Interpreting $^1$H (Proton) NMR Spectra

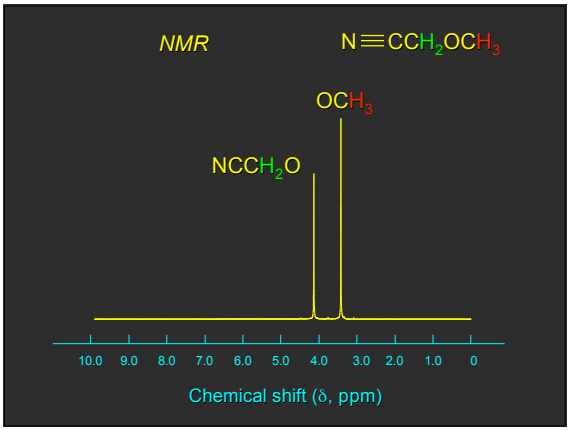
*Information contained in an NMR spectrum includes:*

1. number of signals
2. their intensity (as measured by area under peak)
3. splitting pattern (multiplicity)

*Number of Signals*

protons that have different chemical shifts are chemically nonequivalent

exist in different molecular environment

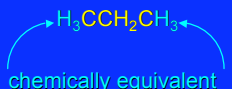



*Chemically equivalent protons*

are in identical environments

have same chemical shift

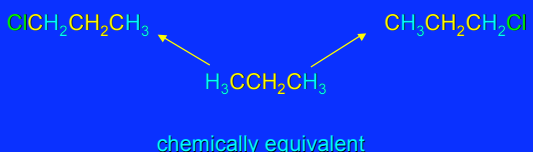
replacement test: replacement by some arbitrary "test group" generates same compound




*Chemically equivalent protons*

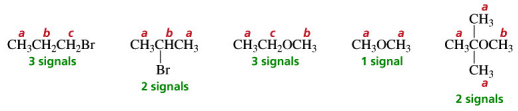
Replacing protons at C-1 and C-3 gives same compound (1-chloropropane)

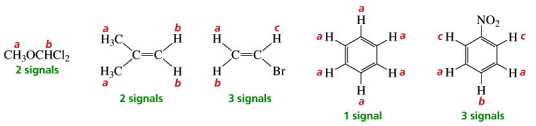
C-1 and C-3 protons are chemically equivalent and have the same chemical shift

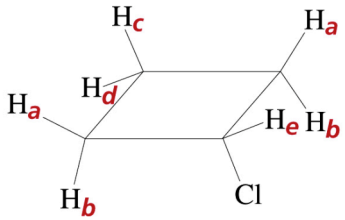


## Chemical Shift: Chemically equivalent protons

Each set of chemically equivalent protons in a compound gives rise to a signal in an $^1$H NMR spectrum of that compound




**chlorocyclobutane**

**the NMR spectrum has 5 signals**

**$H_a$ and $H_b$ are not equivalent**

**$H_c$ and $H_d$ are not equivalent**

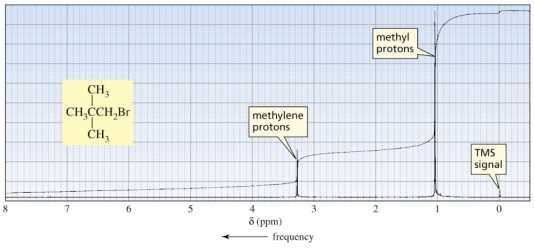
To determine whether similar appearing protons are equivalent, substitute another atom "Z" for each of the protons in question. Then determine their relationship and categorize the atoms as *same, diastereotopic, or enantiotopic*. Consider the green H's then click "Start" to begin.


Definitions Start

## Question

- How many chemically non-equivalent kinds of protons are there in 2,2-dimethylbutane?
- A) 2
- B) 3
- C) 4
- D) 5

## $^1$H NMR spectrum of 1-bromo-2,2-dimethylpropane



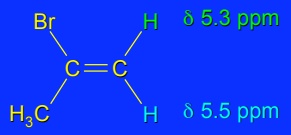
## Question

- How many proton signals would you expect to find in the $^1$H-NMR spectrum of 2-chloropentane?
- A) 2
- B) 3
- C) 4
- D) 5
- E) More than 5

*Diastereotopic protons*

replacement by some arbitrary test group generates diastereomers

diastereotopic protons can have different chemical shifts



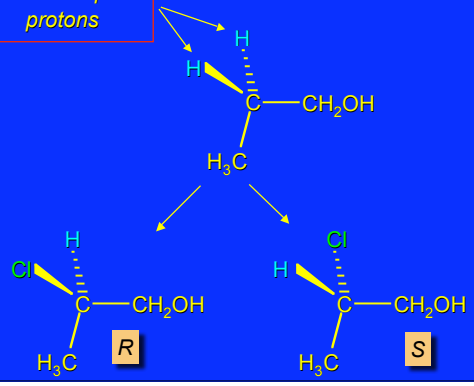

*Enantiotopic protons*

are in mirror-image environments

replacement by some arbitrary test group generates enantiomers

enantiotopic protons have the same chemical shift

*Enantiotopic protons*



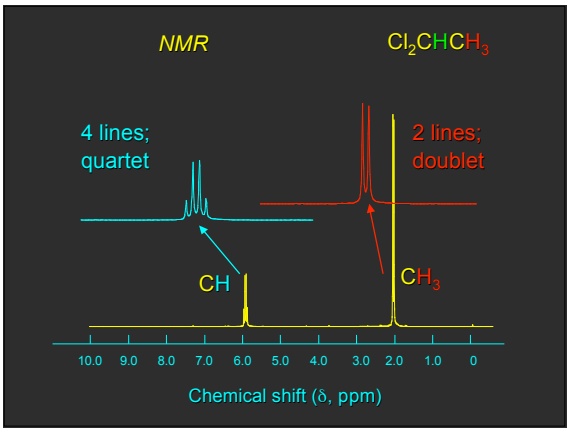

## Question

- How many proton signals would you expect to possibly find in the $^1$H-NMR spectrum of 2-chloropentane?
- A) 6
- B) 7
- C) 8
- D) 9
- E) More than 9

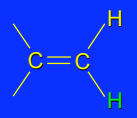
Spin-Spin Splitting
in
NMR Spectroscopy

not all peaks are singlets

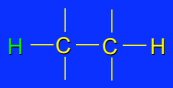
signals can be split by coupling of nuclear spins




*Two-bond and three-bond coupling*

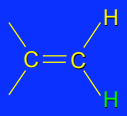


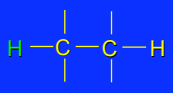
protons separated by two bonds (geminal relationship)



protons separated by three bonds (vicinal relationship)

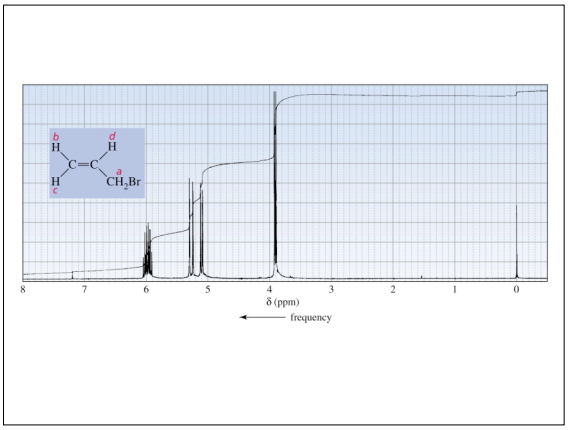
*Two-bond and three-bond coupling*

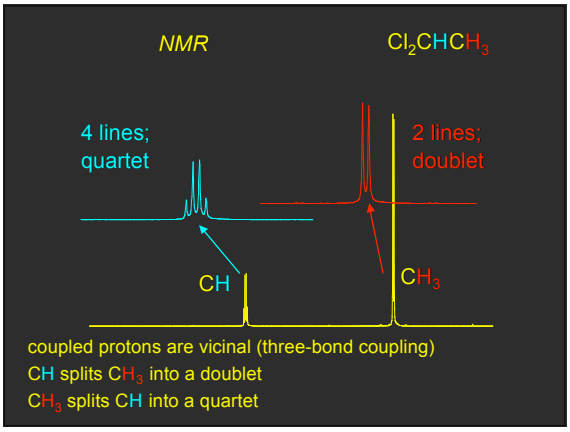




in order to observe splitting, protons cannot have same chemical shift

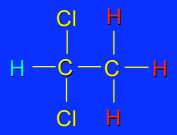
coupling constant ($^2J$ or $^3J$) is independent of field strength




coupled protons are vicinal (three-bond coupling)
CH splits $CH_3$ into a doublet
$CH_3$ splits CH into a quartet

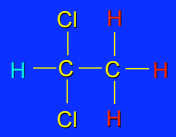
*Why do the methyl protons of 1,1-dichloroethane appear as a doublet?*



signal for methyl protons is split into a doublet

To explain the splitting of the protons at C-2, we first focus on the two possible spin orientations of the proton at C-1

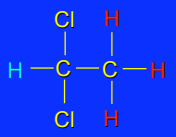
*Why do the methyl protons of 1,1-dichloroethane appear as a doublet?*



signal for methyl protons is split into a doublet

There are two orientations of the nuclear spin for the proton at C-1. One orientation shields the protons at C-2; the other deshields the C-2 protons.

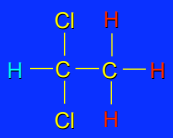
*Why do the methyl protons of 1,1-dichloroethane appear as a doublet?*



signal for methyl protons is split into a doublet

The protons at C-2 "feel" the effect of both the applied magnetic field and the local field resulting from the spin of the C-1 proton.

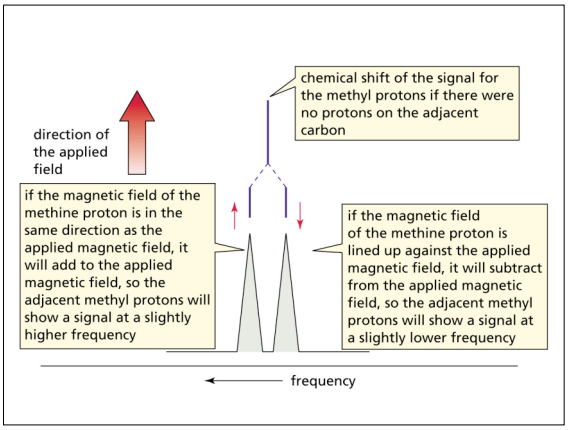
*Why do the methyl protons of 1,1-dichloroethane appear as a doublet?*

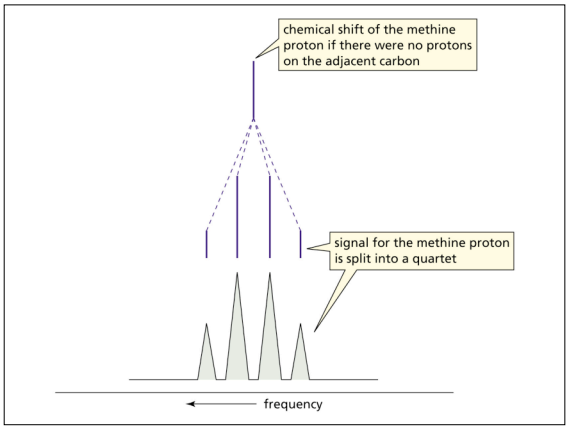


"true" chemical shift of methyl protons (no coupling)

this line corresponds to molecules in which the nuclear spin of the proton at C-1 *reinforces* the applied field

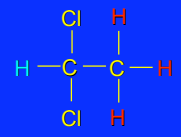
this line corresponds to molecules in which the nuclear spin of the proton at C-1 *opposes* the applied field



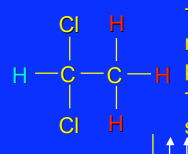

*Why does the methine proton of 1,1-dichloroethane appear as a quartet?*

signal for methine proton is split into a quartet



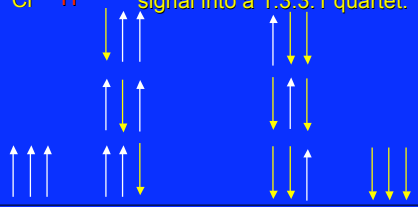
The proton at C-1 "feels" the effect of the applied magnetic field and the local fields resulting from the spin states of the three methyl protons. The possible combinations are shown on the next slide.

*Why does the methine proton of 1,1-dichloroethane appear as a quartet?*




There are eight combinations of nuclear spins for the three methyl protons.

These 8 combinations split the signal into a 1:3:3:1 quartet.



*The splitting rule for $^1H$ NMR*

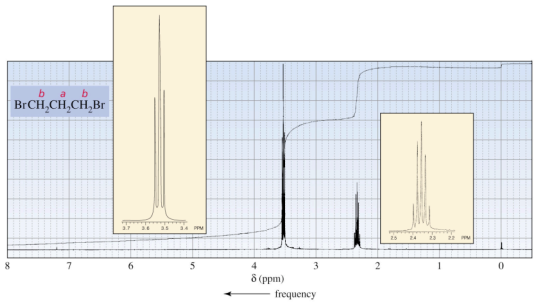
For simple cases, the multiplicity of a signal for a particular proton is equal to the number of equivalent vicinal protons + 1.

*Table*

Splitting Patterns of Common Multiplets

| Number of equivalent protons to which H is coupled | Appearance of multiplet | Intensities of lines in multiplet |
|---|---|---|
| 1 | Doublet | 1:1 |
| 2 | Triplet | 1:2:1 |
| 3 | Quartet | 1:3:3:1 |
| 4 | Pentet | 1:4:6:4:1 |
| 5 | Sextet | 1:5:10:10:5:1 |
| 6 | Septet | 1:6:15:20:15:6:1 |

*$^1H$ NMR Splitting*

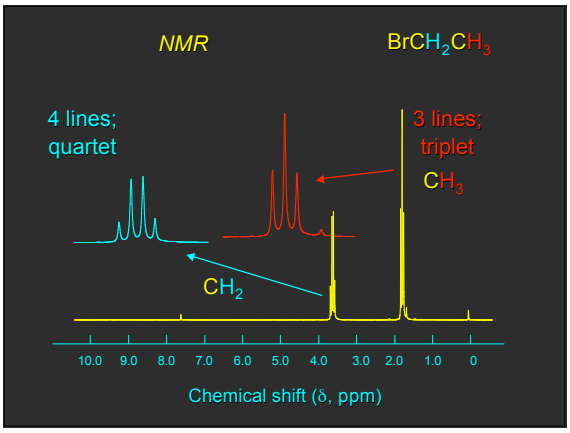



## Question

- What is the multiplicity (spin-spin splitting) of the protons of 1,2-dichloroethane?
- A) one singlet
- B) two singlets
- C) one doublet
- D) one triplet

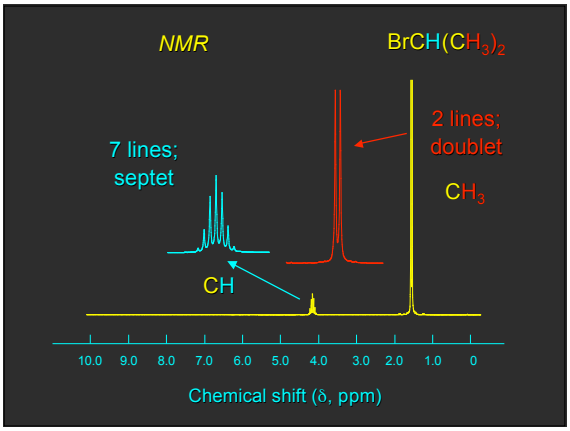
Splitting Patterns:
The Ethyl Group

$CH_3CH_2X$ is characterized by a triplet-quartet pattern (quartet at lower field than the triplet)




Splitting Patterns:
The Isopropyl Group

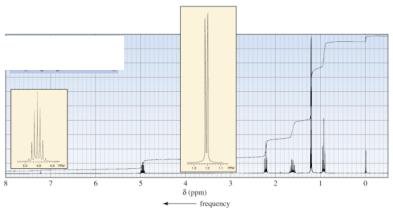
$(CH_3)_2CHX$ is characterized by a doublet-septet pattern (septet at lower field than the doublet)




## Question

- Which isomer of $C_4H_9Br$ has only one peak in its $^1$H-NMR spectrum having the chemical shift δ 1.8?
- A) 1-bromobutane
- B) 2-bromobutane
- C) 1-bromo-2-methylpropane
- D) 2-bromo-2-methylpropane

## Question



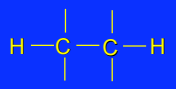

Which compound is the most reasonable for the NMR spectrum above?

A) Ethyl pentanoate
B) Propyl isobutyrate
C) Butyl propanoate
D) Isopropyl butyrate
E) Isopentyl acetate

Splitting Patterns:
Pairs of Doublets

Splitting patterns are not always symmetrical, but lean in one direction or the other when "coupled".

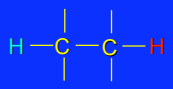
## *Pairs of Doublets*



Consider coupling between two vicinal protons.

If the protons have different chemical shifts, each will split the signal of the other into a doublet.

## *Pairs of Doublets*



Let $\Delta\nu$ be the difference in chemical shift in Hz between the two hydrogens.

Let $J$ be the coupling constant between them in Hz.

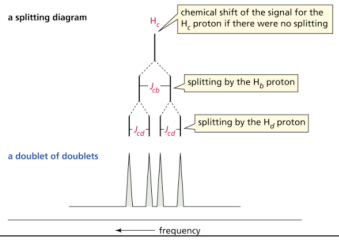
## The Difference between a Quartet and a Doublet of Doublets

a quartet
relative intensities: 1 : 3 : 3 : 1

a doublet of doublets
relative intensities: 1 : 1 : 1 : 1

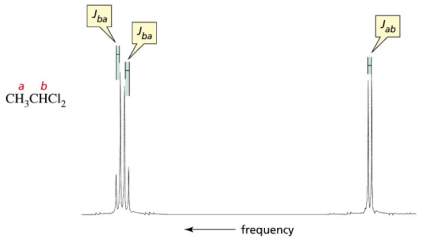
## A Splitting Diagram for a Doublet of Doublets

1,1,2-trichloro-3-methylbutane



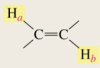
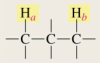
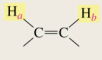
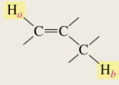

## *Coupling Constants*

The coupling constant ($J$) is the distance between two adjacent peaks of a split NMR signal in hertz

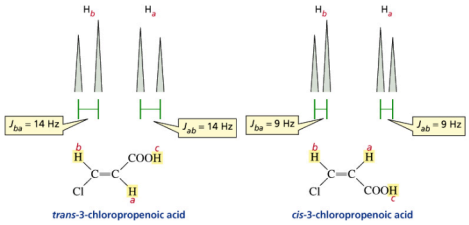



Coupled protons have the same coupling constant

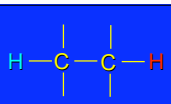
**Approximate Values of Coupling Constants**

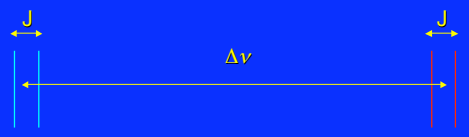
| Approximate value of $J_{ab}$ (Hz) | | Approximate value of $J_{ab}$ (Hz) | |
|---|---|---|---|
|  | 7 |  | 15 (trans) |
|  | 0 |  | 10 (cis) |
|  | 2 (geminal coupling) |  | 1 (long-range coupling) |

A trans coupling constant is greater than a cis coupling constant



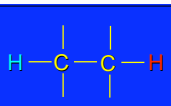

*AX*

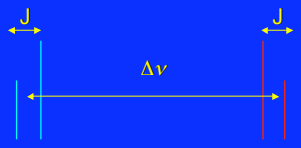





When $\Delta\nu$ is much larger than J the signal for each proton is a doublet, the doublet is symmetrical, and the spin system is called AX.

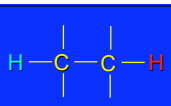
*AM*

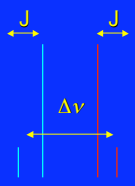





As $\Delta\nu$/J decreases the signal for each proton remains a doublet, but becomes skewed. The outer lines decrease while the inner lines increase, causing the doublets to "lean" toward each other.

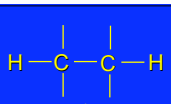
*AB*






When $\Delta\nu$ and J are similar, the spin system is called AB. Skewing is quite pronounced. It is easy to mistake an AB system of two doublets for a quartet.

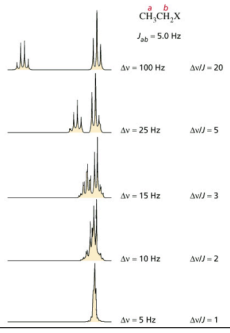
*$A_2$*

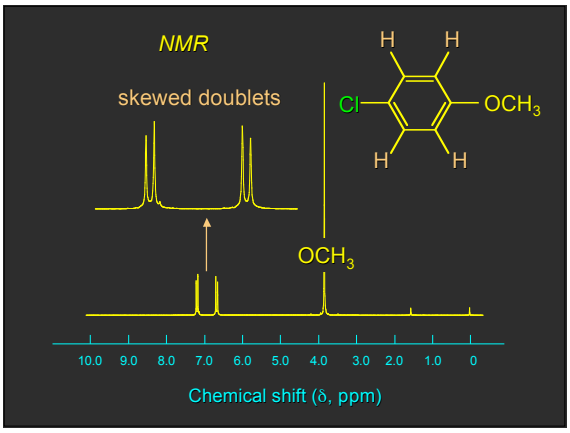




When $\Delta\nu$ = 0, the two protons have the same chemical shift and don't split each other. A single line is observed. The two doublets have collapsed to a singlet.

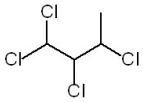
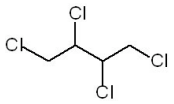
*To observe well-defined splitting patterns, the difference in the chemical shifts (in Hz) must be 10 times the coupling constant values*

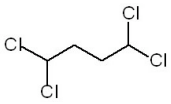





## Question

- Which isomer of formula $C_4H_6Cl_4$ has two signals at δ 3.9 (doublet, 4H) and δ 4.6 (triplet, 2H) in its $^1$H-NMR spectrum?

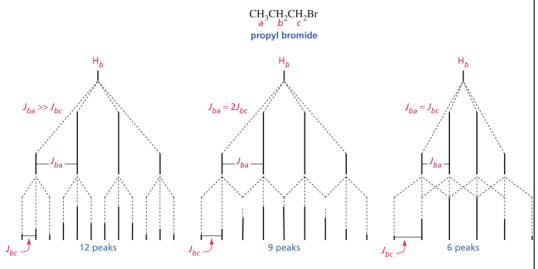
- A 


- C 

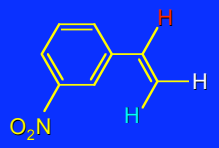

## Complex Splitting Patterns

Multiplets of multiplets
MESS-plets

## A Splitting Diagram for a Quartet of Triplets




## *m*-Nitrostyrene

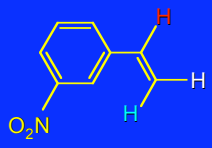


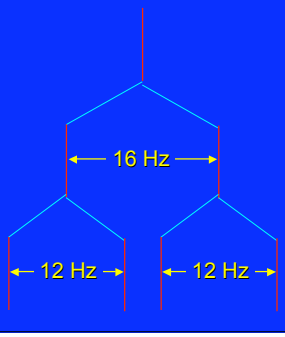

Consider the proton shown in red.

It is unequally coupled to the protons shown in blue and white.

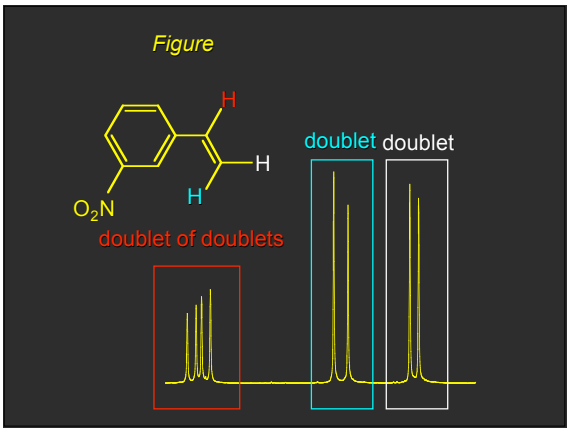
$J_{cis}$ = 12 Hz; $J_{trans}$ = 16 Hz

## *m*-Nitrostyrene




The signal for the proton shown in red appears as a doublet of doublets.



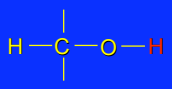

The object of this exercise is to assign each proton in a known chemical structure to its corresponding NMR signal. This procedure is necessary for any products you may isolate in lab. Click "Start" to begin.

Start

$^1$H NMR Spectra of Alcohols & Amines

What about H bonded to O and N?

*O—H*




The chemical shift for O—H is variable (δ 0.5-5 ppm) and depends on temperature and concentration.

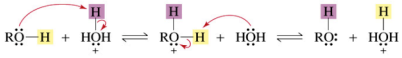
Splitting of the O—H proton is sometimes observed, but **often is not**. It usually appears as a broad peak.

Adding $D_2O$ converts O—H to O—D. The O—H peak disappears.

## *Protons Bonded to Oxygen and Nitrogen*

*The greater the extent of the hydrogen bond, the greater the chemical shift*

mechanism for acid-catalyzed proton exchange



*These protons can undergo proton exchange with deuterium.*

*They appear as broad signals.*

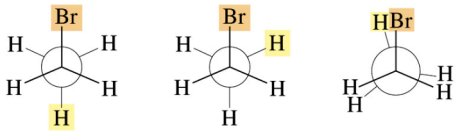
## Question

Which of the following statements is false?

- A) Splitting of the hydroxyl proton of an alcohol is not usually observed.
- B) Alcohol protons shift to lower fields in more concentrated solutions.
- C) Addition of $D_2O$ to alcohol will result in an increased intensity of the hydroxyl proton signal.
- D) The chemical shift of the hydroxyl proton depends on solvent, temperature, and concentration of the solution.

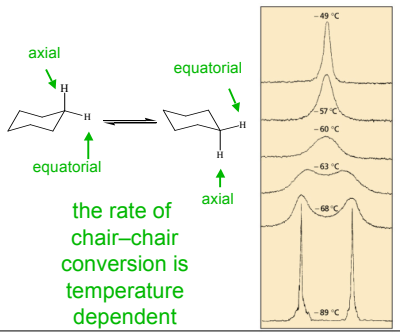
NMR and Conformations

*The three methyl protons are chemically equivalent due to rotation about the C–C bond*




*One signal is observed for the methyl group.*

*$^1$H NMR spectra of cyclohexane-$d_{11}$ at various temperatures*



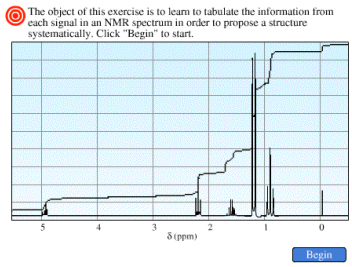

the rate of chair–chair conversion is temperature dependent

*NMR is "slow"*

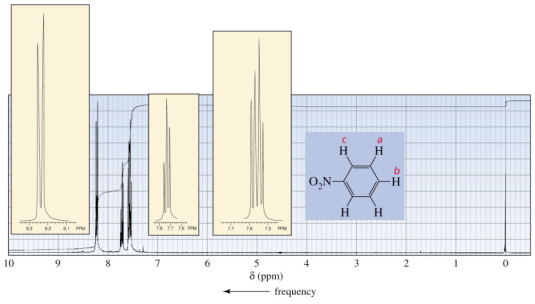
Most conformational changes occur faster than NMR can detect them.

An NMR spectrum is the weighted average of the conformations.

For example: Cyclohexane gives a single peak for its H atoms in NMR. Half of the time a single proton is axial and half of the time it is equatorial. The observed chemical shift is half way between the axial chemical shift and the equatorial chemical shift.




The signals for the $H_a$, $H_b$, and $H_c$ protons do not overlap



The signals for the $H_c$, $H_d$, and $H_e$ protons overlap