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Title: Light Modulation of Properties of Arylazoisoxazole Photoswitches and their Benzene- 1,3,5-tricarboxamide (BTA) Functionalized Derivatives

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Abstract: Light modulation of properties of arylazoisoxazole photoswitches and their benzene-1,3,5-tricarboxamide (BTA) functionalized derivatives Abstract Azobenzenes undergo reversible photoisomerization between two isomeric states, namely trans (E) (thermodynamically more stable) and cis (Z) isomers. Forward (E-Z) isomerization occurs with light (UV or visible), and reverse (Z-E) occurs through light (visible light) or under thermal conditions. Among the various classes of photoswitches reported so far, azobenzene is one of them exhibiting robustness and high stability and is easily accessible through simple synthetic steps. Apart from this, azobenzenes can be easily functionalized and utilized in various applications such as molecular machines, data storage, molecular recognition, liquid crystals, etc. In recent times, the resurgence of azoarene chemistry is being witnessed mainly due to the emergence of azoheteroarenes, where one of the aryl rings in azobenzene is replaced by five-membered heterocyclic rings. Depending on the heteroaryl ring, they have shown comparatively better forward and reverse bidirectional photoswitching, variable cis (Z) isomer stability, and exhibit a wide range of applications in photochemical, photobiological, optochemical, data storage devices, energy storage materials, etc. In this relevance, we have introduced arylazo-3,5-dimethyl isoxazole as a new class of photoswitches. We synthesized 37 derivatives with different aryl substituents using a simple synthetic strategy. To understand the effect of substitution on the photoswitching properties and Z-isomer stability, we performed UV-vis and ^1H NMR spectroscopic studies. They all showed good to excellent reversible photoswitching in solution and solid state, and high thermal stability of Z-isomeric state. For the unsubstituted aryl derivative, we have estimated the $t_{1/2}$ as 45.5 days in DMSO- d_6 , making it one of the long-lived Z-isomeric forms. Activation parameters (E_a , ΔH^\ddagger , ΔG^\ddagger , ΔS^\ddagger) have also been estimated from Eyring and Arrhenius plots using the thermal reverse isomerization kinetics data of Z-isomer at variable temperatures that showed consistency with the literature reports on stable Z-isomers. Apart from this, we also observed a light-induced phase transition in the parent phenylazo-3,5-dimethylisoxazole which is followed by POM, DSC, and further supported by the crystal packing. In the next part of the work, we functionalized the o-, m-, and p- aminophenylazoisoxazoles and their N-methylated analogues into a C₃-symmetric benzene-1,3,5-tricarboxamide (BTA) core. The resulting tripodal photoswitches were explored for their photoswitching characteristics and supramolecular assemblies. Particularly, the possibilities of multistate photochromic properties, concentration dependency in photoswitching, and estimation of PSS composition of individual photoisomers have been obtained through UV-vis and ^1H -NMR spectroscopic studies. The results revealed the existence of bistability between all-trans and all-cis isomers with excellent and reversible photoswitching and high thermal stability of ZZZ-isomeric state, which are the salient features of these tripodal molecules. Activation parameters have also been obtained through variable temperature kinetics studies and Eyring and Arrhenius plots. Interestingly, a reversible light-induced sol-gel phase transition has also been observed in the case of benzene-1,3,5-tricarboxamide derivatives, which was supported by POM studies. In the last part of the work, we synthesized C₃-symmetric molecules for photoswitchable liquid crystalline properties where phenylazoisoxazole units are present at terminal positions and separated from the core part through alkoxy spacer units of variable lengths (C₈, C₁₀, C₁₂). All three molecules showed discotic liquid crystalline (DLC) properties in a nematic manner at room temperature, confirmed by POM (Polarized optical microscopy), SAXS/WAXS (Small angle/wide angle X-ray scattering), and DSC (Differential scanning calorimetry) studies. Besides this, excellent and reversible photoswitching has been observed in the solution state, solid state, and thin film state by using UV-vis, POM, ^1H NMR, and AFM studies. Also, high Z-isomer stability and photostability are the other salient features of these functional molecules. Furthermore, activation parameters for the reverse thermal isomerization step have been estimated from Eyring and Arrhenius plots. Interestingly, we also observed a reversible light-induced mesophase change that was confirmed by POM and SAXS/WAXS studies.


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