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Synthesis of New Mono- and Bis- Photochromic Compounds Based on Isatins

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Abstract

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Among various photochromic compounds, 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives are the subject of intense research due to their photochromic behavior even in the crystalline state, although molecules which show photochromic reactivity in the crystalline state are rare. In this research synthesis of several mono- and bis-1,3-diazabicyclo[3.1.0]hex-3-enes with isatin linkage are enclosed. All synthesized compounds undergo reversible photochromic reactions not only in the solution but also in crystalline state by irradiation with UV light (254 nm).

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

Introduction

Photochromic molecules undergo a reversible color change, which originates from their structural change upon light irradiation.

In photochromic phenomenon, in addition to changes in the absorption spectra (color), various chemical and physical properties such as refractive index, dielectric constant, oxidation–reduction potential, geometric structure, internal energy, viscosity, solubility and etc. chang as well, so they have received remarkable attention for their potential applications to various photo switches and optical memory systems and ion transport through membranes [1-4].

In general, different types of organic photochromic compounds such as azobenzenes [5-6], spirobenzopyrans [7-8], spirooxazines [9], fulgides [10] and diarylethenes [11-12] have been reported so far, but compounds that show significant photochromic behavior in crystalline state are very rare [13-14].

In our group, new mono-, bis- and tris- photochromic compounds based on 1,3-diazabicyclo[3.1.0]hex-3-ene have been synthesized recently [15-24], which show significant photochromic behavior and change in color in solid state as well as solution. Here for first time the role of isatin in the structure of targets photochromic synthesized compounds are considered.

Experimental

Instrumentation and Reagents

The UV/Vis absorption spectra in the range 1900–800 nm (EtOH) as well as position of absorption band maxima for the initial A (λ^A_{max} nm) and photoinduced B (λ^B_{max} nm) photoisomers were measured with a Shimadzu UV-2100 spectrophotometer. Chemicals were purchased from Merck. Melting points were uncorrected and determined by Electrothermal 9100 melting point apparatus. Products were characterized by IR, ^{1}H NMR, ^{13}C NMR, TLC, and m.p. IR spectra were obtained on a FTIR-470. All NMR data were recorded in $CDCl_3$ and DMSO-d_6 using Bruker Avance 500 MHz spectrometer. Chemical shifts are reported in ppm (δ) using deuterated solvents as internal references.

Chemistry

General procedure for preparation of compounds 6a-6c

To a solution of isatin (4 mmol) in dry DMF (8.5 mL), NaH (6 mmol) (washed with dry *n*-hexane 3×10 ml) was added dropwise under argon atmosphere at 0° C. After stirring for 30 min a dark violet solution was produced. Then, the corresponding dihalogenated compound (2 mmol) was added dropwise. After the completion of the reaction 12 mL water was added and stirring was continued for 2 hours at 0° C. The produced solid was filtered off and recrystallized from EtOH.

1-(4-(2,3-dioxoindoline-1-yl)butyl)indoline-2,3-dione (6a*)*

Orange powder, yield: 95%, m.p. 189˚C. IR (KBr): 3108, 3050, 2963, 2860, 1728, 1602, 1554, 1517, 1463, 1353, 754 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 7.62 (m, 4H), 7.16 (d, J = 7.51 Hz, 2H), 6.96 (d, J = 7.48 Hz, 2H), 3.84 (br, 4H), 1.86 (br, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): ; 183.5, 158.8, 150.9, 139, 125.9, 124.3, 117.9, 110.6, 39.9, 24.8 ppm.

1-(5-(2,3-dioxoindoline-1-yl)pentyl)indoline-2,3-dione (6b)
Orange powder, yield: 92%, m.p. 89˚C. IR (KBr): 3050, 2925, 2858, 1737, 1610, 1467, 1353, 759 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 7.61 (m, 4H), 7.13 (t, J = 7.5 Hz, 2H), 6.93 (d, J = 8 Hz, 2H), 3.73 (t, J = 7 Hz, 2H), 3.73 (t, J = 7 Hz, 4H), 1.92 (m, 4H), 1.48 (m, 2H) ppm. ^{13}CNMR (125 MHz, $CDCl_3$/DMSO): 183.4, 158.2, 150.7, 138.4, 125.4, 123.7, 117.5, 110.1, 39.7, 59.2, 23.8 ppm.

1-(6-(2,3-dioxoindoline-1-yl)hexyl)indoline-2,3-dione (6c)
Orange powder, yield: 89%, m.p. 76˚C. IR (KBr): 3100, 3050, 2937, 2864, 1735, 1610, 1510, 1465, 1357, 1288, 1095, 857, 765, 619, 551, 476 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 7.59-7.62 (m, 4H), 7.12 (t, J = 7.5 Hz, 2H), 6.87 (d, J = 8 Hz, 2H), 3.73 (t, J = 7 Hz, 2H), 1.72 (br, 4H), 1.45 (br, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 183.5, 158.1, 150.8, 183.3, 125.4, 123.6, 117.5, 110.1, 39.9, 27.0, 29.3 ppm.

General procedure for preparation of compounds 5a-5b
A solution of isatin 4 (1 mmol), ketoaziridine **3a-3b** (1 mmol), NH_4OAc (10 mmol) in EtOH (10 mL) was stirred at room temperature for required time after the completion of the reaction the solid was filtered off and recrystallized from EtOH or other suitable solvents.

6-(4-nitrophenyl)-4-phenyl-1,3-diazaspiro[bicycle[3.1.0]hex-3-ene-2,3´-indoline]2´-one (5a)
Open form 36.5%, closed form 63.5%. Yellow powder, yield: 85%, m.p. 222 ˚C. IR (KBr): 3213, 3105, 3050, 1728, 1600, 1512, 1471, 1340, 1200, 856, 742, 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$):; 10.8 (s, 0.5H), 10.7(s, 1H), 8.19 (d, J = 8.89 Hz, 1.2H), 8.18 (d, J = 8.08 Hz, 2H),8.01 (d, J = 8.42 Hz, 2H), 7.98 (d, J = 8.46 Hz, 1.2H), 7.61 (m, 5.8H), 7.55 (d, J = 7.27 Hz, 2H), 7.52 (d, J = 7.25 Hz, 1.2H), 7.34 (t, J=7.72 ,1.6H), 7.16 (d, =J 7.26 Hz, 0.6H), 7.03 (t, J = 7.52 Hz, 0.6H), 6.99 (t, J= 7.49 Hz, 0.7H), 6.95 (d, J = 7.49 Hz, 0.7H),4.48 (s, 1H),3.96 (s, 0.5H) ,3.65 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): ; 175.7, 175, 174.5, 174.1, 1476., 146.4, 146.1, 143.6, 141.4, 133.1, 133, 131.7, 131.5, 131.4, 131.1, 129.8, 129.5, 129, 127.6, 126.2 , 125.1, 124.2, 123.2, 123, 111.1, 97.6, 95.4, 56.7 ,56.3, 41.6 ppm.

6-(3-nitrophenyl)-4-phenyl-1,3-diazaspiro[bicycle[3.1.0]hex-3-ene-2,3´-indoline]2´-one (5b)
White powder, yield: 80%, m.p. 218 ˚C. IR (KBr): 3220, 3105, 3045, 2084, 1726, 1612, 1526, 1346, 759 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): 10.4 (br, 1H), 8.18 (s, 1H), 8.10(d, J = 8.19 Hz, 1H), 8.01 (d, J = 8.42 Hz, 2H), 7.80 (d, J = 7.78 Hz, 1H), 7.63 (m, 3H), 7.54 (t, J = 7.55 Hz, 2H), 7.33 (t, J =7.41Hz, 1H), 7.01(t, J =7.60 Hz, 1H) ,6.96 (d, J = 7.74 Hz, 1H), 4.50 (s, 1H), 3.67 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): ; 175.8, 174.1, 148.6, 143.6, 140.9, 134.3, 133.1, 131.4, 130.6, 129.8, 129.5, 127.7, 126.2, 123.1, 123, 122.8, 111.1, 97.6, 56.1, 41.3 ppm.

General procedure for preparation of compounds 8a-8e
A similar procedure such as **5a-5b** was applied for **8a-8b**, but instead ketoaziridine **3a-3b** (1 mmol) we used ketoaziridine **3a-3b** (2 mmol).

1,4-bis-4-(4-nitrophenyl)-4-phenyl-1,3-diazaspiro[bicycle[3.1.0]hex-3-ene-2,3´-indoline]2´-one (8a)
Open form 70%, closed form 30%. Yellow powder, yield: 79%, m.p. 254 ˚C. IR (KBr): 3100, 3072, 2929, 2862, 1712, 1649, 1614, 1519, 1465, 1352, 1230, 1110, 1054, 1002, 750, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.16 (d, J = 7.57 Hz, 4H), 8.01(d, J = 8 Hz, 4H), 7.59 (d, J = 7.2Hz, 2H), 7.54 (m, 6H), 7.34 (d, J = 7.2 Hz, 4H), 7.38(d, J =7.6 Hz, 2H), 7.11 (d, J =8 Hz, 1H), 7.20 (d, J = 7.20 Hz, 2H) , 6.93 (t, J = 7.4 Hz, 2H), 4.24 (br, 1H), 3.99 (m, 4H) ,3.18 (s, 2H), 1.92 (br, 1H), 1.62 (br, 2H), 1.27 (t, J = 7.4 Hz, 2H) ppm.

1,4-bis-4-(3-nitrophenyl)-4-phenyl-1,3-diazaspiro[bicycle[3.1.0]hex-3-ene-2,3´-indoline]2´-one (8b)
Open form 63.5%, closed form 36.5%. White powder, yield: 76%, m.p. 288 ˚C. IR (KBr): 3100, 3064, 2931, 2860, 1730, 1649, 1606, 1519, 1461, 1350, 1232, 1170, 1108, 1053, 929,750, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (br, 4H), 8.13 (d, J = 6.8 Hz, 2H), 8 (d, J = 6.8 Hz, 4H), 7.67 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.51(m, 6H) ,7.35 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 2H), 7.03-7.09 (m, 4H),4.03(s, 2H), 3.94 (br, 4H), 3.21(s, 1H), 1.98 (br, 2H), 1.60 (br, 4H) ppm.

1,5-bis-6-(4-nitrophenyl)-4-phenyl-1,3-diazaspiro[bicycle[3.1.0]hex-3-ene-2,3´-indoline]2´-one-pentane (8c)
yellow powder, yield: 71%, m.p. 269 ˚C. IR (KBr): 3100, 3058, 2935, 2869, 1728, 1606, 1566, 1531, 1473, 1352, 1168, 1107, 759,690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.19 (d, J = 8.8 Hz, 4H), 8 (d, J = 6.8 Hz, 4H), 7.49-7.61 (m, 4H), 7.39 (d, J = 7.6 Hz, 4H), 7.14(d, J = 7.2 Hz, 2H), 7.35 (d, J =7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 2H), 7.16 (d, J = 7.2 Hz, 2H), 7.04 (t, J = 6.8 Hz, 2H), 6.94(t, J = 7.2 Hz, 2H), 4.25 (s, 1H), 3.86-3.72 (m, 4H), 3.18 (s, 2H), 2.04 (br, 2H), 1.88(br, 4H), 1.59 (br, 2H) ppm.

1,5-bis-6-(3-nitrophenyl)-4-phenyl-1,3-diazaspiro[bicycle[3.1.0]hex-3-ene-2,3′-indoline]2′-one-pentane (8d)
Open form 66%, closed form 34%. White powder, yield: 76%, m.p. 245 ˚C. IR (KBr): 3100, 3072, 2923, 2860, 1726, 1647, 1614, 1531, 1452, 1361, 1168, 1107, 759,692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$):8.23 (br, 2H), 8.12 (d, J = 7.2 Hz, 2H) , 8-8.02 (m, 6H), 7.71 (d, J = 7.6 H, 2H), 7.59 (t, J = 7.2 Hz, 2H), 7.49-7.53 (m, 6H), 7.39-7.42 (m, 2H), 7.07 (d, J = 7.4 Hz, 2H), 6.94 (d, J =7.6 Hz, 2H),4.02 (s, 2H), 3.80-3.86 (m, 2H), 3.69-3.76 (m, 4H), 3.21 (s, 1H), 2.64 (s, 1H), 2.20 (s, 2H), 1.90 (br, 2H),1.61(br, 4H), 1.27 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 175.7, 172.3, 148.3, 144, 139.2, 133.5, 132.6, 132.3, 130.9, 129.5, 128.5, 128.3, 126.2, 124.1, 123, 122.8, 122.7, 121.9 ppm.

1,6-bis-6-(3-nitrophenyl)-4-phenyl-1,3-diazaspiro[bicycle[3.1.0]hex-3-ene-2,3′-indoline]2′-one-hexane (8e)
White powder, yield: 71%, m.p. 284 ˚C. IR (KBr): 3100, 3058, 2925, 2858, 1712, 1668, 1614, 1519, 1465, 1350, 1224, 1168, 894, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.22-8.24 (br, H), 8.12 (t, J = 6.4 Hz, 2H), 8.01 (d, J = 7.6 Hz, 4H), 7.67 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 7.8 Hz, 2H), 7.48-7.58 (m, 6H), 7.36 (t, J = 6.8 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.02-7.08 (m, 4H) , 4.02 (s, 2H), 3.93 (t, J = 8.2 Hz, 4H), 3.21 (s, 2H), 1.96 (br, 4H), 1.27 (t, J = 7 Hz, 4H) ppm.

Results and Discussion

In this research new mono- and bis- photochromic compounds **5a**-**5b** and **8a**-**8e** based on isatin were prepared and their UV-Vis behavior in solid and solution forms was investigated. The derivatives of bis-isatins **7a**-**7c** were prepared via reaction of isatin **4** with dihalogenated alkenes **6a-6c** as link in the presence of NaH in dry DMF under argon atmosphere at 0˚ C. The desired products were prepared by the reaction of **7a**-**7c**, ketoaziridine **3a**-**3b** and 10 equivalents (NH_4OAc) in dry DMF or absolute EtOH (Scheme 1, 2). Compounds **3a**-**3b** were prepared according to the literature [15].

Scheme 1. General procedure for preparation of compounds **5a-b**

Scheme 2. General procedure for preparation of compounds **8a**-**8e**
All the photochromic compounds after exposing to the sun light or UV lamp (254 nm) show a change in their color which is due to the formation of open form. The intensity of color enhances as the duration of irradiation increases as a result of increasing the population of open form (Scheme 3).

Scheme 3. Photochromic behavior of compound **8a**.
The photochromic behavior of these compounds was investigated in EtOH. According to the figure 1 compound **8a** showed photochromic behavior in solution, however after 20 min of irradiation the absorption decreased.

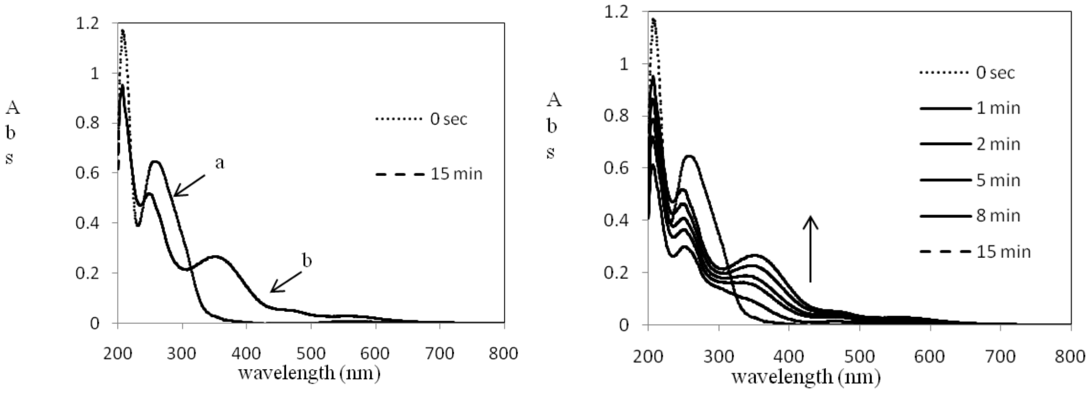

Figure 1. UV-Visible spectra of compound **8a** before irradiation (a) and after irradiation (b).

This phenomena shows that in solution photocyclization between their closed isomer and open isomer can not be repeated as well as solid state. As the figure 1 shows the compound does not have any absorption in visible region before irradiation, the absorption in UV region before and after irradiation is related to $\pi \rightarrow \pi^*$ transformations. After irradiation the absorption in visible region emerges and increases by 15 min. UV-Vis data of compounds **5a-b** and **8a-e** are shown in table 1.

Table 1. Spectroscopic data of compounds **5a-5b** and **8a-8e**

Entry	λ^A_{max} (nm)	λ^B_{max} (nm)	Color (before)	Color (after)
5a	262	370, 480	yellow	blue
5b	250, 288	480	white	pink
8a	252, 270	383, 480	white	red
8b	251, 264	489, 580	Light pink	Dark pink
8c	250, 266	388, 481	yellow	blue
8d	268	380, 487	white	pink
8e	251, 262	380, 391, 480	yellow	blue

The ^{1}H NMR spectra of compounds **5a**, **8a-b** and **8d** in $CDCl_3$ solution indicates the equilibrium ratio for open:closed isomers (the spectra are available in supplementary material). The identity of the two isomers was easily assigned based on an analysis of the integration of characteristic signals for each isomer.

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