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Title:	Tailoring Secondary Interactions to Influence H- $\pi$ versus n- $\sigma^*$ Competition in Hydrogen Bonded Complexes: A Matrix Isolation and Ab Initio Study
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**Abstract:** Hydrogen bonded complexes of 2,6-dichlorophenylacetylene (2,6-DCPhAc) with H<sub>2</sub>O were studied experimentally using Matrix Isolation Infrared Spectroscopy, and corroborated through ab initio computations. The question addressed in this thesis concerns the competition between H- $\pi$  and n- $\sigma^*$  hydrogen bonded structures in phenylacetylene systems with H<sub>2</sub>O and the factors that govern the relative stability of the two isomers. It was shown earlier that while in Acetylene (Ac)-H<sub>2</sub>O complex, Ac served as the proton donor, forming the n- $\sigma^*$  complex, the PhAc-H<sub>2</sub>O system manifested a H- $\pi$  structure, where H<sub>2</sub>O was the proton donor to the acetylenic  $\pi$  cloud of PhAc. The switch in roles was attributed to the presence of a secondary contact involving a hydrogen bonding interaction between the aromatic C-H of PhAc and the oxygen of H<sub>2</sub>O (i.e. C-H ... O interaction). The question asked here is the following: If the C-H group involved in the secondary interaction is replaced with a C-Cl group, thereby suppressing the C-H ... O interaction, would there be a change in the relative stability of the H- $\pi$  and n- $\sigma^*$  isomers? Towards finding an answer to the above question, hydrogen bonding interactions in 2,6-DCPhAc-H<sub>2</sub>O system was studied. Ab initio computations were performed using M06-2X and MP2 methods with 6-311++g\*\* and aug-cc-pVDZ basis sets, using Gaussian-09 software. Interaction energies of the complexes were also computed using single point calculations at the CCSD(T) level at the CBS limits. Frequency calculations were performed to assign our experimental features and to confirm if the structure corresponding to a stationary point is a minimum. AIM and NBO calculations were done to understand the nature of the interactions in the complexes. Calculations showed that the energy gap between the H- $\pi$  and n- $\sigma^*$  isomers in the chloro derivative is smaller than in the unsubstituted PhAc-H<sub>2</sub>O system; pointing to the loss of stabilization of the H- $\pi$  complex relative to the n- $\sigma^*$  structure in the chloro system. At the MP2/aug-cc-pVDZ level, BSSE corrected interaction energies actually show a flipping of the relative energies of the complexes, indicating the n- $\sigma^*$  complex to be more stable than the H- $\pi$  isomer. Matrix isolation experiments also confirmed the presence of the n- $\sigma^*$  structure in the matrix. This work has therefore highlighted the important role of the secondary interaction, alluded to in the earlier work. This work has also highlighted that by suitably tailoring the structure of the precursor molecules, one can tune the competition between nearly degenerate structures.


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