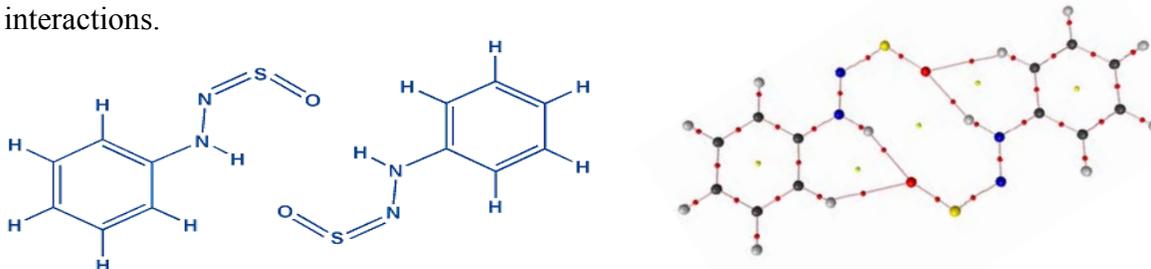


Computational Study into Proton Chemical Shift Changes in the Dimerization of N-Sulfinylhydrazines

Martha N. Kariuki and Heidi M. Muchall

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montreal, QC, Canada

From previous experimental (IR) as well as computational vibrational studies,¹ it has been shown that aromatic N-sulfinylhydrazines (Ar-NH-N=S=O) can form hydrogen bonded dimers dictated by the nature of substitution on the aromatic ring. Dimerization has been observed to occur in all but *ortho* substituted compounds. While from an X-ray structure analysis on the roughly planar dimer of Ph-NH-N=S=O in its crystalline state, where only N-H...O interactions had been suggested,² the hydrogen bonding network observed within the framework of the quantum theory of Atoms in Molecules (AIM), from the computed electron density, actually involves two N-H...O and two C-H...O interactions.



Vibrational studies have illustrated the nature of these weak interactions through an observation of the change in C-H and N-H vibrational stretching frequencies (ν) upon dimerization.¹ The N-H...O interaction illustrates a red shift in $\nu(\text{N-H})$, while the C-H...O interaction shows an improper blue shift in $\nu(\text{C-H})$ attributed to the shortening of this C-H bond. While the N-H...O interaction is shown readily in IR dilution studies, an interpretation of the $\nu(\text{C-H})$ region was not attempted because of its complexity and the weakness of this C-H...O interaction. ¹H NMR dilution studies, on the other hand, are expected to reveal the C-H...O interaction, because of the deshielding that occurs upon hydrogen bond formation.

In this contribution we present computational results on various *meta* and *para* substituted N-sulfinylhydrazines, chosen based on the spread in Hammett substituent constants. From orbital interactions, electron densities, frequencies and isotropic shieldings for both monomers and dimers, we characterize the C-H...O interactions and provide a prediction as to which substituents lead to the largest changes in ¹H chemical shift upon hydrogen bonding.

[1] P. Malla, *Structural analysis of N-phenyl-N'-sulfinylhydrazines and their hydrogen bonded dimers*. MSc thesis, Concordia University, Montreal, Quebec, 2005.

[2] A. Gieren, B. Dederer, *Angew. Chem. Int. Ed. Engl.* **16**, 179 (1977).