

# Berea College Undergraduate Research Program

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The BCURP has supported research studying the use of magnetic resonance of liquid crystalline systems to determine quadrupolar coupling constants. This research was undertaken by E. Dinesh Pillai, rising sophomore chemistry/physics major. This work was carried out over the summer of 1999 using our new high field NMR spectrometer (purchased with NSF-ILI grant in February 1999) to acquire spectra of our samples and using a Pentium II LINUX workstation (purchased with this grant) to simulate the observed spectra.

The samples were prepared by dissolving 10-100  $\mu\text{L}$  of acetone ( $\text{CH}_3\text{COCH}_3$ ) in an NMR tube filled with 1.0 g of liquid crystal (4,4'-dihexylazoxybenzene). These molecules are shown in figure 1. Note that the

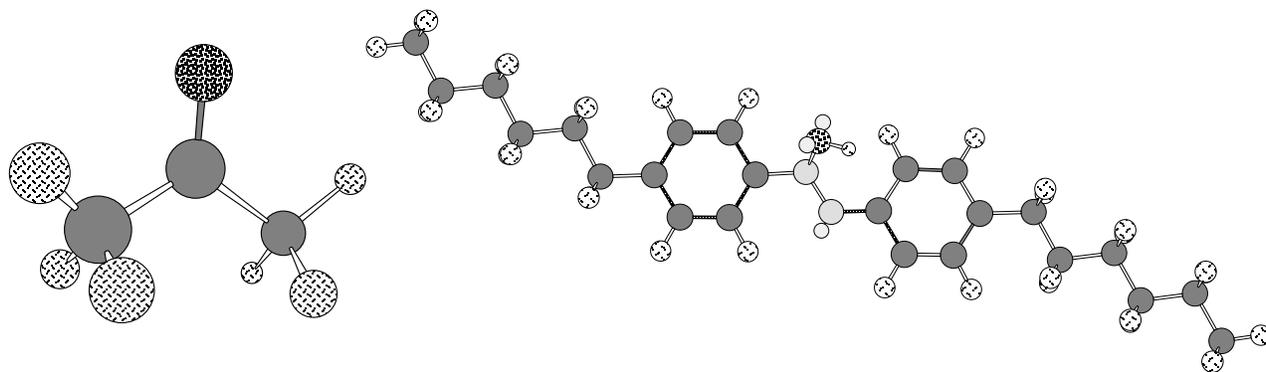


Figure 1. Three dimensional structure of acetone (left) and 4,4-dihexyl-azoxybenzene (right). Notice long tube-like appearance of the molecule on the right (leading to the liquid crystalline phase).

liquid crystalline molecule has a structure which is long and cylindrical. This tube-like structure allows the 4,4'-dihexylazoxybenzene molecules to align with one another when the temperature is lowered and the samples are placed in an aligning field (electric or magnetic) giving rise to the nematic phase. For the acetone sample, we heated the mixture in the NMR spectrometer to  $50^\circ\text{C}$  and then cooled slowly through the nematic phase transition where the liquid crystalline solvent goes from an isotropic solution to a partially ordered solution. This ordered material appears cloudy to the eye, but flows easily like a liquid. This cloudy appearance is a result of the liquid crystalline molecules aligning with the magnetic field and creating partially ordered regions which interact with light in an anisotropic fashion (this is the basis for a LC display). The acetone molecule in

this matrix would be partially ordered as well through its random interactions with the solvent. Normally, the isotropic spectrum for acetone would be a single sharp line at about 1-2 ppm. This is due to the isotropic random motion of the molecule averaging out all interactions between the various hydrogen atoms of the molecule. When the isotropic solution is cooled, the acetone molecule experiences a restricted motion which leads to only a partial averaging of the interactions between the hydrogen atoms. This gives rise to a spectrum shown in figure 2 (this is a simulation which matches nearly perfectly the experimentally observed data). The NMR data

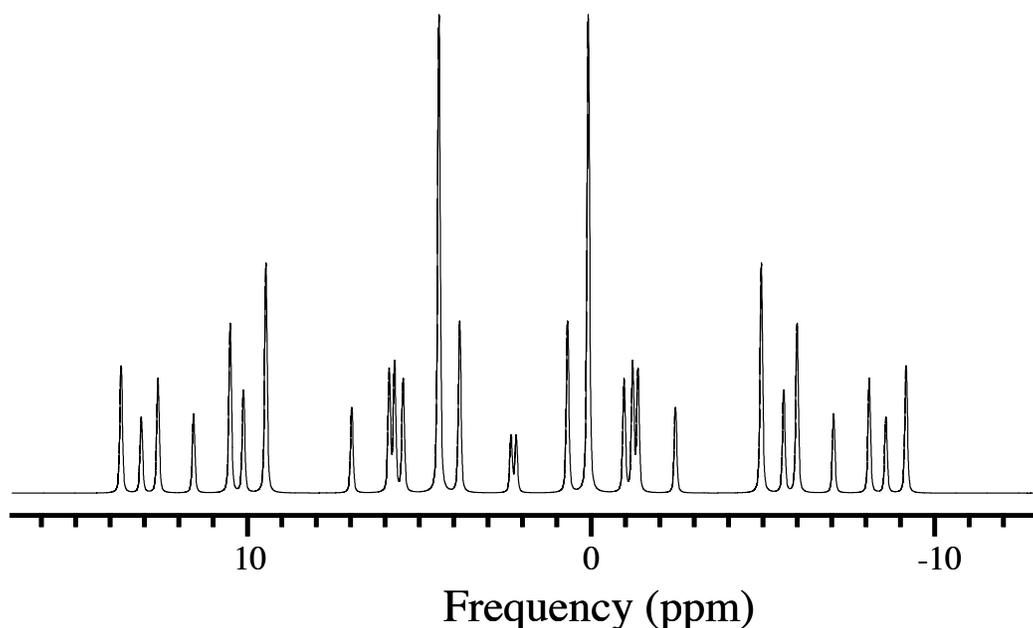


Figure 2. Sample spectrum (simulated) of acetone dissolved in liquid crystal cooled slowly from 50°C to 25°C

was simulated using a program written at Berea by Jay Baltisberger over the course of the summer. This program allows the user to input the various coupling and chemical shift parameters for up to 10 spins (the acetone system is a 6 spin problem) and generate an observed NMR spectrum. The dipolar coupling was observed to be -796 (between methyl groups) and +329 (within a methyl group) Hz between the hydrogen atoms in the acetone molecule. These dipolar couplings represent the average of the equation:

$$D_{obs} = \frac{D_{ij}}{r_{ij}^3} \left( \frac{3 \cos^2 \theta - 1}{2} \right)$$

where  $D_{ij}$  is a fundamental constant,  $r_{ij}$  is the distance between the pair of hydrogen atoms and  $\theta$  is the angle between the internuclear vector and the static magnetic field. A second program was written to simulate the rotation of the acetone molecule and study the effect of anisotropic rotation on the averaged coupling constants.

This program suggested that the coupling constants should be opposite in sign and that the coupling between methyl groups should be stronger. This result was surprising since the distance between hydrogen atoms within a single methyl group is much shorter (and would give rise to a much larger constant normally). Upon further study it was determined that the rapid methyl rotation caused the inter-methyl coupling to be averaged much less than the intra-methyl coupling. This seems to agree with our observed coupling constants. We purchased a  $^{13}\text{C}$  labeled sample of acetone so that we could attempt to measure the  $^{13}\text{C}$  dipolar couplings as well as the  $^{13}\text{C}$  chemical shift tensor. In theory, both of these parameters should be averaged in a manner similar to the proton dipolar couplings. These studies were not finished by the end of the summer and will be studied further throughout the course of this year and next summer. The ultimate goal of studying the  $^{17}\text{O}$  quadrupolar coupling was not achieved. We did try to acquire some  $^{17}\text{O}$  spectra of the acetone in both the isotropic and nematic phases. These studies indicate that the signal is very weak and will require extensive signal averaging (on the order of 1-2 weeks of continuous observation). This kind of time was unavailable this summer but will be available at the Christmas break this December, 1999. We saw some indications in the data we acquired in 24 hour runs that the expected 5 peak multiplet was present and that the quadrupolar coupling constant would be able to be extracted from a higher quality data set. This opens the door to our long term goal of looking at a biological sample in which the C=O bond in an Fe-porphyrin ring system may be studied.