INTRINSIC OPTICAL ACTIVITY AND ENVIRONMENTAL PERTURBATIONS: SOLVATION EFFECTS IN CHIRAL BUILDING BLOCKS

PAUL M LEMLER, PATRICK VACCARO, *Department of Chemistry, Yale University, New Haven, CT, USA*.

The non-resonant interaction of electromagnetic radiation with an isotropic ensemble of chiral molecules, which causes the incident state of linear polarization to undergo a signed rotation, long has served as a metric for gauging the enantiomeric purity of asymmetric syntheses. While the underlying phenomenon of circular birefringence (CB) typically is probed in the condensed phase, recent advances in ultrasensitive circular-differential detection schemes, as exemplified by the techniques of Cavity Ring-Down Polarimetry (CRDP), have permitted the first quantitative analyses of such processes to be performed in rarefied media. Efforts to extend vapor-phase investigations of CB to new families of chiral substrates will be discussed, with particular emphasis directed towards the elucidation of intrinsic (e.g., solvent-free) properties and their mediation by environmental perturbations (e.g., solvation). Specific species targeted by this work will include the stereoselective building blocks phenylpropylene oxide and α-methylbenzyl amine, both of which exhibit pronounced solvent-dependent changes in measured optical activity. The nature of chiroptical response in different environments will be highlighted, with quantum-chemical calculations serving to unravel the structural and electronic provenance of observed behavior.