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In Search of the Structural Determinants of Optical Activity. Kacey Claborn, Werner Kaminsky, Bart Kahr, Dept. of Chemistry, Univ. of Washington, Seattle, WA 98195, USA.

Polarimetric measurement of enantio-purity is a mainstay in the chemical laboratory, yet this reliance belies our understanding of how molecular structure gives rise to the effect. Recent advances in quantum computing make desktop calculations of optical activity viable. However, comparisons to the existing catalog of experimental specific rotations in the fluid phase require averaging the computed second rank tensors, obviating much of the power of theory. In crystals, molecules have well defined geometries and orientations making them superior candidates for comparison to theory and potential vehicles for interpretation.

Molecular crystals of tetraphenyl-C, -Si, -Ge, -Sn, and -Pb belong to the non-enantiomorphous yet optically active space group $P\text{-}42_1c$, providing a unique system for comparing chiroptical response by isomorphous substitution. Solid state polarimetric measurements were accomplished by the 'tilter' method developed by Kaminsky and Glazer (1996). The absolute orientations of the two independent tensor components with respect to the degenerate axes were assigned on the basis of anomalous dispersion. Calculations of optical rotation using both classical and quantum theories have been employed for comparison and guidance in the structural interpretation of optical activity.