

Nuclear Magnetic Resonance spectroscopy

(Ref: Kemp, Pavia, Dyer, Silverstein-Webster, Clayden, Paula/Bruice, Solomons and others)

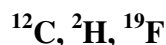
THEORY: NMR spectroscopy deals with those nuclei, which behave as a tiny magnet. Those nuclei which possess a mechanical spin or angular momentum would behave as a tiny magnet. Since a nucleus is associated with a (+) ve charge and so if it spins around its axis it would generate a magnetic field whose axis is coincident with the axis of its spin. The total angular momentum depends upon the nuclear spin or spin number (I), which may have values 0, 1/2, 1, 3/2, depending upon the particular nucleus. The numerical values of spin number I is related to the mass number and the atomic number as follows-

Type	Mass NO.	Atomic NO.	Spin NO.	e.g.
1.	odd	even or odd	1/2, 3/2, 5/2	$^1\text{H}_1$, $^{13}\text{C}_6$, $^{15}\text{N}_7$, $^{19}\text{F}_9$, $^{31}\text{P}_{15}$ all have $I = 1/2$ and $^{11}\text{B}_5$ has $I = 3/2$
2.	even	odd	1, 2, 3	$^2\text{H}_1$, $^{14}\text{N}_7$ have $I = 1$
3.	even	even	0	$^{12}\text{C}_6$, $^{16}\text{O}_8$

**** Note-** 1) Nuclei of the type 1 and 2 having $I \neq 0$ come under the preview of NMR spectroscopy.

2) Nuclei of the type having $I = 0$ cannot be studied by NMR.

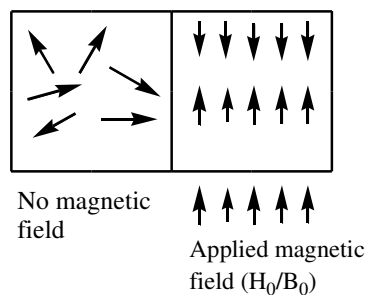
Q. Which of the following is / are not NMR active? Explain.



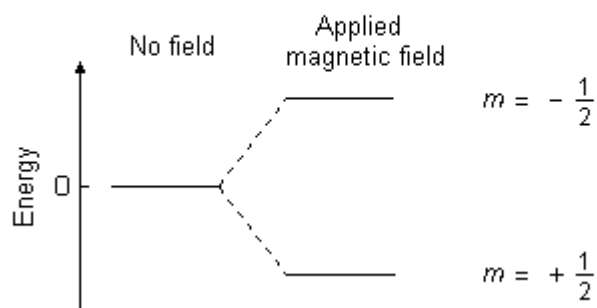
Ans. For ^{12}C ($^{12}\text{C}_6$) mass no. (12) and atomic no. (6), both are even. Hence spin no. (I) = 0 and the nuclei is NMR inactive

For ^2H ($^2\text{H}_1$) atomic no. (1) is odd and for ^{19}F ($^{19}\text{F}_9$) mass no. (19) is odd, hence spin no. (I) $\neq 0$ and so they are both NMR active.

****** When such a tiny nuclear magnet ($I \neq 0$) is placed in an external magnetic field, it takes up any of the possible orientations given by the relation $(2I+1)$. Each orientation being characterized by a definite energy level. Thus for hydrogen having $I = 1/2$, the number of such possible orientation, that the nuclear magnet can assume when placed in a uniform magnetic field is equal to $(2 \times 1/2 + 1) = 2$, one is a lower energy and the other is a higher energy level orientation. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number*, m .



Energy levels for a nucleus with spin quantum number 1/2

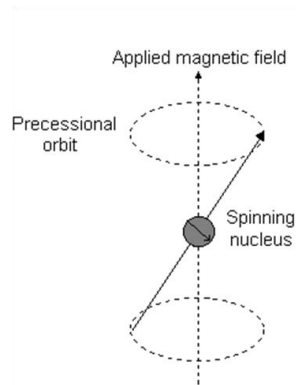


It is now possible to induce a transition from lower energy level to higher energy level by absorption of energy of appropriate frequency and corresponding to this absorption of energy, one gets an NMR signal for the nucleus.

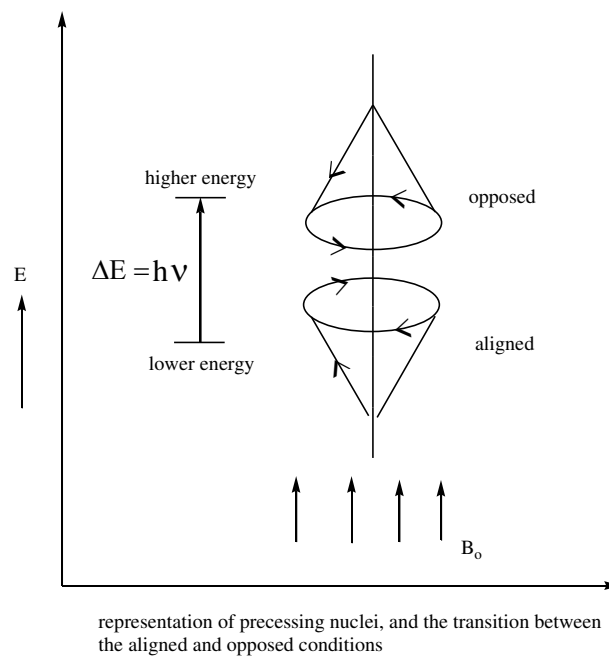
[** For $^2\text{D}_1$ and $^{14}\text{N}_7$, $I = 1$, so they can take up 3 orientations. These nuclei do not simply possess magnetic dipoles, rather possess electric quadrupoles. So they can interact both with magnetic and electric field gradients.]

Precessional motion

Unless the axis of the nuclear magnet is oriented exactly parallel or antiparallel with the applied magnetic field, there will be certain force by the external magnetic field to so orient it. But because the nucleus is spinning, the effect is that its rotational axis draws out a circle perpendicular to the applied field. This motion of the nucleus is called *precession*.

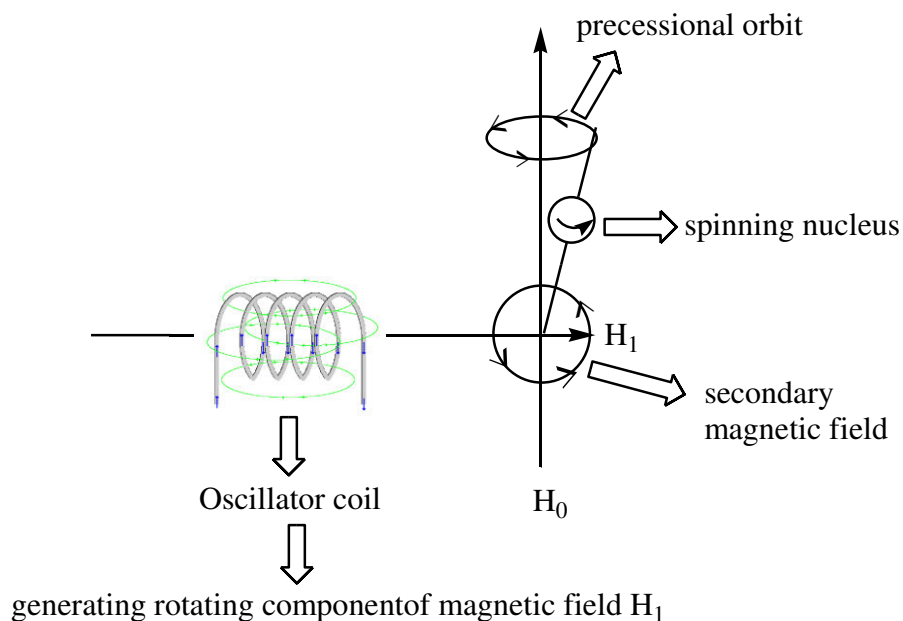


Thus as the proton is a spinning magnet it will precess around the axis of an external magnetic field and can do so in two principle orientations either aligned with the field (low energy) or opposed to the field (high energy).

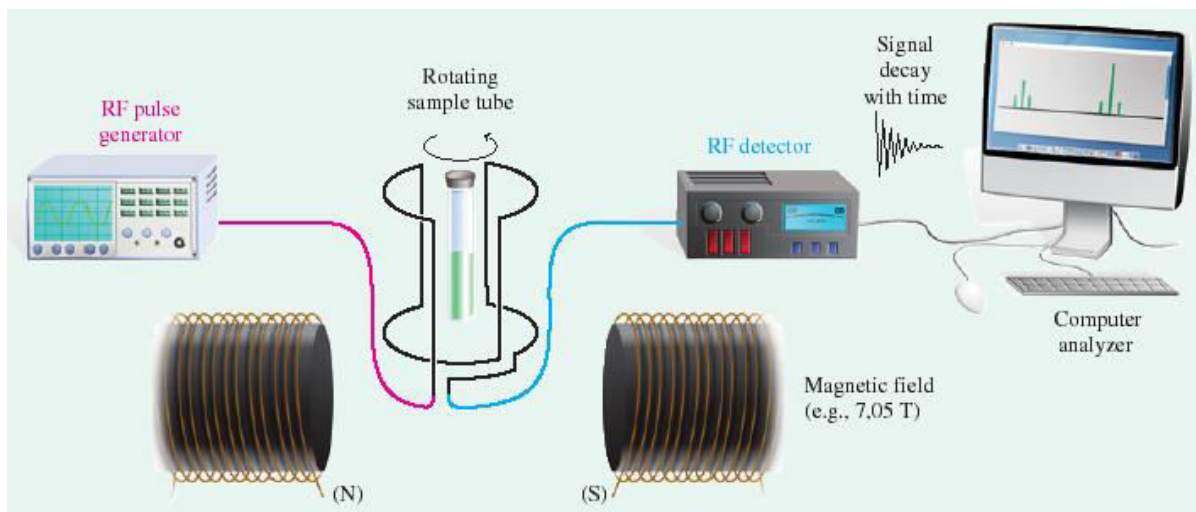


The act of turning over the nucleus from one orientation to the other can be brought about by the application of a secondary magnetic field H_1 in a direction perpendicular to the main magnetic field. Furthermore if this new magnetic field H_1 is to be continually effective, it must rotate in a plane perpendicular to the direction of H_0 in phase with the precessing nucleus. The secondary magnetic field is actually the magnetic vector component of electromagnetic radiation supplied by the radio frequency oscillator.

When the frequency of the rotating magnetic field H_1 becomes exactly equal to the precessional frequency of the nucleus, the precessional nucleus and the rotating magnetic field are said to be in resonance and the absorption of energy by the nucleus can occur.



*** The precessional frequency, ν , is directly proportional to the strength of the external magnetic field B_0 : that is, $\nu \propto B_0$. As an example, a proton exposed to an external magnetic field force of 1.4T (14000gauss) will precess 60 million times per second, so that $\nu = 60$ MHz. For an external field to 2.3T, $\nu = 100$ MHz, and so on (Tesla is a measure of magnetic flux density, not field strength)



*** Nuclei in the lower energy state undergo transitions to the higher energy state; the population of the two states may approach equality and if this arises no further net absorption of energy can occur, and the observed resonance signal will fade out. This situation is described as saturation of the signals. In the recording of a normal NMR spectrum, however, the populations in the two spin states do not become equal, because higher energy nuclei are constantly returning to the lower energy spin state.

Of great important factor, however, are two radiationless processes, which enable high energy to lose energy.

The high-energy nucleus can undergo energy loss (or relaxation) by transferring ΔE to some electromagnetic vector present in the surrounding environment. For example, a nearby solvent molecule, undergoing continuous vibrational and rotational changes, will have associated electrical and magnetic changes, which might be properly oriented and of the correct dimension to absorb ΔE . Since the nucleus may be surrounded by a whole array of the neighbouring atoms, either in the same molecule or in the solvent molecules, etc., this relaxation process is termed as spin lattice relaxation, where lattice implies the entire framework or aggregate of neighbours.

A second relaxation process involves transferring ΔE to a neighbouring nucleus, provided that the particular value of ΔE is common to both nuclei: this mutual exchange of spin energy is termed as spin spin relaxation. While one nucleus loses energy, the other nucleus gains energy, so that no net change in the populations of the two spin states is involved.

The mean half-life of spin-lattice relaxation process is designated as T_1 , and that of the spin spin relaxation process as T_2 . If T_1 and T_2 are small, then the lifetime of an excited nucleus is short and it has been found that this gives rise to very broad absorption lines in the NMR spectrum. If T_1 and T_2 are large, perhaps of the order of 1 second, then sharp spectral line arises.

For nonviscous liquids (and that includes solutions of solids in nonviscous solvents) molecular orientations are random and transfer of energy by spin lattice relaxation is inefficient. In consequence T_1 is large, and this is one reason why sharp signals are obtained in NMR studies on nonviscous systems.

The important relationship between relaxation times and line broadening can be understood qualitatively by using the uncertainty principle in the form $\Delta E \cdot \Delta t \approx h/2\pi$ or since $\Delta E = h \Delta \nu$, $\Delta \nu \cdot \Delta t \approx 1/2\pi$. If Δt is large (that is the lifetime of a particular energy state is large), $\Delta \nu$ must be small that is the uncertainty in the measured frequency must be small, so that there is very little *spread* in the frequency, and line widths are narrow). Conversely if Δt is small (fast relaxation) then $\Delta \nu$ must be large, and broad lines appear in the spectrum.

Q. Why ^{14}N -H peak appears as broad peak in PMR spectroscopy?

Ans. The ^{14}N nucleus possesses an electrical quadrupole moment and is therefore able to interact with both electric and magnetic field gradients, which causes the nucleus to tumble rapidly; spin lattice relaxation is highly effective and therefore T_1 is small, NMR signals for the ^{14}N nucleus are very broad indeed, and for the same reason the NMR signals for the most protons attached to ^{14}N (in N-H groups) are broadened.

Q. What do you mean by chemical shift?

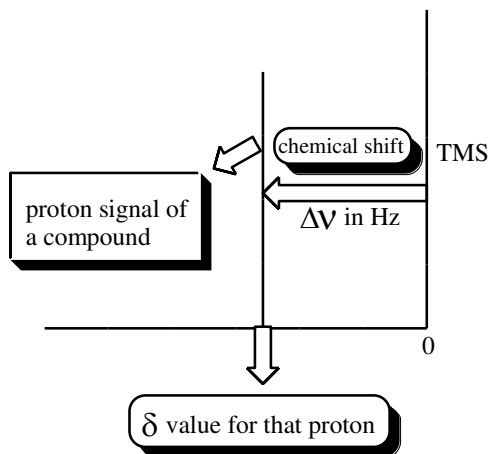
Ans. Absolute resonance frequencies of nuclei are difficult to measure. However relative proton resonance frequencies can be easily determined. The separation of resonance frequencies of nuclei in different structural environment from that of arbitrary chosen standard is termed as the chemical shift or relative resonance frequency.

*** Since chemical shifts are always very small (typically < 5000 Hz) compare to the total field strength (commonly the equivalent of 60, 300, 600 etc. million Hz), it is convenient to express this fractions in units of parts per million (ppm). This is origin of the delta scale (δ) for the expression of chemical shifts relative to TMS (tetramethyl silane- Me_4Si).

$$\delta = \frac{(\text{Observed shift from TMS in Hz}) \times 10^6}{(\text{Operating frequency of the instrument in Hz})}$$

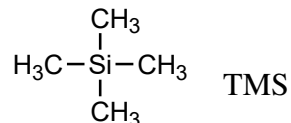
δ value remains always fixed for a particular type of proton whichever instrument (60 or 300 or 600 MHz) is used.

The resonance frequency of the protons of TMS, used as an internal standard, is arbitrarily taken as zero. The chemical shift of a proton of an organic compound is given by the separation of its signal from that of the TMS signal.



Q. Why TMS is chosen as an internal standard or reference compound in NMR?

Ans.



- i) Because of high electropositive nature of Si, it enhances the electron density toward the methyl groups. As a result the protons of the methyl groups become most shielded and the corresponding ^1H NMR signal occurs at highest upfield range than any other normal organic compounds.
- ii) Here all the methyl hydrogens are equivalent. So we get just one peak for one type of hydrogen for TMS. If the hydrogens are different then more than one signal will be observed in the printed spectra, which may lead ambiguity
- iii) Except D_2O or H_2O it is soluble in almost any other organic solvents.
- iv) It is chemically inert and has low boiling point. So recovery of the sample is easier after taking the NMR spectra.

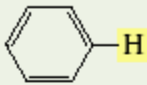
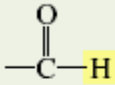
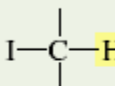
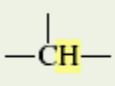
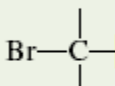
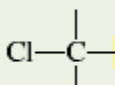
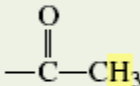
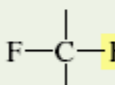
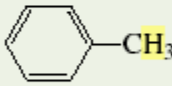
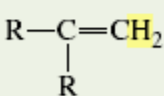
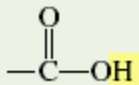
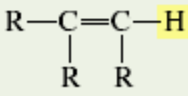
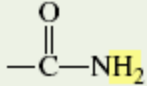
****In case of D_2O or H_2O , sodium salt of 3-(trimethylsilyl)-propanesulphonic acid is used.**



****Sometimes τ units are used instead of δ units**

$$\tau = 10 - \delta$$

Approximate Values of Chemical Shifts for ^1H NMR^a

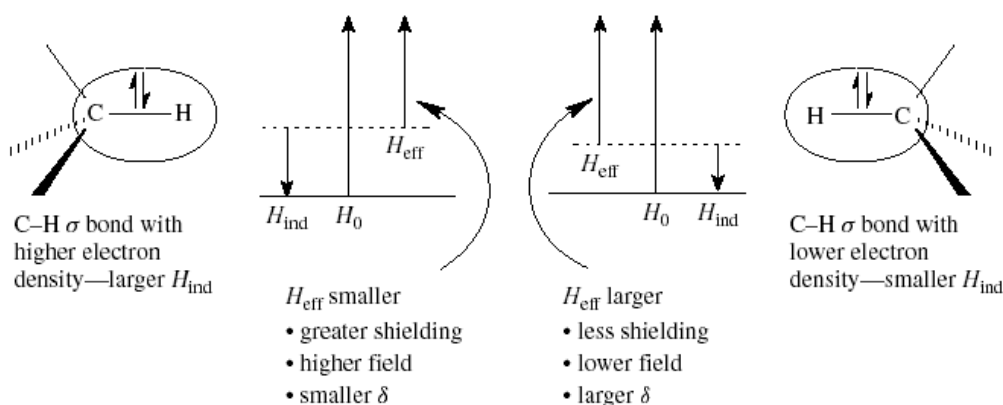
Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0		6.5–8
$-\text{CH}_3$	0.9		9.0–10
$-\text{CH}_2-$	1.3		2.5–4
	1.4		2.5–4
$-\text{C}=\text{C}-\text{CH}_3$	1.7		3–4
	2.1		4–4.5
	2.3	$\text{R}-\text{NH}_2$	Variable, 1.5–4
$-\text{C}\equiv\text{C}-\text{H}$	2.4	ROH	Variable, 2–5
$\text{R}-\text{O}-\text{CH}_3$	3.3	ArOH	Variable, 4–7
	4.7		Variable, 10–12
	5.3		Variable, 5–8

^aThe values are approximate because they are affected by neighboring substituents.

Factors influencing chemical shift

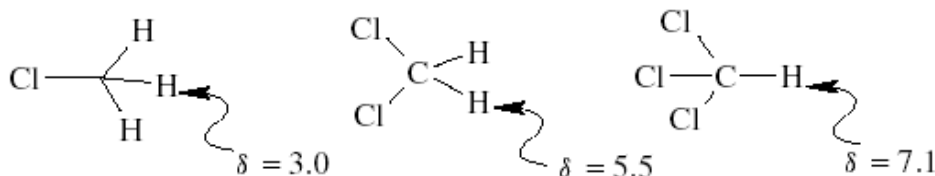
a) Electronegativity-shielding and deshielding: -

With a method available to measure differences in chemical shifts between protons, it is appropriate to ask why different protons experience different H_{eff} 's even though a single B_0 is applied to the sample. The explanation lies in the fact that nuclei are surrounded by electron clouds. In the applied field B_0 , electron pairs in bonds surrounding the hydrogens act to counter the applied field by induced fields (H_{ind}). The result is that the nucleus is shielded from the applied field by its electron cloud. (Nuclei, which are more shielded, come at higher fields and have lower chemical shifts.) Thus it is the electron density around the nucleus, which shields the nucleus from the applied field. It follows that the greater the electron density around a proton, the larger will be the induced field H_{ind} and that proton will be more shielded. It will appear more upfield and will have a smaller chemical shift (δ value). Conversely the lower the electron density around a proton, the less shielded it will be, the more downfield it will be, and it will have a larger δ value.

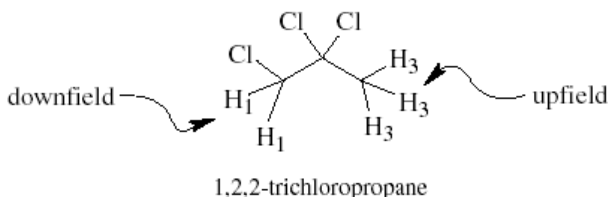


Changes in chemical shift due to electron density around the proton.

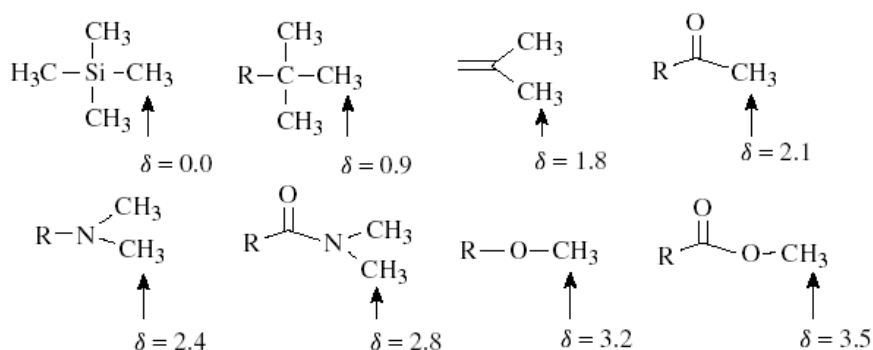
Structural features, which withdraw electrons from protons, cause downfield shifts and larger δ values, while structural features, which increase electron density around protons, cause upfield shifts and lower δ values. For example, chemical shifts for methyl chloride, dichloromethane, and chloroform are $\delta = 3.0$, $\delta = 5.5$, and $\delta = 7.1$, respectively. The inductive effects of increasing numbers of chlorine atoms decrease the electron density about the hydrogens and result in increasing chemical shifts.



Likewise 1,2,2-trichloropropane discussed previously has the two-proton signal downfield from the three-proton signal. This is because the methylene protons are influenced by the inductive effects of three chlorine atoms, two vicinal and one geminal, while the methyl group is influenced by only two vicinal chlorine atoms. The electron density is higher at the methyl hydrogens, which are more shielded and occur at higher fields than the two protons of the methylene group.



Consideration of a series of compounds containing methyl groups illustrates clearly the influence of the electron density on chemical shift. As the electron-withdrawing ability of groups attached to the methyl group increase, progressive downfield shifts are evident and δ values increase. Conversely TMS comes very far upfield because silicon-carbon bonds are polarized toward carbon and result in very high electron density about the methyl hydrogens of TMS.



Q. Arrange the following halides in order of increasing chemical shift (δ values) of the α -protons with explanation.



Ans. The explanation lies in the fact that nuclei are surrounded by electron clouds. In the applied field B_0 , electron pairs in bonds surrounding the hydrogens act to counter the applied field by induced fields (H_{ind}). It follows that the greater the electron density around a proton, the larger will be the induced field H_{ind} and that proton will be more shielded. It will appear more upfield and will have a smaller chemical shift (δ value). Conversely the lower the electron density around a proton, the less shielded it will be, the more downfield it will be, and it will have a larger δ value.

F is most electronegative and iodine is least, so the marked protons will be least shielded in (A) and most in (D) with successive decrease in electronegativities of the halogens. Hence the order of increasing chemical shift (δ values) of the α -protons will be (A) > (B) > (C) > (D).

Same answer

Q. What differences in chemical shift values are expected for the protons of CH_3F , CH_3Cl and CH_3Br and why?

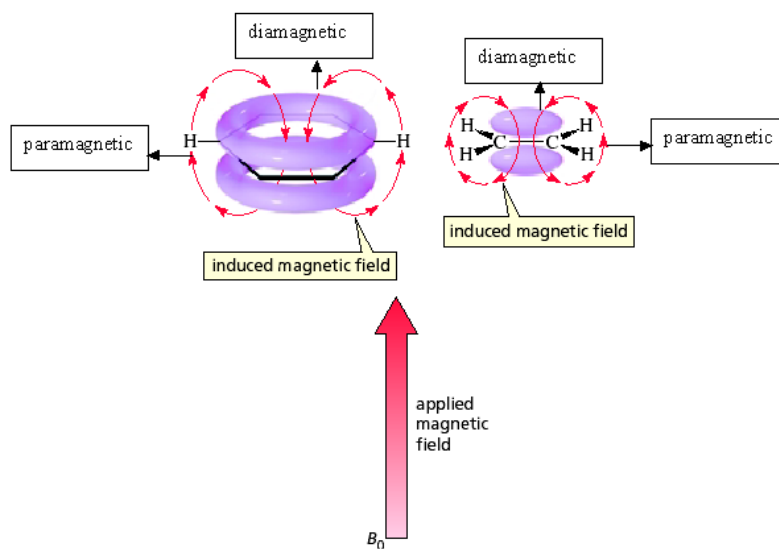
Q. Explain the terms i) downfield and ii) upfield shifts in NMR spectroscopy.

b) Anisotropic effect

The chemical shifts of hydrogens bonded to sp^2 hybridized carbons are at a higher frequency than one would predict, based on the electronegativity of the sp^2 carbons. For example, a hydrogen bonded to a terminal sp^2 carbon of an alkene appears at 4.7 ppm, a hydrogen bonded to an internal sp^2 carbon appears at 5.3 ppm, and a hydrogen on a benzene ring appears at 6.5–8.0 ppm.

The unusual chemical shifts associated with hydrogens bonded to sp^2 carbons that form bonds are due to *anisotropy*. **Anisotropy** describes an environment in which different magnetic fields are found at different points in space. Because π electrons are less tightly held by nuclei than are σ electrons, π electrons are more free to move in response to a magnetic field. When a magnetic field is applied to a compound with π electrons, the π electrons move in a circular path. This electron motion causes an induced magnetic field. How this induced magnetic field affects the chemical shift of a proton depends on the direction of the induced magnetic field—in the region where the proton is located—relative to the direction of the applied magnetic field.

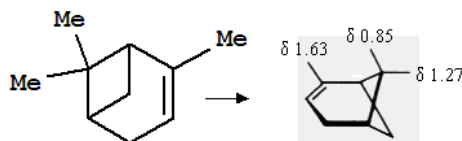
The magnetic field induced by the π electrons of a benzene ring—in the region where benzene's protons are located—is oriented in the same direction as the applied field. The magnetic field induced by the π electrons of an alkene—in the region where the protons bonded to the sp^2 carbons of the alkene are located—is also oriented in the same direction as the applied field. Thus, in both cases, the protons sense a larger effective magnetic field—the sum of the strengths of the applied field and the induced field. Because frequency is proportional to the strength of the magnetic field experienced by the protons, the protons resonate at higher frequencies (downfield region- higher δ value, paramagnetic anisotropy) than they would have if the π electrons had not induced a magnetic field.



Any group held above or below the plane of the double bond will experience a shielding effect, since in these areas the induced field opposes B_0 . So here diamagnetic anisotropic effect will shift the proton to upfield region (lower δ value, diamagnetic anisotropy).

Some examples

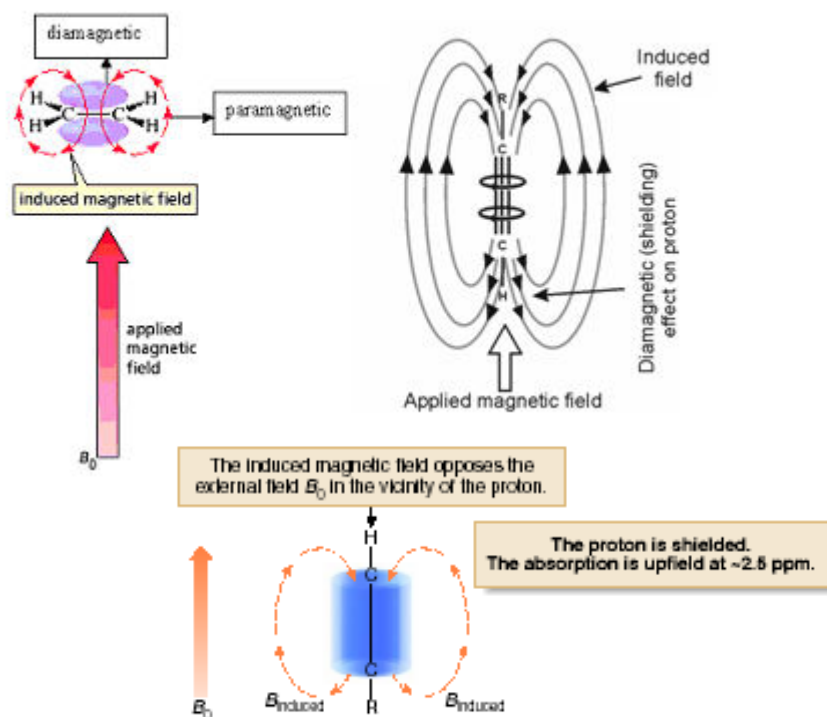
**In α pinene one of the geminal methyl groups is held in just such a shielded position, and comes to resonance at significantly lower δ value (upfield) than its twin. The third methyl group appears at higher δ value (downfield) since it lies in the plane of the double bond and is thus deshielded (paramagnetic anisotropic effect)



Q. Why do acetylenic protons resonate at upfield region with respect to ethlenic protons though acetylenic hydrogens are more acidic than ethylenic hydrogens?

Ans. The unusual chemical shifts associated with hydrogens bonded to sp^2 carbons that form bonds are due to *anisotropy*. The magnetic field induced by the π electrons of an alkene—in the region where the protons bonded to the sp^2 carbons of the alkene are located—is also oriented in the same direction as the applied field. Thus, the protons sense a larger effective magnetic field—the sum of the strengths of the applied field and the induced field. Because frequency is proportional to the strength of the magnetic field experienced by the protons, the protons resonate at higher frequencies (downfield region- higher δ value, paramagnetic anisotropy) than they would have if the π electrons had not induced a magnetic field.

But alkyne protons appear at comparatively much lower δ value (upfield region). When the axis of the alkyne group lies parallel to the direction of applied field, the cylindrical sheath of π electrons is induced to circulate around the axis, and the resultant annulus shaped magnetic field acts in a direction that opposes B_0 in the vicinity of the protons. Higher B_0 values are needed to bring the protons to resonance, therefore acetylenic protons appear at low δ values in the spectrum.



Q. Acetylenic protons appear at lower δ value than ethylenic protons despite the higher electronegativity of acetylenic carbons than ethylenic carbons. Explain.

Q. Aromatic protons are more deshielded than ethylenic protons, although both the types of protons are attached to sp^2 -hybridised carbon atoms-explain.

Ans. The unusual chemical shifts associated with hydrogens bonded to sp^2 carbons that form bonds are due to *anisotropy*. **Anisotropy** describes an environment in which different magnetic fields are found at different points in space. Because π electrons are less tightly held by nuclei than are σ electrons, π electrons are more free to move in response to a magnetic field.

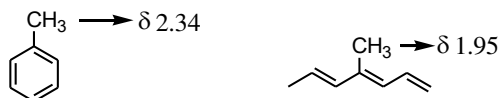
The magnetic field induced by the π electrons of a benzene ring and ethylene is oriented in the same direction as the applied field. Thus, in both cases, the protons sense a larger effective magnetic field—the sum of the strengths of the applied field and the induced field. Because frequency is proportional to the strength of the magnetic field experienced by the protons, the protons resonate at higher frequencies (downfield region- higher δ value, paramagnetic anisotropy) than they would have if the π electrons had not induced a magnetic field.

The greater deshielding influence of the ring current in aromatic compounds (paramagnetic anisotropic effect) is due to cyclically delocalised π electrons which has much pronounced effect compared to the deshielding of ethylene having no cyclic delocalisation).

Draw the picture

Q. Compare the δ values of methyl protons of toluene and 4-methyl-1,3,5- heptatriene?

Ans.

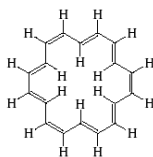


In toluene, the methyl protons resonate at higher ppm compared to that of methyl protons of 4-methyl-1,3,5-heptatriene. This is some measure of the greater deshielding influence of the ring current in aromatic compounds (paramagnetic anisotropic effect due to cyclically delocalised π electrons) compared to the deshielding of conjugated alkene groups (having no cyclic delocalisation)

Draw the picture

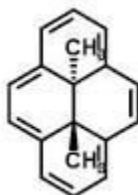
(*** Methyl protons are upfield compared to aromatic protons since they are separated from the ring current through linking with carbon atom and so enjoying paramagnetic deshielding effect in lesser amount compared to aromatic protons)

Q. [18]-Annulene shows two signals in its ^1H NMR spectrum: one at 9.25 ppm and the other very far upfield (beyond TMS) at -2.8 ppm. What hydrogens are responsible for each of the signals?



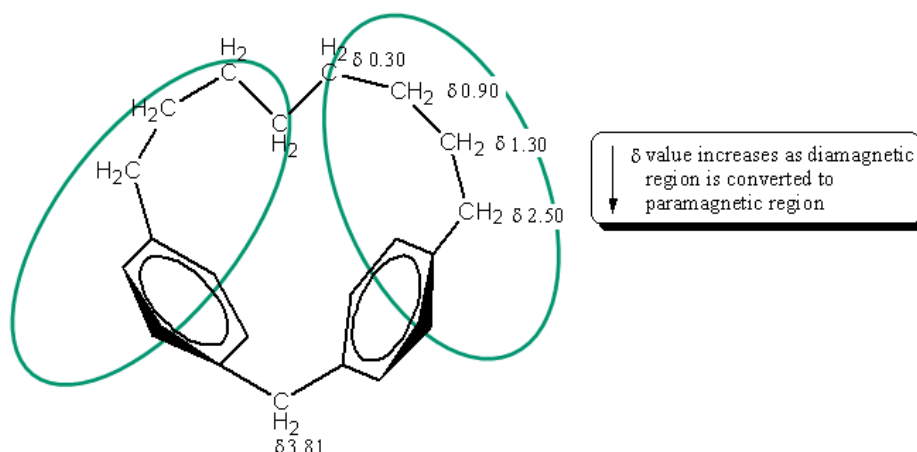
Hint: Notice the direction of the induced magnetic field outside (paramagnetic anisotropic effect) and inside (diamagnetic anisotropic effect) the benzene ring.

*** On of the most dramatic observations in NMR work on aromatic systems involves the dimethyl derivative of pyrene, in which the methyl protons appear at -4.2 ppm (far upfield than TMS).



This shows that the cyclic π electron system around the periphery of the molecule sustains a substantial ring current, and therefore indicates aromatic character in a nonbenzenoid ring system. The methyl groups are deep in the shielding zone of this ring current, and it is for this reason that they appear at such extraordinary δ value.

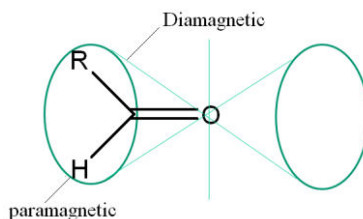
*** Any group that is sterically held above or below the plane of the aromatic nucleus will, obviously, be abnormally shielded because of the ring current effect (diamagnetic anisotropic effect).



The central methylene groups of [1,8] paracyclophane (an ansa compound) are shielded by about 1 ppm more than ordinary methylene groups because they are held rigidly above the plane of the benzene rings.

Q. Explain why aldehydic protons are highly deshielded?

Ans. The word "anisotropic" means "non-uniform". Magnetic anisotropy means that there is a "non-uniform magnetic field". Electrons in π systems (*e.g.* aromatics, alkenes, alkynes, carbonyls *etc.*) interact with the applied field, which induces a magnetic field that causes the anisotropy. As a result, the nearby protons will experience 3 fields: the applied field, the shielding field of the valence electrons and the field due to the π system. Depending on the position of the proton in this third field, it can be either shielded (smaller δ) or deshielded (larger δ).



Two cone shaped volumes, centered on oxygen atom, lie parallel to the axis of the C=O bond; protons within these cones experience deshielding due to the paramagnetic anisotropic effect, so that aldehydic protons (and the formyl protons of the formate esters, HCOOR) appear at high δ value (downfield region).

Similar case-

All the ring protons of acetophenone are deshielded because of the ring current effect. Moreover, the ortho protons are further deshielded (meta, para $\delta \sim 7.40$; ortho $\delta \sim 7.85$) because of the additional deshielding effect of the carbonyl group. In Figure , the carbonyl bond and the benzene ring are coplanar. If the molecule is oriented so that the applied magnetic field B_0 is perpendicular to the plane of the molecule, the circulating π electrons of the C=O bond shield the conical zones above and below them and deshield the lateral zones in which the ortho protons are located. Both ortho protons are equally deshielded since another, equally populated, conformation can be written in which the "left-hand" ortho proton is deshielded by the anisotropy cone. Nitrobenzene shows a similar effect.

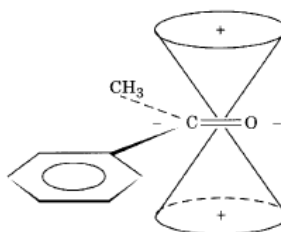


FIGURE . Shielding (+) and deshielding (–) zones of acetophenone.

Chemical Shift Equivalence

The concept of chemical shift equivalence is central to NMR spectrometry. Chemical-shift equivalent (isochronous) nuclei comprise a *set* within a *spin system*.

The immediate question is: Are selected nuclei in a molecule chemical shift equivalent, or are they not? If they are, they are placed in the *same set*. The answer can be framed as succinctly as the question: Nuclei are chemical shift *equivalent if they are interchangeable through any symmetry operation or by a rapid process*. This broad definition assumes an achiral environment (solvent or reagent) in the NMR experiment; the common solvents are achiral.

***Determination of Chemical
Shift Equivalence by Interchange
Through Symmetry Operations***

There are three symmetry operations: *rotation about a simple axis of symmetry* (C_n), *reflection through a plane of symmetry* (σ), and *inversion through a center of symmetry* (i). More rigorously, symmetry operations may be described under two headings: C_n and S_n . The latter is *rotation around an alternating axis of symmetry*. It turns out that S_1 is the same as σ , S_2 is the same as i , and higher subscripts for S_n are rare. We shall use C_n , σ , and i . The subscripts denote the number of such rotations required to make a 360° rotation. Thus C_1 is a 360° rotation, C_2 is a 180° rotation, etc. The designation S_1 requires a 360° rotation followed by a reflection through the plane at a right angle to the axis. S_2 requires a 180° rotation followed by a reflection, and so forth.

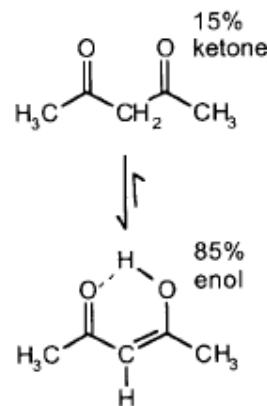
Homotopic and enantiotopic protons are chemical shift equivalence

Diastereotopic protons are chemical shift nonequivalence

Chemical Shift Equivalence by Rapid Interconversion of Structures

If chemical structures can interconvert, the result depends on temperature, catalyst, solvent, and concentration.

Keto–Enol Interconversion—The tautomeric interconversion of acetylacetone (Fig.) at room temperature is slow enough that the absorption peaks of both forms can be observed—i.e., there are two spectra. The equilibrium keto/enol ratio can be determined from the relative areas of the keto and enol CH₃ peaks, as shown. At higher temperatures the interconversion rate will be increased so that a single “averaged” spectrum will be obtained. Chemical shift equivalence for all of the interconverting protons has now been achieved.



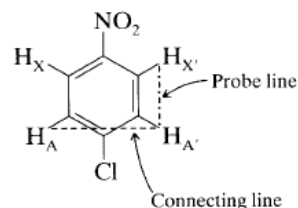
Magnetic Equivalence (Spin–Coupling Equivalence)

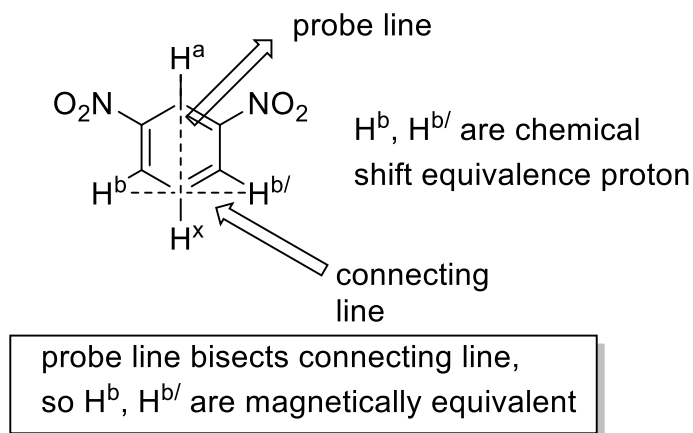
A further refinement involves the concept of *magnetic-equivalent* nuclei, also termed “spin–coupling equivalent nuclei”. If nuclei in the same set (i.e., chemical-shift equivalent nuclei) couple equally to any nucleus (probe nucleus) in the same spin system, they are magnetic equivalent.

Magnetic equivalence presupposes chemical shift equivalence. To determine whether chemical-shift equivalent nuclei are magnetic equivalent, geometrical relationships are examined. If the bond distances and angles from each nucleus in relation to the probe nucleus are identical, the nuclei in question are magnetic equivalent. In other words, two chemical-shift equivalent nuclei are magnetic equivalent if they are symmetrically disposed with respect to each nucleus (probe) in the same spin system. Magnetic-equivalent nuclei *couple identically* with any other nucleus in the same spin system; hence the synonymous term “spin–coupling equivalence”. Note that a test for magnetic equivalence is valid only when the *two nuclei are chemical shift equivalent*; that is, they are in the same set.

These rules are applied readily to conformationally restricted structures. Thus, in *p*-chloronitrobenzene (Fig.) the protons ortho to the nitro group (H_A and $\text{H}_{\text{A}'}$) are chemical shift equivalent to each other, and the protons ortho to the chlorine atom (H_X and $\text{H}_{\text{X}'}$) are chemical-shift equivalent to each other.

To test this conclusion, draw a line connecting H_A and $\text{H}_{\text{A}'}$, select $\text{H}_{\text{X}'}$ (or H_X) as a probe nucleus, then draw a probe line from the probe nucleus, at a right angle to the line connecting H_A and $\text{H}_{\text{A}'}$. If the probe line were to intersect the connecting line at midpoint, H_A and $\text{H}_{\text{A}'}$ would be magnetic equivalent. Obviously, they are not.

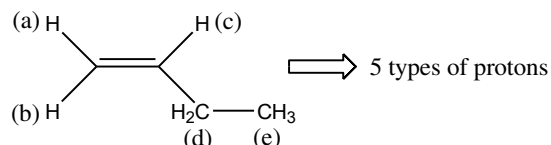




Q. What do you mean by magnetically equivalent and magnetically nonequivalent protons?

Q. How many kinds of non equivalent protons in 1-butene?

Ans.



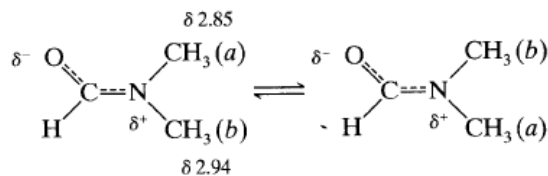
Q. Show with labels the expected number of signals in 2-bromopropane?

Q. Label the different types of magnetically non-equivalent hydrogens of the following compound and justify your answer: $CH_2=C(CH_3)C(CH_3)_3$

Q. “The methyl group of N,N-dimethyl formamide show two different signals”- explain?

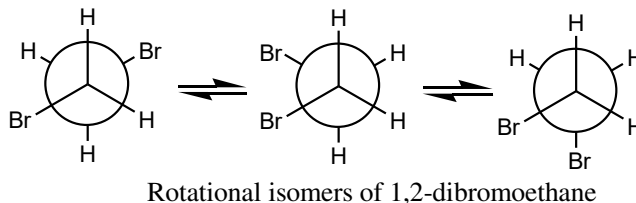
Ans.

Interconversion Around a “Partial Double Bond” (Restricted Rotation)—At room temperature, a neat sample of dimethylformamide shows two CH_3 peaks because the rate of rotation around the hindered “partial double bond” is slow. At $\sim 123^\circ C$, the rate of exchange of the two CH_3 groups is rapid enough so that the two peaks merge.



Q. Comment on the NMR signal(s) of 1,2-dibromoethane.

Ans. The four protons in 1,2-dibromoethane ($\text{BrCH}_2\text{CH}_2\text{Br}$) are chemically indistinguishable, and one might also suppose that they are magnetically equivalent; the Newmann diagram show clearly, however, the protons in the different conformations are not in magnetically equivalent environments.



If the NMR spectrum is recored at low temperature, the rapid molecular rotations around the C-C bond are 'frozen' and different signals should be found. Otherwise at elevated temperatures same time averaged environment leads to one type of signal.

Solvents used in NMR

To satisfy the condition that nonviscous samples give the sharpest NMR spectrum, it is usually necessary to record the spectra of organic compounds in solution.

Choice of solvent is not normally difficult, provided a solubility of about 10 percent is obtainable, but it is clearly an advantage to use aprotic solvents (which do not themselves give an NMR spectrum to superimpose on that of the sample).

Most common solvents \rightarrow CDCl_3 , $(\text{CD}_3)_2\text{SO}$ (DMSO-d_6)

Others \rightarrow CCl_4 , C_6D_6 , D_2O , $(\text{CD}_3)_2\text{CO}$

Q. Why a peak is observed at $\delta 7.3$ when CDCl_3 is used as solvent?

Ans. Greater isotopic impurity means greater cost. Commercially available CDCl_3 solvent for NMR study contains 1% CHCl_3 as impurity. So a peak at $\delta 7.3$ appears for the hydrogen of CHCl_3 in PMR. But simplicity of the peak does not lead to ambiguity too much unless coalesces with the peak(s) of the sample compound (specifically aromatic protons).

(Same case occurs for $\text{DMSO-d}_6 \rightarrow$ peak appears at $\sim \delta 3$ for isotopic impurity coming from $(\text{CH}_3)_2\text{SO}$)

Q. Can CHCl_3 be used as a solvent in ^1H NMR study?

Ans. CHCl_3 itself contains proton that appears at $\delta 7.3$ in PMR spectra. So there is a possible chance that this NMR signal will superimpose with that of the proton(s) of the sample (specifically aromatic protons) and that is why it cannot be used as NMR solvent.

Q. “The NMR spectrum of chloroform dissolved in cyclohexane appears at $\delta 7.3$, but in benzene solution it is $\delta 1.56$ ”- why?

Ans. The NMR signals for protons attached to carbon are, in general, shifted only slightly by changing solvent, except where significant bonding or dipole-dipole interaction might arise; the NMR spectrum for CHCl_3 dissolved in cyclohexane appears at $\delta 7.3$, but in benzene solution the signal is moved upfield by the exceptionally large amount of $\delta 1.56$ (to $\delta 6.74$). Benzene is behaving as a Lewis base to CHCl_3 , and considerable charge transfer is responsible for altering electron density around the CHCl_3 proton, with concomitant upfield shift in the signal.

Q. How the positions of the X-H (X=O, N, S etc.) protons will shift on changing the solvents?

Ans. The positions of the X-H protons move significantly to different region on changing the solvents of different polarity.

This effect is largely associated with hydrogen bonding and it is noted even when different concentrations are used in the same solvent.

At low concentrations, intermolecular hydrogen bonding is diminished in simple OH, NH, and SH compounds: since hydrogen bonding involves electron cloud transfer from the hydrogen atoms to a neighbouring electronegative atom (O, N, S). The hydrogen experiences a net deshielding effect when hydrogen bonding is strong, and is less deshielded when hydrogen bonding is diminished. Thus, at high concentrations (strong hydrogen bonding, strong deshielding) OH, NH and SH protons appear at higher δ than in dilute solutions.

Signal splitting : spin-spin splitting

Signal splitting arises from a phenomenon known as spin spin coupling. Spin-spin coupling effects are transferred primarily through bonding electrons and lead to spin spin splitting.

The most common occurrence of coupling is between hydrogen atoms on adjacent carbons (vicinal hydrogens), where separation between the hydrogens is by three σ bonds. Such coupling is called vicinal coupling.

Hydrogens bonded to the same carbon (geminal hydrogens) can also couple, but only if they are diastereotopic.

Long range coupling can be observed over more than three bond lengths in very rigid molecules such as bicyclic compounds, and in systems where π bonds are involved.

**** Vicinal coupling**

Vicinal coupling generally follows the (n+1) rule, except when diastereotopic hydrogens or conformationally restricted systems are involved.

Q. Where signal splitting would not be observed?

Ans. In general signal splitting is not observed for protons that are chemical shift equivalent (homotopic) or enantiotopic. e.g. $\text{CH}_3\text{-CH}_3$, just one signal.

**** Splitting tree diagrams and the origin of signal splitting**

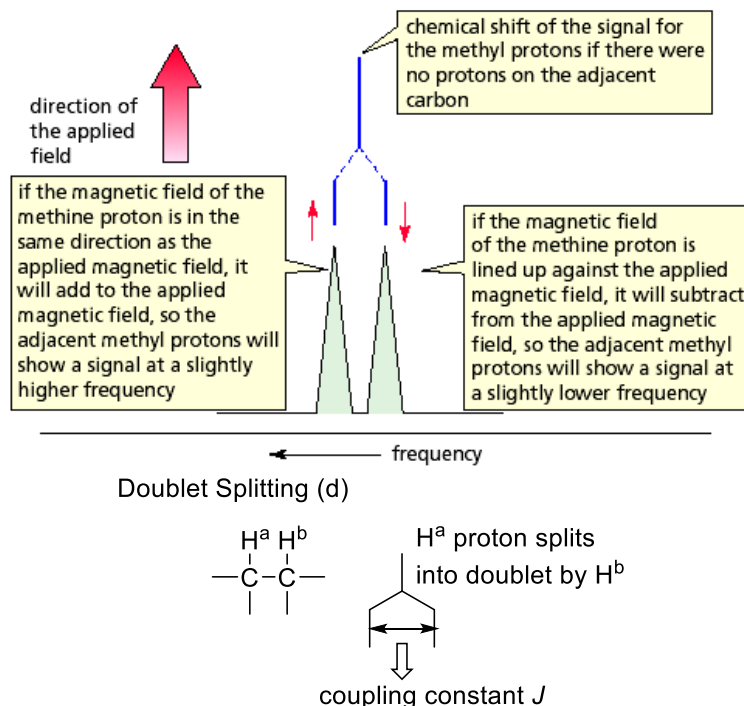
Signal splitting is caused by the magnetic effect of protons that are nearby and nonequivalent to those protons producing a given signal. Nearby protons have magnetic moments that can either add to or subtract from the magnetic field around the proton being observed. This effect splits the energy levels of the protons whose signal is being observed into a signal with multiple peaks.

The origin of the signal splitting can be illustrated by using splitting tree diagrams and by showing the possible combinations of magnetic moment alignments for the adjacent protons.

Splitting is caused by protons bonded to adjacent (i.e., directly attached) carbons. The splitting of a signal is described by the N+1 rule where *N* is the number of *equivalent* protons bonded to *adjacent* carbons. By “equivalent protons,” we mean that the protons bonded to an adjacent carbon are equivalent to each other, but not equivalent to the proton giving rise to the signal. The carbon adjacent to the methyl group in 1,1-dichloroethane is bonded to one proton, so the signal for the methyl protons is split into a doublet. The carbon adjacent to the carbon bonded to the methine proton is bonded to three equivalent protons, so the signal for the methine proton is split into a quartet. The number of peaks in a signal is called the **multiplicity** of the signal. Splitting is always mutual: If the *a* protons split the *b* protons, then the *b* protons must split the *a* protons. The methine proton and the methyl protons are an example of *coupled protons*. **Coupled protons** split each other's signal.

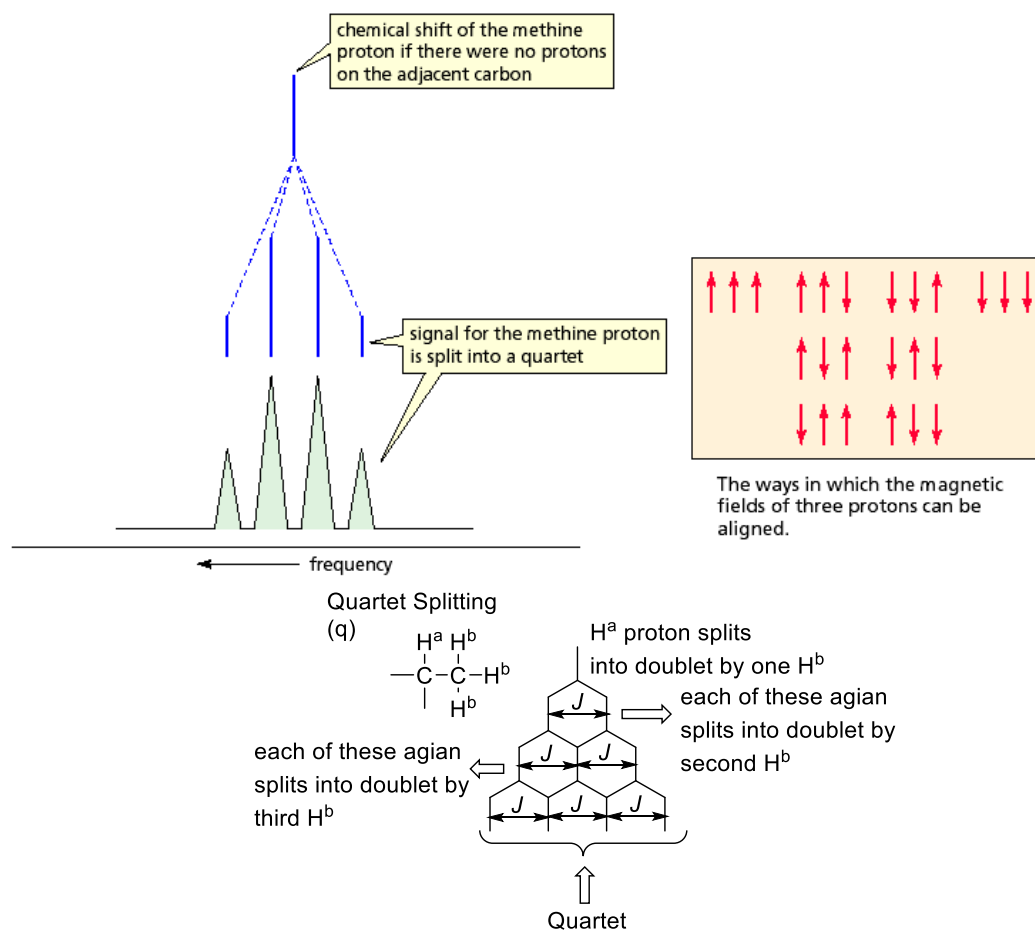
More specifically, the splitting of signals occurs when different kinds of protons are close enough for their magnetic fields to influence one another—called **spin-spin coupling**. For example, the frequency at which the methyl protons of 1,1-dichloroethane show a signal is influenced by the magnetic field of the methine proton. If the magnetic field of the methine proton aligns *with* that of the applied magnetic field, it will add to the applied magnetic field, causing the methyl protons to show a signal at a slightly higher frequency. On the other hand, if the magnetic field of the methine proton aligns *against* the applied magnetic field, it will subtract from the applied magnetic field and the methyl protons will show a signal at a lower frequency. Therefore, the signal for the methyl protons is

split into two peaks, one corresponding to the higher frequency and one corresponding to the lower frequency. Because each spin state has almost the same population, about half the methine protons are lined up with the applied magnetic field and about half are lined up against it. Therefore, the two peaks of the *doublet*(d) have approximately the same height and area.



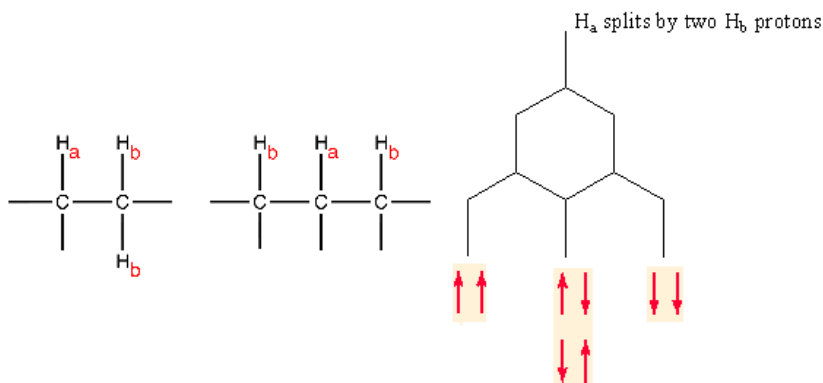
Similarly, the frequency at which the methine proton shows a signal is influenced by the magnetic fields of the three protons bonded to the adjacent carbon. The magnetic fields of each of the three methyl protons can align with the applied magnetic field, two can align with the field and one against it, one can align with it and two against it, or all three can align against it. Because the magnetic field that the methine proton senses is affected in four different ways, its signal is a *quartet*(q).

The relative intensities of the peaks in a signal reflect the number of ways the neighboring protons can be aligned relative to the applied magnetic field. For example, a quartet has relative peak intensities of 1 : 3 : 3 : 1 because there is only one way to align the magnetic fields of three protons so that they are all with the field and only one way to align them so that they are all against the field. However, there are three ways to align the magnetic fields of three protons so that two are lined up with the field and one is lined up against the field. Likewise, there are three ways to align the magnetic fields of three protons so that one is lined up with the field and two are lined up against it.



Splitting analysis for a triplet

Similarly the splitting of a proton into triplet can be explained.

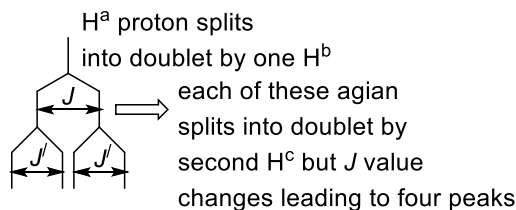
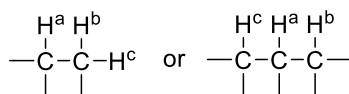
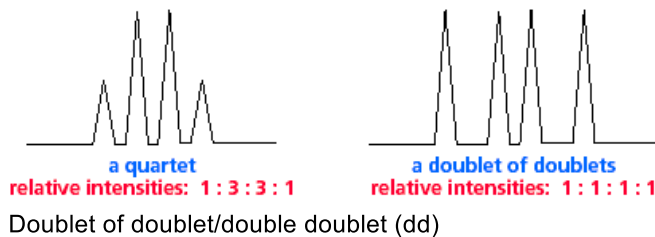


Important Note

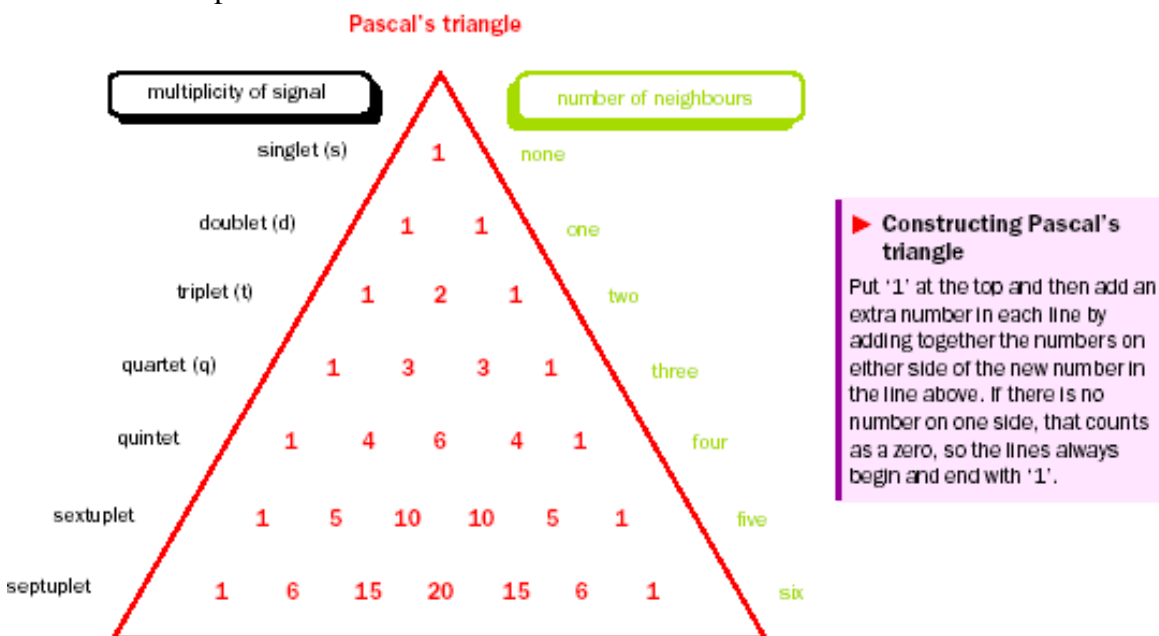
In this example both H_b hydrogens assumed to be homotopic or enantiotopic (chemical shift equivalent). If they are diastereotopic or otherwise chemical shift nonequivalent, each may have had a different coupling constant with H_a , and the splitting pattern would not have been a pure triplet (or not even a triplet at all). For example, if the two coupling

constants has been significantly different, the pattern would have been a doublet of doublets (written as 'dd') instead of triplet. Diastereotopic geminal hydrogens that couple with a vicinal hydrogen typically produce a 'dd'.

Notice the difference between a quartet and a doublet of doublets. Both have four peaks. A quartet results from splitting by *three equivalent* adjacent protons; it has relative peak intensities of 1 : 3 : 3 : 1, and the individual peaks are equally spaced. A doublet of doublets, on the other hand, results from splitting by *two nonequivalent* adjacent protons; it has relative peak intensities of 1 : 1 : 1 : 1, and the individual peaks are not necessarily equally spaced.



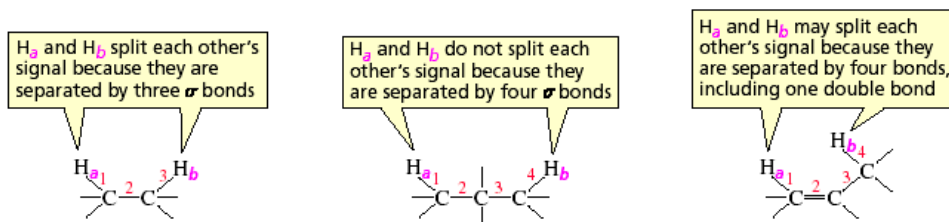
If there are more protons involved, we continue to get more complex systems, but the intensities can all be deduced simply from Pascal's triangle, which gives the coefficients in a binomial expansion.



Abbreviations used for style of signal

Abbreviation	Meaning	Comments
s	singlet	might be 'broad'
d	doublet	equal in height
t	triplet	should be 1:2:1
q	quartet	should be 1:3:3:1
dt	double triplet	other combinations too, such as dd, dq, tq...
m	multiplet	avoid if possible but sometimes necessary to describe complicated signals

***A signal for a proton is never split by *equivalent* protons. Normally, *nonequivalent* protons split each other's signal only if they are on *adjacent* carbons. Splitting is a "through-bond" effect, not a "through-space" effect; it is rarely observed if the protons are separated by more than three σ bonds. If, however, they are separated by more than three bonds and one of the bonds is a double or triple bond, a small splitting is sometimes observed. This is called **long-range coupling**.

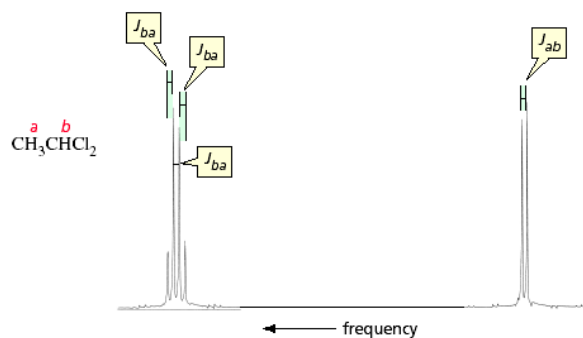


Coupling Constants

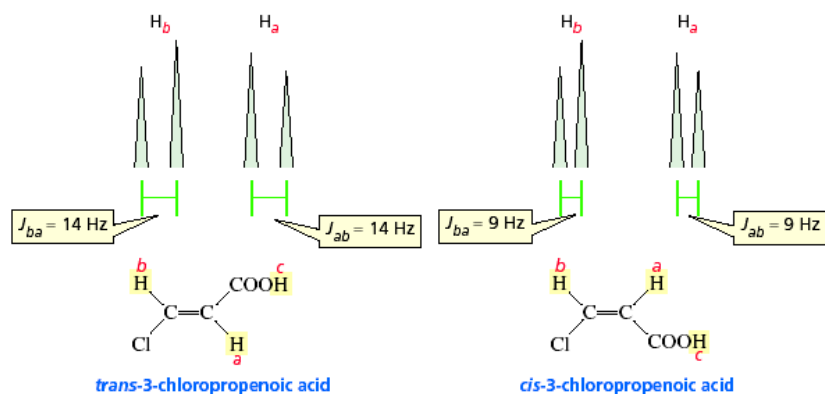
The distance, in hertz, between two adjacent peaks of a split NMR signal is called the **coupling constant** (denoted by J). The coupling constant for being split by is denoted by J . The signals of coupled protons (protons that split each other's signal) have the same coupling constants: in other words $J_{ab} = J_{ba}$. Coupling constants are useful in analyzing complex NMR spectra because protons on adjacent carbons can be identified by identical coupling constants.

The 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.

The coupling constant for two nonequivalent hydrogens on the *same* sp^2 carbon is often too small to be observed, but it is large for nonequivalent hydrogens bonded to *adjacent* sp^2 carbons. Apparently, the interaction between the hydrogens is strongly affected by the intervening π electrons. It has been observed that π electrons also allow long-range coupling—that is, coupling through four or more bonds.



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*).

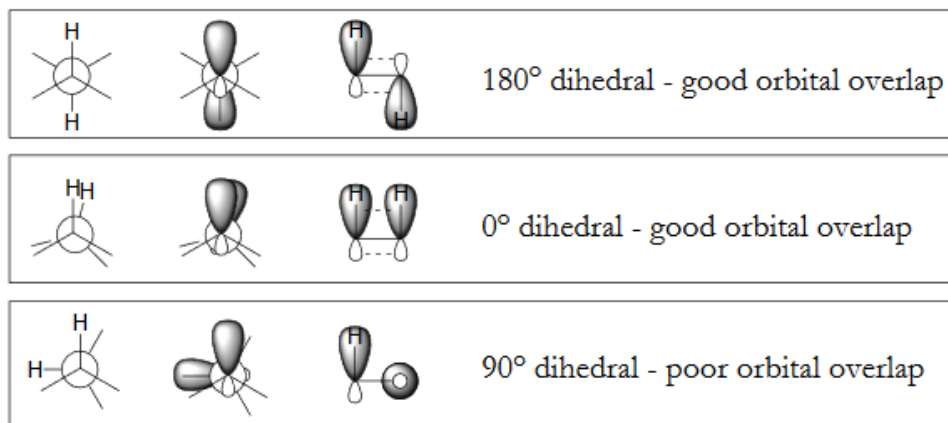


*** Coupling constant value depends on close proximity. Henceforth it is expected

$$J_{\text{gem}} (\text{one carbon separation}) > J_{\text{cis}} > J_{\text{trans}}$$

But actually reverse happens because too much closer proximity brings about the nodal plane of antibonding orbital to come closer and hamper the coupling.

But in general the highest coupling constants will occur between protons that have a dihedral angle of either 0° or 180°, and the lowest coupling constants will occur at 90°. This is due to orbital overlap – when the orbitals are at 90°, there is very little overlap between them, so the hydrogens cannot affect each other's spins very much.



*** **Calculation of coupling constant:**

When two protons couple to each other, they cause splitting of each other's peaks. The spacing between the peaks is the same for both protons, and is referred to as the coupling constant or *J* constant. This number is always given in hertz (Hz), and is determined by the following formula:

$$J \text{ Hz} = \Delta \text{ ppm} \times \text{instrument frequency}$$

Δ ppm is the difference in ppm of two peaks for a given proton.

Figure 1-1 below shows the simulated NMR spectrum of 1,1-dichloroethane, collected in a 30 MHz instrument. This compound has coupling between **A** (the quartet at 6 ppm) and **B** (the doublet at 2 ppm).

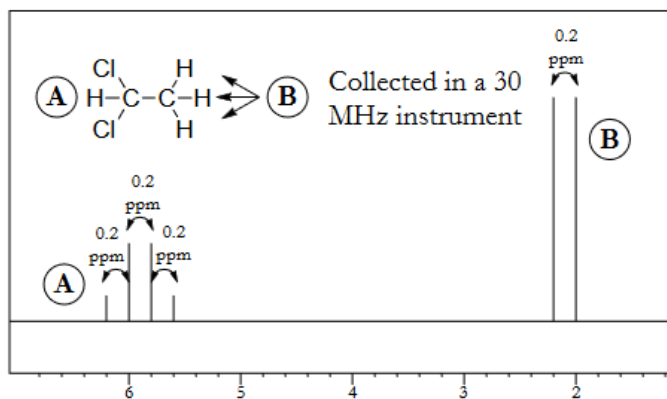


Figure 1-1: The NMR spectrum of 1,1-dichloroethane, collected in a 30 MHz instrument. For both A and B protons, the peaks are spaced by 0.2 ppm, equal to 6 Hz in this instrument.

For both **A** and **B**, the distance between the peaks is equal. In this example, the spacing between the peaks is 0.2 ppm (for example, the peaks for **A** are at 6.2, 6.0, 5.8, and 5.6 ppm). This is equal to a *J* constant of $(0.2 \text{ ppm} \cdot 30 \text{ MHz}) = 6 \text{ Hz}$. Since the shifts are given in ppm or parts per million, you should divide by 10^6 . But since the frequency is in megahertz instead of hertz, you should multiply by 10^6 . These two factors cancel each other out, making calculations nice and simple.

Figure 1-2 below shows the NMR spectrum of the same compound, but this time collected in a 60 MHz instrument.

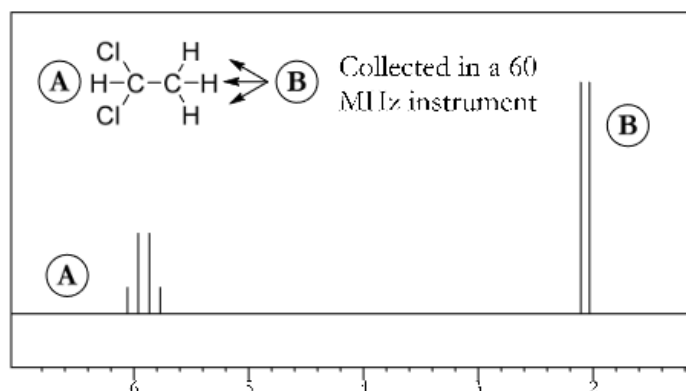
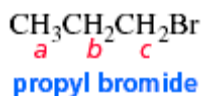


Figure 1-2: The NMR spectrum of 1,1-dichloroethane, collected in a 60 MHz instrument. For both A and B protons, the peaks are spaced by 0.1 ppm, equal to 6 Hz in this instrument.

This time, the peak spacing is 0.1 ppm. This is equal to a J constant of $(0.1 \text{ ppm} \cdot 60 \text{ MHz}) = 6 \text{ Hz}$, the same as before. This shows that the J constant for any two particular protons will be the same value in hertz, no matter which instrument is used to measure it.

Q. Comment on the NMR spectrum of propyl bromide.

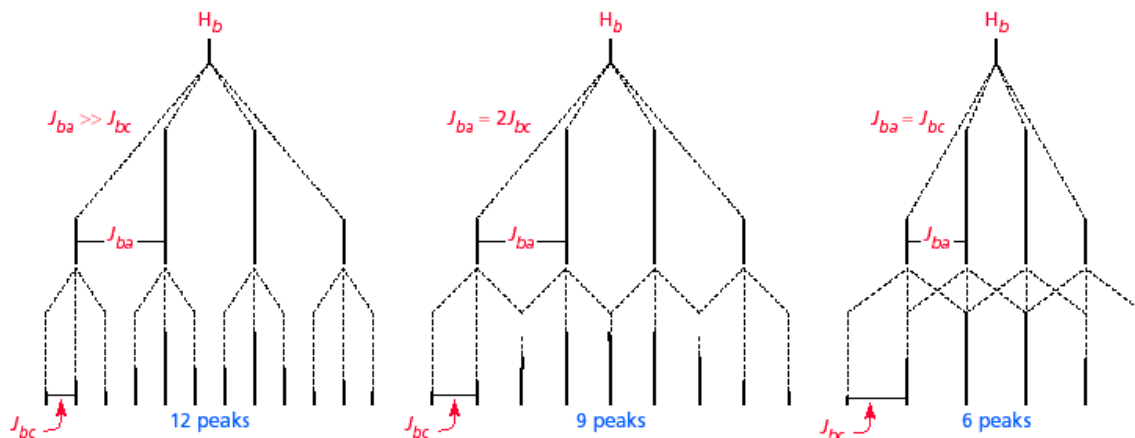
Hint-



The methyl protons (a type) and the c type protons will split into triplet as usual.

The signal for the H_b protons of propyl bromide is split into a quartet by the H_a protons, and each of the resulting four peaks is split into a triplet by the H_c protons.

How many of the 12 peaks are actually seen depends on the relative magnitudes of the two coupling constants, J_{ba} and J_{bc} . For example, the figure shows that there are 12 peaks when J_{ba} is much greater than J_{bc} , 9 peaks when $J_{ba} = 2J_{bc}$, and only 6 peaks when $J_{ba} = J_{bc}$. As you can see, the number of peaks actually observed depends on how many overlap with one another. When peaks overlap, their intensities add together.



A splitting diagram for a quartet of triplets. The number of peaks actually observed when a signal is split by two sets of protons depends on the relative magnitudes of the two coupling constants.

Typical coupling constants

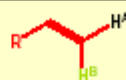
Geminal $^2J_{HH}$

saturated



10–16 Hz

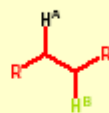
unsaturated



0–3 Hz

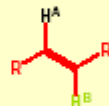
Vicinal $^3J_{HH}$

saturated



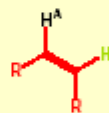
6–8 Hz

unsaturated *trans*



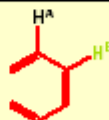
14–16 Hz

unsaturated *cis*



8–11 Hz

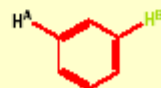
unsaturated aromatic



6–9 Hz

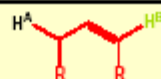
Long-range $^4J_{HH}$

meta



1–3 Hz

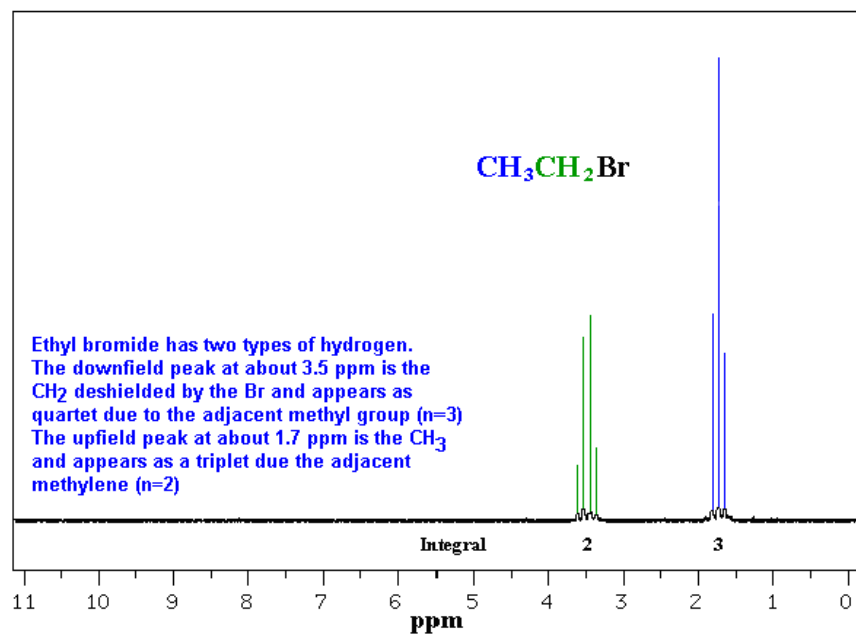
allylic



1–2 Hz

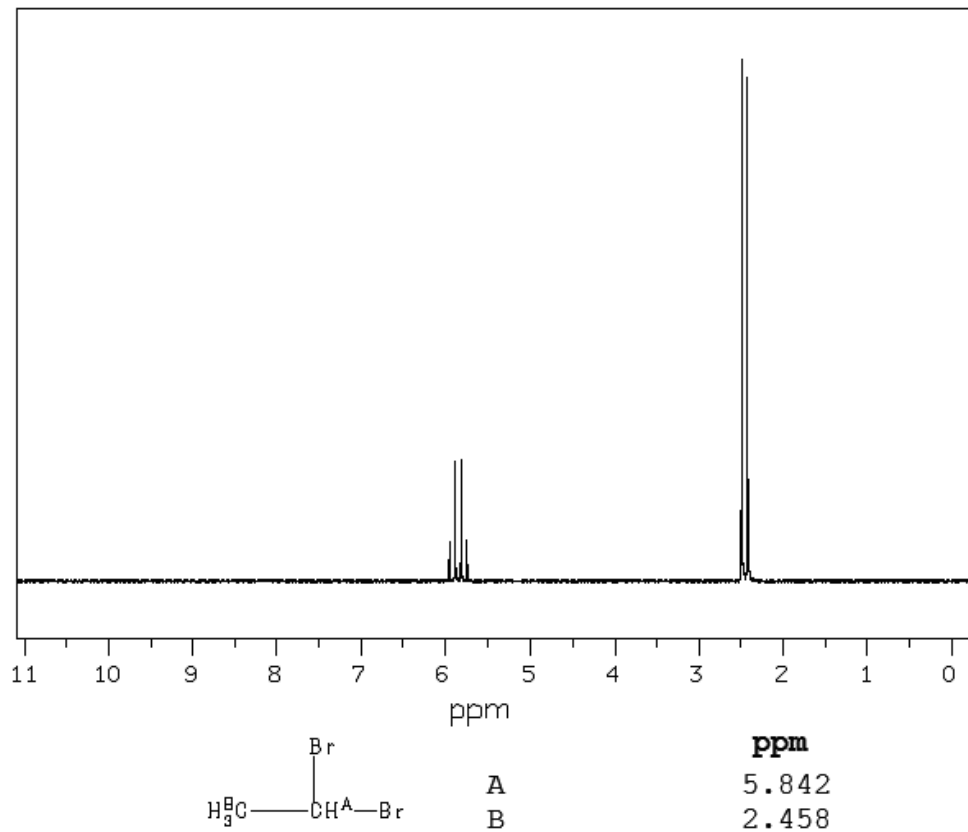
Several examples

1) Ethyl bromide

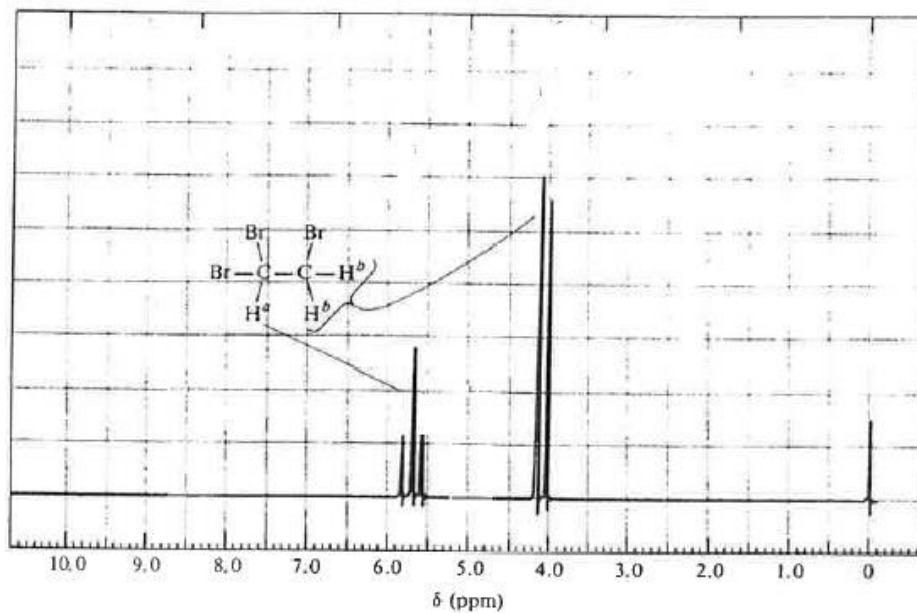


δ 1.7 (3H,t), δ 3.3 (2H,q)

2) 1,1-dibromoethane



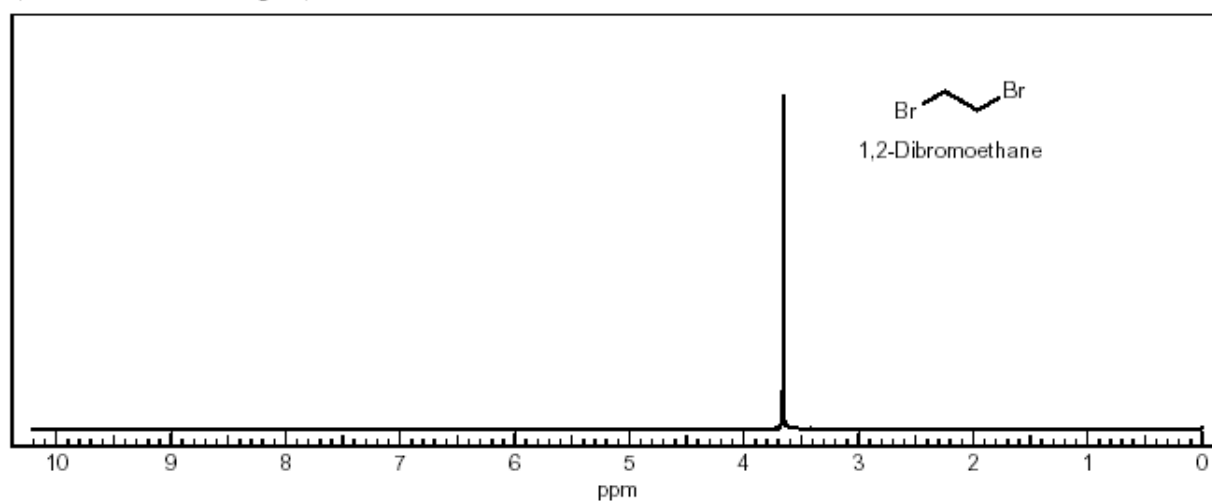
3) 1,1,2-tribromoethane



δ 4.2 (2H, d), δ 5.8 (1H, t)

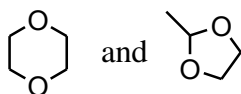
4) 1,2-dibromoethane

Protons that have the same chemical shift do not show spin-spin splitting. Thus the CH_2 groups of 1,2-dibromoethane are singlets,



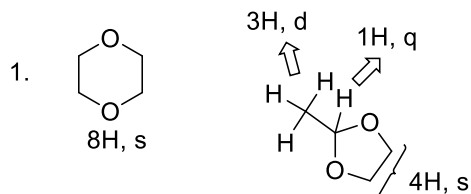
δ 3.7 (4H, s)

Q. Indicate the differences in the NMR spectrum of the followings

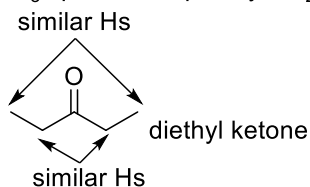


Q. How would you differentiate between di-tert-butyl ketone and diethyl ketone from ^1H NMR spectroscopy?

Q. Indicate, with reasons, how many PMR signals do you expect from each of the followings
i) di-tert-butyl ketone ii) R-2-chlorobutane.

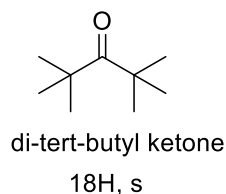


2. each CH_3 splits into triplet by CH_2



each CH_2 splits into quartet by CH_3

overall- 4H, q and 3H, t



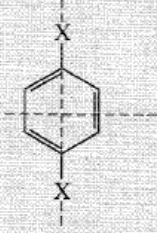
3. \Rightarrow diastereotopic Hs

- H1- splits into doublet by one H2 proton, (3H, d).
 H2- At first splits into quartet by three H1 protons, each of them further split into doublet by H3 proton, each of them further split into doublet by H4 proton, ultimately appear as multiplet (1H, m).
 Number of peaks (theoretically) = $(3+1)(1+1)(1+1) = 16$
 H3 - At first splits into quartet by three H5 protons, each of them further split into doublet by H4 proton, each of them further split into doublet by H2 proton, ultimately appear as multiplet (1H, m).
 Number of peaks (theoretically) = $(3+1)(1+1)(1+1) = 16$
 H4 - At first splits into quartet by three H5 protons, each of them further split into doublet by H3 proton, each of them further split into doublet by H2 proton, ultimately appear as multiplet (1H, m).
 Number of peaks (theoretically) = $(3+1)(1+1)(1+1) = 16$
 H5- splits into doublet by one H3 proton, each of them further splits into doublet by H4 proton (3H, dd).

Q. Distinguish between the compounds of the following pairs by NMR spectroscopy
 CH_3CHBr_2 and $\text{CH}_2\text{BrCH}_2\text{Br}$

AROMATIC COMPOUNDS—SUBSTITUTED BENZENE RINGS

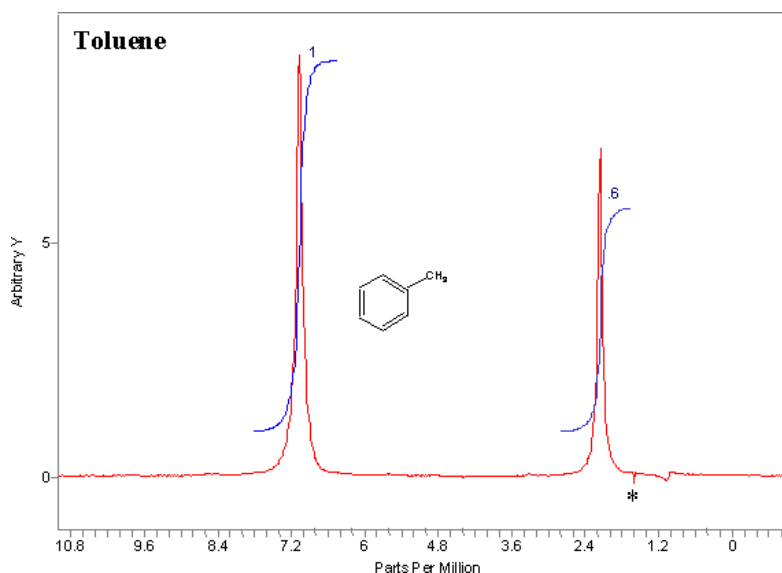
Phenyl rings are so common in organic compounds that it is important to know a few facts about NMR absorptions in compounds that contain them. In general, the ring protons of a benzenoid system have resonance near 7.3 ppm; however, electron-withdrawing ring substituents (e.g., nitro, cyano, carboxyl, or carbonyl) move the resonance of these protons downfield, and electron-donating ring substituents (e.g., methoxy or amino) move the resonance of these protons upfield.

¹ H CHEMICAL SHIFTS IN <i>p</i> -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
	<div> <div>Electron donating</div> <div>Electron withdrawing</div> </div>	

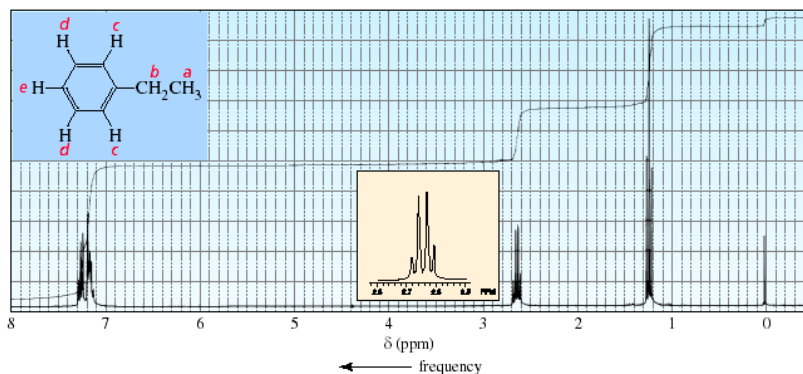
A. Monosubstituted Rings

Alkylbenzenes

In monosubstituted benzenes in which the substituent is neither a strongly electron-withdrawing nor a strongly electron-donating 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. A possible explanation is that the chemical shift differences, which should be small in any event, are somehow eliminated by the presence of the ring current, which tends to equalize them. All of the protons are nearly equivalent under these conditions.



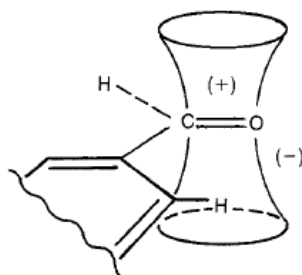
There are five sets of chemically equivalent protons in ethylbenzene. We see the expected triplet for the H_d protons and the quartet for the H_b protons. (This is a characteristic pattern for an ethyl group.) We expect the signal for the H_c protons to be a doublet and the signal for the H_e proton to be a triplet. Because the H_c and H_e protons are not equivalent, they must be considered separately in determining the splitting of the signal for the H_d protons. Therefore, we expect the signal for the H_d protons to be split into a doublet by the H_c protons and each peak of the doublet to be split into another doublet by the H_e proton, forming a doublet of doublets. However, we do not see three distinct signals for the H_c , H_d , and H_e protons in Figure . Instead, we see overlapping signals. Apparently, the electronic effect (i.e., the electron-donating/electron-withdrawing ability) of an ethyl substituent is not sufficiently different from that of a hydrogen to cause a difference in the environments of the H_c , H_d , and H_e protons that is large enough to allow them to appear as separate signals.



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).

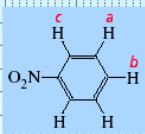
The actual NMR spectra of nitrobenzene and benzaldehyde do not have the appearances that would be predicted on the basis of resonance structures. Instead, the *ortho* protons are much more deshielded than the *meta* and *para* protons, due to the magnetic anisotropy of the π bonds in these groups.



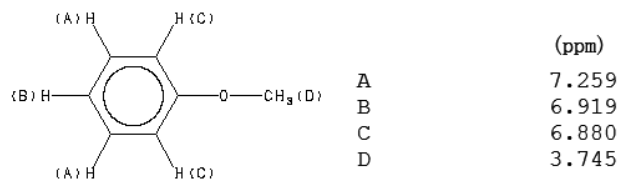
Anisotropic deshielding of the *ortho* protons of benzaldehyde.

In contrast to the H_c , H_d , and H_e protons of ethylbenzene, the H_a , H_b , and H_c protons of nitrobenzene show three distinct signals (Figure), and the multiplicity of each signal is what we predicted for the signals for the benzene ring protons in ethylbenzene (H_c is a doublet, H_b is a triplet, and H_a is a doublet of doublets). The nitro group is sufficiently electron withdrawing to cause the H_a , H_b , and H_c protons to be in different enough environments that their signals do not overlap.

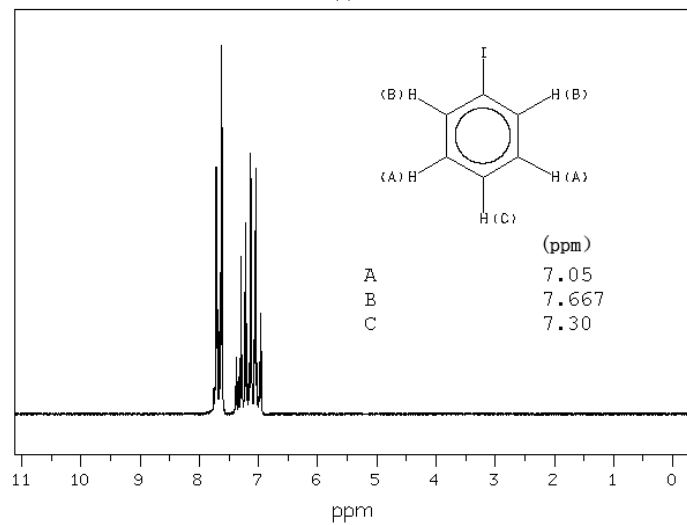
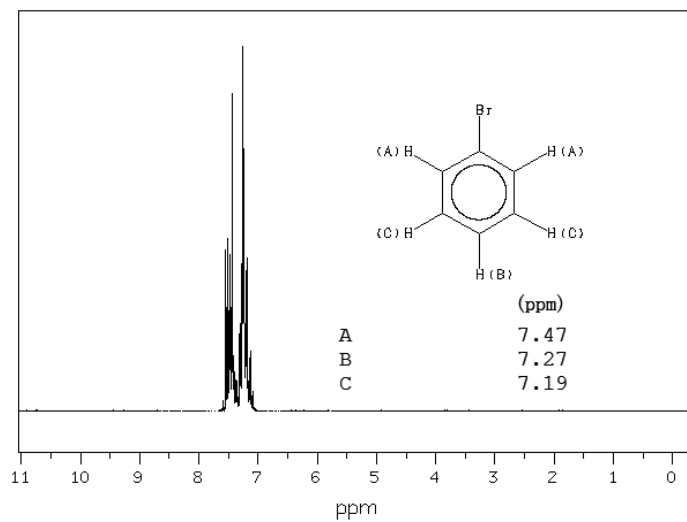
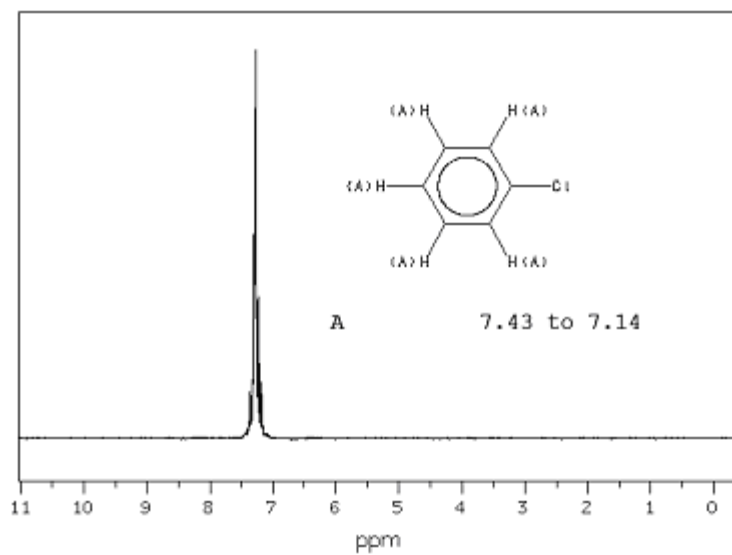
Q. Toluene is oxidized to benzaldehyde. What change in the PMR spectral feature is observed in the product with respect to the starting compound?

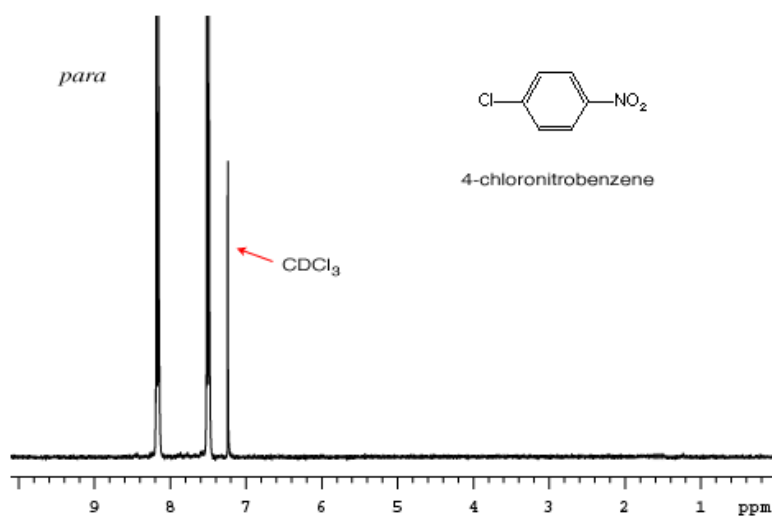
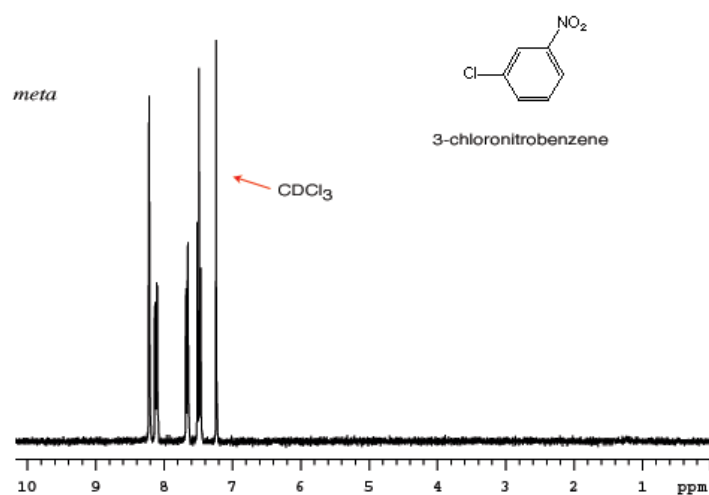
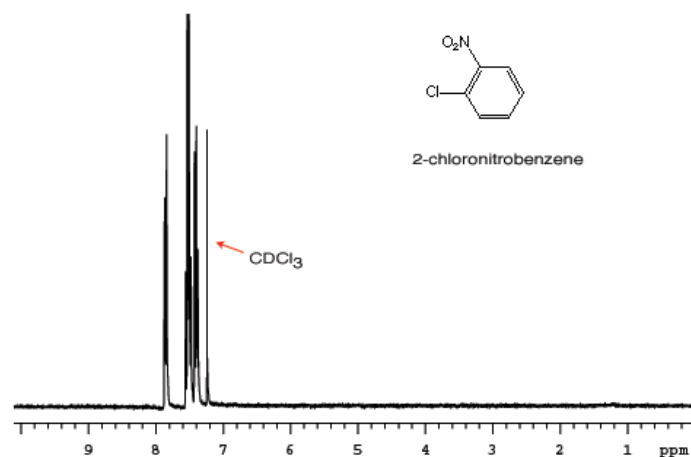


When electron-donating groups are attached to the ring, the ring protons are not equivalent, even at 60 MHz. A highly activating substituent such as methoxy clearly increases the electron density at the *ortho* and *para* positions of the ring (by resonance) and helps to give these protons greater shielding than those in the *meta* positions and, thus, a substantially different chemical shift.

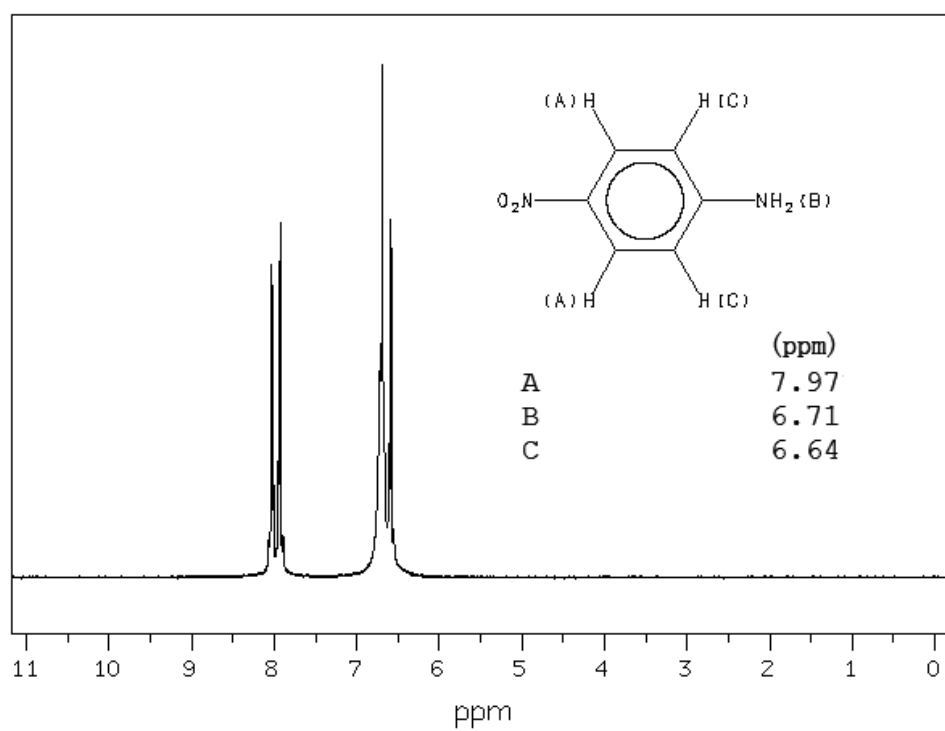
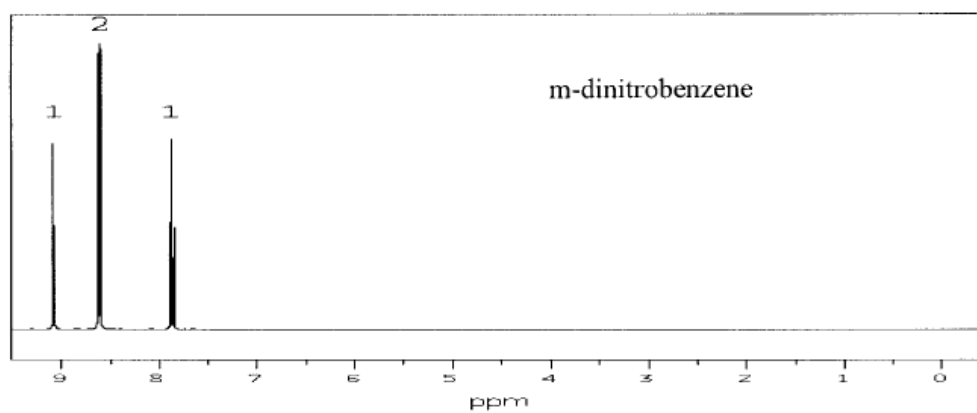
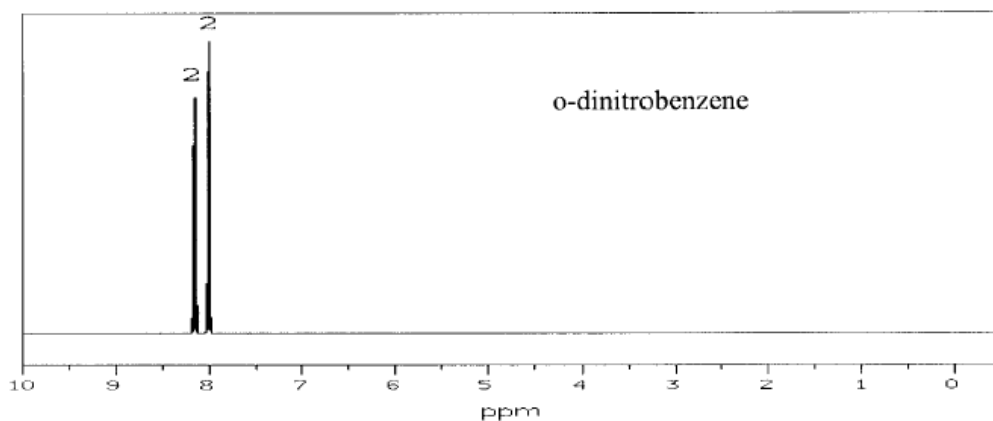


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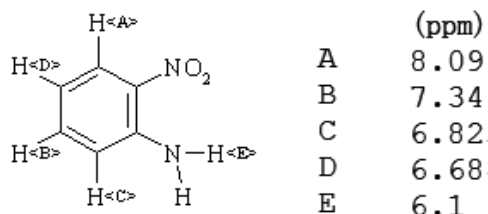
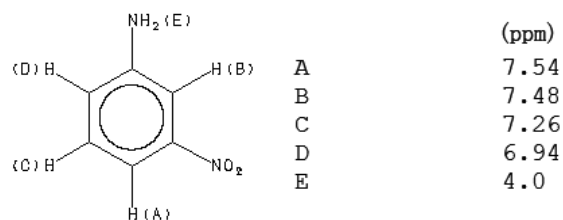


Solve the splitting pattern and mark the protons according to their ppm values.

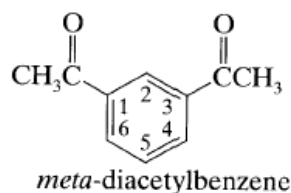


Solve the splitting pattern and mark the protons according to their ppm values.

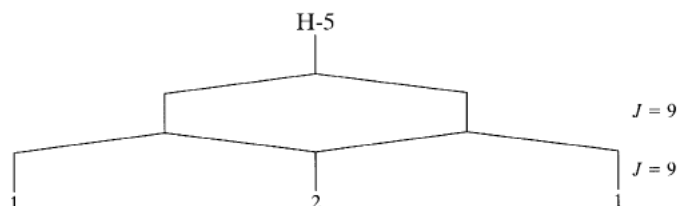
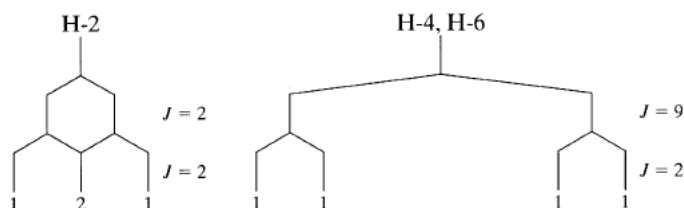
Draw the NMR spectrum of



Important note-In the above examples of aromatic systems, meta coupling is avoided. But if meta coupling is considered, then the splitting pattern will be changed whenever necessary. One example is shown below



coupling constants for the ortho, meta, and para protons as $J = 9$, $J = 2$, and $J \sim 0$, respectively. H-2 is coupled to two meta protons to give a triplet ($J = 2$). The protons at H-4 and H-6 are coupled ortho to the H-5 proton and meta to the H-2 proton ($J = 9$ and 2); the result is a doublet of doublets. The H-5 proton is coupled to two ortho protons to give a triplet ($J = 9$). The small meta coupling may appear only as peak broadening.

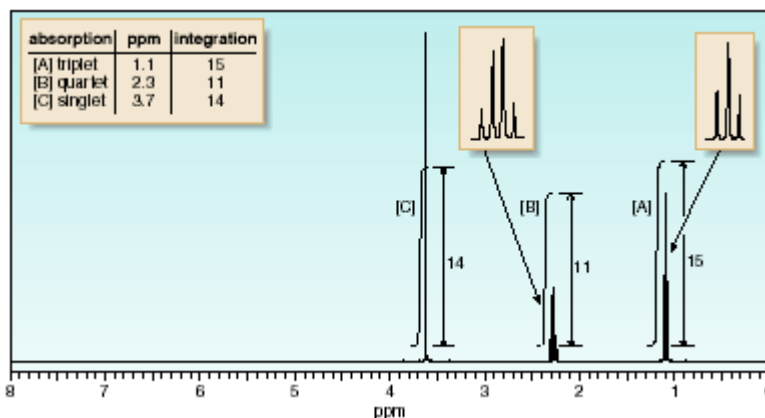


Q. How can you distinguish the following molecules by PMR spectroscopy?

- 1) *p*-dichlorobenzene and *o*-dichlorobenzene.
- 2) *p*-dinitrobenzene and *o*-dinitrobenzene.
- 3) *p*-nitroaniline and *o*-nitroaniline.

HOW TO Use ^1H NMR Data to Determine a Structure

Example- Using its ^1H NMR spectrum, determine the structure of an unknown compound X that has molecular formula $\text{C}_4\text{H}_8\text{O}_2$ and contains a $\text{C}=\text{O}$ absorption in its IR spectrum.

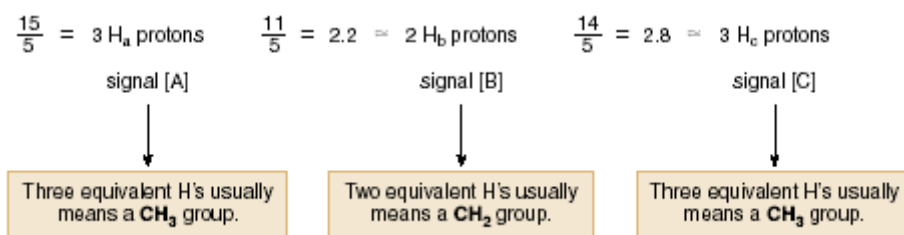


Step [1]- Determine the number of different kinds of protons.

- The number of NMR signals equals the number of different types of protons.
- This molecule has three NMR signals ([A], [B], and [C]) and therefore **three** types of protons (H_a , H_b , and H_c).

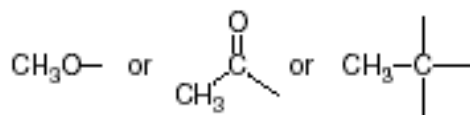
Step [2]- Use the integration data to determine the number of H atoms giving rise to each signal.

- Total number of integration units: $14 + 11 + 15 = 40$ units
- Total number of protons = 8
- Divide: $40 \text{ units} / 8 \text{ protons} = 5 \text{ units per proton}$
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.

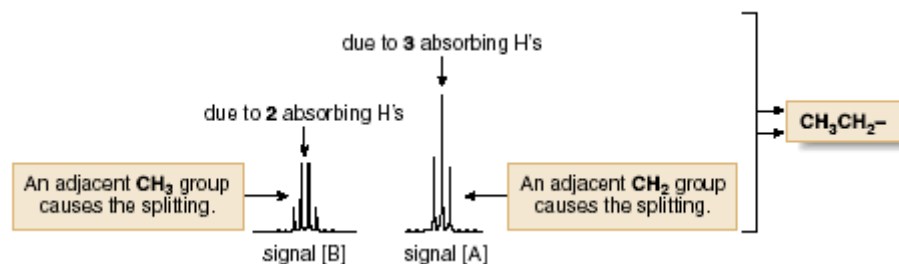


Step [3]- Use individual splitting patterns to determine what carbon atoms are bonded to each other.

- Start with the singlets. Signal [C] is due to a CH_3 group with no adjacent nonequivalent H atoms. Possible structures include:



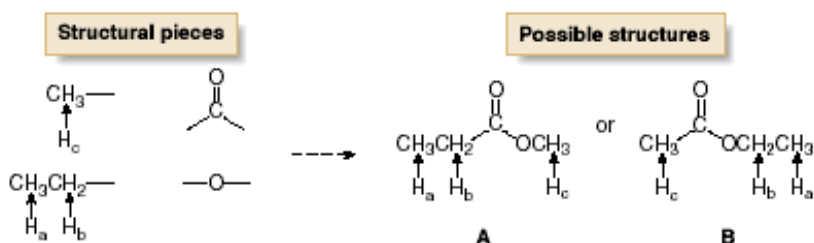
- Because signal [A] is a **triplet**, there must be **2 H's** (CH_2 group) on the adjacent carbon.
- Because signal [B] is a **quartet**, there must be **3 H's** (CH_3 group) on the adjacent carbon.
- This information suggests that **X** has an **ethyl** group CH_3CH_2- .



To summarize, **X** contains CH_3- , CH_3CH_2- , and $\text{C}=\text{O}$ (from the IR). Comparing these atoms with the molecular formula shows that one O atom is missing. Because O atoms do not absorb in a ^1H NMR spectrum, their presence can only be inferred by examining the chemical shift of protons near them. O atoms are more electronegative than C, thus deshielding nearby protons, and shifting their absorption downfield.

Step [4]- Use chemical shift data to complete the structure.

- Put the structure together in a manner that preserves the splitting data and is consistent with the reported chemical shifts.
- In this example, two isomeric structures (**A** and **B**) are possible for **X** considering the splitting data only:



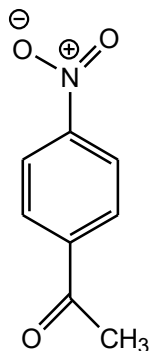
- Chemical shift information distinguishes the two possibilities. The electronegative O atom deshields adjacent H's, shifting them downfield between 3 and 4 ppm. If **A** is the correct structure, the singlet due to the CH_3 group (H_c) should occur downfield, whereas if **B** is the correct structure, the quartet due to the CH_2 group (H_b) should occur downfield.
- Because the NMR of **X** has a singlet (not a quartet) at 3.7, **A is the correct structure.**

Q. An organic compound having molecular formulae ($\text{C}_8\text{H}_7\text{NO}_3$) shows a strong IR band at 1690 cm^{-1} and three signals at δ 8.5 (d), δ 7.9 (d), δ 2.5 (s) in its PMR spectrum. Establish the structure of the compound. How can you synthesise the compound from suitable monosubstituted aromatic hydrocarbon?

Hint- D.B.E = 6. (exceeds 4, so chance of being aromatic)

Peak at 1690 cm^{-1} in IR - indicates decreased carbonyl stretching frequency

Two doublet in PMR indicates p-disubstituted benzene ring. One singlet indicates the presence of isolated protons at the outside of the ring.
So possible structure



Assign the splitting patterns and correlate the δ values

Q. A compound having molecular formulae ($C_6H_{12}O$) shows a strong IR band at 1705 cm^{-1} and two singlets at δ 2.1 and 1.2 in its PMR spectrum. Establish the structure of the compound.

Q. An organic compound having molecular formulae ($C_5H_{10}O$) shows a strong IR band at 1715 cm^{-1} and showed two signals – a triplet and a quartet in its PMR spectrum. Establish the structure of the compound.

Q. An organic compound shows the following spectral data

Mass: 130 (M.W)

IR: $3082\text{--}2860, 1825, 1755, 1455\text{ cm}^{-1}$

^1H NMR: δ 1.30 (t, $J=7.1\text{Hz}$), δ 2.20 (q, $J=7.1\text{Hz}$) & the ratio of two peaks = 3:2

Establish the structure.

Q. An organic compound $C_4H_6O_2$ shows a strong IR band at 1720 cm^{-1} and only one singlet signal in its ^1H NMR spectrum. Analyse the compound.

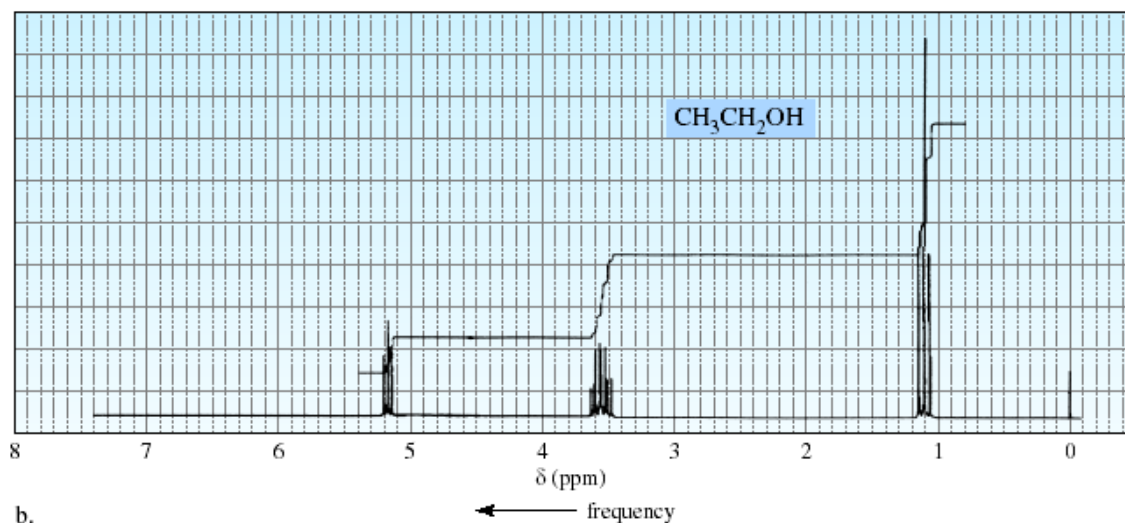
Q. Write the structure of the compound, $C_5H_{11}Cl$, which shows two singlets in its ^1H NMR spectrum.

Q. Compound A (mf $C_6H_{12}O$) shows a peak at 1715 cm^{-1} in its IR spectrum. The PMR spectrum of compound A displays two singlets at δ 0.9 and 2.2 in the ratio of 3:1. Deduce a structure for compound A that fits these spectral data.

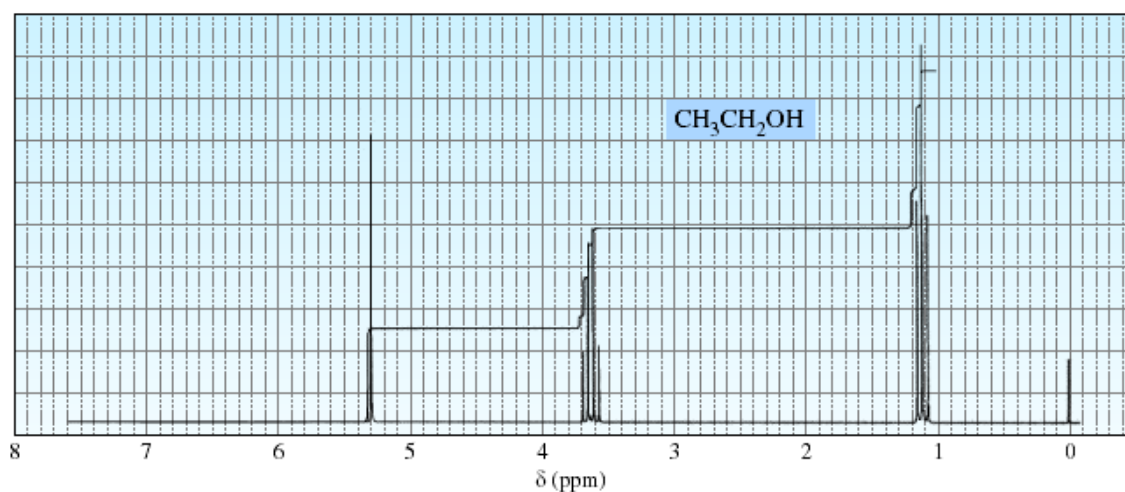
*****Fast proton exchange decouples hydroxy hydrogens**

The ^1H NMR spectrum of pure dry ethanol is shown in Figure (a), and the ^1H NMR spectrum of ethanol with a trace amount of acid is shown in Figure(b). The signal for the proton bonded to oxygen is farthest downfield and is split into a triplet by the neighboring methylene protons; the signal for the methylene protons is split into a multiplet by the combined effects of the methyl protons and the OH proton.

a.



b.



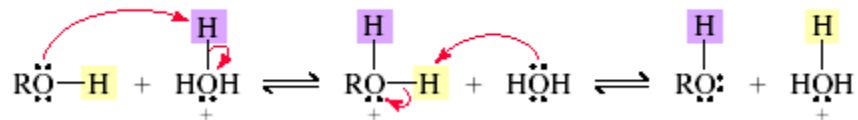
The spectrum shown in Figure (b) is the type of spectrum most often obtained for alcohols. The signal for the proton bonded to oxygen is not split, and this proton does not split the signal of the adjacent protons. So the signal for the OH proton is a singlet, and the signal for the methylene protons is a quartet because it is split only by the methyl protons.

The two spectra differ because protons bonded to oxygen undergo **proton exchange**, which means that they are transferred from one molecule to another. Whether the OH proton and the methylene protons split each other's signals depends on how long a particular proton stays on the OH group.

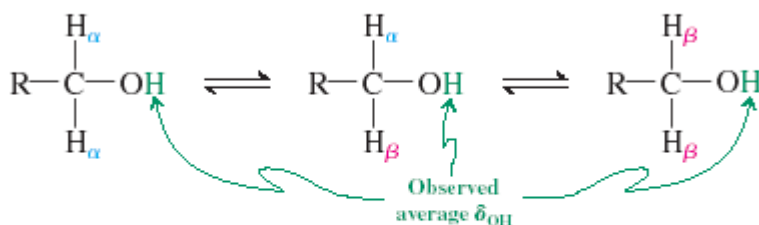
In a sample of pure alcohol, the rate of proton exchange is very slow. This causes the spectrum to look identical to one that would be obtained if proton exchange did not occur. Acids and bases catalyze proton exchange, so if the alcohol is contaminated with just a trace of acid or base, proton exchange becomes rapid. When proton exchange is rapid, the spectrum records only an average of all possible environments. Therefore a rapidly exchanging proton is recorded as a singlet. The effect of a rapidly exchanging

proton on adjacent protons is also averaged. Thus, not only is its signal not split by adjacent protons, the rapidly exchanging proton does not cause splitting.

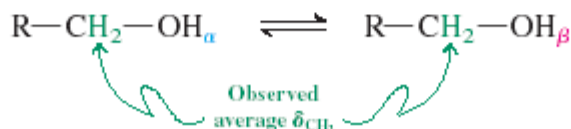
mechanism for acid-catalyzed proton exchange



Rapid Proton Exchange Between Alcohols with Various $CH_2-\alpha, \beta$ Spin Combinations Averages δ_{OH}



Rapid α -Proton with β -Proton Exchange Averages δ_{CH_2}

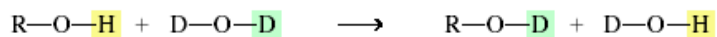


[Important note- The signal for an OH proton is often easy to spot in an 1H NMR spectrum because it is frequently somewhat broader than other signals. The broadening occurs because the rate of proton exchange is not slow enough to result in cleanly split signal, as in Figure (a), or fast enough for a cleanly averaged signal, as in Figure (b).]

Q. The NMR spectrum of commercially available (ordinary grade) ethanol and highly pure ethanol are quite different. Why?

***Use of Deuterium in NMR Spectroscopy

Because deuterium signals are not seen in an 1H NMR spectrum, substituting a deuterium for a hydrogen is a technique used to identify signals and to simplify 1H NMR spectra. If after an alcohol's 1H NMR spectrum is obtained, a few drops of D_2O are added to the sample and the spectrum is taken again, the OH signal can be identified. It will be the signal that becomes less intense (or disappears) in the second spectrum because of the proton exchange process just discussed. This technique can be used with any proton that undergoes exchange.



It is an useful technique for the detection of OH, NH, active methylene groups etc.