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Title: Exploring Hydrogen Bonding Interactions in Multifunctional  $\pi$  Systems using Matrix Isolation Infrared Spectroscopy and Ab Initio Computations

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**Abstract:** This thesis addresses the study of hydrogen bonding interactions in a number of multifunctional  $\pi$  systems. The molecules considered in this study are phenylacetylene (PhAc), acetylene ( $C_2H_2$ ), borazine ( $B_3N_3H_6$ ) and benzene ( $C_6H_6$ ), all of which are  $\pi$  systems with competitive binding sites. These molecules have the potential to serve as proton donors or acceptors and thus, it was interesting to study the competition between the different isomeric forms of the complexes. This work specifically addresses the question as to which amongst the various isomers of the hydrogen bonded complexes would be the global minimum. We have employed the technique of matrix isolation infrared spectroscopy corroborated by ab initio calculations to study these weak hydrogen bonded  $H \dots \pi$  systems. In addition to providing infrared spectral features with small line widths, essential in studying weak non-covalent interactions, matrix isolation spectroscopy, also offers the possibility of trapping both global and local minima, thus providing a better panorama of the hydrogen bonding landscape. One of the first systems we explored, was the PhAc- $C_2H_2$  heterodimer. Both precursors could potentially serve as proton acceptors or donors and our experiments unambiguously pointed to the complex where  $C_2H_2$  was the proton donor to the acetylenic  $\pi$  cloud in PhAc. The reason as to why between PhAc and  $C_2H_2$ ,  $C_2H_2$  was the proton donor was addressed and it was inferred that weak secondary interactions between the phenyl C-H group in PhAc and the  $\pi$  cloud of  $C_2H_2$  may be responsible for determining the structure of the global minimum. Other systems we chose were the complexes of  $B_3N_3H_6$  with a number of  $\pi$  systems.  $B_3N_3H_6$ , also popularly known as inorganic benzene is the isoelectronic and isostructural analogue of  $C_6H_6$ . It is highly moisture sensitive and decomposes rapidly in the presence of water, which makes it a challenge to study this system. The main motivation behind studying the  $B_3N_3H_6$  systems was to compare it with the much studied  $C_6H_6$  systems. While many theoretical and experimental studies in the literature are known on the hydrogen bonding interactions in  $C_6H_6$  systems, very little experimental work has been done on  $B_3N_3H_6$ . One of the first studies on  $B_3N_3H_6$  taken up in the group was the  $B_3N_3H_6-H_2O$  system. This system showed the N-H group of  $B_3N_3H_6$  serving as the proton donor to the O atom of water as the global minimum, which was very different from the  $C_6H_6-H_2O$  system which displays an  $H \dots \pi$  interaction. Thus, it was concluded in this work that the  $B_3N_3H_6-H_2O$  system had a different landscape compared with the  $C_6H_6-H_2O$  system, which motivated us to further explore the nature of interaction of  $B_3N_3H_6$  with  $\pi$  systems. Matrix isolation infrared spectroscopy and ab initio computations were performed on the  $B_3N_3H_6-C_2H_2$ ,  $B_3N_3H_6$  dimer,  $B_3N_3H_6-C_6H_6$  and  $B_3N_3H_6$ -PhAc. One of the highlights of this work, is that in the  $B_3N_3H_6-C_2H_2$ ,  $B_3N_3H_6$  dimer and  $B_3N_3H_6-C_6H_6$ , we experimentally observed more than one minima, which is a unique feature of matrix isolation experiments. In the case of the  $B_3N_3H_6$  dimer, we also observed a dihydrogen bonded dimer, which is the first experimental report of a dihydrogen bond in a system other than a metal hydride. In all the systems studied with  $B_3N_3H_6$ , it was predominantly the N-H of  $B_3N_3H_6$  which served as the proton donor. Atoms in molecules analysis (AIM), Energy Decomposition Analysis (EDA) and Natural Bond Orbital (NBO) analysis was performed for all the complexes to further explore the nature of interactions. This work therefore sheds light on the non covalent interaction landscape offered by the various  $\pi$  systems.


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