AN EXPLORATION OF ELECTRONIC STRUCTURE AND NUCLEAR DYNAMICS IN TROPOLONE

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The interrelated phenomena of proton transfer and hydrogen bonding play pivotal roles in diverse chemical and biochemical phenomena. Tropolone affords a model system for investigating these important concepts, being small enough to retain computational tractability yet sufficiently complex to exhibit the multimode dynamics that govern the behavior of substantially larger complexes. Both the ground ($\tilde{X}\,^1\mathrm{A}_1$) and the first excited singlet ($\tilde{A}\,^1\mathrm{B}_2$) electronic states support a potential energy surface whose predominant feature is a symmetric, double-minimum well characterized by a barrier of finite height, with the exchange of a hydrogen atom between hydroxylic and ketonic oxygen centers (attached to adjacent positions on a conjugated seven-membered ring) being mediated by quantum mechanical tunneling. A series of *ab initio* calculations, built primarily upon methods that allow for extensive treatment of electron-correlation effects, have been performed on tropolone with particular emphasis being directed towards elucidation of the structural and vibrational properties that mediate unimolecular dynamics. In contrast to minimal Hartree-Fock (HF/CIS) and density-functional schemes which yield inconsistent theoretical results for the $\tilde{X}\,^1\mathrm{A}_1$ and $\tilde{A}\,^1\mathrm{B}_2$ manifolds, coupled-cluster methods (CCSD, CCSD(T), and EOM–CCSD) predict proton-transfer barrier heights that are in accord with the experimentally-observed increase in tunneling efficiency following $\pi^* \leftarrow \pi$ electron promotion (fully-relaxed barrier heights of $2557.0\,\mathrm{cm}^{-1}$ and $1270.6\,\mathrm{cm}^{-1}$ for the $\tilde{X}$ and $\tilde{A}$ states, respectively). Detailed analyses suggest that the reduction in barrier height upon electronic excitation stems from a variety of complementary factors, including overall contraction of the C−O−H· · ·O=C reaction center (equilibrium oxygen atom distance drops from 2.53Å to 2.46Å) and concomitant shortening of the hydrogen bond. The potential energy landscape of tropolone, as well as the underlying nature of the vibrationally-mediated hydron migration process, will be discussed within the framework of the encompassing G_4 molecular symmetry group.