NMR III

Practice of NMR

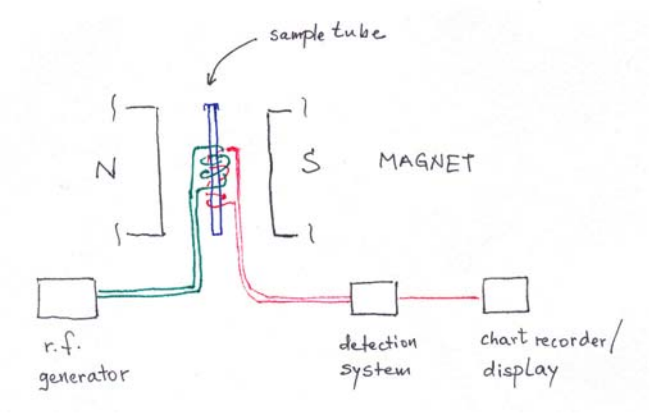
Proton Equivalence

Time Scale

Ref	9 : 3, 7, 9; 8th ed. 9 : 5, 8, 10; 9th ed.
Prob	9 : 1 - 4; 8th ed. 9 : 3 - 6; 9th ed. HMWK #3
Adv Rdg	9 : 8; 8th ed. 9 : 9; 9th ed.

NMR Instrument

Functional Diagram



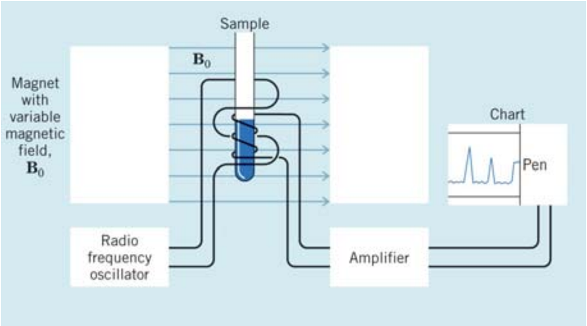
detection of resonance conditions

- "traditional": fixed r.f.; vary B_0
- "alternative": fixed B_0, vary r.f.
- "modern": "Fourier Transform Technology", using fixed magnet
  (*broad shot of rf's, then see how it decays*)

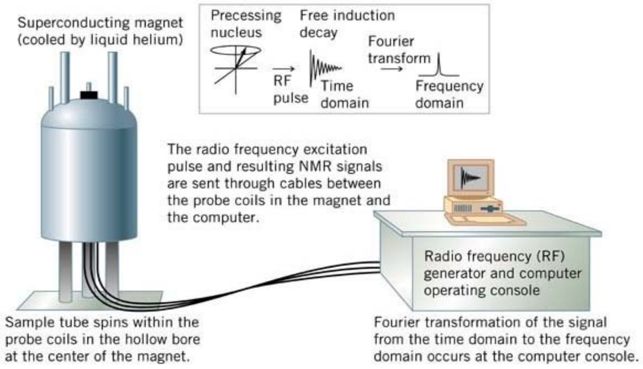
results always displayed as in "alternative"

for illustration, see ......

Solomons 9.3, NMR Instrument, Traditional



Solomons 9.11, NMR Instrument, Modern



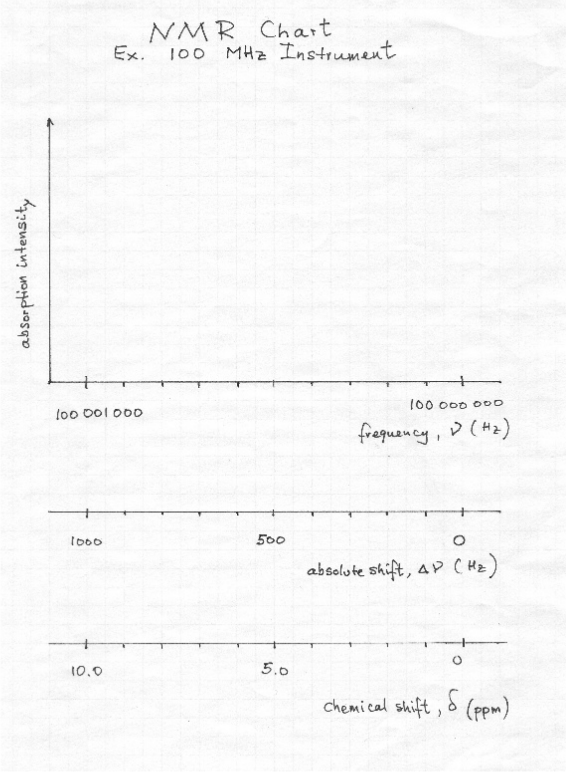
The radio frequency excitation pulse and resulting NMR signals are sent through cables between the probe coils in the magnet and the computer.

Sample tube spins within the probe coils in the hollow bore at the center of the magnet.

Fourier transformation of the signal from the time domain to the frequency domain occurs at the computer console.

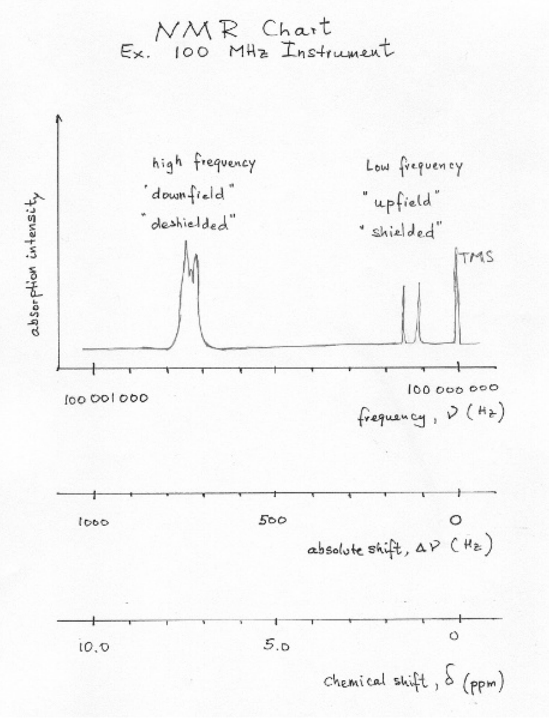
NMR Chart

Ex. 100 MHz Instrument; Blank



NMR Chart

Ex. 100 MHz Instrument; w/ Peaks



Proton Equivalence

(Chem Equivalence only)

- identical (= "equiv") H's give 1 signal
- non-identical (= "non-equiv.") H's give diff. signals

Implication

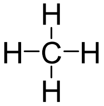
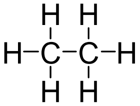
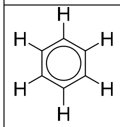
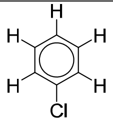
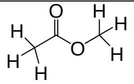
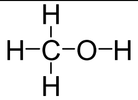
- equiv. H's have same chem. environment
- non equiv. ..... different ....

Terminology:

Usually, several types of H's exist in a molecule,

"each type" = "non-equivalent H"

Practice, Non – Equivalent H's

cmpd	# of non-equivalent H's
	1
	1
	1
	3
	2
	2

Equivalence ...

In difficult cases:

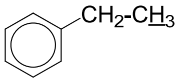
- replace H by "X"
- see if it gives different cmpd
  (*naming might help)*
- if get diff. enantiomers
  ∴ doesn't count
- if get diff. diastereomers
  ∴ counts as non-equivalent

Terminology

if replacement gives — then H's are called

~~achiral~~ identical cmpd — homotopic (*equiv.*)

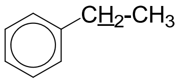
Ex.:



1 signal for 3 H's

enantiomers — enantiotopic (*equiv.*)

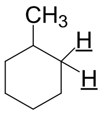
Ex.:



1 signal for 2 H's

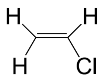
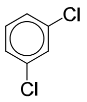
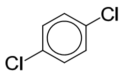
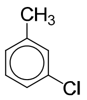
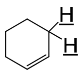
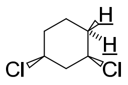
diastereomers — diastereotopic (*non-equiv.*)

Ex.:



2 signals for 2 H's
(*in theory*)

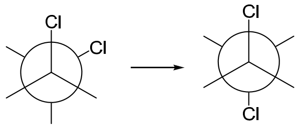
Practice: Non-Equivalent Protons

cmpd	# of non-equivalent H's
	3
	3
	1
	4 (not counting CH_3 group)
	1 (enantiotopic)
	2 (diastereotopic)

Time Scale

- NMR detection is slow
- cannot see individual conformations

e.g., $Cl\text{-}CH_2\text{-}CH_2\text{-}Cl$



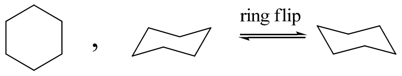
conformational change not detectable,
gives only 1 signal, reflecting avg. of conformations

Applies to:

1.) open chain systems

2.) **mobile** ring systems

e.g., cyclohexane



here, cannot differentiate between ax. & eq.

Note:

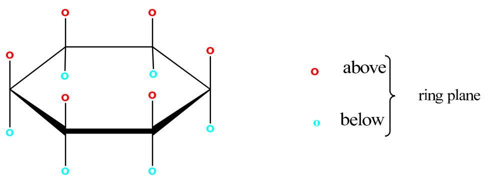
In rigid ring systems, such as trans decalins, steroids

ax. & eq. can be differentiated

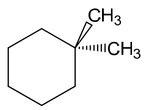
time scale

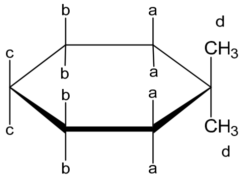
- NMR sees ring(s) (at r.t.)
  as planar structure,
  with H’s above and below the plane

- better 3D visualisation for NMR as follows:

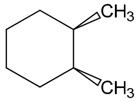


Practice : Count Non-Equivalent Protons





4 signals



6 signals