

IS TROPOLONE PLANAR? THE ROLE OF SYMMETRY ON PROTON-TRANSFER DYNAMICS

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The interrelated phenomena of proton transfer and hydrogen bonding play vital roles in many chemical and biochemical processes. A model compound for investigating these concepts is tropolone where a potential barrier of finite height hinders the symmetric transfer of a hydron between hydroxylic (proton-donating) and ketonic (proton-accepting) oxygen atoms that are attached to adjacent positions on a conjugated seven-membered ring. Tropolone is computationally tractable, yet retains sufficient complexity to exhibit the multimode dynamics that govern proton transfer in substantially larger systems. *Ab initio* calculations on the structure of ground-state tropolone (\tilde{X}^1A_1) have been undertaken with particular emphasis toward evaluating the validity of symmetry constraints often imposed on geometry optimizations. The molecule is found to converge to a slightly nonplanar configuration at levels of theory which incorporate substantial electron correlation. Although small, the resulting barrier to planarity imparts significant anharmonicity to the lowest-frequency (ν_{39}) normal mode, suggesting the importance of other out-of-plane vibrations toward the promotion and state-specificity of proton transfer. The implications of this nonplanarity for the potential energy landscape of tropolone, as well as for the description of attendant proton-transfer pathways, will be discussed within the framework of the encompassing G_4 molecular symmetry group.