Department of Chemistry
NMR Facilities
Director: Dr. Carlos A. Steren

NMR NEWS December 2008

* To check on the **instrumental status** and the **reservation system**, and find tutorials, links and more, visit our website www.chem.utk.edu/nmr

* **NMR Tools package has been added to Origin 7.5 at the University server.** The NMR Tools are nuclear magnetic resonance data processing addons for OriginLab's data analysis and graphing program for Windows. For more information check on the website http://www.nmrtools.com/

* **HSQC or ^{13}C spectrum, which one has the highest sensitivity?** The enhancement in sensitivity with an HSQC experiment is significantly higher than the enhancement obtained using NOE. Numbers I got from the literature are as follow, HSQC relative sensitivity ~32, ^{13}C with NOE relative sensitivity ~3. Sensitivity of a single pulse ^{13}C experiment 1 (one). **However**, if a sample is concentrated enough, sensitivity is not an issue, and a ^{13}C with NOE experiment will be faster than an HSQC.

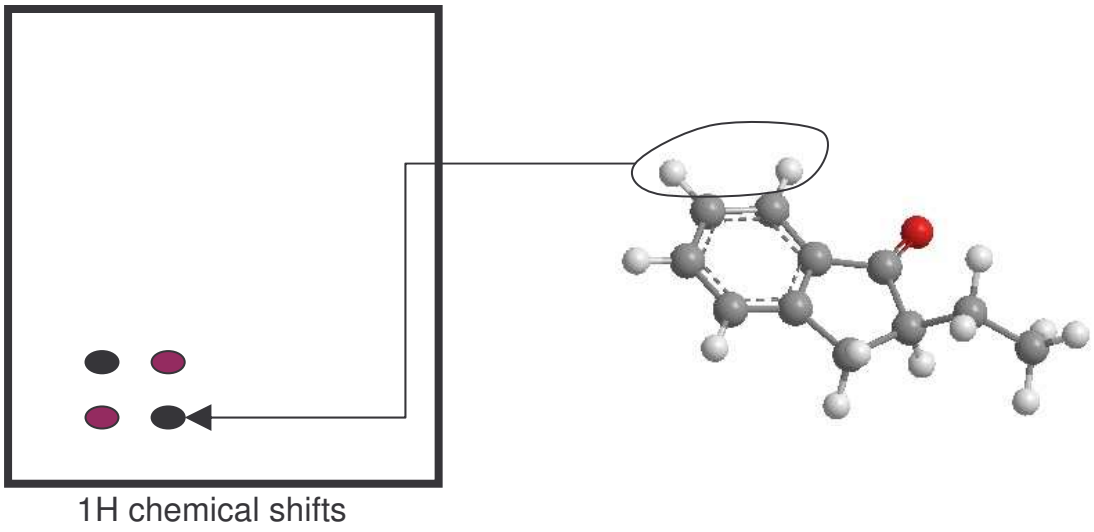
∗ **How hard is to run 2D experiments?** Three of our spectrometers have specific user interfaces that makes running 2D experiments very simple. Just a couple of clicks with the mouse are needed to run them. The interfaces are, Glide on the Varian 300, Icon NMR on the Bruker 400 and Walkup on the Varian 600.

∗ Do you want to save time? ...then run 2D experiments! The fastest 2D experiment: COSY (it takes only 3minutes!).

What does a COSY show? Typically connections between two protons that are not more than three bonds away from each other.

x = ^{1}H chemical shift

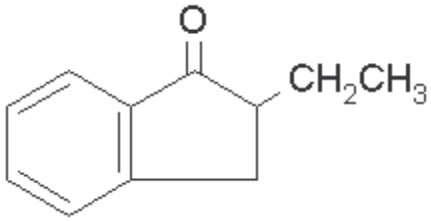
y = ^{1}H chemical shift

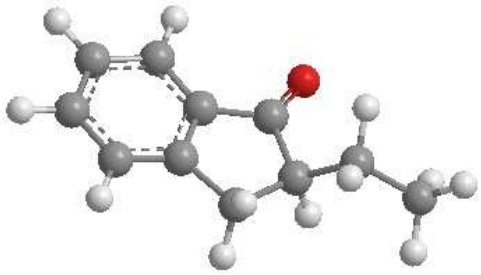


Diagonal peaks and cross peaks ?? An HSQC shows cross peaks that represent correlations between ^{1}H and ^{13}C nuclei. COSY shows correlation between two protons, cross peaks, but also ^{1}H self correlations named diagonal peaks.

Two cross peaks for the same correlation!! Given a correlation between two ^{1}H with chemical shifts δ1 and δ2, cross peaks at coordinates (δ1,δ2) and (δ2,δ1), the transpose cross peak, are observed. Diagonal peaks are found at positions (δ1,δ1) and (δ2,δ2).

Lets analyze a real COSY spectrum acquired for the molecule 2-ethyl-1-indanone.





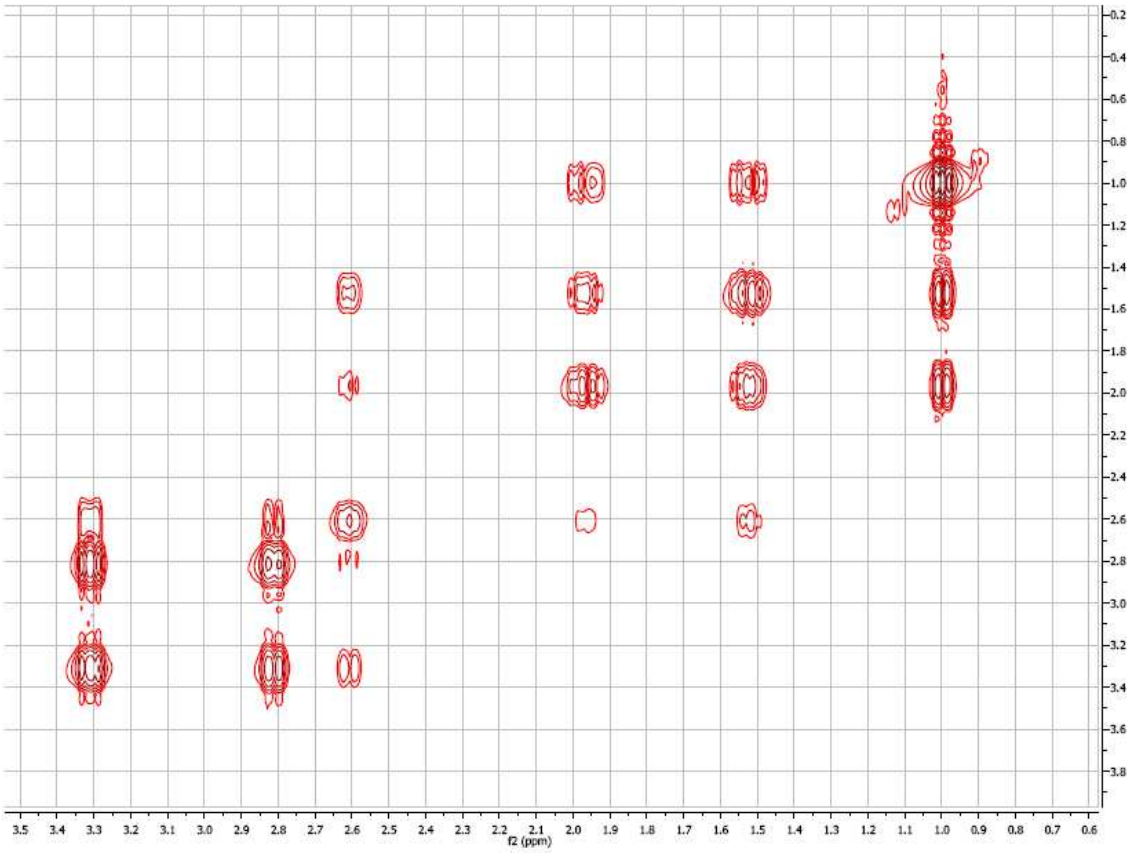
An HSQC spectrum of 2-ethyl-1-indanone was analyzed in October's newsletter, and the following table of chemical shifts was obtained.

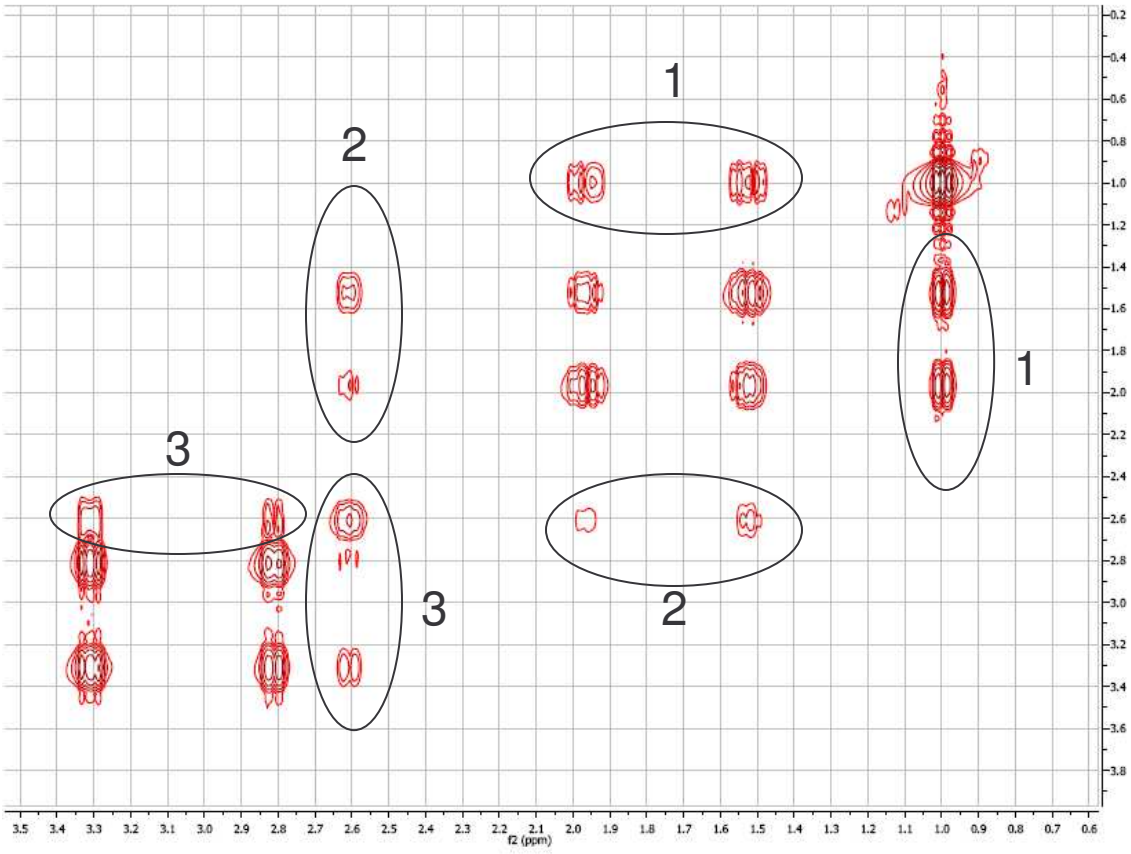
	δ(^{1}H) ppm	δ(^{13}C) ppm
CH_3	1.00	12.1
CH_2	1.97, 1.53	24.5
CH_2	3.31, 2.82	32.5
CH	2.61	49.1
CH	7.74	124.0
CH	7.46	126.7
CH	7.36	127.7
CH	7.57	135.1

The remaining questions back then were, which aromatic peak corresponds to which proton in the molecule and which CH_2 group is which.

Instead of showing the whole COSY spectrum, the aliphatic and aromatic regions are depicted and analyzed.

Aliphatic region





1.- Starting from the top right hand side, the diagonal peak of the methyl group appears at coordinates (1.0,1.0). Cross peaks with coordinates (1.0, δ) and (δ, 1.0), with δ=1.97 αvδ 1.53, are the correlations to the protons of the methylene connected to the methyl group (see figure shown above). Thus, CH_2 (H:1.97, 1.53 ; C: 24.5) is the one linked to the CH_3 group.

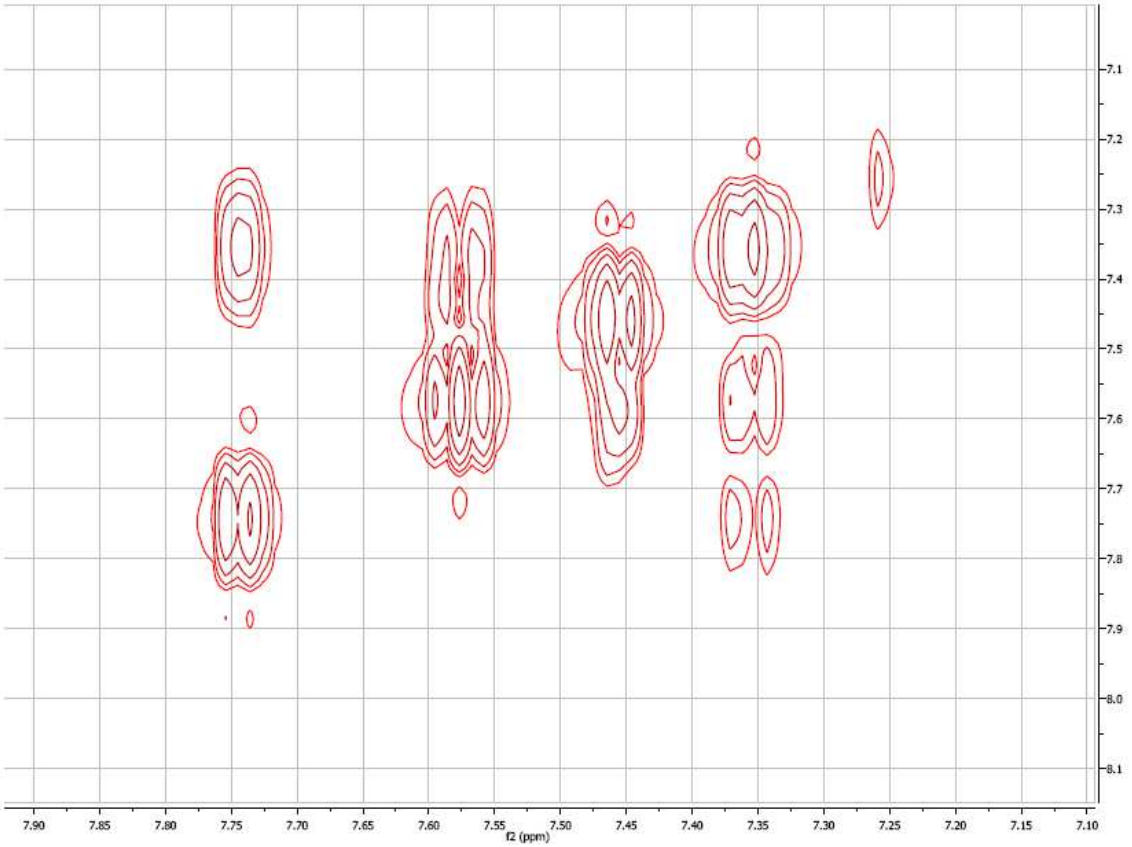
2.- Now starting from the CH_2 (H: 1.97, 1.53) diagonal peaks, cross peaks at 2.6 ppm are observed (weak cross peaks). These are the correlations to the CH methine group (H: 2.61,C: 49.1).

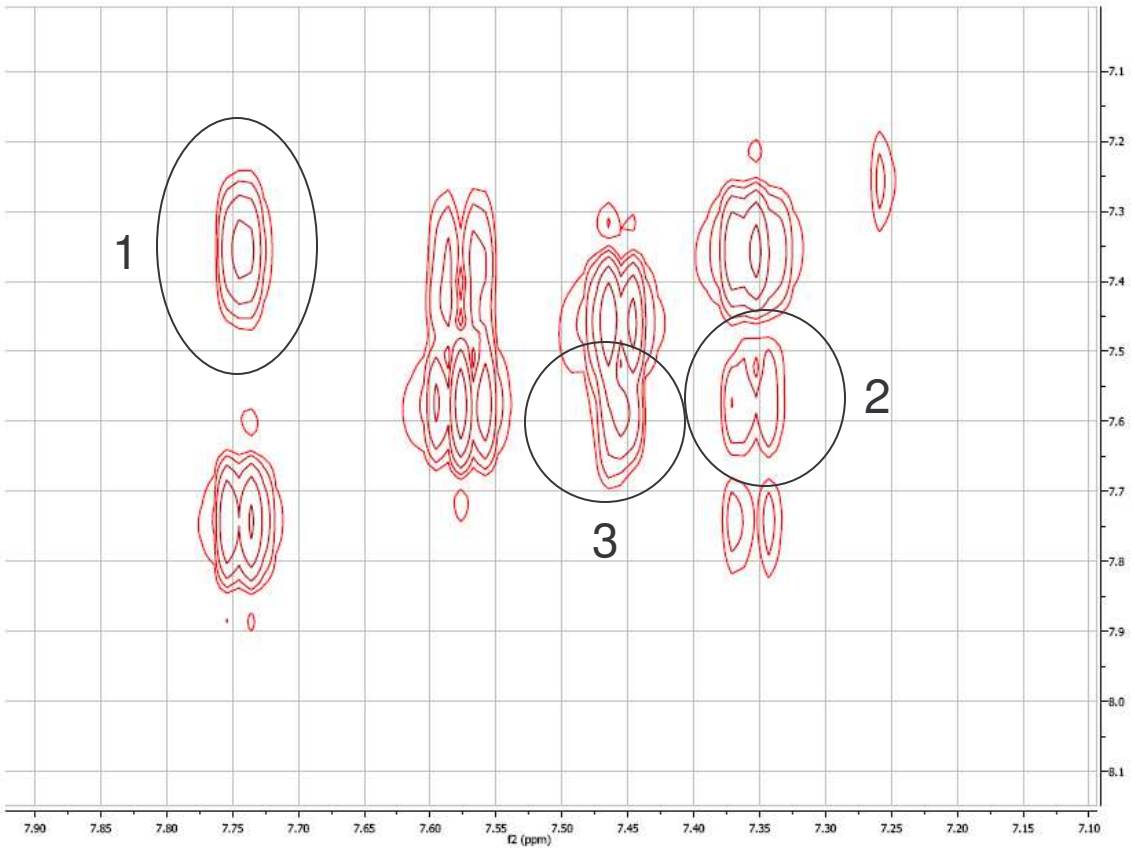
3.- Starting on the diagonal peak of the CH (2.61,2.61), cross peaks to 3.31 and 2.82 ppm are observed. These are the protons of the second methylene group, (H: 3.31, 2.82;C: 32.5).

4.- The cross peaks between the two ^1H of each CH_2 group are easy to identify.

Question left: In the CH_2 groups, which proton has which chemical shift?

Aromatic region





The CHs at both ends of the ring will have connections only to one adjacent group, meaning only one cross peak. Those in the middle have two connections. Thus,

1.- The proton at 7.74 ppm shows only one cross peak. Thus, this is one end and it is connected to CH (H:7.36 , C: 127.7).

2.- Starting from the diagonal peak at 7.36 ppm, two cross peaks are observed (7.36 , 7.74) and (7.36 , 7.57). Thus, CH (H: 7.57, C:135.1) is the next proton in the ring.

3.- Again starting from the diagonal peak, (7.57,7.57) a cross peak at (7.57,7.46) is observed. This is the other end of the ring, CH (H: 7.46, C: 126.7).

Questions left: which end is which in the molecule? How can the connection between the aromatic and aliphatic segments be verifyied?
Will try to address these questions in the following issues.