

DFT Study of the Stereo-Selectivity of Oxygenated Hetero-cycles from 10 to 12 Links

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Intra-Molecular Diels-Alder (IMDA) reactions of tethered trienes can furnish two distinct diastereoisomeric products. The cis (i.e. endo) stereoisomer and the trans (i.e. exo) stereoisomer. Experimental evidences shows a quite high cis stereo-selectivity for 10 links compounds (cis/trans = 70:30) while 11 and 12 links exhibit no particular selectivity. DFT (B3LYP/6-31G*)[1,2] computations provide useful insights into the origins of this amazing stereo-selectivity. The cyclization path towards trans stereo-isomer is always thermodynamically favored whatever the size of the system. The high cis stereo-selectivity displayed by the 10 links system is kinetically controlled by a tug of war between ring strain and electronic effects in the transition structure. The dual descriptor[3,4] of chemical reactivity, a conceptual DFT based descriptor designed to delineate electronic effects, has been used to unravel the stabilizing processes that take place at the TSs.

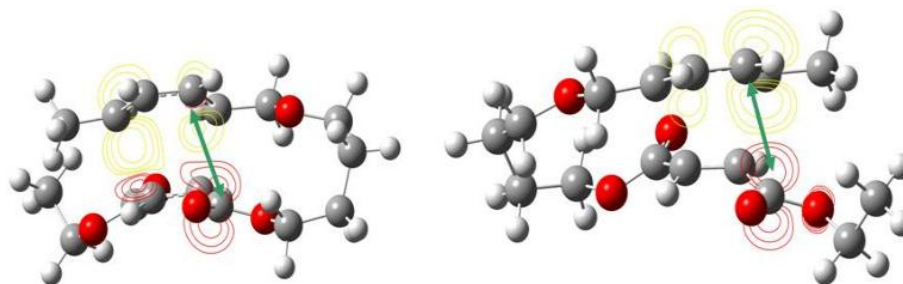


Figure. Δf maps calculated at the B3LYP/6-31G(d) for the TSs and projected on a plan that intersects the carbon involved in the secondary interactions.

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