What is the role of puckering in the thermal ratcheting steps of HTI based molecular motors?

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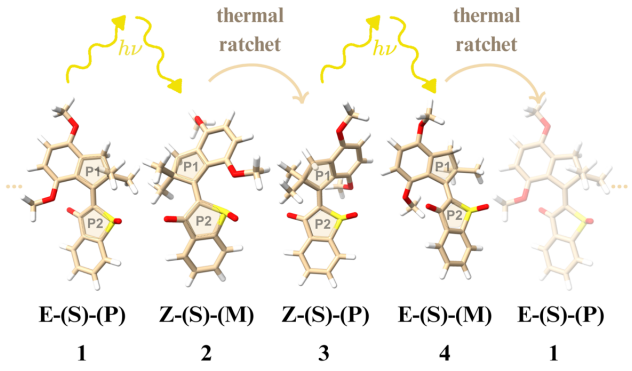
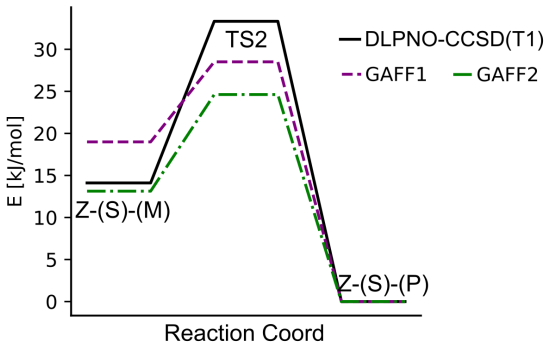
In this contribution, we will employ a combination of classical molecular dynamics simulations and static high-level ab initio calculations to elucidate the role of puckering in the ratcheting mechanism of Hemithioindigoid (HTI)-based molecular motors. HTI based molecular motors are small molecular machines, which utilize visible light to power directional thermal rotations of a small molecular rotor substructure relative to a so-called stator part. The thermal rotations are typically known as thermal ratcheting steps and involve a local unidirectional helix inversion, while the HTI chromophore allows E to Z photoisomerization with nondamaging visible light.[1]





In preliminary calculations, we observed that the motor states 1 to 4 all exhibit distinguished puckering conformations, which are likely induced due to steric effects of the methoxy and methyl substituents. In this work, we further investigate the role of puckering in the full thermal ratcheting mechanism with a combination of static ab initio calculations and molecular mechanics based MD simulations. Using geometric criteria obtained from NEB calculations and steered Molecular Dynamics Simulations, we identify the collective variables that are key to understanding the reaction mechanism of the thermal ratcheting steps. Finally, we perform 1 and 2 dimensional umbrella sampling in dichloromethane to unravel the energetic and geometric factors that underly the thermal ratcheting mechanism.

[1] R. Wilcken, M. Schildhauer, F. Rott, L. A. Huber, M. Guentner, S. Thumser, K. Hoffmann, S. Oesterling, R. d. Vivie-Riedle, E. Riedle, and H. Dube, *J. Am. Chem. Soc,* **2018**, *140*, 5311-5318.