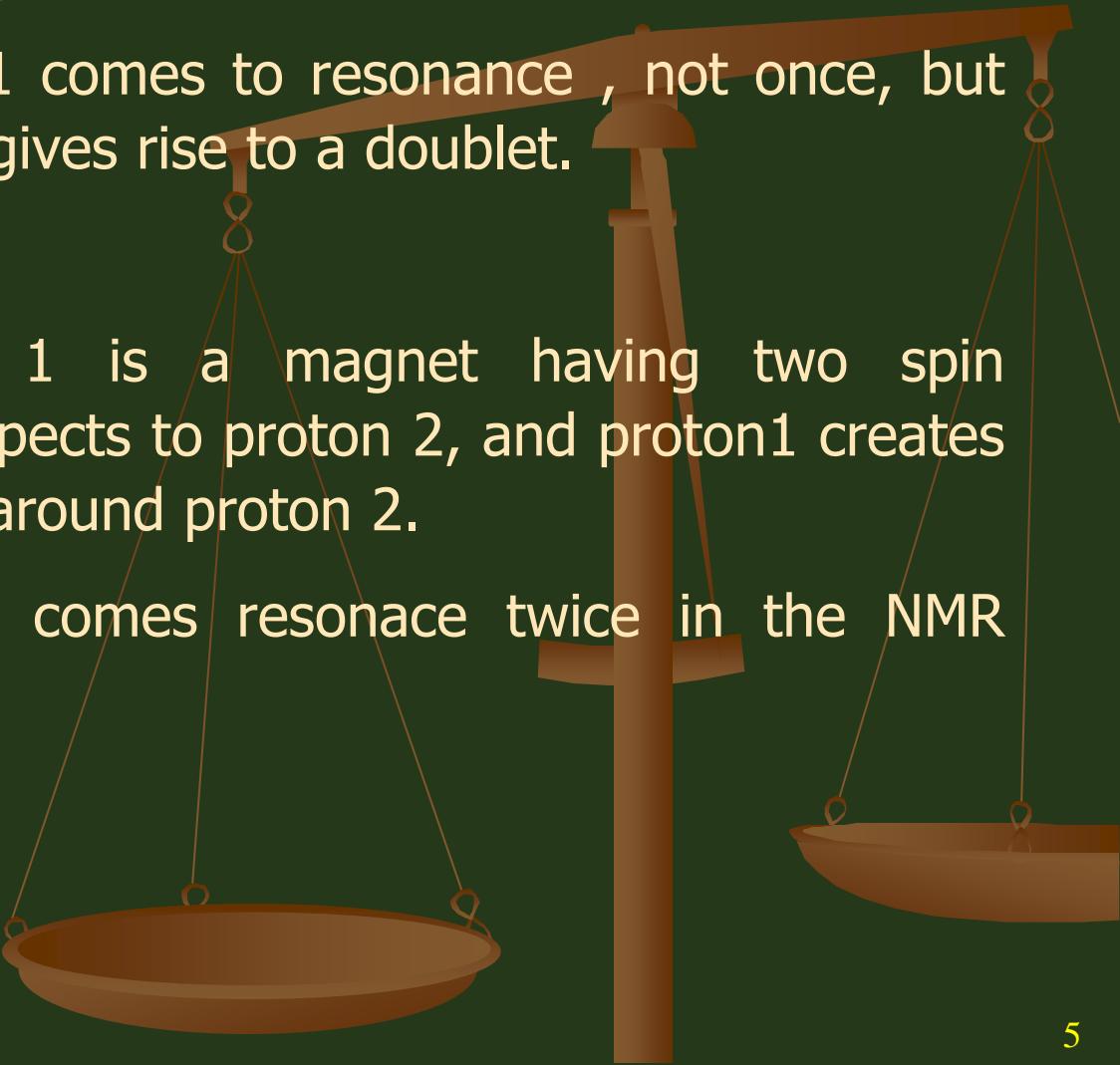
Spin – Spin Splitting (Con't)

- Why is the signal for proton 1 split into a doublet?
- Explanation: The resonance position for a proton 1 depends on its total magnetic environment; part of its magnetic environment is the nearby proton 2.
- Proton 2 is itself magnetic , and proton 2 can have its nuclear magnet either aligned with proton 1 or opposed to proton 1.
- Thus , proton 1 can either increase the net magnetic field experienced by 1(2 aligned) or Decrease it (2 opposed); in fact , it does both.
- The two spin orientations of proton 2 create two different magnetic fields around proton 1.



Spin – Spin Splitting (Con't)

- In roughly half of the molecules the spin orientation of proton 2 creates a shielding field around proton 1, and in the half a deshielding field.
- Therefore , proton 1 comes to resonance , not once, but twice, and proton 1 gives rise to a doublet.
- Similarly , proton 1 is a magnet having two spin orientations with respects to proton 2, and proton1 creates two magnetic fields around proton 2.
- Therefore proton 2 comes resonace twice in the NMR spectrum.



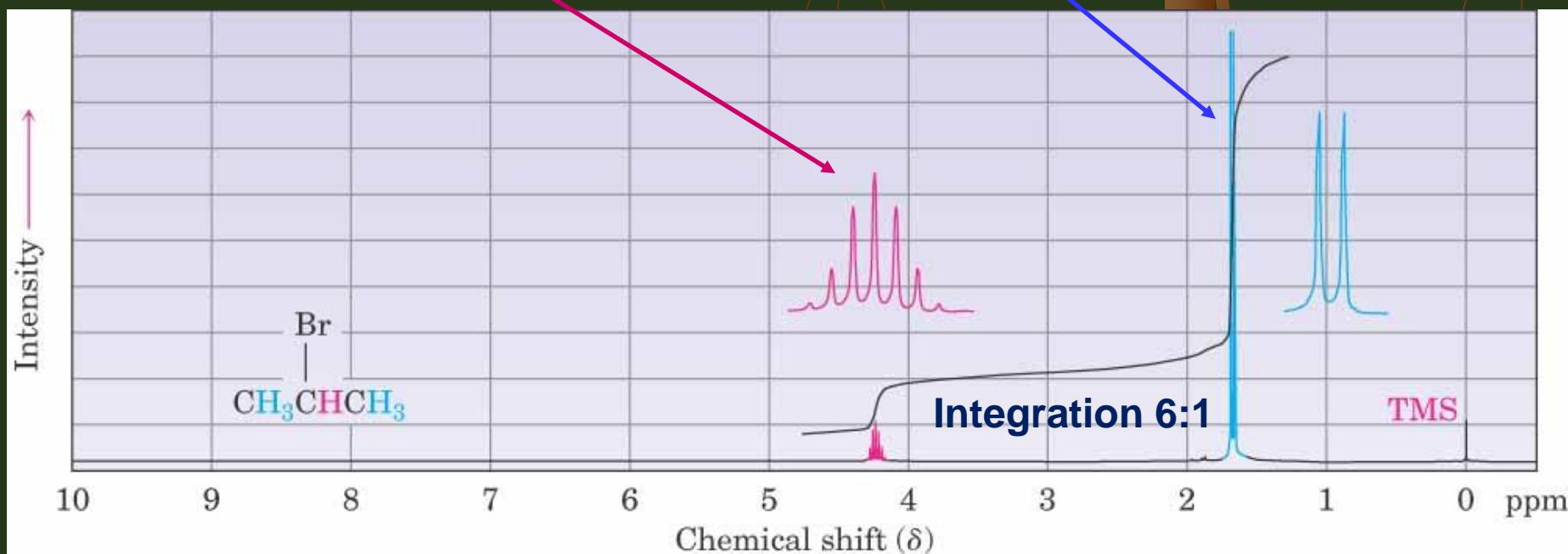
- Example: 2-bromopropane

The -CHBr proton is split by 6 equivalent -CH_3 protons ($n = 6$):
a **septet**

$n = 6$ leads to $6+1 = 7$ peaks

The 6 equivalent -CH_3 protons
are split by 1 -CHBr proton ($n = 1$):
a **doublet**

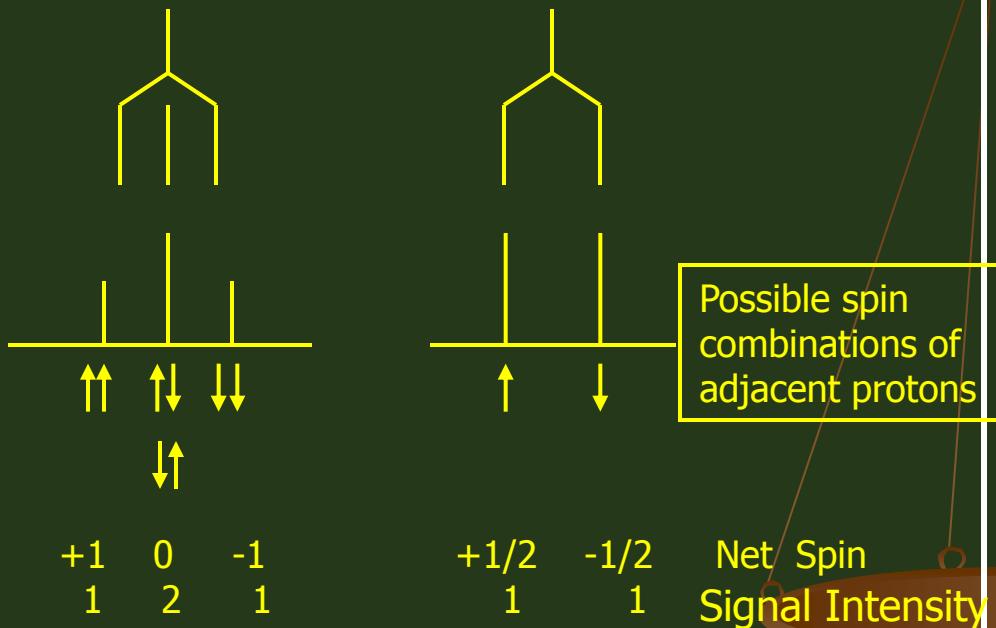
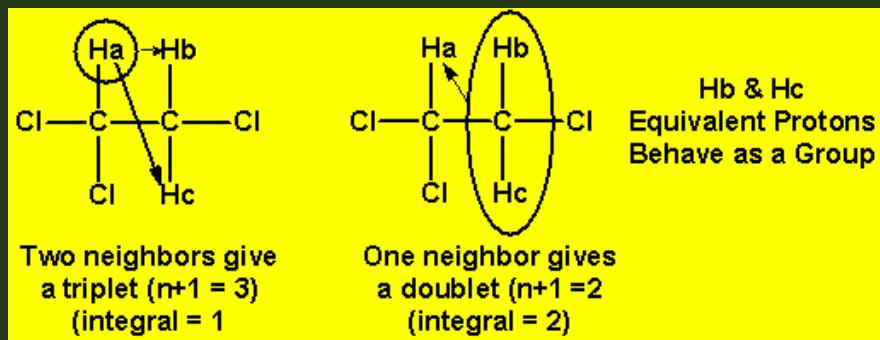
$n = 1$ leads to $1+1 = 2$ peaks



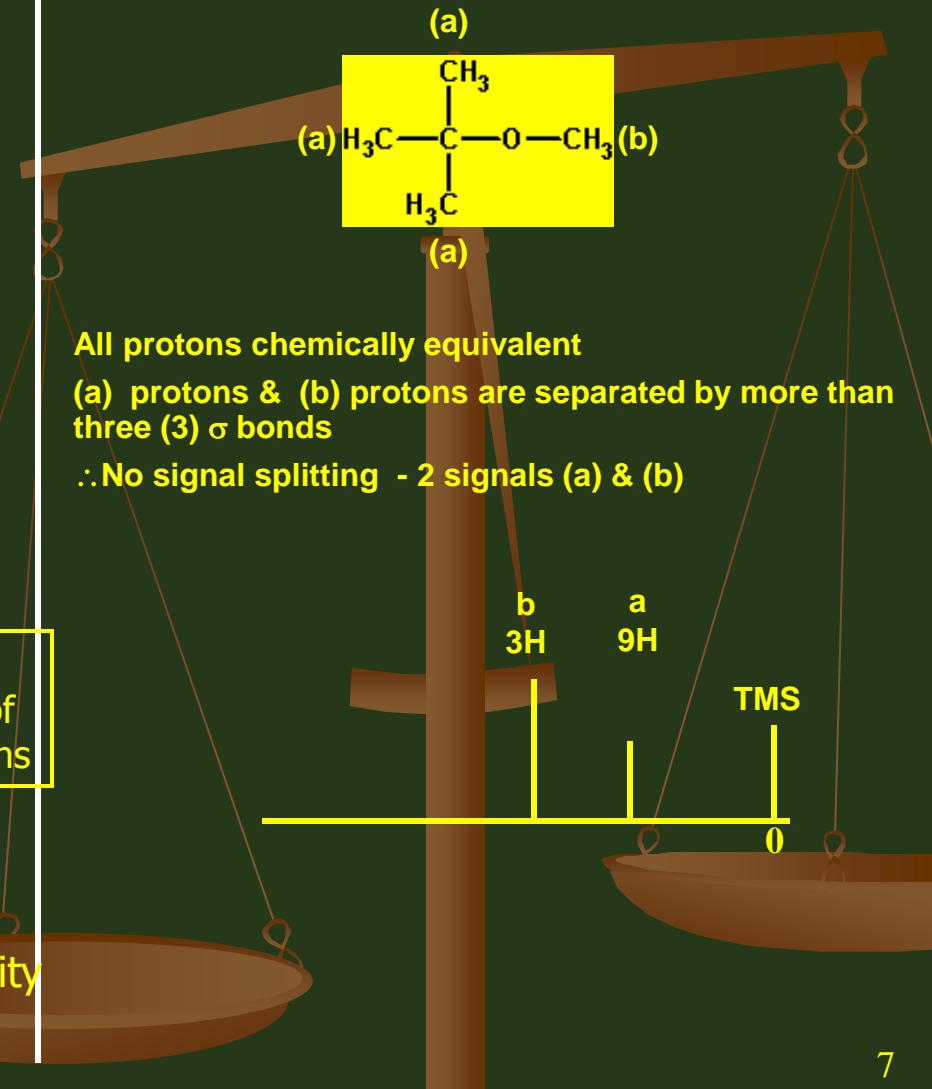
NMR

■ Spin-Spin Splitting (Con't)

1,1,2-Trichloroethane



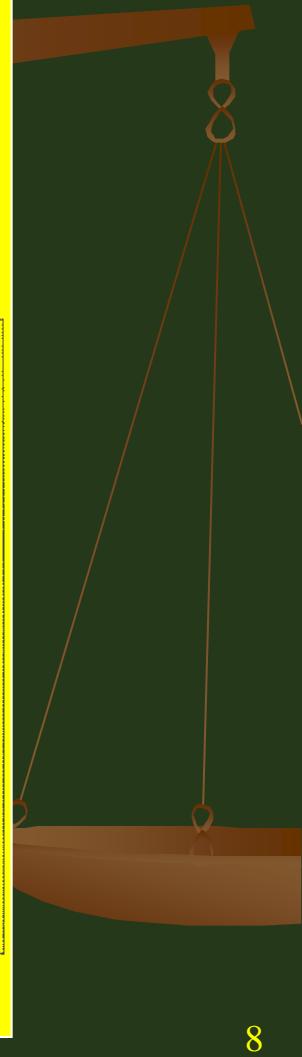
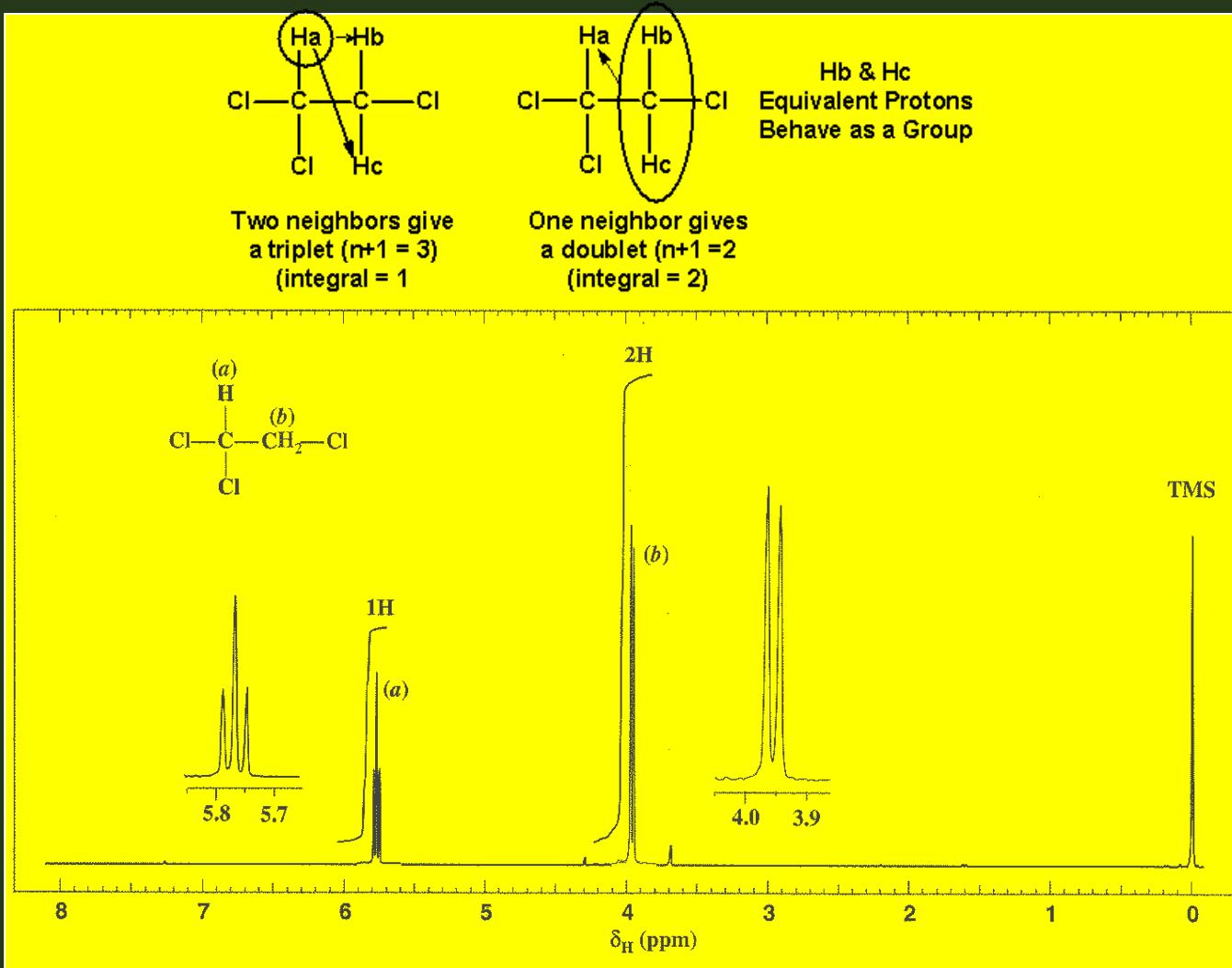
Tert-Butyl Methyl Ether



NMR

■ Spin-Spin Splitting – An example

1,1,2-Trichloroethane

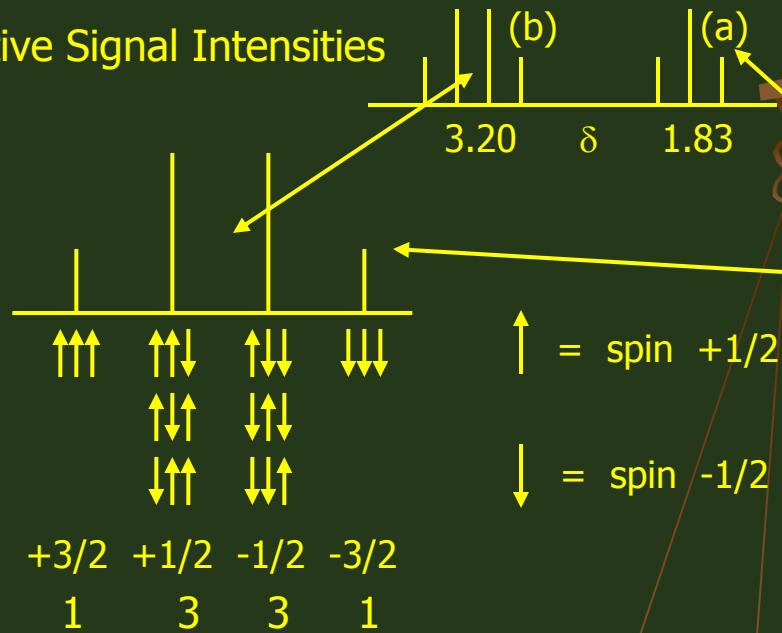


NMR

■ Spin - Spin Splitting - Multiplet Signal Intensities

Example Spectrum: Ethyl group $\left[\text{CH}_3-\overset{\text{(a)}}{\text{CH}_2}-\overset{\text{(b)}}{\text{CH}_2} \right]$

Note Relative Signal Intensities



There are 3 times as many protons with $+1/2$ or $-1/2$ spin arrangements than $+3/2$ & $-3/2$.
Therefore, the signal intensities are greater.

No. Adjacent Protons No. Peaks Seen

0 Singlet

1 Doublet

2 Triplet

3 Quartet

4 Quintet

5 Sextet

6 Septet

Pascal's Triangle

		Relative Intensity							
		1	1	1	1	1	1	1	1
		1	1	1	1	1	1	1	1
		1	2	1	1	2	1	1	1
		1	3	3	1	3	3	1	1
		1	4	6	4	6	4	1	1
		1	5	10	10	10	5	1	1
		1	6	15	20	15	6	1	1
		1	7	21	35	35	21	7	1
		1	8	28	56	70	56	28	8

Intensity ratios derived from the $n + 1$ rule

Each entry is the sum of the two entries above it to the left and right.

The relative intensities of the outer signals in sextet & septet multiplets are very weak and sometimes obscured.

NMR

■ Spin - Spin Splitting - Common Splitting Patterns

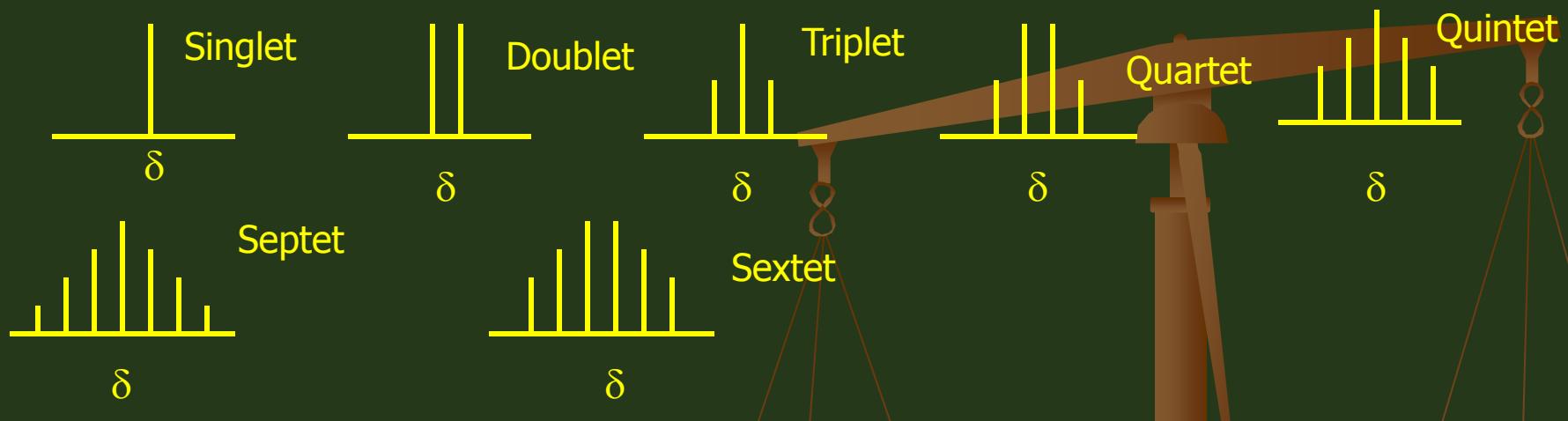


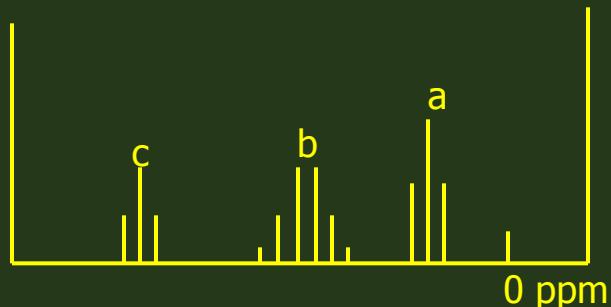
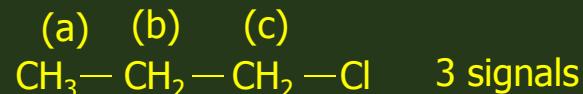
TABLE 13.4 Some Common Spin Multiplicities

Number of equivalent adjacent protons	Type of multiplet observed	Ratio of intensities
0	Singlet	1
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Quintet	1:4:6:4:1
6	Septet	1:6:15:20:15:6:1

NMR

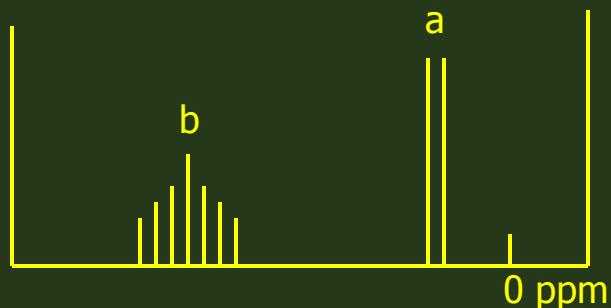
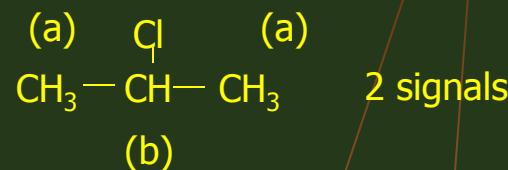
■ Spin - Spin Splitting - Isomer Example

1-Chloropropane



Signal	Rel Chem Shift	Rel Signal Area	Neighbors	Multiplicity
a	lowest	3	2	3 (Triplet)
b	middle	2	5	6 (Sextet)
c	highest	2	2	3 (Triplet)

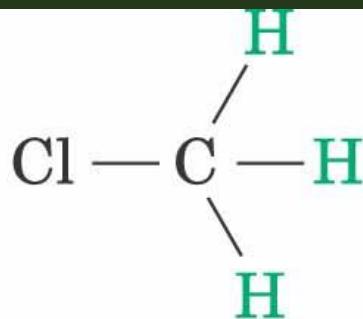
2-Chloropropane



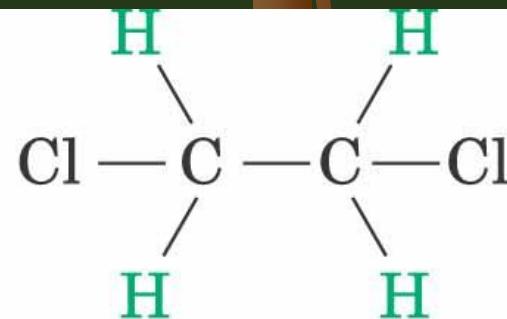
Signal	Rel Chem Shift	Rel Signal Area	Neighbors	Multiplicity
a	lowest	6	1	2 (Doublet)
b	highest	1	6	7 (Septet)

Rules for Spin-Spin Splitting¹

1. Chemically equivalent protons do not show spin-spin splitting.
2. The equivalent protons may be on the same carbon or on different carbons



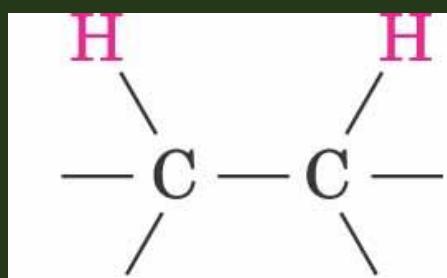
Three C–H protons are chemically equivalent; no splitting occurs.



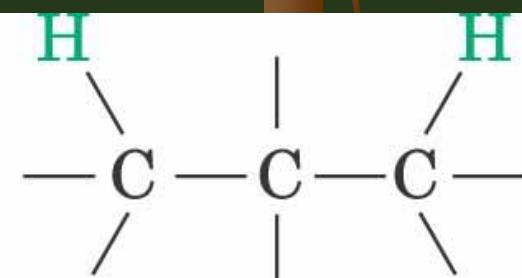
Four C–H protons are chemically equivalent; no splitting occurs.

Rules for Spin-Spin Splitting²

2. Protons that are farther than two carbon atoms apart don't usually couple, although they sometimes show small coupling when they are separated by a π bond.



Splitting observed



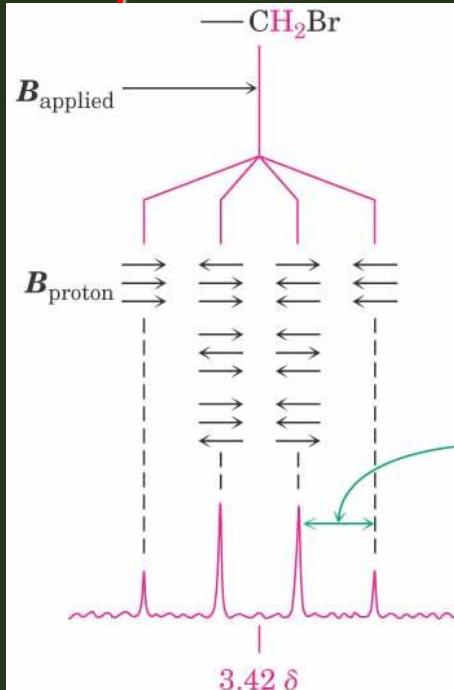
Splitting not usually observed

coupling constant,

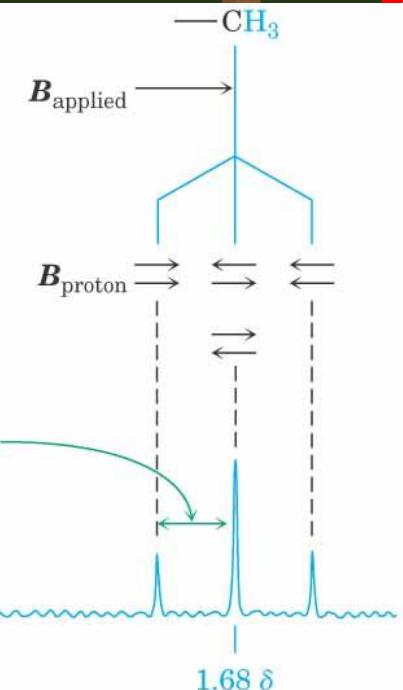
- The distance between peaks in a multiplet is called the **coupling constant**, denoted **J**

It is measured in **Hz** and is in the 0-18 Hz range

It is **dependent on the molecular geometry but independent of the spectrometer field strength**



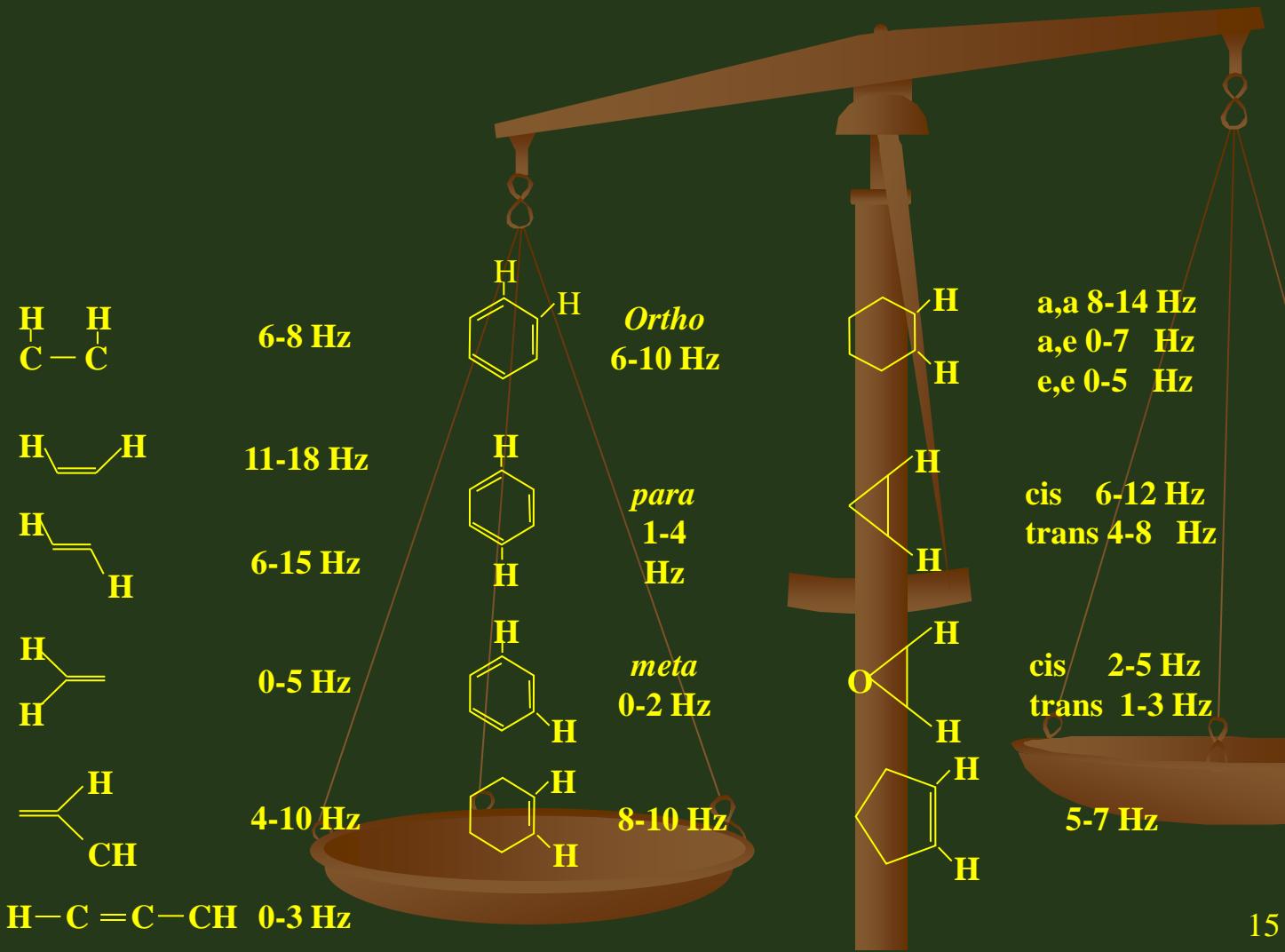
Quartet due to coupling with $\text{—CH}_2\text{Br}$



Triplet due to coupling with —CH_3

NMR

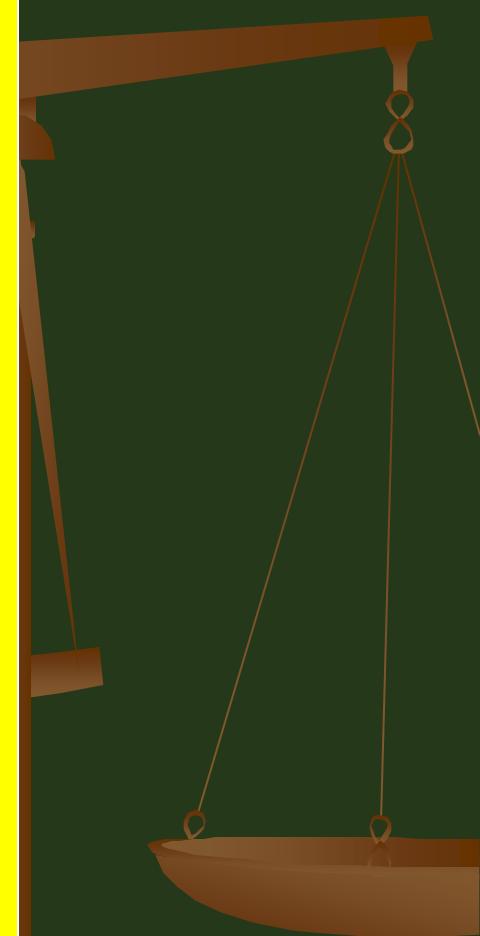
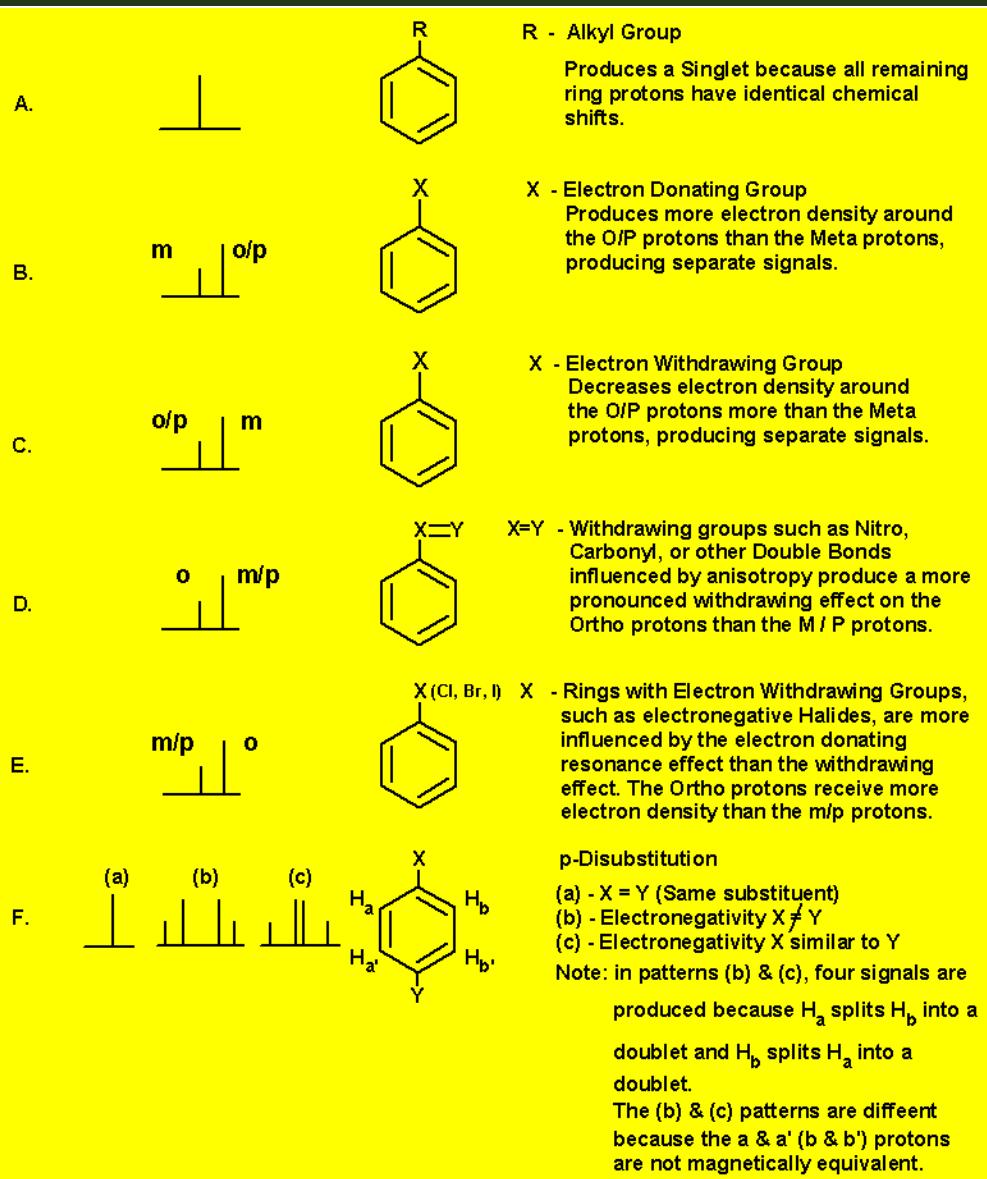
- The Coupling Constant has different magnitudes for different types of protons





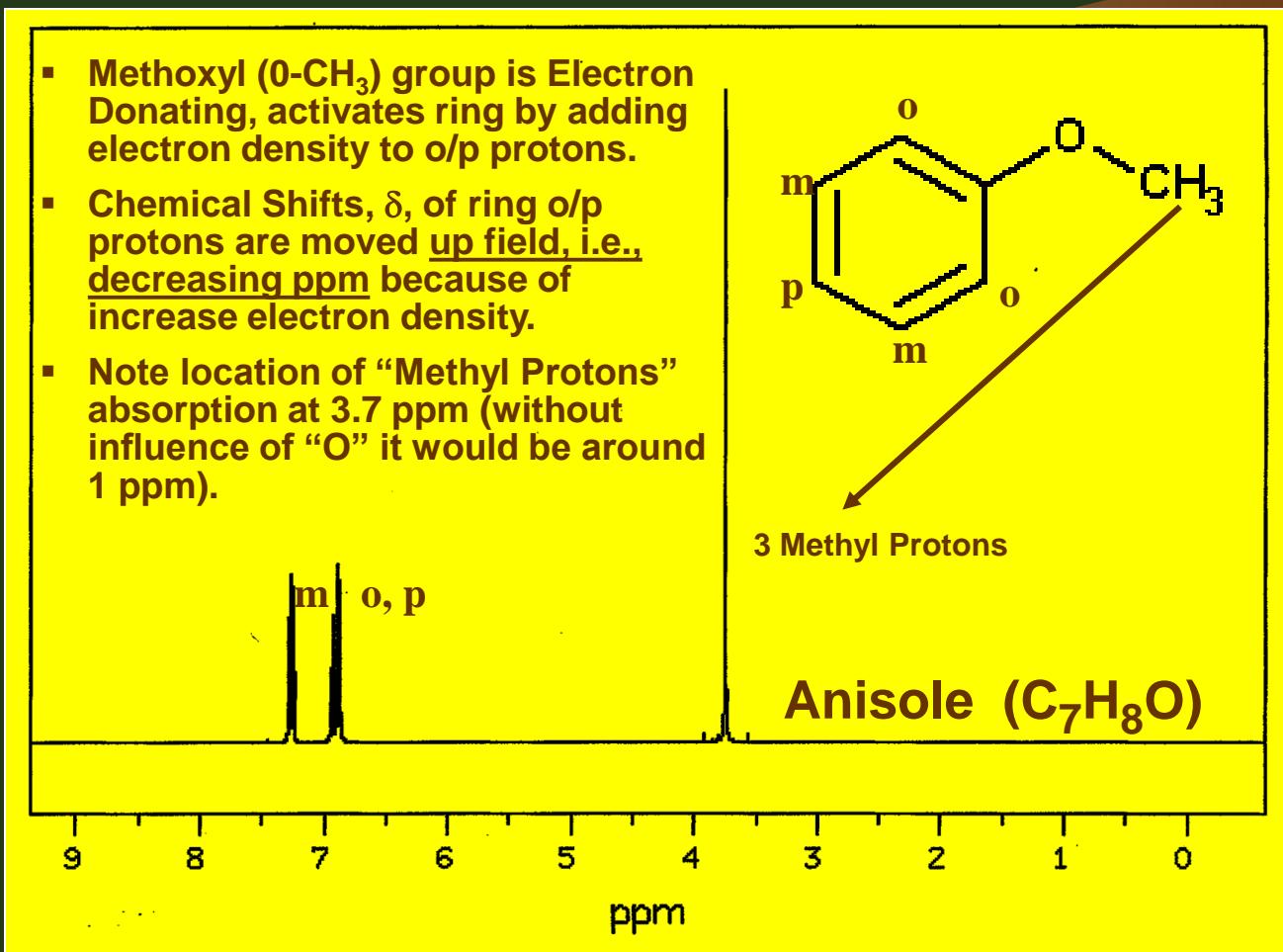
NMR

Common Aromatic Patterns



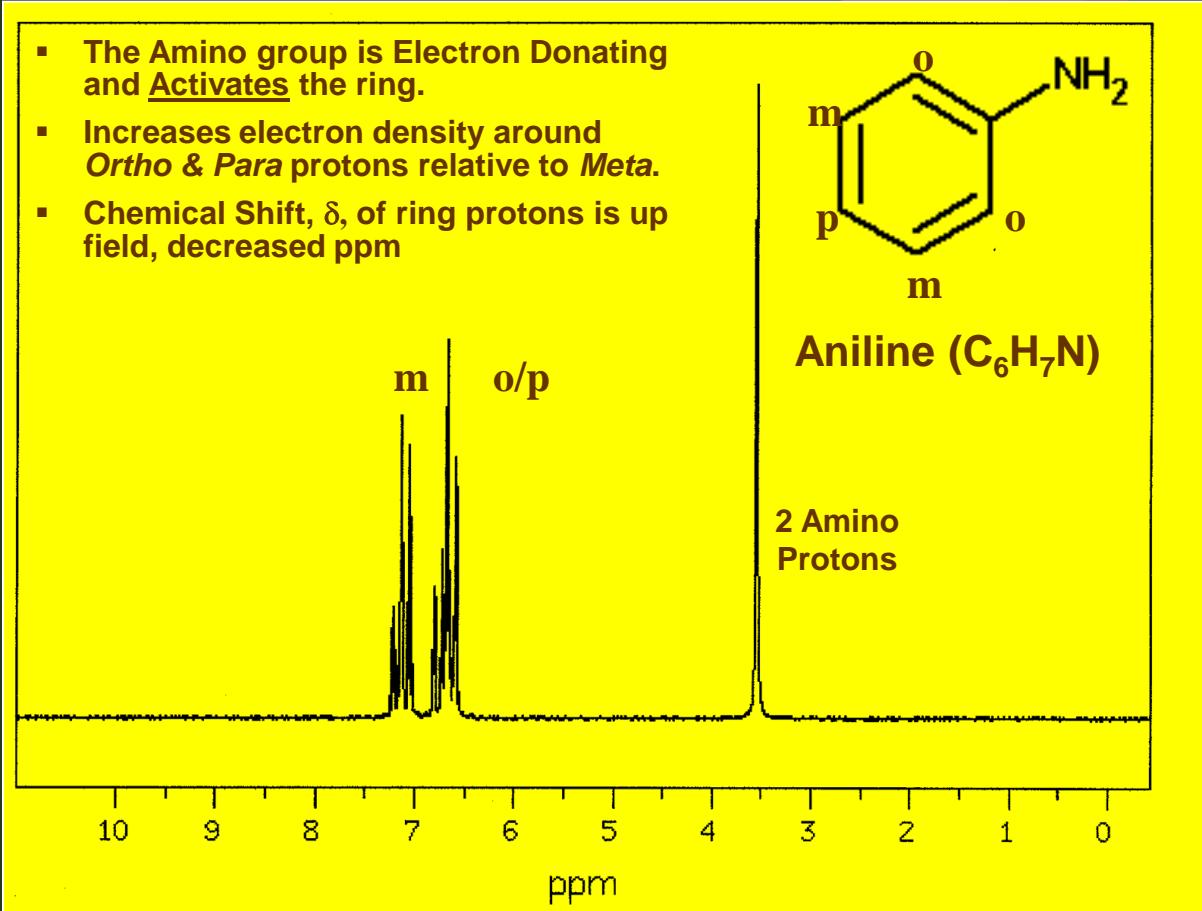
NMR

- “Activating” and “Deactivating” groups and the impact of the changing electron density in the Benzene ring on Chemical Shift of ortho, meta, para protons



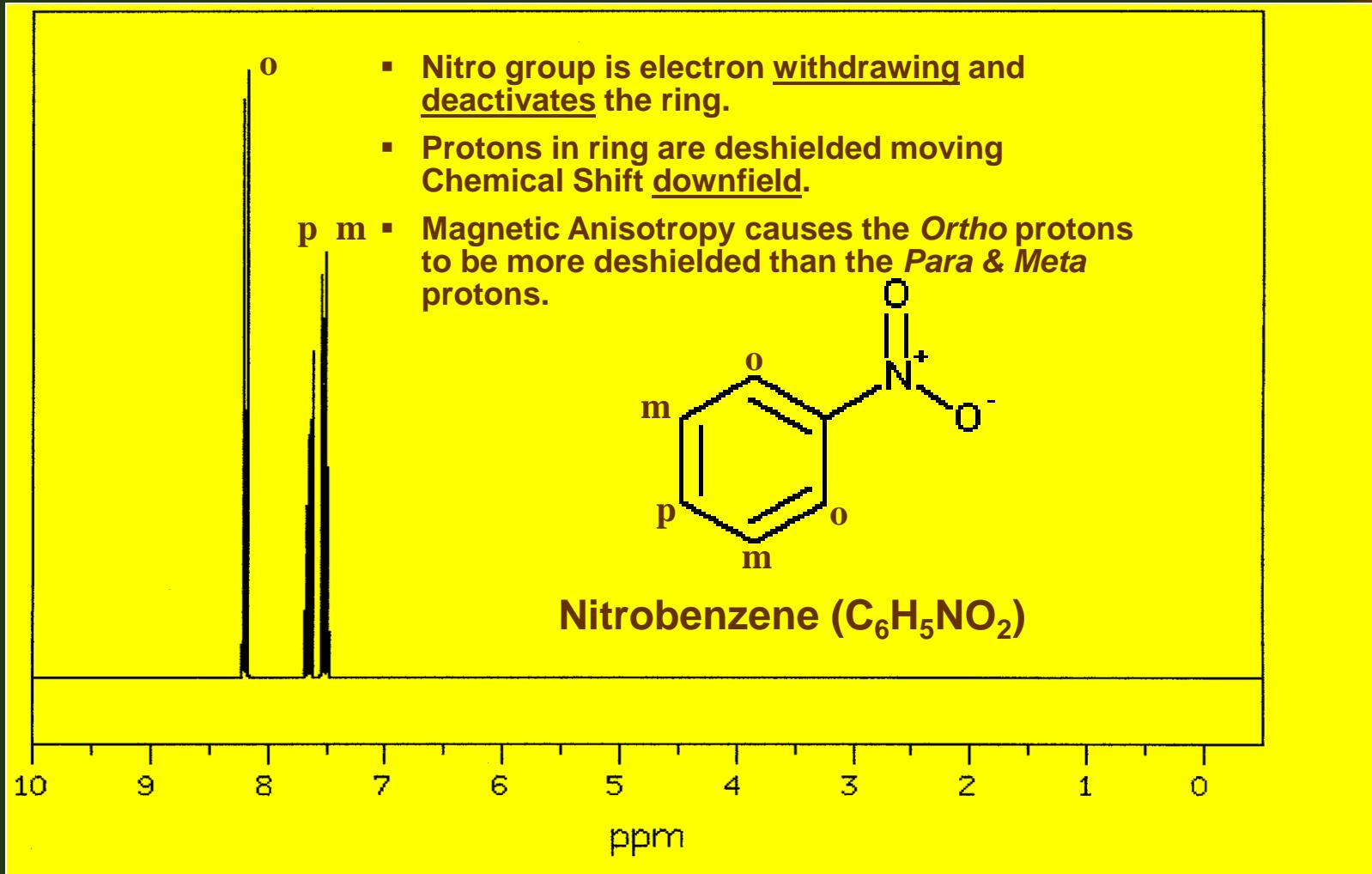
NMR

- “Activating” and “Deactivating” groups and the impact of the changing electron density in the Benzene ring on Chemical Shift of ortho, meta, para protons



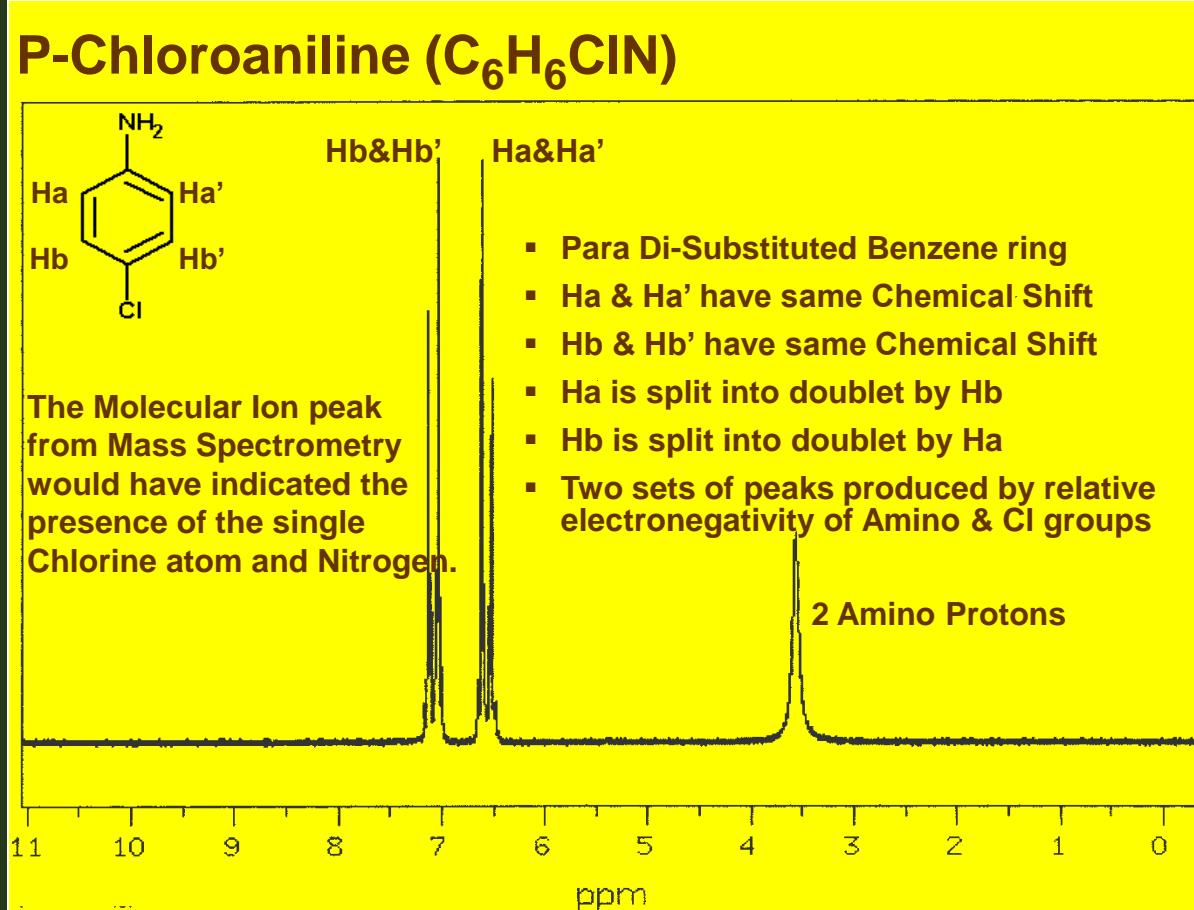
NMR

- “Activating” and “Deactivating” groups and the impact of the changing electron density in the Benzene ring on Chemical Shift of ortho, meta, para protons



NMR

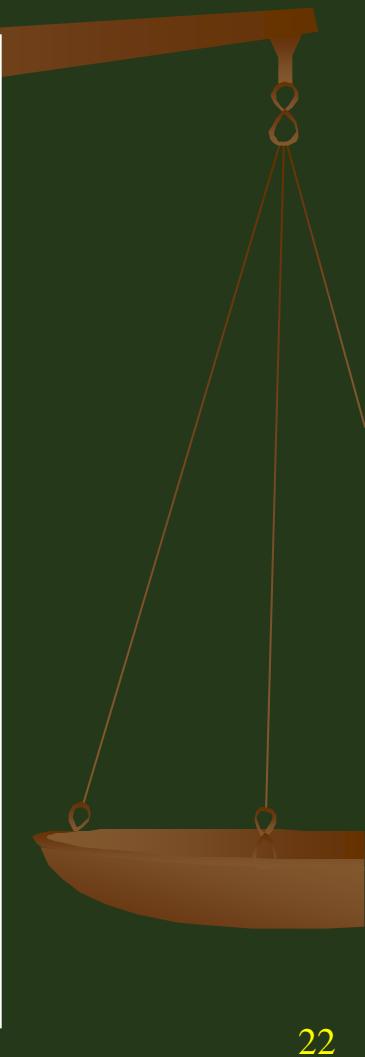
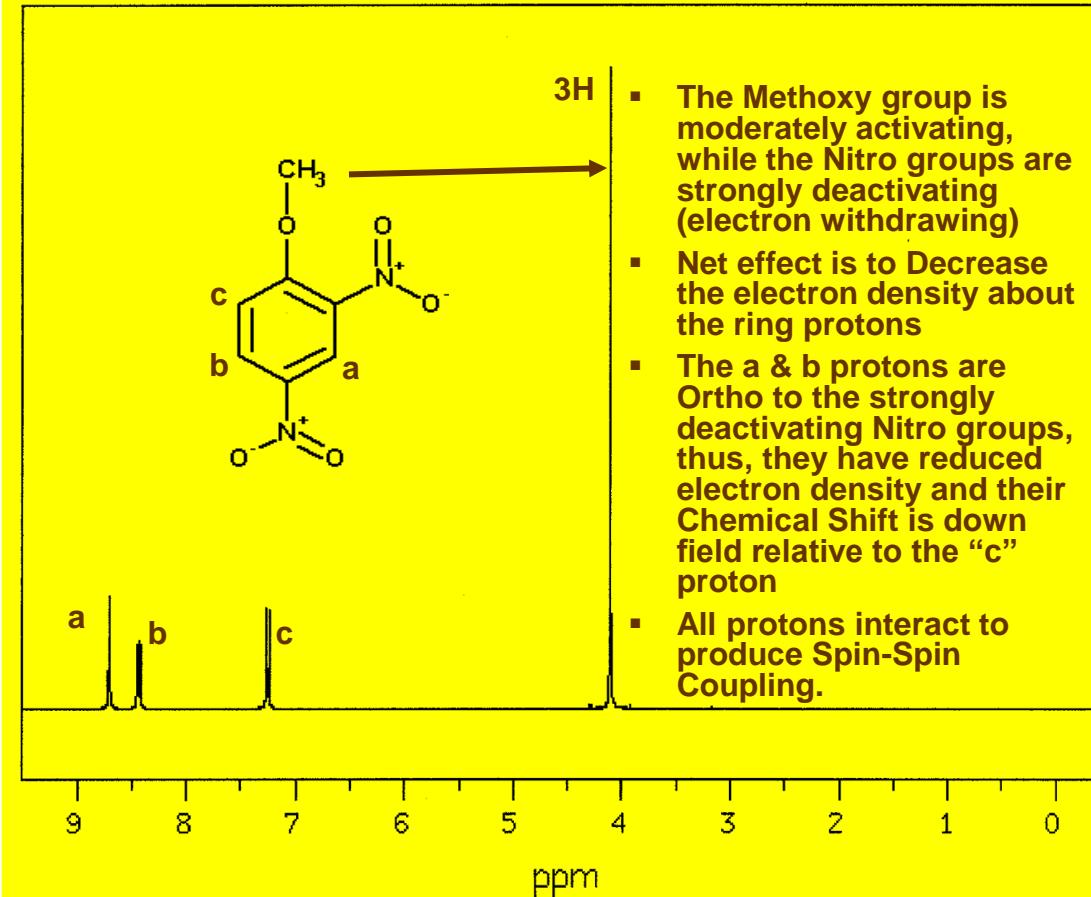
- “Activating” and “Deactivating” groups and the impact of the changing electron density in the Benzene ring on Chemical Shift of ortho, meta, para protons



NMR

- “Activating” and “Deactivating” groups and the impact of the changing electron density in the Benzene ring on Chemical Shift of ortho, meta, para protons

2,4-Dinitroanisole ($C_7H_6N_2O_5$)



NMR

- Example $^1\text{H}_1$ NMR Spectra

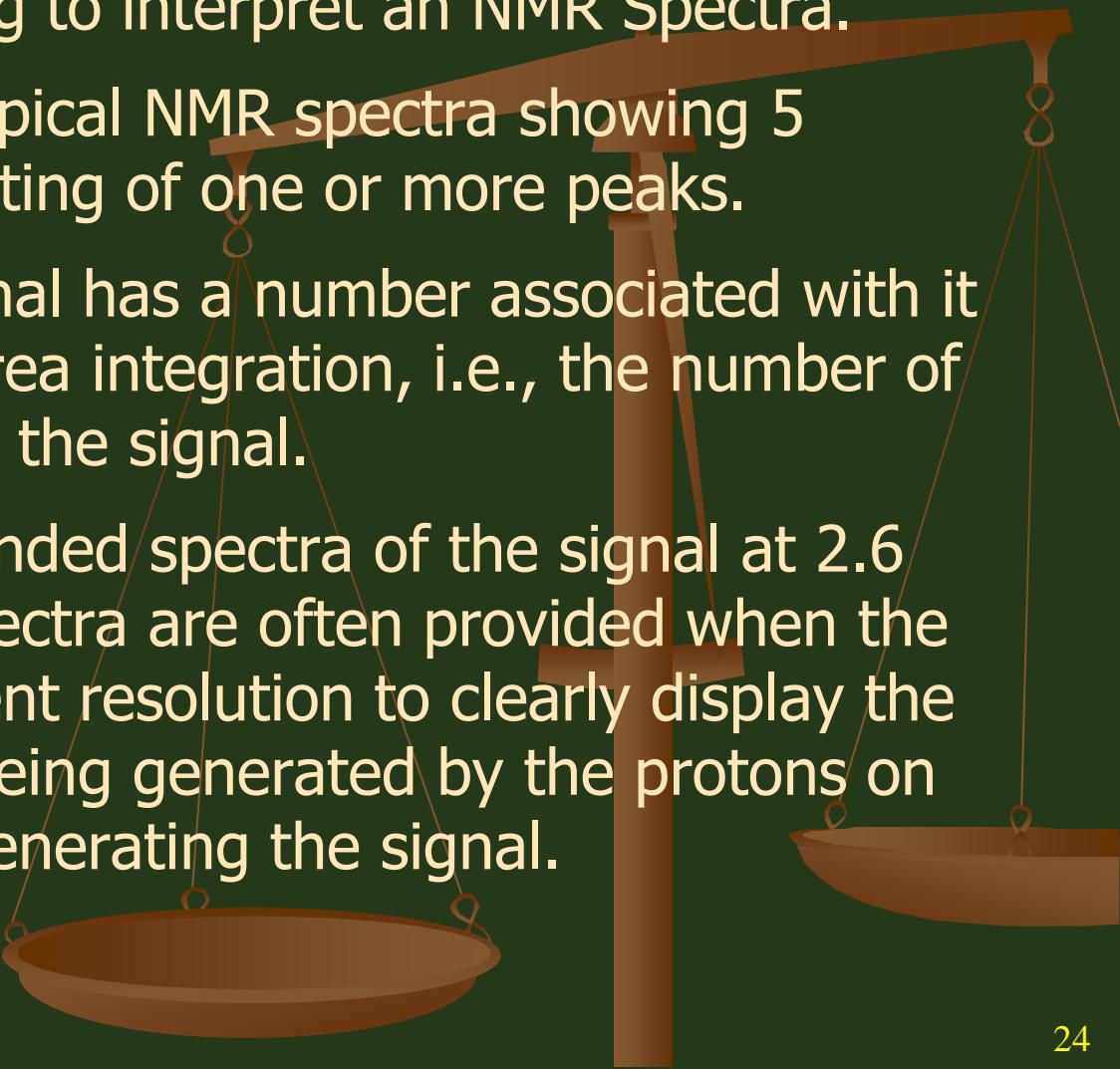
Suggestions
For
Interpreting NMR Spectra



NMR Example Spectra

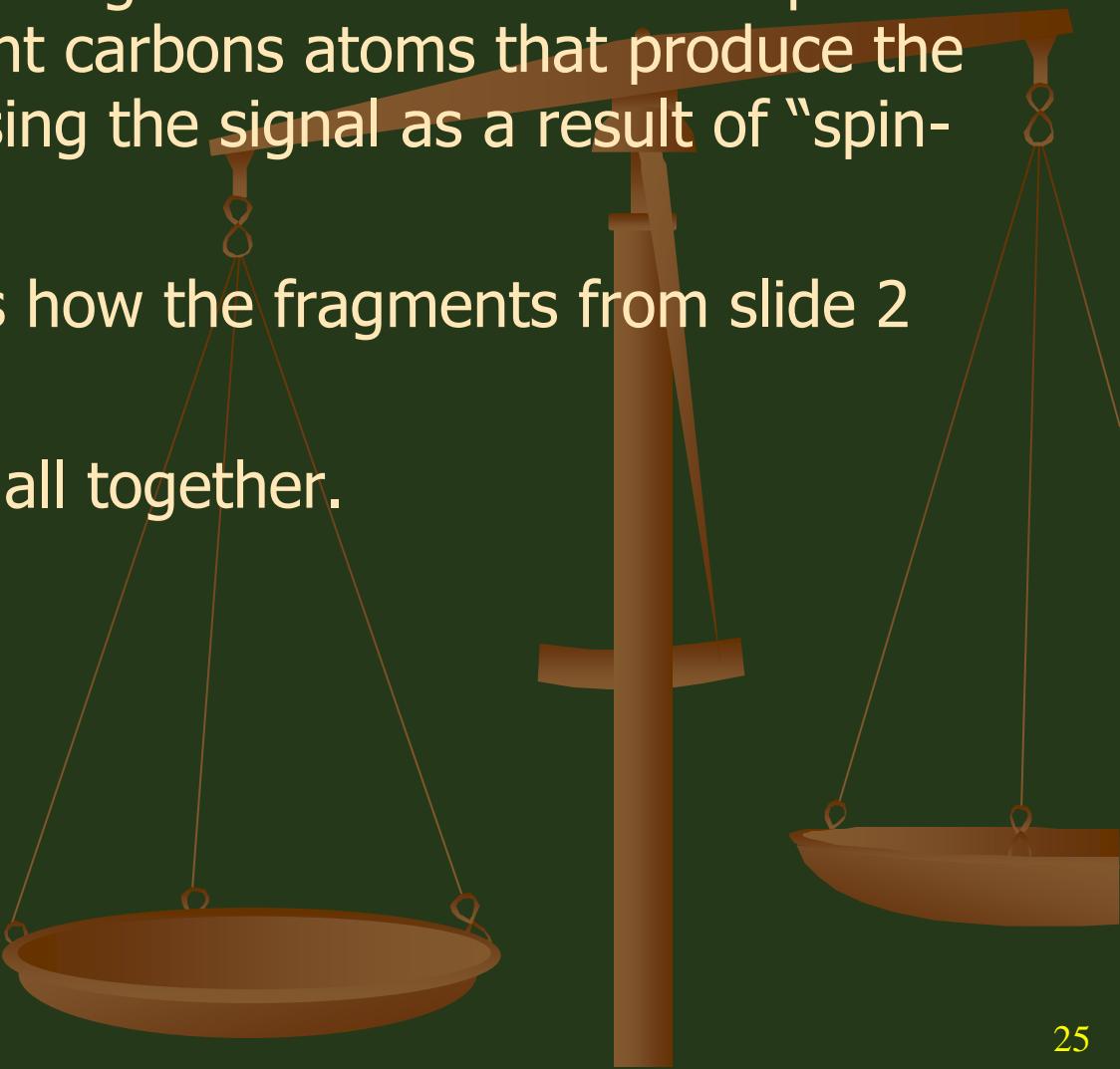
■ NMR Spectra Interpretation Procedure

- The following 4 slides provide a suggested process to follow in attempting to interpret an NMR Spectra.
- The 1st slide is a typical NMR spectra showing 5 signals each consisting of one or more peaks.
- Note that each signal has a number associated with it representing the area integration, i.e., the number of protons generating the signal.
- Also note the expanded spectra of the signal at 2.6 ppm. Expanded spectra are often provided when the signal lacks sufficient resolution to clearly display the number of peaks being generated by the protons on the carbon atom generating the signal.



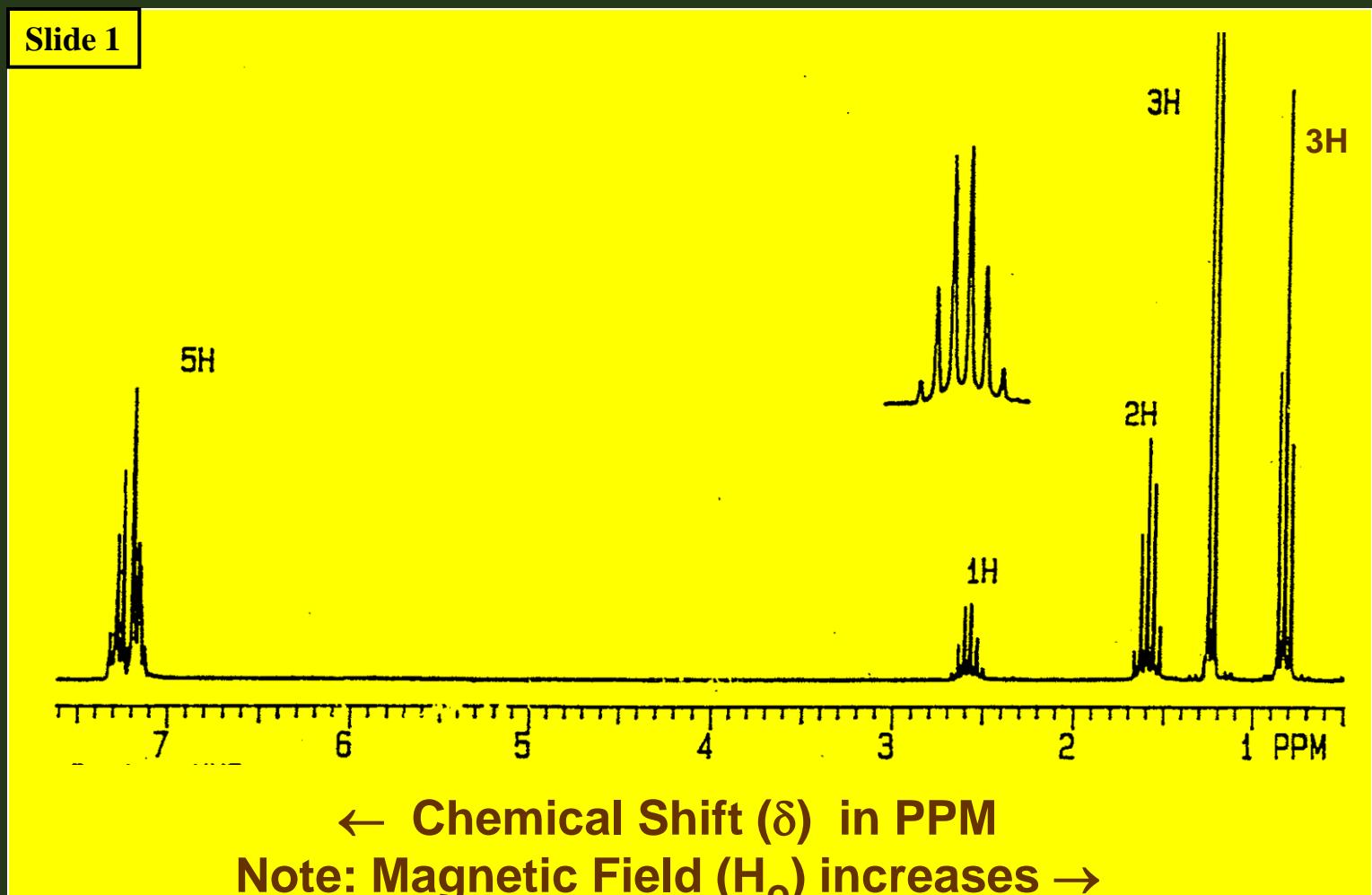
NMR Example Spectra

- The 2nd slide presents interpretations of each signal relative to the number of protons (n) on the carbon atom generating the signal and the number of protons attached to adjacent carbons atoms that produce the n+1 peaks comprising the signal as a result of “spin-spin” splitting.
- The 3rd slide shows how the fragments from slide 2 might fit together.
- The 4th slide ties it all together.



NMR Example Spectra

- Four slides demonstrating a process for interpreting an NMR Spectra

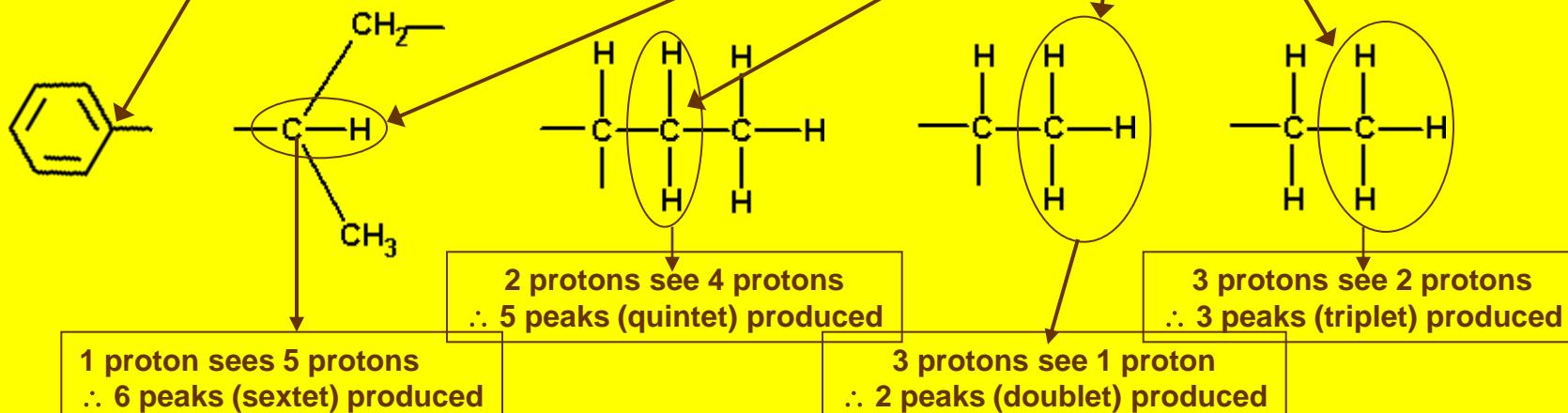
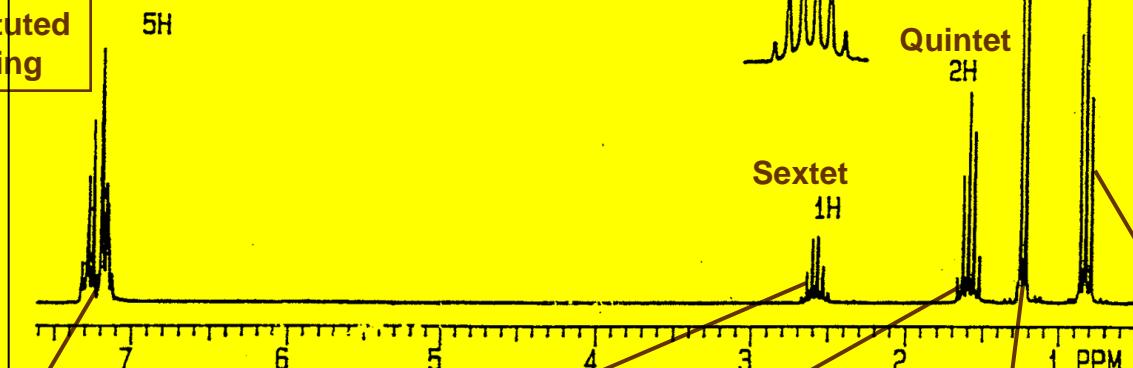


NMR Example Spectra

Slide 2

From chemical shifts, peak integration values, and splitting patterns, develop substructures for each signal.

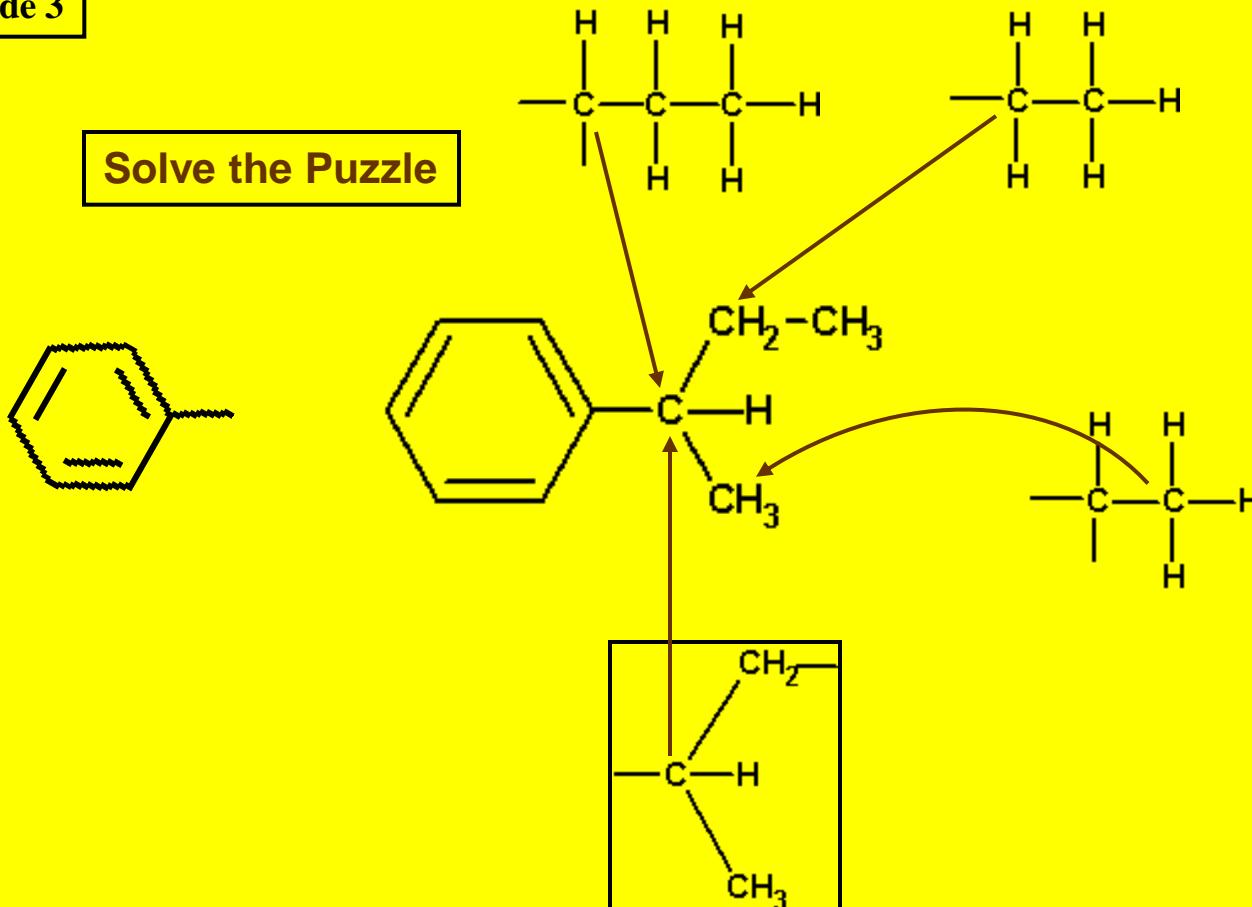
Mono-substituted Benzene Ring



NMR Example Spectra

Slide 3

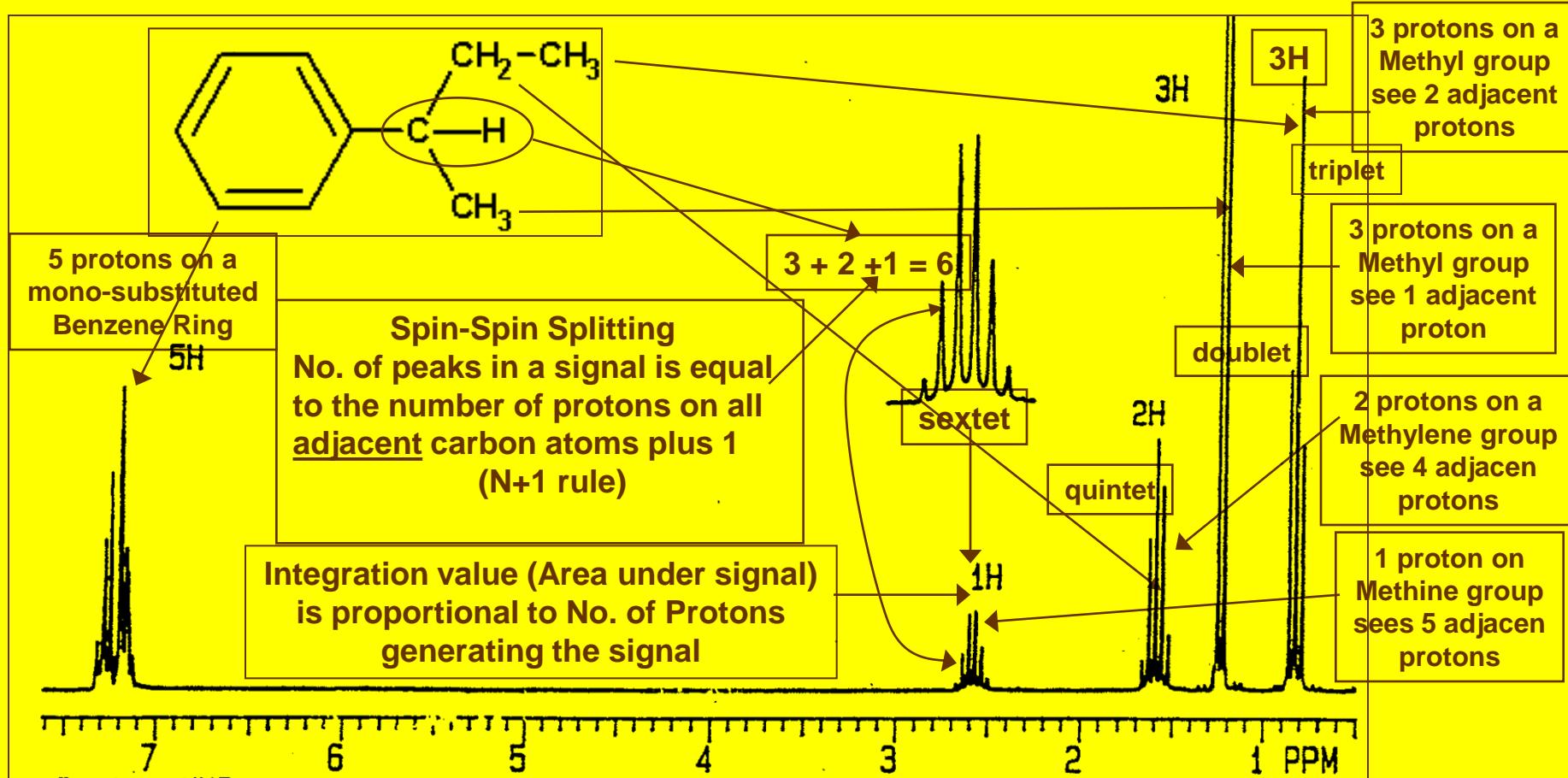
Solve the Puzzle



NMR Example Spectra

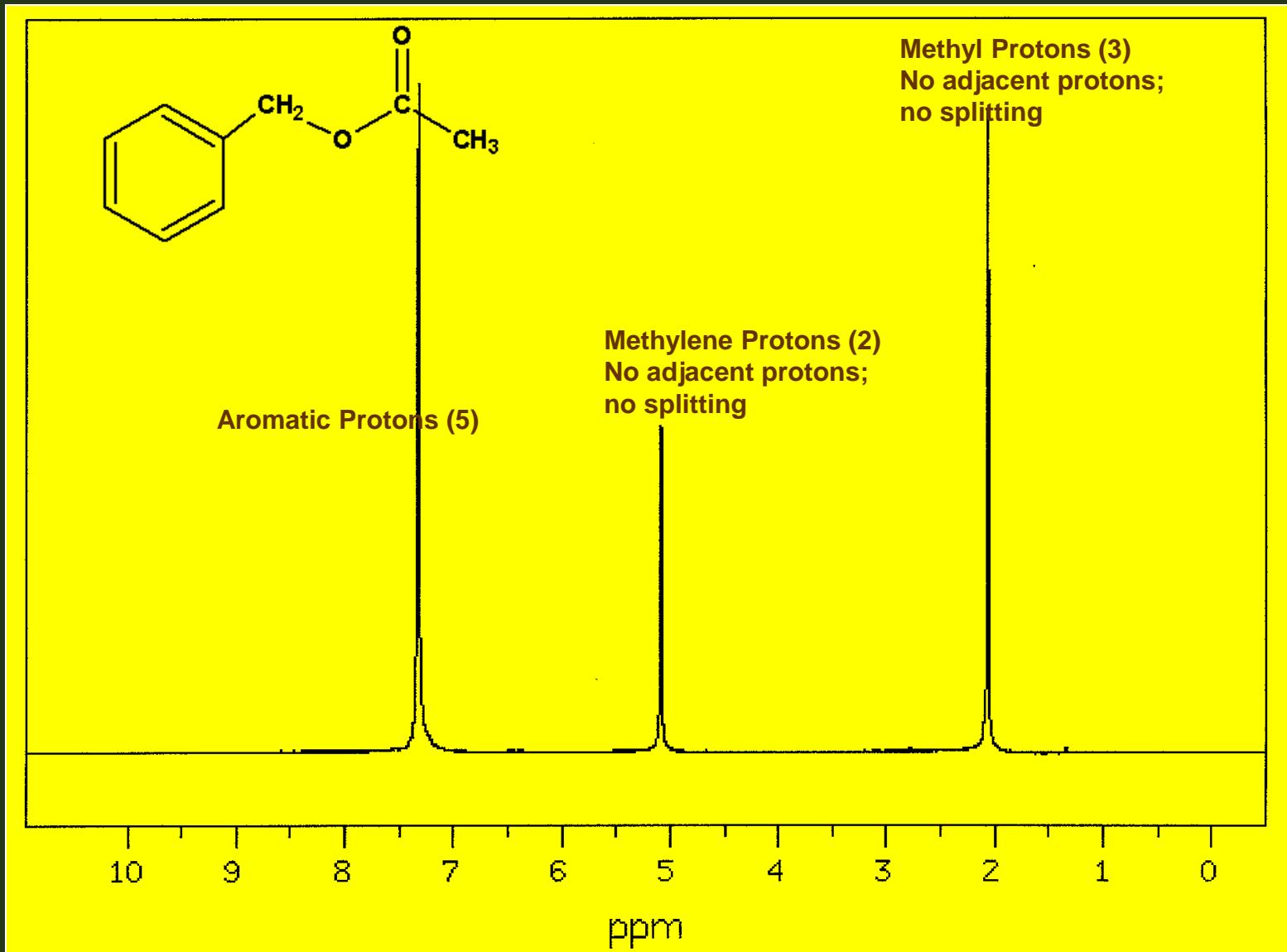
Slide 4

The Solution: 2-Phenylbutane ($C_{10}H_{14}$)



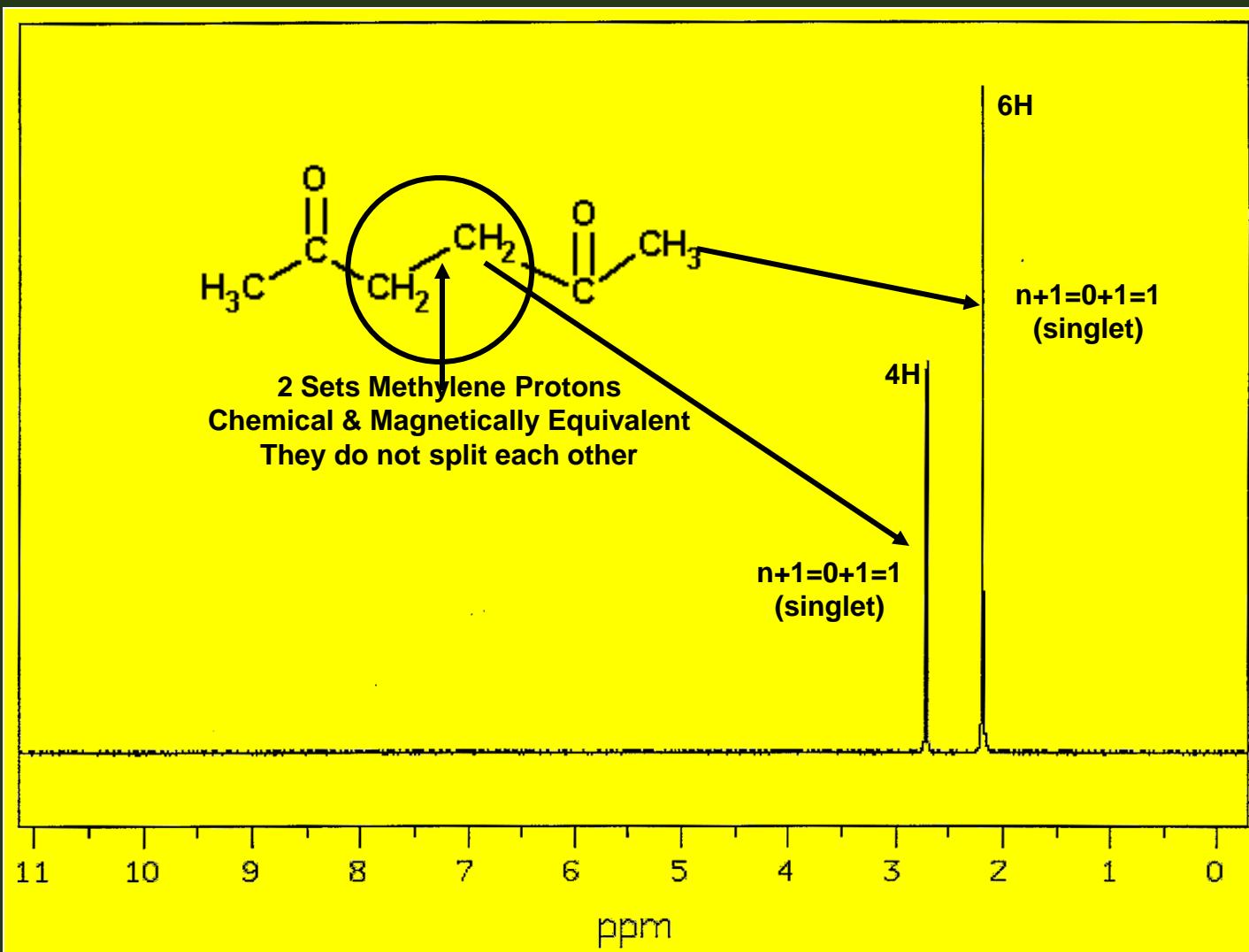
NMR Example Spectra

Benzyl Acetate ($C_9H_{10}O_2$)



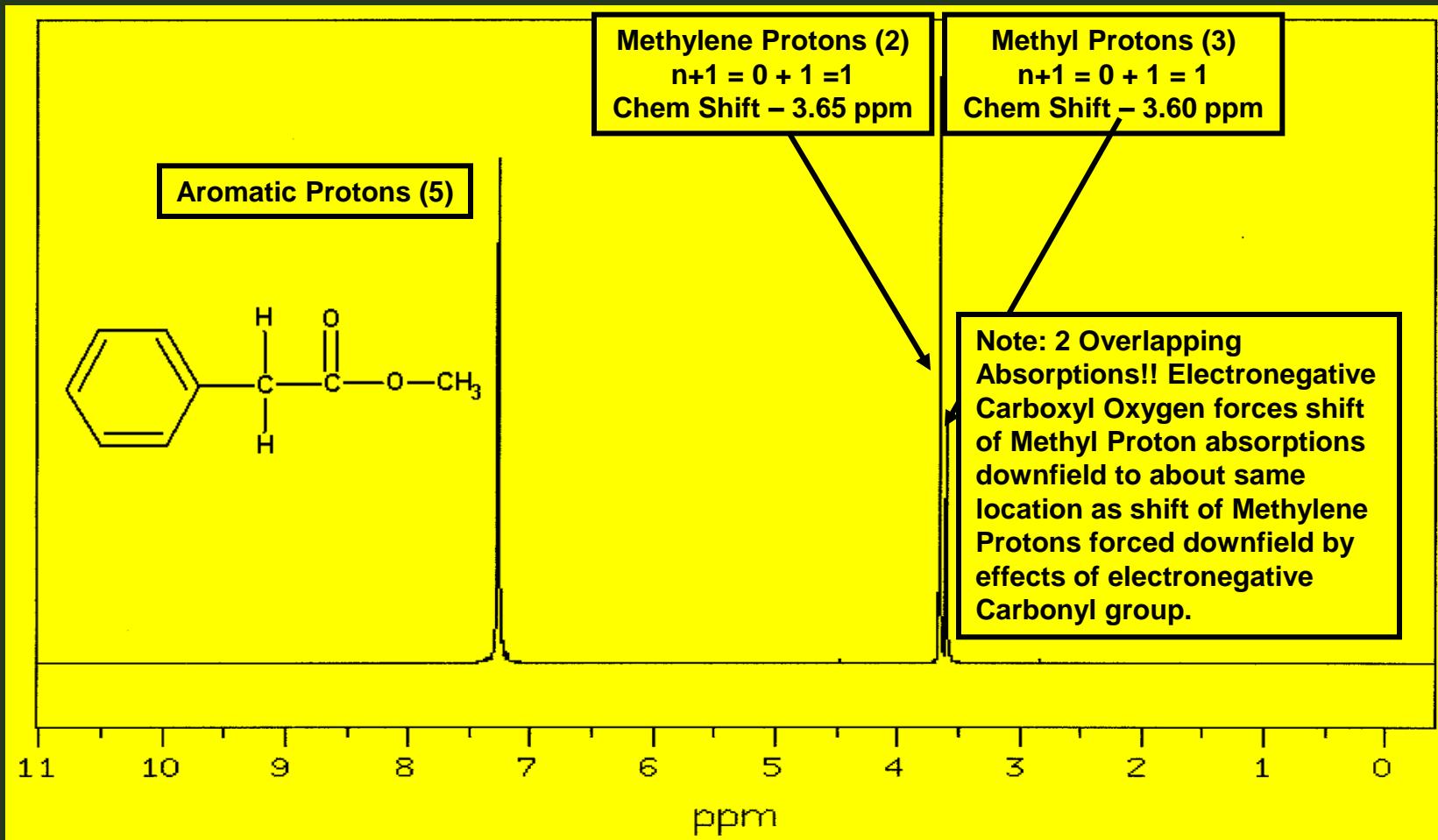
NMR Example Spectra

2,5-Hexanedione (Acetonylacetone) ($C_6H_{10}O_2$)



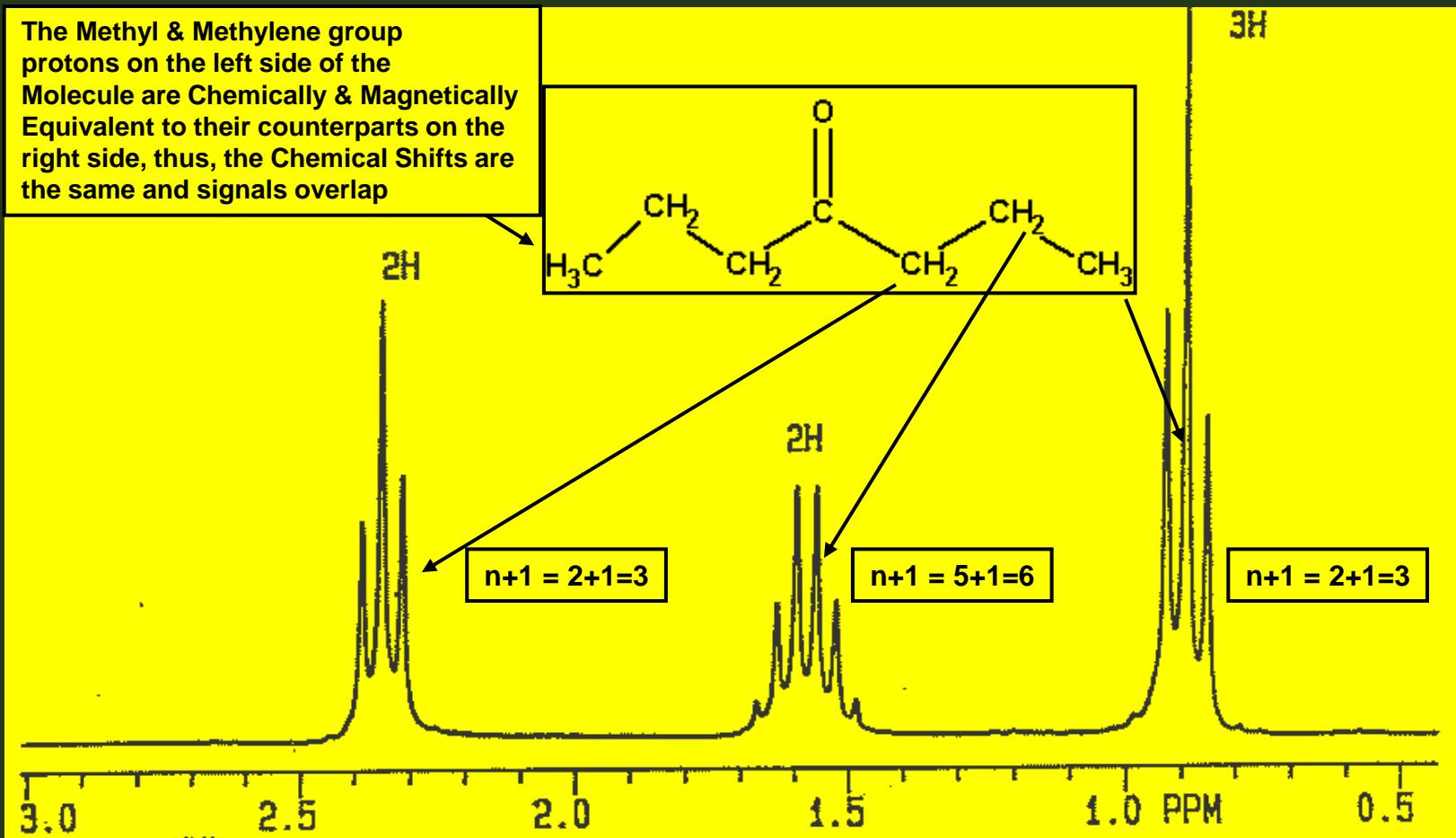
NMR Example Spectra

Methyl Phenyl Acetate ($C_9H_{10}O_2$)



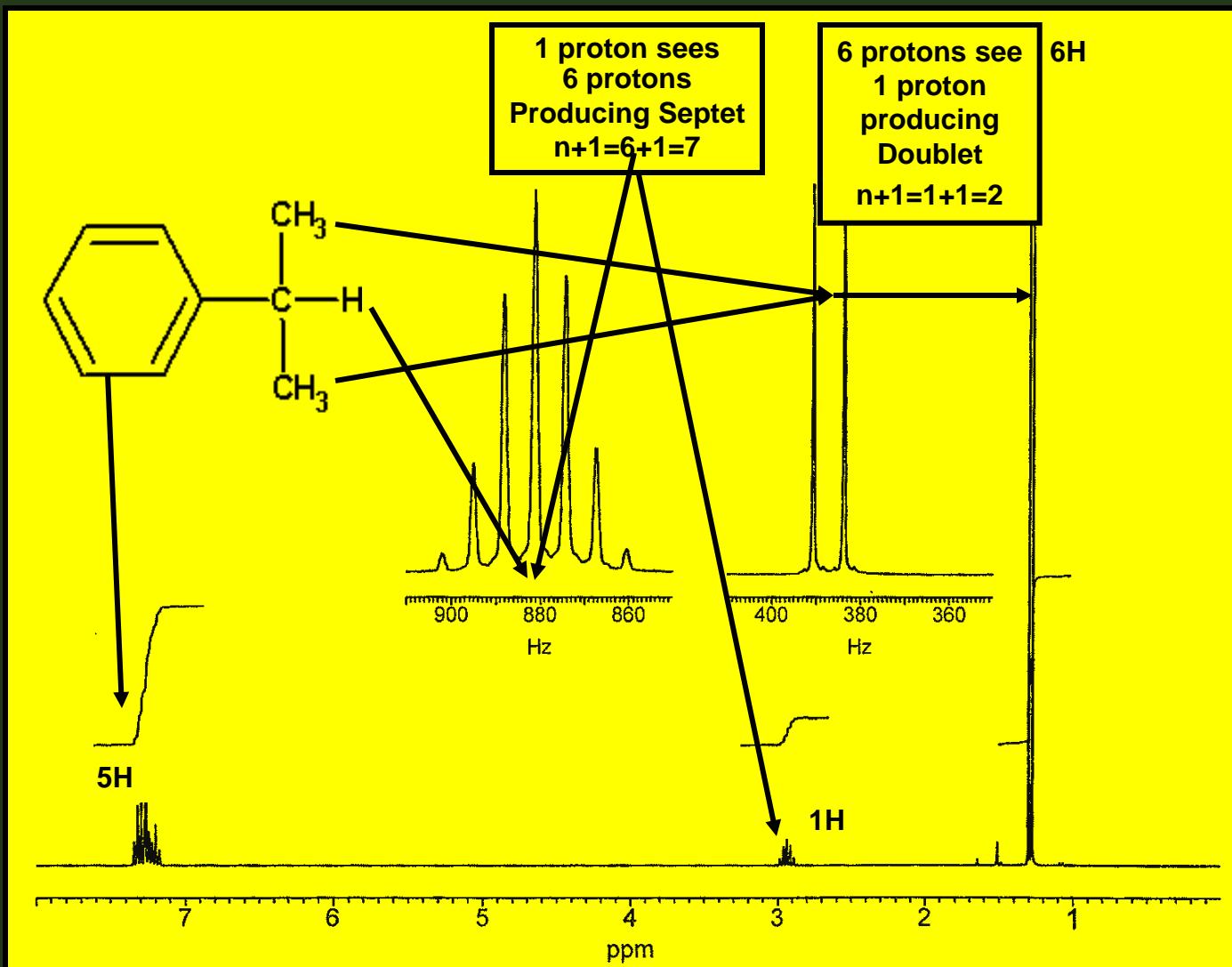
NMR Example Spectra

4-Heptanone ($C_7H_{14}O$)



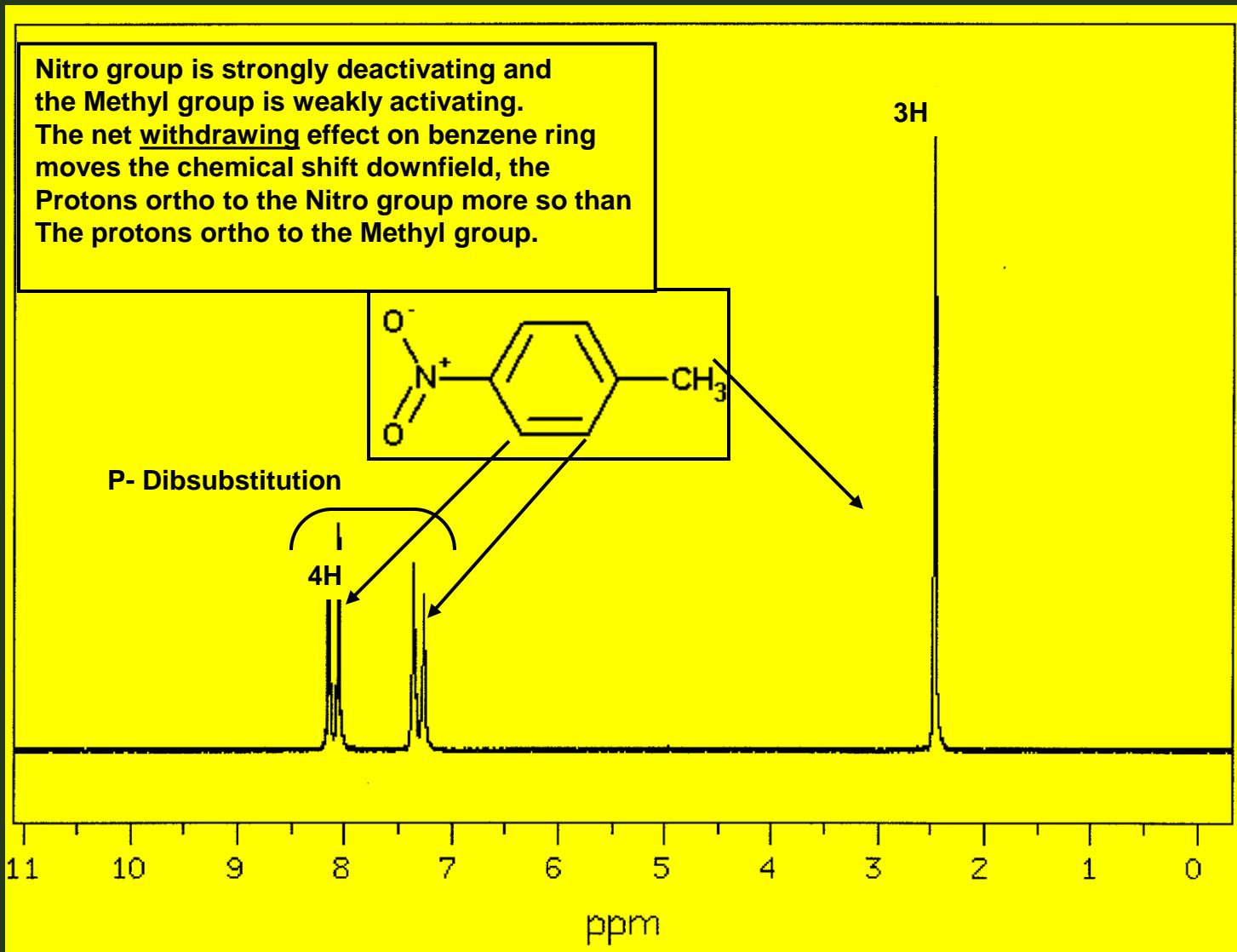
NMR Example Spectra

Isopropyl Benzene (C_9H_{12})



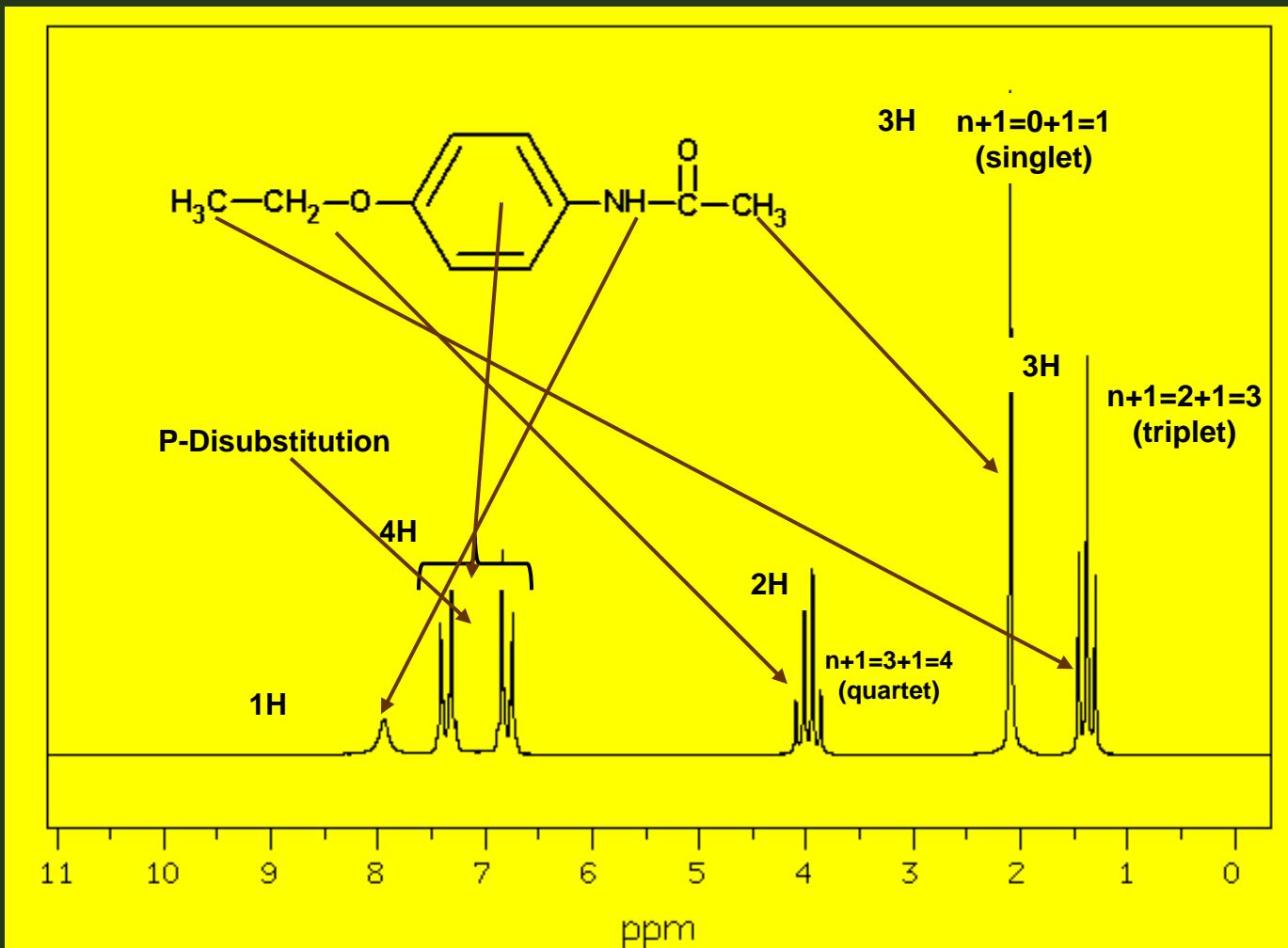
NMR Example Spectra

P-Nitrotoluene ($C_7H_7NO_2$)



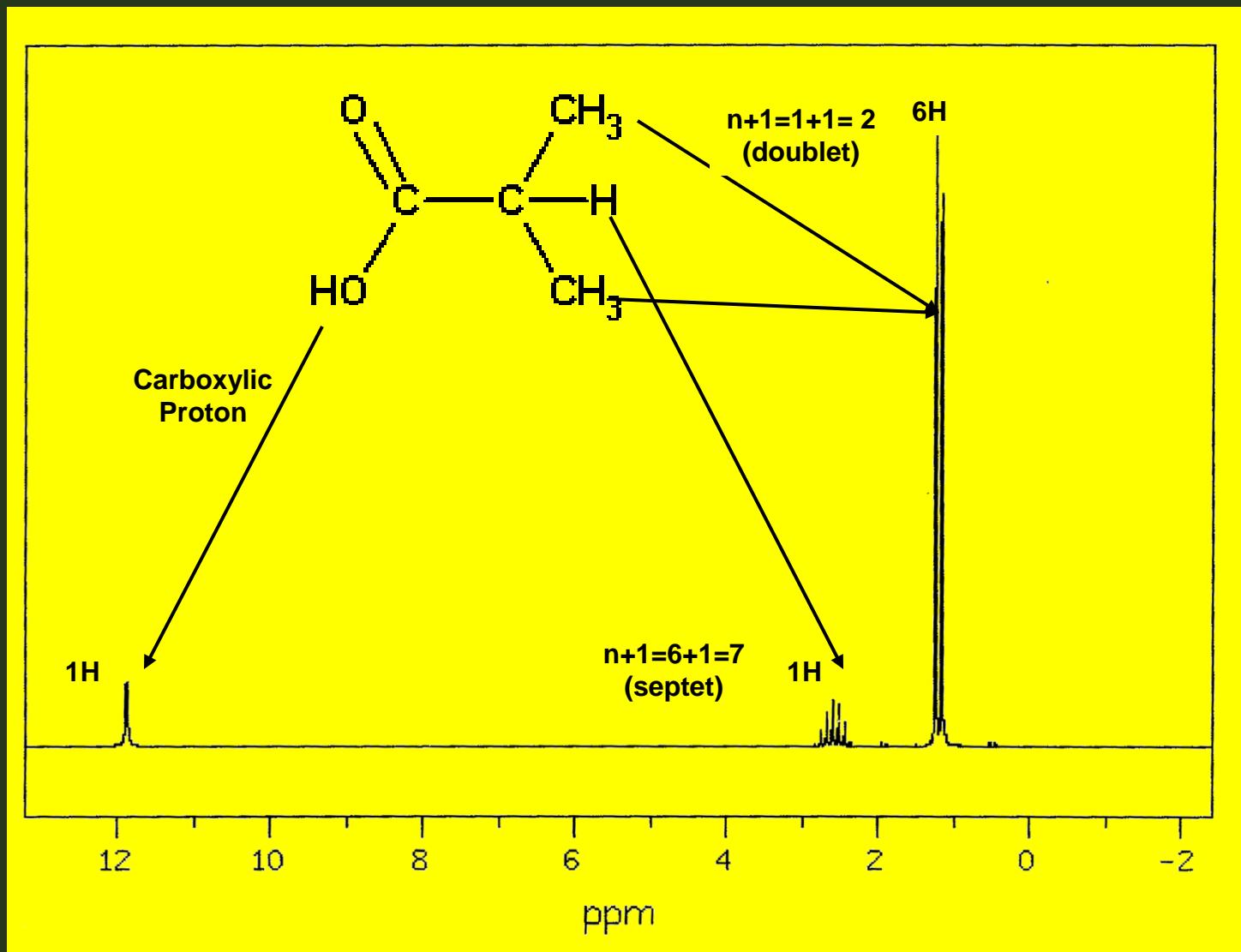
NMR Example Spectra

Phenacetin ($C_{10}H_{13}NO_2$)



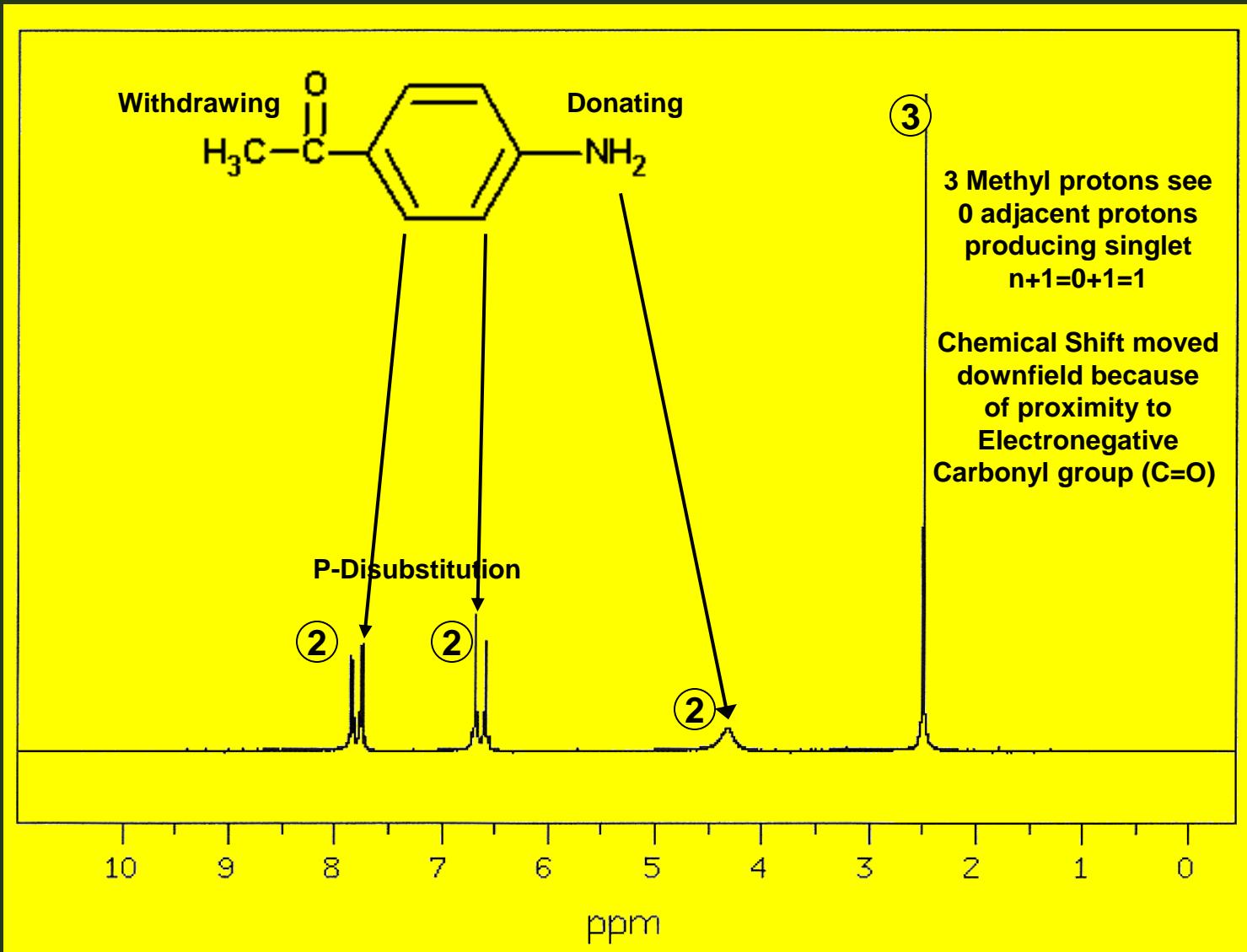
NMR Example Spectra

Isobutyric Acid ($C_4H_8O_2$)



NMR Example Spectra

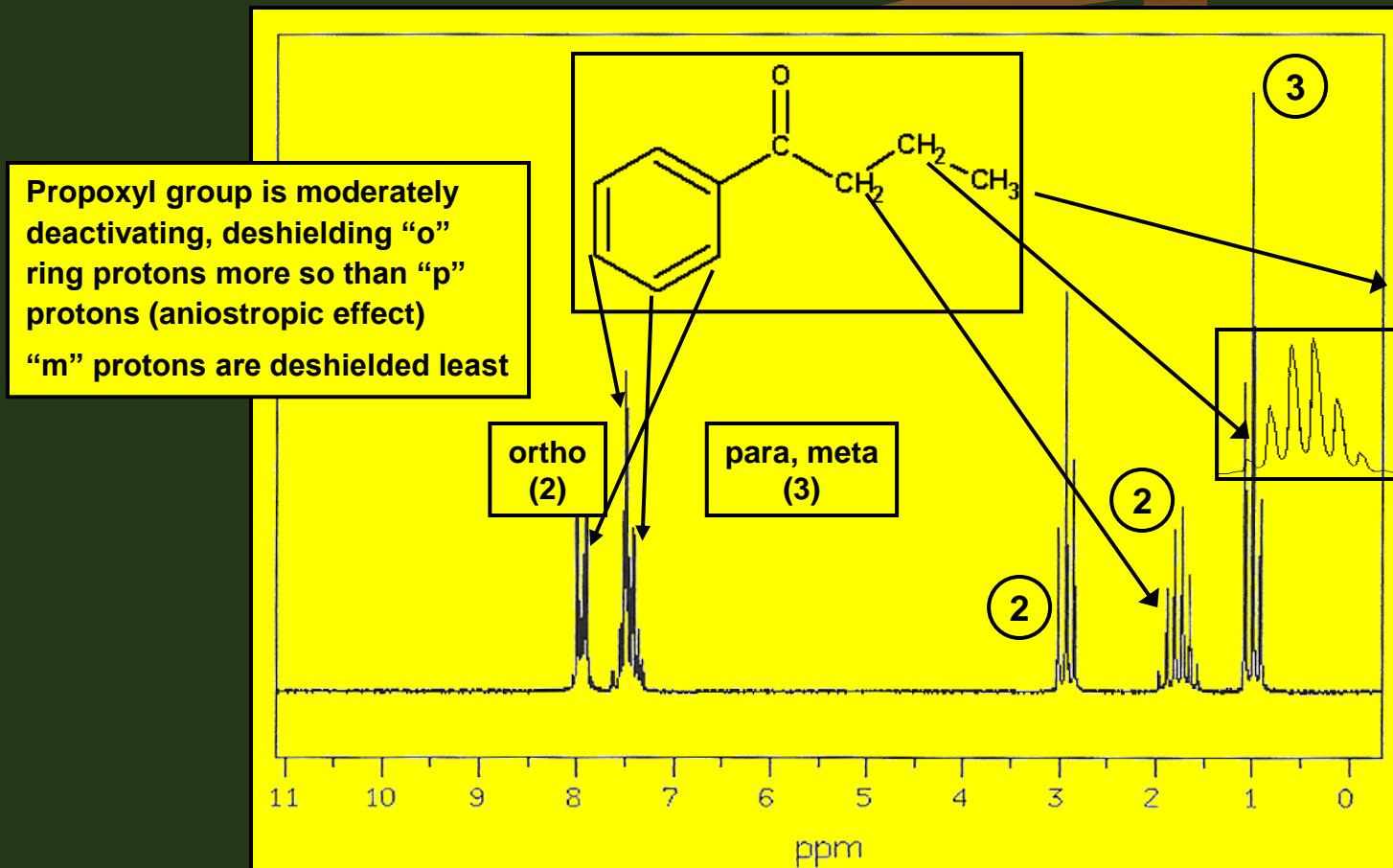
4-Amino-Acetophenone (C_8H_9NO)



NMR Example Spectra

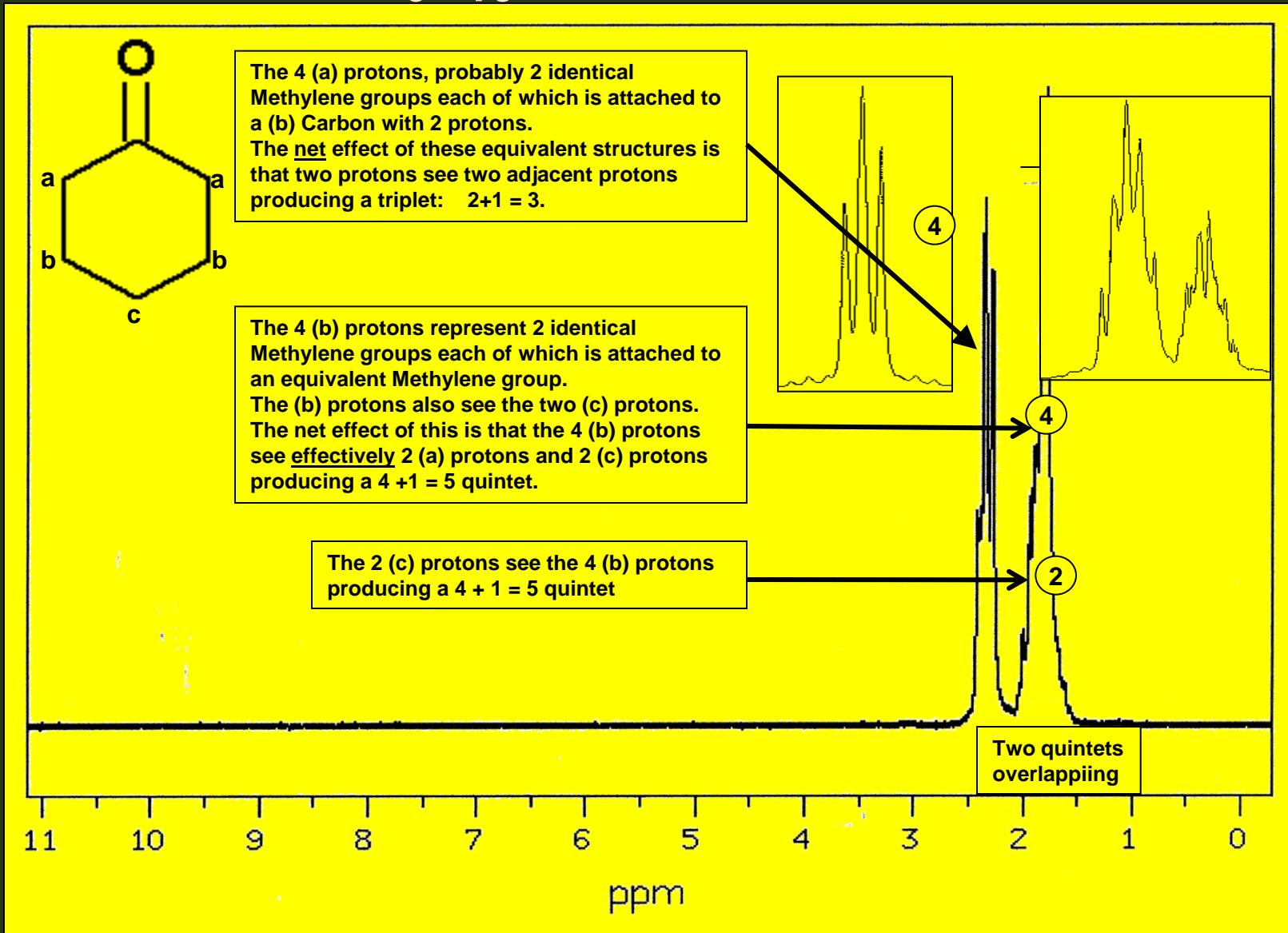
Butyrophenone ($C_{10}H_{12}O$)

The Chemical Shift of the Methylene group nearest the moderately deactivating Carbonyl group is greater than the adjacent Methylene group, because the deactivating effect diminishes with distance



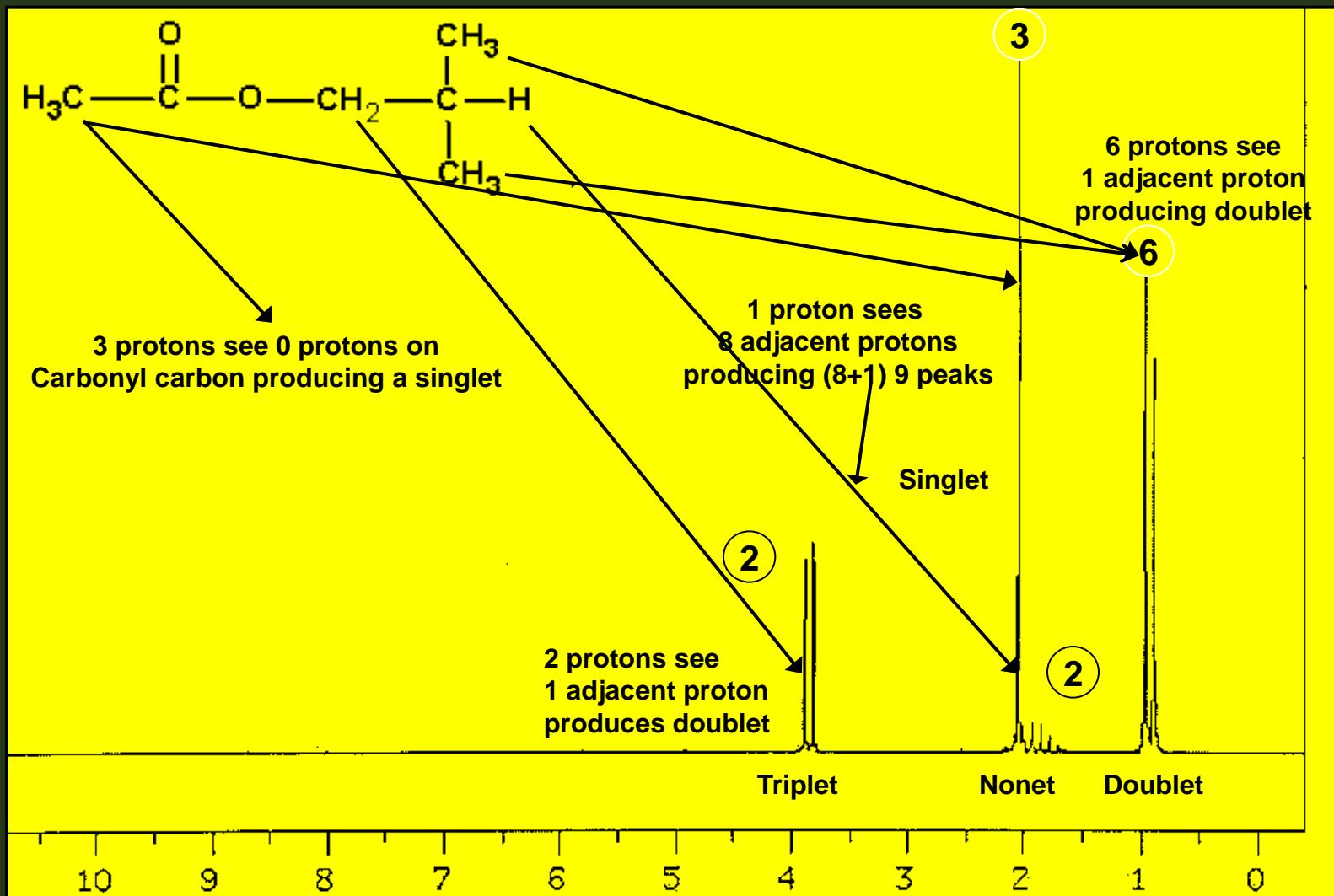
NMR Example Spectra

Cyclohexanone ($C_6H_{10}O$)

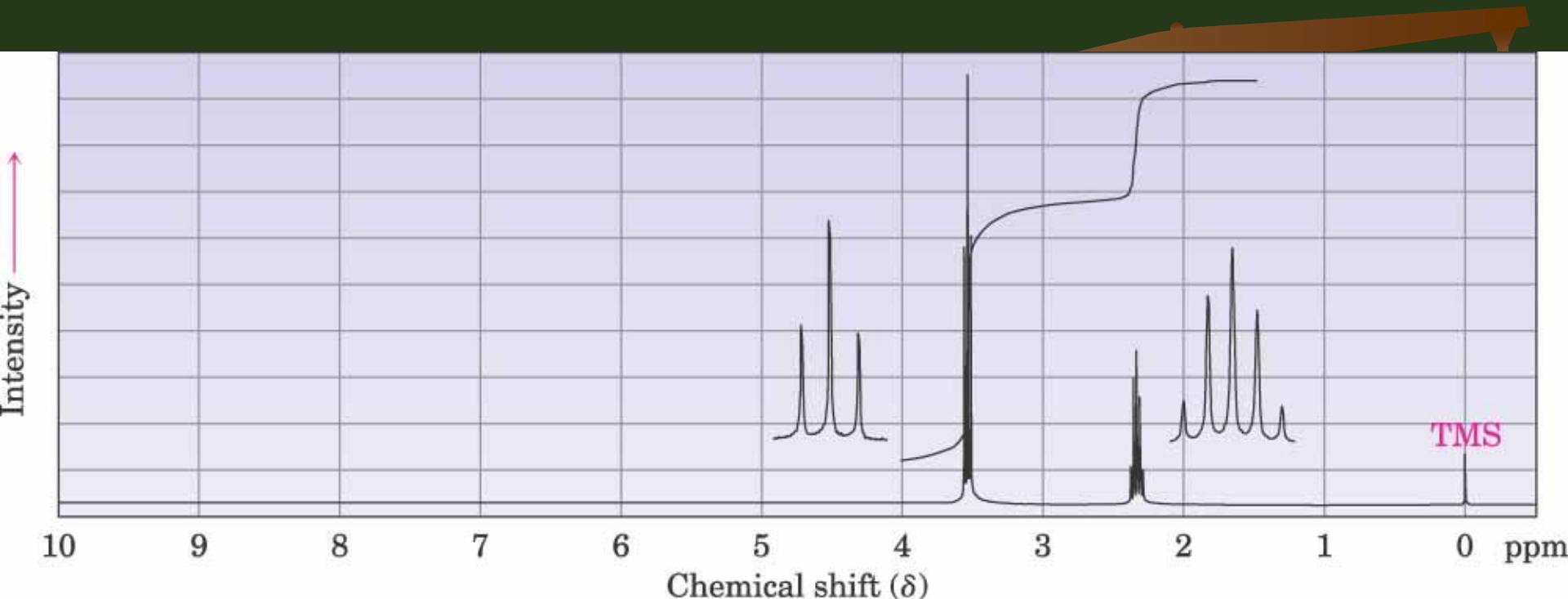


NMR Example Spectra

Isobutyl Acetate ($C_6H_{12}O_2$)



Practice Problem: The compound whose ^1H NMR spectrum is shown has the molecular formula $\text{C}_3\text{H}_6\text{Br}_2$.
Propose a structure.



©2004 Thomson - Brooks/Cole

Practice Problem: The compound whose ^1H NMR spectrum is shown has the molecular formula $\text{C}_4\text{H}_7\text{O}_2\text{Cl}$ has an I.R absorption peak at 1740 cm^{-1} . Propose a structure.

