Chem 227/ Dr. Rusay



## Postlab : Synthesis of DEET NMR: Resonance/ Rotations/ Conformations

## Adapted from: Professor Thomas Nalli, Winona State University http://course1.winona.edu/tnalli/s09/350.htm

Nuclear magnetic resonance occurs on a fairly slow time scale. Therefore, fast conformational/rotational changes are not discernable by NMR and the observed spectrum is the average spectrum of the interconverting molecules. In general, an averaged spectrum is observed when the rate of the process is  $2\pi$  times the frequency difference, i.e.  $(2\pi \times \Delta v)$  between the peaks being observed. For example, consider a hypothetical molecule with two nonequivalent methyl groups with respective <sup>1</sup>H NMR chemical shifts of 3.0 and 3.5 ppm recorded on a 300 MHz instrument. The frequency difference between the two peaks is 150 Hz (0.5 ppm x 300 Hz/ppm). If a bond rotation interconverted these methyl groups faster than 900 times per second (900 s<sup>-1</sup>) as in the example,  $2\pi \times 150$  Hz = 942 Hz = 942 s<sup>-1</sup> = 942 times per second), then these six protons would show up as a single peak at 3.25 ppm. In contrast, if the methyl groups interconverted much slower than 900 times per second, they appear as two distinct signals at 3.0 and 3.5 ppm. When the interconversion rate is greater or approximately equal to  $2\pi x \Delta v$ , the six methyl protons appear as a single broad peak at the average chemical shift (3.25 ppm).

Therefore, at lower temperatures the change is slower and separate peaks are observed as in the DEET spectra above. At higher temperatures, one sharp peak at an average chemical shift value is observed The ethyl groups in the <sup>1</sup>H spectrum above, which was recorded at 5°C, are very poorly resolved. It shows a pair of broad signals that appear to be singlets for each set of chemically equivalent protons in each ethyl group. These pairs represent two different rotational conformers, which can be related to their respective resonance structures.

The energy barrier to rotation about most carbon-carbon single bonds is usually on the order of 3-5 kcal/mol. This low barrier means that these bonds freely rotate. For instance, the C-C bond of ethane rotates approximately than 1011 times per second at room temperature.

However, rotation about the the C-N bond of an amide is constrained relative to the C-C bond. This can be explained by the amide's resonance structures, where the C-N bond has appreciable double bond character. In other words, rotation about the C-N bond disrupts the pi overlap between the carbonyl carbon and the nitrogen resulting in a much higher energy barrier (Ea) for bond rotation and hence additional NMR signals at low temperatures.