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Title: Tuning the Thermal Stability of Z-isomer of Hydroxy Derivatives of Phenylazohetroarene Photoswitches

Authors: Meena, Dheeraj Kumar

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The Z-isomer of arylazo(hetero)arene, particularly azopyrazoles, a class of five-membered azo photoswitches, has exceptional thermal stability and quantitative photoswitching (half-lives up to 1000 days). The substitution pattern influences the thermal half-life of these Z- isomers due to steric and electronic effects. Intriguingly, the half-lives of hydroxy derivatives (at ortho and para position to azo group) of N-Me pyrazoles and isoxazoles are found to be very less due to tautomerization of hydroxy proton at azo-nitrogen. The steric and electronic effects have been used mostly to counter significant substituent impacts. Herein, we report an approach to enhance the thermal stability of photoswitched state by substitution, varying heterocycles and quaternization of N-atom of pyrazoles or

isoxazoles. Accordingly, a new class of such ionic photoswitches were created by simply alkylation of N-atom of heterocyclic ring.

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