

Local Ordering: The Effect of Quadrupole Interaction on the Hyperfine Couplings of the Cyclohexadienyl Radical

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An appropriate solvent can significantly increase the rate of formation and the product yield in organic synthesis. The solvent can subtly alter the geometric and electronic structure of the molecules, stabilizing or destabilizing the reactants or transition states, which leads to changes in the reaction rate. The hyperfine coupling constants (hfcs) are a sensitive means of examining the electronic structure of a radical in solution and monitoring how this is altered through solvent interactions.

In an earlier study the methylene muon and the methylene proton hfcs of the muoniated cyclohexadienyl radical were measured in neat solvents and mixtures of various polarities between octadecane and water [1]. The hfcs of the cyclohexadienyl radical's methylene protons are altered by the partial ordering of the dipole moments of the neighboring solvent molecules around the dipole of the muoniated cyclohexadienyl radical [2]. The hfcs were found to be directly proportional to the concentration of solvent dipole moments (μ_S).

A notable exception to this trend is benzene, in which the hfcs are significantly larger than in other nonpolar solvents, such as octadecane or cyclohexane, even though all of these solvents have identical μ_S values. The difference between the solvents is that benzene has a molecular quadrupole moment, which can interact with the dipole moment of the cyclohexadienyl radical. In order to study this effect the hfcs of the muoniated cyclohexadienyl radical were measured by avoided level crossing muon spin resonance (ALC- μ SR) in a series of benzene / cyclohexane mixtures. It was found that the shift in the hfcs was proportional to the benzene concentration. This contradicts the model of Vujosević et al. where the hfc shift was predicted to be proportional to the quadrupole concentration to the 4/3 power [1].

In this work the model of Vujosević et al. has been extended and an analytical method for calculating the internal field was developed. This extended model reproduced the observed linear relationship between the hfcs and the quadrupole concentration, and it was found that the diameter of solvents and solute molecules are of great importance. The new model will be presented and discussed in detail.

[1] D. Vujosević et al., J. Phys. Chem. B 111 (2007) 199.

[2] A. H. Reddoch, and S. Konishi, J. Chem. Phys. 70 (1979) 2121.