

Chapter 12

Spectroscopy and Structure Determination

Principles of Spectroscopy
Nuclear Magnetic Resonance Spectroscopy
Infrared Spectroscopy
Mass Spectrometry
UV-Visible Spectroscopy

Important questions about the structure of an organic compound

How are the atom arranged?

The carbon skeleton-cyclic or acyclic?

Aromatic or not?

Saturated or unsaturated?

What functional group/s are present?

What elements are in a compound and in what proportions?

Attempts to provide answers to the questions

Chemists have used

- Elemental analysis
- Chemical tests for functional groups
- Chemical conversions and breakdowns

In modern times

- Spectroscopy has provided great advantages such as: rapid response, detailed structural information, small sample materials, and consistency of results.

Principles of Spectroscopy

$$E = h\nu$$

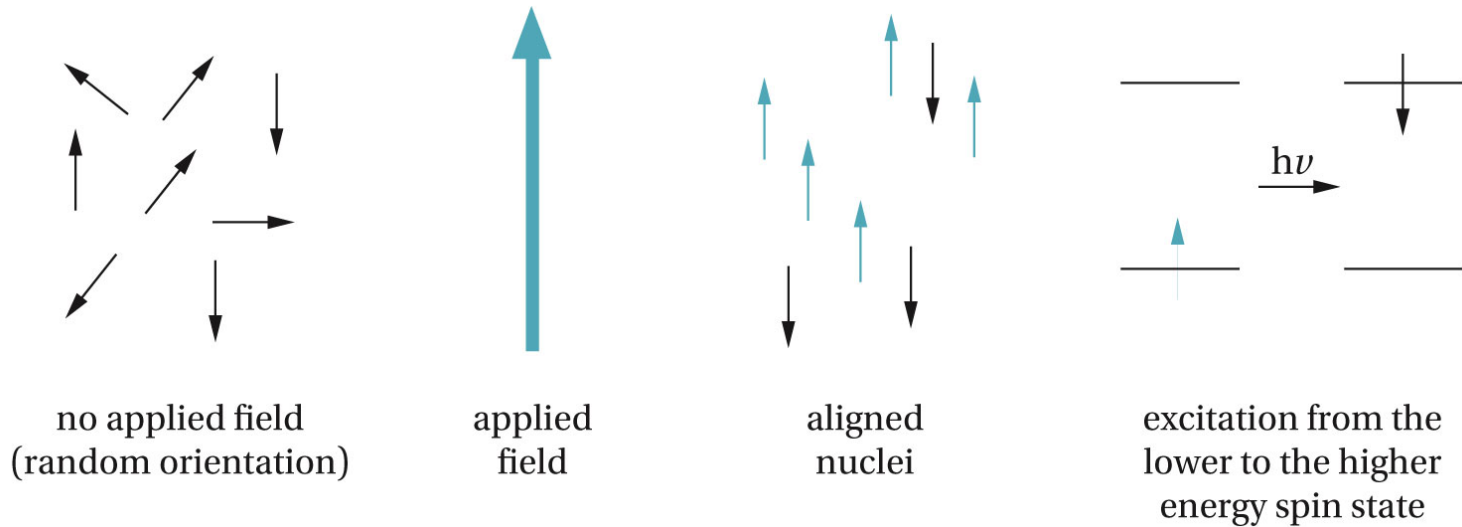
or

$$E = hc/\lambda$$

Type of spectroscopy	Radiation source	Energy (Kcal/mol)	Type of transition
NMR	Radio waves	6-60 x 10 ⁻⁶	Nuclear spin
IR	Infrared light	2-12	Molecular vibrations
UV-Visible	Visible or ultraviolet light	37-150	Electronic states

Nuclear Magnetic Resonance (NMR) Spectroscopy

Commonly used nuclei in NMR are ^1H and ^{13}C



Chemical Shifts

^1H and ^{13}C nuclei in a particular organic compound may differ in their electronic environments, therefore show peaks at different chemical shifts measured in δ (delta) units from the reference peak. Which is TMS (tetramethylsilane $(\text{CH}_3)_4\text{Si}$)

The chemical shift is ***independent*** of the instrument on which it is measured.

Chemical shift = $\delta = \frac{\text{distance of peak from TMS, in Hz}}{\text{spectrometer frequency in MHz}}$ ppm

Peak Areas

Different kinds of ^1H nuclei will give different peaks. The relative number of equivalent ^1H nuclei are proportional to their peak area.

The relative ratios of peak areas is captured in the ***integration*** of the spectrum.

However for ^{13}C NMR integration is not normally used as it does not give accurate information.

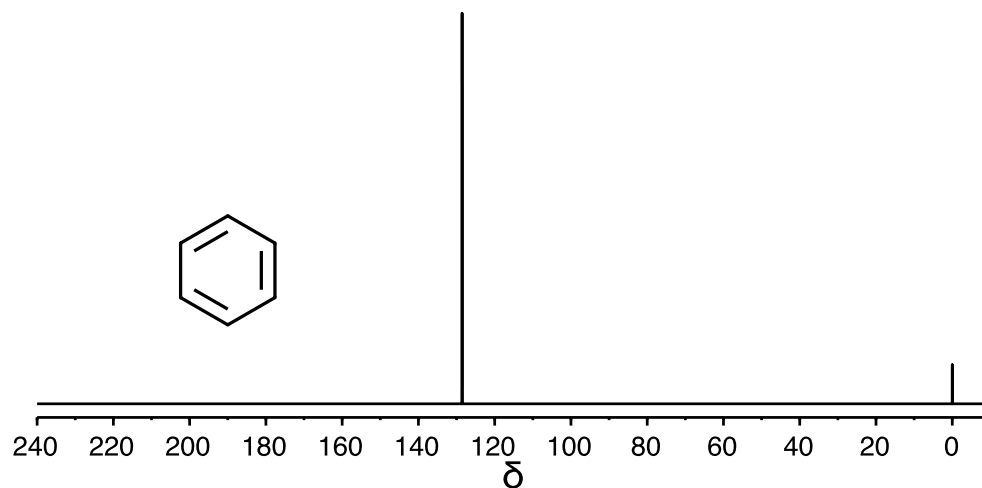
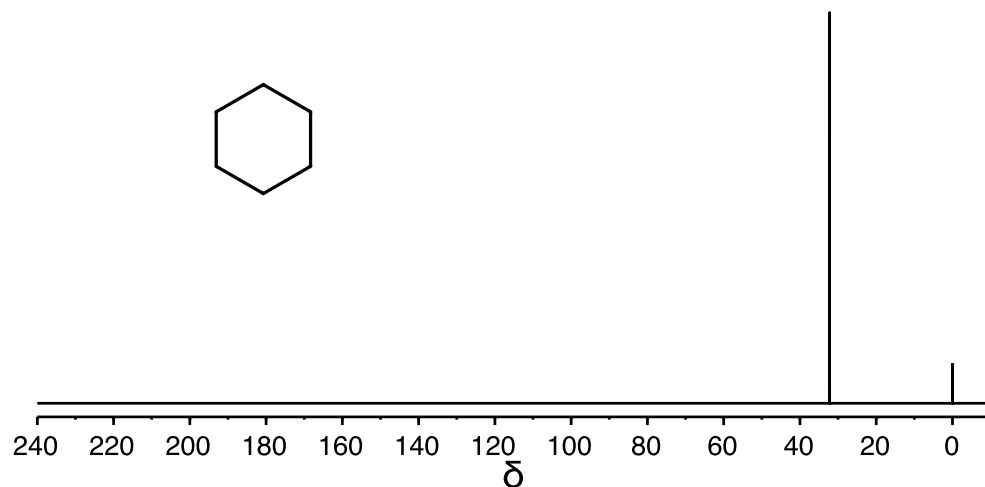
^{13}C NMR Spectroscopy

^{13}C NMR spectroscopy provides information about the carbon skeleton of the compound.

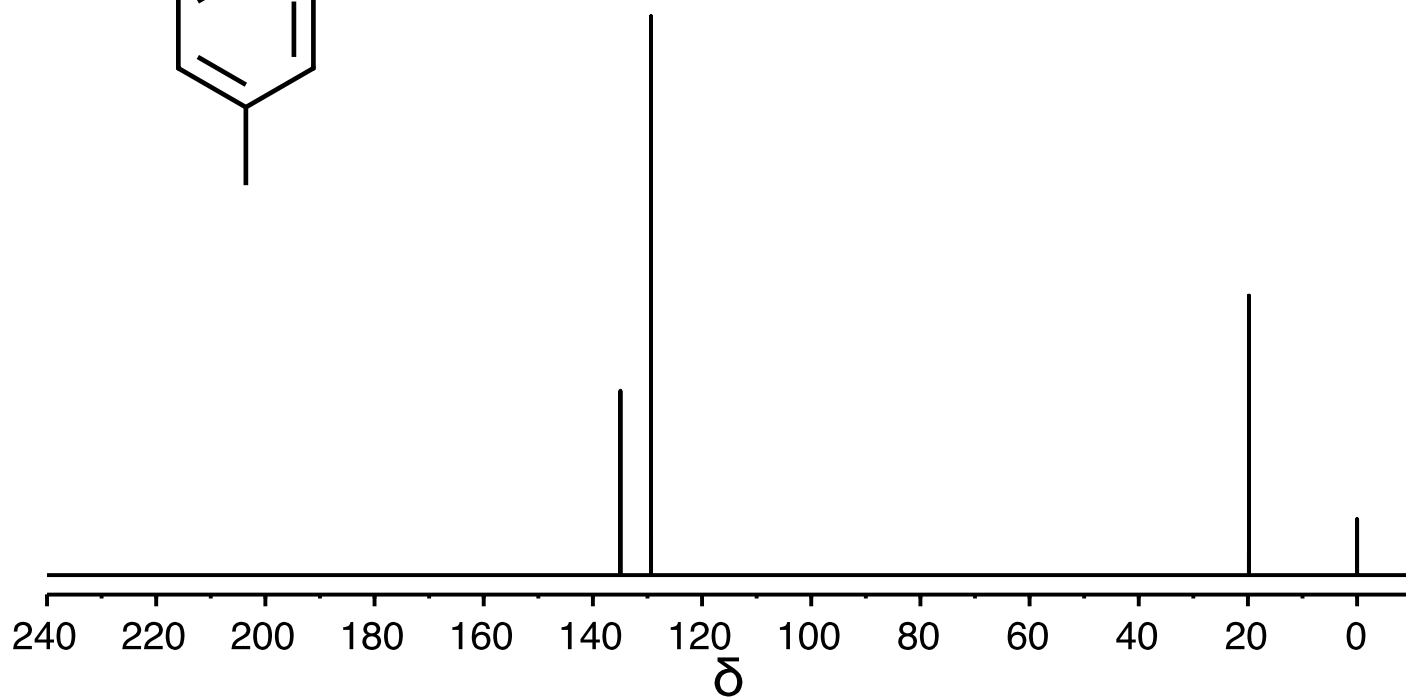
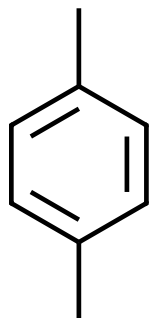
The abundant ordinary ^{12}C isotope does not have a nuclear spin. However, the ^{13}C , which has 1.1% natural abundance, has a nuclear spin.

Typical chemical shift range for ^{13}C is 0 ppm to 200 ppm downfield from TMS.

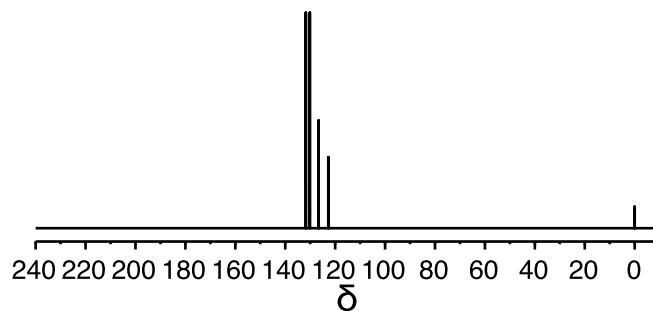
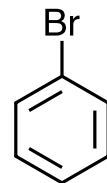
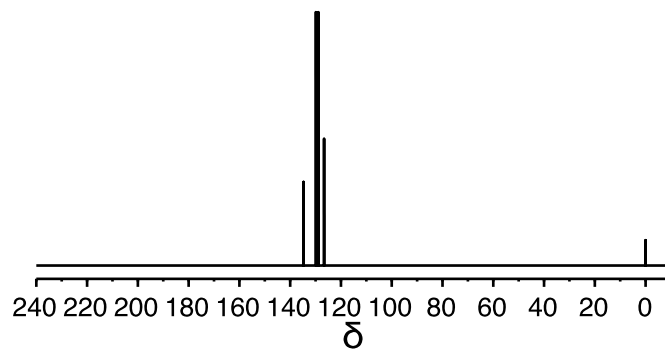
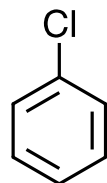
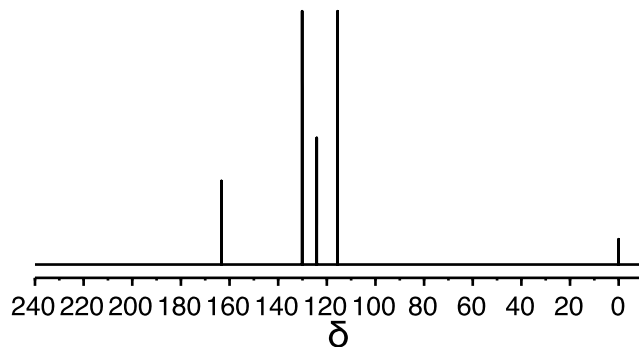
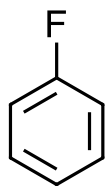
^{13}C NMR spectra of cyclohexane vs benzene



p-Xylene



Effect of electronegativity



Splitting in ^{13}C NMR

Due to low natural abundance of ^{13}C , the chance of finding two adjacent ^{13}C atoms in the same molecule is small. Hence ^{13}C - ^{13}C splitting is ordinarily not seen.

However, ^{13}C - ^1H spin-spin splitting can occur, but the ^{13}C spectrum is usually run such that this splitting do not appear (*called a proton decoupled spectrum*)