Interpreting ^1H (Proton) NMR Spectra

Information contained in an NMR spectrum includes:

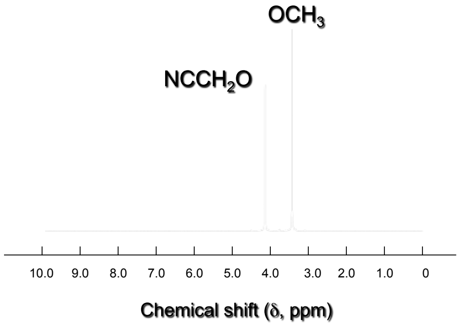
1. number of signals
2. their intensity (as measured by area under peak)
3. splitting pattern (multiplicity)

Number of Signals

protons that have different chemical shifts are chemically nonequivalent, that is,

exist in different molecular environments

NMR $N{\equiv}CCH_2OCH_3$

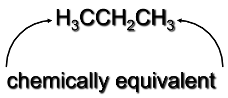


Chemically equivalent protons ("homotopic")

are in identical environments

have same chemical shift

replacement test: replace Hs with an arbitrary "test group" ➔ generates the same compound

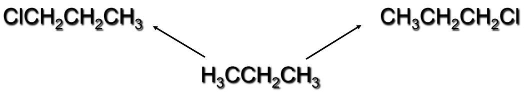

$H_3CCH_2CH_3$

chemically equivalent

Chemically equivalent protons ("homotopic")

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


$ClCH_2CH_2CH_3$ $CH_3CH_2CH_2Cl$

$H_3CCH_2CH_3$

chemically equivalent

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

Corollary: protons are equivalent if there is an axis of rotational symmetry that allows one proton to be rotated onto the other without changing the molecule.

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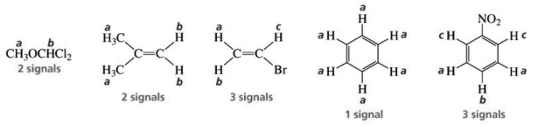

Question

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

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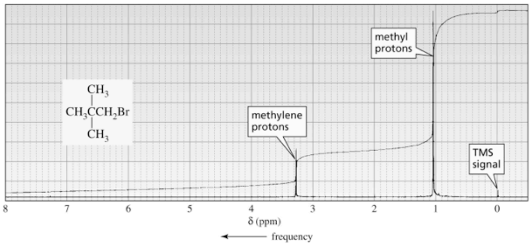
^{1}H NMR spectrum of 1-bromo-2,2-dimethylpropane



Question

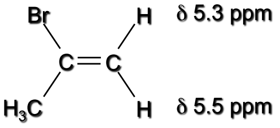
- How many proton signals would you expect to find in the ^{1}H-NMR spectrum of 2-chloropentane?
- A) 2
- B) 3
- C) 4
- D) 5
- E) More than 5

Diastereotopic protons

Consider ***two geminal protons*** (a "***methylene***" group):

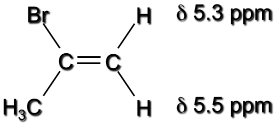
replacement by some arbitrary test group generates diastereomers: non-superimposable, non-mirror images; eg. multiple chiral carbon atoms

diastereotopic protons have different chemical shifts



Diastereotopic protons

Corollary: diastereotopic protons do not have an axis of rotational symmetry nor a plane of symmetry.



Enantiotopic protons

Consider ***two geminal protons*** (a "***methylene***" group).

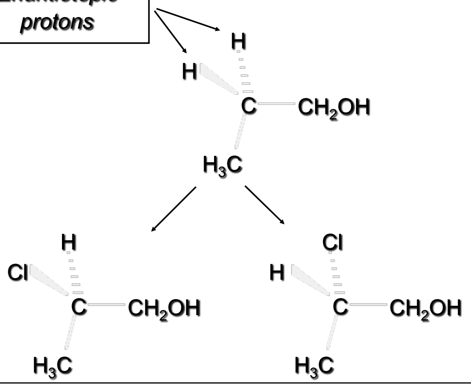
They are enantiotopic if they:

in replacement by some arbitrary test group generate enantiomers.

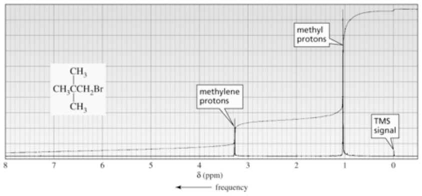
are mirror-images (have a plane of symmetry).

Enantiotopic protons have the same chemical shift.

Enantiotopic protons



Enantiotopic protons



If the methylene protons are replaced by some arbitrary test group, enantiomers are generated.

There is a molecular plane of symmetry, mirroring the methylene protons, which produces only one signal.

Chiral Protons & Racemic Mixtures

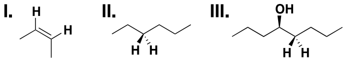
Consider ***a single proton*** bonded to a chiral carbon atom.

A proton bonded to a chiral carbon with an absolute R-configuration has the same chemical shift as one bonded in the S- isomer, which follows the pattern seen in all enantiomers, i.e. they only differ in their rotation of a beam of polarized light.

Chiral protons have the same chemical shift and produce only one signal whether in a racemic mixture or as a pure stereoisomer.

Question

Indicate if the two protons in the following are chemically equivalent (homotopic), enantiotopic or diastereotopic.



A. Diastereotopic
B. Enantiotopic
C. Chemically equivalent (homotopic)

A. I = A; II = B; III = C
B. I = A; II = C; III = B
C. I = B; II = A; III = C
D. I = B; II = C; III = A
E. I = C; II = B; III = A

Question

How many proton signals would you expect to find in the ^{1}H-NMR spectrum of the following compound?

$CH_3CH_2CH_2CH_2CH_2Cl$

- A) 4
- B) 5
- C) 6
- D) 7
- E) 8

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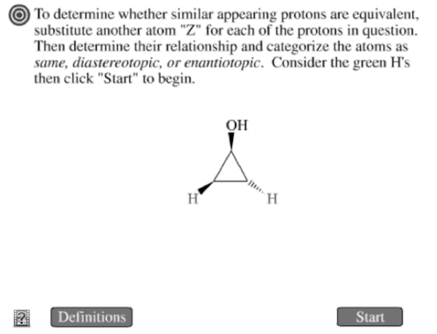
http://chemconnections.org/organic/Movies%20Org%20Flash/nmr-chem-equivalence-Flash/W13_06v3.swf



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.

Question

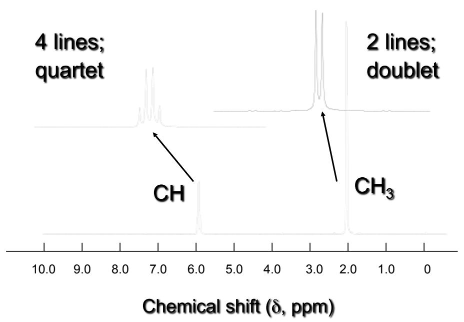
- How many proton signals would you expect to possibly find in the ^{1}H-NMR spectrum of 2-chloropentane?
- A) 6
- B) 7
- C) 8
- D) 9
- E) More than 9

Spin-Spin Splitting in NMR Spectroscopy

not all peaks are singlets

signals can be split by coupling of nuclear spins

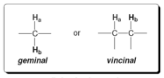
NMR **Cl_2CHCH_3**



Two-bond and three-bond coupling

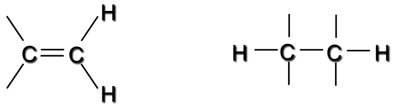
protons separated by two bonds (geminal relationship)

protons separated by three bonds (vicinal relationship)



splitting is observed

Two-bond and three-bond coupling



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

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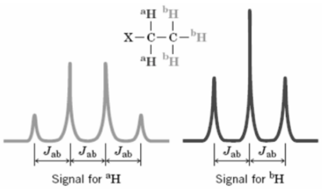
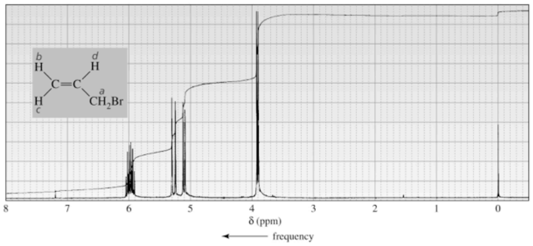
Multiplicity / Coupling

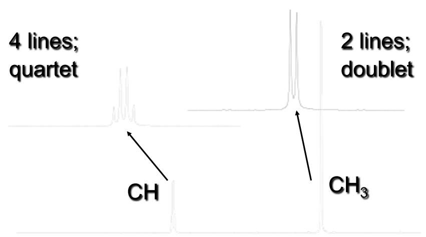
- The degree to which a neighboring proton will shield or deshield its neighbor is called a COUPLING CONSTANT.



  - The coupling constant or ***J* value** is the distance between peaks of a splitting pattern measured in units of Hz.
  - When protons split each other, their coupling constants will be equal.
  - $J_{ab} = J_{ba}$



NMR Cl_2CHCH_3

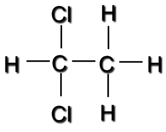


coupled protons are vicinal (three-bond coupling)

CH splits CH_3 into a doublet

CH_3 splits CH into a quartet

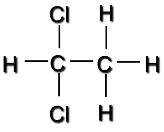
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



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

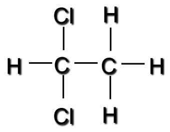
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



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.

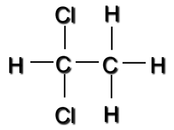
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?

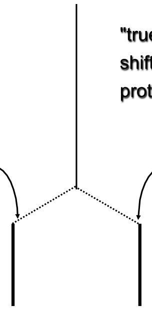


signal for methyl protons is split into a doublet

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

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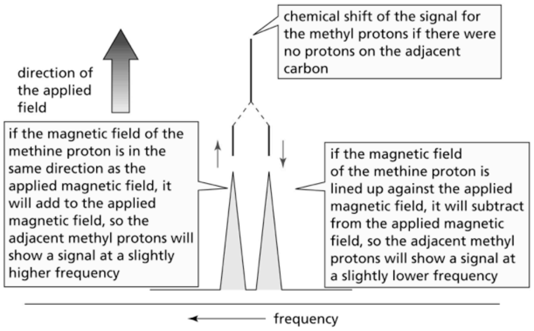

chemical shift of the signal for the methyl protons if there were no protons on the adjacent carbon

direction of the applied field

if the magnetic field of the methine proton is in the same direction as the applied magnetic field, it will add to the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly higher frequency

if the magnetic field of the methine proton is lined up against the applied magnetic field, it will subtract from the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly lower frequency

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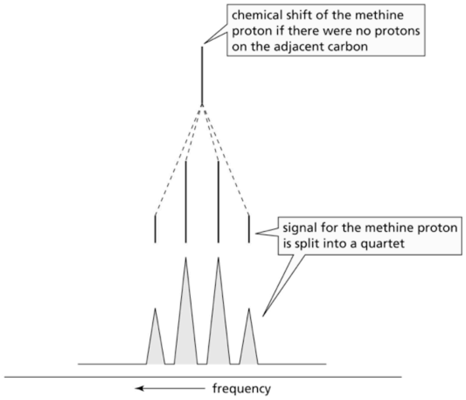
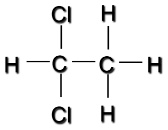


chemical shift of the methine proton if there were no protons on the adjacent carbon

signal for the methine proton is split into a quartet

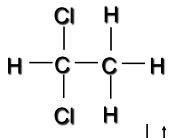
Why does the methine proton of 1,1-dichloroethane appear as a quartet?

signal for methine proton is split into a quartet



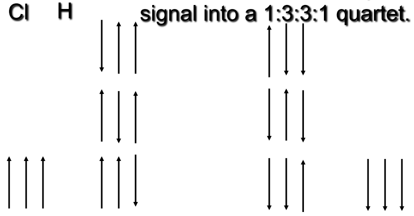
The proton at C-1 "feels" the effect of the applied magnetic field and the local fields resulting from the spin states of the three methyl protons. The possible combinations are shown on the next slide.

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.



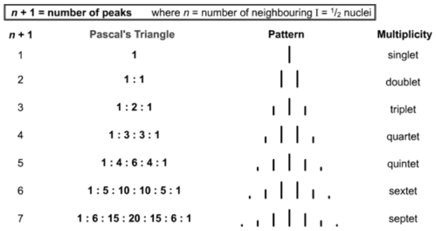
The splitting rule for ^{1}H NMR

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

Commonly known as the n + 1 rule.

Splitting Patterns of Common Multiplets

of equivalent coupled protons   Intensities of lines   Appearance



***n* + 1 = number of peaks**   where *n* = number of neighbouring I = $^1/_2$ nuclei

n	*n* + 1	Pascal's Triangle	Pattern	Multiplicity
0	1	1	ǀ	singlet
1	2	1 : 1	ǀ ǀ	doublet
2	3	1 : 2 : 1	ǀ ǀ ǀ	triplet
3	4	1 : 3 : 3 : 1	ǀ ǀ ǀ ǀ	quartet
4	5	1 : 4 : 6 : 4 : 1	ǀ ǀ ǀ ǀ ǀ	quintet
5	6	1 : 5 : 10 : 10 : 5 : 1	ǀ ǀ ǀ ǀ ǀ ǀ	sextet
6	7	1 : 6 : 15 : 20 : 15 : 6 : 1	ǀ ǀ ǀ ǀ ǀ ǀ ǀ	septet

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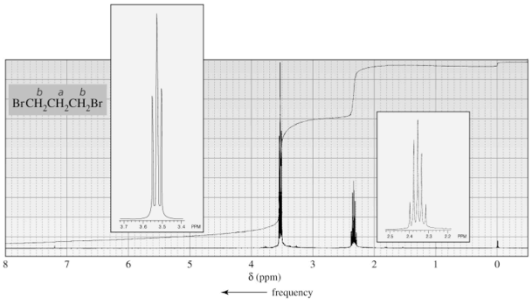
^{1}H NMR Splitting



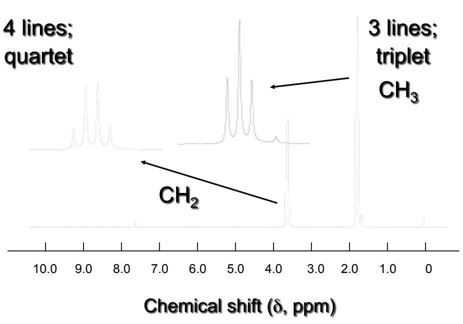
Question

- 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)

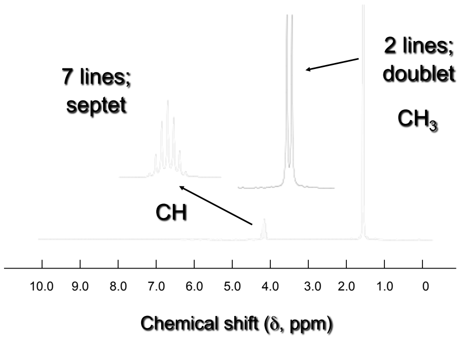
NMR **$BrCH_2CH_3$**



Splitting Patterns:
The Isopropyl Group

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

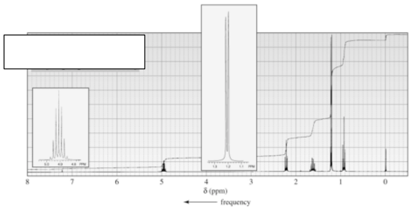
NMR $BrCH(CH_3)_2$



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



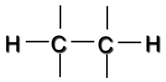
Which compound is the most reasonable for the NMR spectrum above?

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".

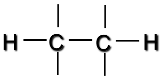
Pairs of Doublets



Consider coupling between two vicinal protons.

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

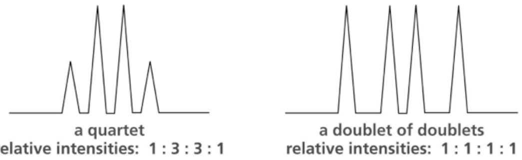
Pairs of Doublets



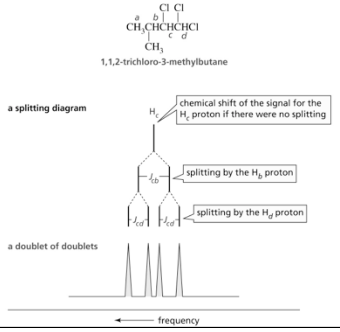
Let $\Delta\nu$ be the difference in chemical shift in Hz between the two hydrogens.

Let J be the coupling constant between them in Hz.

The Difference between a Quartet and a Doublet of Doublets

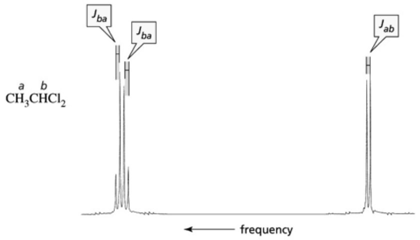


A Splitting Diagram for a Doublet of Doublets



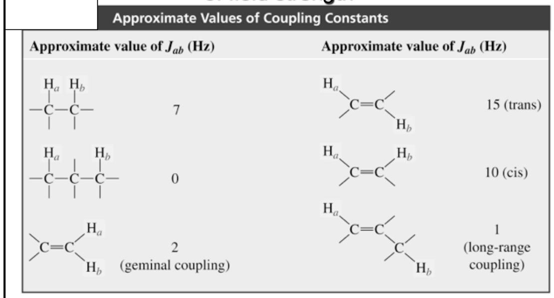
Coupling Constants

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

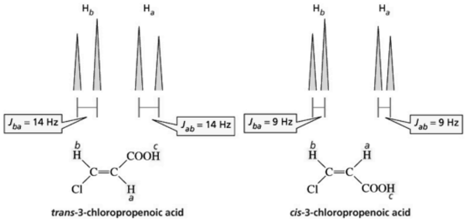
Coupling constants (^2J or ^3J) are independent of field strength



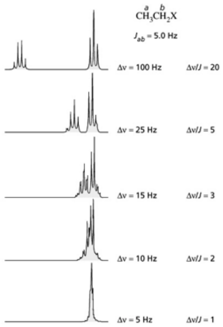
Approximate Values of Coupling Constants

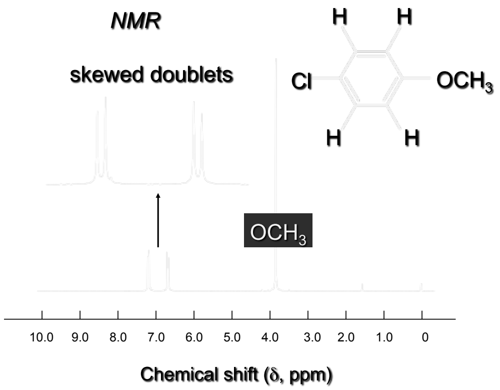
Approximate value of J_{ab} (Hz)		Approximate value of J_{ab} (Hz)	
	7		15 (trans)
	0		10 (cis)
	2 (geminal coupling)		1 (long-range coupling)

A trans coupling constant is greater than a cis coupling constant



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

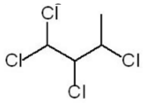




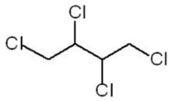
Question

- 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 spe

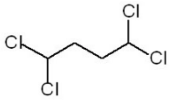
- A)



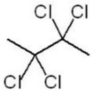
B)



- C)



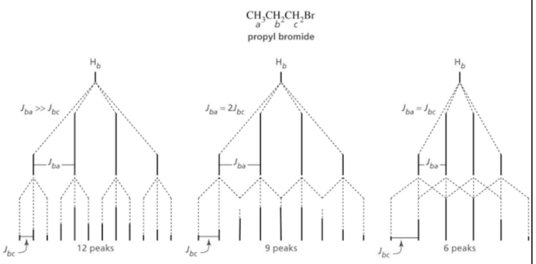
D)



Complex Splitting Patterns

Multiplets of multiplets
aka “Mess-plets” *
* Dr. L. Burns

A Splitting Diagram for a Quartet of Triplets



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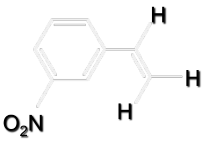
m-Nitrostyrene

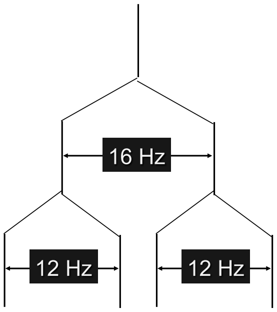


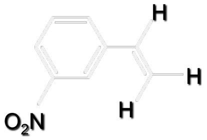
Consider the proton shown in red.

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

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

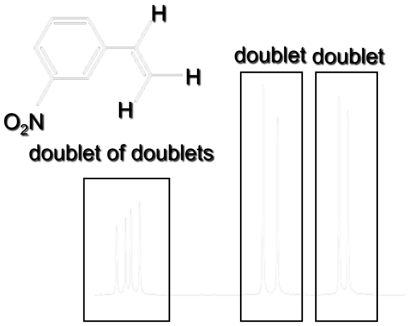
m-Nitrostyrene





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

Figure



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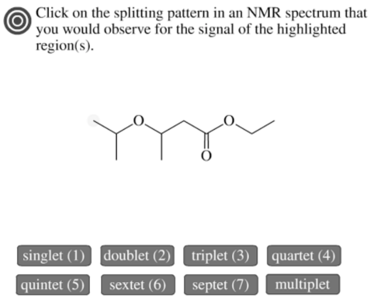
http://chemconnections.org/organic/Movies%20Org%20Flash/nmr-splitting.swf



Click on the splitting pattern in an NMR spectrum that you would observe for the signal of the highlighted region(s).

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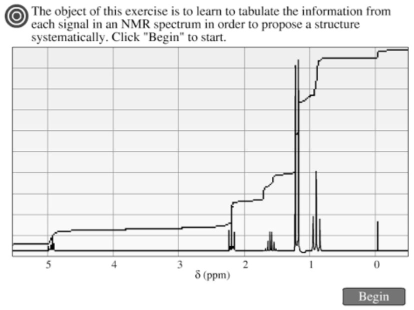
http://chemconnections.org/organic/Movies%20Org%20Flash/nmr-1H-spectra-interpret/AACFLFR0.swf



The object of this exercise is to learn to tabulate the information from each signal in an NMR spectrum in order to propose a structure systematically. Click "Begin" to start.

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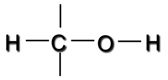
^{1}H NMR Spectra of Alcohols & Amines

H- bonded to O and N

O—H



$H-C-O-H$

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

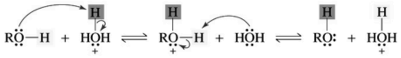
Splitting of the O—H proton is sometimes observed, but **often is not**. *It usually appears as a broad peak.*

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.

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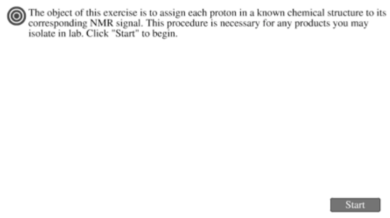
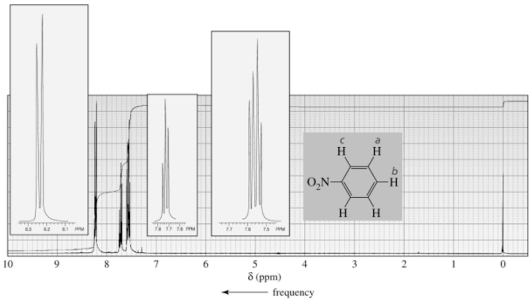
http://chemconnections.org/organic/Movies%20Org%20Flash/nmr-peak-assignments.swf

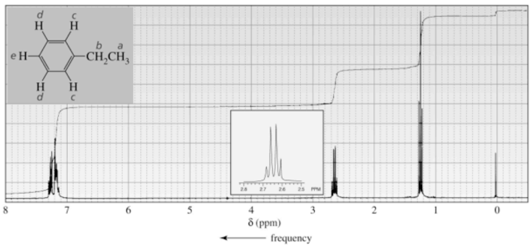


The object of this exercise is to assign each proton in a known chemical structure to its corresponding NMR signal. This procedure is necessary for any products you may isolate in lab. Click "Start" to begin.

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

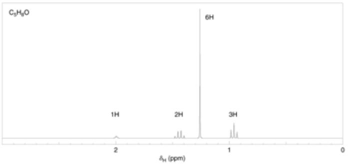


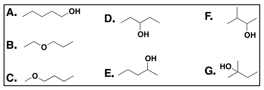
The signals for the H_c, H_d, and H_e protons overlap



Question

Which compound corresponds to the 1H NMR spectrum below?

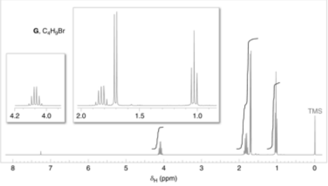




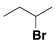
A. A
B. D
C. E
D. F
E. G

Question

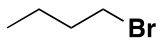
Which compound corresponds to the 1H NMR spectrum below?



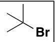
A.



B.



C.



D.