

NMR III

Chemical Shift

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

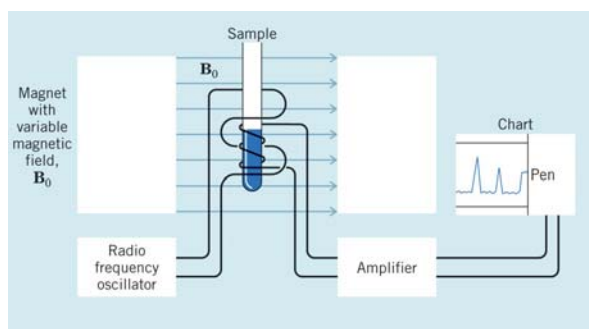
detection of resonance conditions

- “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)

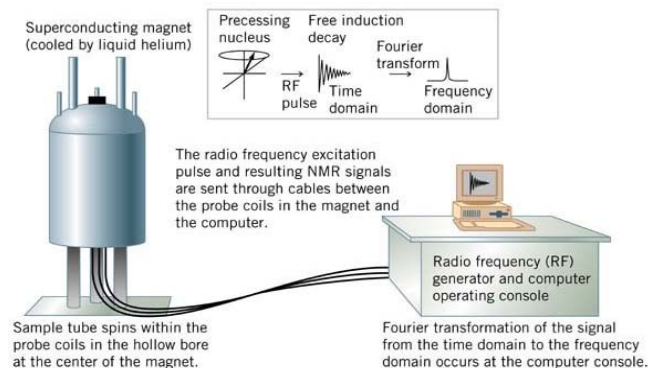
results always displayed as in the “alternative”

for illustration, see p. 3.5

Solomons 9.3, NMR Instrument, Traditional



Solomons 9.11, NMR Instrument, Modern

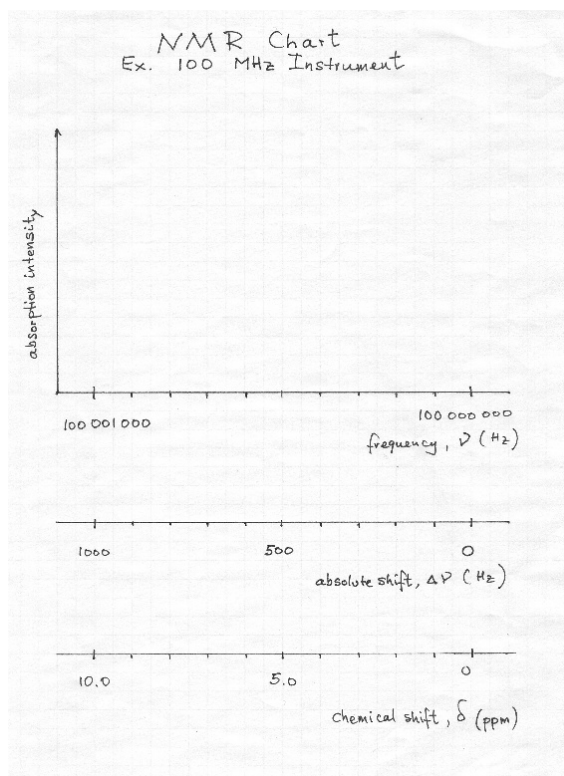


NMR Chart

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

Rationale

- 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
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	
$\begin{array}{c} \text{H} \\ \\ \text{H} \quad \text{C} \quad \text{H} \\ / \quad \backslash \\ \text{H} \quad \text{C} \quad \text{H} \\ \\ \text{H} \end{array}$	
$\begin{array}{c} \text{H} \\ \\ \text{H} \quad \text{C} \quad \text{H} \\ / \quad \backslash \\ \text{H} \quad \text{C} \quad \text{H} \\ \\ \text{Cl} \end{array}$	
$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$	

Equivalence ...

In difficult cases:

- replace H by “X”
- see if it gives different compd
(*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 compd homotopic (*equiv.*)

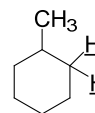
Ex.:

enantiomers enantiotopic (*equiv.*)

Ex.:

diastereomers diastereotopic (*non-equiv.*)

Ex.:



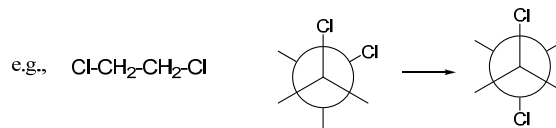
2 signals for 2 H's
(*in theory*)

Practice: Non-Equivalent Protons

compd	# of non-equivalent H's
	(not counting CH ₃ group)

Time Scale

- NMR detection is slow
- cannot see individual conformations



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:

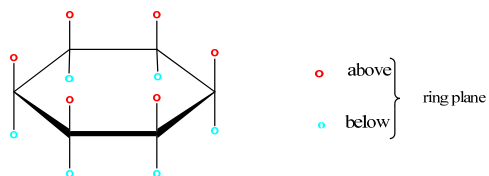
In rigid ring systems, such as trans decalins, steroids

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

