

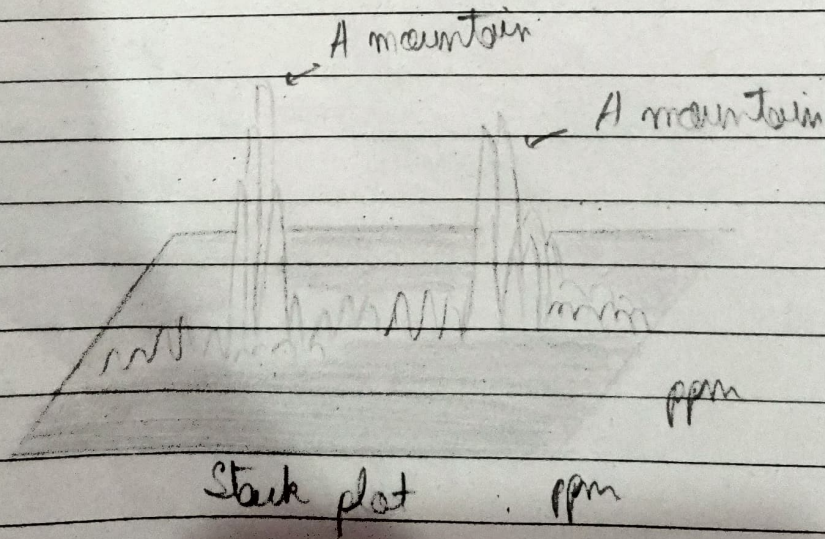
Unit - 2

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Two Dimensional NMR Spectroscopy

The COSY Technique → Introduction

- A conventional ^1H NMR spectrum has a frequency axis and an intensity axis, 2-D NMR spectra have two frequency axes and one intensity axis.
- The common 2-D spectra are ^1H - ^1H shift correlation in which both frequency axes show ^1H chemical shifts. This is known as ^1H - ^1H shift correlated spectroscopy, which is known by COSY (Correlated Spectroscopy).
- COSY identifies pairs of protons which are coupled to each other.

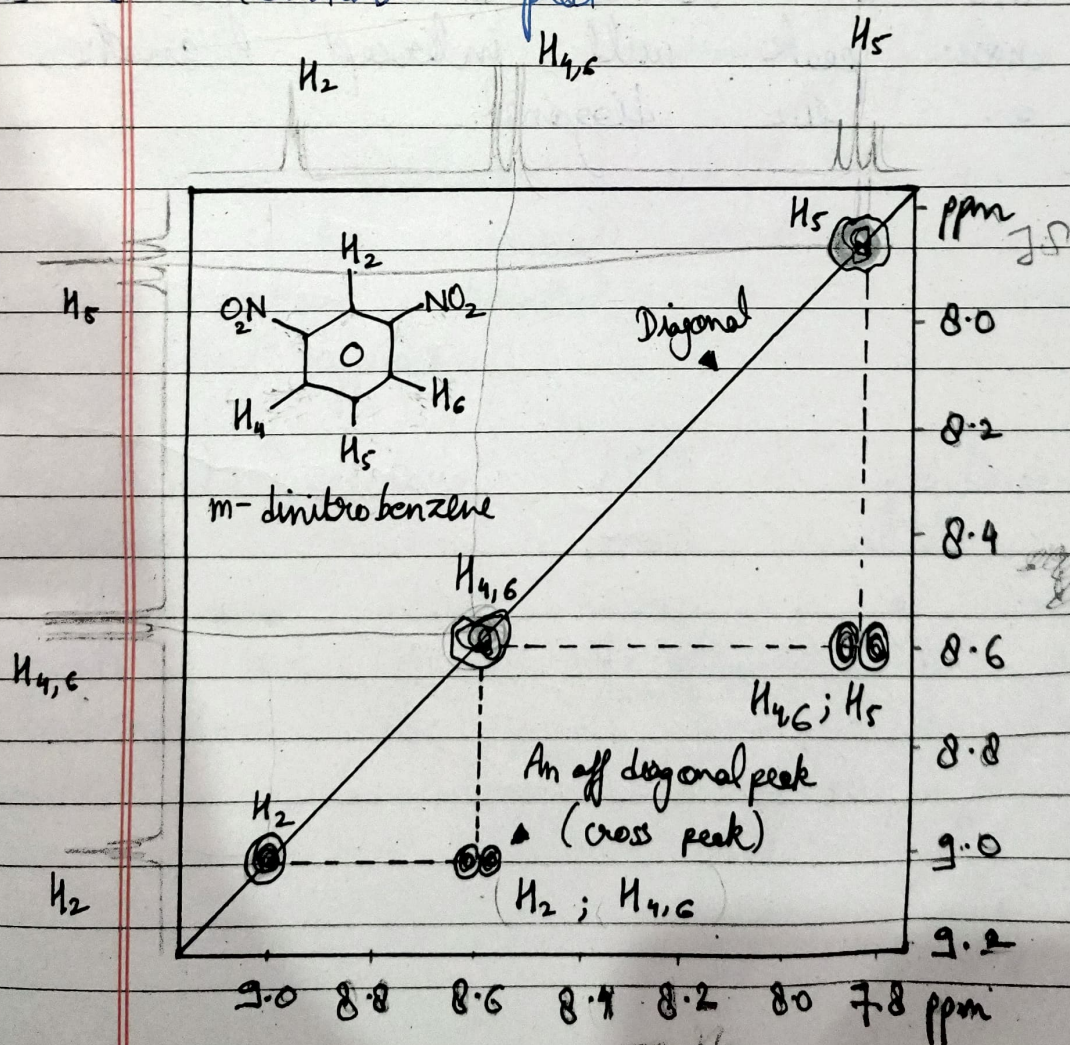


A portion of the COSY spectrum of a compound gives a look of a mountain range viewed from the air.

These "mountain-like" spectra (known as stack plots) are not the spectra which are used in practice to study a compound.

COSY Correlation Spectroscopy (Cross-Peak Correlation)

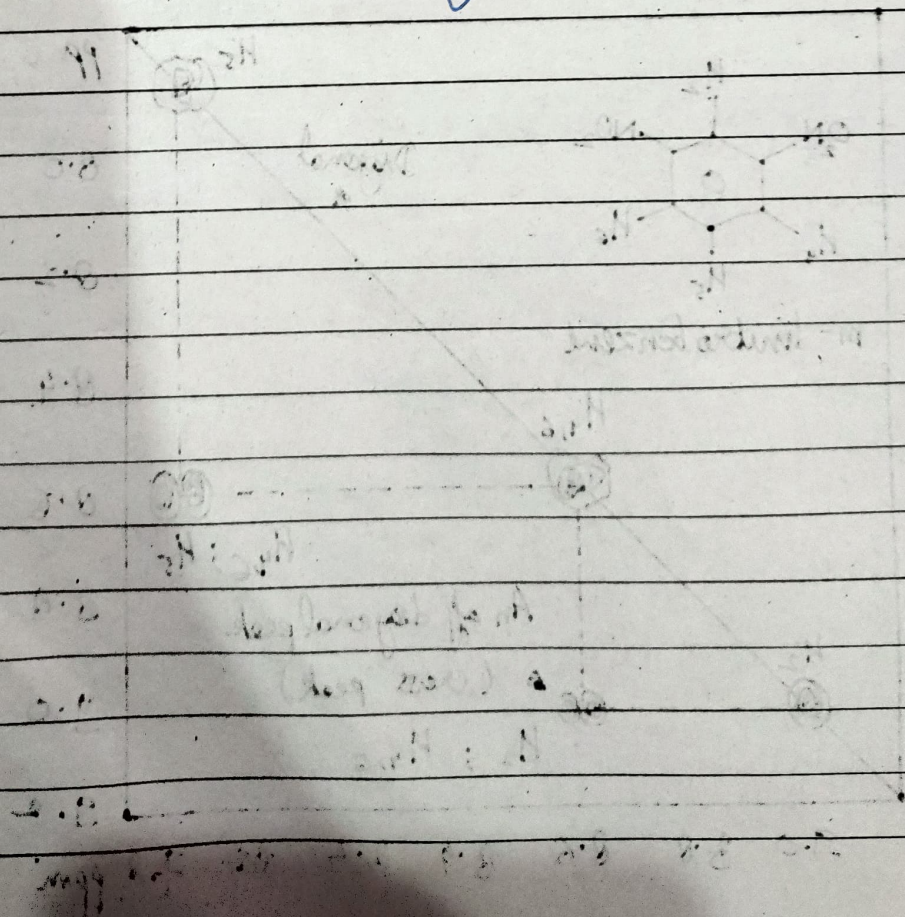
The COSY spectrum of m-dinitrobenzene is presented as a contour plot.



• COSY spectrum is the ^1H NMR spectrum run both along the X-axis and then at the Y-axis and the signals are repeated yet again as spots on the diagonal.

• In the COSY spectrum of m-dinitrobenzene the diagonal runs from upper right corner to lower left corner.

If a proton couples with another proton i.e., if a correlation is established then a horizontal line drawn from a cross peak will intercept a contour on the diagonal and a vertical line from the same cross peak will intercept another contour on the diagonal.



DEPT ¹³C Spectra

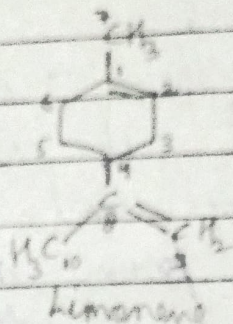
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- In several of the recent advances (i.e., COSY and HETCOR spectra) it is now possible to establish coupling and therefore, bonding between at least close proximity b/w these lying hydrogens are connected carbon and hydrogen atoms.
- In a yet another advancement — a DEPT experiment (distortionless enhanced polarisation transfer) three spectra are obtained.
- One is a normal broadband ^{decoupled} spectrum.
- The second spectrum (DEPT 90° spectrum) is obtained under special conditions in which only carbons bonded to a single hydrogen (CH's) appear.
- A third spectrum (DEPT 135° spectrum) is obtained under ~~which~~ conditions in which CH's and CH₃'s appear as a normal signals, but CH₂'s appear as negative absorptions, and no peak for quaternary carbons.

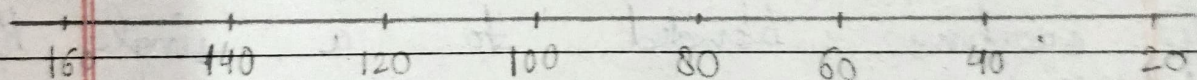
For e.g. ~~limonene~~ limonene illustrates this.

broad-band decoupled spectrum



DEPT-90 spectrum

DEPT-135 spectrum



The spectrum 1 is the usual broad-band decoupled spectrum which displays the expected no. of 10 lines for ten carbons and groups these into six alkyl carbon signals at high field (20-40 ppm) and four alkyl carbon signals at low field (100-150 ppm).

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The spectrum 2 is DEPT-90 spectrum in which only two CH signals for carbons C-2 and C-4 appear.

Spectrum 3 is DEPT-135 spectrum which displays positive absorptions for two CH_2 groups (C-7 and C-10) and for two CH groups (C-2 and C-4), moreover it shows negative peaks for four CH_2 groups (C-3, C-5, C-6 and C-9) while no signal for C-1 and C-8.