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# New 1,3-diazabicyclo-[3.1.0]hex-3-ene photochromic azo dyes: Synthesis, characterization and spectroscopic studies

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ABSTRACT

Ten new 1,3-diazabicyclo-[3.1.0]hex-3-ene-based azo dyes (**3a**–**3k**) were synthesized via three-component reaction between [3-(x-phenyl)aziridin-2-yl](phenyl)methanone (x = 4-$NO_2$, 3-$NO_2$), $NH_4OAc$ and azo-coupled *o*-vanillin or salicylaldehyde precursors (**1a**–**1e**) and characterized by UV–Vis, IR and $^1H$ NMR spectroscopic techniques. The synthesized azo dyes undergo ring opening in EtOH by irradiation with 254 nm UV light. The properties and photochromic structural behavior relationship (PSBR) of these dyes has been analyzed. The spectroscopic information show that the close-*E* photoisomer prevails in ordinary room light, however by irradiation with UV light the open-*Z* photoisomer is prominent.



## 1. Introduction

Photochromism is a vast field encompassing well known phenomena associated with reversible transformations of photoisomers having different absorptions upon irradiation with UV and visible light. This phenomena is not limited to the color or absorption spectra, as the changes are based on two different molecules with different physical and chemical properties [1,2]. There has been significant scientific interest in the photochromic compounds used in optical memories, photo-switches, data-storage systems, full color displays, molecular motors and mechanical machines, optoelectronic systems, liquid-crystalline actuators and responsive photonic crystals [3–8]. 1,3-Diazabicyclo-[3.1.0]hex-3-ene derivatives possess exclusive photochromic properties and display good photochromic properties both in the solid and solution states. 1,3-Diazabicyclo[3.1.0]hex-3-ene photochromic compounds can undergo reversible photocyclization between their closed-ring isomer and open-ring isomer under irradiation using a light source of appropriate wavelength [9–15]. Recently, we used a novel type of potentiometry with membrane sensors based on 6-(4-nitrophenyl)-2,4-diphenyl-3,5-diazabicyclo[3.1.0]hex-2-ene and 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diazabicyclo[3,1,0] hex-2-ene for detection of Sn(II) and Sr(II) ions at trace levels in real samples, respectively [16–18].

Azo dyes are an important class of organic colorants used in many practical applications [19,20]. The photochromism and thermochromism of aromatic azo dyes make them suitable as optical sensors and molecular memory storage [21–26]. Reversible *E*/*Z* isomerization of azobenzenes, a representative family of photochromic molecules, is usually induced by alternating irradiation with ultraviolet (UV) and blue lights, which conduct *E* to *Z* and vice versa isomerization through azo π–π* and azo n–π* excitations, respectively [27,28]. Recently, several reports regarding synthesis of azo dyes bearing heterocyclic moieties such as thiophene, pyrrole and azoles have been published. These azo dyes were used for multiple optical and electronic applications such as second harmonic generation, optical switching, chemosensing, organic sensitized solar cells and memories [29–33].

In consideration of these characteristics, it is of interest to examine for the first time the coupling of the photoactive azo group and 1,3-diazabicyclo-[3.1.0]hex-3-ene to give single azo-1,3-diazabicyclo-[3.1.0]hex-3-ene dyes (**3a**–**3k**) and investigate their PSBR (Scheme 1).

## 2. Experimental

### 2.1. Materials and apparatus

All reagents were purchased from Fluka, Merck and Aldrich and used without further purification. [3-(4-Nitrophenyl)aziridin-2-yl](phenyl) methanone (**2a**), and [3-(3-nitrophenyl) aziridin-2-yl](phenyl) methanone (**2b**), were prepared as described previously [9]. Azo dyes precursors, **1a**–**1e**, were prepared according to the well known literature procedure [34].

The absorption spectra of azo dyes were measured by Shimadzu UV-2100 spectrophotometer in the range 200–800 nm (EtOH, $c = 2 \times 10^{-4}$ M, cell path length 1 cm). A light at 254 nm from a low-pressure Hg lamp was used for the photoisomerization from the close-*E* form to the open-*Z*. The structure of all synthesized compounds was confirmed by $^1H$ and $^{13}C$ NMR spectra, recorded on

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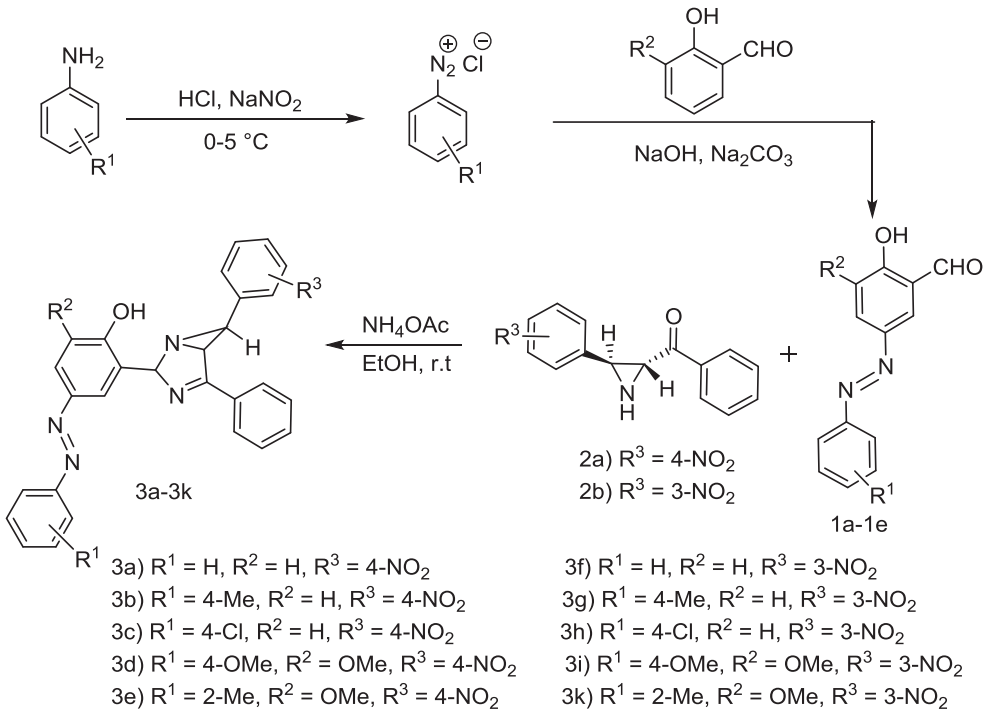



**Scheme 1.** Synthesis of azo-1,3-diazabicyclo-[3.1.0]hex-3-ene dyes.

Bruker Avance 500 and 400 MHz spectrometers. IR spectra were recorded on a Shimadzu IR 470 spectrophotometer in the region of 400–4000 $cm^{-1}$ in KBr pellets. Melting points of all prepared compounds were determined on Mettler FP-5 melting point apparatus and are uncorrected. C. H. N. analyses were performed on a Vario-EL III elemental analyzer.

### 2.2. General procedure for the synthesis of photochromic azo dyes 3a–3k

Ketoaziridine **2a** or **2b** (0.268 g, 1 mmol) and $NH_4OAc$ (0.77 g, 10 mmol) were dissolved in absolute EtOH (10 ml) and the solution was stirred vigorously for 10 min at r.t. To this, an azo aldehyde **1a–1e** (1 mmol) was added and the mixture stirred at r.t. The reaction was monitored by TLC (EtOAc:petrol, 2:6). The reaction was completed after 24 h and the product was collected by filtration, washed with EtOH and recrystallized from EtOH or MeOH.

### 2.3. Spectral data for the synthesis of dye derivatives

*2-[6-(4-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]-4-(phenylazo)phenol* (Table 1, **3a**): Yield 78%, M.p 135–137 °C, $^1$H NMR (500 MHz, $CDCl_3$) δ: 2.68 (s, 1H), 3.98 (s, 1H), 6.84 (s, 1H), 7.06 (d, 1H, $J$ = 8.6 Hz), 7.43 (t, 1H, $J$ = 7.18 Hz), 7.48 (t, 2H, $J$ = 7.39 Hz), 7.56 (t, 4H), 7.64 (t, 1H, $J$ = 7.3 Hz), 7.75 (d, 2H, $J$ = 8.1 Hz), 7.87 (dd, 1H, $J$ = 8.6, 2.4 Hz), 7.99 (dd, 2H, $J$ = 8.4, 1.03 Hz), 8.06 (s, 1H), 8.25 (d, 2H, $J$ = 8.7 Hz). $^{13}$C NMR (500 MHz, $CDCl_3$) δ: 43.81, 57.61, 95.00, 118.05, 122.89, 123.77, 123.82, 124.31, 124.88, 127.91, 129.25, 129.44, 129.57, 130.54, 130.86, 133.29, 144.72, 147.01, 148.08, 152.94, 158.79, 171.90. IR (KBr, $cm^{-1}$): 1595, 1500, 1440, 1340, 1280. Anal. Calcd. for $C_{28}H_{21}N_5O_3$: C 70.73, H 4.45, N 14.73, found C 70.65, H 4.57, N 14.79.

*2-[6-(4-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]-4-(p-tolylazo)phenol* (Table 1, **3b**): Yield 84%, M.p 181–183 °C, Close form, 81%, $^1$H NMR (500 MHz, $CDCl_3$) δ: 2.43 (s, 3H), 2.67 (s, 1H), 3.97 (s, 1H), 6.83 (s, 1H), 7.05 (d, 1H, $J$ = 8.7 Hz), 7.28 (d, 2H, $J$ =8.15 Hz), 7.57–7.52 (m, 4H), 7.66–7.61(t, 3H, $J$ =8.1 Hz), 7.85 (dd, 1H, $J$ = 10.4, 2.04 Hz), 7.99 (d, 2H, $J$ = 7.5 Hz), 8.00 (s, 1H), 8.25 (d, 2H, $J$ = 8.6 Hz), 9.80 (s, 1H). $^{13}$C NMR (500 MHz, $CDCl_3$) δ: 21.86, 43.80, 57.59, 95.04, 118.00, 122.89, 123.46, 123.80, 124.29, 124.82, 127.93, 129.24, 129.55, 130.10, 130.58, 133.26, 141.36, 144.76, 147.07, 148.05, 151.02, 158.52, 171.84. After irradiation with UV light converted to the open form, 19%, $^1$H NMR (500 MHz, $CDCl_3$) δ: 2.47 (s, 1H), 2.99 (s, 1H), 3.88 (s, 1H), 6.50 (s, 1H), 7.08 (d, 1H, $J$ = 8.6 Hz), 7.34 (d, 2H, $J$ = 8.1 Hz), 7.57–7.52 (m, 4H), 7.66–7.61 (m, 3H), 7.89 (dd, 1H, $J$ =10.9, 2.27 Hz), 7.98 (d, 2H, $J$ = 8.4 Hz), 8.00 (s, 1H), 8.31 (d, 2H, $J$ =8.6 Hz). $^{13}$C NMR (500 MHz, $CDCl_3$) δ: 21.86, 47.94, 57.15, 95.00, 118.27, 122.99, 123.46, 123.80, 124.39, 124.82, 127.76, 129.33, 129.51, 130.14, 130.58, 133.12, 141.36, 144.76, 146.91, 148.05, 151.02, 158.52, 171.84. IR (KBr, $cm^{-1}$): 1600, 1510, 1480, 1340, 1260. Anal. Calcd. for $C_{29}H_{23}N_5O_3$: C 71.15, H 4.74, N 14.31, found C 71.03, H 4.73, N 14.42.

*4-(4-Chlorophenylazo)-2-[6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo [3.1.0]hex-3-en-2-yl] phenol* (Table 1, **3c**): Yield 70%, M.p 170–172 °C, Close form 81%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.64 (s, 1H), 3.96 (dd, 1H, $J$ = 0.8, 2 Hz), 6.80 (s, 1H), 7.04 (d, 1H, $J$ = 8.8 Hz), 7.43 (d, 2H, $J$ = 8.8 Hz), 7.57–7.48 (m, 4H), 7.69–7.60 (m, 3H), 7.85 (dd, 1H, $J$ = 1.6, 5.6 Hz), 7.97 (d, 2H, $J$ = 8.4 Hz), 8.00 (s, 1H), 8.24 (d, 2H, $J$ = 8.8 Hz), 9.90 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 43.38, 57.22, 94.54, 117.73,

**Table 1**
Properties of photochromic azo compounds **3a–3k**.

| Entry | $\lambda_{max}$(nm)(EtoH) | m.p.(°C) | Color | Purification | Yield% |
|---|---|---|---|---|---|
| 1a[35] | 233, 335 | 128–129 | Brown | EtOH/$H_2O$ | 78 |
| 3a | 250, 347 | 135–137 | Orange-green | EtOH | 78 |
| 3f | 250, 350 | 140–141 | Yellow | EtOH | 68 |
| 1b[35] | 238, 340 | 150–152 | Brown | EtOH/$H_2O$ | 87 |
| 3b | 250, 355 | 181–183 | Orange | MeOH | 84 |
| 3g | 250, 350 | 159–160 | Yellow | MeOH | 79 |
| 1c[36] | 237, 346 | 213–215 | Yellow | EtOH | 90 |
| 3c | 250, 360 | 170–172 | Orange | MeOH | 70 |
| 3h | 250, 355 | 163–165 | Orange | EtOH | 63 |
| 1d | 249, 386 | 172–173 | Brown | EtOH/$CHCl_3$ | 78 |
| 3d | 255, 368 | 149–151 | Yellow | EtOH | 86 |
| 3i | 251, 368 | 174–176 | Pea green | EtOH | 81 |
| 1e | 240, 272, 379 | 102–104 | Brown | EtOH/$H_2O$ | 73 |
| 3e | 257, 368 | 156–158 | Yellow | EtOH | 83 |
| 3k | 251, 368 | 147–149 | Yellow | EtOH | 80 |

123.47, 123.57, 123.73, 123.89, 124.47, 127.47, 128.82, 129.16, 129.26, 130.08, 132.91, 136.24, 144.26, 146.40, 147.66, 150.86, 158.63, 171.52. After irradiation with UV light converted to the open form, 19%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.98 (d, 1H, $J$ = 2 Hz), 3.88 (dd, 1H, $J$ = 0.4,2.4 Hz), 6.50 (s, 1H), 7.07 (d, 2H, $J$ = 8.8 Hz), 7.43 (d, 2H, $J$ = 8.8 Hz), 7.57–7.48 (m, 4H), 7.69–7.60 (m, 3H), 7.85 (dd, 1H, $J$ = 1.6, 5.6 Hz), 7.95 (d, 2H, $J$ = 7.6 Hz), 8.00 (s, 1H), 8.32 (d, 2H, $J$ = 8.8 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 48.20, 56.00, 96.47, 117.96, 123.47, 123.57, 123.73, 123.84, 124.47, 127.32, 128.88, 129.11, 129.26, 130.08, 132.73, 136.24, 144.26, 146.40, 147.66, 150.80, 158.60, 171.50. IR (KBr, $cm^{-1}$): 1600, 1520, 1480, 1340, 1280. Anal. Calcd. for $C_{28}H_{20}N_5O_3Cl$: C 65.95, H 3.95, N 13.73, found C 65.87, H 3.87, N 13.74.

*2-Methoxy-4-(4-methoxyphenylazo)-6-[6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]phenol* (Table 1, **3d**): Yield 86%, M.p 149–151 °C, Close form, 70%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.69 (s, 1H), 3.89 (s, 3H), 3.91 (s, 1H), 4 (s, 3H), 6.90 (s, 1H), 7 (d, 2H, $J$ =9.2 Hz), 7.47 (d, 1H, $J$ = 2 Hz), 7.50–7.63 (m, 6H), 7.80 (d, 2H, $J$ =9.2 Hz), 8 (d, 2H, $J$ = 7.2 Hz), 8.21 (d, 2H, $J$ = 8.8 Hz), 9.29 (br, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 42.83, 55.58, 56.14, 57.19, 93.81, 102.1, 114.21, 118.85, 123.14, 123.82, 124.33, 127.5, 128.76, 129.09, 130.4, 132.67, 144.65, 146.18, 146.83, 147.42, 147.53, 148.74, 161.66, 171.50. After irradiation with UV light converted to the open form, 30%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.94 (s, 1H), 3.89 (s, 1H), 3.91 (s, 3H), 4.03 (s, 3H), 6.62 (d, 1H, $J$ = 2.8 Hz), 7.03 (d, 2H, $J$ = 8.8 Hz), 7.50–7.63 (m, 7H), 7.91 (d, 2H, $J$ = 9.2 Hz), 8 (d, 2H, $J$ = 7.2 Hz), 8.27 (d, 2H, $J$ = 8.4 Hz), 8.6 (br, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 47.82, 55.58, 56.24, 56.99, 93.84, 101.21, 114.21, 119.33,123.86, 124.38, 125.54, 127.38, 128.85, 128.97, 130.79, 132.28, 144.48, 146.13, 146.48, 147.01, 147.61, 148.45, 161.61, 170.2. IR (KBr, $cm^{-1}$): 1595, 1510, 1500, 1465, 1340, 1285. Anal. Calcd. for $C_{30}H_{25}N_5O_5$: C 67.28, H 4.71, N 13.08, found C 67.18, H 4.86, N 13.07.

*2-Methoxy-4-(2-methylphenylazo)-6-[6-(4-nitrophenyl)-4-phenyl-1, 3-diazabicyclo[3.1.0] hex-3-en-2-yl]phenol* (Table 1, **3e**): Yield: 83%, M.p 156–158 °C, Close form, 72%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 3H), 2.7 (s, 1H), 3.91 (t, 1H, $J$ = 1.6 Hz), 4.01 (s, 3H), 6.90 (s, 1H), 7.23 (td, 1H, $J$ = 8, 1.6 Hz), 7.27–7.36 (m, 2H), 7.50–7.65 (m, 7H), 7.68 (dd, 1H, $J$ = 2, 0.8 Hz), 7.98–8.02 (m, 2H), 8.22 (d, 2H, $J$ = 8.8 Hz), 9.65 (br, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 17.22, 43, 56.12, 57.36, 93.98, 104.6, 115.34, 116.91, 123.23, 123.86, 126.42, 127.42, 128.78, 129.12, 130.24, 130.41, 131.16, 132.77, 137.41, 144.59, 146.54, 147.58, 147.93, 148.76, 150.55, 171.44. After irradiation with UV light converted to the open form, 28%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.73 (s, 3H), 2.96 (d, 1H, $J$ = 1.6 Hz), 3.89 (t, 1H, $J$ = 2.4 Hz), 4.03 (s, 3H), 6.63 (d, 1H, $J$ = 2.8 Hz), 7.27–7.36 (m, 3H), 7.50–7.65 (m, 8H), 7.98–8.02 (m, 2H), 8.27 (d, 2H, $J$ = 8.8 Hz), 8.66 (br, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 17.52, 47.82, 56.19, 56.95, 93.73, 101.88, 115.52, 119.51, 132.86, 125.53, 126.49, 127.36, 128.91, 129.01, 130.31, 130.63, 131.16, 132.41, 137.32, 144.75, 146.54, 146.9, 147.64, 148.45, 150.84, 170.3. IR (KBr, $cm^{-1}$): 1600, 1510, 1450, 1340, 1260. Anal. Calcd. for $C_{30}H_{25}N_5O_4$: C 69.35, H 4.85, N 13.48, found C 69.52, H 4.89, N 13.37.

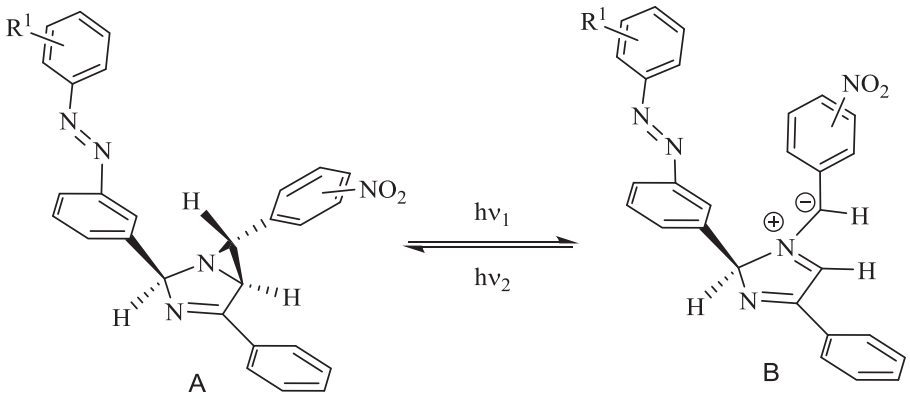
*2-[6-(3-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]-4-(phenylazo)phenol* (Table 1, **3f**): A similar procedure as applied for **3a** was practical but instead of **2a** same amount of **2b** was utilized. Yield 68%, M.p 140 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ 2.70 (s, 1H), 3.98 (s, 1H), 6.84 (s, 1H), 7.07 (d, 1H, $J$ = 8.7 Hz), 7.43 (t, 1H, $J$ = 7.2 Hz), 7.48 (t, 2H, $J$ = 7.34 Hz), 7.56 (t, 3H), 7.64 (t, 1H, $J$ = 7.4 Hz,), 7.72 (d, 1H, $J$ = 7.6 Hz,), 7.76 (d, 2H, $J$ = 7.4 Hz), 7.88 (dd, 1H, $J$ = 8.6, 2.2 Hz), 8.01 (d, 2H, $J$ = 7.3 Hz), 8.09 (s, 1H), 8.21 (dd, 1H, $J$ = 1.22, 9.39 Hz), 8.26 (s, 1H), 10 (s, 1H). $^{13}$C NMR (500 MHz, $CDCl_3$) δ: 43.61, 57.36, 94.98, 118.06, 121.89, 122.91, 123.33, 123.79, 123.86, 124.94, 129.27, 129.41, 129.56, 130.00, 130.57, 130.79, 133.28, 133.36, 139.66, 146.99, 149.00, 152.99, 158.82, 171.96. IR (KBr, $cm^{-1}$): 1600, 1560, 1540, 1470, 1340, 1270. Anal. Calcd. for $C_{28}H_{21}N_5O_3$: C 70.73, H 4.45, N 14.73, found C 70.76, H 4.57, N 14.81.

*2-[6-(3-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]-4-(p-tolylazo)phenol* (Table 1, **3g**): Yield 79%, M.p 160 °C, $^1$H NMR (500 MHz, $CDCl_3$) δ: 2.43 (s, 3H), 2.69 (s, 1H), 3.98 (s, 1H), 6.83 (s, 1H), 7.06 (d, 1H, $J$ = 8.7 Hz), 7.28 (d, 2H, $J$ = 8.1 Hz), 7.57–7.54 (t, 3H), 7.64 (t, 1H, $J$ = 6.7 Hz), 7.66 (d, 2H, $J$ = 8.1 Hz), 7.72 (d, 1H, $J$ = 7.67 Hz), 7.85 (dd, 1H, $J$ = 8.6, 2.19 Hz), 8.01 (d, 2H, $J$ = 7.3 Hz), 8.07 (s, 1H), 8.22 (d, 1H, $J$ = 8.1 Hz), 8.26 (s, 1H), 9.92 (s, H). $^{13}$C NMR (500 MHz, $CDCl_3$) δ: 21.85, 43.60, 57.34, 95.03, 118.00, 121.90, 122.89, 123.30, 123.52, 123.84, 124.83, 129.24, 129.54, 130.00, 130.06, 130.61, 133.23, 133.39, 139.70, 141.00, 147.00, 149.00, 151.00, 158.54, 171.89. IR (KBr, $cm^{-1}$): 1600, 1580, 1520, 1480, 1340, 1260. Anal. Calcd. for $C_{29}H_{23}N_5O_3$: C 71.15, H 4.74, N 14.31, found C 71.08, H 4.81, N 14.22.

*4-(4-Chlorophenylazo)-2-[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo [3.1.0]hex-3-en-2-yl] phenol* (Table 1, **3h**): Yield 63%, M.p 164 °C, Close form, 72%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.66 (s, 1H), 3.97 (s, 1H), 6.80 (s, 1H), 7.04 (d, 1H, $J$ = 8.8 Hz), 7.42 (d, 2H, $J$ = 8.8 Hz), 7.49 (d, 1H, $J$ = 8.4 Hz), 7.58–7.52 (m, 2H), 7.63–7.61 (m, 1H), 7.68 (d, 2H, $J$ = 8.4 Hz), 7.85 (dd, 1H, $J$ = 8.8, 2.4 Hz), 7.88 (d, 1H, $J$ = 8.8 Hz), 7.98 (d, 2H, $J$ = 7.2 Hz), 8.00 (s, 1H), 8.20 (d, 1H, $J$ = 8 Hz), 8.24 (s, 1H), 10.00 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 43.19, 56.94, 94.51, 117.72, 121.49, 122.92, 123.51, 123.71, 123.75, 124.60, 128.84, 129.15, 129.22, 129.60, 130.00, 132.88, 132.89, 136.15, 139.22, 146.37, 148.57, 150.90, 158.67, 171.58. After irradiation with UV light converted to the open form, 28%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.90 (s, 1H), 3.89 (s, 1H), 6.40 (s, 1H), 7.07 (d, 1H, $J$ = 8.8 Hz), 7.42 (d, 2H, $J$ = 8.8 Hz), 7.49 (d, 1H, $J$ = 8.4 Hz), 7.58–7.52 (m, 2H), 7.63–7.61 (m, 1H), 7.70 (d, 2H, $J$ = 6.4 Hz), 7.82 (d, 1H, $J$ = 8.8 Hz), 7.88 (d, 1H, $J$ = 8.8 Hz), 7.96 (d, 2H, $J$ = 8 Hz), 8.25 (s, 1H), 8.34 (s, 1H), 8.52 (s, 1H), 10.26 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 47.39, 56.43, 95.14, 117.90, 121.64, 123.11, 123.54, 123.83, 123.89, 125.59, 128.90, 129.00, 129.27, 129.80, 130.20, 132.42, 132.70, 136.00, 139.28, 146.24, 148.57, 151.14, 158.20, 170.26. IR (KBr, $cm^{-1}$): 1600, 1580, 1520, 1480, 1340, 1260. Anal. Calcd. for $C_{28}H_{20}N_5O_3Cl$: C 65.95, H 3.95, N 13.73, found C 65.88, H 3.98, N 13.65.

*2-Methoxy-4-(4-methoxyphenylazo)-6-[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo [3.1.0]hex-3-en-2-yl]phenol* (Table 1, **3i**): Yield 81%, M.p 174–176 °C, Close form, 65%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.71 (s, 1H), 2.89 (s, 3H), 3.92 (s, 1H), 4 (s, 3H), 6.91 (s, 1H), 6.98 (d, 2H, $J$ = 8.8 Hz), 7.47–7.64 (m, 5H), 7.67 (m, 2H), 7.78–7.81 (m, 2H), 8 (d, 2H, $J$ = 7.2 Hz), 8.1 (d, 1H, $J$ = 8 Hz), 8.22 (s, 1H), 9.35 (br, 1H). $^{13}$C NMR(100 MHz, $CDCl_3$) δ: 42.63, 55.57, 56.14, 56.94, 93.8, 102.12, 114.18, 118.93, 121.56, 122.76, 123.2, 124.34, 128.77, 129.08, 129.52, 130.43, 132.64, 132.91, 139.55, 146.15, 146.87, 147.46, 148.52, 148.76, 161.61, 171.55. After irradiation with UV light converted to the open form, 35%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.95 (s, 1H), 3.74 (quar, 1H, $J$ = 6.8 Hz), 3.9 (s, 3H), 4.02 (s, 3H), 6.62 (d, 1H, $J$ = 2.4 Hz), 7.02 (d, 2H, $J$ = 8.8 Hz), 7.47–7.64 (m, 5H), 7.78–7.81 (m, 1H), 7.91–7.93 (m, 3H), 8 (d, 2H, $J$ = 7.2 Hz), 8.21 (m, 1H), 8.3 (s, 1H), 8.61 (br, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 47.71, 55.57, 56.22, 56.62, 93.8, 101.26, 114.2, 119.3, 121.69, 122.87, 124.4, 125.63, 128.89, 128.97, 129.63, 130.8, 132.28, 132.57, 139.78, 146.11, 146.48, 147.01, 148.44, 148.48, 161.58, 170.26. IR (KBr, $cm^{-1}$): 1600, 1575, 1525, 1470, 1345, 1280. Anal. Calcd. for $C_{30}H_{25}N_5O_5$: C 67.28, H 4.71, N 13.08, found C 67.34, H 4.76, N 13.01.

*2-Methoxy-4-(2-methylphenylazo)-6-[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0] hex-3-en-2-yl]phenol* (Table 1, **3k**): Yield 80%, M.p 147–149 °C, Close form, 54%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.5 (s, 3H), 2.72 (s, 1H), 3.89–3.91 (m, 1H), 4.01 (s, 3H), 6.91 (s, 1H), 7.24 (td, 1H, $J$ = 7.4, 2 Hz), 7.27–7.32 (m, 1H), 7.35 (d, 1H, $J$ = 4 Hz), 7.5–7.63 (m, 5H), 7.68–7.71 (m, 2H), 7.8 (d, 1H, $J$ = 7.6 Hz), 7.99–8.02 (m, 2H), 8.18 (dd, 1H, $J$ = 8.4, 1 Hz), 8.24 (s, 1H), 9.68 (br, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 17.24, 42.79, 56.12, 57.15, 93.98, 104.55, 115.37, 117.06, 121.48, 122.79, 123.31, 126.41, 128.78, 129.1, 129.58, 130.28, 131.11, 132.73, 132.77, 137.4, 139.54, 149.53, 147.97, 148.43, 148.78, 150.58, 171.47. After irradiation with UV light converted to the open form, 46%, $^1$H NMR (400 MHz, $CDCl_3$) δ: 2.74 (s, 3H), 2.96 (d, 1H, $J$ = 1.6 Hz), 3.89–3.91 (m, 1H), 4.02 (s, 3H), 6.63 (d, 1H, $J$ = 2.4 Hz), 7.27–7.32 (m, 2H), 7.35 (d, 1H, $J$ = 4 Hz), 7.5–7.63 (m, 7H), 7.99–8.02




**Scheme 2.** Photoisomerization of photochromic dyes via imine ylide upon the UV–light irradiation.

(m, 3H), 8.21 (dd, 1H, $J = 8.4$, 1.2 Hz), 8.31 (s, 1H), 8.70 (br, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 17.52, 47.68, 56.17, 56.62, 93.8, 102.18, 115.54, 119.14, 121.64, 122.88, 125.72, 126.46, 128.87, 128.98, 129.63, 130.35, 130.77, 131.16, 132.3, 132.54, 137.4, 139.77, 146.53, 146.88, 148.51, 148.57, 150.84, 170.34. IR (KBr, $cm^{-1}$): 1605, 1575, 1525, 1475, 1345. Anal. Calcd. for $C_{30}H_{25}N_5O_4$: C 69.35, H 4.85, N 13.48, found C 69.28, H 4.91, N 13.52.

## 3. Result and discussion

In our approach, *o*-vanillin or salicylaldehyde in the first step was coupled with the diazonium chloride obtained from aniline derivatives to give **1a**–**1e**. In the next efforts, the photochromic azo dyes **3a**–**3k** were synthesized via three-component reactions between ketoaziridine **2a** or **2b**, $NH_4OAc$ and azo dye precursor, as shown in Scheme 1 and Table 1.

The characteristic IR absorption bands of compounds were determined in KBr disk. In the IR spectra of **3a**–**3k**, absence of a C=O absorption related to the azo precursors **1a**–**1e** and the N – H stretching related to the ketoaziridines **2a**–**2b** in addition to the appearance of a new C=N absorption band in the range of 1597–1605 $cm^{-1}$ indicated that 1,3-diazabicyclo[3.1.0]hex-3-en moiety was formed.

The NMR spectra of dyes were recorded in $CDCl_3$ at 25 °C. All of the synthesized azo dyes except for **3a**, **3f** and **3g** showed a new set of signals in $^1$H and $^{13}$C NMR in addition to the original ones because of Photoisomerization between their closed-ring **A** photoisomer and open-ring **B** photoisomer via conrotatory (σ2s + n2s) heterolytic cleavage of the three-member ring under irradiation with light source of appropriate wavelength (254 nm) [9–11]. Photoisomerization of these photochromic azo dyes via proposed zwitter ionic double-charged imine ylides were depicted in Scheme 2.

The $^1$H NMR spectra of compound **3c** in $CDCl_3$ indicate mixture of two photoisomers with ratio of 78:22 (**3c**:**3c′**) closed to open forms upon exposure to UV light. The ratios of close to open photoisomers were measured from integral ratio of certain peaks in $^1$H NMR spectra. The characteristic shifts of their $H_a$, $H_b$, $H_c$ were observed in the

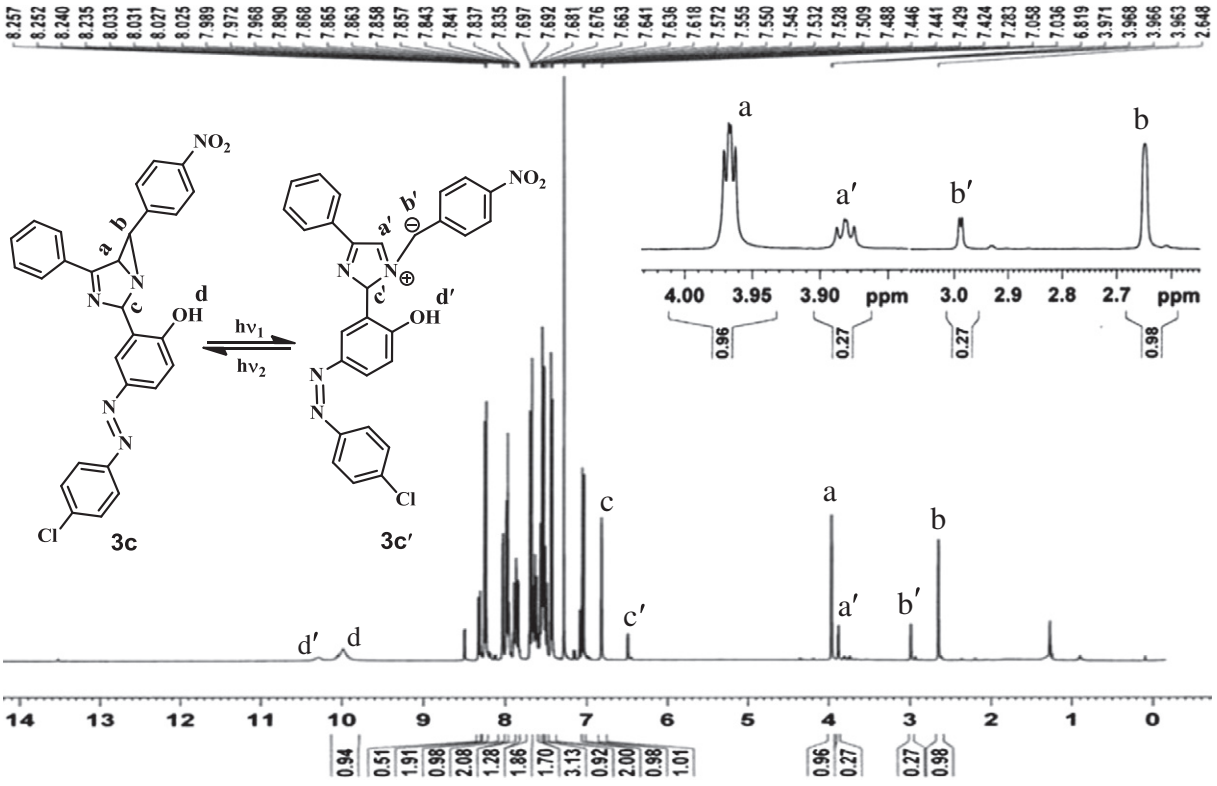



**Fig. 1.** $^1$HNMR of **3c** indicates mixture of two photoisomers with ratio of 78:22 for close and open forms.

**Table 2**
$^1$H NMR chemical shifts of close and open-ring isomers for **3a**–**3k**.

| Entry | δb,b′ | δa,a′ | δc,c′ | δOH,OH′ | Close/open form ratio (%) |
|---|---|---|---|---|---|
| 3a | 2.67, – | 3.97, – | 6.83, – | – | 100/0 |
| 3b | 2.67, 2.99 | 3.97, 3.88 | 6.83,6.50 | 9.8, – | 81/19 |
| 3c | 2.64, 2.98 | 3.96, 3.88 | 6.80, 6.50 | 9.90, – | 78/22 |
| 3d | 2.69, 2.94 | 3.91, 3.89 | 6.90, 6.62 | 9.29, 8.60 | 70/30 |
| 3e | 2.70, 2.96 | 3.91, 3.89 | 6.90, 6.63 | 9.65, 8.66 | 72/28 |
| 3f | 2,70, – | 3.98, – | 6.84, – | 10, – | 100/0 |
| 3g | 2.69, – | 3.98, – | 6.83, – | 9.92, – | 100/0 |
| 3h | 2.66, 2.90 | 3.97, 3.89 | 6.80, 6.40 | 10, – | 68/32 |
| 3i | 2.71, 2.95 | 3.92, 3.74 | 6.91, 6.62 | 9.35, 8.61 | 65/35 |
| 3k | 2.72, 2.96 | 3.90, 3.90 | 6.91, 6.63 | 9.68, 8.70 | 54/46 |

$^1$H NMR spectra (Fig. 1). As shown in Fig. 1 and Table 2, the $^1$H NMR signal of $H_b$ appeared at δ = 2.64 ppm for **3c** (close form) and δ = 2.98 ppm for **3c′** (open form), and the $^1$H NMR signals of the $H_a$ and $H_c$ of the imidazole ring appeared at δ = 3.96 and 6.80 ppm for **3c** and δ = 3.88 and 6.50 ppm for **3c′** respectively. The $H_b$ proton located above the plane of imidazole ring is shielded by anisotropic effect, thus it chemical shift appeared at higher field compared to $H_a$ and $H_c$. Similar chemical shift changes have also been observed in the $^1$H NMR spectra of other photochromic dyes. $^1$H NMR spectra in Fig. 1 shows broad peak of O – H at 10 ppm attributed to the intramolecular H-bonding with $N_1$ or $N_3$ of imidazoline ring.

The electronic absorption spectra of **3a**–**3k** were recorded in EtOH upon irradiation with 254 nm light at room temperature. Before UV light irradiation, compound **3b** showed two strong bands at 252 and 354 nm. When **3b** was irradiated, the absorption intensity at 354 nm gradually increased and a new absorption peak at 440 nm appeared. When **3g** was irradiated, the absorption intensity at 248 and 354 nm increased without appearance of a peak at 440 nm (Fig. 2). This implies that both azo and aziridine moieties are affected by UV irradiation and the imine ylide of photoisomer **3b** with a *p*-$NO_2$ group is more highly stabilized than photoisomer **3g** with *meta*-$NO_2$ substitution. This phenomenon is attributed to the *p*-$NO_2$ conjugation effect.

By increasing the duration of irradiation or exposure to the sun light the intensity of color for all of the photochromic dyes due to population of open-*Z* photoisomer both in the solid and solution forms were increased.

## 4. Conclusion

New azo dyes with 1,3-diazabicyclo-[3.1.0]hex-3-ene moiety were synthesized via three-component reaction between (3-(x-phenyl) aziridin-2-yl)(phenyl)methanone (x = 4-$NO_2$, 3-$NO_2$), $NH_4OAc$ and azo-coupled *o*-vanillin or salicylaldehyde precursor. The photochromic azo dyes **3a**–**3k**, upon exposure to UV light showed the equilibrium ratio between close and open photoisomers. The spectroscopy data showed that the close photoisomers prevail in ordinary room light; however by irradiation with UV light the open photoisomers are prominent.

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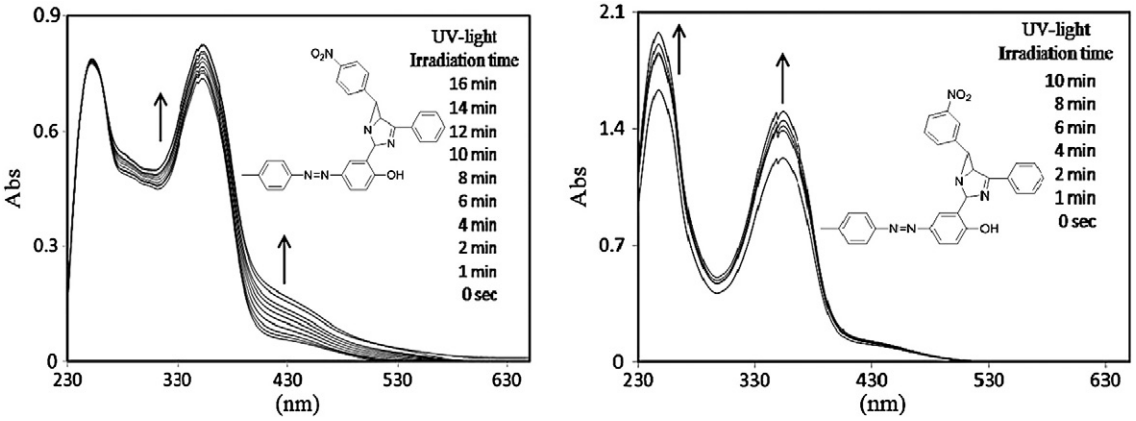


**Fig. 2.** Absorption spectra character in EtOH ($2 \times 10^{-4}$ M) before and after successive UV irradiation, for **3b** ring opening prevailed (left); **3g** (right).

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