

Two-Dimensional NMR Techniques

1. COSY (correlated spectroscopy)

A type of two-dimensional experiment used to establish proton-proton correlations

A COSY spectrum is acquired as a series of one-dimensional experiments

One dimension represents the computer memory used to store each experiment; one dimension represents the number of experiments or slices

$256 \times 512 = 256$ experiments each collected with 512K of computer memory

$512 \times 1024 = 512$ experiments each collected with 1024K of computer memory (four times as much data)

Can take some time to acquire a COSY; anywhere from 15 minutes to two hours

In a COSY spectrum spectrum, the one-dimensional spectrum appears along the diagonal

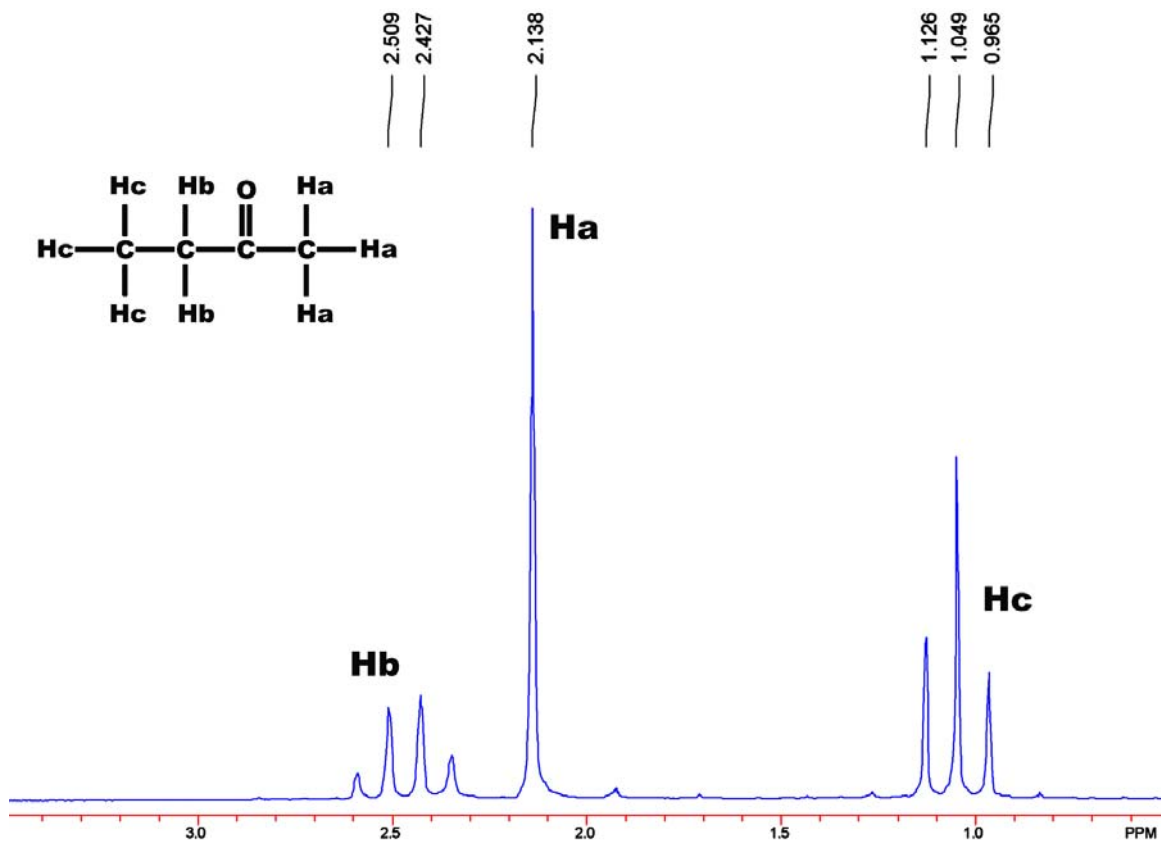
Cross peaks connect those protons that are coupled

Half of the spectrum is a reflection of the other half (the spectrum may be reflected through the diagonal)

A process known as *symmetrization* is often used to improve spectra; everything that does not have a mirror image across the diagonal is discarded

Example 1: 2-butanone

Recall proton spectrum of 2-butanone:

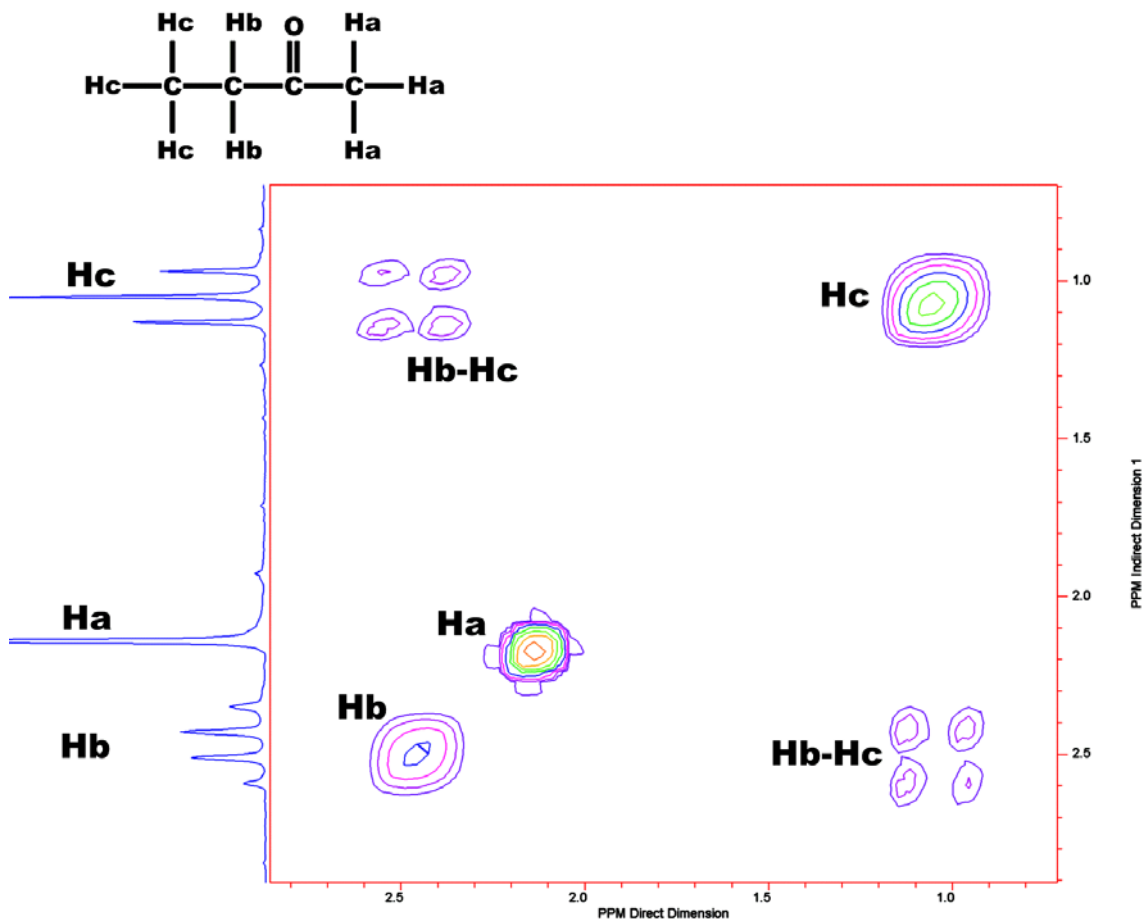


Hc split into a triplet by two equivalent Hb atoms

Hb split into quartet by three equivalent Hc atoms

Ha appears as a singlet; no other H-atoms within three bonds

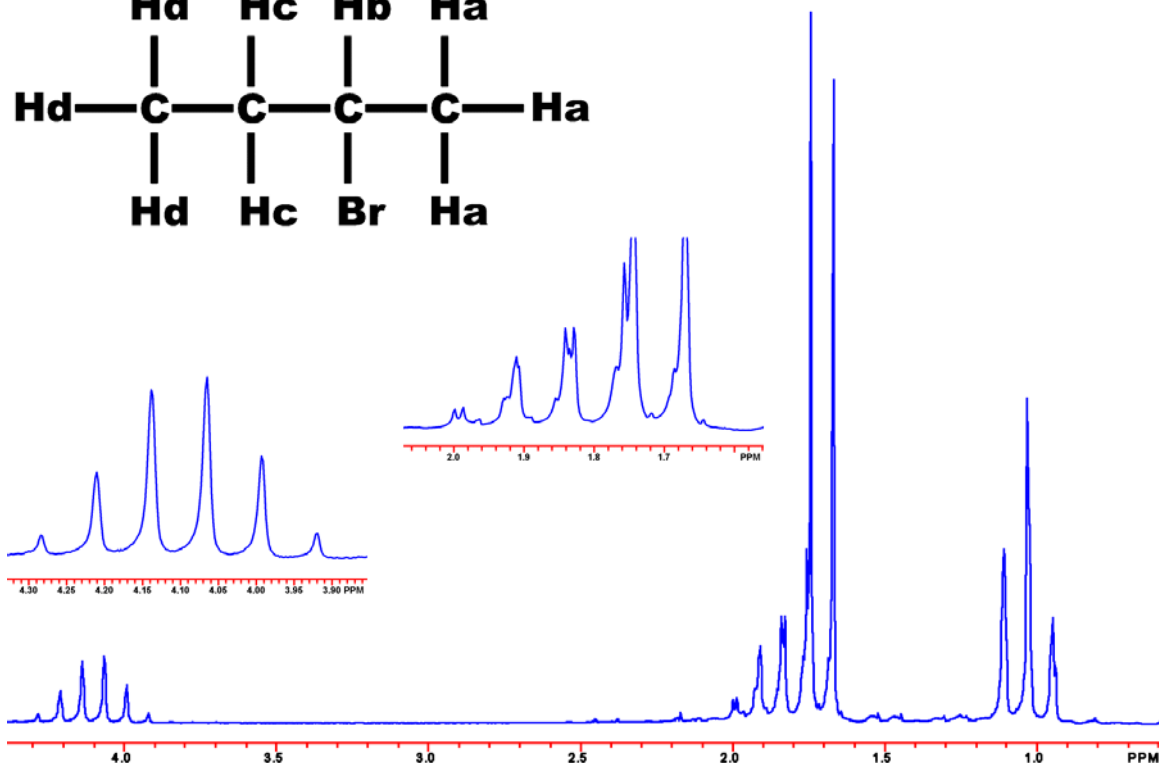
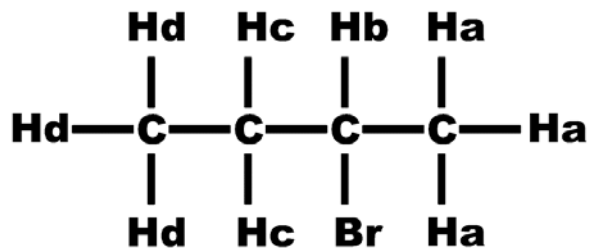
90-MHz COSY Spectrum of 2-Butanone



Hb and Hc are connected by a *cross peak* (labeled Hb-Hc on spectrum) because they are coupled

Ha does not show any cross peaks because it is not coupled to any other protons

Example 2: 2-bromobutane



90-MHz proton spectrum of 2-bromobutane

The Ha protons are split only by the Hb proton into doublet; appear at approximately 1.7 ppm

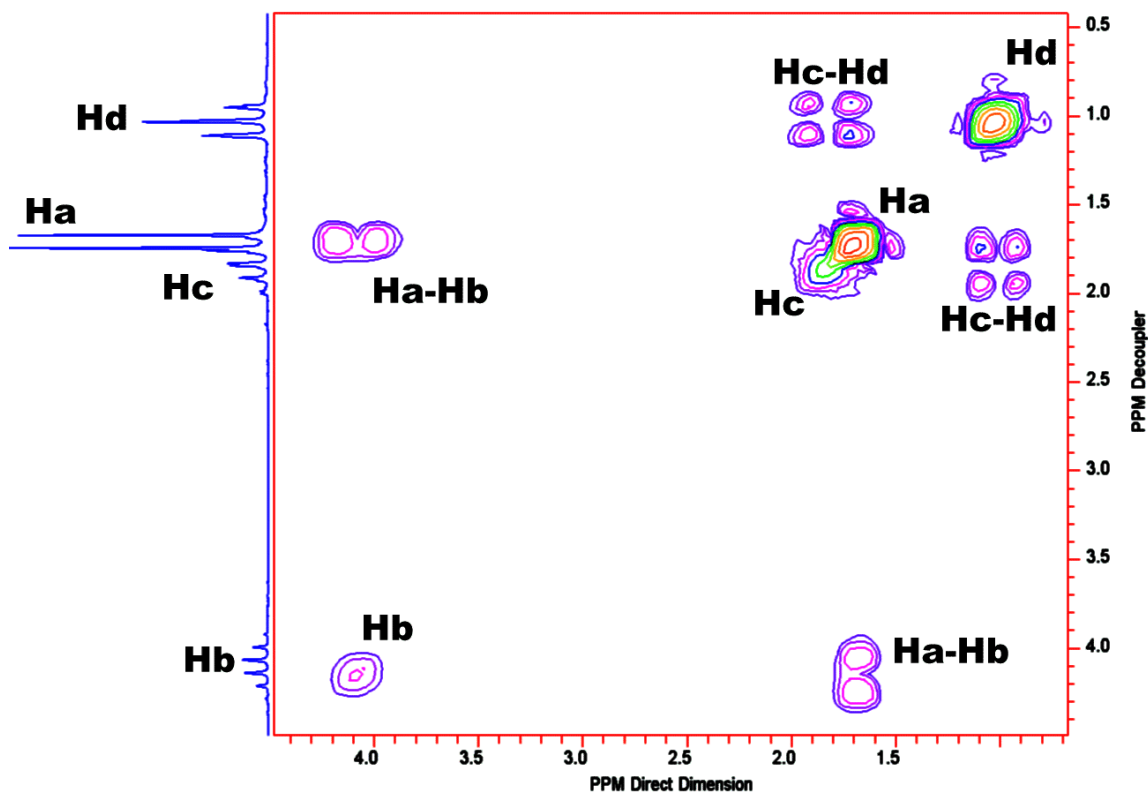
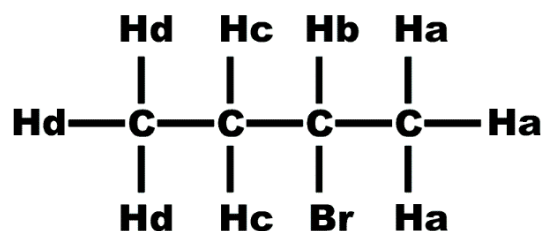
The Hd protons are split by only by the Hc protons into a triplet; appear at approximately 1.1 ppm

The Hc protons are split both by the Hd protons into a quartet and again by the Hb proton into a doublet; appear as a multiplet at approximately 1.75 ppm

The Hb proton is split by the Ha protons into a quartet and again by the Hc protons into a triplet; appears as a multiplet at approximately 1.5 ppm

Note that the Hb and Hc multiplets are partially overlapped

90-MHz COSY Spectrum of 2-Bromobutane



There is a cross peak between Ha and Hc; these protons are coupled

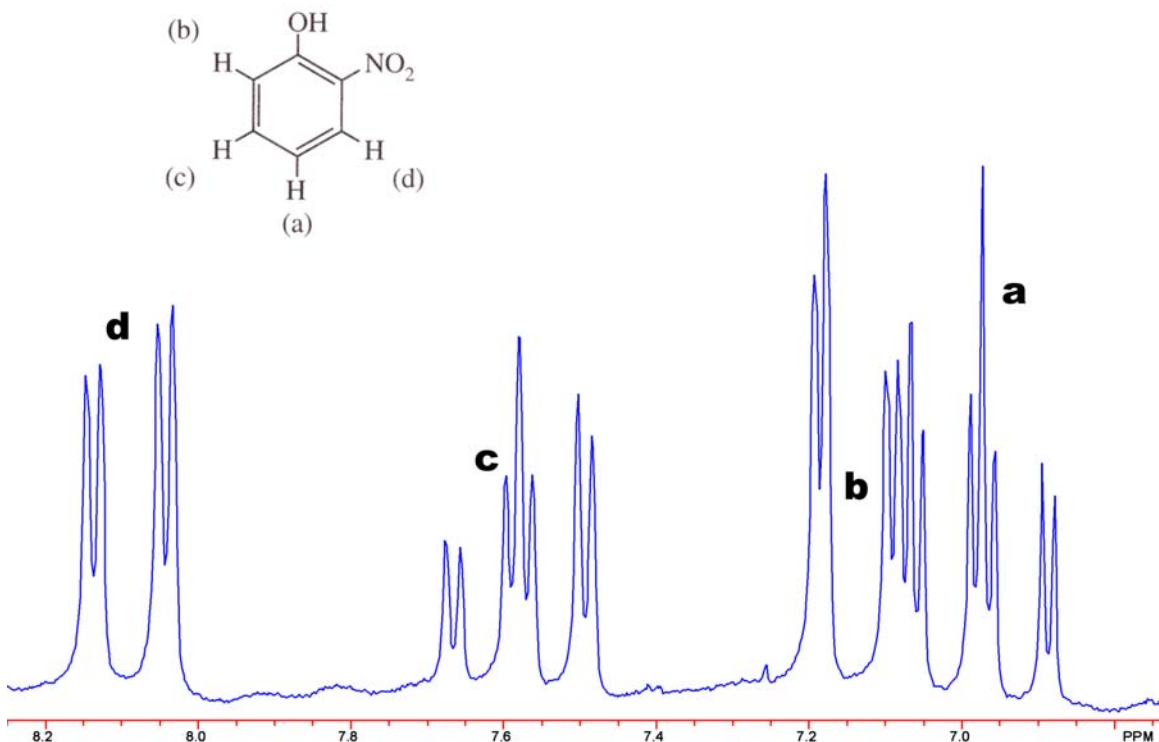
There is a cross peak between Hc and Hd; these protons are coupled

No cross peak between Hb and Hd because these are *not* coupled

No cross peak between Ha and Hc because these are *not* coupled

No cross peak between Ha and Hd because these are *not* coupled

Example 3: 2-nitrophenol



Both *ortho* and *meta* couplings are present in this case

The *b* and *d* protons experience two couplings, one large and one small, and appear as a doublet of doublets

The large coupling is an *ortho* coupling

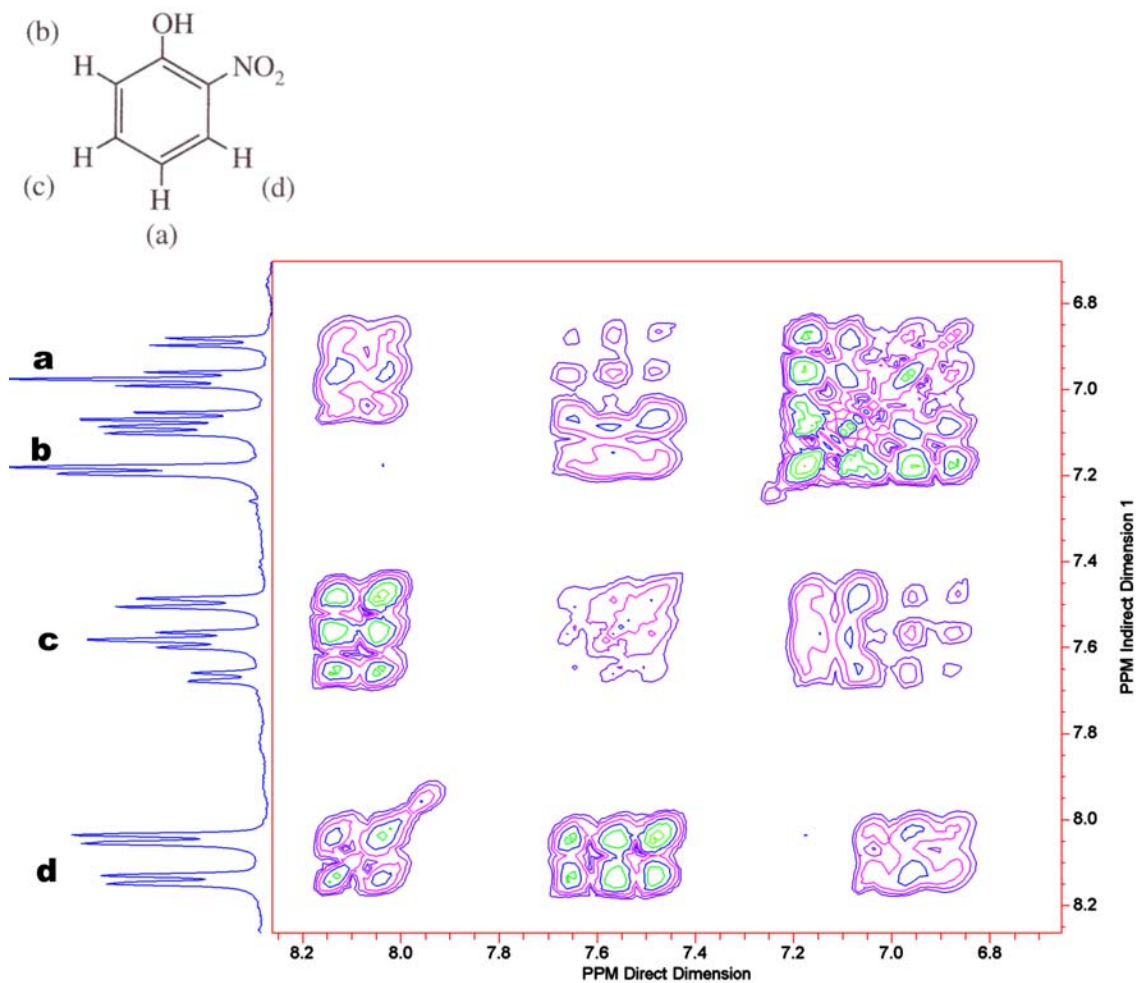
The small coupling is a *meta* coupling

The *a* and *c* protons experience two large couplings (causing a split into doublet of doublets, which appear as a triplet) and one small coupling (causing each component of the triplet to be split)

The large coupling is an *ortho* coupling

The small coupling is a *meta* coupling

90-MHz COSY Spectrum of 2-Nitrophenol



Proton *a* shows cross peaks with protons *b*, *c* and *d*

Proton *b* shows cross peaks with protons *c* and *a*

Proton *c* shows cross peaks with protons *a*, *b*, and *d*

Proton *d* shows cross peaks with protons *a* and *c*

There are *no cross peaks* between protons *d* and *b*

Other Types of Two-Dimensional Experiments

NOESY - (Nuclear Overhauser Spectroscopy)

In appearance similar to a COSY

Cross peaks appear as a result of through-space interactions
(rather than through-bond interactions)

HETCOR – (Heteronuclear Correlation)

Heteronuclear in that it involves both proton and carbon nuclei

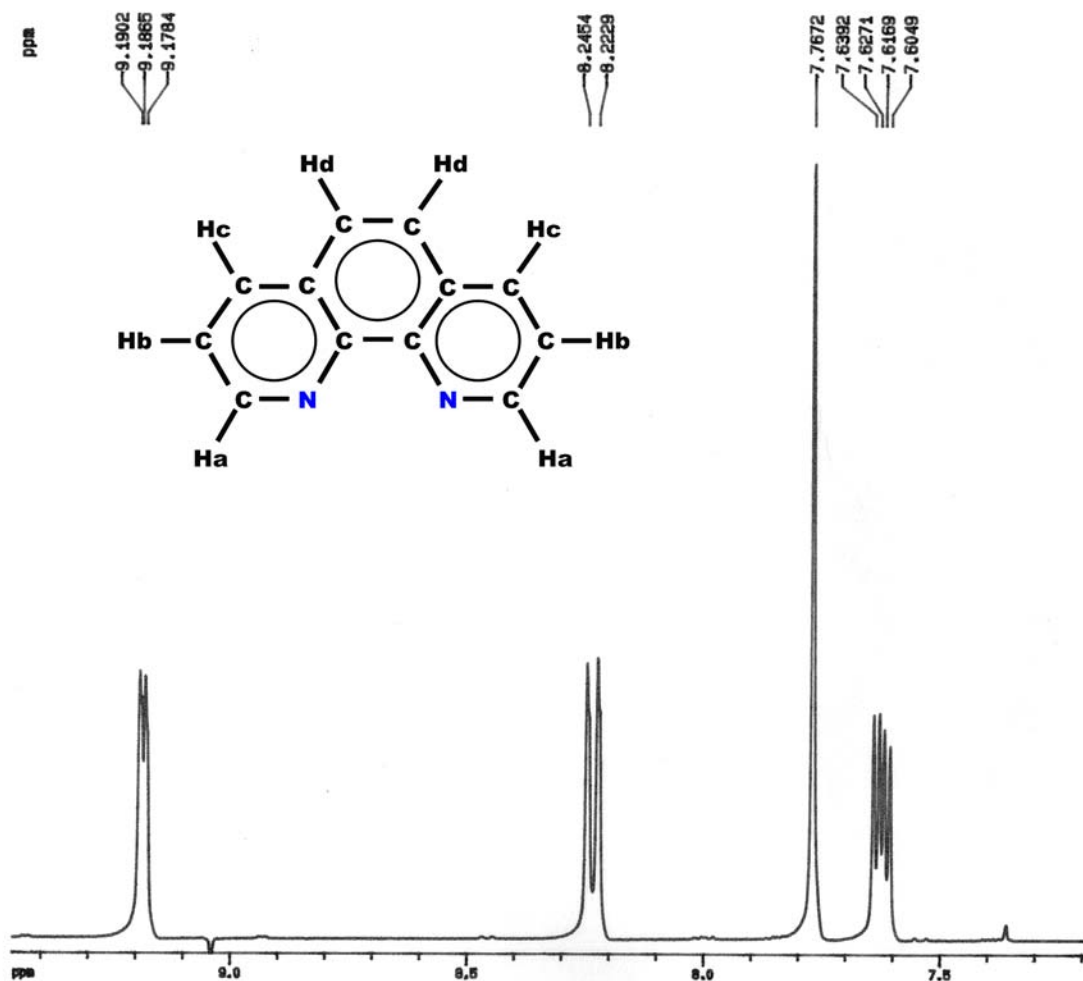
Carbon spectrum appears along one axis, proton spectrum appears
along the other

Cross peaks appear between carbon atoms and their attached
protons

If proton assignments are known, can be used to aid in carbon
assignments (and vice-versa)

An Example: 1,10-phenanthroline

Recall proton spectrum of 1,10-phenanthroline



360-MHz Spectrum of 1,10-Phenanthroline

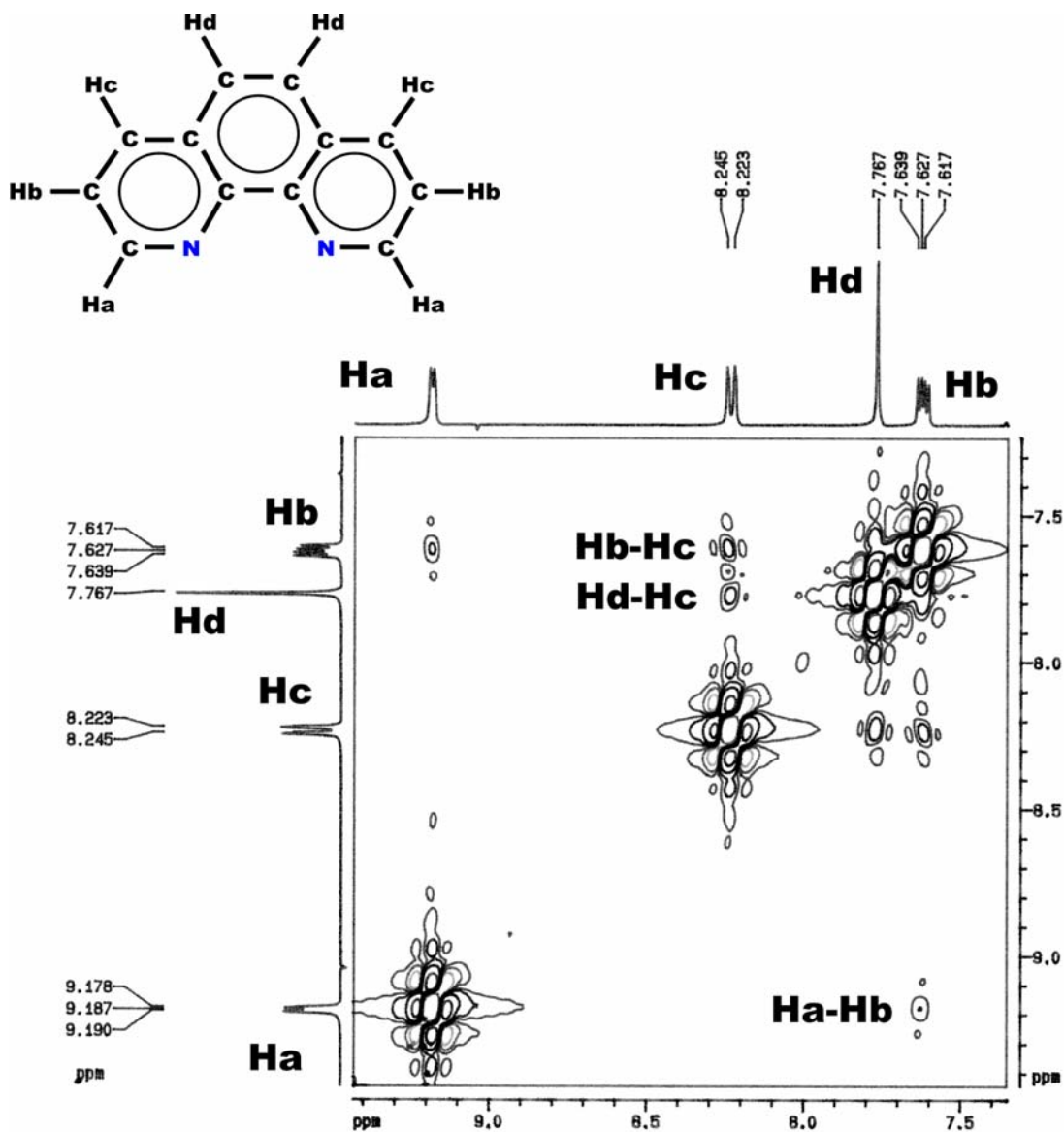
9.18 = Ha (doublet, closest to N atom shifted furthest downfield)

8.24 = Hc (split only by Hb, this is only other doublet)

7.62 = Hb (based on multiplicity, split by Ha and Hc)

7.76 = Hd (no splitting, appears as a singlet)

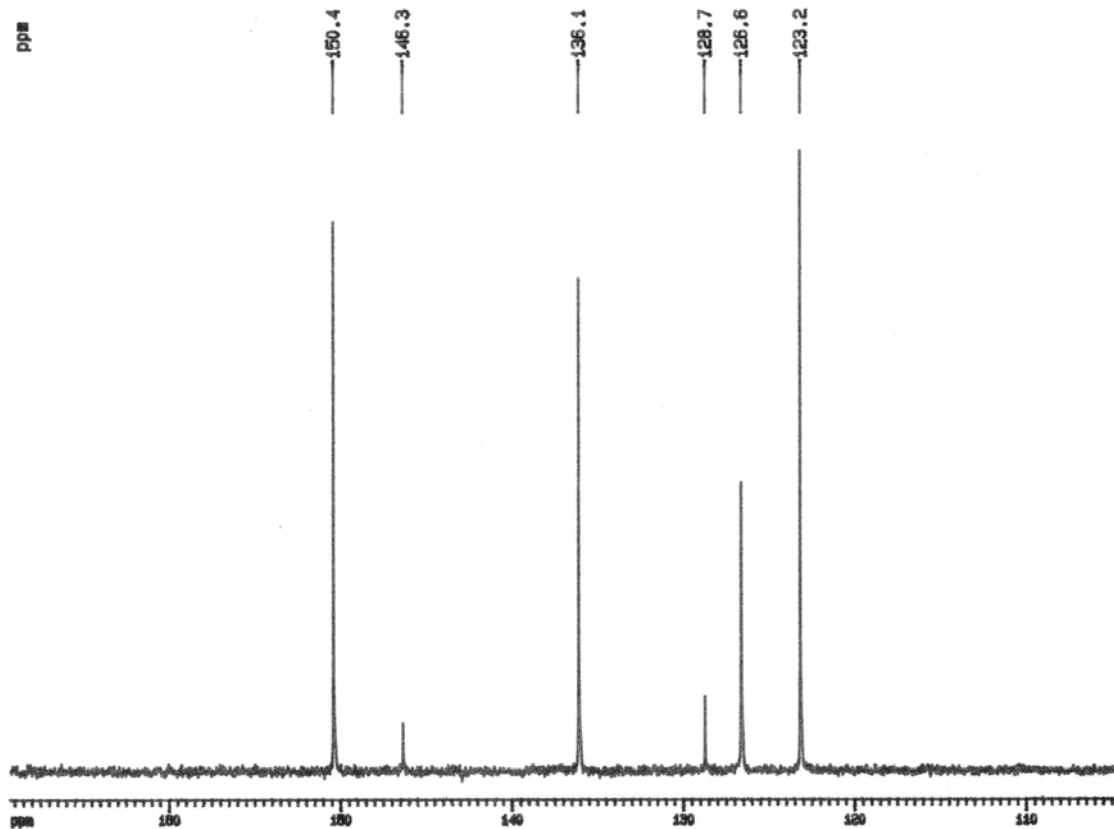
NOESY Spectrum of 1,10-Phenanthroline



Hd singlet shows cross peak only to Hc doublet (confirms assignment of doublet at 8.24 ppm to Hc and not Ha)

Hb quartet shows cross peaks to Ha and Hc doublets

Carbon Spectrum of 1,10-Phenanthroline

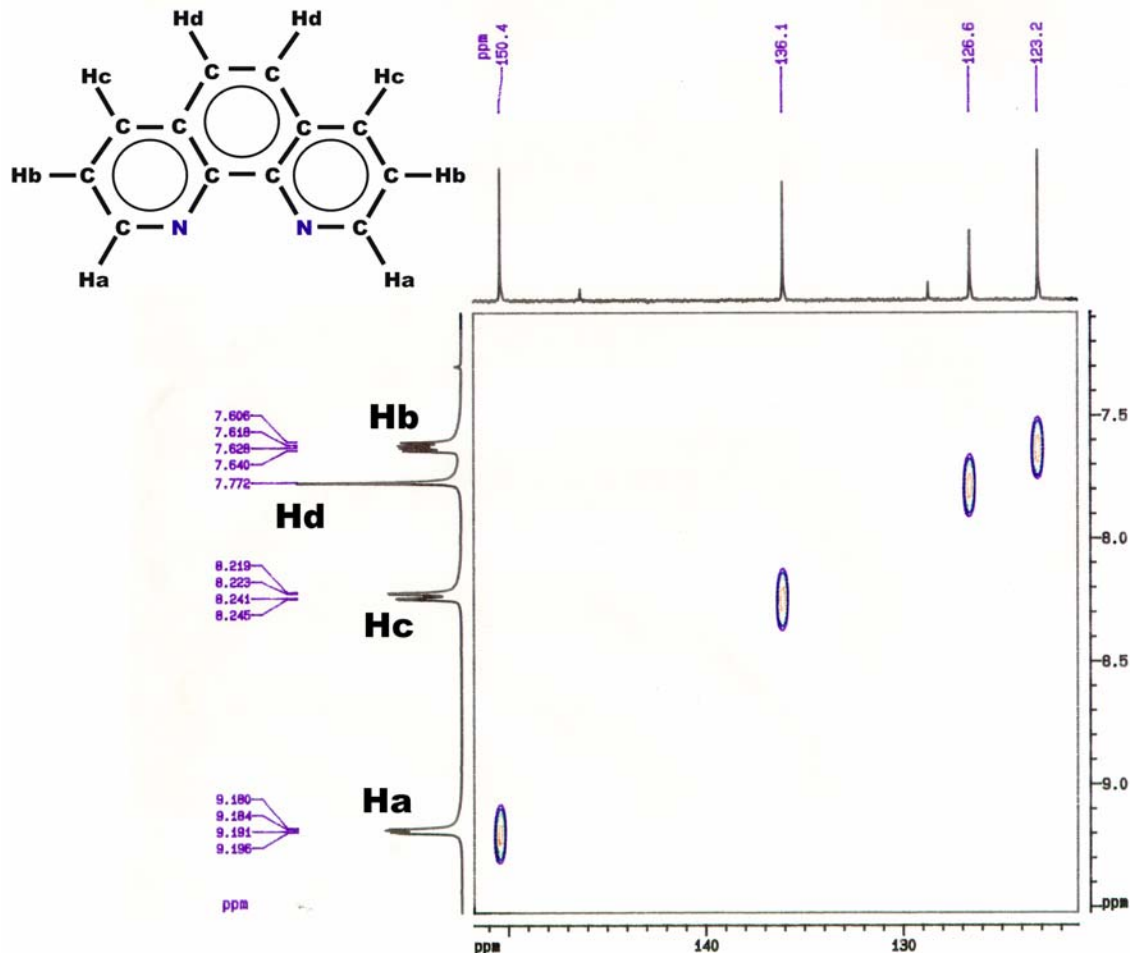


Can we make assignments in this spectrum?

Not beyond a couple of guesses

What we need is a HETCOR

Heteronuclear Correlation Spectrum of 1,10-Phenanthroline



Ha correlates to carbon signal at 150.4 ppm

Hb correlates to carbon signal at 123.2 ppm

Hc correlates to carbon signal at 136.1 ppm

Hd correlates to carbon signal at 126.6 ppm

The two quaternary carbon atoms do not show any correlations because they do not have attached protons; of these two we can make an educated guess that the one closest to the nitrogen atom is shifted furthest downfield.