Title:	H−π Landscape of the Phenylacetylene–HCl System: Does This Provide the Gateway to the Markovnikov Addition?
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Abstract:	Non covalently bonded complexes of phenylacetylene–HCl were studied using matrix isolation infrared spectroscopy and ab initio calculations. Phenylacetylene (PhAc) is an interesting hydrogen bond precursor as it has multiple sites for weak interactions, and it was therefore considered worthwhile to study PhAc–HCl landscape. The interactions in PhAc–HCl were identified using the shifts in the infrared frequencies of the precursor molecules, as a result of complex formation. Our experiments unambiguously revealed spectral signatures of two types of H−π complexes, in both of which HCl was the proton donor. In one complex, the acetylenic π cloud (H−πAc) was the proton acceptor, while in the second, the role of the proton acceptor was played by the phenyl π cloud (H−πPh). The H−πAc and H−πPh complexes were evidenced by a 124 and 80 cm–1 red shift respectively, in the fundamental HCl stretch, relative to that of the uncomplexed HCl monomer. Ab initio calculations performed at M06-2X and MP2 level of theory using 6-311++G(d,p) and aug-cc-pVDZ basis functions indicated the H−πAc complex to be the global minimum and the H−πPh complex to be a local minimum; thus corroborating our experimental results. These conclusions were also confirmed by calculations at MP2/CBS and CCSD(T)/CBS limits. Interestingly, there were two isomers for the H−πAc complex, and it appears from an analysis of the charge densities, that one of the two isomers may serve as the gateway complex for the Markovnikov addition reaction. Computations identified a number of other minima, characterized by n−σ* and possibly Cl−π bonded structures, on the PhAc–HCl potential surface. AIM, NBO, and LMO-EDA analyses were also performed to characterize the non covalent interactions in the PhAc–HCl heterodimer.
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