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Effect of PEG-200 and Tween-20 on photoisomerization of 1-alkyl-2-(arylazo)imidazoles in toluene

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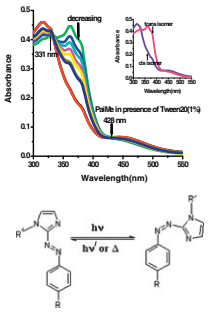
HIGHLIGHTS

- Photoisomerization of 1-alkyl-2-(arylazo)imidazoles, *trans*-to-*cis*, in PEG-200 and Tween-20 is reported.
- The rate and quantum yields increase in emulsion and follows free state < PEG-200-phase < Tween-20-phase.
- The reverse, *cis*-to-*trans* has been carried out by thermal process.
- The E_a of *cis*-to-*trans* isomerization follows: free state > PEG-200-phase > Tween-20-phase.

GRAPHICAL ABSTRACT

The photoisomerization of 1-alkyl-2-(arylazo)imidazole in presence of PEG-200 and Tween-20, in toluene solution by UV light irradiation has been reported. The rate and quantum yields of *trans*-to-*cis* isomerization are decreased in presence of microemulsion. The *cis*-to-*trans* isomerization is carried out by thermal route. The activation energy (E_a) follows as free state > PEG-200-phase > Tween-20-phase. The branched polyhydroxo structure of Tween-20 may help to wrap the polar photochrome more efficiently than major ether functionalized PEG-200 and stabilizes *trans*-isomer.



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ABSTRACT

The photoisomerization of 1-alkyl-2-(arylazo)imidazole, *trans*-to-*cis*, has been studied in the matrix of PEG-200 and Tween-20 in toluene medium by UV light irradiation. The *trans* and *cis*-isomers have different absorption spectra. The *cis*-to-*trans* isomerization proceeds slowly in visible light irradiation while it is appreciably fast in thermal process. The rate of *trans*-to-*cis* isomerization is decreased by 30–60% in presence of PEG-200 and Tween-20. The quantum yield of the photoisomerization is also decreased by 35–55% and follows the rate sequence: free state > PEG-200-phase > Tween-20 phase. The activation energy (E_a) of *cis* → *trans*, thermal backward isomerization, is reduced in PEG-200 and Tween-20 phase following free state > PEG-200-phase > Tween-20-phase. The branched polyhydroxo structure of Tween-20 may help to wrap the polar photochrome more efficiently than major ether functionalized PEG-200 and stabilizes *trans*-isomer.

Introduction

The ordered molecular aggregates are of much interest because of their special properties and possible technological applications [1–3]. The physical, chemical, luminescence, catalytic, biological, electrochemical etc., properties of the active molecular units have sharply been influenced in the microenvironment of molecular aggregates [4–6]. Photochromism, a reversible photo-induced transformation between two molecular states whose absorption spectra differ significantly [7,8], has been influenced by microenvironments in solution [9–13]. The reversible photoisomerization has enormous applications for controlling the properties of functional polymeric materials [14], useful for the photo-control of

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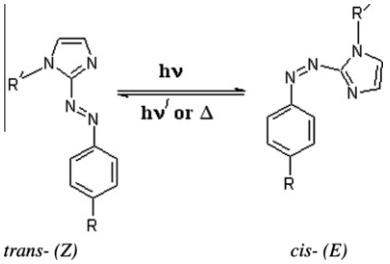


Scheme 1. Isomerization of 1-alkyl-2-(arylazo)imidazole ($\nu > \nu'$).

biomolecules [15] and for novel applications such as data storage [16,17] and self-assembling systems [18,19]. We have been investigating the *trans-to-cis* photoisomerization of 1-alkyl-2-(arylazo)imidazoles and their metal complexes [20–27]. The influence of microenvironment on the photoisomerization has been studied from different aspects and has mainly been focused to explain the mechanism of the *trans-to-cis* conversion [28]. The solvent properties (density, polarity, viscosity, hydrogen bonding ability, van der Waals, electrostatic activity etc.) and the presence of noninteracting (innocent) and interacting (noninnocent) foreign molecules have controlled the isomerization rate and quantum yields [9–13,29,30]. In this work we report the effect of microenvironment originated by adding PEG-200 (polyethylene glycol) and Tween-20 on the photoisomerization of four different 1-alkyl-2-(arylazo)imidazoles. Only a few reports have been published to count the effect of micelle on the photochromic activity of active molecules [11–13] while the photochromic molecules solubilized in micelles have been suggested as probes for the study of the hydrodynamics of fluids [31].

Experimental

Reagents/materials

1-Alkyl-2-(arylazo)imidazoles were synthesized by reported procedure [32] Imidazole, aniline, *p*-toluidine were of Analytical reagent grade collected from SRL, India. PEG-200 (Polyethylene glycol) and Tween-20 were collected from Sigma–Aldrich. All other chemicals and solvents were reagent grade as received.

Physical measurements

Spectroscopic data were obtained using the following instruments: UV–Vis spectra from Perkin Elmer Lambda 25 spectrophotometer; photoexcitation has been carried out using Perkin Elmer LS-55 spectrofluorimeter.

Photometric measurements

Absorption spectra were taken with a Perkin Elmer Lambda 25 UV/VIS Spectrophotometer in a 1 × 1 cm quartz optical cell maintained at 25 °C. The light source of a Perkin Elmer LS 55 spectrofluorimeter was used as an excitation light, with a slit width of 10 nm. An optical filter was used to cut off overtones when necessary. The absorption spectra of the *cis* isomers were obtained by extrapolation of the absorption spectra of a *cis*-rich mixture for which the composition is known from ^{1}H NMR integration. Quantum yields (ϕ) were obtained by measuring initial *trans*-to-*cis* isomerization rates (v) in a well-stirred solution within the above instrument using the equation,

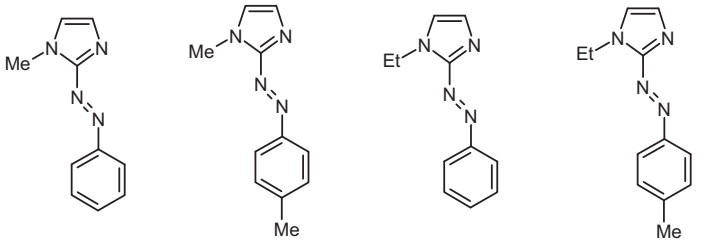
$$v = (\phi I_0/V)(1 - 10^{-\mathrm{Abs}})$$

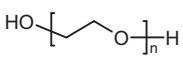
where I_0 is the photon flux at the front of the cell, V is the volume of the solution, and Abs is the initial absorbance at the azobenzene (ϕ = 0.11 for π–π^* excitation [33]) under the same irradiation condition.

Results and discussions

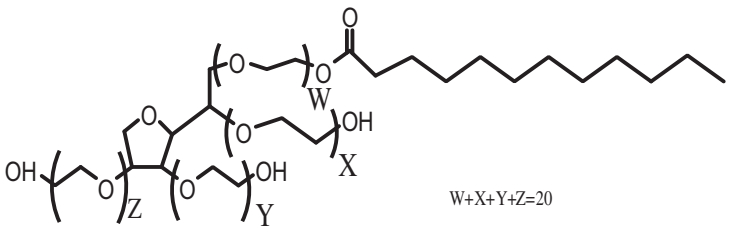
The compounds

The photoisomerization (Scheme 1) of 1-methyl-2-(phenylazo)imidazole (Pai-Me, **1a**), 1-methyl-2-(*p*-tolylazo)imidazole





PEG-200 (Polyethylene glycol 200)



Polyoxyethylene (20) sorbitan monolaurate (Tween 20)

Scheme 2. Ligands, PEG-200 and Tween-20 used in this work.