Effect of 1,10-Phenanthroline Aromaticity in Carboxylic Acids: GIAO Calculations and ^{1}H NMR Spectroscopy

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INTRODUCTION

Hydrogen bonding influences the functionalities of molecular species, as well as the understanding of several physical properties, such as energetic stabilities, structural properties and the vibrational properties[1-2]. In this work, we examine the pronounced effects associated with the process of formation of the hydrogen bonds as they appear in the chemical shifts of the acidic hydrogens in the complexes between 1,10-phenantroline and benzoic acid in stoichiometric ratios 1:1 and 1:2, PHEN:ACID. Subsequently, we studied the NBO charges transferred due to hydrogen bonds in theses complexes.

METHODS

We performed B3LYP/6-31++G(d,p) calculations to optimize the geometry of the hydrogen bonded complexes, followed by the GIAO method to predict the acidic hydrogen chemical shift. As reference, TMS was also calculated with the same methodology. We also prepared solutions of the 1,10-phenantroline, the carboxylic acids, and their 1:1 and 1:2, PHEN:ACID, mixtures, all dissolved in $CDCl_3$. Further, the experimental ^{1}H NMR chemical shift values were obtained using a Unity Plus 400 MHz Varian equipment.

RESULTS AND DISCUSSION

Figure 1 shows the calculated, δ^{GIAO}, and experimental, δ^{NMR}, chemical shifts for the acidic hydrogen of the 1:1 and 1:2 complexes. We also show the shielding effect in the acidic hydrogen due hydrogen bonds in the complexes by the difference between the values of the chemical shifts obtained for the acidic hydrogen, both in the complex as well as in the acid dimer ($\Delta\delta=\delta^{\text{in complex}} - \delta^{\text{in acid dimer}}$). The pronounced effect in the 1:1 complex, $\Delta\delta^{GIAO}$ and $\Delta\delta^{NMR}$ can be explained by the transferred NBO charge, ΔQ^{NBO}.

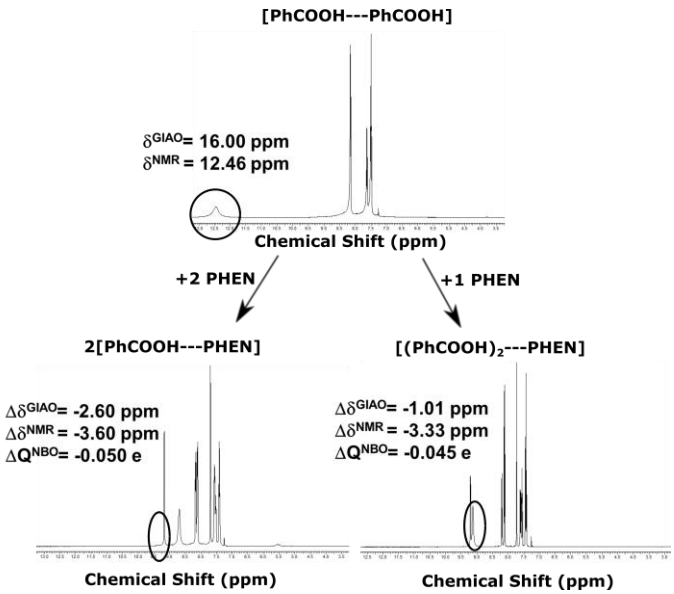

Figure 1. Calculated and experimental chemical shifts of acidic hydrogen nucleus of the benzoic acid (δ^{GIAO} and δ^{NMR}), the shielding effect due hydrogen bonds in complexes 1:1 and 1:2, PHEN:ACID, ($\Delta\delta^{GIAO}$ and $\Delta\delta^{NMR}$) and the NBO charges transferred, ΔQ^{NBO}, due hydrogen bonds.

CONCLUSIONS

The GIAO calculations agree with the ^{1}H NMR experiments in predicting a shielding of the acidic hydrogen of the hydrogen bonded complexes between 1,10-phenantroline and benzoic acid in ratios 1:1 and 1:2, PHEN:ACID, being the 1:1 complex the most affected.

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