



# Synthesis of anthracene derivatives of 1,3-diazabicyclo[3.1.0]hex-3-ene



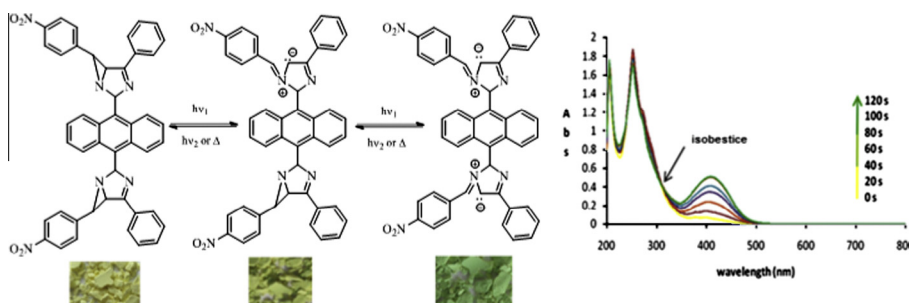
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## HIGHLIGHTS

- Synthesis of *mono*- and *bis*-1,3-diazabicyclo[3.1.0]hex-3-enes with anthracene moiety.
- Photochromic behavior of both *mono*- and *bis*-compounds.
- Photochromic behavior in solution and in solid state.
- Irradiation under UV light at 254 nm.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Novel *mono*- and *bis*-photochromic compounds of 1,3-diazabicyclo[3.1.0]hex-3-enes based on anthracene moiety were synthesized efficiently. Photochromic compounds were synthesized through the reaction of 10-(hydroxymethyl)anthracene-9-carbaldehyde and anthracene-9-carbaldehyde or 9,10-anthracenedi-carbaldehyde as *bis*-aldehydes with ketoaziridines in dry DMF at room temperature. Photochromic compounds exhibited photochromic behavior both in solution and in solid state by irradiation under UV light at 254 nm. Compounds bearing 4-NO<sub>2</sub> on aziridine moiety showed intensive color change. Compounds were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and UV-Vis.

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## Introduction

Photochromism is a phenomena defined as a reversible transformation between two isomeric species induced by light. Photochromic compounds are interesting as their physical properties such as geometrical structures, luminescence, optical rotation, absorption spectra, internal energy, viscosity, and refractive index can be manipulated by light.

Synthesis and study of the photochromic compounds have attracted a great attention due to their significant applications in optical data storage [1,2], optoelectronic devices [3,4], photo-switches and liquid-crystalline actuators [5,6]. Spiropyrans [7–9], fulgides [10,11], diarylethenes [12,13], and azobenzenes [14,15]

are most known photochromic systems. Although a great numbers of photochromic compounds have been synthesized that a few of them have shown photochromism in crystalline state. In continuation to our recent synthesis of *mono*, *bis*- and *tris*-photochromic systems based on 1,3-diazabicyclo[3.1.0]hex-3-ene with considerable photochromic properties both in solution and crystalline state [16–26], here, we report expansion of our photochromic systems by incorporating anthracene backbone.

## Results and discussion

First, ketoaziridine compounds **4a–b** was prepared according to our previous method as following: chalcones were prepared by Claisen–Schmidt reaction, brominated in chloroform, and then transformed to the corresponding ketoaziridines by reaction with NH<sub>4</sub>OAc (see supplementary data, Fig. S1) [16].

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Second, anthracene dicarbaldehyde **10** was synthesized in a three-step reaction with some modification according to the previous report [27]. In the first step, anthraquinone **5** was transformed to diepoxide **7** in the presence of trimethylsulfonium iodide **6**, NaH and DMSO under argon atmosphere. Diepoxide **7** was reacted with LiBr in CH<sub>3</sub>CN under reflux to produce 10-(hydroxyl methyl)anthracen-9-carbaldehyde **9**.

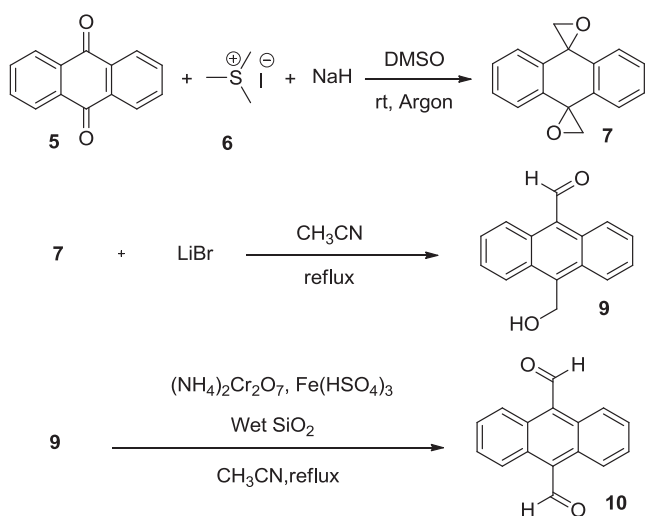
In the third step, anthracene-9,10-dicarbaldehyde **10** was prepared by utilizing a new selective oxidation method using ammonium chromate and ferric hydrogen sulfate in presence of wet silica gel to oxidize the hydroxyl group of **9** to aldehyde without further oxidation of the other aldehyde group [28,29] (Scheme 1).

We can propose that ferric hydrogen sulfate and wet silica gel is able to produce H<sup>+</sup> which will produce chromic acid (HCrO<sub>4</sub><sup>-</sup>) in the reaction with ammonium chromate. The produced chromic acid can oxidize benzylic alcohol to corresponding aldehyde. The proposed mechanism for oxidation of **9** to anthracene-9,10-dicarbaldehyde **10** was shown in supplementary data (Fig. S2).

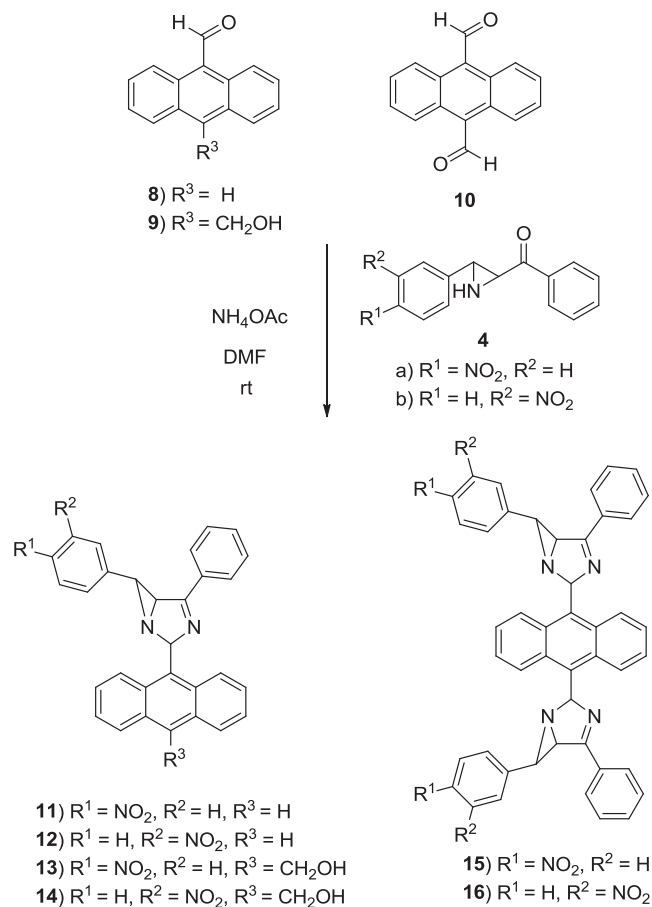
The IR spectra of diepoxide **7** indicated disappearance of C=O stretch and appearance of four absorption bands at 1318, 896, 916, and 840 cm<sup>-1</sup> due to epoxy C—O—C stretch. The <sup>1</sup>H NMR spectra displayed a singlet of 4 protons intensity at 3.27 ppm in addition to aromatic protons. Its <sup>13</sup>C NMR spectra exhibited 5 types of carbon atom; signals at 54.5 and 63.8 ppm which are indications of methylene and quaternary aliphatic carbon, respectively. The IR spectra of **9** reveals the presence of OH and aldehyde carbonyl stretch at 3400 and 1675 cm<sup>-1</sup>, respectively. In the <sup>1</sup>H NMR spectra of **9**, hydroxyl, methylene, and aldehyde protons appeared as singlets at 3.43, 5.75, and 11.54 ppm, respectively. The IR spectra of anthracene-9,10-dicarbaldehyde **10** showed absorption of C=O at 1670 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra displayed a singlet of 2 protons intensity at 11.51 ppm in addition to other aromatic protons.

Several photochromic products **11–14** were prepared via 3-multicomponent reaction of **8** and **9** with ketoaziridines **4** and excess NH<sub>4</sub>OAc at room temperature, respectively (Scheme 2). Formation of these compounds was confirmed on the basis of their IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra.

The IR spectra of compounds **11** and **12** confirmed disappearance of N—H and C=O groups in the starting materials and appearance of C=N stretching band at 1600 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra of compounds **11** and **12** showed signals at 2.86–3.82 ppm due to aziridine protons, imidazole protons appeared at 7.80 and 7.81 ppm as singlet, aromatic and anthracene protons appeared at expected chemical shifts. Further support for the structure of **11** and **12**



Scheme 1. Synthesis of dialdehyde **10** from **5**.



Scheme 2. Preparation of photochromic compounds **11–16**.

was provided by <sup>13</sup>C NMR spectra, which exhibits signals at 121.6–148.1 ppm for aromatic carbons, olefinic carbon appeared at 168.3 and 168.4 ppm and aliphatic carbons appeared at 40.7–95.6 ppm.

In the IR spectra of compounds **13** and **14** an absorption band appeared at region 3400–3428 cm<sup>-1</sup> due to O—H stretch, absorption band at 1600 cm<sup>-1</sup> indicates the presence of C=N, and absorption band at region 1040–1045 cm<sup>-1</sup> specify the presence of C—O bond. The <sup>1</sup>H NMR spectra of compounds **13** and **14** displayed signals of aziridine ring protons at regions 2.83–3.83 ppm, signal of methylene group at 5.68 and 5.72 ppm, signal of OH group at 3.41 ppm, signal of imidazole proton at 7.77 and 7.83 ppm, and anthracene protons at 7.55–8.81 ppm respectively. In <sup>13</sup>C NMR spectra olefinic carbon appeared at 108.2 and 168.2 ppm, aromatic carbons appeared at 121.4–148 ppm, and aliphatic carbons appeared at 40.6–95.6 ppm.

Two bis-photochromic products **15–16** were prepared via the reactions of pre-made **10** with two moles ketoaziridines **4** and excess NH<sub>4</sub>OAc at room temperature.

In the IR spectra of bis-photochromic **15** and **16** absorption bands at 1604–1614 cm<sup>-1</sup> are indication of C=N functional group. The <sup>1</sup>H NMR analysis of **15** and **16** showed signals of aziridine protons as singlet at 2.83–3.88 ppm, signal of imidazole proton at 7.81 and 7.84 ppm, aromatic and anthracene protons at 8.40–7.25 and 7.67–8.77 ppm, respectively. In <sup>13</sup>C NMR spectra olefinic carbon for both of them appeared at 169.8 ppm, aromatic carbons appeared at 121.6–148.2 ppm, and aliphatic carbons appeared at 40.8–95.8 ppm. These photochromic derivatives in their NMR spectra at room light showed only structure of close-ring photoisomers. This can be due to the more stability of the close-ring

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