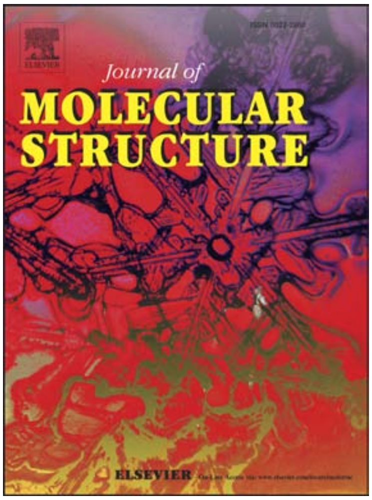


Synthesis of Anthracene Derivatives of 1,3-Diazabicyclo[3.1.0]hex-3-ene

Nosrat O. Mahmoodi, Safoura Mirkhaef, Atefeh Ghavidast

PII: S0022-2860(14)01021-7
DOI: http://dx.doi.org/10.1016/j.molstruc.2014.10.019
Reference: MOLSTR 21015

To appear in: *Journal of Molecular Structure*

Received Date: 18 August 2014
Revised Date: 7 October 2014
Accepted Date: 9 October 2014

Please cite this article as: N.O. Mahmoodi, S. Mirkhaef, A. Ghavidast, Synthesis of Anthracene Derivatives of 1,3-Diazabicyclo[3.1.0]hex-3-ene, *Journal of Molecular Structure* (2014), doi: http://dx.doi.org/10.1016/j.molstruc.2014.10.019

Synthesis of Anthracene Derivatives of 1,3-Diazabicyclo[3.1.0]hex-3-ene

Nosrat O. Mahmoodi*, Safoura Mirkhaef, Atefeh Ghavidast

Chemistry Department, Faculty of Science, Guilan University, P. O. Box 41335-1914, Rasht, Iran

Corresponding Author. e-mail: mahmoodi@guilan.ac.ir

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-anthracenedicarbaldehyde 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_2 on aziridine moiety showed intensive color change. Compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, and UV-Vis.

Keywords: Photochromic, Anthracene, Anthraquinone, Bis-1,3-diazabicyclo[3.1.0]hex-3-ene

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, etc. can be manipulated by light.

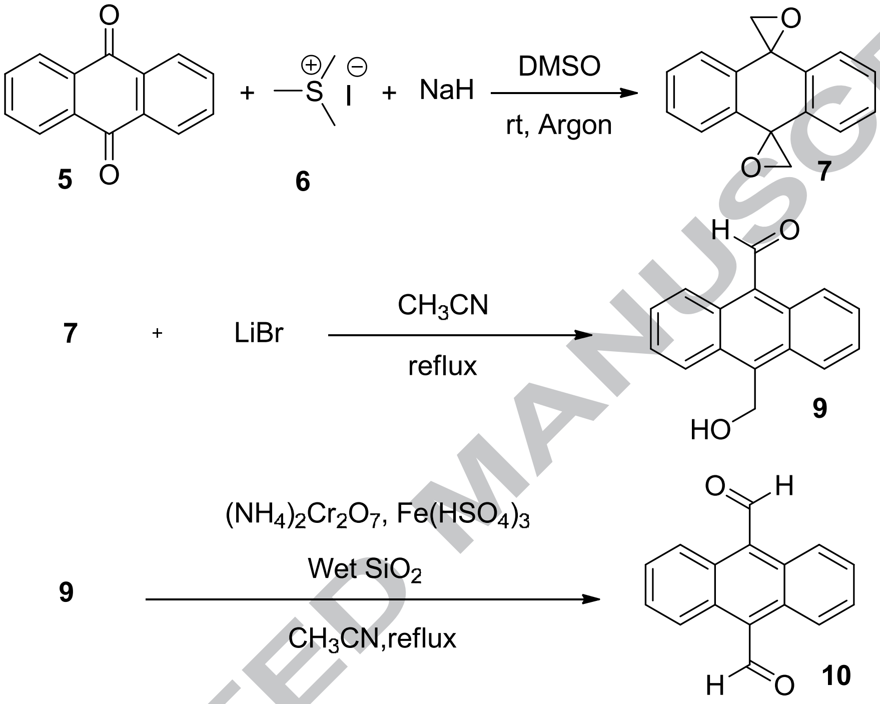
Synthesis and study of the photochromic compounds have attracted a great attention due to their significant applications in optical data storage [1,2], optoelectronic devices [3,4], photo-switches and liquid-crystalline actuators [5,6]. Spiropyrans [7,9], fulgides [10,11], diarylethenes [12,13], and 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_4OAc (see supplementary data, Fig. S1) [16].

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 trimethylsolfunium iodide **6**, NaH and DMSO under argon atmosphere. Diepoxide **7** was reacted with LiBr in CH_3CN 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).

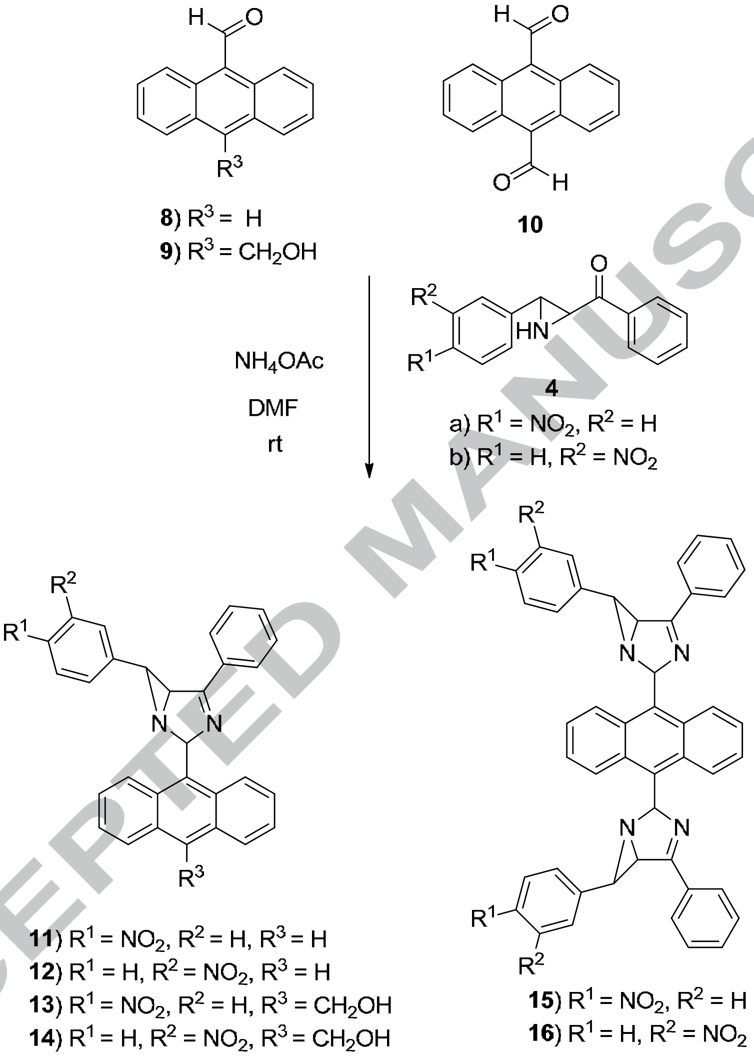


Scheme 1. Synthesis of dialdehyde **10** from **5**

We can propose that ferric hydrogen sulfate and wet silica gel is able to produce H^+ which will produce chromic acid ($HCrO_4^-$) 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^{-1} due to epoxy C-O-C stretch. The ^1H NMR spectra displayed a singlet of 4 protons intensity at 3.27 ppm in addition to aromatic protons. Its ^{13}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^{-1}, respectively. In the ^1H 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^{-1}. The ^{1}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$_4$OAc at room temperature, respectively (Scheme 2). Formation of these compounds was confirmed on the basis of their IR, ^{1}H NMR, and ^{13}C NMR spectra.



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

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^{-1}. The ^{1}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** was provided by ^{13}C NMR spectra, which exhibits signals at121.6-148.1 ppm for aromatic carbons, olefinic carbon appeared at 168.3 and168.4 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^{-1} due to O–H stretch, absorption band at 1600 cm^{-1} indicates the presence of C=N, and absorption band at region 1040-1045 cm^{-1} specify the presence of C-O bond. The ^{1}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 protone at 7.77 and 7.83 ppm, and anthracene protons at 7.55-8.81 ppm respectively. In ^{13}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 premade **10** with two moles ketoaziridines **4** and excess NH_4OAc at room temperature.

In the IR spectra of *bis*-photochromic **15** and **16** absorption bands at 1604-1614 cm^{-1} are indication of C=N functional group. The ^{1}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 ^{13}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 photoisomer in the presence of anthracene ring. According to our prior experiences, appearance of the singlet signals with lower intensity in the vicinity of aziridine protons and singlet signal at 6.0-7.0 ppm attributable to imidazoline proton that proved the formation of the open-ring photoisomer [20,22,24-25]. These statements are included in the revised manuscript and indicated as red pen in the text.

Photochromic compounds **11**, **13**, and **15** showed strong color change upon exposure to sun light in crystalline state, while compounds **12**, **14**, and **16** did not show obvious color change in crystalline form. For **11** upon exposure to sun light a color change from yellow to green was observed and for **13** yellow to bright brown and for **15** yellow to bright green and by further exposure changed to dark green were observed. This can be due to the resonance in these compounds; for *para* NO_2 derivatives **11**, **13**, and **15** the resonance is better and longer than *meta* NO_2 derivatives **12**, **14**, and **16**. Also, increasing of the color intensity can be due to enhancement of population of open form rather than closed form.

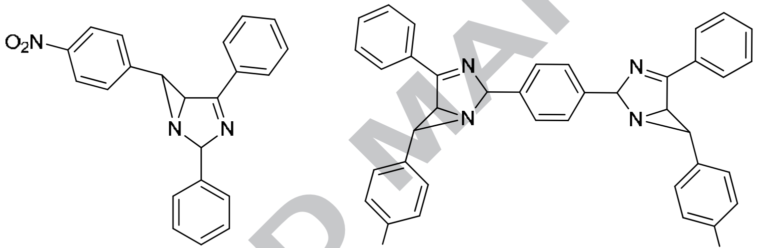
The formation of open-ring photoisomer and photochromic behavior of compounds **11-16** were confirmed by UV-Vis spectra in EtOH under irradiation with UV light at 254 nm for different times. After UV irradiation, the ethanolic solutions promptly turned to yellow color and the absorbance band at visible region emerged and increased due to the formation of the open-ring photoisomer. The maximum absorptions are shown in Table 1. All compounds showed isosbestic points in their UV-Vis studies which means that the close-ring and open-ring photoisomers are in equilibrium at this wavelength. The isosbestic points for compounds **11**, **13**, and **15** are higher than the others; it might be due to the nitro group.

Table 1. Spectra and data of λ^{A}_{max}, λ^{B}_{max} , $\lambda_{isosbestic}$ for products **11-16**

Compound	**λ^{A}_{max} (nm)**	**λ^{B}_{max} (nm)**	**$\lambda_{isosbestic}$**
11	205, 253.5, 350, 368, 388	205, 254, 368, 389, 431	301
12	206, 256, 351, 369, 389	256, 363, 424	296
13	205, 259, 356, 375, 396	205, 259, 375, 396, 436	302
14	205, 256, 339, 355, 375, 396	206, 258, 356, 376, 396	264
15	206, 253, 379, 398	205, 253, 410	313
16	212, 256, 360, 378, 400	208, 253, 365	280

λ^{A}_{max}: before irradiation, λ^{B}_{max}: after irradiation

More important the comparison of λ^{A}_{max}, λ^{B}_{max} , $\lambda_{isosbestic}$ for **11** and **15** with our previous synthesized **20** and **21** with phenyl as an alternative of anthracene [17,18, 20] exhibit a better photocoloration/photobleaching ratio and acceptable light sensitivity due to continuous red shift absorption up to 400 nm (Fig. 1) (Table 2) .



20 **21**

Fig. 1. Structure of **20** and **21** with phenyl as an alternative of anthracene

Table 2. Spectra and data of λ^{A}_{max}, λ^{B}_{max} , $\lambda_{isosbestic}$ for products **20** and **21**

Compound	**λ^{A}_{max} (nm)**	**λ^{B}_{max} (nm)**	**$\lambda_{isosbestic}$ (nm)**
20	281	401	318
21	207, 251	207, 261, 405	238

λ^{A}_{max}: before irradiation, λ^{B}_{max}: after irradiation

A UV-Vis spectrum of compound **11** is depicted in Fig. 2. The compound was exposed to the UV light and its absorption was recorded by 20 seconds intervals. The study showed that by increasing the UV irradiation time the intensity of absorption increased while after 120 seconds it decreased. This phenomenon indicates that in solution the photochromic properties of these compounds have lower repeatable cycle than in the solid form. Also, a well-defined isosbestic point at 301 nm is observed (Fig. 2).

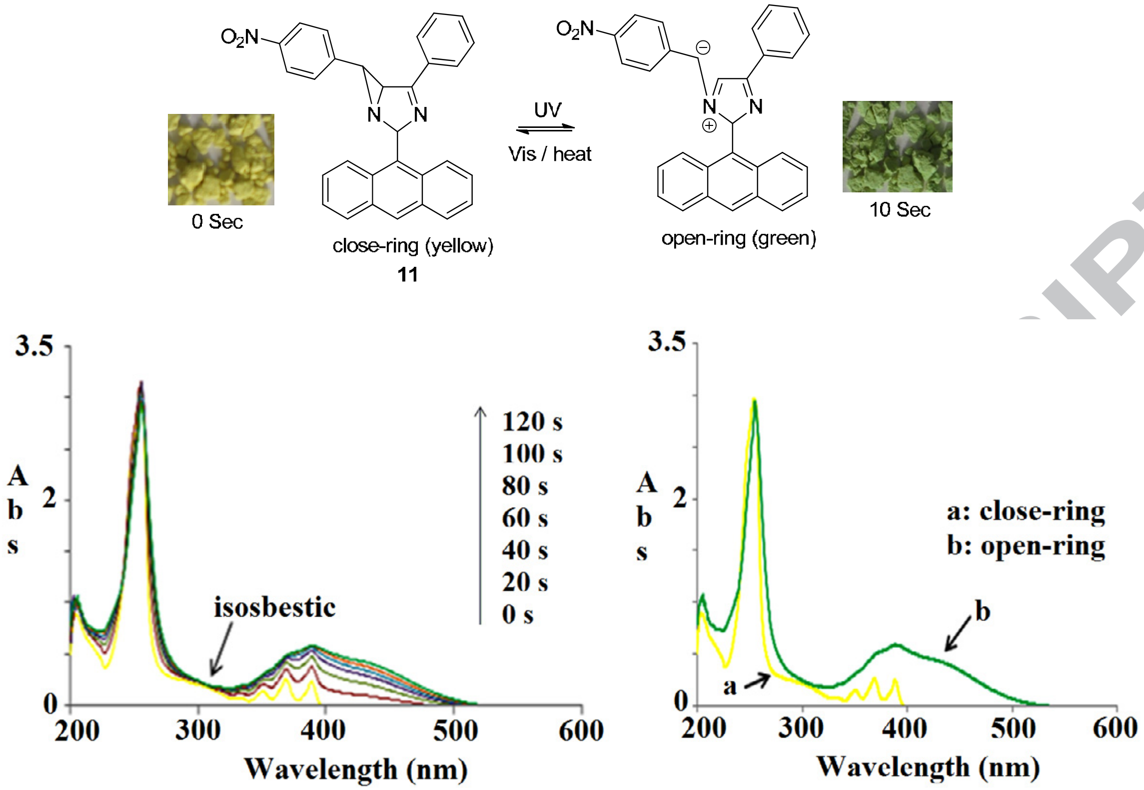


Fig. 2. Photochromic performance and UV-Vis spectra of **11** before and after UV light irradiation for different times in EtOH (C = 1.0 × 10^{-4} M, 293 K).

Fig. 3 shows the UV-Vis spectra of **15** with two photochromic center in EtOH. The UV-Vis spectra were recorded in 20 seconds intervals, and similar to **11** its intensity decreased after 120 seconds. Compound **15** exhibited λ^{A}_{max} at 206 and 253 nm before irradiation and λ^{B}_{max} at 206, 253 and 410 nm after irradiation. Isosbestic point revealed at 313 nm.

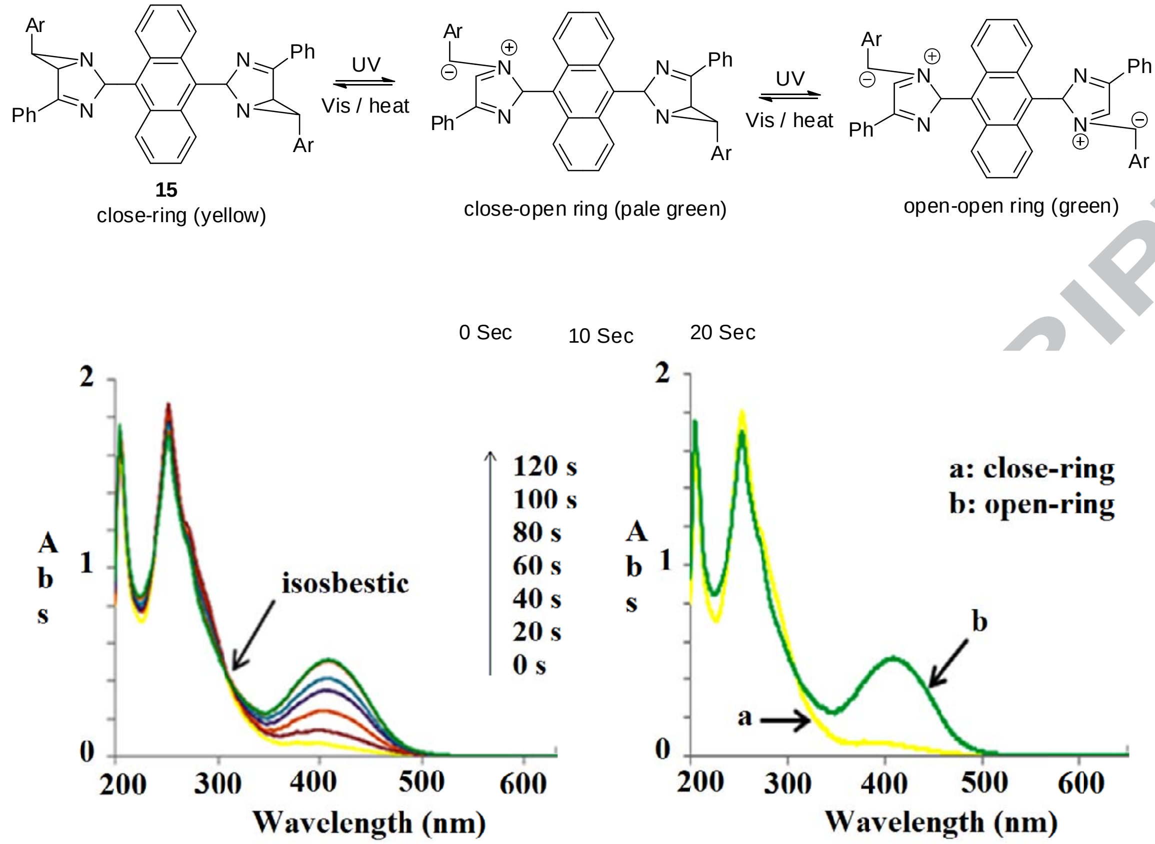


Fig. 3. Photochromic performance and UV-Vis spectra of **15** before and after UV light irradiation for various times in EtOH ($C = 1.0 \times 10^{-4}$ M, 293 K).

Experimental Section

Chemicals were purchased from Fluka and Merck. Melting points were uncorrected and determined by Electrothermal 9100 melting point apparatus. Products were characterized by m. p., IR, ^{1}H NMR, ^{13}C NMR and TLC. IR spectra were obtained on a Shimadzu IR-470. All NMR data were recorded in $CDCl_3$ using Bruker Avance 500 MHz and 400 MHz spectrometer. Chemical shifts are reported in ppm (δ) using deuterated solvents as internal references. The UV-Vis absorption spectra in the range 200-600 nm (EtOH) as well as position of λ_{max} for the initial A (λ^{A}_{max} nm) and photoinduced B (λ^{B}_{max} nm) photoisomers were measured with a Shimadzu UV-2100 spectrophotometer. Plate chromatography was conducted over silica gel 60, F_{254} Merck.

Preparation of trans-dispiro[oxirane-2,9′[10′*H*]-anthracene-10′,2″-oxirane] **7**:

To a two-necked flask NaH (13 mmol, 0.52 g, 60% in oil) was added under argon atmosphere and washed with *n*-hexane (3×20 mL). Then trimethylsolfunium iodide (12.64 mmol, 2.58 g) in dry DMSO (30 mL) was added slowly in darkness. The mixture was stirred for 8 hours at rt. After that, anthraquinone (5.62 mmol, 1.17 g) in dry DMSO (30 mL) was added and stirred for 16 hours at rt. After completion of the reaction, flask was put onto an ice bath; crushed ice (100 g) was added to the mixture and stirred for 30 min at 0˚C. The white or yellow precipitate was filtered off, washed with water and dried. Yield 80%. m. p. 117-120 °C, colorless solid, IR (KBr, ν/cm^{-1}): 3040, 2980, 1479, 1450, 1318, 916, 896, 840, 762, 740. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.27 (s, 4H, CH_2), 7.29-7.44 (m, 8H, H_b, H_c). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 54.5, 63.8, 122.3, 128.4, 135.4.

Preparation of 10-(hydroxymethyl) anthracene-9-carbaldehyde **9**:

To a solution of LiBr (23 mmol, 2 g) in dry CH_3CN (80 mL) was added **7** (5 mmol, 1.18 g) and stirred for 18 hours in darkness at rt. After completion of the reaction, flask was put onto an ice bath and cooled down to -20 °C. Golden crystals gradually formed upon cooling, filtered off and dried on air. Yield 80%. m. p. 180-182 °C, golden crystals, IR (KBr, ν/cm^{-1}): 3400, 2950, 2900, 2750, 2700, 1675, 1620, 1540, 1030, 750. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.43 (s, 1H, OH), 5.75 (s, 2H, CH_2), 7.68-7.74 (m, 4H, H_b, H_c), 8.57 (d, *J* = 8.0 Hz, 2H, H_d), 8.94 (d, *J* = 8.0 Hz, 2H, H_a), 11.54 (s, 1H, CHO).

Preparation of 9,10-anthracenedicarbaldehyde **10**:

To flask containing $(NH_4)_2Cr_2O_7$ (1 mmol, 0.252 g), wet silica gel (0.3 g) and $Fe(HSO_4)_3$ (1 mmol, 0.347 g) in dry CH_3CN (5 mL) was added compound **9** (1 mmol, 0.236 g) and refluxed for 3 hours. The mixture was filtered off and washed with CH_3CN (3×3 mL). The organic layer was dried with $MgSO_4$, filtered and evaporated under reduced pressure. Yield 60%. m. p. 237-240 °C, orange solid, IR (KBr, ν/cm^{-1}): 3068, 2921, 2850, 2780, 1670, 1586, 1445, 752, 695. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.73 (dd, *J* = 5.8, 3.4 Hz, 4H, H_b), 8.76 (dd, *J* = 5.6, 3.6 Hz, 4H, H_a), 11.51 (s, 2H, CHO).

Preparation of 2-(anthracene-9-yl)-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene **11**:

A solution of **4a** (1 mmol, 0.268 g), **8** (1 mmol, 0.236 g) and NH_4OAc (5 mmol, 0.4 g) in dry DMF (3 mL) was stirred at rt for 24 hours. The reaction was monitored by TLC (EtOAc/ether, 6/3). After completion of the reaction, the mixture was collected by filtration, washed with EtOH (60 °C) and dried. The crud product was recrystallized from EtOH. After irradiation with UV it converted to light green. Yield 76%. m. p. 191-193 °C, yellow solid, IR (KBr, ν/cm^{-1}): 3040, 2980, 2880, 1600, 1510, 1470, 1440, 1340, 830, 720, 690. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.84 (s, 1H, H_1), 3.82 (s, 1H, H_2), 7.25 (d, *J* = 8.8 Hz, 2H, H_b), 7.48 (t, *J* = 7.4 Hz, 2H, H_h), 7.55 (broad, 2H, H_g), 7.61-7.70 (m, 3H, H_e, H_d), 7.80 (s, 1H, H_4), 7.99 (d, *J* = 8.8 Hz, 2H, H_c), 8.02 (d, *J* = 8.4 Hz, 2H, H_a), 8.19 (d, *J* = 8 Hz, 2H, H_i), 8.50 (s, 1H, H_j), 8.72 (broad, 2H, H_f); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 40.9, 55.7, 95.6, 123.4, 124.8, 125.6, 126.6, 127.4, 128.3, 128.6, 129.2, 129.6, 130.9, 131.6, 132.0, 145.3, 147.0, 168.4; UV-Vis (EtOH) $\lambda_{max/nm}$: 205.0, 253.5, 350.0, 368.0, 388.5 nm before irradiation and 205.0, 253.5, 350.0, 368.0, 388.5, 430.34 nm after irradiation. HRMS ((+)-ESI): *m/z* = 455.1641 (calcd. 455.1634 for $C_{30}H_{21}N_3O_2$).

Preparation of 2-(anthracene-9-yl)-6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene **12**:

A similar procedure for synthesis of **12** as described for **11** was applied compounds **8** and **4b** were used. The reaction completed over 5 days. After irradiation with UV light its color did not changed obviously. Yield 65%. m. p. 143-145 °C, cream solid, IR (KBr, ν/cm^{-1}): 3050, 2980, 2880, 1600, 1508, 1470, 1442, 1340, 830, 740, 690. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.86 (s, 1H, H_1), 3.82 (s, 1H, H_2), 7.27-7.30 (t, *J* = 7.6 Hz, 1H, H_c), 7.39 (d,

J = 7.6 Hz, 1H, H_d), 7.48 (t, J = 7.2 Hz, 2H, H_j), 7.55 (broad, 2H, H_i), 7.62-7.69 (m, 3H, H_f, H_g), 7.81 (s, 1H, H_4), 7.96 (d, J = 8 Hz, 2H, H_e), 8.02 (d, J = 8.4 Hz, 1H, H_b), 8.05 (s, 1H, H_a), 8.20 (d, J = 7.6 Hz, 2H, H_k), 8.50 (s, 1H, H_l), 8.74 (broad, 2H, H_h); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 40.7, 55.5, 95.6, 121.62, 122.2, 124.8, 125.6, 126.6, 127.3, 128.4, 128.6, 129.07, 129.10, 129.13, 129.5, 131.0, 131.6, 131.9, 132.0, 132.8, 134.2, 140.1, 148.1, 168.4; UV-Vis(EtOH) $\lambda_{max/nm}$: 206.0, 255.5, 351.0, 368.5, 388.5 nm before irradiation and 206.0, 255.5, 362.5, 423.22 nm after irradiation. HRMS ((+)-ESI): *m/z* = 455.1639 (calcd. 455.1634 for $C_{30}H_{21}N_3O_2$).

Preparation of (10-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2 -yl)anthracene-9-yl)methanol **13**: A similar procedure as described for **11**, for synthesis of **13** was applied compound **9** was used instead of **8** with **4a**. The reaction completed over 3 days. Yield 70%. m. p. 190-192 °C, yellow solid, IR (KBr, ν/cm^{-1}): 3400, 3050, 2910, 2850, 1600, 1510, 1490, 1440, 1340, 1040, 800, 740, 695. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.83 (s, 1H, H_1), 3.41 (s, 1H, OH), 3.80 (s, 1H, H_2), 5.68 (s, 2H, CH_2), 7.23 (d, J = 8.8 Hz, 2H, H_b), 7.55-7.57 (m, 4H, H_h, H_g), 7.61-7.68 (m, 3H, H_d, H_e), 7.77 (s, 1H, H_4), 7.97 (d, J = 8.8 Hz, 2H, H_c), 8.18 (d, J = 8.4 Hz, 2H, H_a), 8.47 (d, J = 8 Hz, 2H, H_i), 8.79 (broad, 2H, H_f); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 40.7, 55.6, 57.7, 95.6, 123.4, 124.4, 125.8, 126.2, 126.4, 127.3, 128.6, 129.2, 130.0, 130.2, 130.8, 131.9, 132.0, 133.2, 145.1, 147.0, 168.2; UV-Vis (EtOH) $\lambda_{max/nm}$: 204.5, 258.5, 356.0, 374.5, 395.5 nm before irradiation and 204.5, 258.5, 356, 374.5, 395.5, 435.9 nm after irradiation. HRMS ((+)-ESI): *m/z* = 485.1734 (calcd. 485.1739 for $C_{31}H_{23}N_3O_3$).

Preparation of (10-(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2 -yl)anthracene-9-yl)methanol **14**: A similar procedure as described for **11**, for synthesis of **14** was applied compound **9** and **4b** were used. The reaction completed over 5 days. After irradiation with UV light its color did not changed obviously. Yield 50%. m. p. 150-153 °C, yellow solid, IR (KBr, ν/cm^{-1}): 3428, 3063, 2962, 1604, 1515, 1446, 1344, 1045, 862, 800, 695. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.83 (s, 1H, H_1), 3.41 (s, 1H, OH), 3.83 (s, 1H, H_2), 5.72 (s, 2H, CH_2), 7.25-7.29 (t, 1H, H_c), 7.41 (d, J = 7.6, 1H, H_d), 7.56-7.59 (broad, 4H, H_i, H_j), 7.62-7.68 (m, 4H, $H_{f,g}$), 7.83 (s, 1H, H_4), 8.01 (d, J = 8 Hz, 2H, H_e), 8.18 (d, J = 8.4 Hz, 2H, H_b), 8.24 (s, 1H, H_a), 8.47 (d, J = 8 Hz, 2H, H_k), 8.81 (broad, 2H, H_h); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 40.6, 55.4, 57.7, 95.5, 121.4, 122.0, 124.4, 125.9, 126.2, 126.4, 127.4, 128.6, 129.2, 130.0, 130.2, 130.8, 131.9, 132.0, 133.2, 134.2, 140.1, 148.0, 168.2; UV-Vis (EtOH) $\lambda_{max/nm}$: 205.0, 256.0, 338.5, 355.0, 375.0, 395.5 nm before irradiation and 206.0, 257.5, 356.0, 375.7, 395.5 nm after irradiation. HRMS ((+)-ESI): *m/z* = 485.1743 (calcd. 485.1739 for $C_{31}H_{23}N_3O_3$).

Preparation of 9,10-bis(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl) anthracene **15**:
A similar procedure as described for **11**, for synthesis of **15** was applied, however compound **10** 1 eq with 2eq **4a** and 2eq NH_4OAc were used. The reaction completed over 7 days. After irradiation with UV light it converted to bright green. Yield 70%. m. p. 198-200 °C, yellow solid, IR (KBr, ν/cm^{-1}): 3052, 2934, 1604, 1513, 1440, 1343, 845, 734, 695. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.84 (s, 2H, H_1), 3.82 (s, 2H, H_2), 7.25 (d, J = 8.4 Hz, 4H, H_b), 7.49-7.58 (m, 6H, H_e, H_d), 7.67 (dd, J = 5.6, 3.6 Hz, 4H, H_g), 7.81 (s, 2H, H_4), 8.02 (d, J = 8.4 Hz, 4H, H_c), 8.20 (d, J = 8.4 Hz, 4H, H_a), 8.74 (broad, 4H, H_f); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 41.0, 55.9, 95.8, 123.4, 125.7, 126.6, 127.4, 128.6, 129.3, 130.7, 131.6, 132.0, 145.5, 147.3, 169.8. UV-Vis (EtOH) $\lambda_{max/nm}$: 205.5,

253.0, 379.0, 398.0 nm before irradiation and 205.0, 253.0, 409.5 after irradiation. HRMS ((+)-ESI): *m/z* = 732.2491 (calcd. 732.2485 for $C_{46}H_{32}N_6O_4$).

Preparation of 9,10-bis(6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl) anthracene **16**:
A similar procedure as described for **15**, for synthesis of **16** was applied, compounds **10** and **4b** were used. The reaction completed over 7 days. After irradiation with UV light its color did not changed obviously. Yield 65%. m. p. 149-151 $^{\circ}$C, yellow solid, IR (KBr, ν/cm^{-1}): 3060, 2964, 1614, 1528, 1445, 1394, 1348, 879, 803, 734, 692. ^{1}H NMR (100 MHz, CDCl$_3$, ppm): δ 2.83 (s, 2H, H$_1$), 3.88 (s, 2H, H$_2$), 7.29 (t, 2H, H$_c$), 7.34 (d, *J* = 7.6 Hz, 2H, H$_d$), 7.47 (m, 6H, H$_f$, H$_g$), 7.67 (dd, *J* = 5.4, 3.4 Hz, 4H, H$_i$), 7.84 (s, 2H, H$_4$), 8.04 (d, *J* = 8 Hz, 4H, H$_e$), 8.16 (d, *J* = 8.4 Hz, 2H, H$_b$), 8.20 (s, 2H, H$_a$), 8.77 (broad, 4H, H$_h$); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 40.8, 55.8, 95.8, 121.6, 122.3, 125.7, 126.6, 127.4, 128.6, 129.3, 130.7, 131.7, 132.1, 133.1, 134.0, 140.5, 148.2, 169.8; UV-Vis (EtOH) $\lambda_{max/nm}$: 212, 255.5, 359.5, 378, 399.5 nm before irradiation and 208, 252.5, 358.5 nm after irradiation. HRMS ((+)-ESI): *m/z* = 732.2489 (calcd. 732.2485 for $C_{46}H_{32}N_6O_4$).

Conclusion

In summary, anthracene-9-carbaldehyde, 10-(hydroxymethyl)anthracene-9-carbaldehyde and 9,10-anthracene dicarbaldehyde was used in synthesis of *mono*- and *bis*-photochromic compounds successively. The photochromic compounds showed color change in crystalline state and also their wavelength change under UV irradiation in EtOH solution that confirms their photochromic behavior.

References

[1] S. Kawata, Y Kawata, Three-Dimensional Optical Data Storage Using Photochromic Materials, Chem. Rev. 100 (2000) 1777-1788. DOI: 10.1021/cr980073p.

[2] JA Delaire, K Nakatani, Linear and Nonlinear Optical Properties of Photochromic Molecules and Materials, Chem. Rev. 100 (2000) 1817-1845. DOI: 10.1021/cr980078m.

[3] H Durr, H Bouas- Laurent Photochromism Molecules and Systems. Elsevier (1990), Amsterdam.

[4] BL Feringa, WF Jager, B de Lange, Organic Materials for Reversible Optical Data Storage, Tetrahedron. 49 (1993) 8267-8310. DOI: 10.1016/S0040-4020(01)81913-X.

[5] D Dulic, Kudernac, A Puzys, BL Feringa, BJ VanWees, Temperature Gating of The Ring-Opening Process in Diarylethene Molecular Switches, Adv. Mater. 19 (2007) 2898–2902. DOI: 10.1002/adma.200700161.

[6] VA Barachevsky, TYP Strokach, A Puankov, MM Krayushkin, Thermally Irreversible Organic Photochromic Compounds for Optical Memory, J. Phys. Org. Chem. 20 (2007) 1007-1021. DOI: 10.1002/poc.1191.

[7] MQ Zhu, L Zhu, JJ Han, W Wu, JK Hurst, ADQ Li, Spiropyran-Based Photochromic Polymer Nanoparticles with Optically Switchable Luminescence, J. Am. Chem. Soc. 128 (2006) 4303-4309. DOI: 10.1021/ja0567642.

[8] D Levy, D Avnir, Effects of the Changes in the Properties of Silica Cage Along the Gel/Xerogel Transition on the Photochromic Behavior of Trapped Spiropyrans, J. Phys. Chem. 92 (1988) 4734-4738. DOI: 10.1021/j100327a035.

[9] S Benard, P Yu, New Spiropyrans Showing Crystalline-State Photochromism, Adv. Mater. 12 (2000) 48-50. DOI: 10.1002/(SICI)1521-4095(200001)12:1<48::AID-ADMA48>3.0.CO;2-G.

[10] A Santiago, RS Becker, Photochromic Fulgides. Spectroscopy and Mechanism of Photoreactions, J. Am. Chem. Soc. 90 (1968) 3654-3658. DOI: 10.1021/ja01016a009.

[11] M Seibold, H Port, Mid-Infrared Recognition of the Reversible Photoswitching of Fulgides, Chem. Phys. Lett. 252 (1996) 135-140. DOI: 10.1016/S0009-2614(96)00131-5.

[12] M Irie, O Miyatake, K Uchida, T Eriguchi, Photochromic Diarylethenes with Intralocking Arms, J. Am. Chem. Soc. 116 (1994) 9894-9900. DOI: 10.1021/ja00101a010.

[13] S Pu, G Liu, L Shen, J Xu, Efficient Synthesis and Properties of Isomeric Photochromic Diarylethenes Having a Pyrrole Unit, Org. Lett. 9 (2007) 2139-2142. DOI: 10.1021/ol070622q.

[14] JM Mativetsky, G Pace, M Elbing, MA Rampi, M Mayor, P Samorì, Azobenzenes as Light-Controlled Molecular Electronic Switches in Nanoscale Metal-Molecule-Metal Junctions, J. Am. Chem. Soc. 130 (2008) 9192–9193. DOI: 10.1021/ja8018093.

[15] C Barrett, A Natansohn, P Rochon, Cis-Trans Thermal Isomerization Rates of Bound and Doped Azobenzenes in a Series of Polymers, Chem. Mater. 7 (1995) 899–903. DOI: 10.1021/cm00053a014.

[16] NO Mahmoodi, H Kiyani, Synthesis of Thiophene Derivatives of 1,3-Diazabicyclo[3,1,0]hex-3-ene, Bull. Korean. Chem. Soc. 25 (2004) 1417-1420. DOI: http://dx.doi.org/10.5012/bkcs.2004.25.9.1417.

[17] NO Mahmoodi, MA Zanjanchi, H Kiyani, Photochromism of Several Synthesised 1,3-Diazabicyclo[3,1,0]hex-3-ene derivatives, J. Chem. Res. (2004). 438-440.

[18] NO Mahmoodi, MR Yazdanbakhsh, H Kiyani, B Shrifzadeh, Synthesis and Photochromic Properties of New Heterocyclic Derivatives of 1,3-Diazabicyclo[3.1.0]Hex-3-Ene, J. Chin. Chem. Soc. 54 (2007) 635-641. DOI: 10.1002/jccs.200700091.

[19] NO Mahmoodi, H Kiyani, K Tabatabaeian, MA Zanjanchi, M Arvand, B Sharifzadeh, NMR Structural Elucidation and Photochromic Behavior of New 1,3-Diazabicyclo[3.1.0]hex-3-ene Derivatives, Russ. J. Org. Chem. 46 (2010) 884-893. DOI: 10.1134/S1070428010060175.

[20] H Kiyani, NO Mahmoodi, K Tabatabaeian, MA Zanjanchi, Photochromic Behavior of Several New Synthesized Bis-1,3-diazabicyclo[3.1.0]hex-3-enes, J. Phys. Org. Chem. 22 (2009) 559-567. DOI: 10.1002/poc.1550.

[21] H Kiyani, NO Mahmoodi, K Tabatabaeian, MA Zanjanchi, Synthesis and Photochromism of 1,3-diazabicyclo[3.1.0]hex-3-ene Phenol Rings, Mendeleev. Commun. 19 (2009) 203-205. DOI: 10.1016/j.mencom.2009.07.010.

[22] NO Mahmoodi, K Tabatabaeian, H Kiyani, Two 1,3-Diazabicyclo[3.1.0]hex-3-enes with a ‘Tripod’ Core, Helv. Chim. Acta. 95 (2012) 536-542. DOI: 10.1002/hlca.201100333.

[23] NO Mahmoodi, K Tabatabaeian, A Ghavidast, Synthesis and Photochromic Behavior of Mono-, and Bis-Photochromic System Linked by *p*-Phenylene Bridge, Chin. Chem. Lett. 21 (2010) 1199-1202. DOI: 10.1016/j.cclet.2010.04.036.

[24] T Besharati-Seidani, NO Mahmoodi, Synthesis of New Bicyclic Aziridines Containing Chalcone Analogs and Investigation of Their Photochromic Properties, Bull. Korean. Chem. Soc. 34 (2013) 875-883. DOI: http://dx.doi.org/10.5012/bkcs.2013.34.3.875.

[25] NO Mahmoodi, M Mamaghani, T Behzadi, Synthesis and Structure–Behavior Relationships of *Tetra*-Substituted Imidazole Derivatives of 1,3-diazabicyclo[3,1,0]hex-3-ene, Mol. Divers. 16 (2012) 737-747. DOI: 10.1007/s11030-012-9409-7.

[26] NO Mahmoodi, A Ghavidast, Synthesis of Photochromic Bis-1,3-diazabicyclo-[3.1.0]hex-3-ene Derivatives Having a Bisindole Linkage, Chem. Heterocycl. Compd. 49 (2014) 1451-1457. DOI: 10.1007/s10593-014-1395-5.

[27] Y Lin, SA Lang, J Christina, M Seifert, RG Child, GO Morton, PF Fabio, Aldehyde Syntheses. Study of the Preparation of 9,10-anthracenedicarboxaldehyde, J. Org. Chem. 44 (1979) 4701-4703. DOI: 10.1021/jo00393a050.

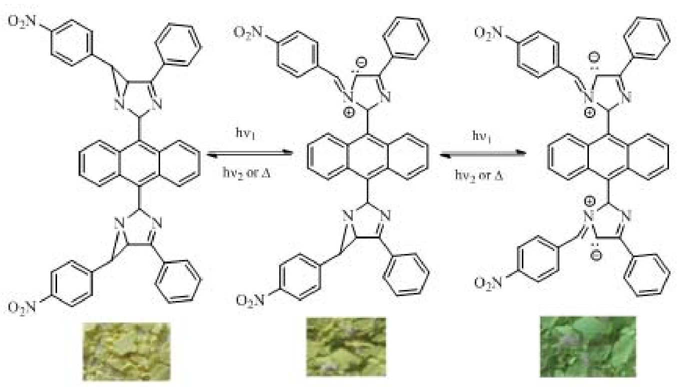
[28] F Shirini, MA Zolfigol, M Khaleghi, Oxidation of Alcohols Using $(NH_4)_2Cr_2O_7$ in the Presence of Silica Chloride/Wet SiO_2 in Solution and under Solvent Free Conditions, Bull. Korean. Chem. Soc. 24 (2003) 1021-1022. DOI: http://dx.doi.org/10.5012/bkcs.2003.24.7.1021.

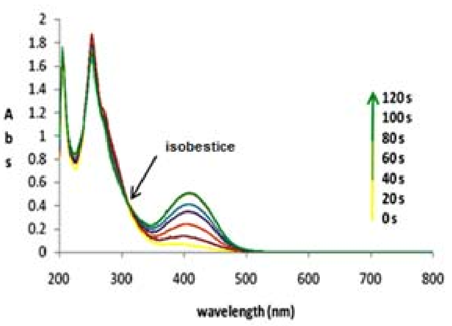
[29] F Shirini, MA Zolfigol, MR Azadbar, Oxidation of Benzyl Alcohols Under Mild Heterogeneous Conditions, Russ. J. Org. Chem. 37 (2001) 1600-1602. DOI: 10.1023/A:1013816422004.

GRAPHICAL ABSTRACT

Synthesis of Anthracene Derivatives of 1,3-Diazabicyclo[3,1,0]hex-3-ene

Nosrat O. Mahmoodi, Safoura Mirkhaef





Highlight for Reviewer

- 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.