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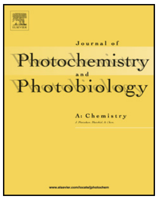

Short note

Photochromism of dihydroindolizines. Part XX: Synthesis and photophysical behavior of fluorenyldihydroindolizines photochromes based “Click” chemistry strategy

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ABSTRACT

Novel type of photochromic dihydroindolizines (DHIs) bearing substituted 2,7- disubstituted triazolofluorene (region A) with different acetylenic linker-conjugates and substituted pyridazines as heterocyclic base (region B) have been productively synthesized through “Click” chemistry strategies by different chemical and photochemical pathways. The chemical structures of the new photochromic triazolo-dihydroindolizines were established on the bases of analytical and spectroscopic tools. Polychromatic light irradiation of the photochromic DHIs led to ring opened colored betaines, which underwent reversible thermal 1,5-electrocyclization. The red to reddish-violet betaines returned back through 1,5-electrocyclization to the corresponding DHIs with diverse rate constants depending on the subsitutents in fluorene terminal triazole moieties. The unique photochromic properties of newly synthesized compounds maybe useful for a plethora of new applications.

1. Introduction

The Synthesis of functionalized optical materials having photoswitchable characters has considered as one of the most interesting topics in the field of materials chemistry. These materials are used in the fabrication of huge number of optoelectronic devices such as optical memories, switches, and holograms. These materials normally produced from polymer doping with photoactive materials [1–7]. It is famous that the organic photochromic materials are competent of altering their geometrical and electronic structures underneath the influence of ultraviolet light irradiation and return-back to their preliminary state when the glowing irradiation ceases. The back-reaction to the initial state may be promoted by a thermal process (spontaneous) or triggered through irradiation with poly- or monochromatic visible light [8–10]. Since the reversible structural changes arise at a single-molecule Stage, the photochromism phenomenon become latent interesting in miniaturizing optic mechanism down to the molecular level and for applications in molecular opto-electronics, namely for information and photoswitching technologies with offering the possibility to control, the physico-chemical properties of materials such as fluorescence, electrical conductivity, magnetism, permeability and reactivity through photochromic reactions [10–19]. Of course, the extraordinary and browbeaten characteristic of these materials is the remarkable reversible color change.

Photochromic dihydroindolizines, discovered and developed by Dürr [20–25], are well-known photochromic family that attracted much attention from the viewpoints of both fundamental elucidation of electrocyclization reactions (Scheme 1) and their potential applications include variable optical density, optical filters, miscellaneous optical devices, decorative objects, novelty items and toys, smart windows and visors, security inks [25–36]. These organic photochromes, based on the 1,5-electrocyclization between two discrete isomeric states: ring-open form (betaine-form) and ring closed form (DHI-form), are potential candidates for optical storage media and electronic devices [33–36].

Since the pioneer discovery of the Huisgen terminal alkyne-azide 1,3-cycloaddition [37] by the Meldal [38] and Sharpless

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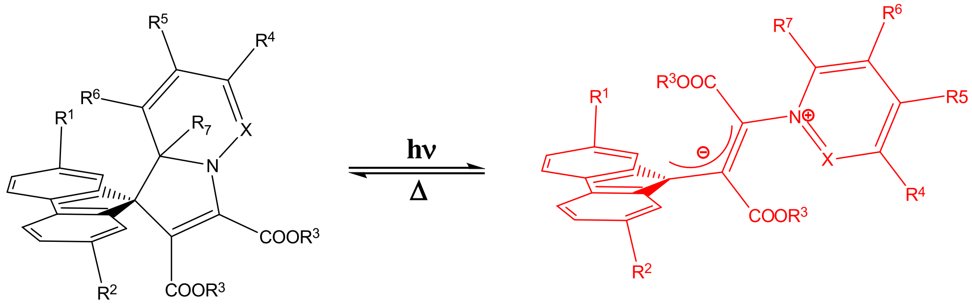


Scheme 1. Photo-induced ring opening of the photochromic DHI (closed form) to colored betaine (open form) and vise-versa through thermally 1,5-electrocyclization.

[39–42], many reserches have been done with describing the use of this simple “Click” methodology [43–50] to link together polyfunctionalized building blocks of “Click” chemistry through the copper(I)-catalyzed variant [51–53]. The 1,3-dipolar cycloaddition of alkynes and azides [54,55] (AAC) to give substituted 1,2,3-triazoles has considered as a influential linking reaction in both uncatalyzed [56] and metal-catalyzed [57,58] forms. Its application in plenteous areas has highlighted from the value of its benevolent reaction conditions, simple workup and purification procedures. “Click” chemistry shows a modular approach in the synthesis of enormous number of functionalized compounds based on practical chemical transformations for making the molecular connections with excellent fidelity.

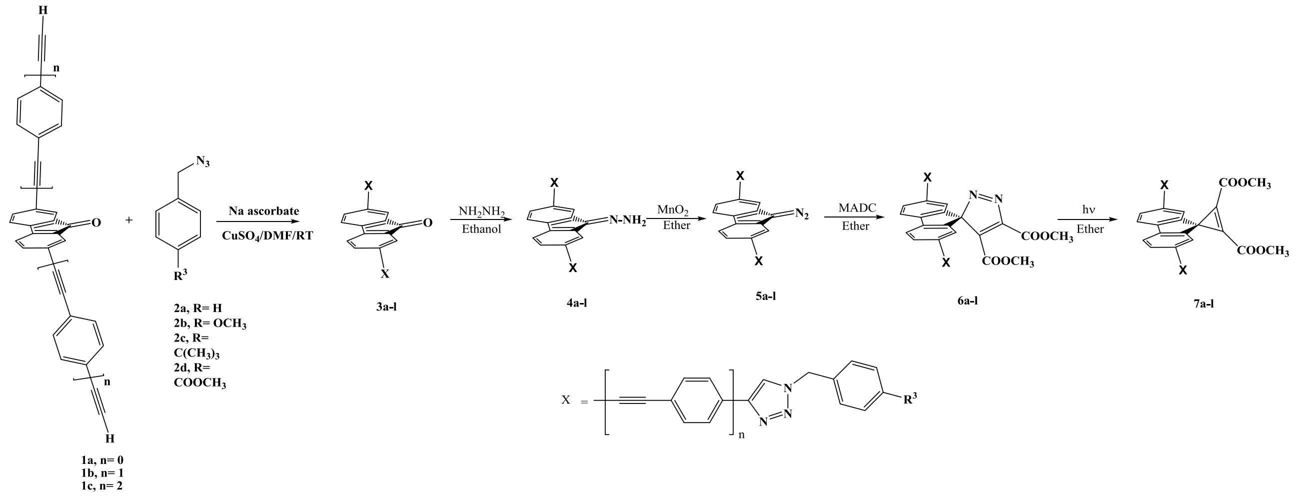
Shrestha et al. [33][33b] have synthesized a maleimide group capable of performing “click chemistry”, as defined in the very recent literature [59]. Moreover, we have successfully designed and synthesized carbon-rich photochromic dihydroindolizines by using different coupling reaction conditions [33–36]. These results motivated us to go deeply for the synthesis of new substituted DHIs from carbon-rich fluorenyldihydroindolizines incorporating substituted triazoles via “Click” chemistry condition aiming to get hold of new-fangled properties and applications. In continuation of our focused research interest on the synthesis and photochromic performance of dihydroindolizines (DHIs), this manuscript will shed more light on synthesis and photophysical properties of fluorenyldihydroindolizines photochromes via “Click” chemistry and study their photochromic behaviors in solution.

2. Results and discussion

2.1. Synthesis of fluorenylacetylene spirocyclopropene precursors via “Click” chemistry

2,7-Bis((4-ethynylphenyl)ethynyl)-9*H*-fluoren-9-one **1a–c** (n = 0–3) were previously synthesized by us via Sonogashira-coupling reactions [34–36]. The spirocyclopropenes **7a–o** were synthesized in five steps in both chemical and photochemical reactions (Scheme 2). The first synthetic pathways of spirocyclopropenes **7a–l** were done through the copper catalyzed azide-alkyne cycloaddition reactions [37–42]. Therefore, treatment of 2,7-bis((4-ethynylphenyl)ethynyl)-9*H*-fluoren-9-one **1a–c** as alkyne derivatives with two equivalent substituted phenyl azides **2a–d** in presence of $CuSO_4{\cdot}5H_2O$ as catalyst, sodium ascorbate in DMF as solvent at ambient temperature for 12 h, afforded the desired triazole derivatives **3a–l** in moderate to good yield (52–77%). Condensation of triazole derivatives **3a–l** with hydrazine hydrate in boiling ethanol for 4 h led to the formation of the corresponding hydrazone derivatives **4a–l** in high yield (81–93%) after crystallization from ethanol.

Oxidation of the hydrazone derivatives **4a-l** with active manganese dioxide in dry ether under nitrogen atmosphere at room temperature in absence of light afforded the 9- diazafluorene pyrazole derivatives **5a-l** in moderate yield (57–69%). 1,3-cycloaddition of methyl acetylene-dicarboxylate (MADC) to the 9-diazofluorene pyrazole derivatives **4a-l** in dry ether under dark condition and nitrogen atmosphere for 24 h led to the



Scheme 2. Synthetic pathway synthesis of fluorenylacetylene spirocyclopropenes precursors via “Click” chemistry methodology.