

ISOELECTRONIC HOMOLOGS AND ISOMERS: TROPOLONE, 5-AZATROPOLONE, 1-H-AZEPINE-4,5-DIONE
SADDLE-POINTS, AND IONS

RICHARD L. REDINGTON, *Department of Chemistry and Biochemistry, Texas Tech University, Lubbock
Texas 79409.*

The experimental availability of 1-H-azepine-4,5-dione (45Di), together with the interesting tunneling structures observed for gaseous tropolone (Tp), motivate the high level MO investigation of these and other 64 electron homologs and isomers. The family is comprised of the tautomer structures of Tp, 5-azatropolone (5Aztp), its protonated cation (5AztpH⁺), their C_{2v} saddle-point configurations, the tropolonate (Tp⁻) and 5-azatropolonate (5Aztp⁻) anions, and 45Di. The results suggest 5Aztp and 5AztpH⁺ will be synthesized and that their tautomerization dynamics and tunneling behaviors will strongly resemble those of Tp. Isolated 45Di is predicted to be more stable than its 5Aztp isomer by about 3 kJmol⁻¹ and solvation in polar solvents significantly increases this margin. The MO-computed protonation energy to form 5AztpH⁺ from 45Di is -974 kJmol⁻¹. Isolated 45Di is predicted to have nonplanar twisted geometry with PES minima at C₂ point group symmetry, a very low C_{2v} intermediate barrier, and fluxional dynamical behavior.