

Rotation about Aromatic Amide Bonds II: A Computational Project

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Previously we showed that the solvent induced change in the proton NMR spectrum of 2-nitroacetanilide could not be explained by a change in H bonding in CDCl₃ vs DMSO. Rather a change in the angle of the acetamido group to the plane of the benzene ring explains this. Calculations using Gaussian can trace the change of ¹H chemical shifts of the ring protons as the angle of the acetamido group to the plane of the benzene ring is varied. These suggest that in CDCl₃ the energy minimum for this rotation is about 50° while in DMSO it is close to 90°. In N-methyl-2-nitroacetanilide, where H bonding is removed there also is a change in spectrum in going from CDCl₃ to DMSO. The ¹³C spectrum shows this more clearly. Here rotation is along the amide bond rather the C1C2NH axis. Since amides have partial double bond character, separate signals are observed for *cis* and *trans* conformers. Calculations using Gaussian confirm that the *trans* [E] conformer is the major one in both solvents. The ratio of these conformers goes from approx 3:1 in CDCl₃ to 3:2 in DMSO. This corresponds to a difference in ΔG between conformers of about 2.2 KJ/mole in CDCl₃ and 1KJ/mole in DMSO.