

COMPUTATIONAL INVESTIGATIONS OF SUBSTITUTED TETRAPHENYLETHYLENES: MOLECULAR GEOMETRY AND THE CAPTODATIVE EFFECT, Karl C. Flanagan, Allison K. Macia, Michael J. Vineburg, and Louise L. Stracener*, Edgewood College, Chemistry, Geoscience, and Physics Department, Madison, WI 53711, lstracener@edgewood.edu

Tetraphenylethylenes substituted with $-\text{OCH}_3$ and $-\text{CN}$ groups, as well as *ortho*- and *meta*- CH_3 groups, have been investigated computationally at the B3LYP/6-31G(d) level of theory in order to determine a.) whether and to what extent the combination of electron-donating ($-\text{OCH}_3$) and electron-accepting ($-\text{CN}$) groups exert a stabilizing effect (the so-called "captodative effect") on the radical transition state for *cis-trans* isomerization, and b.) what effect sterically demanding substituents ($-\text{CH}_3$) on the phenyl rings have on this stabilization. Geometry optimizations of these species indicate that the presence of both an electron donor and an electron acceptor does appear to have a synergistic effect on the geometries of these tetraphenylethylenes (including the alkene bond length, alkene twist angles, and phenyl torsional angles) that suggests the possibility of captodative stabilization of the diradical transition state for isomerization, in agreement with prior experimental studies (i.e., the geometric changes are greater than the sum of changes brought about by donor substitution and acceptor substitution). However, the presence of methyl groups on the phenyl rings causes those rings to twist further out of the plane of the central alkene and appears to attenuate (and, in some cases, completely eliminate) these donor-acceptor effects.