B.Sc. Semester-VI Paper CC-XIV Organic Chemistry-V



III. Nuclear Magnetic Resonance Spectroscopy



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Nuclear Magnetic Resonance Spectroscopy Introduction to NMR Spectroscopy

- Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.
- Two common types of NMR spectroscopy are used to characterize organic structure: ¹H NMR is used to determine the type and number of H atoms in a molecule; ¹⁸C NMR is used to determine the type of carbon atoms in the molecule.
- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.
- When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including ¹H and ¹³C.

- When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.
- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B_0 , they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy.
- The energy difference between these two states is very small (<0.1 cal).



- In a magnetic field, there are now two energy states for a proton: a lower energy state with the nucleus aligned in the same direction as B0, and a higher energy state in which the nucleus aligned against B0.
- When an external energy source (hn) that matches the energy difference (DE) between these two states is applied, energy is absorbed, causing the nucleus to "spin flip" from one orientation to another.
- The energy difference between these two nuclear spin states corresponds to the low frequency RF region of the electromagnetic spectrum.

• Thus, two variables characterize NMR: an applied magnetic field B0, the strength of which is measured in tesla (T), and the frequency n of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz)–(1 MHz = 10⁶ Hz).



 A nucleus is in resonance when it absorbs RF radiation and "spin flips" to a higher energy state.

• The frequency needed for resonance and the applied magnetic field strength are proportionally related:



- The stronger the magnetic field, the larger the energy difference between the two nuclear spin states, and the higher the v needed for resonance.
- NMR spectrometers are referred to as 300 MHz instruments, 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance.
- These spectrometers use very powerful magnets to create a small but measurable energy difference between two possible spin states.



An NMR spectrometer. The sample is dissolved in a solvent, usually $CDCl_3$ (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded. The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.

- Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The frequency at which a particular proton absorbs is determined by its electronic environment.
- The size of the magnetic field generated by the electrons around a proton determines where it absorbs.
- Modern NMR spectrometers use a constant magnetic field strength B_0 , and then a narrow range of frequencies is applied to achieve the resonance of all protons.
- Only nuclei that contain odd mass numbers (such as ¹H, ¹³C, ¹⁹F and ³¹P) or odd atomic numbers (such as ²H and ¹⁴N) give rise to NMR signals.

Nuclear Magnetic Resonance Spectroscopy

¹H NMR–The Spectrum

• An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in parts per million (ppm).



Nuclear Magnetic Resonance Spectroscopy

¹H NMR–The Spectrum

- NMR absorptions generally appear as sharp peaks.
- Increasing chemical shift is plotted from left to right.
- Most protons absorb between 0-10 ppm.
- The terms "upfield" and "downfield" describe the relative location of peaks. Upfield means to the right. Downfield means to the left.
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the d scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.

Nuclear Magnetic Resonance Spectroscopy

¹H NMR–The Spectrum

• The chemical shift of the *x* axis gives the position of an NMR signal, measured in ppm, according to the following equation:



- By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.
- Four different features of a ¹H NMR spectrum provide information about a compound's structure:
 - a. Number of signals
 - b. Position of signals
 - c. Intensity of signals.
 - d. Spin-spin splitting of signals.

Thank You



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