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Chinese Chemical Letters 21 (2010) 1199–1202

CHINESE CHEMICAL LETTERS

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Synthesis and photochromic behavior of mono-, and biphotochromic system linked by *p*-phenylene bridge

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Received 3 March 2010

Abstract

The synthesis of mono- and bis-1,3-diazabicyclo[3.1.0]hex-3-ene derivatives with indole ring and *p*-phenylene spacer, which behave as photochromic materials, is reported. The structure–photochromic behavior relationship (SPBR) of the synthesized compounds has been analyzed.

Keywords: Biphotochromic; *p*-Phenylene bridge; Bis-1,3-diazabicyclo[3.1.0]hex-3-ene

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Photochromic compounds undergo a photo-induced reversible isomerization process between two isomers with different absorption spectra upon irradiation with light of appropriate wavelength [1–3]. Although many types of photochromic compounds have been synthesized so far, few molecules that show photochromic reactivity in the crystalline state are reported [4–6]. Solid-state organic photochromic molecules have attracted much attention due to their potential applications in various optoelectronic devices such as optical memory, optical switch, electronic display, information storage, and so on. Among them, the 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives are a class of unique photochromic compounds, which generate bistable molecules and undergo photochromism in the crystalline state. In continuation to our prior work in the field of synthesis of 1,3-diazabicyclo[3.1.0]hex-3-ene systems and their applications in photochromism organic chemistry [7–13].

In this paper, a novel mono-**1**, **2** and bis-**3**, **4** photochromic compounds contain indole moiety and *p*-phenylene spacer for first time is reported (Scheme 1).

The general preparation of the photochromic compounds **1**–**4** is depicted in Scheme 2. Reaction of indole with 1,4-bis(chloromethyl)benzene in the presence of NaH in dry DMF under nitrogen atmosphere leads to the preparation of bis-indole **8** in 72% yield. This recrystalized pure bis-indole was taken for Vilsmeier–Haack reagent ($POCl_3$, DMF) at room temperature, to produce a bis-aldehyde **7** in 89% yield [14]. Reaction of both one equivalent of indole 3-carbaldehyde or half-equivalent of bis-aldehyde **7** together with one equivalent of ketoaziridines (**5** or **6**) and 10 hg equivalents of NH_4OAc under anhydrous conditions afforded the desired compounds **1**–**4** in good yields (70–80%). Ketoaziridines **5**, **6** was prepared according to literature [7,9,10]. DMF was dried over activated 0.4 nm molecular

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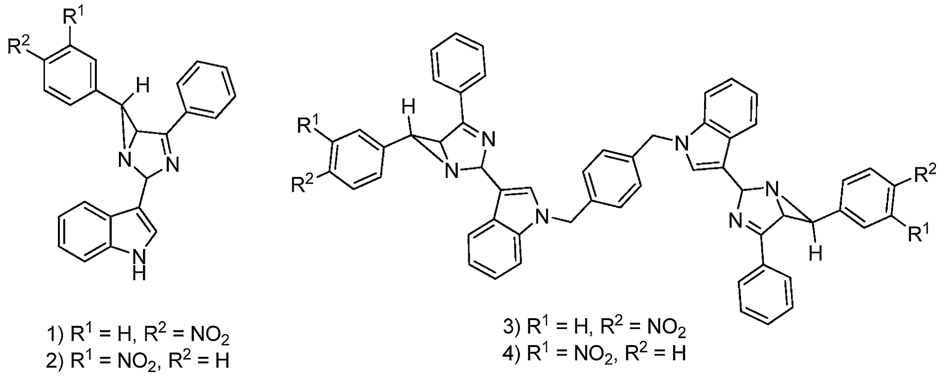
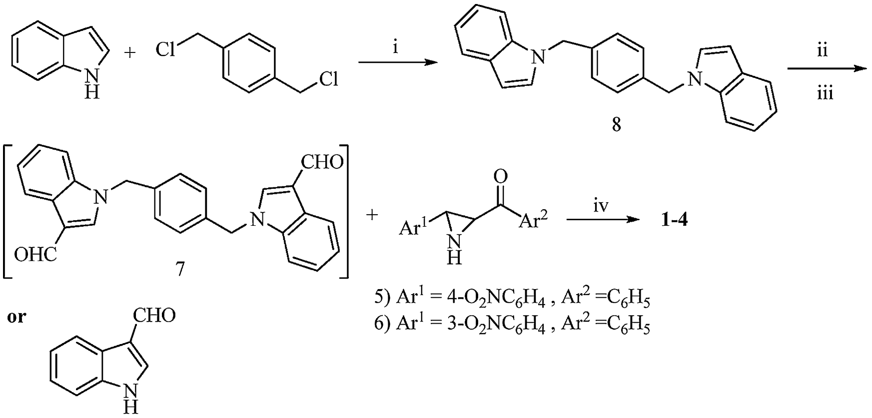
doi:10.1016/j.cclet.2010.04.036



Scheme 1. Structure of photochromic compounds **1**–**4**.



i) NaH/DMF, 0 °C, ii) $POCl_3$/DMF, iii) NaOH/H_2O, 0 °C, iv) NH_4OAc, EtOH, rt

Scheme 2. Synthetic route for the preparation of compounds **1**–**4**.

sieves and EtOH was distilled from Mg, the other reagents and solvents were commercial and used without further purification.

The colorless solids **1** and **2**, after remaining for ~5–10 s under the sunlight, changed the color; this due to the formation of zwitterionic double charged imine ylide **B** (open formed) [7,10]. Compound **1A** with NO_2 group in *para* position changed to deep green **1B**, while compound **2A** with NO_2 group in *meta* position changed to pink **2B** (Fig. 1). Compounds **1** and **2** with one photochromic center in solid state were bleached by heating them in the oven for 4–

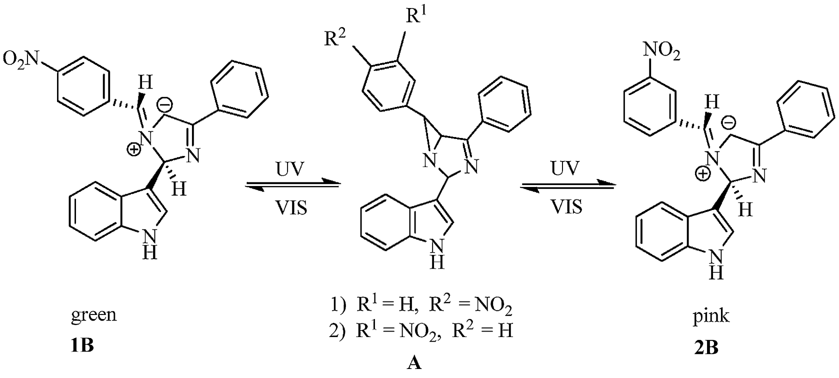
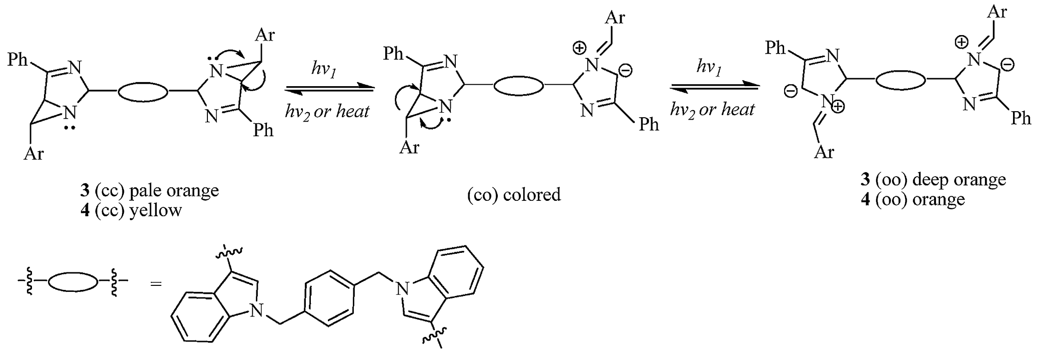


Fig. 1. The photoinduced (UV and VIS) transformations of colorless photochromic compounds **1A** and **2A**, and conversion to **1B** (green) and **2B** (pink).



Scheme 3. Photochromic reactions of bis-1,3-diazabicyclo[3.1.0]hex-3-enes **3** and **4**.

5 min. However, compounds **3** and **4** with two photochromic centers after 10–12 min heating in oven was converted to the initial forms. The repeatable cycle number in solid phase for **1** and **2** is estimated to be $>10^4$ times. Upon alternating irradiation with UV and visible light, the bis- and mono-bicyclic aziridine derivatives undergo reversible cycloreversion/cyclization photochromic reactions between the **cc**, **co** and **oo** isomers.

Compounds **3** and **4** contain two photochromic centers that linked by premade *p*-phenylene spacer, upon exposure to the light sources undergo reversible photocyclization concerning their close–close ring isomer (**cc**), close–open ring isomer (**co**) and open–open ring isomer (**oo**) forms. Photoisomerization of these photochromic compounds with a *p*-phenylene spacer unit are illustrated in Scheme 3. The nitrile ylide of photoisomers **3** (**oo**) and **1B** with a *para*-NO_2 group is more highly stabilized than photoisomers **4** (**oo**) and **2B** with *meta*-NO_2 substitution. The pale orange **3** (**cc**) after 15 s exposure to sunlight converted to the deep orange **3** (**oo**), while yellow **4** (**cc**) changes to orange **4** (**oo**).

The photochromic behavior of **1–4** in ethanol induced by photoirradiation at room temperature was also studied [15]. Fig. 2 shows the absorption spectral change of EtOH solution of compound **3** upon irradiation with 254 nm light ($c = 1.0 \times 10^{-4}$ mol/L). Upon irradiation with UV light, colorless solution of the close-ring isomer **3** (**cc**) changed to the yellow color open-ring isomers **3** (**co**) and **3** (**oo**). The absorption spectrum returned to its initial state when it was irradiated with visible light at longer wavelength than 450 nm.

The wavelengths maximum absorption of 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives **1–4** before (λ^{A}_{max}, nm) and after (λ^{B}_{max}, nm) irradiation in EtOH at 254 nm wavelength are shown in Table 1. Photochromic compounds **1** and **3** with NO_2 group in *para* position, exhibit a bathochromic shift in comparison with compounds **2** and **4** with NO_2 group in *meta* position. This noticeable bathochromic shift (~38–44 nm) means that *para*-NO_2 group participates in the π conjugation of the central photochromic backbone more effective than *meta*-NO_2 group.

Detailed procedures for synthesis of compounds **1–4** and **8** and analytical data of compounds **1–4** and **8** are available in supporting information.

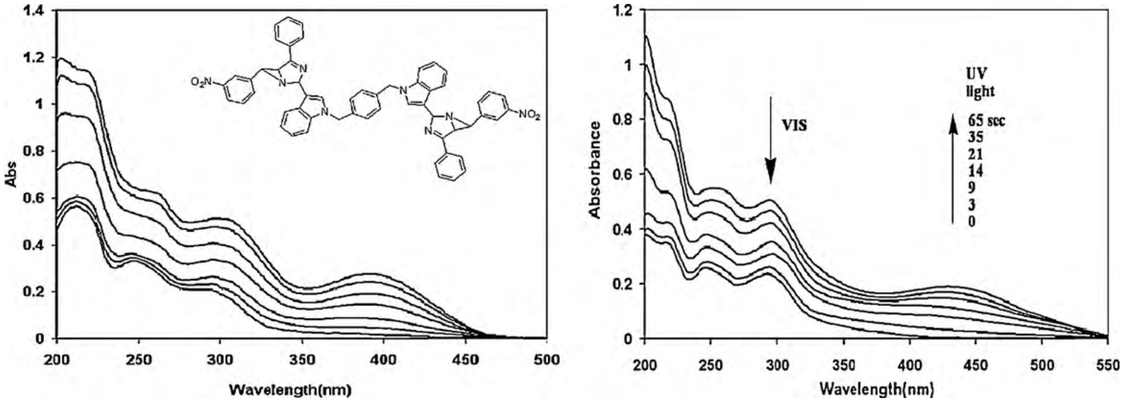


Fig. 2. UV–vis absorption spectra of **3** (left) and **4** (right) upon irradiation under 254 nm light in EtOH ($c = 1.0 \times 10^{-4}$ mol/L) before and after successive UV irradiation for 65 s.

Table 1
UV–vis data of the 1,3-diazabicyclo[3.1.0]hex-3-enes in EtOH.

Compound	λ_{max}^{A} (nm)	λ_{max}^{B} (nm)
1	201, 266	219, 254, 284, 434
2	219, 243	213, 260, 307, 390
3	202, 217, 247, 296	202, 257, 292, 429
4	212, 246, 288	202, 296, 391

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2010.04.036.

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[14] The typical procedure for the synthesis of 1-((4-((3-formyl-1H-indol-1-yl)methyl)phenyl)methyl)-1*H*-indole-3-carbaldehyde 7 was described as follows: $POCl_3$ (1.8 mL, 19.8 mmol) was added slowly to dry DMF (9.1 mL) at 0 °C, after 30 min a solution of 8 (2.2 g, 6.64 mmol) in DMF (46 mL) was added drop wise over 1 h at 0 °C. The mixture was stirred at r.t. for 6 h and poured into 5 mol/L sodium hydroxide (95.24 mL). The mixture heated at 100 °C for 30 min and allowed to cool. The white precipitate was filtered off. Washed with water and purified by silica gel column chromatography to give a pale yellow solid 2.3 g (89%), mp = 294 °C, IR (KBr): 3100, 3050, 2910, 2750, 2800, 1657, 1610, 1528, 1461, 1400 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.92 (s, 2H), 8.43 (s, 2H), 8.11–8.09 (m, 2H), 7.56–7.54 (m, 2H), 7.29 (s, 4H), 7.26–7.23 (m, 4H), 5.5 (S, 4H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 185.56, 141.79, 137.79, 137.27, 128.60, 125.65, 124.5, 123.43, 121.95, 118.29, 112.21, 50.25; HRMS *m/z* (EI) calcd. for $C_{26}H_{20}N_2O_2$ 392.1525. Found 392.1529; Anal. calcd. for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14; Found: C, 79.56; H, 5.13; N, 7.16.

[15] The photoinduced (open) form **B** was formed upon UV irradiation (Hg lamp DRSh-260+ UV-transmitting glass filters), and visible light was generated by a 500 W Xe lamp with a standard band-pass filter 550 AF10 (omega).