May 2017
Appendix VI: DEPT, COSY and HETCOR (HMQC, HSQC & HMBC) NMR Spectra.

Explanation of DEPT spectra:

DEPT is an acronym for **D**istortionless **E**nhancement by **P**olarization **T**ransfer. The result of this experiment is a carbon spectrum that shows the multiplicities (methyl, methylene, methine and quaternary) for the different carbons. DEPT is a 1D experiment, but unlike decoupling and NOE, it involves a multiple pulse sequence. The experiment also requires that both protons and carbons are excited by the pulses. The techniques and theory behind the DEPT experiment are very complicated, but the results are easily interpreted.

There are three types of DEPT spectra that can be acquired. They are noted by numbers. DEPT-45 will give a positive[1] signal for any carbon with an attached proton. DEPT-90 spectra will give a positive signal for methine carbons. DEPT-135 spectra will give positive signals for methine and methyl carbons, and negative signals for methylene carbons. By a linear combination of these three spectra and the normal ^{13}C spectrum, the multiplicities of all of the carbons in a molecule may be determined. The example spectra below show the appearance of each type of carbon in the different DEPT spectra.
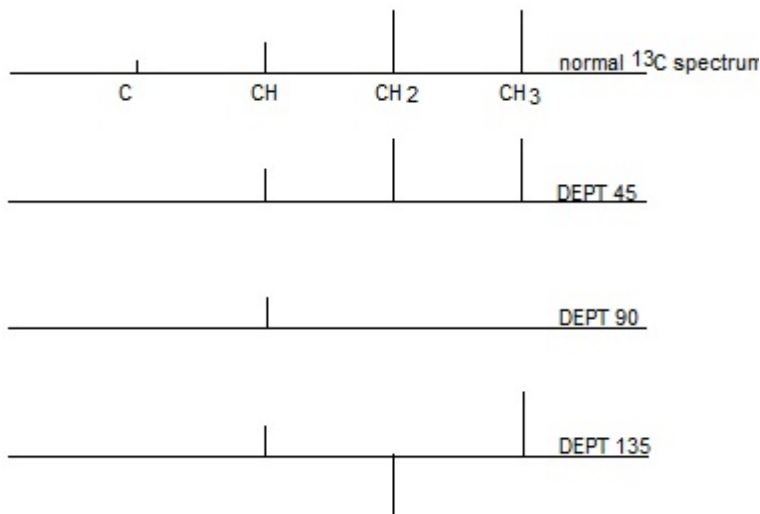
The 45° and 135° subspectra contain peaks associated with carbons bearing protons (no quaternary carbons visible). They differ only by the phase of the CH_2 peaks (up and down respectively). Thus, 45° subspectrum - 135° subspectrum = a subspectrum of just CH_2 peaks

and 45° subspectrum + 135° subspectrum = a subspectrum of CH and CH_3 peaks

The 90° subspectrum contains only the CH peaks, so subtracting this from the 45° + 135° combination will give only the CH_3 peaks.

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[1]The descriptors *positive* and *negative* have been used, but in fact the spectrum may appear either way up i.e. the positive direction may be pointing either up or down.

In many cases, there is not much confusion between the chemical shifts of CH and CH_3 protons, so the 135° subspectrum effectively discriminates between each type of carbon.

COSY NMR Spectra

It is not intended that you tackle the theory behind two dimensional nmr spectra at this stage, but there is no reason why you cannot use the results of the technique! If a spectrum contains coupled resonances that are close together, the signals invariably become muddled to the point of not providing any useful information. In which case, a COSY spectrum may well provide the answer. Below is a brief summary of what happens in this type of experiment.

The regular pulse procedure for acquiring a spectrum is to have three different time intervals in each cycle of scans. The first interval is when nothing happens and the spins are allowed to settle to their natural distribution of states. The second is when a pulse of excitation energy is applied and the spins respond to the stimulus. The detector is then switched on and measurement is taken for a time t. The spectrum is obtained by transforming the data with respect to time t.

In a 2D experiment, a series of spectra are collected where the time between stimulus and detection (t_1) is increased by a small amount in each case. So not only can the spectra be transformed with respect to the detection time (t_2) but also to t_1. This results in a contour plot with the same (but rather crudely resolved) spectrum along each of two axes and a diagonal (bottom left to top right usually) of the contours of the regular spectrum. The interest lies in the off-diagonal contours. Where correlation between coupled resonances exists, a contour should appear in both halves of the spectrum. Values of coupling constants cannot be determined by this method (unless certain conditions are applied) but the fact that two resonances are coupled can aid in the interpretation of the spectrum.

Figure 2 shows a COSY spectrum of 1-propanol containing three resonances. One is coupled to the other two, but they are not coupled to each other. This is reflected in the size of the contours (ie how big the blobs are!).
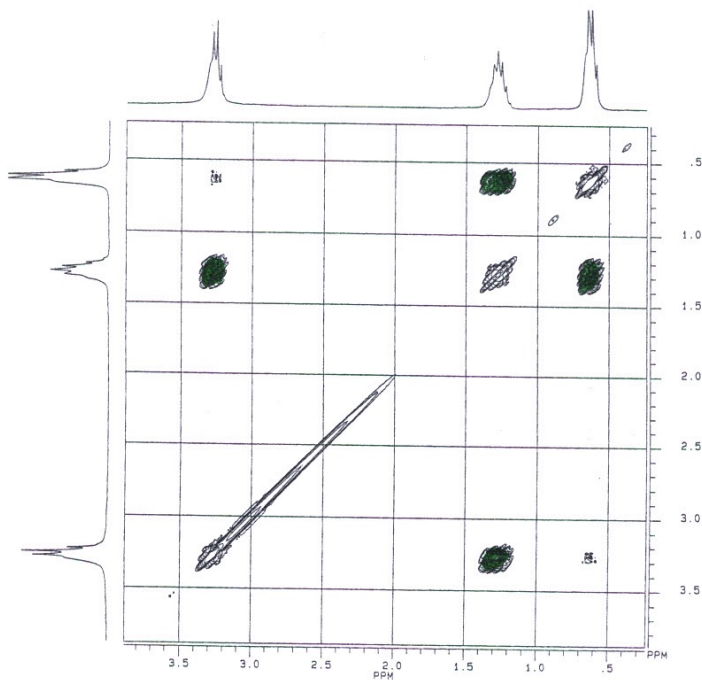

Figure 2: COSY of 1-propanol

C-H Correlated Spectra including HMQC, HSQC & HMBC
Essentially, this type of spectrum is the same as a COSY, with the correlation between two different nuclei. This means that there is no diagonal, but the correlation is signified by intensity at the cross point. Figure 3 shows the HETCOR of 1-propanol.
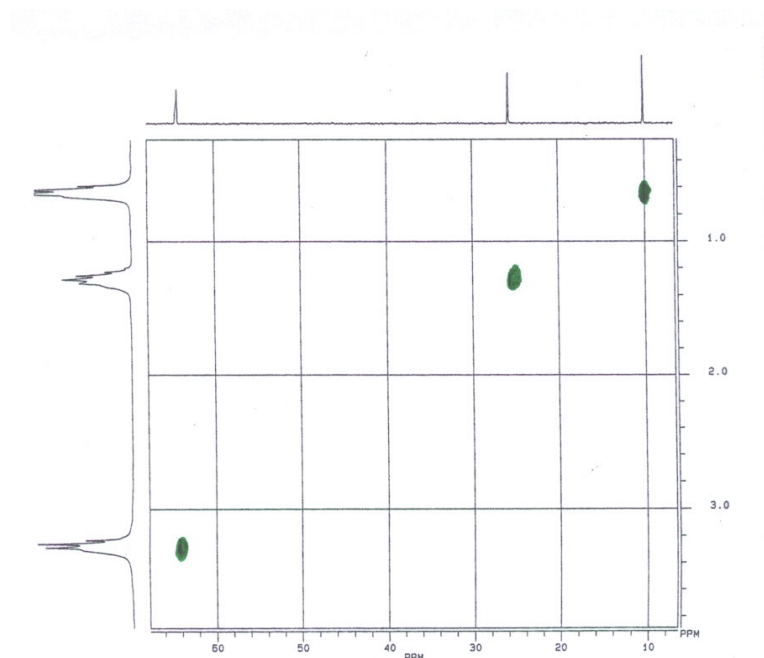

Figure 3: HETCOR of 1-propanol

Modern instruments do the same experiment but using different pulse programs. HMQC and HSQC both look at the correlation over ^1J (ie direct coupling). If correlations over several bonds must be observed, a filter is used to remove all ^1J coupling of J>10 Hz. This is known as HMBC, or long-range HETCOR.

References:
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