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Switching mechanisms and role of entropy in chemically controlled hydrazone-based switches[1] RENE DERIAN, IVAN STICH, Inst. of Physics, Slovak Academy of Sciences — Chemically controlled synthetic rotary switches are important as they resemble rotary motors found in nature. In order to elucidate the recent experiments [1], using hybrid QM/MM methods we have studied chemically controlled hydrazone-based switches in a strongly polar solvent. The experiments indicate a controlled $E \rightarrow Z\text{-}H^{+}$ switching by addition of acid and thermal backward isomerization. We have studied the $Z \rightarrow E$ switching mechanisms and the role of entropy. We find use of explicit MM solvent crucial for understanding the huge dipole moments (>10D) in the Z conformation and significantly smaller (≈5D) in the E conformation and at the transition state, pointing toward very different ordering in those states. Furthermore, the internal and free energy surfaces from thermodynamic integration are qualitatively very different with the free energy surface exhibiting much smaller energy differences between E and Z. In addition, the solvent causes a pronounced shift (≈30°) in the position of the Z states from internal and free energies. Both finding highlight the role of the entropy in the switching process and help a quantitative understanding of the switching in the solvent.

[1] S. M. Landge et al., J. Am. Chem. Soc. **133**, 9812 (2011).

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