

Experimental Measurement and Theory of Substituent Effects in π -Hydrogen Bonding: Complexes of Substituted Phenols with Benzene

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IR spectroscopic experiments and DFT computations reveal the effects of aromatic substituents on π -hydrogen bonding between substituted phenol derivatives and benzene. B3LYP and PBE0 density functionals combined with the 6-311++(2df,2p) basis set were employed in modeling the interactions in simulated CCl₄ solution. Unexpectedly stable and almost identical structures were established for all twenty studied complexes. Simultaneous formation of two π -hydrogen bonds (red-shifting O-H... π and blue-shifting *ortho*-C-H... π) contribute to the stability of these T-shaped complexes. The interaction of the acidic phenol O-H proton-donating group with the benzene π -system dominates the complex formation. The shifts of O-H stretching frequencies for the different phenols are much higher (44 - 74 cm⁻¹) than the isolated C-H frequency variations (2 - 12 cm⁻¹). Strong effects on hydrogen bonding energies and frequency shifts of electron-withdrawing aromatic substituents and very weak influence of electron-donating groups on the π -hydrogen bonding are established. Experimental quantities and theoretical parameters are employed in rationalizing the properties of these π -hydrogen bonded complexes. The experimental pK_a constants for the entire series of twenty substituted phenols correlate excellently ($r = 0.991$) with the measured O-H frequency shifts ($\Delta\nu_{\text{OH}}$). Thus, the acidities of the proton-donating phenols describe quantitatively the hydrogen bonding process. The computed interaction energies correlate well with three theoretical parameters, reflecting properties of the O-H hydrogen: NBO and Hirshfeld atomic charges (q_{H}), and electrostatic potential at nuclei values (V_{H}). The results obtained show that the variations of π -hydrogen bonding energies and $\Delta\nu_{\text{OH}}$ for the systems considered are governed by the classic aromatic substituent effects, comprising both resonance and direct through-space influences.