**1HNMR spectrometry in structural elucidation of organic compounds**

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**ABSTRACT**

1HNMR Spectrometry is the most useful tool available to the organic chemist.-One can perform the structure elucidation of various synthesized organic compounds. This spectral technique gives the information about the molecular structure of organic compounds that is different kinds of protons with different chemical, electronic environments and tells about the relative number of protons of one type.

Present paper includes some important terms involved in this spectral technique and applications in detection of some structural characterization of compounds with examples. The characteristics may be hydrogen bonding, aromaticity isomerism, presence of electro negative atom or group, functional group present in a given compound. NMR spectra also used in various fields like medical diagnostics and physics.

**Keywords**: 1HNMR Spectrometry, proton NMR

**INTRODUCTION**

Nuclear magnetic resonance spectroscopy is a powerful analytical technique for structural elucidation of unknown compounds. The basic principle involved in this technique is resonance. Resonance can be defined as matching of frequency or energy of a system with that of electromagnetic radiation at the strength of magnetic field and it includes flipping of proton from lower energy to higher energy level. This process of absorption of energy and giving a signal in the form of spectrum is called as NMR spectroscopy. The nuclei which are magnetically active only considered for NMR like H\(^1\), C\(^{13}\), F\(^{19}\), P\(^{31}\), N\(^{14}\)/N\(^{15}\) and B\(^{11}\). The nucleus of an isotope whose spin quantum number (I) is greater than zero, shows absorption NMR spectroscopy.

**Important terms and definitions:**

**Precessional frequency**: It is the number of revolutions per second made by magnetic moment vector of the nucleus around the external magnetic field H\(_0\).

**Spin- spin relaxation**: It is due to the natural exchange of spins by two processing nuclei which are in close proximity to each other.

**Spin-lattice relaxation**: It involves the transfer of energy from the nucleus in its higher energy state to the molecular lattice.

**Chemical shift (δ)**: The shift in the positions of NMR absorptions which arises due to shielding and deshielding of the protons by electrons is called chemical shift.

**Coupling constant (J)**: The distance between the centres of two adjacent peaks in a particular multiplet is shown by the value of J and is called as coupling constant.

**Solvents to be used in the NMR spectroscopy**: In order to record the proton NMR spectrum of a substance it must be dissolved in suitable in which it sufficiently soluble (preferably 10-50mg per ml). The substance free of proton should be used as solvent, i.e. which does not give absorption of its own in NMR spectrum. The majority of solvents used are deuterated analogues of the organic solvents. The solvents which are commonly used in NMR spectroscopy are.

a) Carbon tetrachloride- CCl\(_4\)
b) Carbon disulfide-CS2
c) Dueterochloroform-CDCl\(_3\)
d) Hexadueteroacetone-(CD\(_3\))\(_2\)C=O etc.

These solvents differ considerably as regards their polarity clearly, NMR spectrum of a compound measured in one solvent may be slightly different from that measured in another solvent of different polarity. Hence it is important to mention the solvent used in NMR spectrum.
Reference compound used in NMR spectroscopy: A small amount of reference compound usually Tetra methylsilane (CH₃)₄Si is added as internal standard. Due to low electronegativity of silicon, the shielding of equivalent protons in TMS is greater than most of the organic compounds. Therefore, NMR signal for TMS is taken as reference and chemical shifts for different kinds of protons are measured relative to it. The assigned chemical shift value of TMS is zero.

TMS is the most convenient reference and has the following characteristics:

a) It is miscible with almost all organic substances.
b) It is highly volatile and is readily removed from the system.
c) It does not take part in intermolecular associations with the sample.

The values of chemical shift (δ) is given by: \( \frac{V_{\text{sample}} - V_{\text{reference}}}{V_{\text{Reference}}} \) Operating frequency in mega cycles/chemical Shift is expressed in parts per million (ppm).

Interpretation of NMR spectra: NMR spectrum of a substance gives very valuable information about its molecular structure. This information is gathered as follows:

1. The number of signals in the PMR spectrum tells us how many kinds’ protons in different chemical environments are present in the structure under examinations.
2. The positions of signals tells us about the electronic environment of each kind of proton.
3. The intensities of different signals tell us about the relative number of protons of different kinds.
4. The splitting of signals tell us about the environments of the absorbing proton with respect to the environments of the neighbouring protons.

Note: In the case of signals where splitting takes place, the position of the signals is judged from the centre of doublet, triplet, etc.

Applications: The NMR spectroscopy is very widely used for the detailed investigation of an unknown compound.

Identification of structural isomers: The distinction between the following isomers can be easily made from their NMR spectra.

1. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \) (1-chloro propane)
2. \( \text{CH}_2\text{CHClCH}_3 \) (2-chloro propane)

In the isomer (A) 3 signals are observed where as we see only 2 signals in the spectrum for (B), which is clear distinction between the above isomers. The 3 signals for isomer (A) in order of decreasing tau values are: a) A 3 proton triplet (CH3-). A 2 proton sextet (-CH2-) and A2 proton triplet (-CH2Cl). The 2 signals for isomer (B) as: A 6 Proton doublet (CH2-) and A1 proton septet (-CHCl-).

Detection of hydrogen bonding: The NMR technique can be used to study the hydrogen bonding in organic compounds as well as metal chelates. Hydrogen bonding affects the value δ. As hydrogen bonding involves electron cloud transfer from hydrogen to neighbouring electronegative atom like O, N, S etc. So the hydrogen experiences a net deshielding effect and higher δ value. With increasing in concentrations the hydrogen bonding increases, in turn the value of δ increases and with increases in temperature the hydrogen bonding falls, in turn the value of δ decreases. But in case of compounds showing intermolecular hydrogen bonding the concerned δ value remains unchanged even if the solution diluted, such as for carboxylic acids.

Quantitative analysis: The NMR is used to determine the molar ratio of components in a mixture. For example NMR spectrum of a mixture of benzene and cyclohexane which shows peaks at 7.27 δ and 8.56 δ respectively and the integrated area of former peak will be proportional to 6 protons where as that of the latter peak will be proportional to 12 protons. Obviously if the integrated areas of the 2 bands in the spectrum of the mixture are equal, then the molecular ratio of benzene to cyclohexane in the mixture must be 2:1.

Detection of aromaticity: Protons attached to the benzoyl, polynuclear and heterocyclic compounds whose π electrons follow Huckel rule (i.e. no. of π electrons = \(4n+2\)) π where n=0, 1, 2 etc.) are extremely deshielded due to the circulating sextet (ring current) of π electrons. As a result of this, the signal for the aromatic protons appears at a very low field than that observed even for benzene. From this, the aromatic character of the compound under investigation can be predicted.
Structure determination:
1. Structure of metal complex as WF₆L.
2. Structure of SOF₄.
4. Structure of HF₂.
5. Structure of Polyethylene.

Distinction between Cis-trans isomers and conformers: The cis and trans isomers of a compound can easily distinguished as the concerned protons have different values of the Chemical Shifts (δ) as well as the coupling constants (J). Similarly, the various conformations of compound, the axial and equatorial positions of the proton or group carrying proton can be distinguished from their different values of coupling constants.

Detection of electronegative group or atom: It is known that the presence of electronegative atom or group in the neighbourhood of the proton cause deshielding and the signal is shifted downfield. Greater the electronegativity of the adjacent atom, smaller is the tau value of absorption for the concerned proton. Fluorine causes more downward shift as compared to oxygen.

Detection of some double bond character due to resonance: In some compounds, the molecule acquires a little double bond character due to resonance. Due to this, two signals can be expected for apparently equivalent protons. It is due to the hindered rotation which changes the geometry of the molecules. Consider N, N-dimethyl formamide. For structure (a) 2 signals (singlets) should be expected with peak areas 6:1 as the 2-methyls are exactly equivalent. In structure (b), the presence of double bond restricts rotation and now the 2-methyl groups remain no longer equivalent (geometrical isomers) for this structure, 2 signals appear for 2 methyl groups.

Some more applications in chemical analysis are as follow:
- Finding of keto-enol tautomerism in acetyl acetone.
- Intramolecular conversions in PF₅.
- Exchange effects in some organic acids.
- Intermolecular exchange reactions in acid hydrolysis of ethanol.
- Determination of activation energy in N, N-dimethyl acetamide (DMA).
- Elemental analysis like accurate amount of hydrogen present in given organic compound.
- Useful to study rates of certain reactions which are too fast for measurement by ordinary techniques like reaction of hydrolysis of acetic acid.

Limitations of NMR spectroscopy:
1) One of the serious problem with NMR is its lack of sensitivity. The minimum sample size is about 0.1ml having minimum concentration of about 1%.
2) In some compounds, two different types of hydrogen atoms resonate at similar resonance frequencies, this results in an overlap of spectra and makes such spectra difficult to interpret.
3) While characterizing, the organic compounds, no information about molecular weight is given but the relative number of different protons present are only known.
4) It does not tell us directly how much of compound that present.

5) In most of the cases, only liquids can be studied by NMR spectroscopy, although polymers, preheated with solvents, frequently become fluids which can be treated as liquids which results error in $\delta$ values.

In spite of the above mentioned limitations, NMR is one of the most useful analytical tool yet developed for the elucidation of many organic inorganic and different bimolecular structural problems.

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