Spectroscopy

Study of NMR spectra deals with the study of following points:

(i) ***The number of signals*** **:** This tells aboutthe number of different kinds of protons in the molecule.

(ii) ***The position of signals:*** This tells about the electronic environment of each kind of proton.

(iii) ***The intensities of signals:*** This tells about the number of each type of proton.

(iv) The splitting of a signal into several peaks: This tells about the environment of a proton with respect to its neighbouring protons.

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Instrumentation

Two types of NMR spectrometers are in use :

(i) Wide line NMR spectrometers: These are useful for quantitative elemental analysis and for studying physical environment of a nucleus.

(ii) High resolution NMR spectrometers : This type of instrument can resolve the fine structure that is associated with the absorption peak for a particular nucleus, the chemical environment of which reveals the nature of this fine structure.

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Number of Signals :

Equivalent and Non-Equivalent Protons : The protons with the same environment *(i.e., equivalent protons)* absorb at the same applied field strength and produce only one signal while protons with different environment *(i.e., non-equivalent protons)* absorb at different applied strengths and produce different signals. Thus, the **number of signals** in the NMR spectrum tells us how many kinds of protons are present in a given molecule.

The equivalence of protons can be judged by following the method of isomer number. We imagine each hydrogen or proton in the molecule to be substituted by some other atom (say Z). If the substitution of two protons by Z is expected to furnish either the same product or two enantiomeric products (i. e., mirror images), the two protons are chemically and magnetically equivalent, otherwise not.

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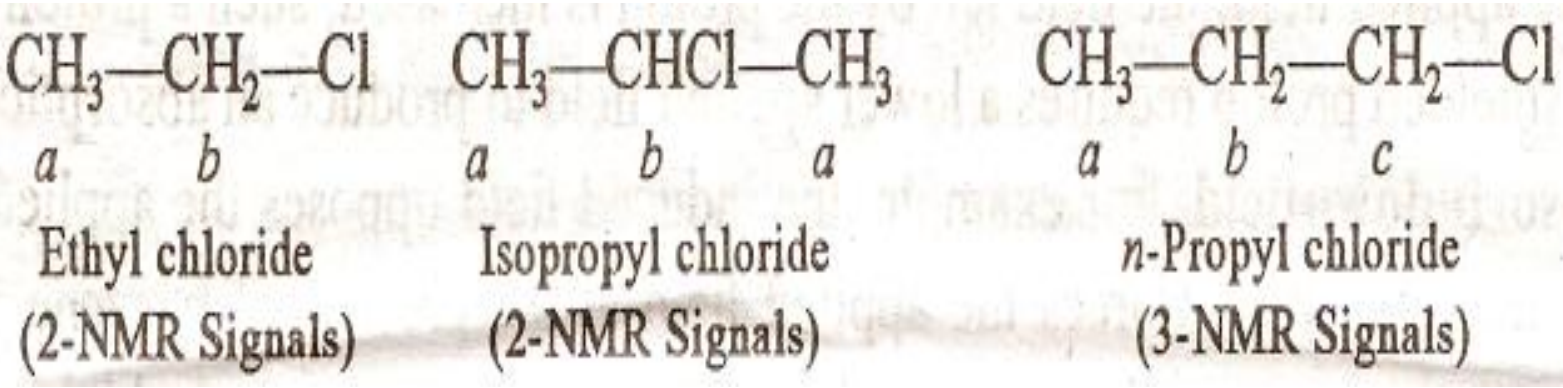
Examples :



Equivalent protons are represented by the same letter, and non-equivalent protons by different letters. In the above example n-propyl chloride gives 3-NMR signals and has 3-non-equivalent set of protons, whereas its isomer isopropyl chloride gives 2-NMR signals and has two sets of equivalent protons and one non-equivalent proton.

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Position of Signals :

The position of the signals reveals the electronic environment of various protons and thus indicates their nature, i *e.,* whether they are aliphatic or aromatic; primary, secondary, tertiary, acetylenic, vinylic or benzylic; adjacent to halogen or to other atoms or groups, etc.

Shielding : When a molecule is placed in a magnetic field, its electron are made to circulate and thus generate a secondary magnetic field called induced magnetic field which may either reinforce or oppose the applied magnetic field. In case the induced field opposes the applied field, the field felt by the proton is diminished; such a proton is said to be shielded. A shielded proton requires a stronger magnetic field to produce an absorption signal and thus is said to absorb upfield.

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Deshielding : If the induced field reinforces the applied field, the field felt by the proton is increased; such a proton is said to be deshielded. A deshielded proton requires a lower applied field to produce an absorption signal and thus is said to absorb down field.

Chemical shift : The shifts in the position of NMR signals arising from the shielding or deshieldingl,by electrons are referred to as chemicals shifts.

Measuring and Expressing the Chemical Shift :

Chemical shifts are measured with reference to Tetramethyl silane (TMS), $(CH_3)_4Si$, which is the standard used in proton magnetic resonance spectroscopy. A small quality of TMS is added to the sample while running its NMR spectrum.

The choice of TMS ,as the standard is one to following advantages: (i) TMS is chemically inert.

(ii) It is miscible with almost all organic substances.

(iii) It is highly volatile and is readily removed from the system.

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The most commonly used scale is the (delta) scale. The position of the tetramethyl Silane (reference) signalis taken as 0.0 ppm. Most chemical shifts have values between 0 arid 10. A small value represents a small down field shift; and a large value represents a large down field shift. Some times tau (ζ) scale is used where the $(CH_3)_4Si$ signal is taken as 10.0 ppm. ζ = 10 - .

The proton-NMR spectrum of a molecule thus gives information about:

(i) The number of signals or peaks which enables us to know about the kinds of protons present in a molecule.

(ii) The intensities of the peaks which tell us about the number of protons of each kind that are

present.

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(iii) The positions of the peaks which tell us about the electronic environment of each kind of proton.

(iv) The spin-spin splitting or multiplicity reveals the possible arrangements of groups in the molecule. At high resolution, the main peak for each group may split into two or more peaks, which indicates the number of protons present in the adjacent carbon.