Organic Chemistry

Advanced Spectroscopy

So far we have talked about 1D NMR. Advanced spectroscopy includes 2D, 3D and 4D NMR. An example of 2D NMR is given in your book in section 13.19. 2D NMRs have two frequency axis and are used to correlate the two items represented by the axis.

Some examples of 2D NMR

1)

Name	Long Name	Use
COSY	Correlated Spectroscopy,	correlates protons with protons

How to Read

Cosy has the same proton spectrum on each axis. Cosy also has a diagonal going from the bottom left to top right of the spectrum. Identify a peak in the 1H NMR and go to the diagonal representing the peak. Trace from the diagonal peak either vertically or horizontally until you come to a cross peak. Return from the cross peak back to the diagonal different than the way you came to the diagonal. If you came horizontally to the cross peak, return to the diagonal vertically. The cross peaks tell you that the peaks in the one dimensional NMR are coupled. Now, from this new peak on the diagonal go either vertically or horizontally until you reach a new cross point.

Example: Figure 13.28, pg 557

2)

Name	Long Name	Use
Hetcor	Heteronuclear chemical shift correlation	correlates protons with carbons

How to Read

The proton spectrum is on the Y axis and the carbon is on the X axis Identify a peak in the 1H NMR and trace vertically until you reach a cross peak. Trace horizontally to the 13C NMR. The protons causing the signal you identified in the 1H NMR are on the carbon that gives the peak in the 13C with the cross peak.

Example: Figure 13.29, pg. 558

3)

Name	Long Name	Use
HMQC	Heteronuclear Multiple Quantum Coherence	correlates protons with carbons

How to Read

Very similar to # 2 except proton is on the X axis and carbon is on the Y axis. This is called the proton or inverse detected version. The advantage is at least an eightfold increase in sensitivity which saves you substantial time required to obtain the spectrum.

4) Name	Long Name	Use
Inadequate	Incredible Natural Abundance DoublE Quantum Transfer Experiment	correlates carbon to carbon

How to Read

Carbon spectrum is on the X axis. Frequency in Hz is on the Y axis. Identify a peak in the 13C NMR. Go down vertically until you reach a cross point. From this cross point, trace horizontally until you reach another cross point. From this second cross point, trace vertically back to the 13C NMR. These two 13C NMR peaks are directly attached. Continue from this peak around the molecule.

5) Name	Long Name	Use
HMBC	Heteronuclear Multiple Bond Coherence	shows long range proton carbon couplings

How to Read

The Carbon NMR is on the Y axis and the proton is on the X axis. The HMBC is very similar to the HMQC except that the the one bond couplings are gone while there are two and three bond couplings present. HMBC spectra are more difficult to read and more detail can be obtained from advanced spectroscopy books.

OTHER 2D NMR Techniques

Name	Long Name	Use
TOCSY	Totally Correlated Spectroscopy	not directly coupled nuclei but in the same spin system

Name	Long Name	Use
NOESY	Nuclear Overhauser Effect ???	Uses NOE to correlate protons (in peptides)

Name	Long Name	Use
ROESY	Rotating Frame Overhauser Effect Spectroscopy	Through space correlations

New Types of NMR

Gradient Field NMR, 3D NMR

NMR Time Scale

The NMR machine only "sees" slower chemical reactions. For example, 1,2,2,3,3,4,4,5,5,6,6-undecadeuterocyclohexane has one hydrogen in the ^{1}H NMR. This hydrogen can be in either the axial position or the equatorial position. At high temperatures, an average spectrum appears. At lower temperatures, it is possible to get a peak for the hydrogen in both the equatorial AND axial positions.

For ethanol, how many types of protons are there? It depends on the speed of the rotation and the speed of exchange for the OH peak.

Example 1 – High Purity Ethanol- Slow exchange speed for OH

CH_3CH_2OH

The CH_3 shows up as a triplet, the CH_2 COUPLES to the OH and shows up as a pentet AND the alcohol proton shows up as a TRIPLET.

Example 2 – "Normal" Ethanol – Fast exchange speed of OH

CH_3CH_2OH

The CH_3 shows up as a triplet. The CH_2 shows up as a quartet and DOES NOT couple with the OH peak. The OH peak shows up as a broad peak and DOES NOT couple to the CH_2.

MRI- Magnetic resonance Imaging

See page 546 for an explanation of MRI with an example.