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Title:	The "Strange Case" of Phenylacetylene: Competition between H- $\pi$ and n- $\sigma^*$ Contacts, Studied using Matrix Isolation Infrared Spectroscopy and Ab Initio Computations
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**Abstract:** Hydrogen bonded interactions of phenylacetylene (PhAc) with a number of partner molecules were studied using matrix isolation infrared spectroscopy and ab initio computations. Phenylacetylene (PhAc) is a multifunctional molecule having an aromatic  $\pi$  and a non-aromatic  $\pi$  system, and an acidic hydrogen at the acetylenic  $\equiv\text{C-H}$  group, thereby presenting more than one site to interact with its partner to form a hydrogen bonded complex. PhAc can be involved in either an  $n-\sigma^*$  interaction through the acidic hydrogen or in a  $\text{H}-\pi$  interaction through either of its two  $\pi$  systems. It therefore presents an interesting case of competitive hydrogen bonding interactions between  $\text{H}-\pi$  and  $n-\sigma^*$  contacts. We chose diethylether (DEE), water ( $\text{H}_2\text{O}$ ), methanol (MeOH), formic acid (FA) and HCl, as hydrogen bonding partners with PhAc to study this competition. On the one hand, DEE presents an exclusive  $n-\sigma^*$  structure, while HCl at the other extreme shows a dominant  $\text{H}-\pi$  interaction. All the other molecules,  $\text{H}_2\text{O}$ , MeOH and FA, show both  $n-\sigma^*$  and  $\text{H}-\pi$  structures. This thesis attempts to understand the competition between the  $n-\sigma^*$  and  $\text{H}-\pi$  interactions in PhAc, as a function of the partner molecules. The hydrogen bonded complexes of PhAc with the above mentioned partners had interaction energies in the range of -1 to -6 kcal/mol. An important aspect of this work has been the experimental observation, in a number of cases, of local minima. While cold molecules studies in the gas phases only identify the global minimum, our experiments using matrix isolation spectroscopy, has experimentally observed local minima as well, thus allowing for a better understanding of the potential surface of the complex. The complex formation was evidenced by the vibrational shifts in the frequencies of the submolecules. The experiments were corroborated using high level ab initio computations using both DFT and MP2 methods together with a 6-311++g\*\* and aug-cc-pVDZ basis sets. Interaction energies of the complexes were also computed using single point calculations at the CCSD(T) level at the CBS limits. AIM, NBO and LMOEDA calculations were also performed to understand the nature of interaction in all the complexes. In the case of PhAc-HCl, it was shown that HCl forms a hydrogen bonded complex where the hydrogen of HCl was bonded to the  $\pi$  cloud of acetylene. It was further inferred that the HCl can in fact freely rotate around the triple bond. It was shown that one of the orientations of HCl, where it was in plane with the phenyl ring, could in fact serve as the gateway complex for Markovnikov addition. The complexes of PhAc- $\text{H}_2\text{S}$  and PhAc-CO were also studied and the computational results on the structure, vibrational frequencies and analysis of the weak intermolecular interactions are presented. However, our experiments on these systems did not yield any definitive assignments and hence no experimental results have been presented. As a result of this work, it has become evident that weak secondary  $\text{C-H} \cdots \text{O}$  interactions, can play a decisive role in deciding the stability of the hydrogen bonded structures. Hitherto it has been assumed that the weak interactions, such as  $\text{C-H} \cdots \text{O}$  play only a supportive role and our work is a paradigm shift in this concept. This thesis has also shown that some of these interactions can, in fact, be gateway structures for organic reactions.


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