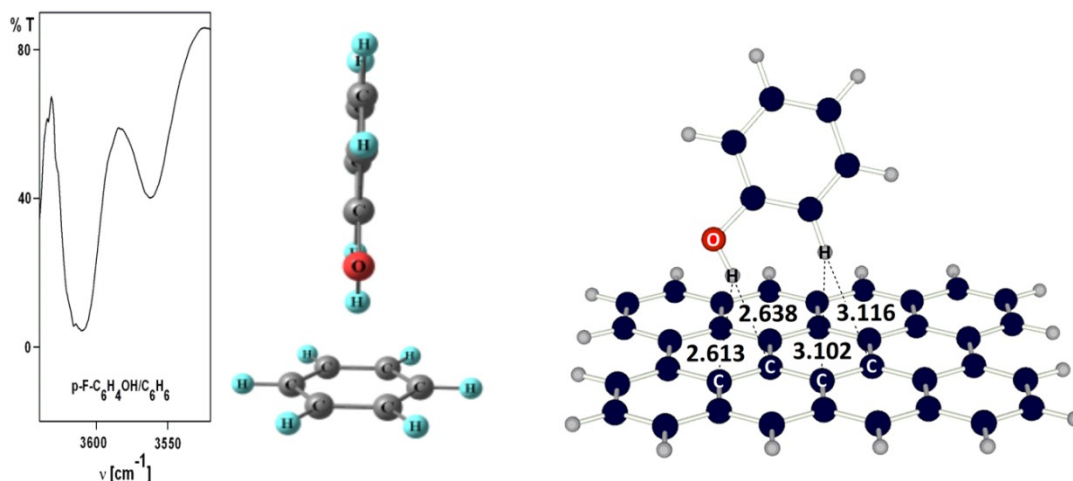


Experimental measurement and theory of substituent effects in π -hydrogen bonding: complexes of substituted phenols with benzene and graphene

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IR spectroscopic experiments and theoretical DFT computations reveal the effects of aromatic substituents on π -hydrogen bonding between monosubstituted phenol derivatives and benzene. 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 complexes. The theoretical computations suggest the presence of equilibria between alternative configurations of the complexes formed. The interaction of the acidic phenol O-H proton-donating group with the benzene π -system dominates the complex formation. *Strong* effects on hydrogen bonding energies and frequency shifts of electron-withdrawing aromatic substituents and *very weak* influence of electron-donating groups are established. Experimental quantities and theoretical parameters are employed in rationalizing the properties of these complexes. The results obtained provide clear evidence that when the structural variations are in the proton-donating species, the substituent effects on π -hydrogen bonding follow classic mechanisms, comprising both resonance and direct through-space influences. The performance of three alternative DFT functionals [B3LYP, B97-D, and PBE0 combined with the 6-311++G(2df,2p)] basis set in predicting the O-H frequency shifts upon complexation is examined.

In contrast, the structure of complexes of phenols with graphene is distinctly different. The substituent effects do not follow the trends established for the benzene complexes. Simultaneous influence of two types of non-covalent interaction – π -stacking and π -hydrogen bonding – determines the unusual structure of complexes and unexpected variations of frequency shifts and energies.

¹ V. Nikolova, S. Ilieva, B. Galabov, H. F. Schaefer, *J. Org. Chem.* (2014) DOI: 10.1021/jo500732m.