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Using bond analysis for the rational design of photoswitches...and it worked!

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Abstract: Photoswitchable compounds, which can be reversibly switched between two isomers (E and Z) by light, continue to attract significant attention for a wide array of applications: from molecular motors, memory, and manipulators to solar thermal storage.[1] Azoheteroarenes represent a relatively new but understudied type of photoswitch, where one of the aryl rings from the conventional azobenzene class has been replaced with a five-membered heteroaromatic ring. Initial studies have suggested the azoheteroarenes –the arylazopyrazoles in particular– to have excellent photoswitching properties (quantitative switching and long Z isomer half-life).[2]

Here we present a systematic computational study to elucidate the origin of the long thermal half-lives and excellent addressability of the arylazopyrazoles, and apply this understanding to determine important structure-property relationships for a wide array of comparable azoheteroaryl photoswitches. We identify compounds with Z isomer half-lives ranging from seconds to hours, to days and to years, and variable absorption characteristics; all through tuning of the heteraromatic ring. On the one hand, the compounds with the longest isomerization half-lives adopt a T-shaped ground state Z isomer conformation and proceed through a T-shaped isomerization pathway. On the other hand, the most complete photoswitching is achieved for compounds that have a twisted (rather than T-shaped) Z-isomer conformation. By balancing chemical bonding factors, we report on a new azopyrazole, which has been experimentally demonstrated to quantitatively switch between Z and E isomers, and has a very long half-life for thermal isomerisation (t1/2 = 74 d at 25 °C).[3]

Keywords: photoswitches, inverse design, chemical bond

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