

HYDROGEN BOUND COMPLEXES WITH TROPOLONE: BINDING MOTIFS, BARRIER HEIGHTS, AND THE SEARCH FOR BIFURCATING SYSTEMS

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The potentially frustrated transfer of a proton between the hydroxylic (proton-donating) and ketonic (proton-accepting) oxygen atom centers in tropolone (TrOH) long has served as a model system for the study of coherent (symmetrical) proton-transfer events. A litany of hydrogen-bound complexes [TrOH · X_n] can be formed *in situ* by docking amphoteric ligands onto the TrOH substrate under supersonic free-jet expansion conditions. Binary ($n = 1$) and higher order ($n = 2, 3, \dots$) complexes formed with formic acid, hydrogen fluoride, acetic acid and propionic acid (X = FA, HF, AA, and PA) have been synthesized and interrogated using a variety of spectroscopic probes built upon the intense $\tilde{A}^1B_2 - \tilde{X}^1A_1$ ($\pi^* \leftarrow \pi$) near-ultraviolet absorption system of bare tropolone, thereby providing vibronically resolved information through combined use of laser-induced fluorescence (LIF), dispersed fluorescence (DF), fluorescence hole-burning (FHB), and stimulated emission pumping (SEP) methods. Experimental results reveal the propensity for binary complexes to adopt a higher-energy external binding motif (ligand attached to the seven membered aromatic ring) over the energetically preferred internal form (ligand bound to the O–H ··· O reaction center), where the latter cleft-bound species can undergo unique symmetric (coherent) double proton-transfer reactions. These findings will be discussed in light of supporting quantum-chemical calculations.