CHEM202

Organic Chemistry

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Module 1: Spectroscopy and Characterisation

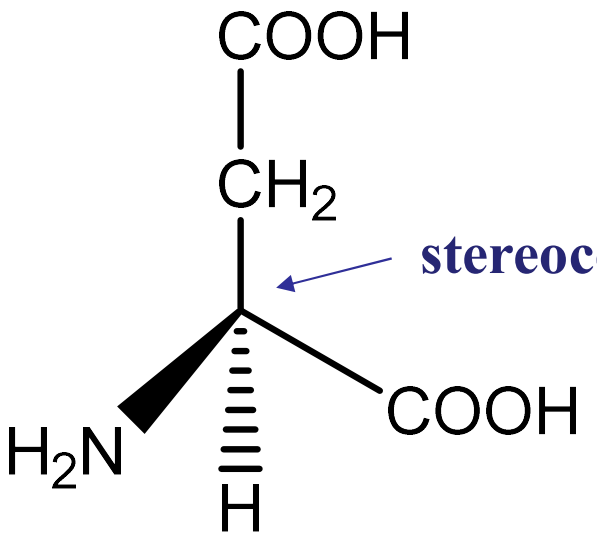
Lecture 8: NMR Spectroscopy

Certain NMR experiments can be used to distinguish enantiomers!

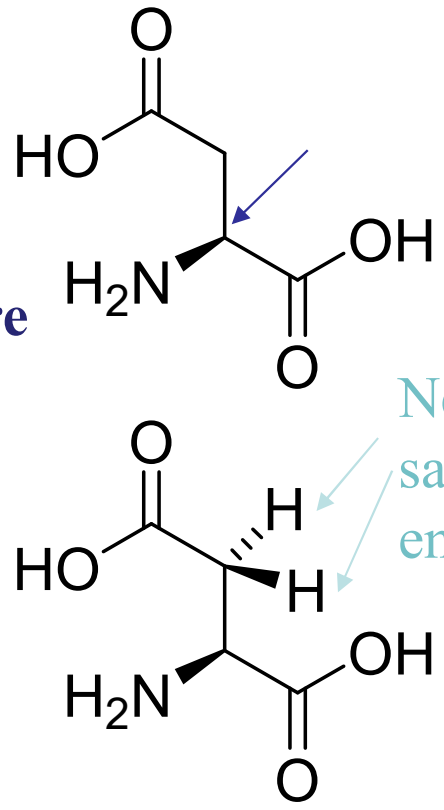
Lecture 8

- Chirality and ^{1}H NMR
- COSY, 2D-NMR.
- NOE, NOESY

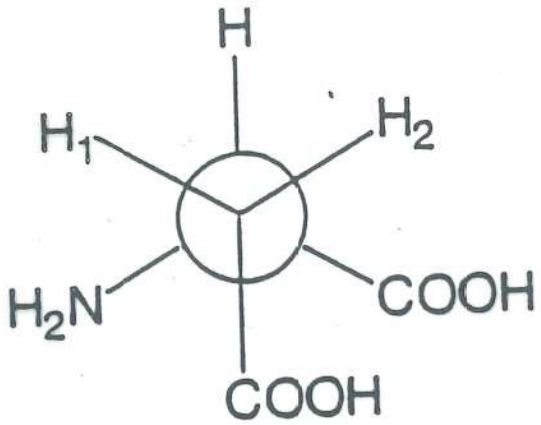
Chirality and ^{1}H NMR

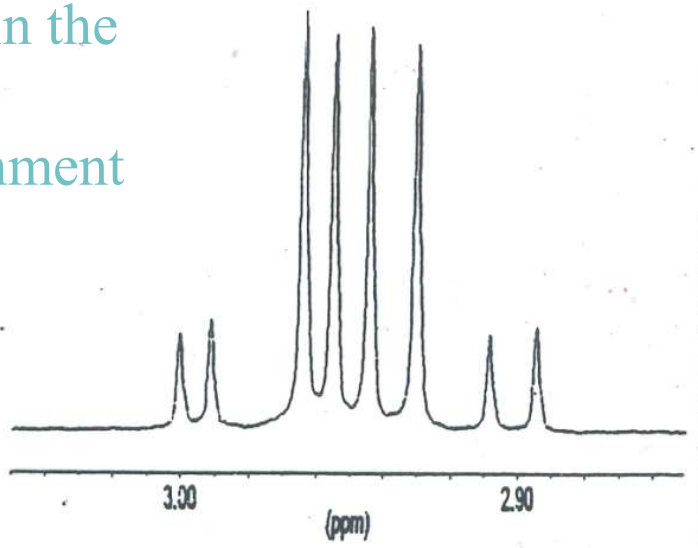


***L*-aspartic acid**



Never in the same environment





The CH_2 group of aspartic acid displays resonances characteristic of the AB part of an ABX system. The protons are inequivalent and are said to be ***diastereotopic***.

There is free rotation about the bond, **but H1 and H2 will never occupy an equivalent pair of envonments.**

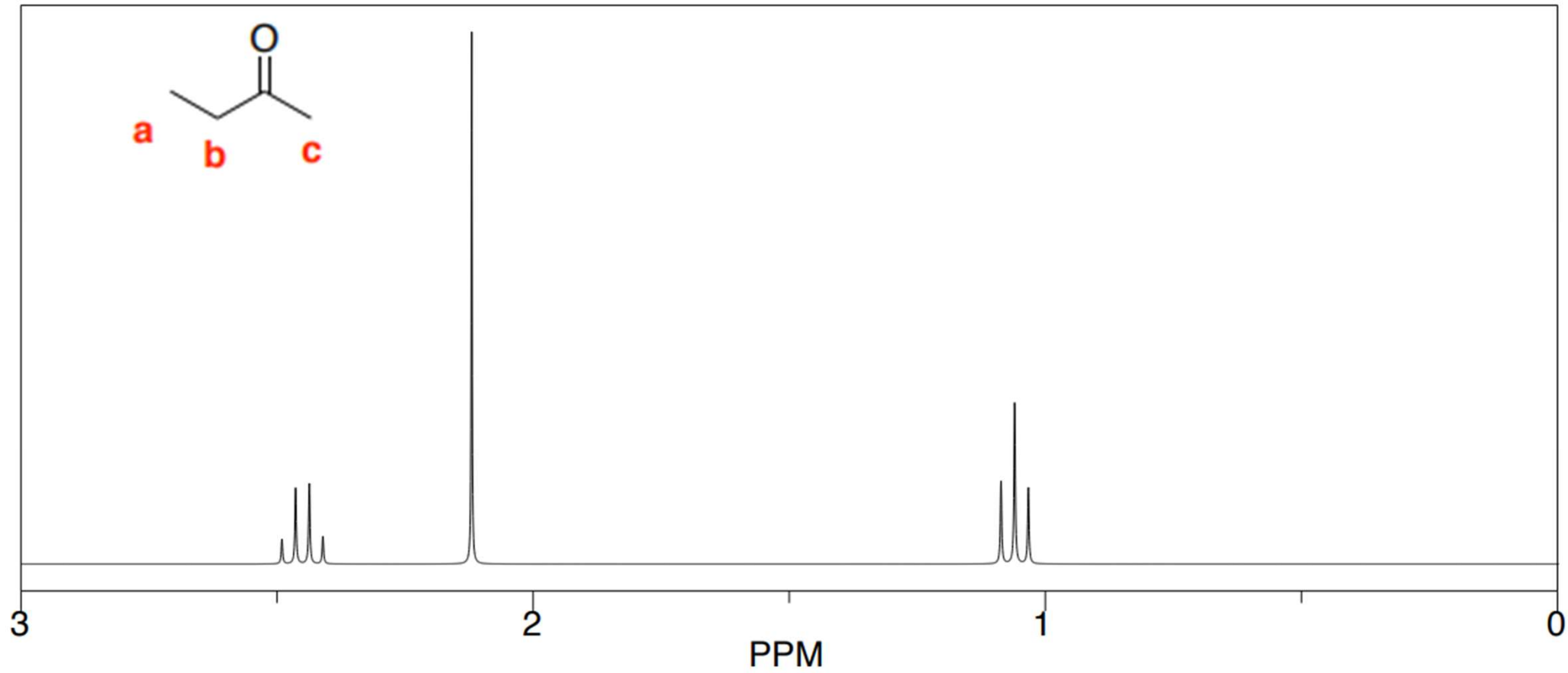
The test for diastereotopic protons is: if you replace either with a deuterium atom, will it create a pair of diastereomers?

Correlation Spectroscopy (COSY)

- COSY provides a map of all coupling networks between protons in a molecule spectroscopy in a single experiment (cf with spin decoupling).
- **Coupling provides connectivity through the bonds**
- It is an example of a two-dimensional (2D) NMR technique.
- Refer Appendix 12; Advanced NMR techniques **(Expt. 3, 4 & 5)**

1D spectrum for 2-butanone

Coupling for this simple molecule can be extracted from the 1D spectrum. But what does a 2D spectrum look like?

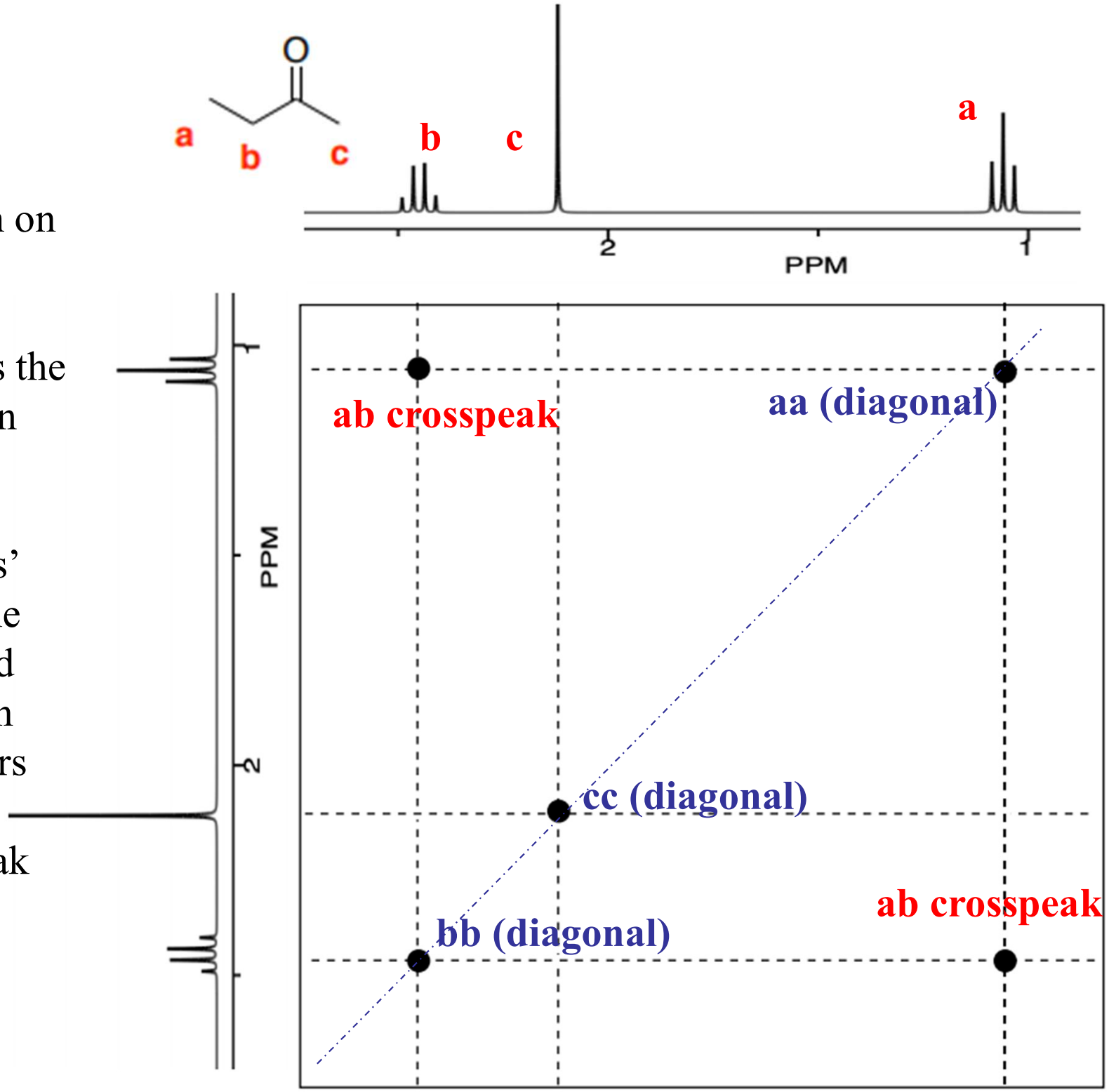


1D spectrum on x and y axis

'Diagonal' is the same peak on each axis

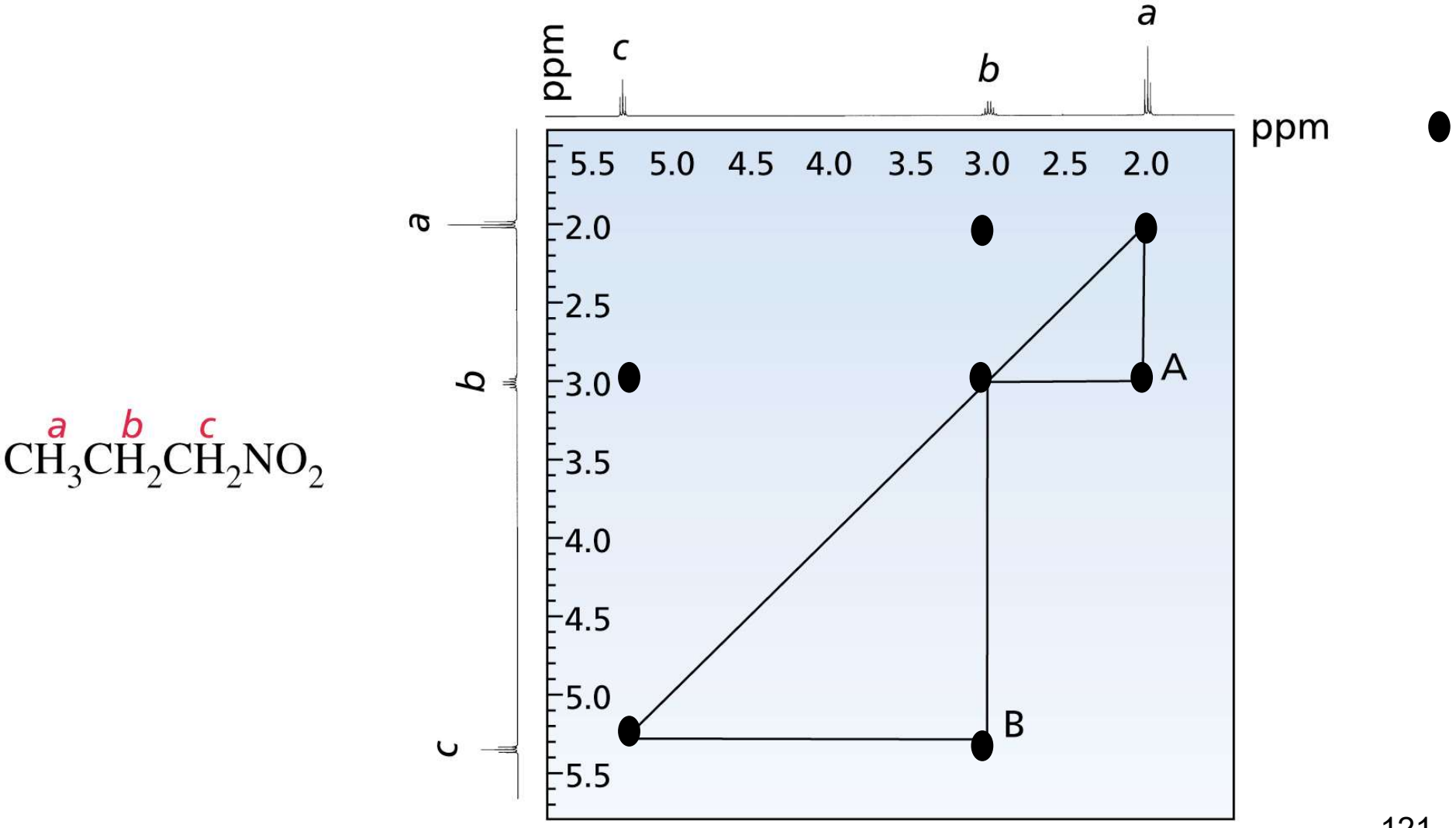
'Cross-peaks' appear off the diagonal, and only between coupling pairs

No cross-peak when no coupling



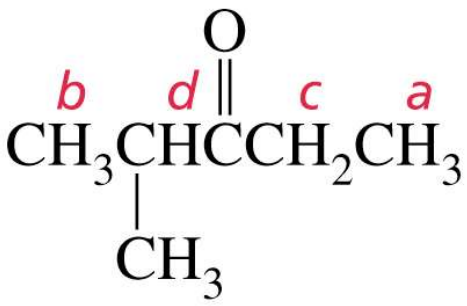
COSY spectrum of 1-nitropropane.

Notes: "A" shows that "a" is coupled to "b" and "B" shows that "b" is coupled to "c."

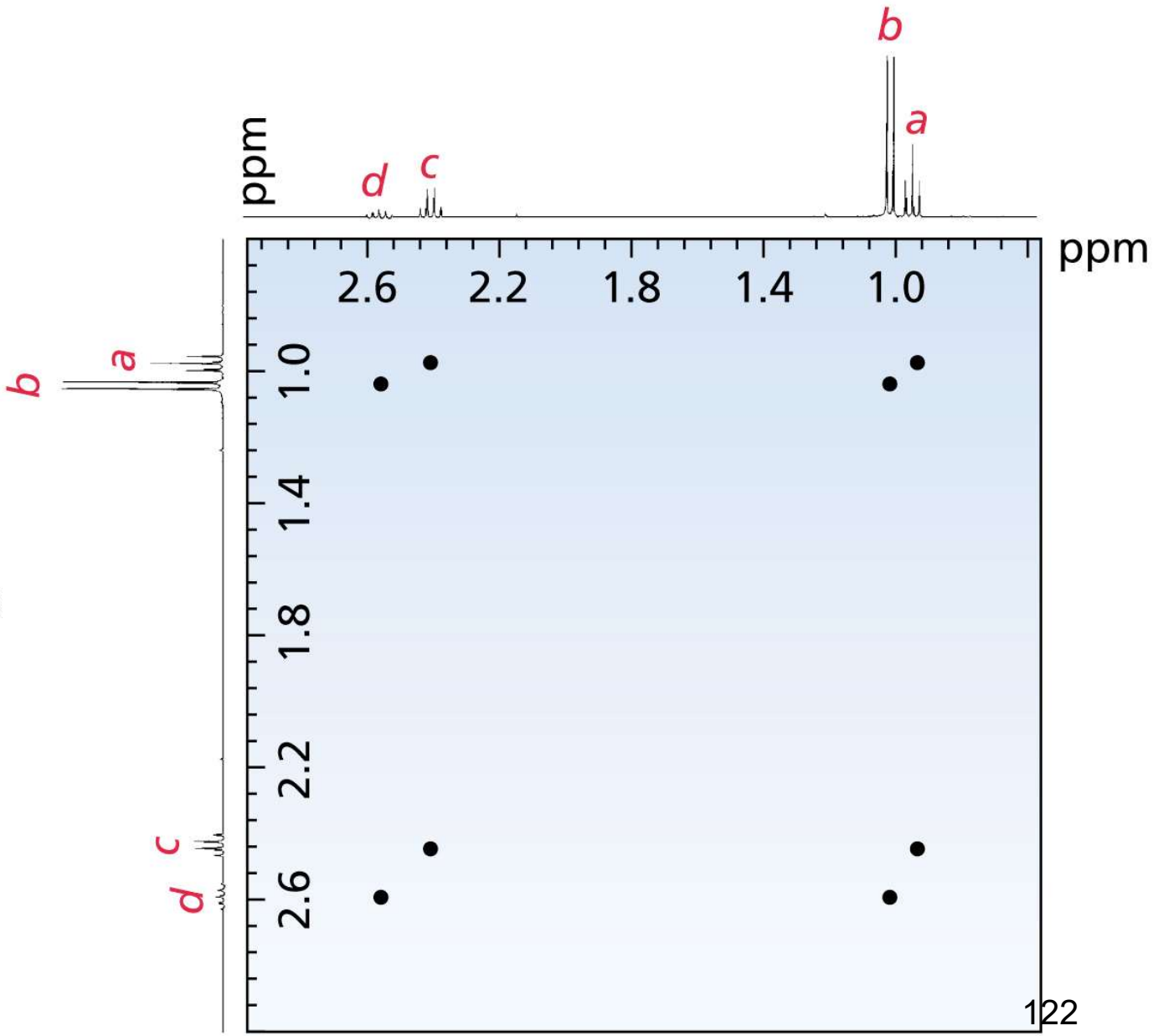


COSY spectrum of 2-methyl-3-pentanone

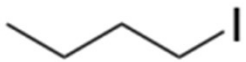
A spin system is a group of protons connected (indirectly) by coupling.

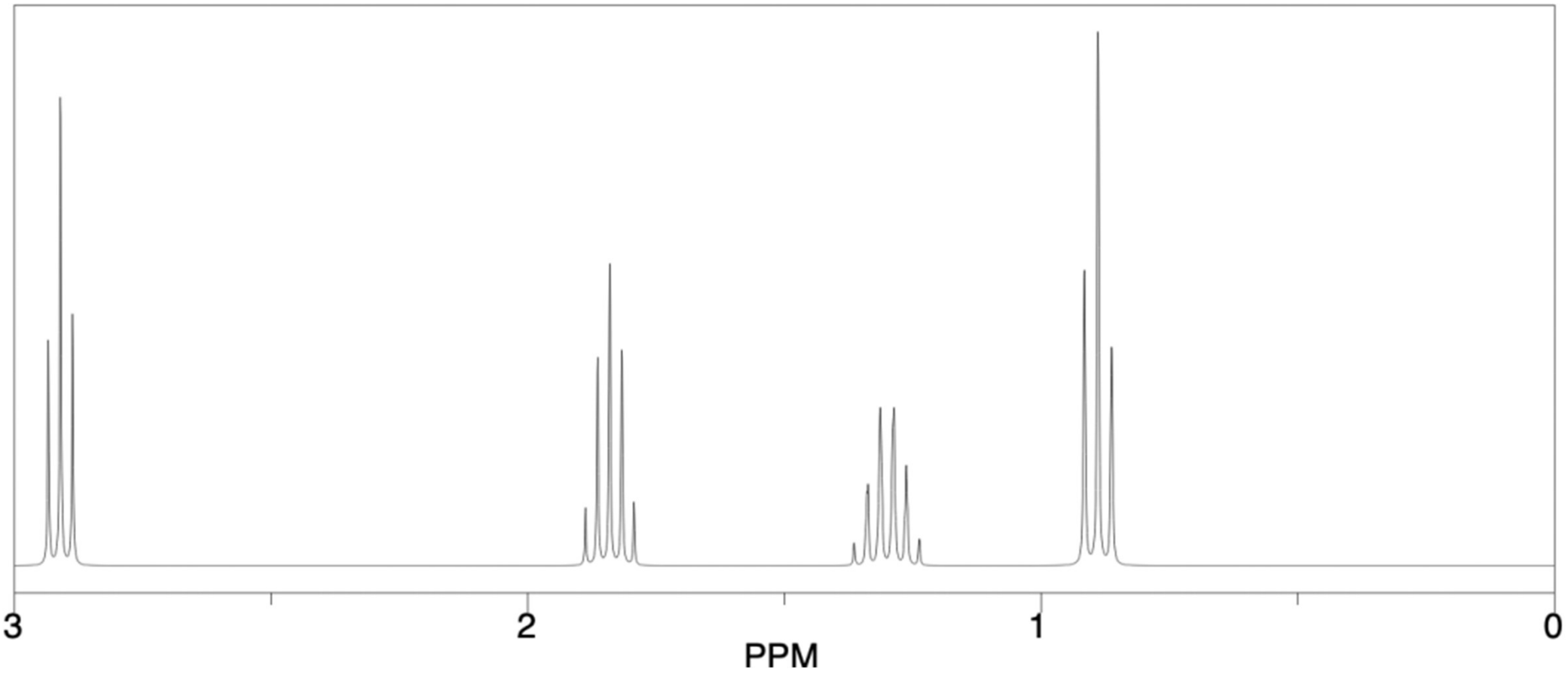


This molecule has two discrete spin systems.



Iodobutane

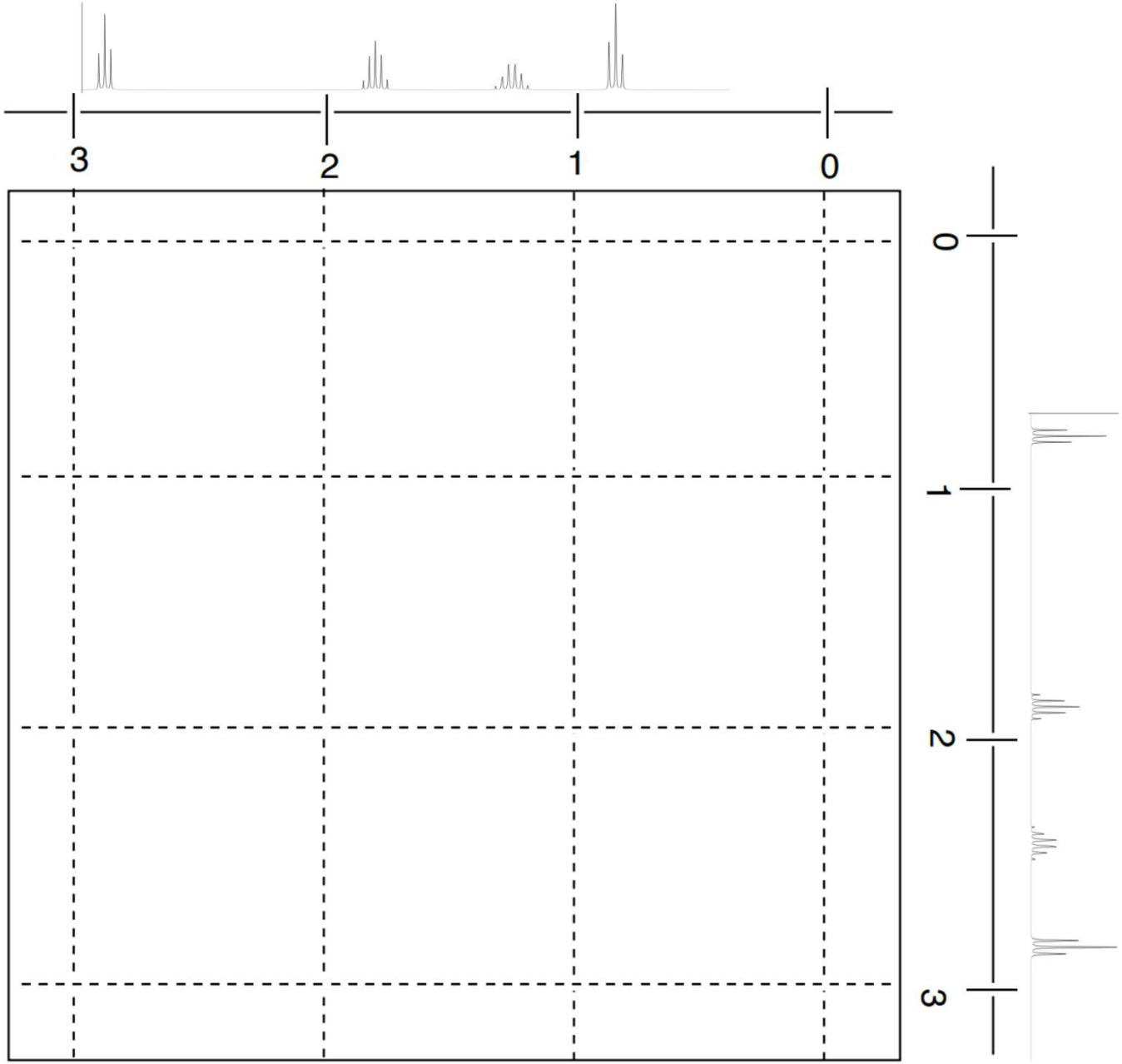




All four signals are part of one spin system.
Thus, we expect all signals to be (indirectly) connected through the COSY

Iodobutane

Predict the COSY for this molecule



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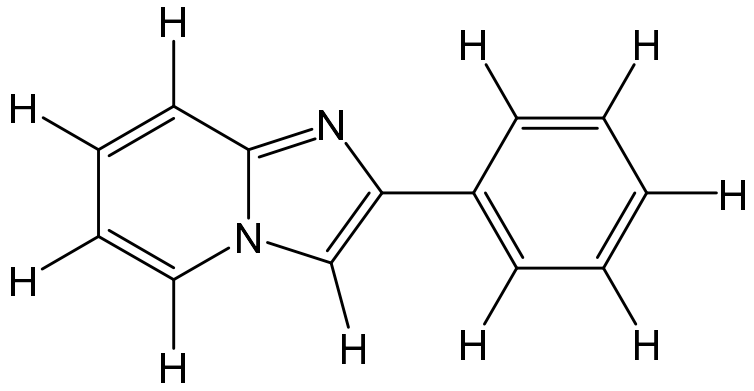
NOESY (Nuclear Overhauser Effect Spectroscopy)

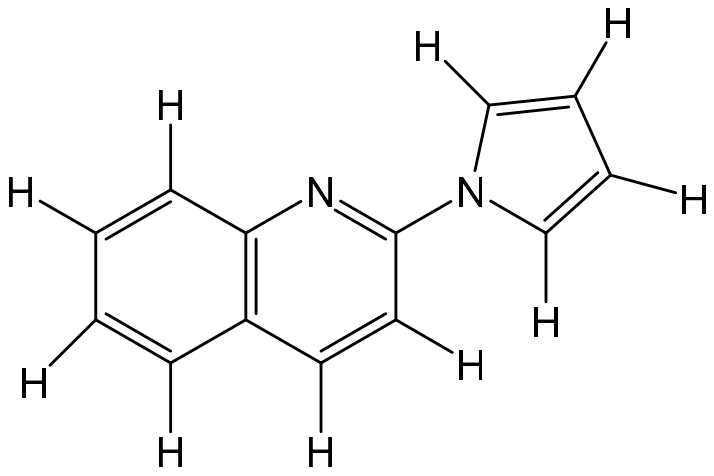
- Enables the molecular geometry to be defined
- Effect (NOE) is transmitted **through space** (not bonds) between interacting nuclei
- Interaction is based on relaxation processes following excitation of the nuclei
- The NOE rapidly diminishes with distance (depends on d^{-6})
- Nuclei must be relatively close together ($d < 0.5$ nm)

- Refer Appendix 12; Advanced NMR techniques **(Expt. 4)**

A synthetic unknown, $C_{13}H_{10}N_2$
- could be structure A or B?



A



B

A synthetic unknown, $C_{13}H_{10}N_2$
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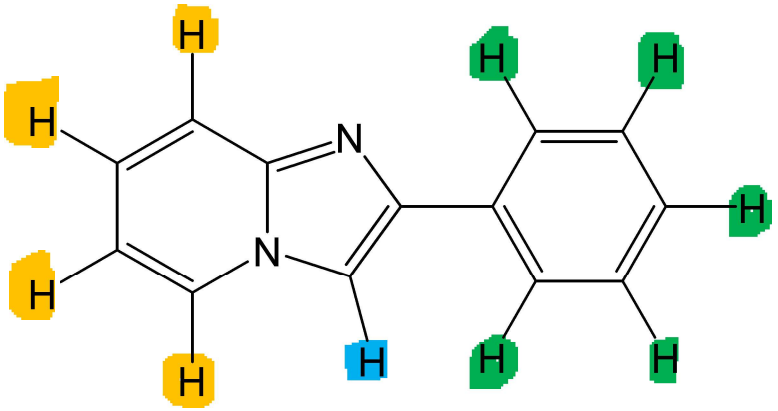
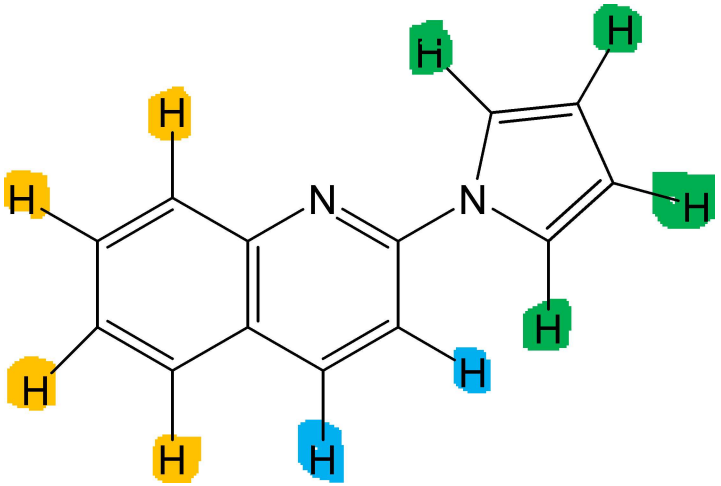


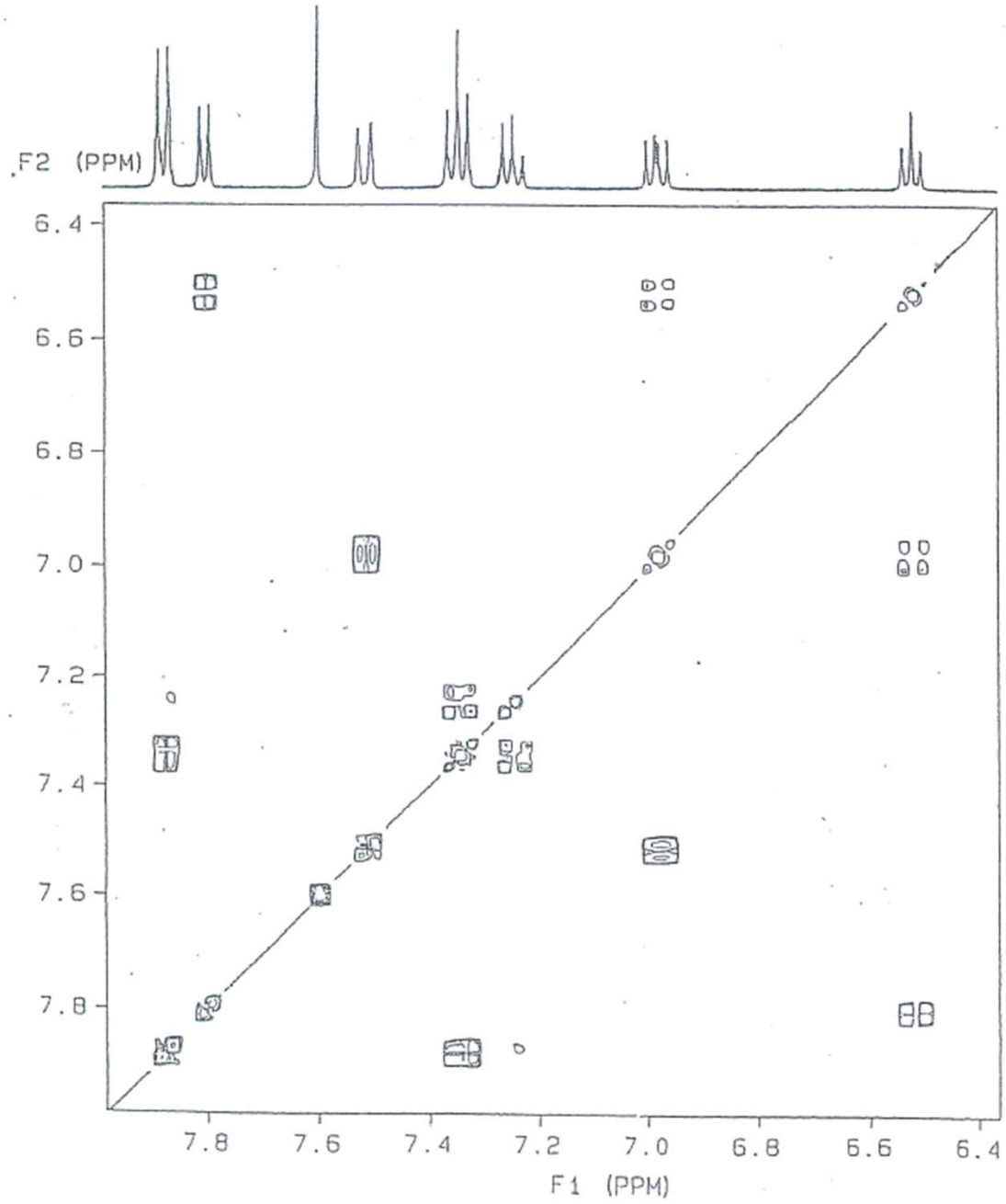
A

Spin systems colourised.
The difference in number of protons in each spin system will be diagnostic.



B

COSY spectrum of unknown



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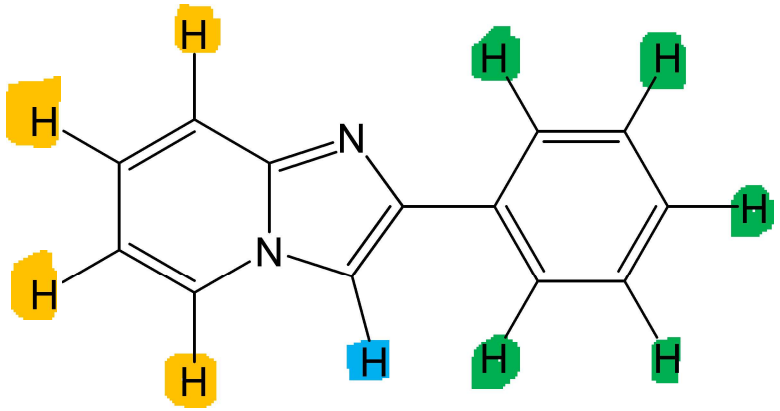
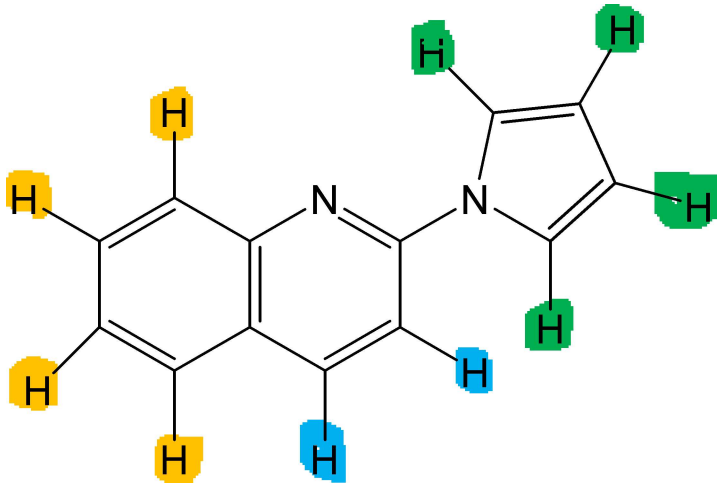
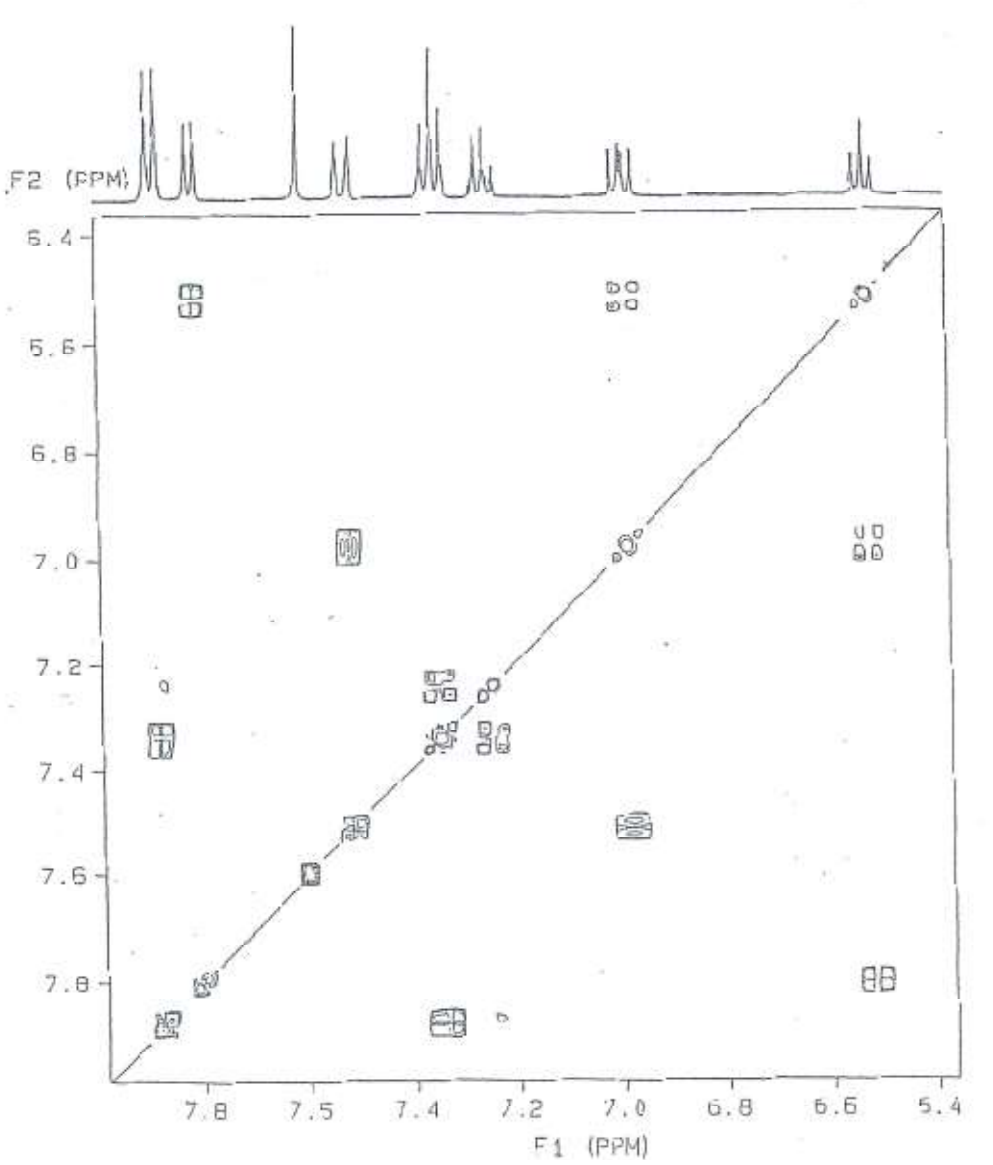


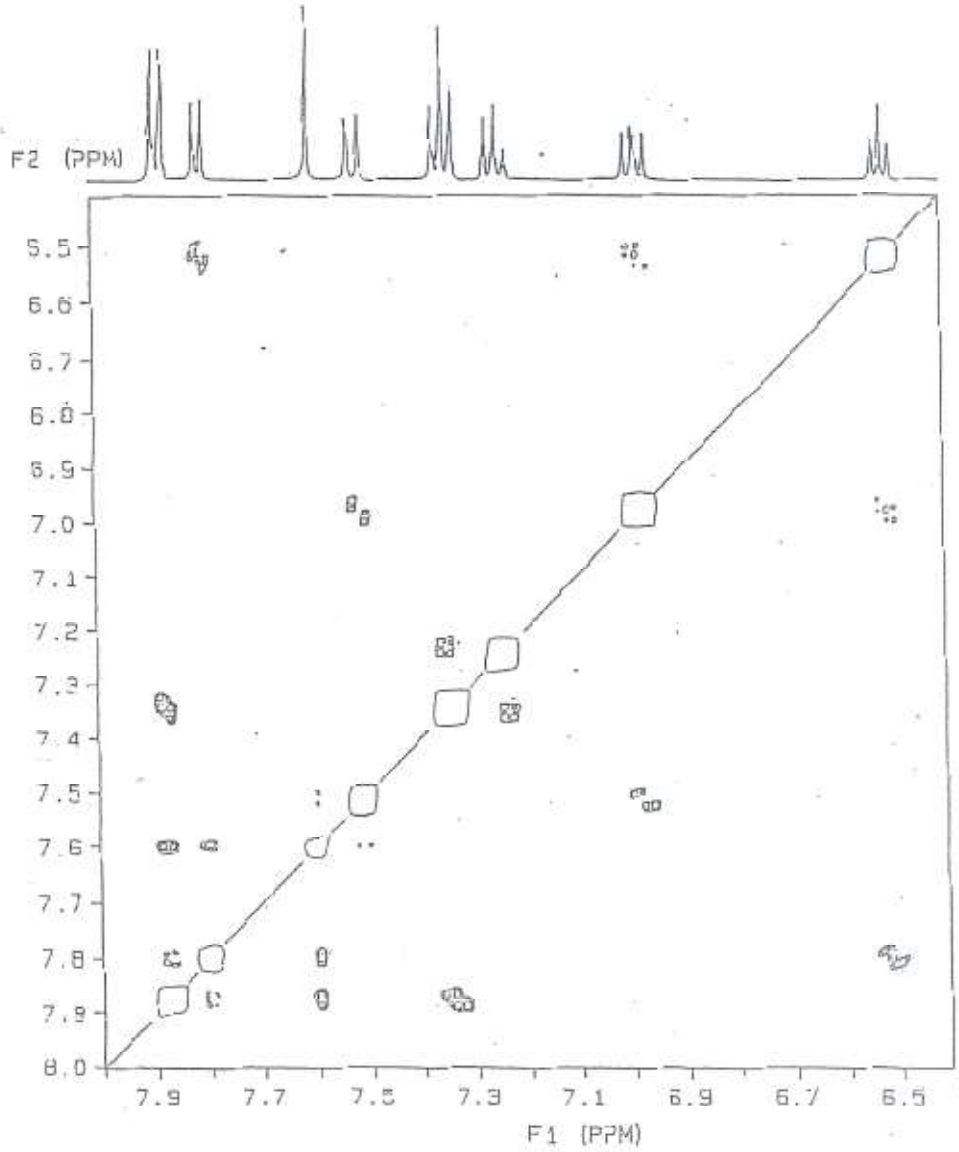
A



B

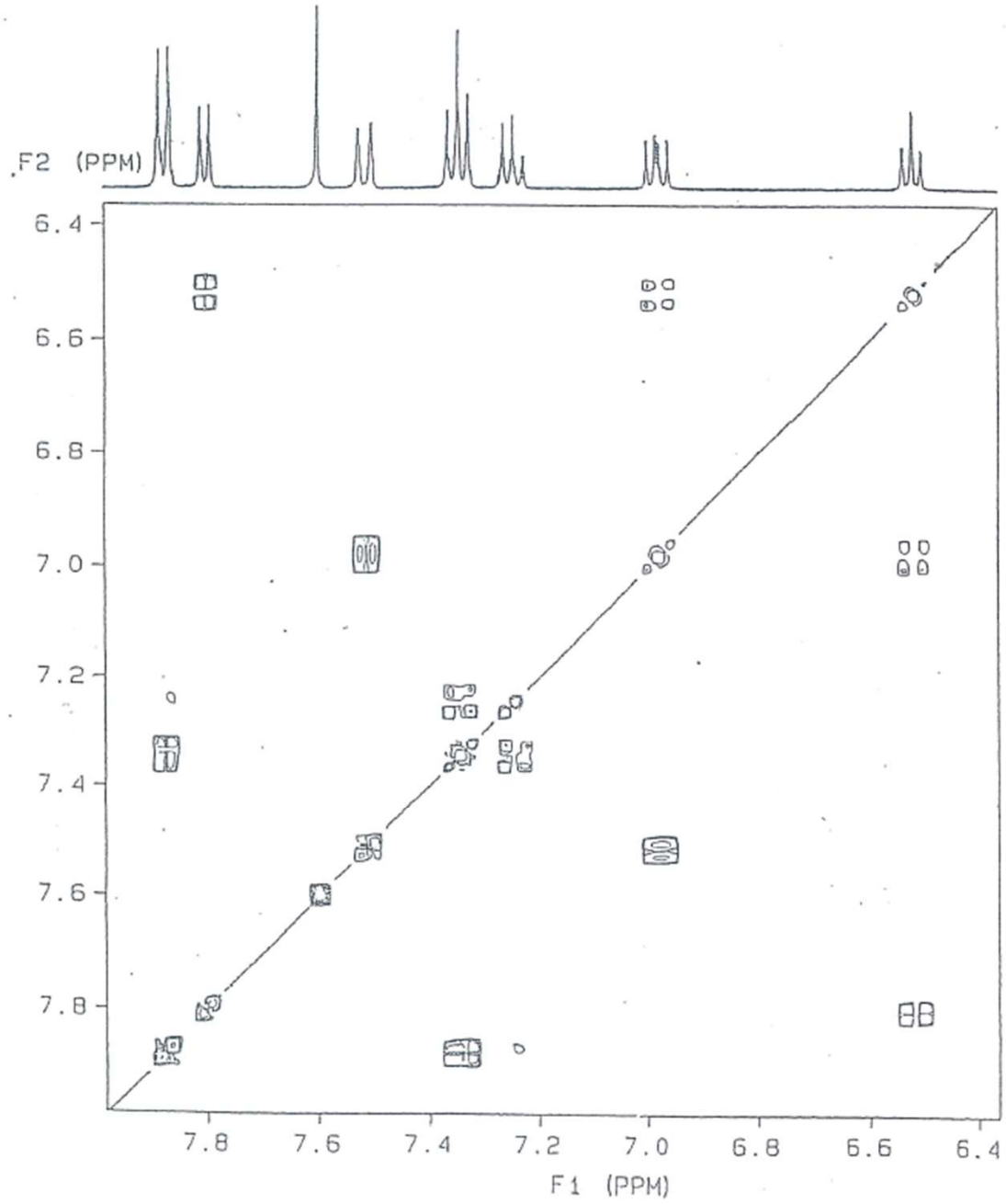


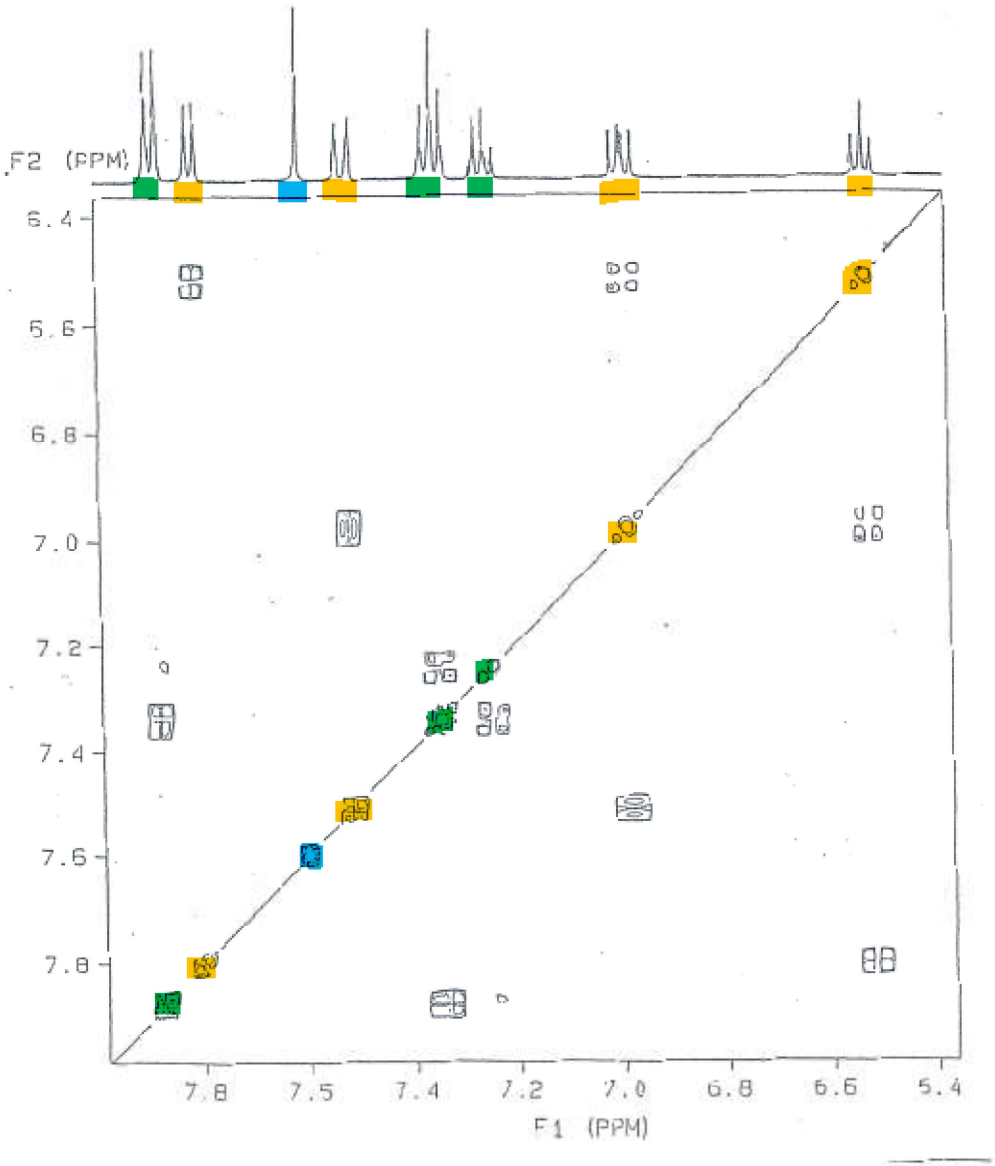
COSY spectrum of unknown:



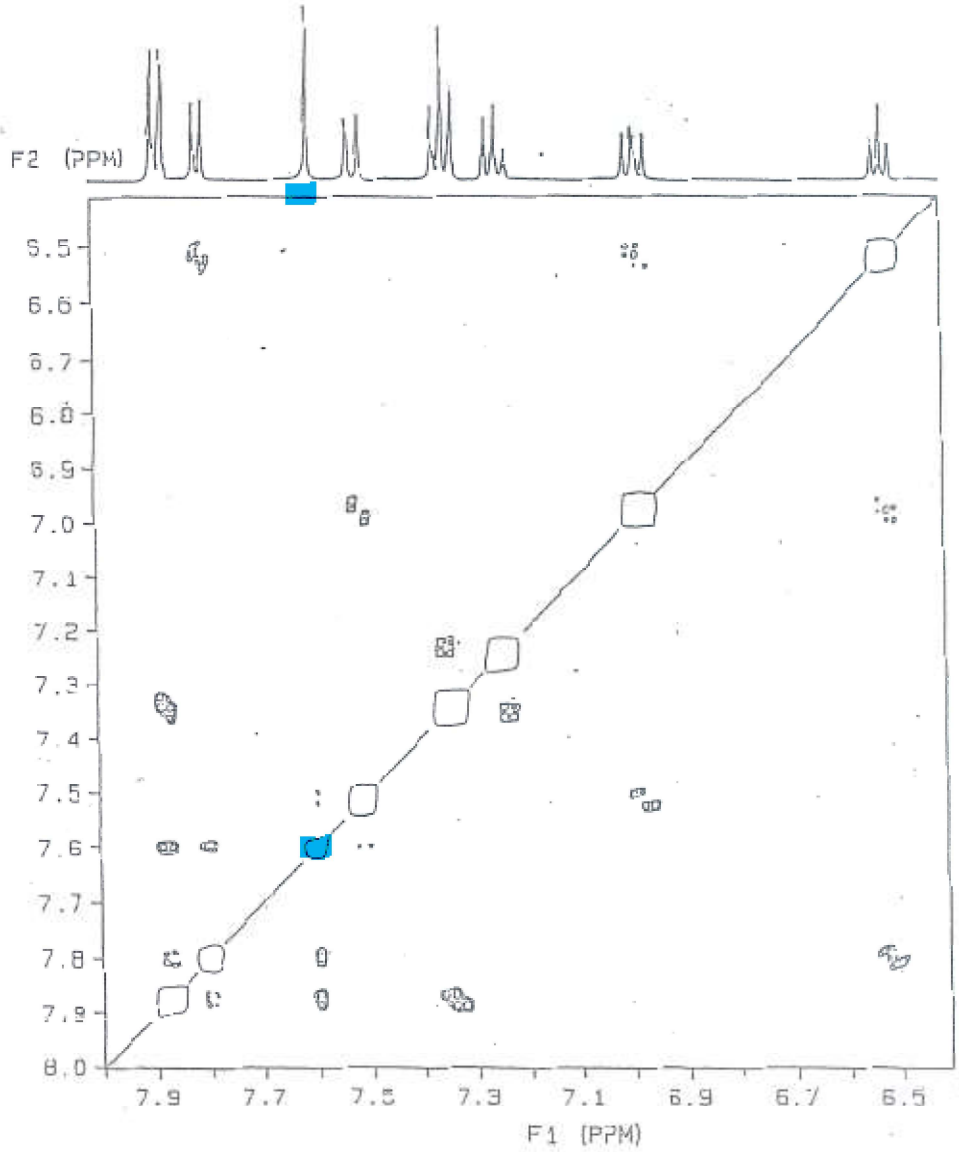
NOESY spectrum of unknown:

COSY spectrum of unknown

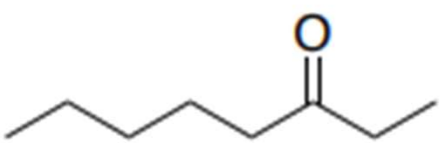




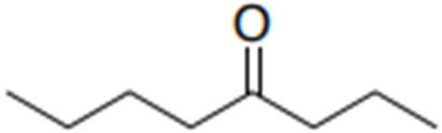
COSY spectrum of unknown:



NOESY spectrum of unknown:



or



?

Use the number of signals expected in each set of spin systems to decide.

(Note: because the COSY is always symmetrical about the diagonal, we only need one axis shown)