

NATURAL OPTICAL ACTIVITY OF CHIRAL EPOXIDES: THE INFLUENCE OF STRUCTURE AND ENVIRONMENT ON THE INTRINSIC CHIROPTICAL RESPONSE

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Chiral epoxides built upon nominally rigid frameworks that incorporate aryl substituents have been shown to provide versatile backbones for asymmetric syntheses designed to generate novel pharmaceutical and catalytic agents. The ubiquity of these species has motivated the present studies of their intrinsic (solvent-free) circular birefringence (CB), the measurement of which serves as a benchmark for quantum-chemical predictions of non-resonant chiroptical behavior and as a beachhead for understanding the often-pronounced mediation of such properties by environmental perturbations (e.g., solvation). The optical rotatory dispersion (or wavelength-resolved CB) of (R)-styrene oxide (R-SO) and (S,S)-phenylpropylene oxide (S-PPO) have been interrogated under ambient solvated and isolated conditions, where the latter efforts exploited the ultrasensitive techniques of cavity ring-down polarimetry. Both of the targeted systems display marked solvation effects as evinced by changes the magnitude and (in the case of R-SO) the sign of the extracted specific optical rotation, with the anomalously large response evoked from S-PPO distinguishing it from other members of the epoxide family. Linear-response calculations of dispersive optical activity have been performed at both density-functional and coupled-cluster levels of theory to unravel the structural and electronic origins of experimental findings, thereby suggesting the possible involvement of hindered torsional motion along dihedral coordinates adjoining phenyl and epoxide moieties.