The Nature of the Hydrogen Bond and the Resonance Effect on the Formamide-Water Complexes.

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Introduction

The amide group is encountered in biomolecules, such as proteins and nucleic acids, and in synthetic polymers. Formamide is the simplest molecule containing the amide group, so it is usually selected as model for studies involving biological systems that display bonds similar to those found in peptides and DNA structures.[1] The nature of the hydrogen bonds formed between formamide and water may aid the understanding of the mechanism expected for hydrogen bonds in protein hydration.[1]

In this work, the geometric and electronic effects of the interaction of formamide and the two transition states of its amide group rotation with water molecules have been studied. The Hartree-Fock and post-Hartree-Fock (MP2 and QCISD(T)) methods, as well as methods based on the density functional theory (B3LYP and B3PW91) have been used. The effects of the hydrogen bonds on the electronic structure of formamide and the transition states of its amide group rotation have been studied by means of the NBO, NRT, and ELF.

Results and Discussion

The interactions of formamide and the transition states of its amide group rotation with water present relatively intense hydrogen bonds. The most stable complexes are those where the water molecule interacts with O(1), specially in the X position (Figure 1). For the transition states, the interaction of water with the N(4) lone pair was also rather intense. The water molecules O-H stretching band was red-shifted. The energetic analysis proposed by Xantheas revealed that the greater contributions to the total relaxation energies are due to distortions taking place in formamide upon complex formation , especially in the complexes with water in X. The NBO method provided information concerning interactions between the localized orbitals that most contributed to the stabilization or destabilization of the complexes.

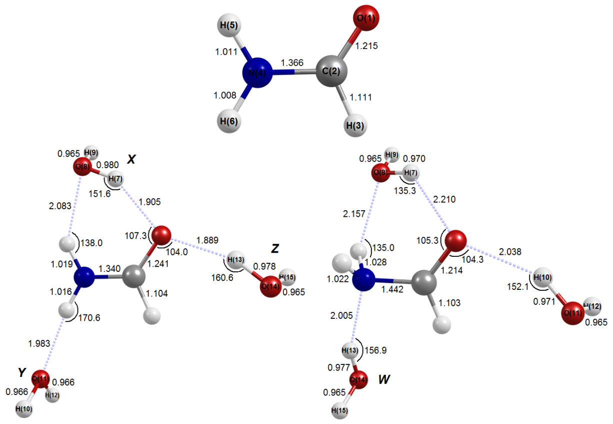

Figure 1. Numbering and solvation sites of formamide.

According to NBO results The interaction with water molecules makes the formamide N(4)-H(5), N(4)-H(6) and C(2)-H(3) bond orders, as well as the water OH bond order (hydrogens closer to formamide) decrease, showing that the hydrogen bonds are significantly strong. The NRT method showed that there is an increase in the contribution of the bipolar resonance structure upon complexation, as well as an increase in the formamide resonance. The ELF analysis, particularly, the population of synaptic basins of formamide confirms the increase of resonance.

Conclusions

All the results show that the hydrogen bonds studied herein are strong, and they exert a major influence on the geometric, energetic and electronic properties of the monomers constituting the complex, leading to an increment in the formamide resonance.

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