

Applied Spectroscopy

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References

- 1: Introduction to spectroscopy; 3rd, 4th and 5th edition, Donald L. Pavia
- 2: Elementary Organic Spectroscopy; Y.R. Sharma
- 3: Spectroscopic Identification of Organic Compounds
7th edition, Robert M. Silverstein
- 4: Organic Structures From Spectra; 4th edition, L. D. Field
- 5: Mass spectrometry; 2nd edition, Jurgen H. Gross
- 6: Organic Chemistry 4th edition, Paula Bruice

Coupling Constants

The distance, in hertz, between two adjacent peaks of a split NMR signal is called the coupling constant (denoted by J). The coupling constant for H_a being split by H_b is denoted by J_{ab} . $J_{ab}=J_{ba}$. Coupling constants are useful in analyzing complex NMR spectra because protons on adjacent carbons can be identified by identical coupling constants.

The simple triplet and quintet is easy to read J values, because can calculate J from the shift difference between any adjacent peak in the multiplet.

$\Delta\delta = 0.006$ ppm



$$\begin{aligned} J &= (\Delta\delta)(\nu_{\text{Larmor}}) \\ &= (0.006 \text{ ppm})(270 \text{ MHz}) \\ &= \mathbf{1.6 \text{ Hz}} \end{aligned}$$

(or, you could also say
 $J_1 = J_2 = 1.6 \text{ Hz}$)

$\Delta\delta = 0.022$ ppm

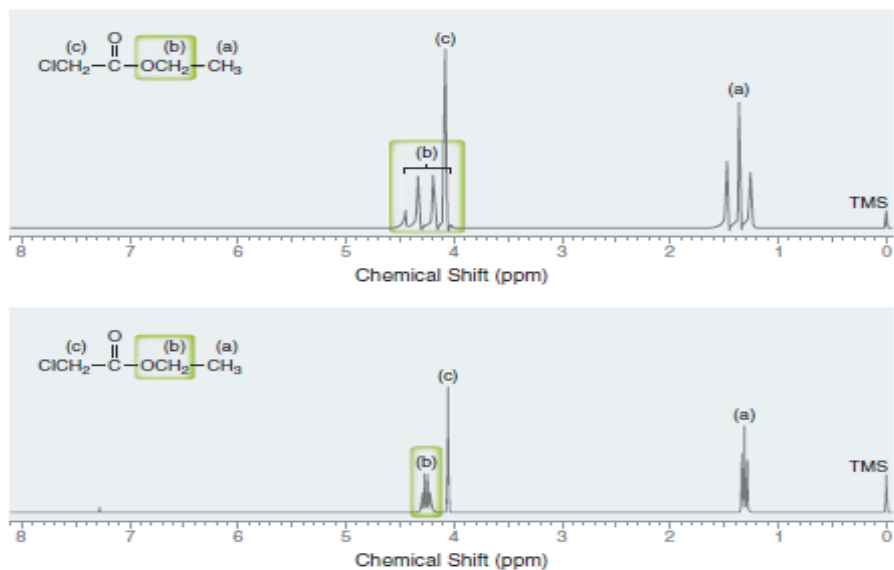


$$\begin{aligned} J &= (\Delta\delta)(\nu_{\text{Larmor}}) \\ &= (0.022 \text{ ppm})(270 \text{ MHz}) \\ &= \mathbf{5.9 \text{ Hz}} \end{aligned}$$

(or, you could also say
 $J_1 = J_2 = J_3 = J_4 = 5.9 \text{ Hz}$)

The magnitude of a coupling constant is independent of the operating frequency of the spectrometer—the same coupling constant is obtained from a 300-MHz instrument as from a 600-MHz instrument. The magnitude of a coupling constant is a measure of how strongly the nuclear spins of the coupled protons influence each other. It, therefore, depends on the **number** and **type of bonds** that connect the coupled protons, as well as the **geometric** relationship of the protons. As a result, NMR spectrometers with higher

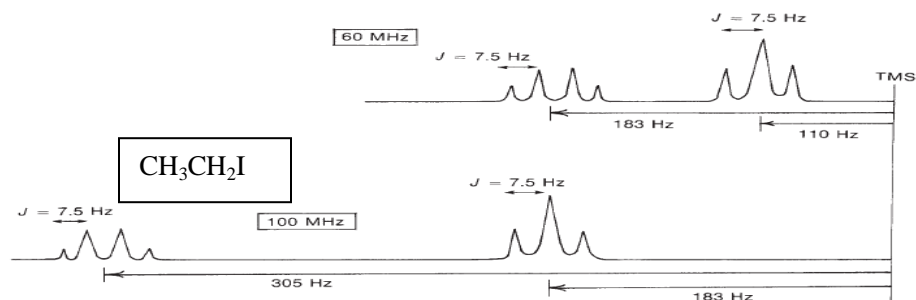
operating frequencies produce spectra in which different signals are less likely to overlap. As an example, compare the two spectra of ethyl chloroacetate as shown:



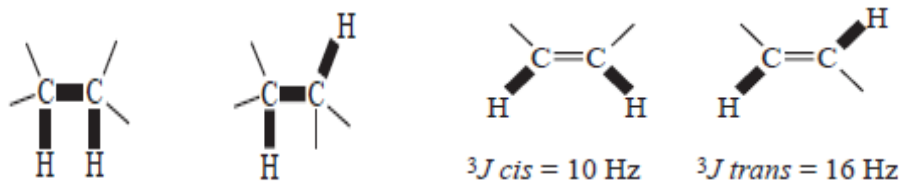
The 60-MHz ^1H NMR spectrum (top) of ethyl chloroacetate and the 300-MHz ^1H NMR spectrum (bottom) of ethyl chloroacetate. The 300-MHz spectrum avoids overlapping signals.

In each spectrum, the coupling constant (J_{ab}) is approximately 7 Hz. The coupling constant only appears to be larger in the 60-MHz ^1H NMR spectrum, because each ppm corresponds with 60 Hz. The distance between each peak (7 Hz) is more than 10% of a ppm. In contrast, the coupling constant appears much smaller in the 300-MHz ^1H NMR spectrum, because each ppm corresponds with 300 Hz, and as a result, the distance between each peak (7 Hz) is only 2% of a ppm. This example illustrates why spectrometers with higher operating frequencies avoid overlapping signals.

The chemical shift in Hertz for the CH_3 and CH_2 protons is much larger in the 100-MHz than 60 MHz spectrum, while identical in (ppm). Despite the expansion of the spectrum determined at the higher spectrometer frequency, careful examination of the spectra indicates that the coupling constant between the CH_3 and CH_2 protons is 7.5 Hz in both spectra.



For the interaction of most aliphatic protons in non-cyclic systems, the magnitudes of coupling constants are always near 7.5 Hz. Compare, for example, 1,1,2-trichloroethane for which $J = 6$ Hz, and 2-nitropropane for which $J = 7$ Hz. These coupling constants are typical for the interaction of two hydrogens on adjacent sp^3 -hybridized carbon atoms. Two hydrogen atoms on adjacent carbon atoms can be described as a three-bond interaction and abbreviated as 3J . Typical values for this most commonly observed coupling is approximately 6 to 8 Hz. The bold lines in the diagram show how the hydrogen atoms are three bonds away from each other.



Coupling constants on modern FT-NMR spectrometers are more easily determined by printing Hertz values directly on the peaks. It is a simple matter of subtracting these values to determine the coupling constants in Hertz.

There are various types of coupling constants associated with two-bond (2J), three-bond (3J), four-bond (4J) and five-bond (5J) interactions.

In alkenes, the 3J coupling constants for hydrogen atoms that are *cis* to each other have values near 10 Hz, while the 3J coupling constants for hydrogen atoms that are *trans* are larger, 16 Hz. A study of the magnitude of the coupling constant can give important structural information.

Coupling constants can be used to distinguish between the spectra of cis and trans alkenes. The coupling constant of trans-vinylic protons is significantly greater than the coupling constant of cis-vinylic protons, because the coupling constant depends on the dihedral angle between the two C-H bonds in the (H-C=C-H) unit. The coupling constant is greatest when the angle between the two C-H bonds is 180° (trans) and smaller when it is 0° (cis).

See pages (142-162) in Pavia fifth editions to get coupling constants of all types of compounds.

***J* is a constant.** Coupling between two nuclei of the same type is called **homonuclear coupling**. The homonuclear three-bond couplings 3J between hydrogens on adjacent carbon atoms (vicinal coupling), which gave multiplets governed by the $n + 1$ Rule.

Coupling between two different types of nuclei is called **heteronuclear coupling**. The couplings between ^{13}C and attached hydrogens are one-bond heteronuclear coupling.

The magnitude of the coupling constant depends to a large extent on the number of bonds intervening between the two atoms or groups of atoms that interact, in general, one-bond couplings are larger than two-bond couplings, which in turn are larger than three-bond couplings, and so forth. Consequently, coupling constant represent information about the type of atoms involved and the number of bonds through which the coupling constant operates.

Types of (*J*-value):

A. One-Bond Couplings (1J) Complex Splitting

A one-bond coupling occurs when a single bond links two spin-active nuclei such as:








SOME ONE-BOND COUPLING CONSTANTS (1J)

$^{13}\text{C}-^1\text{H}$	110–270 Hz sp^3 115–125 Hz (ethane = 125 Hz) sp^2 150–170 Hz (ethene = 156 Hz) sp 240–270 Hz (ethyne = 249 Hz)
$^{13}\text{C}-^{19}\text{F}$	-165 to -370 Hz
$^{13}\text{C}-^{31}\text{P}$	48–56 Hz
$^{13}\text{C}-\text{D}$	20–30 Hz
$^{31}\text{P}-^1\text{H}$	190–700 Hz

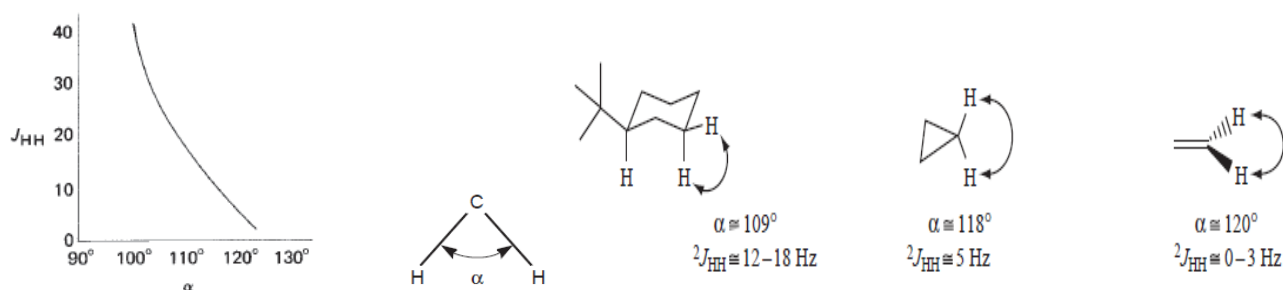
B. Two-Bond Couplings (2J)

Two-bond couplings are quite common in NMR spectra. They are usually called **geminal couplings**. Two-bond coupling constants are typically, although not always, smaller in magnitude than one-bond couplings

SOME TWO-BOND COUPLING CONSTANTS (2J)

 -9 to -15 Hz	 ~50 Hz ³
 0 to 2 Hz	 ~5 Hz ³
 ~2 Hz ³	 7–14 Hz ³
 ~160 Hz ³	

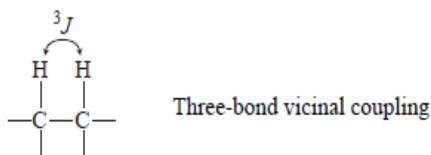
The amount of geminal coupling depends on the H-C-H angle (α). In general, 2J geminal coupling constants increase as the angle (α) decreases.



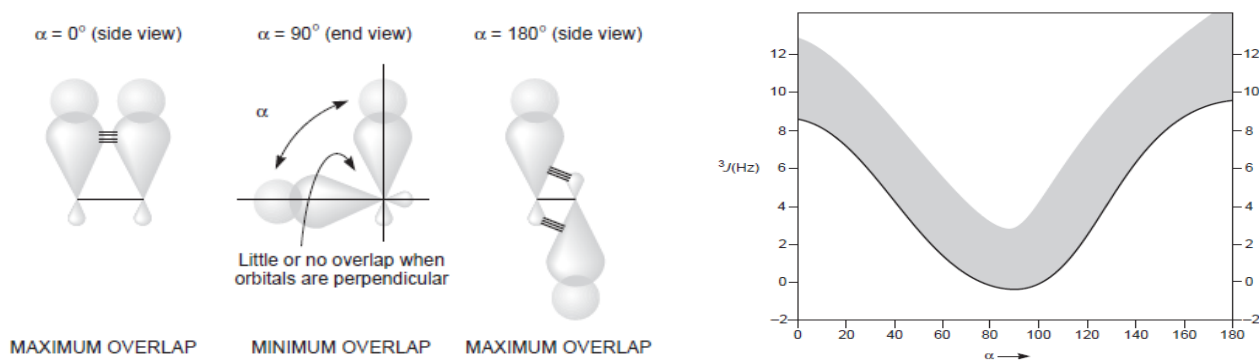
C. Three-Bond Couplings (3J)

In a typical hydrocarbon, the spin of a hydrogen nucleus in one C-H bond is coupled to the spins of those hydrogens in adjacent C-H bonds. These H-C-C-H couplings are usually called **vicinal couplings**. 3J .

In these couplings produce spin-spin splitting patterns that follow the $n + 1$ Rule in simple aliphatic hydrocarbon chains.



The actual magnitude of the coupling constant between two adjacent C-H bonds can be shown to depend directly on the dihedral angle (α) between these two bonds. Figure below defines the dihedral angle (α) as a perspective drawing and a Newman diagram. The magnitude of the splitting between H_A and H_B is greatest when (α) = 0° or 180° and is smallest when (α) = 90° . The side-to-side overlap of the two C-H bond orbitals is at a maximum at 0° , where the C-H bond orbitals are parallel, and at a minimum at 90° , where they are perpendicular. At (α) = 180° , overlap with the **back lobes** of the sp^3 orbitals occurs

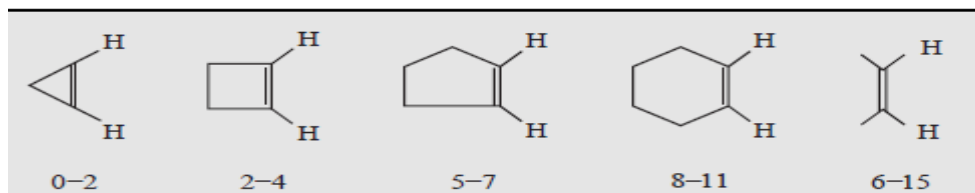


The Karplus relationship—the approximate variation of the coupling constant 3J with the dihedral angle (α).

SOME THREE-BOND COUPLING CONSTANTS ($^3J_{XY}$)

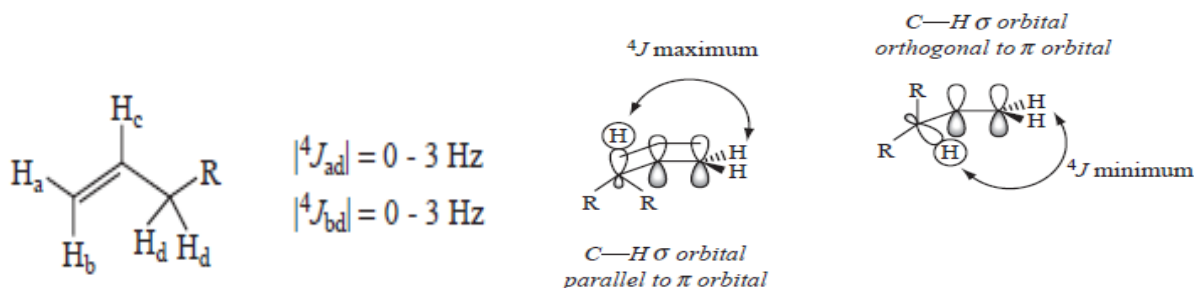
H—C—C—H	6–8 Hz	H—C=C—H	<i>cis</i>	6–15 Hz
			<i>trans</i>	11–18 Hz
^{13}C —C—C—H	5 Hz	H—C=C— ^{19}F	<i>cis</i>	18 Hz
			<i>trans</i>	40 Hz
^{19}F —C—C—H	5–20 Hz	^{19}F —C=C— ^{19}F	<i>cis</i>	30–40 Hz
			<i>trans</i>	–120 Hz
^{19}F —C—C— ^{19}F	–3 to –20			
^{31}P —C—C—H	13 Hz			
^{31}P —O—C—H	5–15 Hz			

VARIATION OF $^3J_{\text{HH}}$ WITH VALENCE ANGLES IN CYCLIC ALKENES (Hz)



D. Long-Range Couplings (4J – nJ)

Only under special circumstances coupling occur between protons that are separated by four or more covalent bonds, and these are collectively referred to as **long-range couplings**. Long-range couplings are common in allylic systems, aromatic rings, and rigid bicyclic systems. Long-range couplings are communicated through specific overlap of a series of orbitals and as a result have a stereochemical requirement. In alkenes, small couplings between the alkenyl hydrogens and protons on the carbon(s) α to the opposite end of the double bond are observed:



Aromatic compounds

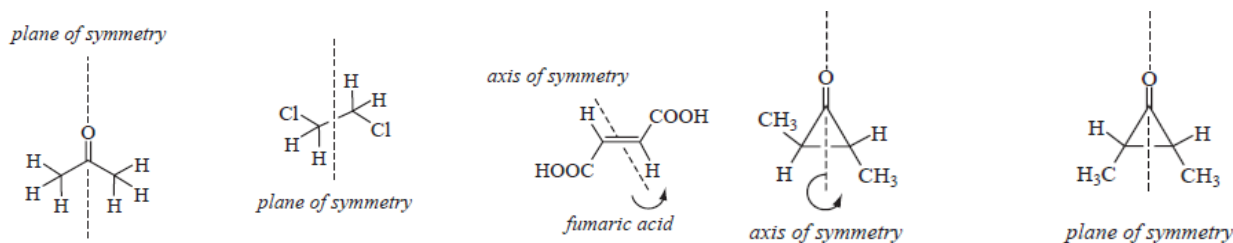
$^3J_{\text{ortho}} \approx 7\text{--}10 \text{ Hz}$, $^4J_{\text{meta}} \approx 2\text{--}3 \text{ Hz}$, $^5J_{\text{para}} \approx 0\text{--}1 \text{ Hz}$

In the splitting patterns for the protons on a benzene ring, it is often possible to determine the positions of the substituents on the ring from these splitting patterns and the magnitudes of the coupling constants.

MAGNETIC EQUIVALENCE

If a plane of symmetry or an axis of symmetry renders two or more nuclei equivalent by symmetry, they are said to be **chemically equivalent**.

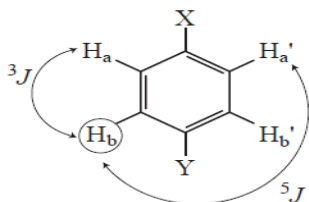
hydrogens appear as a single peak in the ^1H NMR spectrum, and no spin–spin splitting is seen. Such as: Acetone and 1,2-dichloroethane have plane of symmetry. In fumaric acid, there is a twofold axis of symmetry that renders the carbons and hydrogens chemically equivalent. Because of symmetry, the adjacent *trans* vinyl hydrogens in fumaric acid do not show spin–spin splitting, and they appear as a singlet (both hydrogens having the same resonance frequency). The two ring hydrogens and methyl groups in *trans*-2,3-dimethylcyclopropanone (axis of symmetry) are also chemically equivalent, as are the two ring hydrogens and methyl groups in *cis*-2,3-dimethylcyclopropanone (plane of symmetry).



In most cases, chemically equivalent nuclei have the same resonance frequency (chemical shift), do not split each other, and give a single NMR signal. When this happens, the nuclei are said to be **magnetically equivalent** as well as chemically equivalent. However, it is possible for nuclei to be chemically equivalent but magnetically *inequivalent*. As we will show, magnetic equivalence has requirements that are more stringent than those for chemical equivalence. For a group of nuclei to be magnetically equivalent, their magnetic environments, including *all coupling interactions*, must be of identical types. Magnetic equivalence has two strict requirements:

1. Magnetically equivalent nuclei must have identical chemical shifts.
2. Magnetically equivalent nuclei must have equal coupling (same J values) to all other nuclei in the molecule.

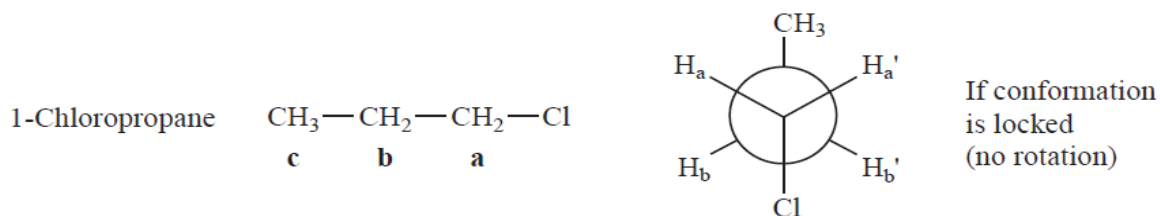
Now, consider a *para*-disubstituted benzene ring, in which the *para* substituents X and Y are not the same. This molecule has a plane of symmetry that renders the hydrogens on opposite sides of the ring chemically equivalent. What about magnetic equivalent? Let us label the chemically equivalent hydrogens H_a and $H_{a'}$ (and H_b and $H_{b'}$). We would expect both H_a and $H_{a'}$ or H_b and $H_{b'}$ to have the same chemical shift, but *their coupling constants to the other nuclei are not the same*. H_a , for instance, does not have the same coupling constant to H_b (three bonds, 3J) as $H_{a'}$ has to H_b (five bonds, 5J). Because H_a and $H_{a'}$ do not have the same coupling constant to H_b , they cannot be magnetically equivalent, even though they are chemically equivalent. This analysis also applies to $H_{a'}$, H_b , and $H_{b'}$, none of which has equivalent couplings to the other hydrogens in the molecule.



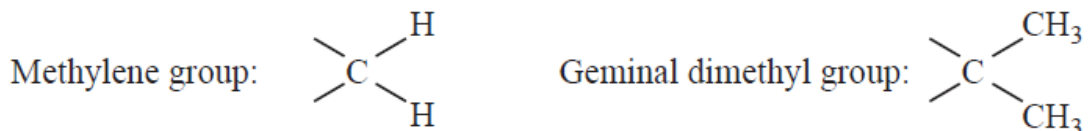
Often, protons that are chemically equivalent are also magnetically equivalent; however, when chemically equivalent protons are *not* magnetically equivalent, there are usually consequences in the appearance of the NMR spectrum. Nuclei that are magnetically equivalent will give “**first-order spectra**” that can be analyzed using the $n + 1$ Rule or a simple “tree diagram”. Nuclei that are not magnetically equivalent sometimes give **second-order spectra**, in which unexpected peaks may appear in multiplets.

Now consider 1-chloropropane. The hydrogens within a group (those on C_1 , C_2 , and C_3) are isochronous, but each group is on a different carbon, and as a result, each *group* of hydrogens has a different chemical shift. The hydrogens in each group experience

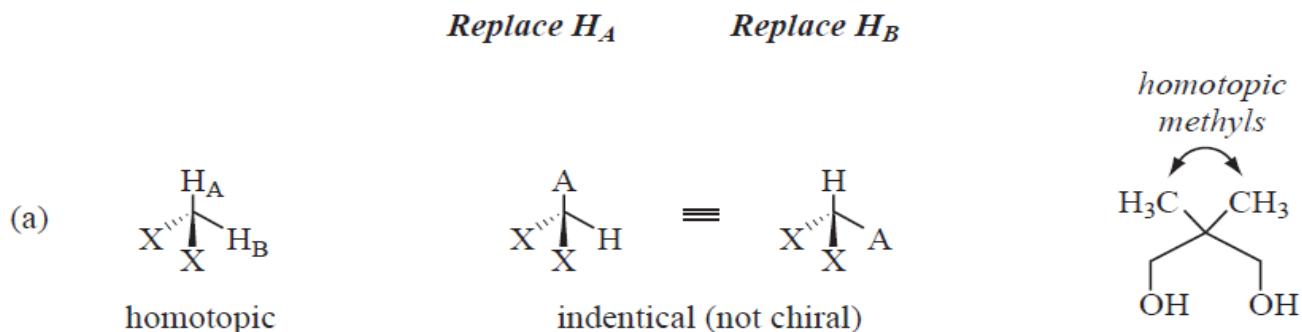
identical *average* magnetic environments, mainly because of free rotation, and are magnetically equivalent. While without free rotation there would be no magnetic equivalence. Because of the fixed unequal dihedral angles ($H_a-C-C-C_b$ versus $H_a-C-C-H_{b'}$), J_{ab} and $J_{ab'}$ would not be the same. Free rotation can be slowed or stopped by lowering the temperature, in which case H_b and $H_{b'}$ would become magnetically inequivalent. This type of magnetic inequivalence is often seen in 1,2-disubstituted ethane groups in which the substituents have sufficient steric bulk to hinder free rotation around the C-C axis enough that it becomes slow on the NMR time-scale.



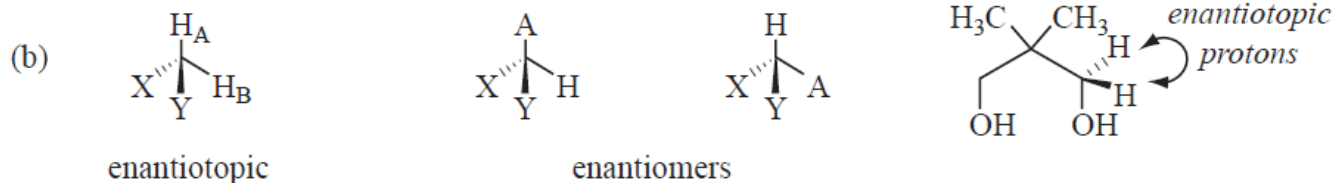
Are the (geminal groups) equivalent or nonequivalent? Methylene groups (geminal protons) and isopropyl groups (geminal methyl groups) are frequently the subjects of interest. It turns out that there are three possible relationships for such geminal groups: They can be **homotopic**, **enantiotopic**, or **diastereotopic**.



Homotopic groups are always equivalent, and in the absence of couplings from another group of nuclei, they are isochronous and give a single NMR absorption. Homotopic groups are interchangeable by rotational symmetry.



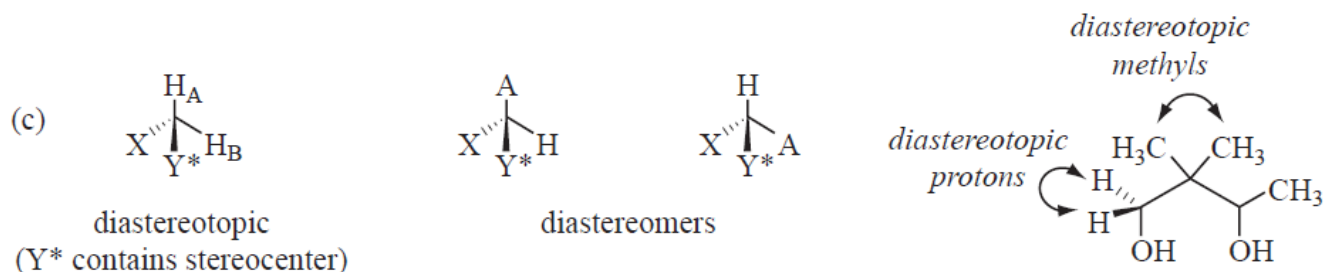
Enantiotopic groups appear to be equivalent, and they are typically isochronous and give a single NMR absorption—except when they are placed in a chiral environment or acted on by a chiral reagent. Enantiotopic groups can also be recognized by the substitution test. The replacement of first H_A and then H_B are *enantiomers*, each hydrogen giving a different enantiomer. Notice that the structure of this enantiotopic molecule is not chiral, but that substituents X and Y are different groups. There is a *plane* of symmetry, but no rotational axis of symmetry. Enantiotopic groups are sometimes called **prochiral** groups. When one or the other of these groups is replaced by a different one, a *chiral* molecule results. The reaction of prochiral molecules with a chiral reagent, such as an enzyme in a biological system, produces a chiral result. If these molecules are placed in a chiral environment, the two groups are no longer equivalent.



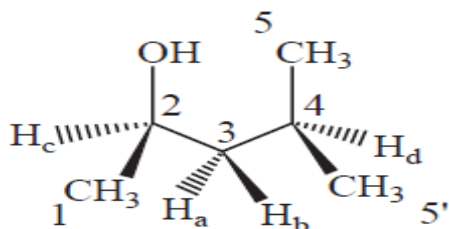
Diastereotopic groups are not equivalent and are not isochronous; they have different chemical shifts in the NMR spectrum. When the diastereotopic groups are hydrogens, they frequently split each other with a geminal coupling constant 2J .

In such molecule, the replacement of first H_A and then H_B yields a pair of *diastereomers*. Diastereomers are produced when substituent Y* already contains an

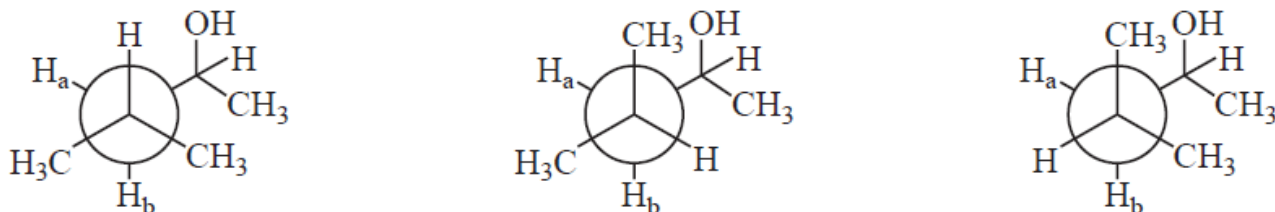
adjacent stereocenter. Diastereotopic groups are also found in prochiral compounds in which the substitution test simultaneously creates two stereogenic centers.



Example: A. Diastereotopic Methyl Groups: 4-Methyl-2-pentanol



This molecule has diastereotopic methyl groups (labeled 5 and 5') on carbon 4. The spectrum shows three methyl peaks because methyl groups (labeled 5 and 5') are diastereotopic and show signals at 23.18 and 22.37 ppm. The two methyl groups have slightly different chemical shifts because of the nearby stereocenter at C-2. The two methyl groups are always nonequivalent in this molecule, even in the presence of free rotation. You can confirm this fact by examining the various fixed, staggered rotational conformations using Newman projections. There are no planes of symmetry in any of these conformations; neither of the methyl groups is ever enantiomeric.

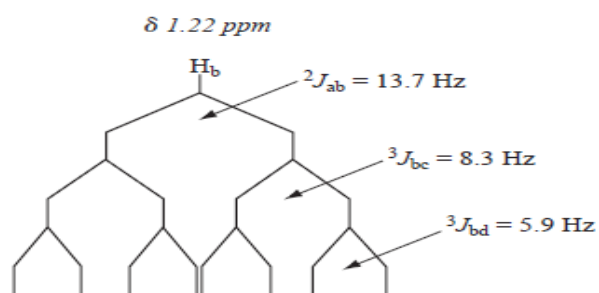
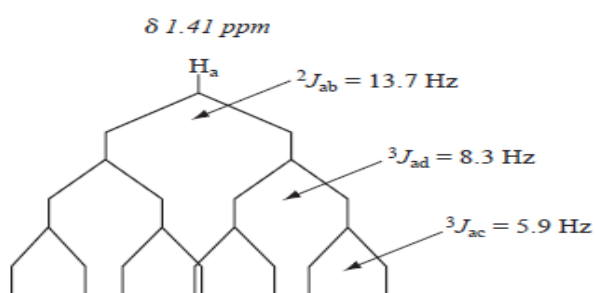
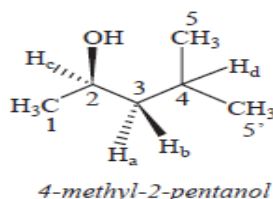


The ^1H proton NMR spectrum is a bit more complicated. The hydrogen atom attached to C-4 splits each methyl group into a doublet. The chemical shift difference between the

methyl protons is very small, however, and the two doublets are partially overlapped. One of the methyl doublets is observed at 0.92 ppm ($J = 6.8$ Hz), and the other diastereotopic methyl doublet is seen at 0.91 ppm ($J = 6.8$ Hz). The C-1 methyl group is also a doublet at 1.18 ppm, split by the hydrogen on C-2 ($J = 5.9$ Hz).

B. Diastereotopic Hydrogens: 4-Methyl-2-pentanol:

A pair of hydrogens located on a carbon atom adjacent to a stereocenter is expected to be diastereotopic. In some compounds expected to have diastereotopic hydrogens, the difference between the chemical shifts of the diastereotopic geminal hydrogens H_A and H_B is so small that neither this difference nor any coupling between H_A and H_B is easily detectable. In this case, the two protons act as a single group. In many other compounds, however, the chemical shifts of H_A and H_B are quite different, and they split each other ($^2J_{AB}$) into doublets. If there are other adjacent protons, large differences in the magnitude of the vicinal coupling constants are seen as well due to unequal populations of conformers arising from differential steric and torsional strain.

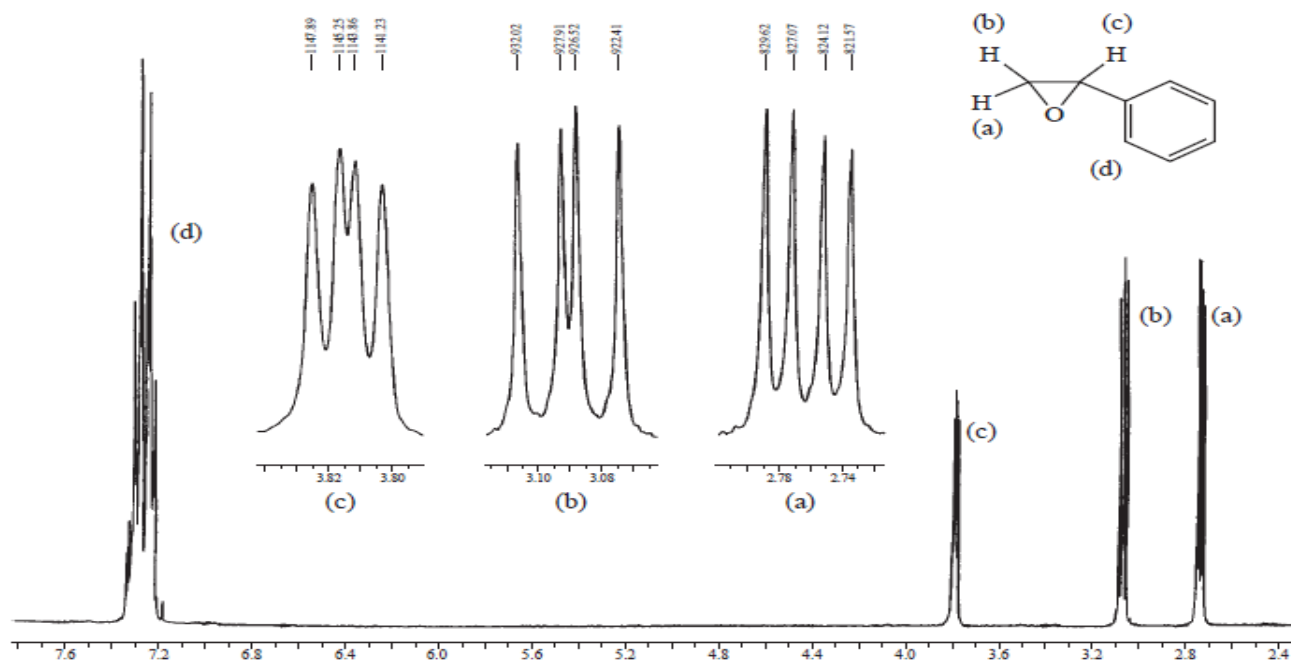


Splitting diagrams for the diastereotopic methylene protons in 4-methyl-2-pentanol.

The geminal coupling constant ${}^2J_{ab} = 13.7$ Hz, which is a typical value for diastereotopic geminal coupling in acyclic aliphatic systems. The coupling constant ${}^3J_{bc}$ (8.3 Hz) is somewhat larger than ${}^3J_{ac}$ (5.9 Hz), which is in agreement with the average dihedral angles predicted from the relevant conformations and the Karplus relationship. The hydrogen on C-2, H_c, is coupled not only to H_a and H_b but also to the C₋₁ methyl group, with ${}^3J(\text{H}_c\text{C}-\text{CH}_3) = 5.9$ Hz. Because of the more complex splitting of H_c, a splitting analysis tree is not shown for this proton. Similarly, the hydrogen on C₋₄ has a complex splitting pattern due to coupling to both H_a and H_b as well as the two sets of diastereotopic methyl protons on C₋₅ and C_{-5'}.

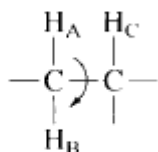
***NONEQUIVALENCE WITHIN A GROUP—THE USE OF TREE DIAGRAMS
WHEN THE $n + 1$ RULE FAILS:**

When the protons attached to a single carbon are chemically equivalent (have the same chemical shift), the $n + 1$ Rule successfully predicts the splitting patterns. In contrast, when the protons attached to a single carbon are chemically nonequivalent (have different chemical shifts), the $n + 1$ Rule no longer applies. We shall examine two cases, one in which the $n + 1$ Rule applies (1,1,2-trichloroethane) and one in which it fails (styrene oxide). In case one due to free rotation around the C-C bond, the methylene protons each experience the same averaged environment, are isochronous (have the same chemical shift), and do not split each other. As a result, they behave as a group, and germinal coupling between them does not lead to any splitting. The $n + 1$ Rule correctly applied. While the ${}^1\text{H}$ spectrum of styrene oxide, shows how chemical nonequivalence complicates the spectrum.



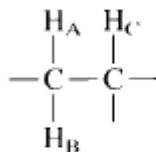
The three-membered ring prevents rotation, causing protons H_A and H_B to have different chemical shift values; they are chemically and magnetically inequivalent. Hydrogen H_A is on the same side of the ring as the phenyl group; hydrogen H_B is on the opposite side of the ring. These hydrogens have different chemical shift values, $H_A = 2.75$ ppm and $H_B = 3.09$ ppm, and they show geminal splitting with respect to each other. The third proton, H_C , appears at 3.81 ppm and is coupled *differently* to H_A (which is *trans*) than to H_B (which is *cis*). Because H_A and H_B are nonequivalent and because H_C is coupled differently to H_A than to H_B (${}^3J_{AC} \neq {}^3J_{BC}$), the $n + 1$ Rule fails, and the spectrum of styrene oxide becomes more complicated. To explain the spectrum, one must examine each hydrogen individually and take into account its coupling with every other hydrogen independent of the others.

(a) Free rotation
The $n + 1$ rule applies



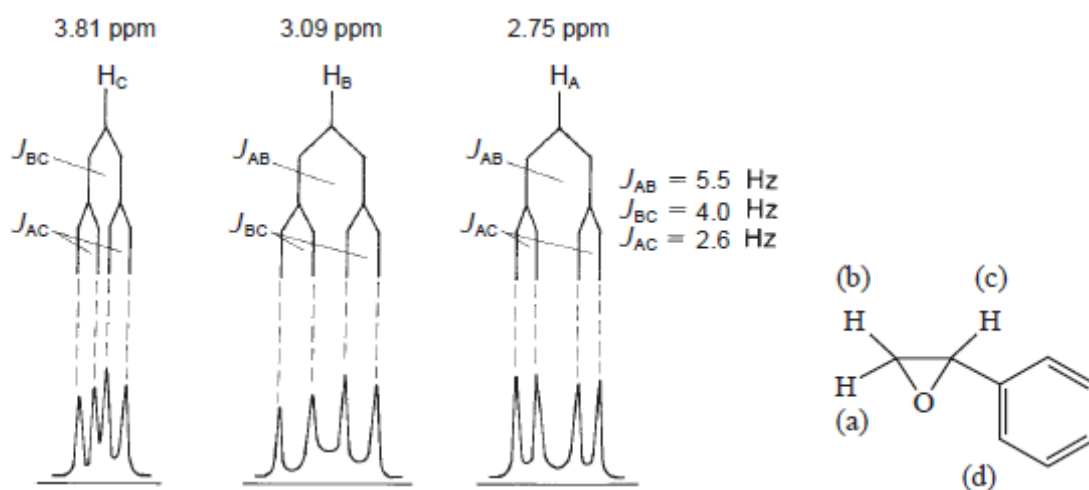
$$\begin{aligned} \delta_A &= \delta_B \\ J_{AC} &= J_{BC} \\ J_{AB} &= 0 \end{aligned}$$

(b) Biased conformation
A tree diagram is required



$$\begin{aligned} \delta_A &\neq \delta_B \\ J_{AC} &\neq J_{BC} \\ J_{AB} &\neq 0 \end{aligned}$$

In the nonequivalence within a group the $n + 1$ Rule Fails must use the Tree Diagrams for spectral analysis. As follows:



An analysis of the splitting pattern in styrene oxide.

MEASURING COUPLING CONSTANTS FROM FIRST-ORDER SPECTRA

The methods given here apply to first-order spectra. What does ‘first-order’ mean, as applied to NMR spectra? For a spectrum to be first-order, the frequency difference ($\Delta\nu$, in Hz) between any two coupled resonances must be significantly larger than the coupling constant that relates them. A first-order spectrum has $\Delta\nu/J > \sim 6.3$.

A. Simple Multiplets—One Value of J (One Coupling):

For simple multiplets, where only one value of J is involved (one coupling), there is little difficulty in measuring the coupling constant. In this case it is a simple matter of determining the spacing (in Hertz) between the successive peaks in the multiplet.

Before we consider multiplets with more than one distinct coupling relationship, it is helpful to review simple multiplets, those adequately described by the $n + 1$ Rule, and begin to consider them as series of doublets by considering each individual coupling relationship separately. For example, a triplet (t) can be considered a doublet of doublets (dd) where two identical couplings ($n = 2$) are present ($J_1 = J_2$). The sum of the triplet's line intensities (1:2:1) is equal to 2^n where $n = 2$ ($1 + 2 + 1 = 2^2 = 4$).

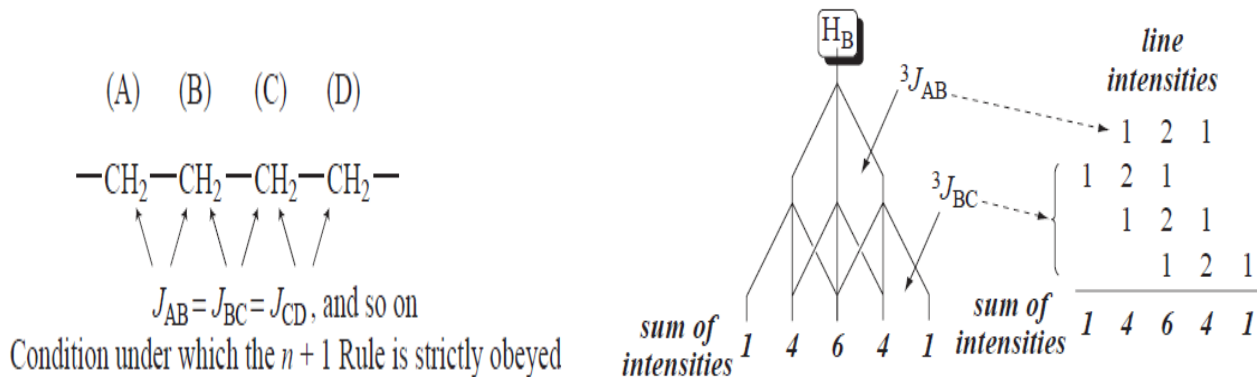
Similarly, a quartet can be considered a doublet of doublet of doublets where three identical couplings ($n = 3$) are present ($J_1 = J_2 = J_3$) and the sum of the quartet's line intensities (1:3:3:1) equals 2^n where $n = 3$ ($1 + 3 + 3 + 1 = 2^3 = 8$). This analysis is continued in this Table.

ANALYSIS OF FIRST-ORDER MULTIPLETS AS SERIES OF DOUBLETS

Number of Identical Couplings	Multiplet Appearance	Equivalent Series of Doublets	Sum of Line Intensities
1	d	d	2
2	t	dd	4
3	q	ddd	8
4	quintet (pentet)	dddd	16
5	sextet	ddddd	32
6	septet	dddddd	64
7	octet	ddddddd	128
8	nonet	ddddddd	256

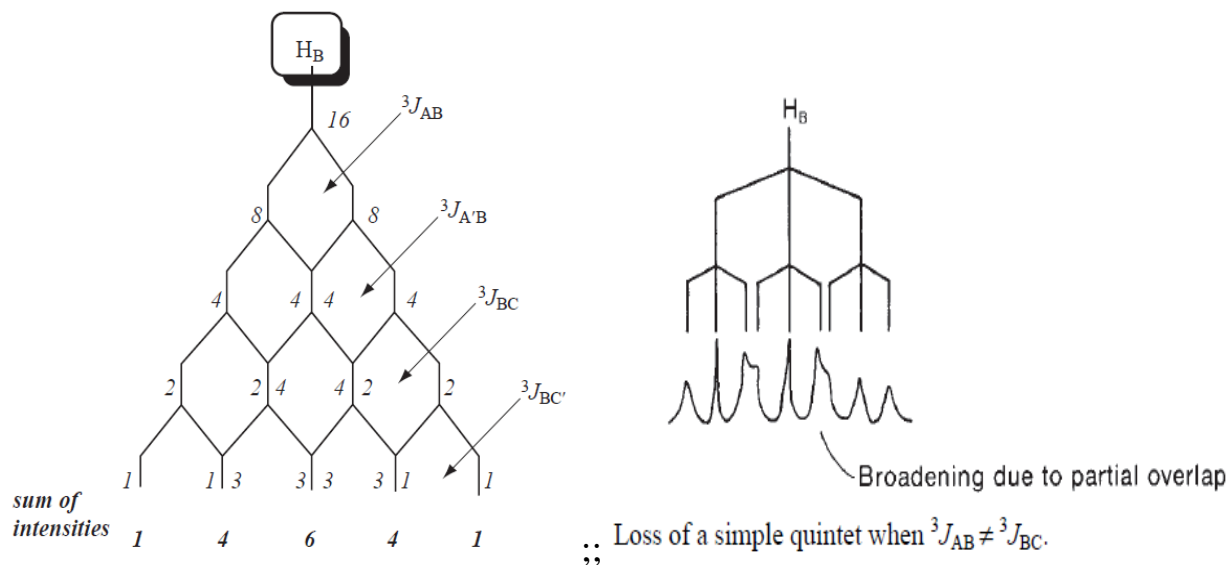
B. Is the $n + 1$ Rule Ever Really Obeyed?

In a linear chain, the $n + 1$ Rule is strictly obeyed only if the vicinal inter-proton coupling constants (3J) are *exactly the same* for every successive pair of carbons.



Construction of a quintet for a methylene group with four neighbors all with identical j -values.

Consider a three-carbon chain as an example. The protons on carbons A and C split those on carbon B. If there is a total of four protons on carbons A and C, the $n + 1$ Rule predicts a pentet. This occurs only if ${}^3J_{AB} = {}^3J_{BC}$ as shown above. Thus, the $n + 1$ Rule depends on a special condition that all of the vicinal coupling constants are identical. While in the case of using dddd (where ${}^3J_{AB} = {}^3J_{A'B} = {}^3J_{BC} = {}^3J_{AC'}$.) can be draw as follows and obtain same quintet. HB multiplet will be $2^4 = 16$; [1:4:6:4:1 = 16].

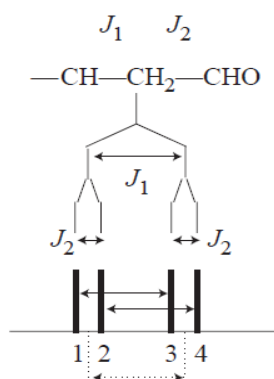


At other times, when there is a large difference between ${}^3J_{AB}$ and ${}^3J_{BC}$, distinct peaks, more than five in number, can be seen. Deviations of this type are most common in a chain of the type X-CH₂CH₂CH₂-Y, where X and Y are widely different in character.

C. More Complex Multiplets—More Than One Value of J :

When analyzing more complicated resonances with more than one distinct coupling, measuring all of the coupling constants presents a challenge. Many chemists take the lazy way out and simply call a complex resonance a “multiplet.” This presents problems on multiple levels. First, coupling constants give valuable information about both the two-dimensional (2-D) structure (connectivity) and three-dimensional (3-D) structure (stereochemistry) of compounds. Some examples for determining coupling constants for a) doublet of doublets (dd), b) doublet of triplets (dt), and c) doublet of doublet of doublets (ddd) patterns:

a)



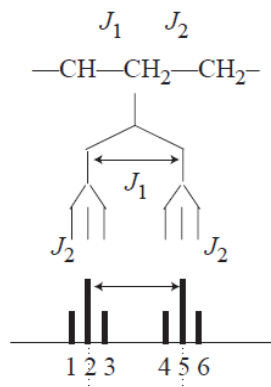
Doublet of Doublets (dd)

To obtain J_1 measure the difference between lines 1 and 3, or 2 and 4, in Hz.*

*Do not try to find the centers of the doublets!

J_2 is the spacing between lines 1 and 2, or 3 and 4

b)

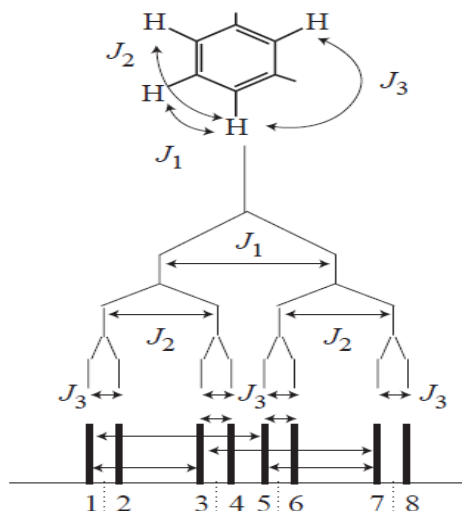


Doublet of Triplets (dt)

To obtain J_1 measure the difference between the most intense lines (2 and 5) in Hz

J_2 is the spacing between lines 1 and 2, or 2 and 3, or those in the other triplet.

c)



A number of approaches are possible. Generally you should choose an appropriately spaced pair of peaks based on their intensities and sharpness.

J values from doublets of doublets (dd's) can be read by looking at the shift differences between peaks 1 and 2 and between peaks 1 and 3. I actually find it a little more reliable to measure a couple of differences (1-2, 3-4) and average them.

$\Delta\delta_{1,2} = 0.022 \text{ ppm}$

$\Delta\delta_{1,3} = 0.030 \text{ ppm}$



$J_{1,2} = 5.9 \text{ Hz}$
 $J_{1,3} = 8.1 \text{ Hz}$

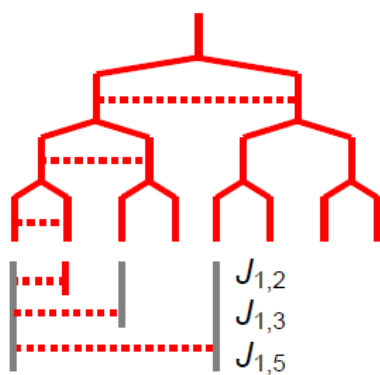
$\Delta\delta_{1,2} = 0.025 \text{ ppm}$

$\Delta\delta_{1,3} = 0.032 \text{ ppm}$



$J_{1,2} = 6.8 \text{ Hz}$
 $J_{1,3} = 8.6 \text{ Hz}$

The last two resonances are actually doublets of doublets of doublets (ddd's). We can actually read coupling constants off of these too, by thinking about how the coupling tree relates to the peaks.



$$J_{1,2} = 1.9 \text{ Hz}$$

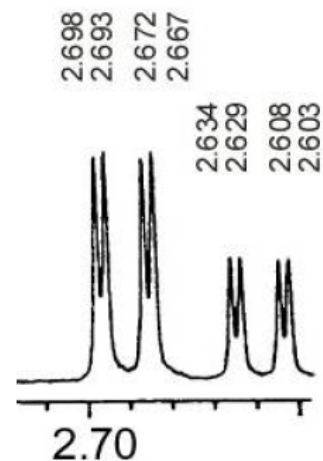
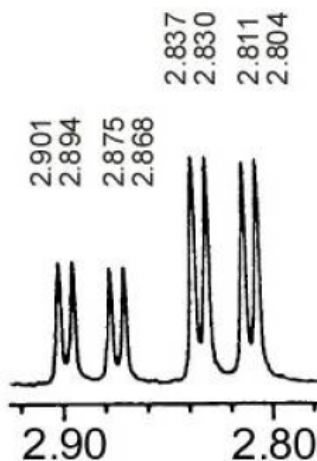
$$J_{1,3} = 7.0 \text{ Hz}$$

$$J_{1,5} = 17.3 \text{ Hz}$$

$$J_{1,2} = 1.4 \text{ Hz}$$

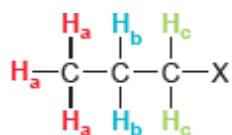
$$J_{1,3} = 7.0 \text{ Hz}$$

$$J_{1,5} = 17.3 \text{ Hz}$$

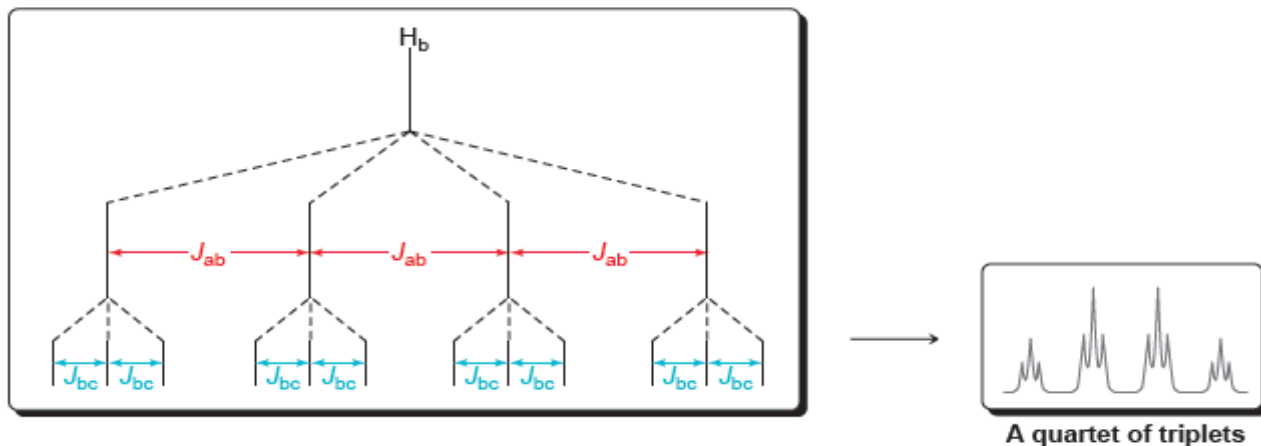


Complex splitting occurs when a proton has two different kinds of neighboring protons.

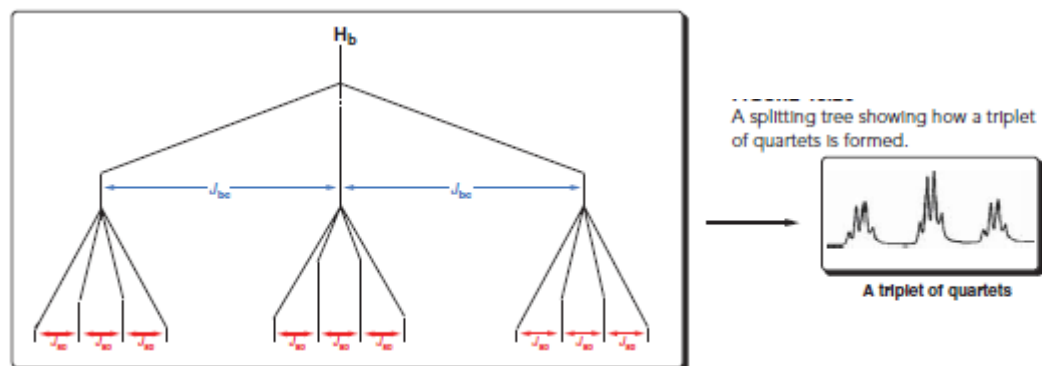
For example:



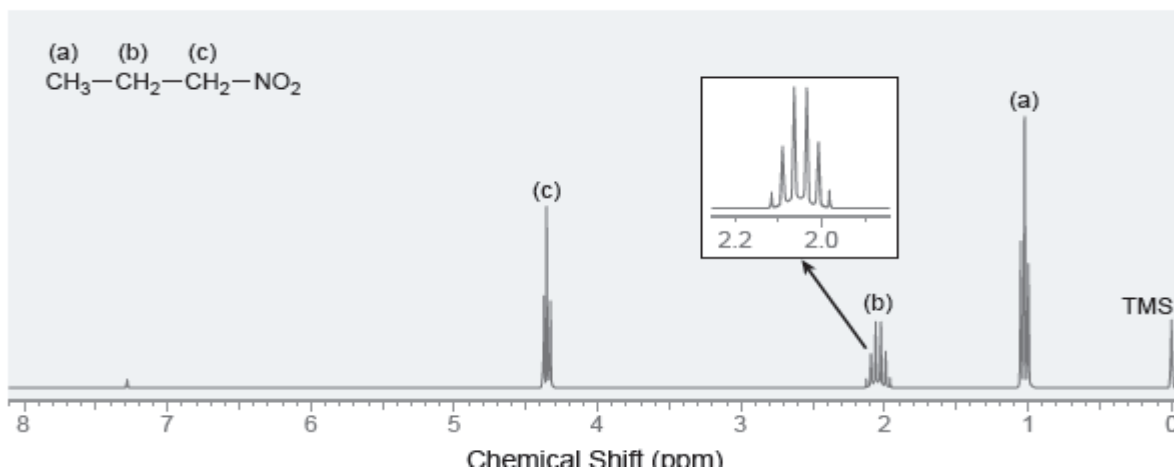
Consider the expected splitting pattern for H_b in this example. The signal for H_b is being split into a quartet because of the nearby H_a protons, and it is being split into a triplet because of the nearby H_c protons. The signal will therefore be comprised of 12 peaks (4 × 3). The appearance of the signal will depend greatly on the *J* values. If *J*_{ab} is much greater than *J*_{bc}, then the signal will appear as a quartet of triplets. This is illustrated in the splitting tree shown in Figure below.



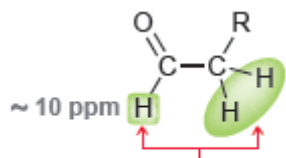
If, however, J_{bc} is much greater than J_{ab} , then the signal will appear as a triplet of quartets (Figure below). In most cases, the J values will be fairly similar, and we will observe neither a clean quartet of triplets nor a clean triplet of quartets. More often, several of the peaks will overlap, producing a signal that is difficult to analyze and is simply called a **multiplet**.



In some cases, J_{ab} and J_{ac} will be almost identical. For example, consider the ^1H NMR spectrum of 1-nitropropane (Figure below). Look carefully at the splitting pattern of the H_b protons (at approximately 2 ppm). This signal looks like a sextet, because the J_{ab} and J_{bc} are so close in value. In such a case, it appears “as if” there are five equivalent neighbors, even though all five protons are not equivalent.

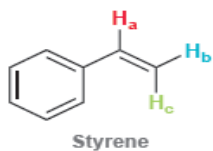


Depending on the size of the J value, splitting may or may not be noticeable. A common examples of neighboring protons that often do not produce observable splitting, are alcohol (hydroxyl group) and aldehydic protons, which generally produce signals near 10 ppm, will often couple only weakly with their neighbors (i.e., a very small J value). The J value is too small, and then the signal near 10 ppm will be appear to be a singlet, despite the presence of neighboring protons.



This J value is often very small

Q/ Each of the three vinylic protons of styrene is split by the other two, and the J values are found to be $J_{ab} = 11$ Hz, $J_{ac} = 17$ Hz, and $J_{bc} = 1$ Hz. Using this information, draw the expected splitting pattern for each of the three signals (H_a , H_b , and H_c).



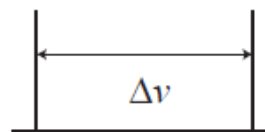
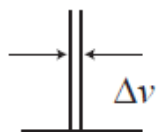
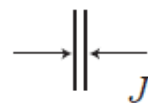
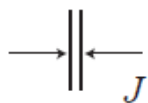
SECOND-ORDER SPECTRA—STRONG COUPLING

A. First-Order and Second-Order Spectra:

The **first-order spectra** is spectra that can be interpreted by using the $n + 1$ Rule or a simple graphical analysis (splitting trees). In certain cases, however, neither the $n + 1$ Rule nor graphical analysis suffices to explain the splitting patterns, intensities, and numbers of peaks observed. In these last cases, a mathematical analysis must be carried out, usually by computer, to explain the spectrum. Spectra that require such advanced analysis are said to be **second order spectra**.

Second-order spectra are most commonly observed when the difference in chemical shift between two groups of protons is similar in magnitude (in Hertz) to the coupling constant J (also in Hertz), which links them. That is, second-order spectra are observed for couplings between nuclei that have *nearly equivalent chemical shifts* but are not exactly identical. In contrast, if two sets of nuclei are separated by a large chemical shift difference, they show first-order coupling.

Another way of expressing this generalization is by means of the ratio $\Delta\nu/J$, where $\Delta\nu$ is the chemical shift difference, and J is the coupling constant that links the two groups. Both values are expressed in Hertz, and their absolute values are used for the calculation. When $\Delta\nu/J$ is large ($> \sim 6$), the splitting pattern typically approximates first-order splitting. However, when the chemical shifts of the two groups of nuclei move closer together and $\Delta\nu/J$ approaches unity, we see second-order changes in the splitting pattern. When $\Delta\nu/J$ is large and we see first-order splitting, the system is said to be **weakly coupled**; if $\Delta\nu/J$ is small and we see second-order coupling, the system is said to be **strongly coupled**.



Strong coupling, second-order spectra
($\Delta\nu/J$ small)

Weak coupling, first-order spectra
($\Delta\nu/J$ large)

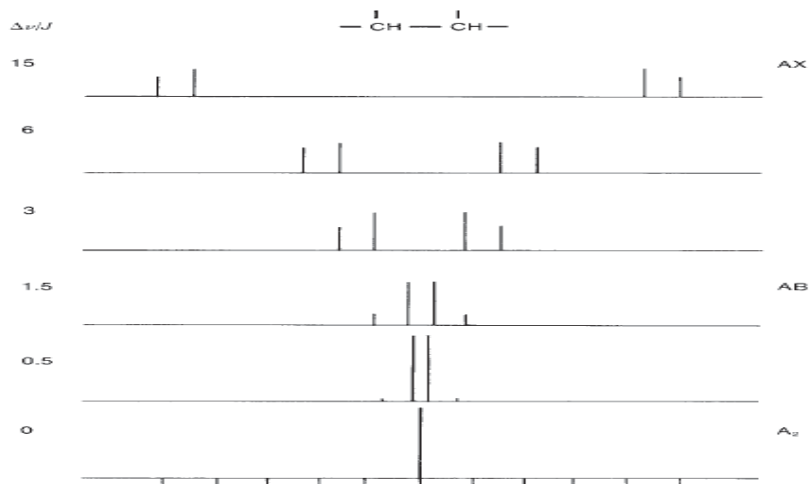
B. Spin System Notation

To designate the type of spin system, each chemically different type of proton is given a capital letter: A, B, C, and so forth. If a group has two or more protons of one type, they are distinguished by subscripts, as in A_2 or B_3 . Protons of similar chemical shift values are assigned letters that are close to one another in the alphabet, such as A, B, and C. Protons of widely different chemical shift are assigned letters far apart in the alphabet: X, Y, Z versus A, B, C. A two proton system where HA and HX are widely separated, and that exhibits first-order splitting, is called an AX system. A system in which the two protons have similar chemical shifts, and that exhibits second-order splitting, is called an AB system. When the two protons have identical chemical shifts, are magnetically equivalent, and give rise to a singlet, the system is designated A_2 . Two protons that have the same chemical shift but are not magnetically equivalent are designated as AA' . If three protons are involved and they all have very different chemical shifts, a letter from the middle of the alphabet is used, usually M, as in AMX. The ^1H NMR spectrum of styrene oxide is an example of an AMX pattern. In contrast, ABC would be used for the strongly coupled situation in which all three protons have similar chemical shifts.

C. The A_2 , AB, and AX Spin Systems

Start by examining the system with two protons, HA and HB, on adjacent carbon atoms. Using the $n + 1$ Rule, we expect to see each proton resonance as a doublet with components of equal intensity in the ^1H NMR spectrum. In actuality, we see two doublets of equal intensity in this situation only if the difference in chemical shift ($\Delta\nu$) between HA and HB is large compared to the magnitude of the coupling constant ($^3J_{AB}$) that links them.

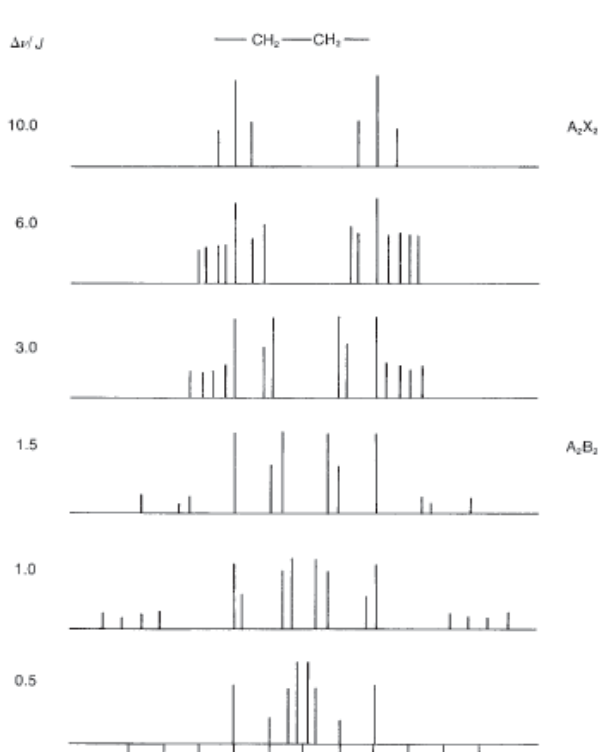
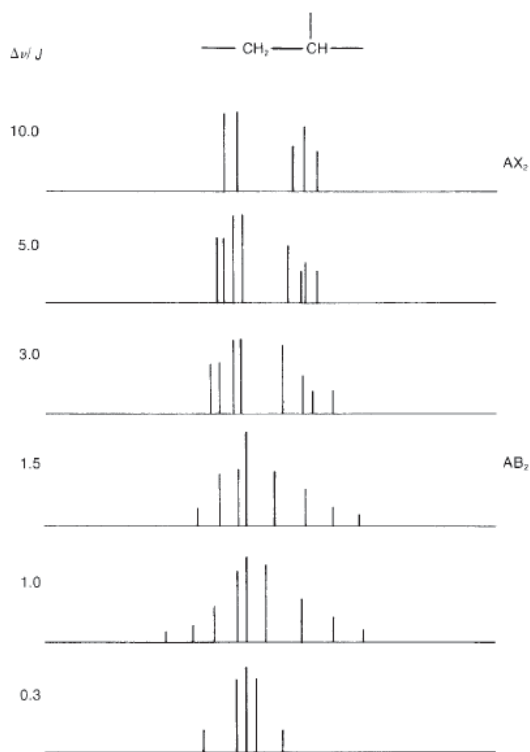
Figure below shows how the splitting pattern for the two-proton system $H_A H_B$ changes as the chemical shifts of HA and HB come closer together and the ratio $\Delta\nu/J$ becomes smaller. The figure is drawn to scale, with $^3J_{AB} = 7$ Hz. When $\delta_{HA} = \delta_{HB}$ (that is, when the protons HA and HB have the same chemical shift), then $\Delta\nu = 0$, and no splitting is observed; both protons give rise to a single absorption peak. Between one extreme, where there is no splitting due to chemical shift equivalence ($\Delta\nu/J = 0$), and the other extreme, the simple first-order spectrum ($\Delta\nu/J = 15$) that follows the $n + 1$ Rule, subtle and continuous changes in the splitting pattern take place. Most obvious is the decrease in intensity of the outer peaks of the doublets, with a corresponding increase in the intensity of the inner peaks. Other changes that are not as obvious also occur.



D. The $AB_2 \dots AX_2$ and $A_2B_2 \dots A_2X_2$ Spin Systems:

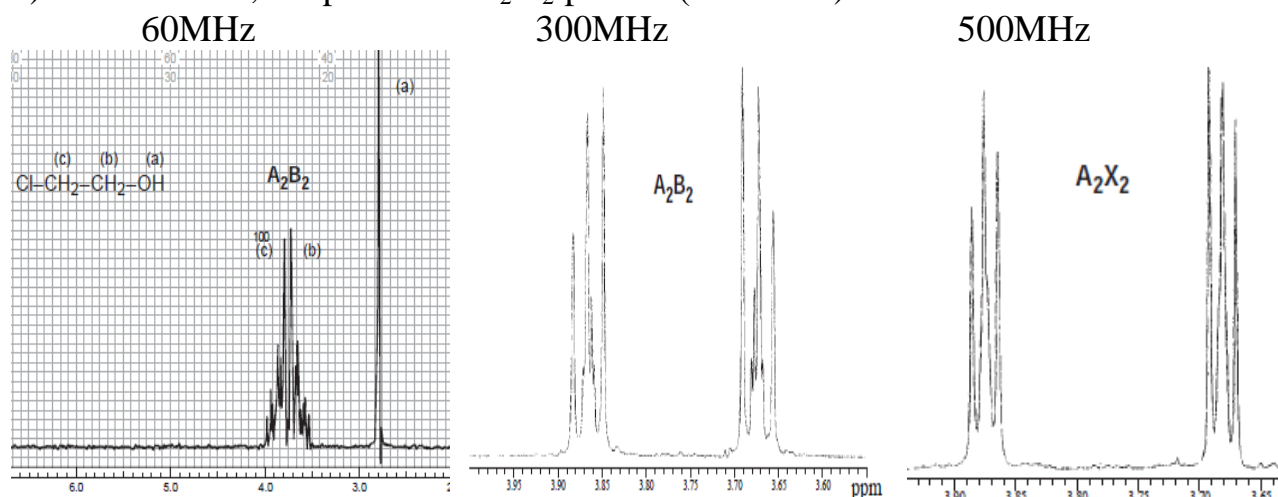
To provide some idea of the magnitude of second-order variations from simple behavior, Figures below illustrate the calculated ^1H NMR spectra of two additional systems ($-\text{CH}-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-$). The first-order spectra appear at the top ($\Delta\nu/J > 10$), while increasing amounts of second-order complexity are encountered as we move toward the bottom ($\Delta\nu/J$ approaches zero).

The two systems shown in Figures are, then, AB_2 ($\Delta\nu/J < 10$) and AX_2 ($\Delta\nu/J > 10$) in one case and A_2B_2 ($\Delta\nu/J < 10$) and A_2X_2 ($\Delta\nu/J > 10$) in the other.



E. The Absence of Second-Order Effects at Higher Field

With routine access to NMR spectrometers with ^1H operating frequencies >300 MHz, chemists today encounter fewer second-order spectra than in years past. We know that the chemical shift increases when a spectrum is determined at higher field, but that the coupling constants do not change in magnitude. This causes the $\Delta\nu/J$ ratio to increase, and second-order effects begin to disappear. At high field, many spectra are first order and are therefore easier to interpret than spectra determined at lower field strengths. As an example: the 60-MHz ^1H NMR spectrum of 2-chloroethanol. This is an A_2B_2 spectrum showing substantial second-order effects ($\Delta\nu/J$ is between 1 and 3). While the ^1H spectrum taken at 300 MHz, the formerly complicated and second-order patterns have *almost* reverted to two triplets just as the $n + 1$ Rule would predict ($\Delta\nu/J$ is between 6 and 8). At 500 MHz, the predicted A_2X_2 pattern ($\Delta\nu/J \sim 12$) is observed, as shown below:



F. Deceptively Simple Spectra:

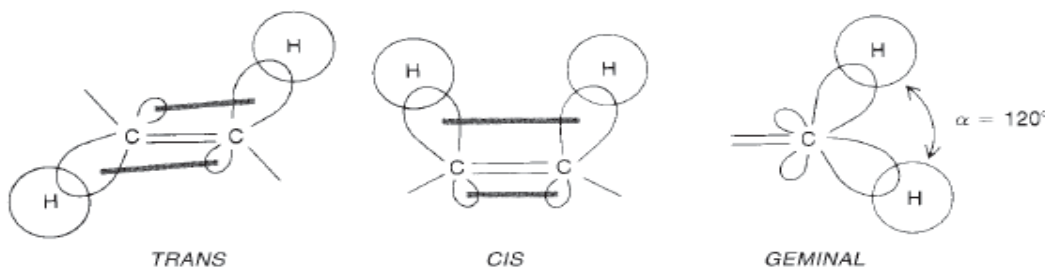
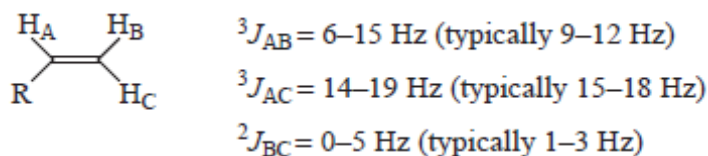
It is not always obvious when a spectrum has become completely first order. Consider the A_2B_2 to A_2X_2 progression. At which value of $\Delta\nu/J$ does this spectrum become truly first order? Somewhere between $\Delta\nu/J = 6$ and $\Delta\nu/J = 10$ the spectrum seems to become A_2X_2 . The number of observed lines decreases from 14 lines to only 6 lines. However, if spectra are simulated, incrementally changing $\Delta\nu/J$ slowly from 6 to 10, we find that the change is not abrupt but gradual.

Some of the lines disappear by decreasing in intensity, and some merge together, increasing their intensities. It is possible for weak lines to be lost in the noise of the baseline or for merging lines to approach so closely that the spectrometer cannot resolve them any longer. In these cases, the spectrum would appear to be first order, but in fact it would not quite be so. A common deceptively simple pattern is that encountered with *para*-disubstituted aromatics, an $AA'BB'$ spectrum.

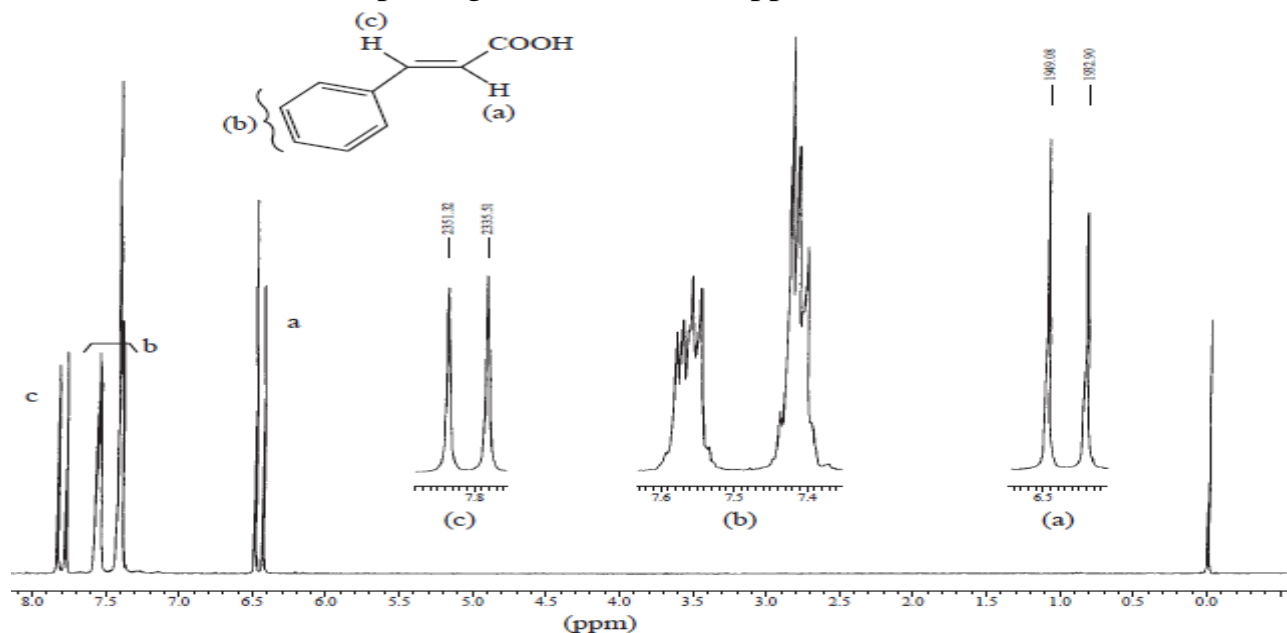
Spectra that appear to be first order, but actually are not, are called **deceptively simple spectra**.

Alkenes:

Just as the protons attached to double bonds have characteristic chemical shifts due to a change in hybridization (sp^2 vs. sp^3) and deshielding due to the diamagnetic anisotropy generated by the π electrons of the double bond, alkenyl protons have characteristic splitting patterns and coupling constants. For monosubstituted alkenes, three distinct types of spin interaction are observed:



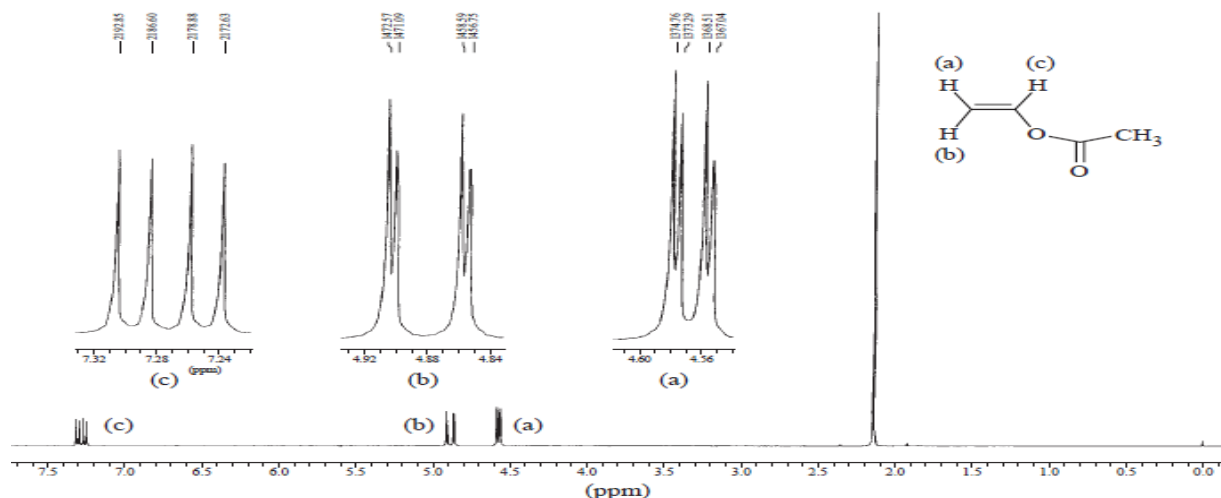
Example (1): *trans* cinnamic acid: The *trans* coupling constant in this case is 15.8 Hz—a common value for *trans* proton–proton coupling across a double bond. The *cis* isomer would exhibit a smaller splitting. Each H_a & H_b appear as doublets.



While a molecule that has a symmetry element (a plane or axis of symmetry) passing through the C–C double bond does not show any *cis* or *trans* splitting since the vinyl protons are chemically and magnetically equivalent. An example of each type can be seen in *cis*- and *trans*-stilbene, respectively. In each compound, the vinyl protons H_A and H_B give rise to only a single *unsplit* resonance peak.



Example (2): The ^1H NMR spectrum of vinyl acetate an (AMX) spin system.

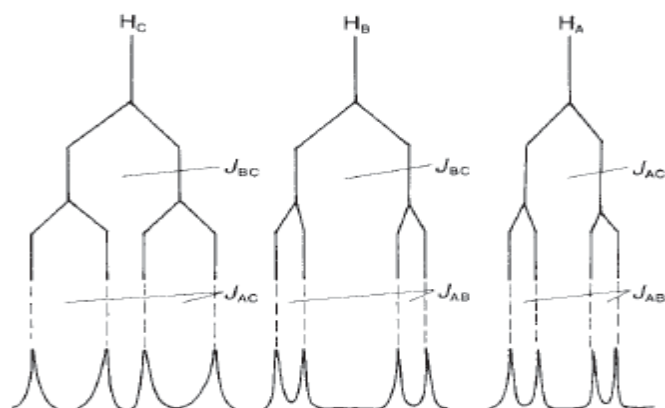


$H_a = 4.57$ ppm, $^3J_{ac} = 6.25$ Hz and $^2J_{ab} = 1.47$ Hz.

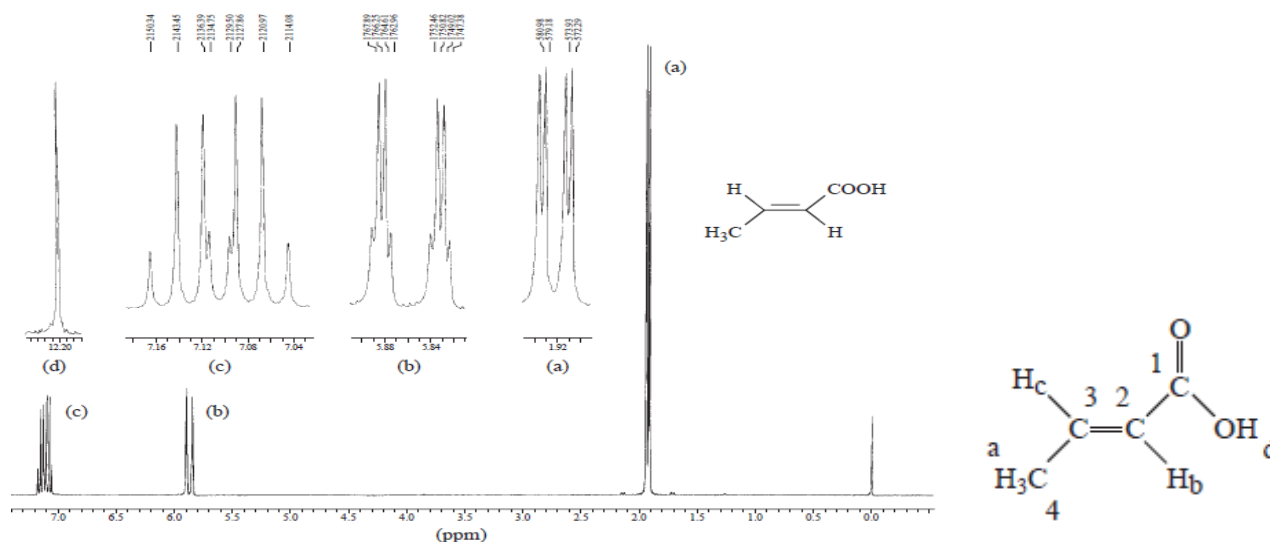
$H_b = 4.88$ ppm. The coupling constants are not consistent; $^3J_{bc} = 13.98$ or 14.34 Hz from the spacing of the peaks. $^2J_{ab} = 1.48$ or 1.84 Hz. It is often the case that the coupling constants are not consistent. More consistent coupling constants can be obtained from analysis of proton H_c .

$H_c = 7.27$ ppm, $^3J_{bc} = 13.97$ Hz and $^3J_{ac} = 6.25$ Hz from the spacing of the peaks.

Summary of coupling constants from the analysis of the spectrum: $^3J_{ac} = 6.25$ Hz, $^3J_{bc} = 13.97$ Hz and $^2J_{ab} = 1.47$ Hz. They can be rounded off to: 6.3, 14.0 and 1.5 Hz, respectively. The graphical analysis will be as follows:



Example (3): a spectrum of crotonic acid. Remember that $^3J_{trans}$ is quite large in an alkene while the allylic couplings will be small. The multiplets may be described as a doublet of doublets (1.92 ppm), a doublet of quartets (5.86 ppm), and a doublet of quartets (7.10 ppm) with the peaks of the two quartets overlapping:



Q/ draw graphical analysis

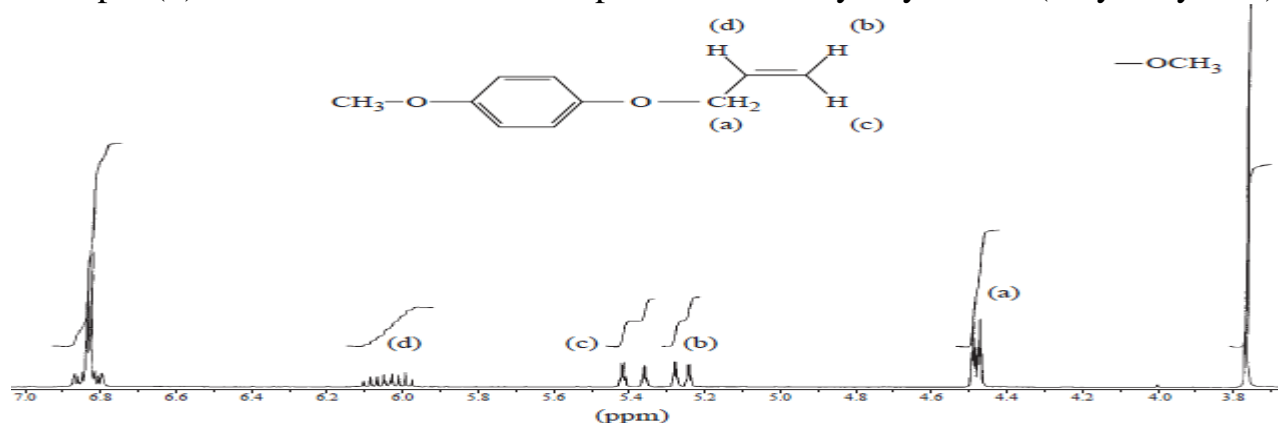
H_a = 1.92 ppm (methyl group at C-4). It appears as a doublet of doublets (dd) because it shows both 3J and 4J couplings; $^3J_{ac} = 6.9$ Hz and $^4J_{ab}$ allylic = 1.6 Hz.

H_b = 5.86 ppm (vinyl proton at C-2). It appears as a doublet of quartets (dq); $^3J_{bc}$ trans = 15.6 Hz and $^4J_{ab}$ allylic = 1.6 Hz.

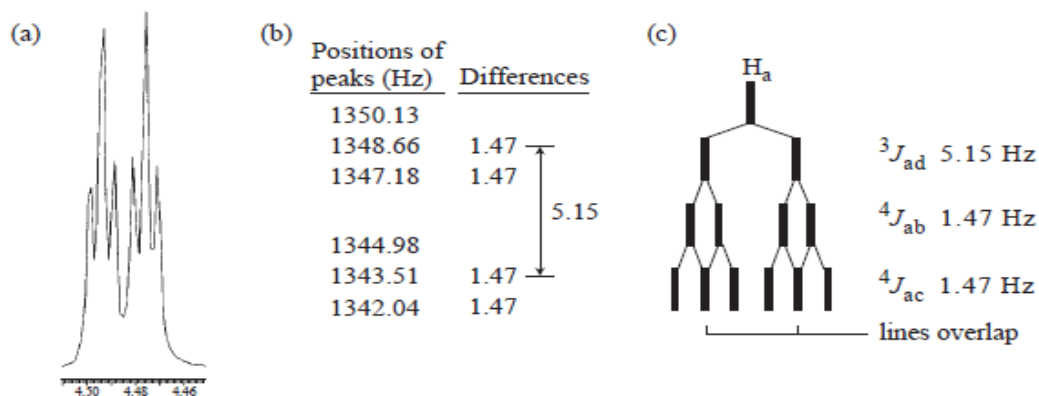
H_c = 7.10 ppm (vinyl proton at C-3). It appears as a doublet of quartets (dq), with some partial overlap of the quartets; $^3J_{bc}$ trans = 15.6 Hz and $^3J_{ac} = 6.9$ Hz. Notice that H_c is shifted further downfield than H_b because of the resonance effect of the carboxyl group and also a through-space deshielding by the oxygen atom in the carbonyl group.

H_d = 12.2 ppm (singlet, acid proton on carboxyl group).

Example (4): The 300-MHz ^1H NMR spectrum of 4-allyloxyanisole (Allylic system):

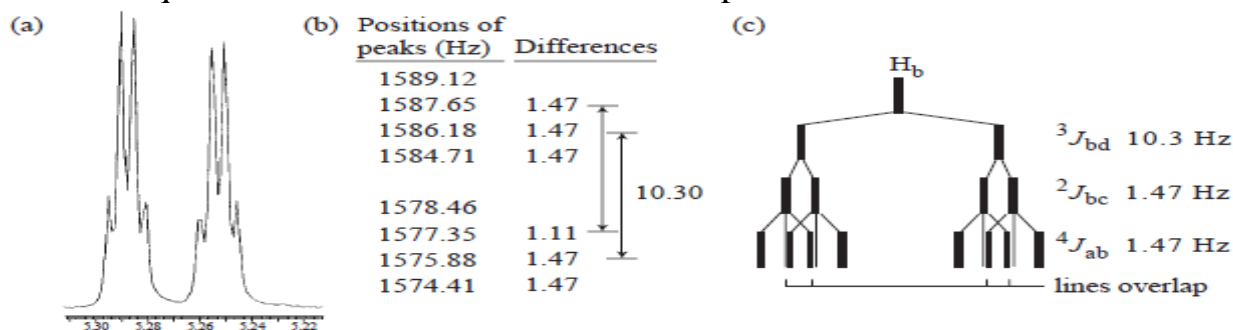


The H_a appears to be a doublet of triplets (dt). However, examination of the molecular structure would lead us to believe that this multiplet should be a doublet of doublets of doublets (ddd), the OCH_2 group being split first by H_d (${}^3J_{ad}$), then by H_b (${}^4J_{ab}$), and then by H_c (${}^4J_{ac}$), each of which is a single proton. A doublet of triplets could result only if (by coincidence) ${}^4J_{ab} = {}^4J_{ac}$. We can find out if this is the case by extracting the coupling constants and constructing a tree diagram.



Allyloxyanisole. (a) Expansion of H_a . (b) Peak positions (Hz) and selected frequency differences. (c) Splitting tree diagram showing the origin of the splitting pattern.

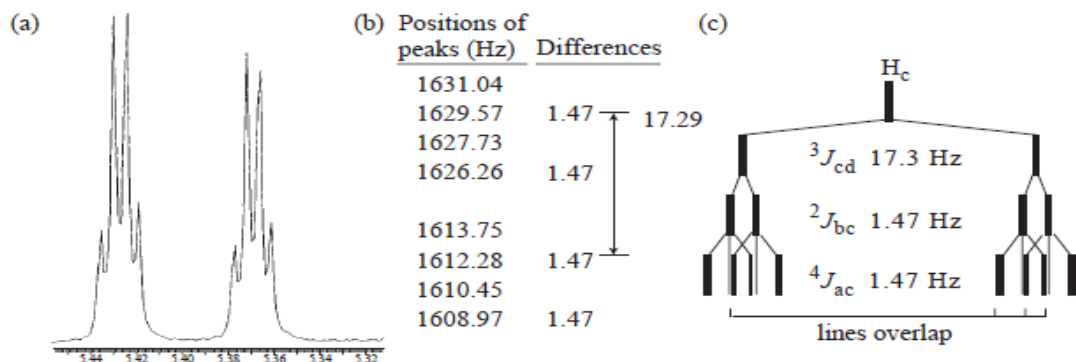
Next consider H_b . The expansion of this multiplet shows it to be an apparent doublet of quartets. The largest coupling should be the *cis* coupling ${}^3J_{bd}$, which should yield a doublet. The geminal coupling ${}^2J_{bc}$ should produce another pair of doublets (dd), and the allylic germinal coupling ${}^4J_{ab}$ should produce triplets (two H_a protons). The expected final pattern would be a doublet of doublet of triplets (ddt) with six peaks in each half of the splitting pattern. Since only four peaks are observed, there must be overlap that could happen if ${}^2J_{bc}$ and ${}^4J_{ab}$ are both small and have nearly the same magnitude. In fact, the two J values appear to be coincidentally the same (or similar), and this is not unexpected. The final solution, a doublet of doublet of triplets (ddt) pattern, which appears to be a doublet of quartets due to the coincidental overlap.



Allyloxyanisole. (a) Expansion of H_b . (b) Peak positions (Hz) and selected frequency differences. (c) Splitting tree diagram showing the origin of the splitting pattern.

H_c is also expected to be a doublet of doublet of triplets (ddt) but shows a doublet of quartets for reasons similar to those explained for H_b. Notice that the first coupling (³J_{cd}) is larger than ³J_{bd}. At this point, we have extracted all six of the coupling constants for the system.

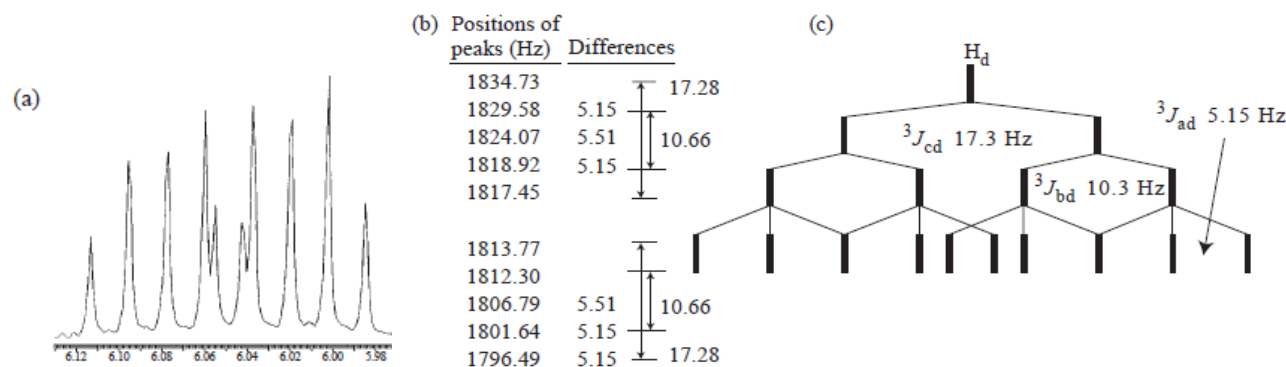
$$\begin{aligned}
 {}^3J_{cd-trans} &= 17.3 \text{ Hz} & {}^2J_{bc-gem} &= 1.5 \text{ Hz} \\
 {}^3J_{bd-cis} &= 10.3 \text{ Hz} & {}^4J_{ab-allylic} &= 1.5 \text{ Hz} \\
 {}^3J_{ad} &= 5.2 \text{ Hz} & {}^4J_{ac-allylic} &= 1.5 \text{ Hz}
 \end{aligned}$$



Allyloxyanisole. (a) Expansion of H_c. (b) Peak positions (Hz) and selected frequency differences. (c) Splitting tree diagram showing the origin of the splitting pattern.

H_d: The predicted pattern is a doublet of doublet of triplets (ddt), which should have six peaks on each half of the symmetrical multiplet. However, due to overlaps, we see what appear to be two overlapping quintets.

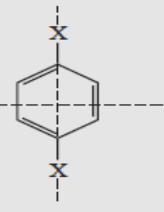
The *cis* coupling (³J_{bd}) was 10.3 Hz. The same coupling measured from the H_d multiplet gives ³J_{bd} = 10.7 Hz. What is the true value of ³J_{bd}? The lines in the H_d resonance are sharper than those in the H_b resonance because H_d does not experience the small long-range allylic couplings that are approximately identical in magnitude. In general, *J* values measured from sharp, uncomplicated resonances are more reliable than those measured from broadened peaks. The true coupling magnitude for ³J_{bd} is likely closer to 10.7 Hz than to 10.3 Hz.



AROMATIC COMPOUNDS—SUBSTITUTED BENZENE RINGS

In general, the ring protons of a benzenoid system appear around 7 ppm; however, E.W ring substituents (e.g., nitro, cyano, carboxyl, or carbonyl) move the resonance of these protons downfield (higher ppm), and E.D ring substituents (e.g., methoxy or amino) move the resonance of these protons upfield (lower ppm), as shown:

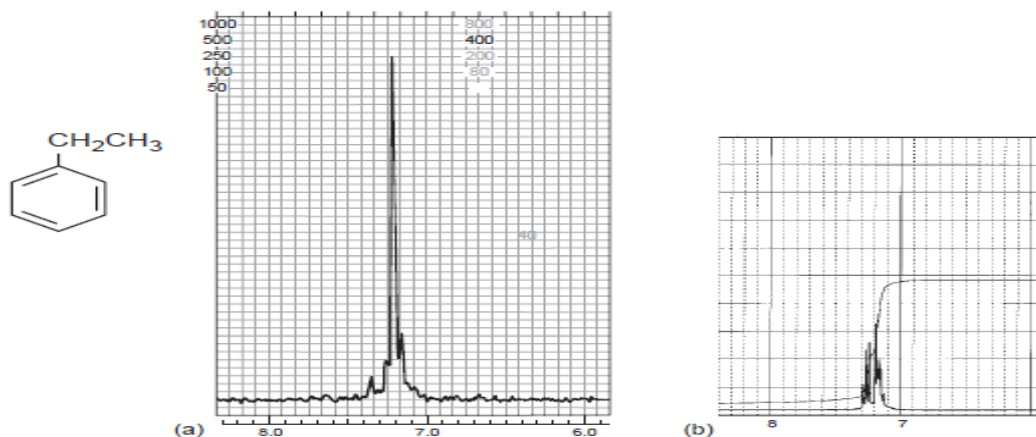
¹H CHEMICAL SHIFTS IN *p*-DISUBSTITUTED BENZENE COMPOUNDS

Substituent X	δ (ppm)	
	-OCH ₃	6.80
	-OH	6.60
	-NH ₂	6.36
	-CH ₃	7.05
	-H	7.32
	-COOH	8.20
	-NO ₂	8.48
		Electron donating
		Electron withdrawing

Many benzenoid rings show second-order splittings at 60 MHz but are essentially first order at 300 MHz or higher field.

A. Monosubstituted Rings:

In monosubstituted benzenes in which the substituent is not a strongly E.w or E.D group, all the ring protons give rise to what appears to be a *single resonance* when the spectrum is determined at 60 MHz. This is a particularly common occurrence in alkyl-substituted benzenes. Although the protons *ortho*, *meta*, and *para* to the substituent are not chemically equivalent, they generally give rise to a single unresolved absorption peak. All of the protons are nearly equivalent under these conditions. The NMR spectra of the aromatic portions of alkylbenzene compounds are good examples of this type of circumstance. Figure below is the 60-MHz and 300-MHz ¹H-NMR spectrum of ethylbenzene. The aromatic protons (that were nearly equivalent at 60 MHz) are neatly separated into two groups. The *ortho* and *para* protons appear upfield from the *meta* protons. The splitting pattern is clearly second order.

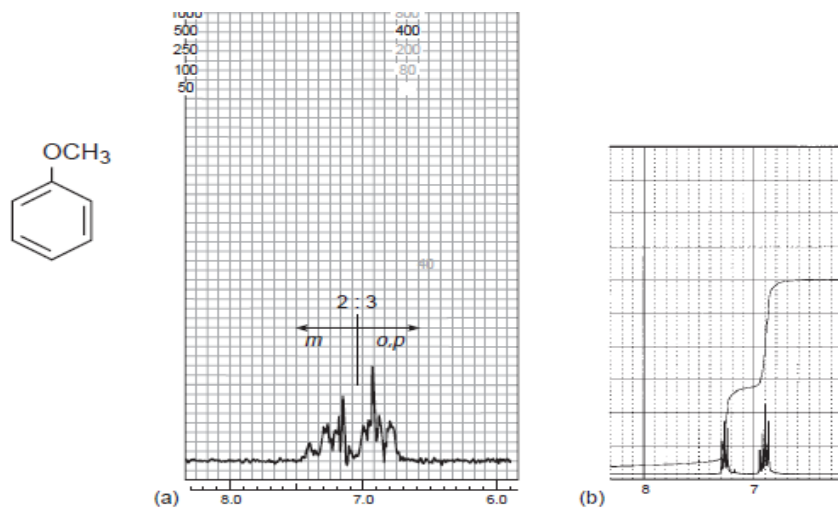


The aromatic ring portions of the ¹H NMR spectrum of ethylbenzene at (a) 60 MHz and (b) 300 MHz.

Electron-Donating Groups

When electron-donating groups are attached to the aromatic ring, the ring protons are not equivalent, even at 60 MHz. A highly activating substituent such as methoxy clearly increases the electron density at the *ortho* and *para* positions of the ring (by resonance) and helps to give these protons greater shielding than those in the *meta* positions and thus a substantially different chemical shift. At 60 MHz, this chemical shift difference results in a complicated second-order splitting pattern for anisole (methoxybenzene), but the protons do fall clearly into two groups, the *ortho/para* protons and the *meta* protons. The 60-MHz NMR spectrum of the aromatic portion of anisole has a complex multiplet for the *o, p* protons (integrating for three protons) that is upfield from the *meta* protons (integrating for two protons), with a clear separation between the two types. Aniline provides a similar spectrum, also with a 3:2 split, owing to the electron-releasing effect of the amino group.

The 300-MHz spectrum of anisole shows the same separation between the *ortho/para* hydrogens (upfield) and the *meta* hydrogens (downfield). However, because the actual shift $\Delta\nu$ (in Hertz) between the two types of hydrogens is greater, there is less second-order interaction, and the lines in the pattern are sharper at 300 MHz. In fact, it might be tempting to try to interpret the observed pattern as if it were first order, but remember that the protons on opposite sides of the ring are not magnetically equivalent even though there is a plane of symmetry. Anisole is an AA'BB'C spin system.

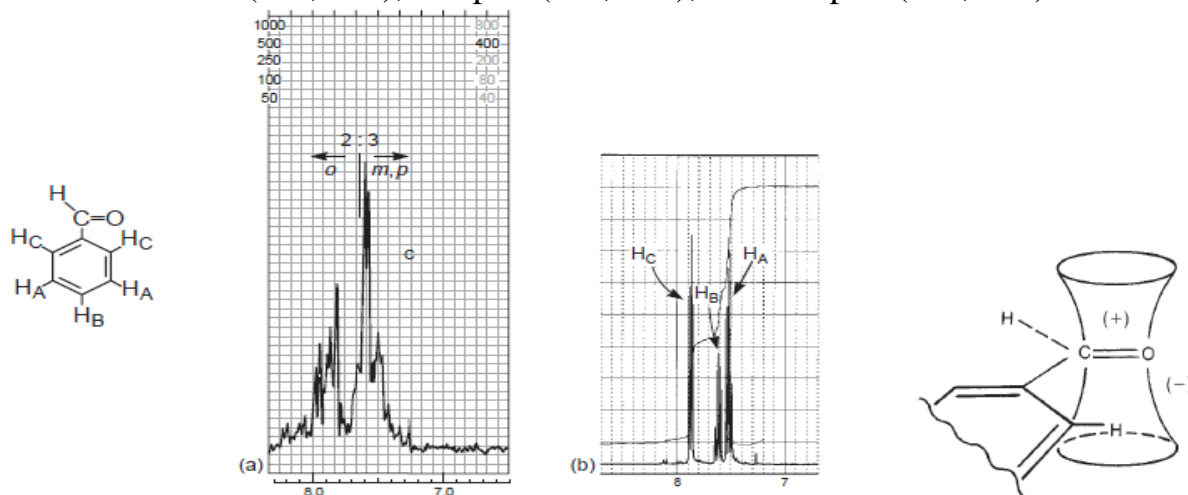


The aromatic ring portions of the ¹H NMR spectrum of anisole at (a) 60 MHz and (b) 300 MHz.

Anisotropy—Electron-Withdrawing Groups

A carbonyl or a nitro group would be expected to show (aside from anisotropy effects) a reverse effect since these groups are electron withdrawing. One would expect that the group would act to decrease the electron density around the *ortho* and *para* positions, thus deshielding the *ortho* and *para* hydrogens and providing a pattern exactly the reverse of the one shown for anisole (3:2 ratio, downfield: upfield). Convince yourself of this by drawing resonance structures. Nevertheless, the actual NMR spectra of nitrobenzene and benzaldehyde do not have the appearances that would be predicted on the basis of resonance structures. Instead, the *ortho* protons are much more deshielded than the *meta* and *para* protons due to the magnetic anisotropy of the π bonds in these groups.

Anisotropy is observed when a substituent group bonds a carbonyl group directly to the benzene ring. Once again, the ring protons fall into two groups, with the *ortho* protons downfield from the *meta/para* protons. Benzaldehyde and acetophenone both show this effect in their NMR spectra. A similar effect is sometimes observed when a carbon-carbon double bond is attached to the ring. The 300-MHz spectrum of benzaldehyde is a nearly first-order spectrum (probably a deceptively simple AA'BB'C spectrum) and shows a doublet (HC, 2 H), a triplet (HB, 1 H), and a triplet (HA, 2 H).

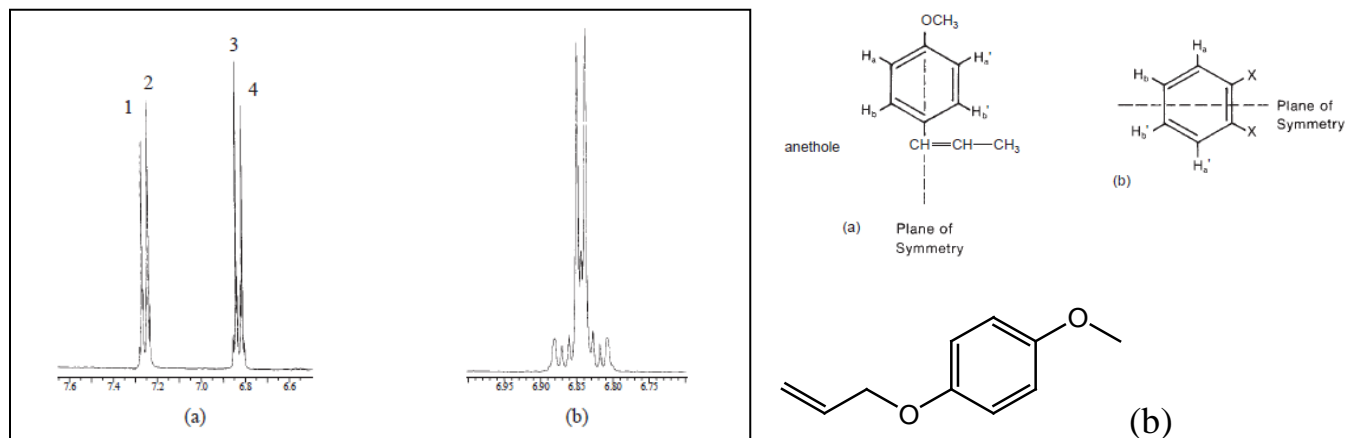


The aromatic ring portions of the ^1H NMR spectrum of benzaldehyde at (a) 60 MHz and (b) 300 MHz.

B. *para*-Disubstituted Rings:

Examine anethole as a first example. Because this compound has a plane of symmetry (passing through the methoxy and propenyl groups), the protons H_a and H_{a'} (both *ortho* to OCH₃) would be expected to have the same chemical shift. Similarly, the protons H_b and H_{b'} should have the same chemical shift. This is found to be the case. You might think that both sides of the ring should then have identical splitting patterns. With this assumption, one is tempted to look at each side of the ring separately, expecting a pattern

in which proton H_b splits proton H_a into a doublet, and proton H_a splits proton H_b into a second doublet.



The aromatic ring portions of the 300-MHz ¹H NMR spectra of (a) anethole and (b) 4-allyloxanisole.

Examination of the NMR spectrum of anethole shows (crudely) just such a four-line pattern for the ring protons. In fact, a *para*-disubstituted ring is easily recognized by this four-line pattern. However, the four lines do not correspond to a simple first-order splitting pattern. That is because the two protons H_a and H_{a'} are *not magnetically equivalent*. Protons H_a and H_{a'} interact with each other and have finite coupling constant $J_{aa'}$. Similarly, H_b and H_{b'} interact with each other and have coupling constant $J_{bb'}$. More importantly, H_a does not interact equally with H_b (*ortho* to H_a) and with H_{b'} (*para* to H_a); that is, $J_{ab} \neq J_{ab'}$. If H_b and H_{b'} are coupled differently to H_a, they cannot be magnetically equivalent. This fact suggests that the situation is more complicated than it might at first appear. A closer look at the pattern shows that this is indeed the case. With an expansion of the parts-per-million scale, this pattern actually resembles four distorted triplets. The pattern is an AA'BB' spectrum. Note, however, that a crude four-line spectrum is characteristic of a *para*-disubstituted ring. It is also characteristic of an *ortho*-disubstituted ring in which the two *ortho* substituents are identical, leading to a plane of symmetry.

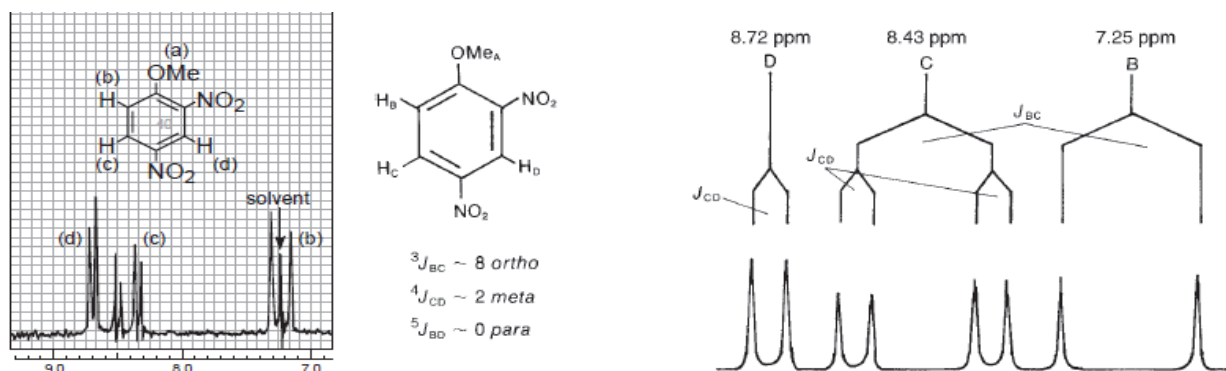
As the chemical shifts of H_a and H_b approach each other, the *para*-disubstituted pattern becomes similar to that of 4-allyloxanisole. The inner peaks move closer together, and the outer ones become smaller or even disappear. Ultimately, when H_a and H_b approach each other closely enough in chemical shift, the outer peaks disappear, and the two inner peaks merge into a *singlet*.

C. Other Substitution:

Other modes of ring substitution can often lead to splitting patterns more complicated than those of the aforementioned cases. In aromatic rings, coupling usually extends beyond the adjacent carbon atoms. In fact, *ortho*, *meta*, and *para* protons can all interact. Following are typical J values for these interactions:

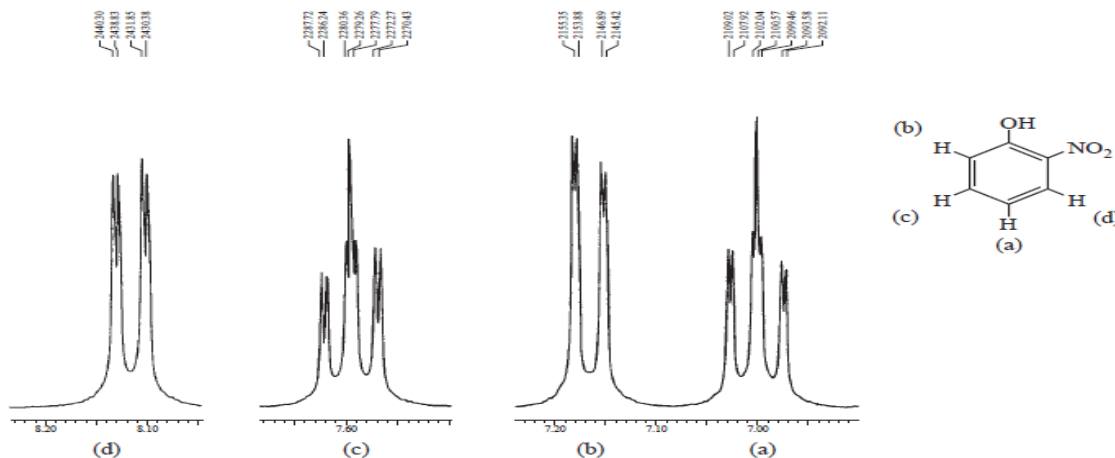
$$\begin{array}{ccc} \textit{ortho} & \textit{meta} & \textit{para} \\ {}^3J = 7-10 \text{ Hz} & {}^4J = 1-3 \text{ Hz} & {}^5J = 0-1 \text{ Hz} \end{array}$$

The trisubstituted compound 2,4-dinitroanisole shows all of the types of interactions mentioned. In this example, as is typical, the coupling between the *para* protons is essentially zero. Also notice the effects of the nitro groups on the chemical shifts of the adjacent protons. Proton H_D , which lies between two nitro groups, has the largest chemical shift (8.72 ppm). Proton H_C , which is affected only by the anisotropy of a single nitro group, is not shifted as far downfield.



The aromatic ring portion of the 60-MHz ^1H NMR spectrum of 2,4-dinitroanisole and its analysis.

Other examples: 2-nitrophenol: The position of each subpeak is given in Hertz. For these spectra, it should be possible not only to assign peaks to specific hydrogens but also to derive tree diagrams with discrete coupling constants for each interaction:



2-Nitrophenol: H_a and H_b are shielded by the electron releasing effect of the hydroxyl group caused by the non-bonded electrons on the oxygen atom being involved in resonance. They can be differentiated by their appearance: H_a is a triplet with some fine structure and H_b is a doublet with fine structure. H_d is deshielded by the electron withdrawing effect and by the anisotropy of the nitro group. Notice that the pattern is a doublet with some fine structure. H_c is assigned by a process of elimination. It lacks any of the above effects that shields or deshields that proton. It appears as a triplet with some fine structure.

$H_a = 7.00$ ppm (ddd); ${}^3J_{ac} \cong {}^3J_{ad} = 8.5$ Hz and ${}^4J_{ab} = 1.5$ Hz. H_a could also be described as a triplet of doublets (td) since ${}^3J_{ac}$ and ${}^3J_{ad}$ are nearly equal.

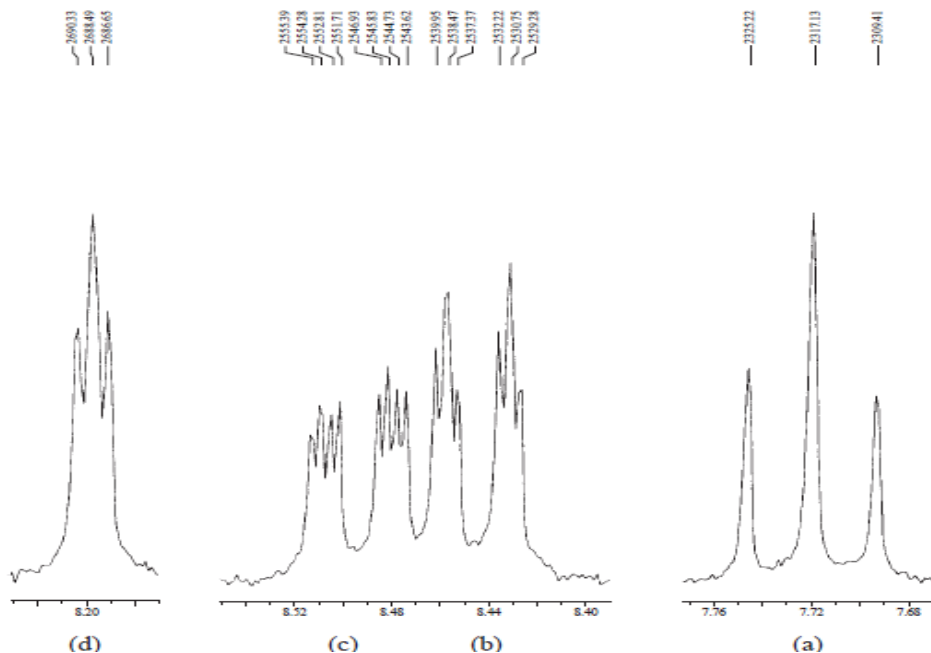
$H_b = 7.16$ ppm (dd); ${}^3J_{bc} = 8.5$ Hz and ${}^4J_{ab} = 1.5$ Hz.

$H_c = 7.60$ ppm (ddd or td); ${}^3J_{ac} \cong {}^3J_{bc} = 8.5$ Hz and ${}^4J_{cd} = 1.5$ Hz.

$H_d = 8.12$ ppm (dd); ${}^3J_{ad} = 8.5$ Hz and ${}^4J_{cd} = 1.5$ Hz; ${}^5J_{bd} = 0$.

The OH group is not shown in the spectrum.

3-Nitrobenzoic acid:



H_d is significantly deshielded by the anisotropy of both the nitro and carboxyl groups and appears furthest downfield. It appears as a narrowly spaced triplet.

This proton only shows 4J couplings. H_b is *ortho* to a carboxyl group while H_c is *ortho* to a nitro group. Both protons are deshielded, but the nitro group shifts a proton further downfield than for a proton next to a carboxyl group. Both H_b and H_c are doublets with fine structure consistent with their positions on the aromatic ring. H_a is relatively shielded and appears upfield as a widely spaced triplet. This proton does not experience any

anisotropy effect because of its distance away from the attached groups. H_a has only 3J couplings ($^5J_{ad} = 0$).

$H_a = 7.72$ ppm (dd); $^3J_{ac} = 8.1$ Hz and $^3J_{ab} = 7.7$ Hz (these values come from analysis of H_b and H_c , below). Since the coupling constants are similar, the pattern appears as an accidental triplet.

$H_b = 8.45$ ppm (ddd or dt); $^3J_{ab} = 7.7$ Hz; $^4J_{bd} \cong ^4J_{bc} = 1.5$ Hz. The pattern is an accidental doublet of triplets.

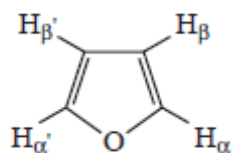
$H_c = 8.50$ ppm (ddd); $^3J_{ac} = 8.1$ Hz and $^4J_{cd} \neq ^4J_{bc}$.

$H_d = 8.96$ ppm (dd). The pattern appears to be a narrowly spaced triplet, but is actually an accidental triplet since $^4J_{bd} \neq ^4J_{cd}$.

The carboxyl proton is not shown in the spectrum.

COUPLING IN HETEROAROMATIC SYSTEMS

Heteroaromatic systems (furans, pyrroles, thiophenes, pyridines, etc.) show couplings analogous to those in benzenoid systems. In furan, for instance, couplings occur between all of the ring protons. Typical values of coupling constants for furanoid rings follow. The analogous couplings in pyrrole systems are similar in magnitude.



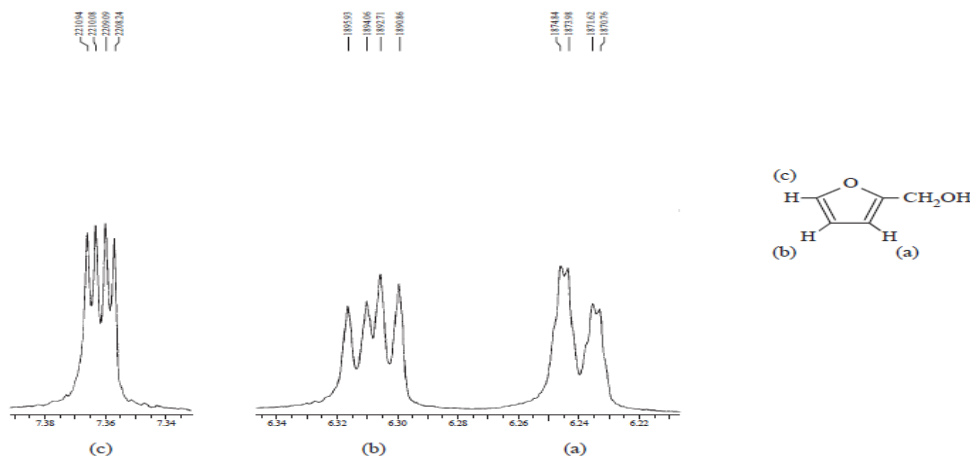
$$^3J_{\alpha\beta} = 1.6 - 2.0 \text{ Hz}$$

$$^4J_{\alpha\beta'} = 0.3 - 0.8 \text{ Hz}$$

$$^4J_{\alpha\alpha'} = 1.3 - 1.8 \text{ Hz}$$

$$^3J_{\beta\beta'} = 3.2 - 3.8 \text{ Hz}$$

The structure and spectrum for furfuryl alcohol are shown below. Only the ring hydrogens are shown—the resonances of the hydroxymethyl side chain ($-\text{CH}_2\text{OH}$) are not included. Notice that proton H_a not only shows coupling to the other two ring hydrogens (H_b and H_c) but also appears to have small unresolved *cis*-allylic interaction with the methylene (CH_2) group.



Furfuryl alcohol:

$H_a = 6.24$ ppm (doublet of quartets); ${}^3J_{ab} = 3.2$ Hz and ${}^4J_{ac} = 0.9$ Hz. The quartet pattern results from a nearly equal 4J coupling of H_a to the two methylene protons in the CH_2OH group and the 4J coupling of H_a to H_c ($n + 1$ rule, three protons plus one equals four, a quartet).

$H_b = 6.31$ ppm (dd); ${}^3J_{ab} = 3.2$ Hz and ${}^3J_{bc} = 1.9$ Hz.

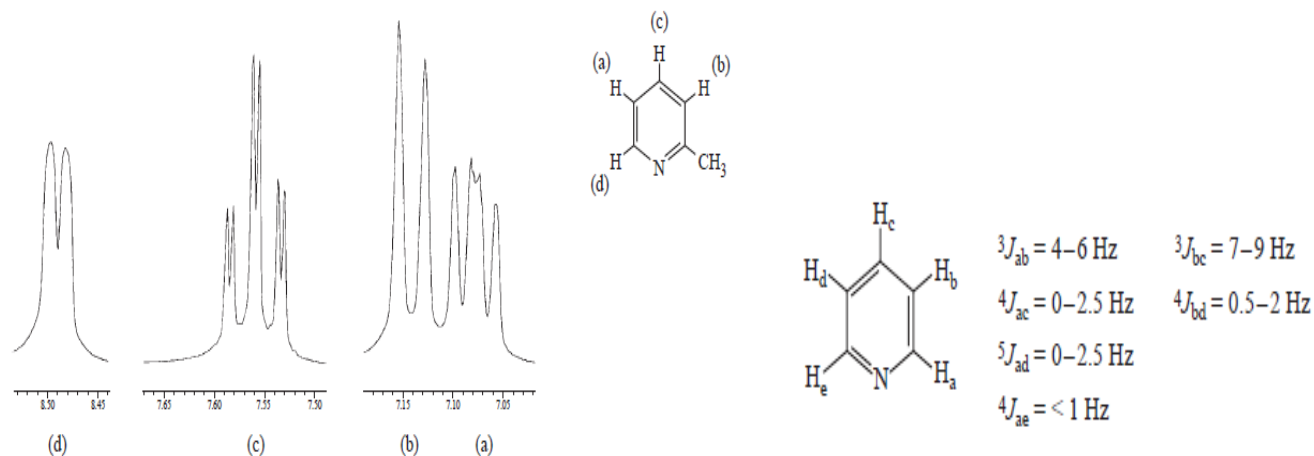
$H_c = 7.36$ ppm (dd); ${}^3J_{bc} = 1.9$ Hz and ${}^4J_{ac} = 0.9$ Hz.

The CH_2 and OH groups are not shown in the spectrum.

2-picoline (2-methylpyridine)

The methyl resonance is not included.

Typical values of coupling constants for a pyridine ring are different from the analogous couplings in benzene:



2-Methylpyridine:

$H_a = 7.08$ ppm (dd); ${}^3J_{ac} = 7.4$ Hz and ${}^3J_{ad} = 4.8$ Hz.

$H_b = 7.14$ ppm (d); ${}^3J_{bc} = 7.7$ Hz and ${}^4J_{ab} \cong 0$ Hz.

$H_c = 7.56$ ppm (ddd or td). This pattern is a likely accidental triplet of doublets because ${}^3J_{ac} \cong {}^3J_{bc}$ and ${}^4J_{cd} = 1.8$ Hz.

$H_d = 8.49$ ppm (“doublet”). Because of the broadened peaks in this pattern, it is impossible to extract the coupling constants. We expect a doublet of doublets, but ${}^4J_{cd}$ is not resolved from ${}^3J_{ad}$. The adjacent nitrogen atom may be responsible for the broadened peaks.