CONFORMATIONAL AND SOLVENT EFFECTS ON OPTICAL ROTATION: SUBSTITUTED EPOXIDES

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Cavity Ring-Down Polarimetry (CRDP)[a] has been used to probe the vapor-phase circular birefringence (or optical rotation) of two conformationally-flexible molecules, *(S)*-1,2-epoxybutane and *(S)*-epichlorohydrin, at the nonresonant excitation wavelengths of 355 and 633nm. Complementary solution-phase studies were performed in solvents possessing a wide range of physical and chemical characteristics, thereby highlighting the pronounced influence of solute-solvent perturbations upon attendant chiro-optical properties. High levels of density functional theory, built upon application of the linear response formalism with the hybrid B3LYP correlation-exchange functional and aug-cc-pVDZ basis set, have been exploited to reveal the subtle interplay of structural and electronic effects that conspire to yield the observed optical activity. In order to elucidate the complications incurred by condensed media, ancillary quantum chemical calculations have been performed by utilizing a polarizable continuum model (PCM) to treat nonspecific solvation phenomena in conjunction with a static isodensity surface technique to generate the requisite solute cavity. Despite explicit exclusion of important "first-shell" effects in the cybotactic region, this IPCM approach affords valuable insights regarding the underlying nature of solvation processes, including the differential stabilization of thermally-populated conformers that usually exhibit antagonistic chiro-optical behavior.

[a] S. M. Wilson, K. B. Wiberg, J. R. Cheeseman, M. J. Frisch, and P. H. Vaccaro, *J. Phys. Chem. A* **109** (51), 11752 (2005).