

## INTRINSIC OPTICAL ACTIVITY AND CONFORMATIONAL FLEXIBILITY: NEW INSIGHTS ON THE ROLE OF RING MORPHOLOGY FROM CYCLIC AMINES

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Electronic circular birefringence (ECB), which causes rotation of the linear-polarization state for non-resonant light traversing an isotropic sample of chiral molecules, long has served as a robust means for assessing enantiomeric purity, but quantitative studies of this important property historically have been restricted to condensed phases where environmental effects (e.g., solvent-solute interactions or crystal-packing forces) can alter the magnitude and even the sign of the intrinsic behavior. As part of a continuing effort to elucidate the structural and electronic origins of such chiroptical phenomena, the dependence of optical rotatory dispersion (or wavelength-resolved ECB) on ring morphology has been explored for two saturated monocyclic amines, (R)-2-methylpyrrolidine and (S)-2-methylpiperidine. To assess the putative role of extrinsic perturbations, ambient measurements of specific optical rotation were performed under both solvated and isolated conditions, where the latter gas-phase work involved use of ultrasensitive cavity ring-down polarimetry. Each of the targeted compounds support active conformational degrees of freedom in the form of large-amplitude puckering motion of the heterocyclic ring combined with internal rotation of methyl substituents, with the antagonistic chiroptical properties exhibited by the resulting conformers combining to yield the overall response observed from a thermally equilibrated ensemble of molecules. Experimental ECB findings will be contrasted with those reported previously for ketones built upon comparable carbocyclic frameworks, and interpreted, in part, by reference to electronic-structure and linear-response calculations performed at various levels of quantum-chemical theory.