

H- π BEATS n- σ IN PHENYLACETYLENE-HCl HYDROGEN BONDED HETERODIMER: A MATRIX ISOLATION INFRARED AND AB INITIO STUDY^a

GINNY KARIR, K S VISWANATHAN, *Chemical Science, Indian Institute of Science Education and Research, MOHALI, PUNJAB, India.*

Hydrogen bonded complexes of phenylacetylene (PhAc) and HCl were studied using matrix isolation infrared spectroscopy and ab initio computations. An H... π complex was observed in our experiments, which was indicated to be the global minimum by our computations. In this complex, HCl serves as the proton donor to the acetylenic π cloud of PhAc. Computations also located two other minima on the PhAc-HCl potential surface. One was an H... π complex where the proton of HCl interacts with the π cloud of the phenyl ring, which was nearly isoenergetic with the global minimum. The other was an n- σ complex, where the acetylenic hydrogen in PhAc interacted with the chlorine of HCl. The phenylacetylene-HCl system was theoretically investigated, employing MP2 and M06-2X methods, with 6-311++G(d,p) and aug/cc-pVDZ basis sets. AIM, EDA and NBO analysis were also performed to explore the nature, physical origin and the strength of the noncovalent interactions. Experiments with phenylacetylene deuterated at the acetylenic hydrogen (PhAcD) were also performed, to confirm the above observation, through the isotopic effect.

This work is part of a study of the hydrogen bonded interactions of phenylacetylene with various precursors, which provide an interesting interaction landscape ranging from a strong n- σ to a strong H- π interaction. As it turns out, HCl is at one end of this range, displaying a strong H- π interaction. While this presentation will give the details of the phenylacetylene-HCl complex, it will also summarize the landscape mentioned above, putting the present study in perspective.

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