

CSIR NET - CHEMISTRY SAMPLE THEORY

NMR SPECTROSCOPY

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1-C-8, Sheela Chowdhary Road, Talwandi, Kota (Raj.) Tel No. 0744-2429714

Web Site www.vpmclasses.com E-mail vpmclasses@yahoo.com

Phone: 0744-2429714

Website: www.vpmclasses.com

Address: 1-C-8, Sheela Chowdhary Road, SFS, TALWANDI, KOTA, RAJASTHAN, 324005

Mobile: 9001297111, 9829567114, 9001297243

E-Mail: vpmclasses@yahoo.com / info@vpmclasses.com

Nuclear Magnetic Resonance Spectroscopy

Introduction

NMR is suitable for studying compounds containing elements with magnetic nuclei and it is particularly important for determining the structures of species containing hydrogen. The nuclei of many elemental isotopes have a characteristic spin (I).

Some nuclei have integral spins (e.g. $I = 1, 2, 3 \dots$), some have fractional spins (e.g. $I = 1/2, 3/2, 5/2 \dots$), and a few have no spin, $I = 0$ (e.g. ^{12}C , ^{16}O , ^{32}S , etc. Nuclei with even atomic numbers and even mass numbers are invisible in NMR).

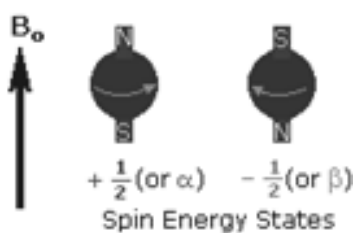
Isotopes of particular interest and use to organic chemists are ^1H , ^{13}C , ^{19}F and ^{31}P , all of which have $I = 1/2$.

NMR phenomenon:

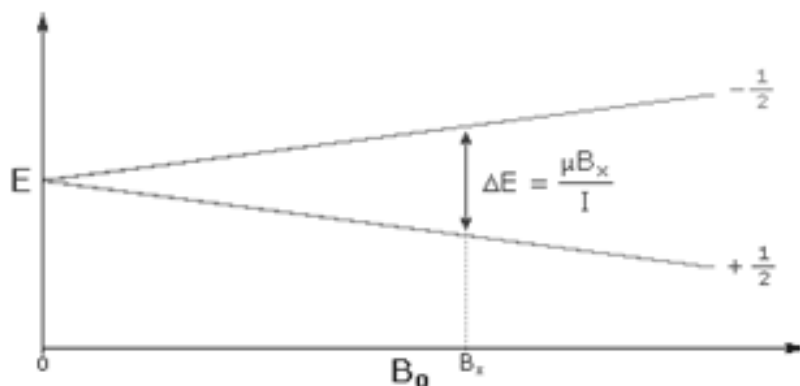
1. A spinning charge generates a magnetic field. The resulting spin-magnet has a magnetic moment (μ) proportional to the spin.



2. In the presence of an external magnetic field (B_0), two spin states exist, $+1/2$ and $-1/2$. The magnetic moment of the lower energy $+1/2$ state is aligned with the external field, but that of the higher energy $-1/2$ spin state is opposed to the external field. The arrow representing the external field points North.



3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The following diagram illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases.



The international unit for magnetic flux is the Tesla (T). The earth's magnetic field is not constant, but is approximately 10^{-4} T at ground level. Modern NMR spectrometers use powerful magnets having fields of 1 to 20 T. Even with these high fields, the energy difference between the two spin states is less than 0.1 cal/mole.

For NMR purposes, this small energy difference (ΔE) is usually given as a frequency in units of MHz (10^6 Hz), ranging from 20 to 900 MHz, depending on the magnetic field strength and the specific nucleus being studied.

Irradiation of a sample with radio frequency (RF) energy corresponding exactly to the spin state separation of a specific set of nuclei will cause excitation of those nuclei in the $+1/2$ state to the higher $-1/2$ spin state. This electromagnetic radiation falls in the radio and television broadcast spectrum. The nucleus of a hydrogen atom (the proton) has a magnetic moment $\mu = 2.7927$.

4. For spin $1/2$ nuclei the energy difference between the two spin states at a given magnetic field strength will be proportional to their magnetic moments. The following gives the approximate frequencies that correspond to the spin state energy separations for each of these nuclei in an external magnetic field of 2.35 T. The formula shows the direct correlation of frequency (energy difference) with magnetic moment ($h = \text{Planck's constant} = 6.626069 \cdot 10^{-34}$ Js).



CHEMICAL SHIFT:

The electron(s) surrounding the proton in covalent compounds and ions are responsible for different NMR spectrum for different compounds. Since electrons are charged particles, they move in response to the external magnetic field (B_0) so as to generate a secondary field that opposes the much stronger applied field. This secondary field **shields** the nucleus from the applied field, so B_0 must be increased in order to achieve resonance (absorption of RF energy).

The frequency of an NMR transition depends on the local magnetic field experienced by the nucleus and is expressed in terms of the **chemical shift**, δ , the difference between the resonance frequency of nuclei in the sample and that of a reference compound:

$$\delta = \frac{\nu - \nu^0}{\nu^0} \times 10^6$$

A common standard for ^1H , ^{13}C or ^{29}Si spectra is Tetramethylsilane $\text{Si}(\text{CH}_3)_4$, abbreviated as TMS. When $\delta < 0$ the nucleus is said to be **shielded** relative to the standard; $\delta > 0$ corresponds to a nucleus that is **deshielded** with respect to the reference.

The H chemical shift in CH_4 is only 0.1 because the H nuclei are in an environment similar to that in Tetramethylsilane, but the H chemical shift is $\delta = 3.1$ for H in GeH_4 . Chemical shifts are different for the same element in inequivalent positions within a molecule.

The sample compounds should possess two characteristics:

- The hydrogen atoms in a given molecule should be structurally equivalent, averaged for fast conformational equilibrium.

- The compounds should be in liquid phase

Factors Affecting Chemical Shift

Inductive effect:

If the electron density about a proton nucleus is relatively high, the induced field due to electron motions will be stronger than if the electron density is relatively low. The shielding effect in such high electron density cases will therefore be larger, and a higher external field (B_0) will be needed for the RF energy to excite the nuclear spin.

Shielded Nucleus:

Since silicon is less electronegative than carbon, the electron density about the methyl hydrogens in Tetramethylsilane is expected to be greater than the electron density about the methyl hydrogens in neopentane (2,2-dimethylpropane), and the characteristic resonance signal from the silane derivative does indeed lie at a higher magnetic field. Such nuclei are said to be **shielded**.

Deshielded Nucleus:

Elements that are more electronegative than carbon should exert an opposite effect (reduce the electron density); and, as the data in the following tables show, methyl groups bonded to such elements display lower field signals (they are **deshielded**).

The deshielding effect of electron withdrawing groups is roughly proportional to their electro negativity, as shown by the table. Furthermore, if more than one such group is present, the deshielding is additive (table) and proton resonance is shifted even further downfield.

Proton Chemical Shifts of Methyl Derivatives

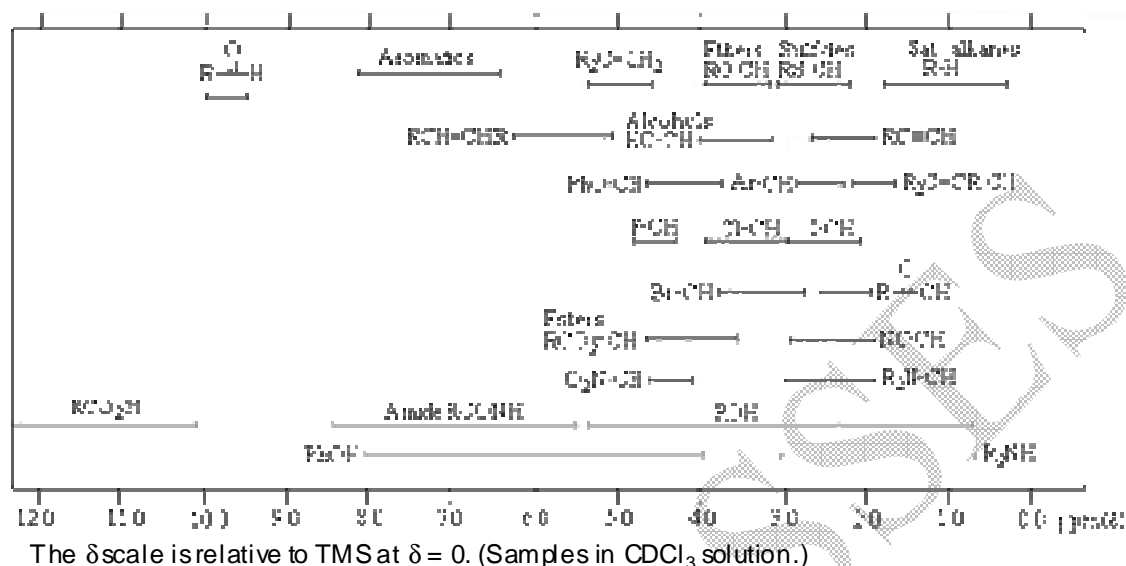
Compound	(CH ₃) ₄ C	(CH ₃) ₃ N	(CH ₃) ₂ O	CH ₃ F
Δ	0.9	2.1	3.2	4.1
Compound	(CH ₃) ₄ Si	(CH ₃) ₃ P	(CH ₃) ₂ S	CH ₃ Cl
Δ	0.0	0.9	2.1	3.0

Proton Chemical Shifts (ppm)

Compound	X=Cl	X=Br	X=I	X=OR	X=SR
CH ₃ X	3.0	2.7	2.1	3.1	2.1
CH ₂ X ₂	5.3	5.0	3.9	4.4	3.7
CHX ₃	7.3	6.8	4.9	5.0	

Proton Chemical Shift Ranges

Low Field Region



Solvent for NMR Spectrum:

- In order to take the **NMR spectra of a solid**, it is usually necessary to dissolve it in a suitable solvent like Carbon Tetrachloride, since it has no hydrogen that could introduce an interfering signal.
- Chloroform-d (CDCl_3) is the most common solvent for NMR measurements, owing to its good solubilizing character and relative unreactive nature (except for 1° and 2° amines).
- Other deuterium labeled compounds, such as deuterium oxide (D_2O), benzene-d6 (C_6D_6), acetone-d6 (CD_3COCD_3) and DMSO-d6 (CD_3SOCD_3) are also available for use as NMR solvents

Signal Strength

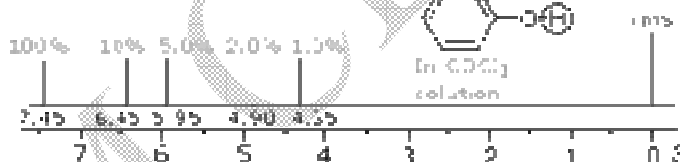
- The magnitude or intensity of NMR resonance signals is displayed along the vertical axis of a spectrum, and is proportional to the molar concentration of the sample.
- Thus, a small or dilute sample will give a weak signal, and doubling or tripling the sample concentration increases the signal strength proportionally.
- If we take the NMR spectrum of equal molar amounts of benzene and cyclohexane in carbon tetrachloride solution, the resonance signal from cyclohexane will be twice as intense as that from benzene because cyclohexane has twice as many hydrogens per molecule.

- This is an important relationship when samples incorporating two or more different sets of hydrogen atoms are examined, since it allows the ratio of hydrogen atoms in each distinct set to be determined.
- To this end it is necessary to measure the relative strength as well as the chemical shift of the resonance signals that comprise an NMR spectrum.

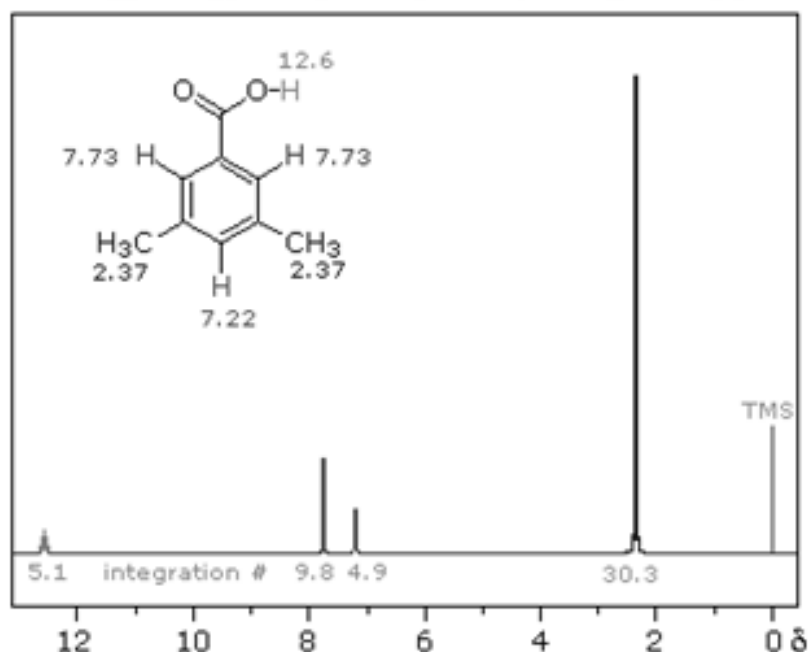
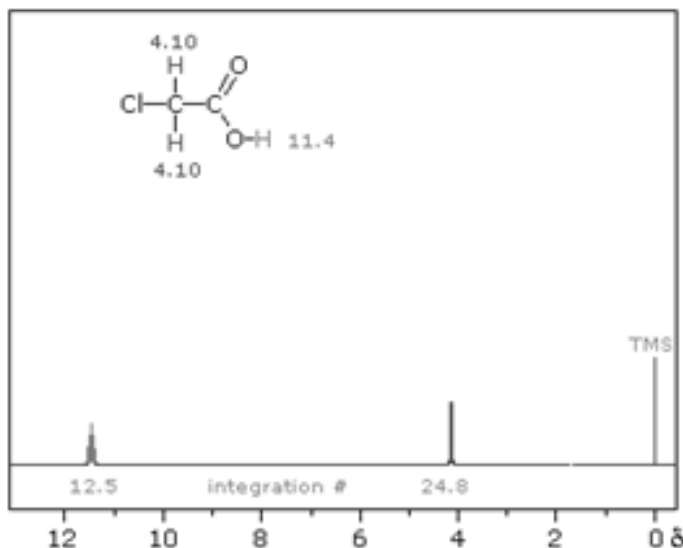
Influence of Hydrogen Bonding:

Hydrogen bonding shifts the resonance signal of a proton to lower field (higher frequency).

- The chemical shift of the hydroxyl hydrogen of an alcohol varies with concentration. Very dilute solutions of 2-methyl-2-propanol, $(\text{CH}_3)_3\text{COH}$, in carbon tetrachloride solution display a hydroxyl resonance signal having a relatively high-field chemical shift ($< 1.0 \delta$). In concentrated solution this signal shifts to a lower field, usually near 2.5δ .
- The more acidic hydroxyl group of phenol generates a lower-field resonance signal, which shows similar concentration dependence to that of alcohols. OH resonance signals for different percent concentration of phenol in chloroform-d are shown in the following diagram (CH signals are not shown).

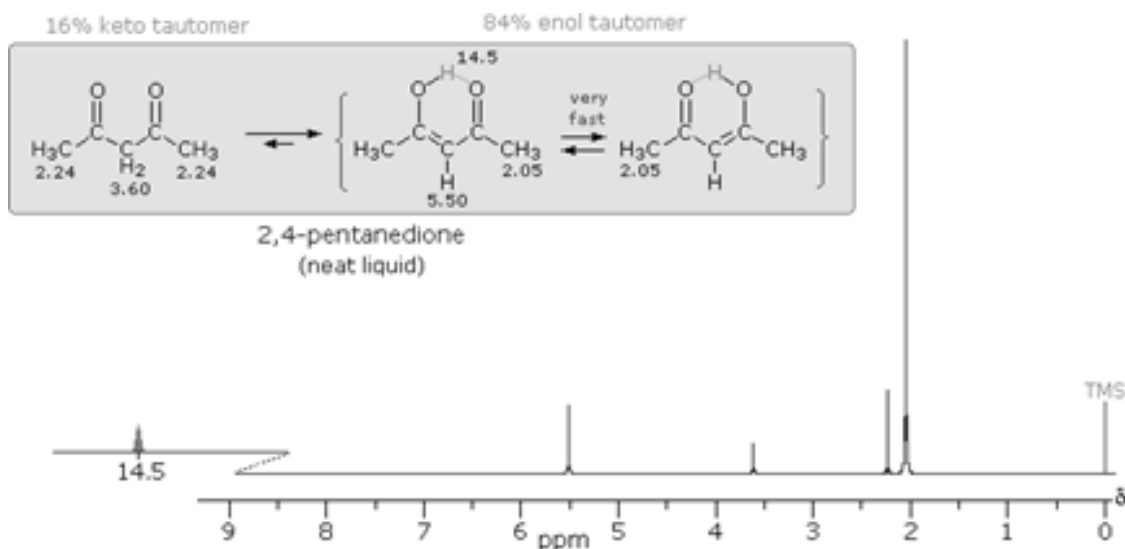


- Because of their favored hydrogen-bonded dimeric association, the hydroxyl proton of carboxylic acids displays a resonance signal significantly down-field of other functions. For a typical acid it appears from 10.0 to 13.0 δ and is often broader than other signals. The spectra shown below for chloroacetic acid (left) and 3,5-dimethylbenzoic acid (right) are examples.



- Intramolecular hydrogen bonds, especially those defining a six-membered ring, generally display a very low-field proton resonance.
- For example 4-hydroxypent-3-ene-2-one (the enol tautomer of 2,4-pentanedione). In the NMR spectrum of the pure liquid, sharp signals from both the ketone and enol tautomers are seen, their mole ratio being 4 : 21.

The chemical shift of the hydrogen-bonded hydroxyl proton is δ 14.5, exceptionally downfield. So the rate at which these tautomers interconvert is slow compared with the time scale of NMR spectroscopy.



These enols are slow to interconvert, we would expect two methyl resonance signals associated with each, one from the allylic methyl and one from the methyl ketone. Since only one strong methyl signal is observed, we conclude that the interconversion of the enols is very fast—so fast that the NMR experiment detects only a single time-averaged methyl group (50% α -ketone and 50% allyl).

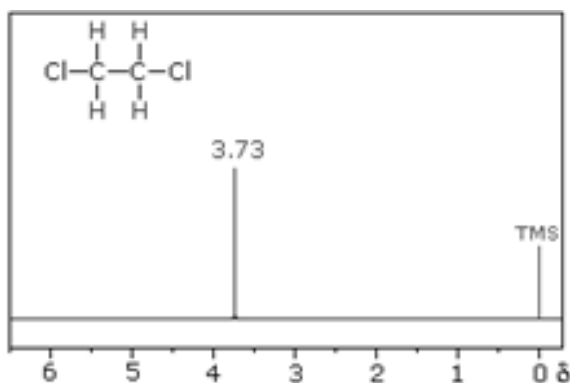
The N-H groups in amines and amides also exhibit hydrogen bonding NMR shifts, although to a lesser degree. The OH and NH groups can undergo rapid proton exchange with each other, so if two or more such groups are present in a molecule, the NMR spectrum will show a single signal at an average chemical shift.

For example, 2-hydroxy-2-methylpropanoic acid, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CO}_2\text{H}$, displays a strong methyl signal at δ 1.5 and a 1/3 weaker and broader OH signal at δ 7.3 ppm. Note that the average of the expected carboxylic acid signal (ca. 12) and the alcohol signal (ca. 2) is 7. Rapid exchange of these hydrogens with heavy water would cause the low field signal to disappear.

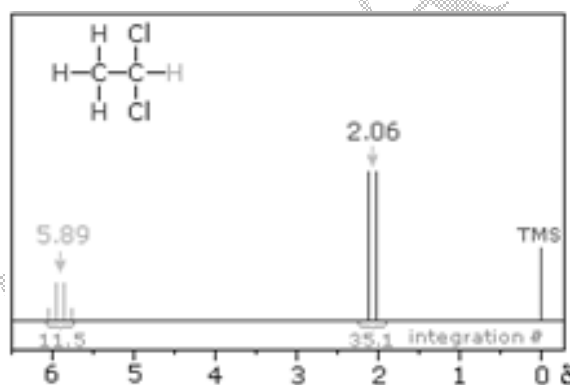
Spin-Spin Interactions:

The NMR spectrum of 1,1-dichloroethane is more complicated than we expect. The 1,2-dichloro-isomer which displays a single resonance signal from the four structurally equivalent hydrogens, the two signals from the different hydrogens are split into close groupings of two or more resonances. This is a common feature in the

spectra of compounds having different sets of hydrogen atoms bonded to adjacent carbon atoms. The signal splitting in proton spectra is usually small, ranging from fractions of a Hz to as much as 18 Hz, and is designated as **J** (the coupling constant). In the 1,1-dichloroethane example all the coupling constants are 6.0 Hz.

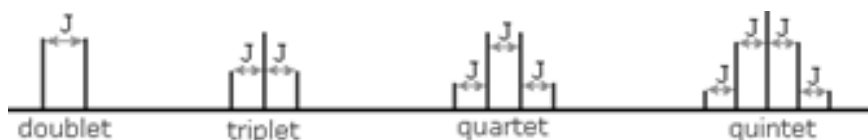


1,2-dichloroethane



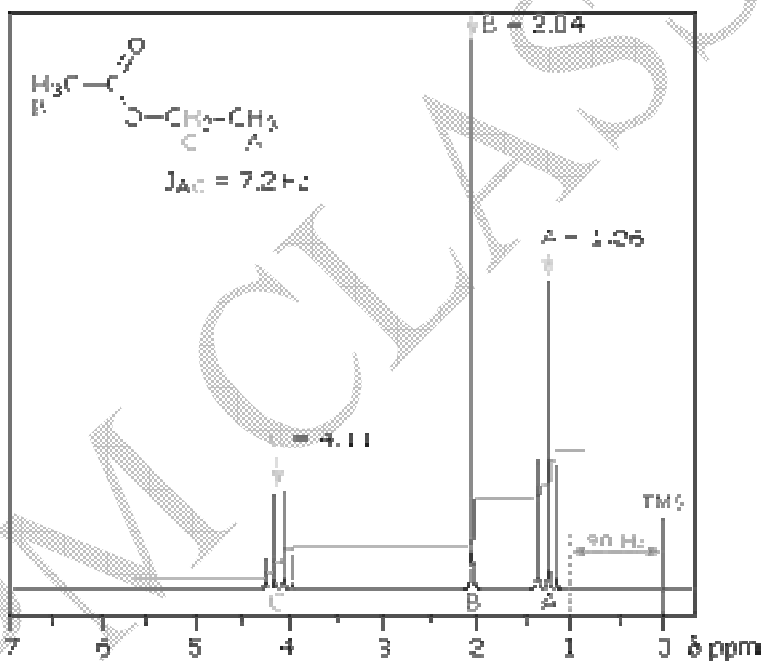
1, 1-dichloroethane

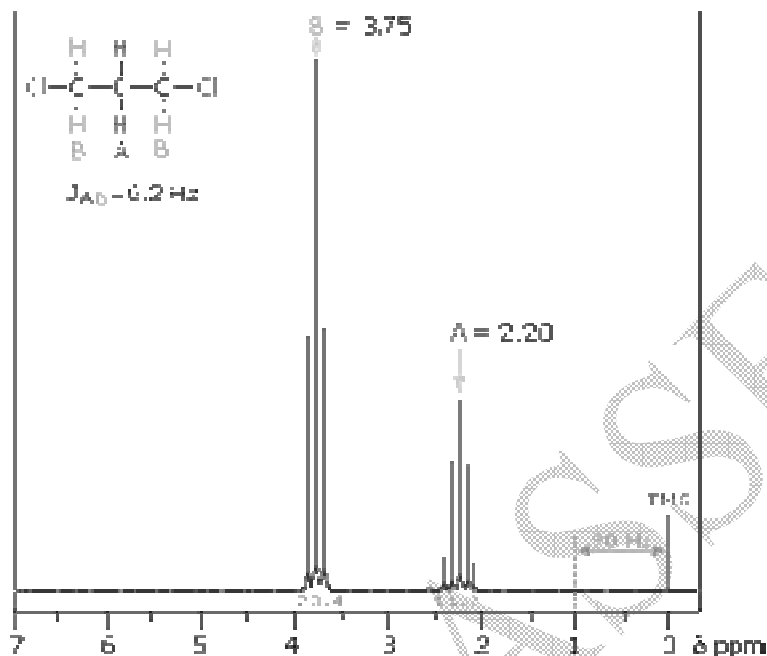
The splitting patterns found in various spectra are easily recognized, provided the chemical shifts of the different sets of hydrogen that generate the signals differ by two or more ppm. The patterns are symmetrically distributed on both sides of the proton chemical shift, and the central lines are always stronger than the outer lines. These patterns have been given names, such as **doublet** (two equal intensity signals), **triplet** (three signals with an intensity ratio of 1:2:1) and **quartet** (a set of four signals with intensities of 1:3:3:1). The line separation is always constant within a given multiple, and is called the **coupling constant (J)**. The magnitude of J, usually given in units of Hz, is magnetic field independent.



The splitting patterns shown above display the ideal or "First-Order" arrangement of lines. This is usually observed if the spin-coupled nuclei have very different chemical shifts (i.e. $\Delta\nu$ is large compared to J). If the coupled nuclei have similar chemical shifts, the splitting patterns are distorted (second order behavior). In fact, signal splitting disappears if the chemical shifts are the same.

The ethyl acetate spectrum on the left displays the typical quartet and triplet of a substituted ethyl group. The spectrum of 1,3-dichloropropane on the right demonstrates that equivalent sets of hydrogens may combine their influence on a second, symmetrically located set.



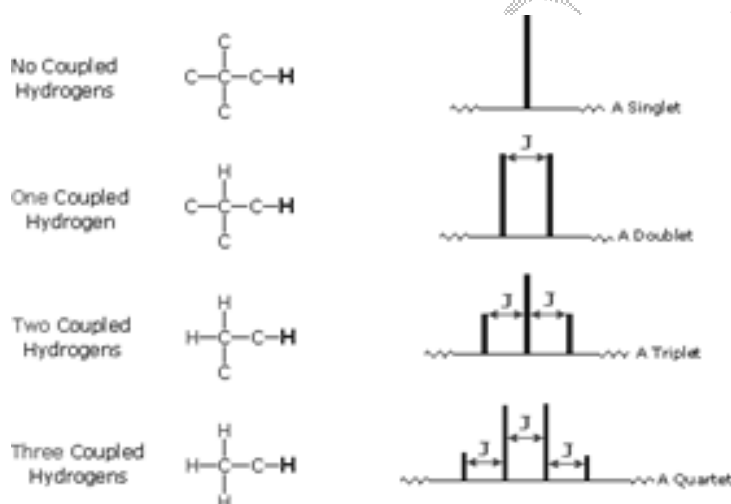


If an atom under examination is influenced by a nearby nuclear spin (or set of spins), the observed nucleus responds to such influences and its response is manifested in its resonance signal. This spin-coupling is transmitted through the connecting bonds, and it functions in both directions. Thus, when the perturbing nucleus becomes the observed nucleus, it also exhibits signal splitting with the same J . For spin-coupling to be observed, the sets of interacting nuclei must be bonded in relatively close proximity (e.g. vicinal and geminal locations), or be oriented in certain optimal and rigid configurations. A number before the symbol J is placed to designate the number of bonds linking the coupled nuclei. Using this terminology, a vicinal coupling constant is 3J and a geminal constant is 2J .

General rules and characteristics for spin 1/2 nuclei:

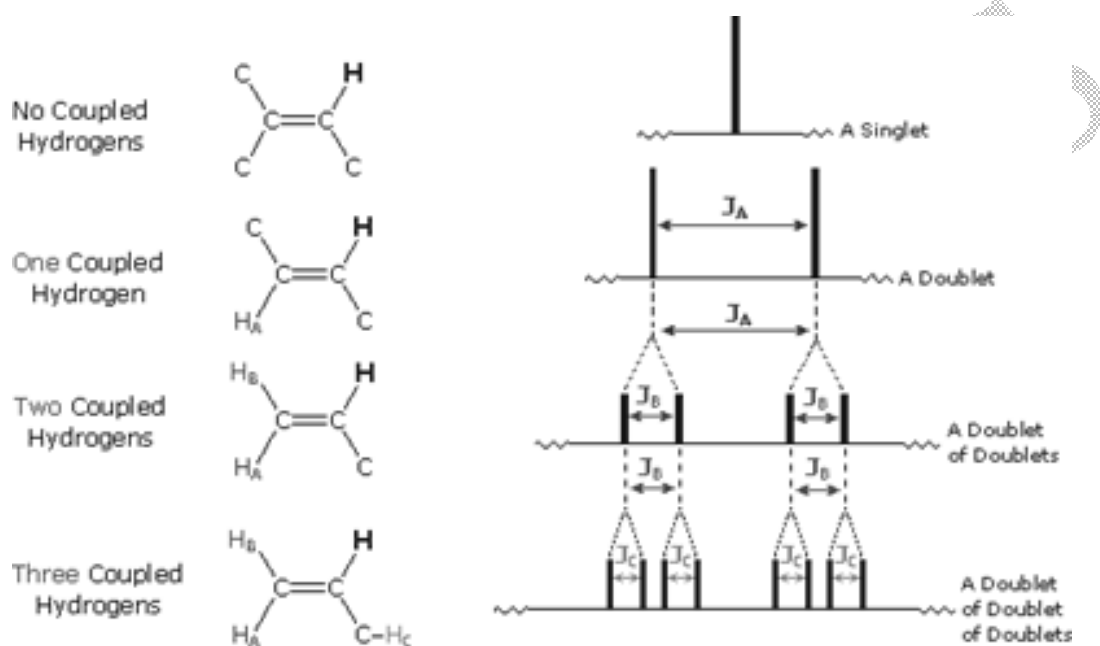
- 1) Nuclei having the same chemical shift (called **isochronous**) do not exhibit spin-splitting. They may actually be spin-coupled, but the splitting cannot be observed directly.
- 2) Nuclei separated by three or fewer bonds (e.g. vicinal and geminal nuclei) will usually be spin-coupled and will show mutual spin-splitting of the resonance signals (same J 's), provided they have different chemical shifts. Longer-range coupling may be observed in molecules having rigid configurations of atoms.

- 3) The magnitude of the observed spin-splitting depends on many factors and is given by the coupling constant J (units of Hz). J is the same for both partners in a spin-splitting interaction and is independent of the external magnetic field strength.
- 4) The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the **$n+1$ rule**; where n is the number of neighboring spin-coupled nuclei with the same (or very similar) J s. If there are 2 neighboring, spin-coupled, nuclei the observed signal is a triplet ($2 + 1 = 3$); if there are three spin-coupled neighbors the signal is a quartet ($3 + 1 = 4$). In all cases the central line(s) of the splitting pattern are stronger than those on the periphery. The intensity ratio of these lines is given by the numbers in Pascal's triangle.



Pascal's Triangle

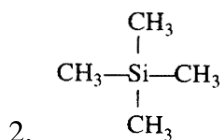
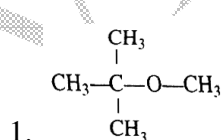
If a given nucleus is spin-coupled to two or more sets of neighboring nuclei by different J values, the $n+1$ rule does not predict the entire splitting pattern. Instead, the splitting due to one J set is added to that expected from the other J sets. Bear in mind that there may be fortuitous coincidence of some lines if a smaller J is a factor of a larger J .

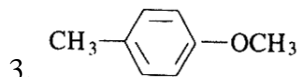


Spin $1/2$ nuclei include ^1H , ^{13}C , ^{19}F & ^{31}P . The spin-coupling interactions described above may occur between similar or dissimilar nuclei. If, for example, a ^{19}F is spin-coupled to a ^1H , both nuclei will appear as doublets having the same J constant. Spin coupling with nuclei having spin other than $1/2$ is more complex.

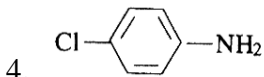
Solved problems

- 1) How many signals in NMR spectra will be obtained from the following compounds respectively?





(A) 2, 1, 4, 3



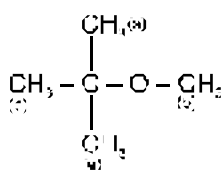
(B) 3, 3, 3, 3

(C) 1, 1, 3, 4

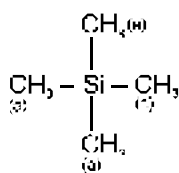
(D) 2, 1, 3, 4

Sol. (A)

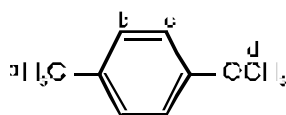
Signals



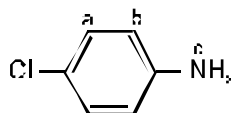
2 signal



1 signal



4 signal



3 signal

- 2) The proton NMR spectrum of a compound with molecular formula C_2H_6O was obtained. Under low resolution three signals with relative intensities of 1 : 2 : 3 were recorded. Under high resolution, the high field signal split into three lines of relative intensities 1 : 2 : 1, medium field signal into four lines of intensities in the ratio of 1 : 3 : 3 : 1. What is the structural formula?

(A) CH_3CH_2OH

(B) CH_3OCH_3

(C) Both will have the same spectrum

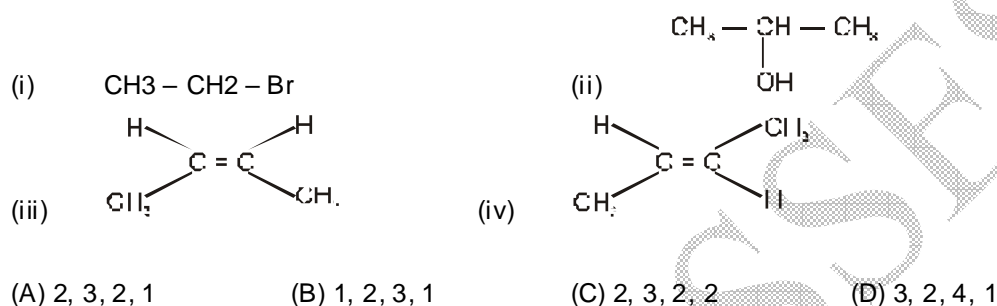
(D) CH_3CHO

Sol. (A) The structural formula is



at low resolution	High field	Medium field	
	1 : 2 : 3	1 : 2 : 1	1 : 3 : 3 : 1

3) How many signals in NMR spectra will be obtained from the following compounds respectively –



Sol.(C)

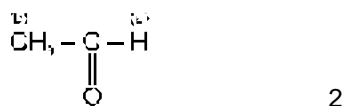
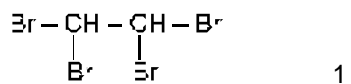
Compounds	Signals
$\overset{b}{\text{C}}\text{H}_3 - \overset{a}{\text{C}}\text{H}_2 - \text{Br}$	2
$\overset{a}{\text{C}}\text{I}_2 - \overset{b}{\text{C}}\text{H} - \overset{c}{\text{C}}\text{I}_2$ OH	3
$\begin{array}{c} \text{H}^a \quad \quad \text{H}^a \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \quad \backslash \\ \text{H}_2\text{C}^b \quad \quad \text{CH}_2^b \end{array}$	2
$\begin{array}{c} \text{H}^a \quad \quad \text{CH}_3^b \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \quad \backslash \\ \text{H}_2\text{C}^b \quad \quad \text{H}^a \end{array}$	2

4) Which one of the following compounds will show more than two signals in its ^1H NMR spectrum?

- (A) $\text{CH}_3 - \text{CH}_2 - \text{Br}$ (B) $\text{CHBr}_2 - \text{CH}_2\text{Br}$ (C) $\text{CH}_3 - \text{CHO}$ (D) $\text{CH}_3 - \text{CH}_2 - \text{OH}$

Sol.(D)

Compounds	Signals
$\overset{(a)}{\text{C}}\text{H}_3 - \overset{(b)}{\text{C}}\text{H}_2 - \text{Br}$	2



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