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Synthesis and photochromism of 1,3-diazabicyclo[3.1.0]hex-3-ene phenol rings

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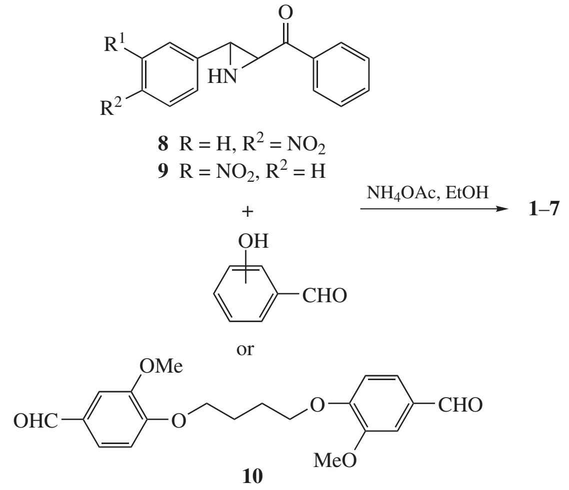
The facile synthesis of mono and bis 1,3-diazabicyclo[3,1,0]hex-3-ene derivatives containing phenol ring, which behave as photochromic materials, is reported.

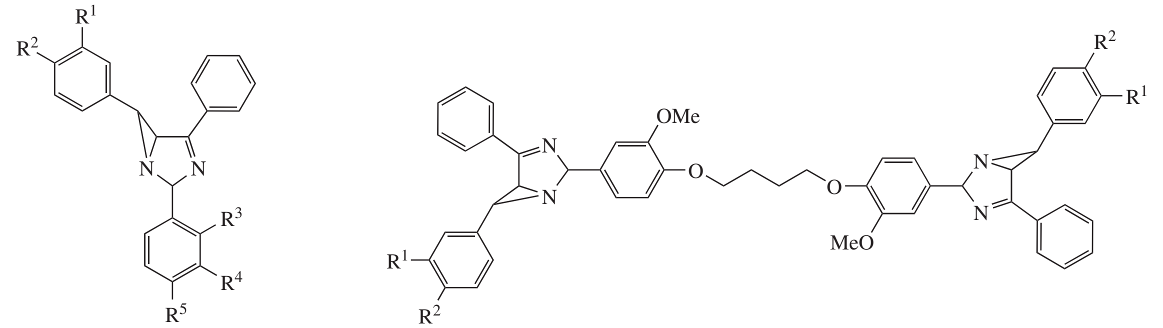
Photochromism is a well-known phenomenon associated with reversible transformations of **A** and **B**, each exhibiting different absorption characteristics upon irradiation with UV and visible light.[1–5] Photochromic compounds reversibly change not only the absorption spectra but also their geometrical and electronic structures upon irradiation.[6] Although many types of photochromic compounds have been reported, those that exhibit photochromic reactions in a crystal state are very rare.[7,8] 1,3-Diazabicyclo[3.1.0]hex-3-ene derivatives possess exclusive photochromic properties. These compounds show photochromic behaviour even in a crystalline state. Depending on the particular structure, 1,3-diazabicyclo[3.1.0]hex-3-ene derivative crystals turn yellow, purple, blue or green upon UV irradiation.[9–13] Recently, we use novel potentiometric membrane sensors based on 6-(4-nitrophenyl)-2,4-diphenyl-1,3-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 the detection of tin(II)[14] and strontium(II)[15] at trace levels in environmental samples, respectively. In this communication, we report the synthesis of new mono-photochromic compounds **1**–**5** and bis-photochromic compounds **6**, **7** (Figure 1).

The general preparation of photochromic compounds **1**–**7** is depicted in Scheme 1. The reaction of vanillin with 1,4-dibromobutane in the presence of K_2CO_3 in DMF leads to bis-aldehyde **10** in 80% yield.[16] Reaction of either one equivalent of hydroxy benzaldehydes or a half-equivalent of bis-aldehyde **10**, and one equivalent of ketoaziridines (**8** or **9**), and 10 equivalents of ammonium acetate under anhydrous conditions afforded desired compounds **1**–**7** in good yields (60–80%).[†]



Scheme 1 Synthetic route for the preparation of compounds **1**–**7**.

The colourless solids **A1**–**A5** after 5–25 s standing under a fluorescence lamp or sunlight change to pale yellow and pink solids for **B1** and **B5**, and to blue solids for **B2**–**B4** (Scheme 2). Visible light did not cause photoinduced (open) form **B** to occur. However, sunlight and fluorescent UV light initiated the photochoromism. Compounds **6** and **7**, which contain two photochromic centres linked by an O-alkyl spacer, upon exposure to the above light sources undergo reversible photocyclization



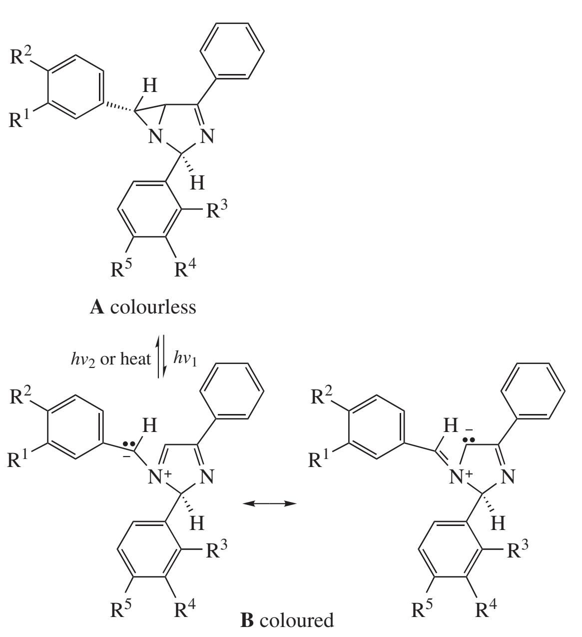
1 $R^1 = R^4 = R^5 = H$, $R^2 = NO_2$, $R^3 = OH$
2 $R^1 = R^3 = R^5 = H$, $R^2 = NO_2$, $R^4 = OH$
3 $R^1 = R^3 = R^4 = H$, $R^2 = NO_2$, $R^5 = OH$
4 $R^1 = R^3 = H$, $R^2 = NO_2$, $R^4 = OMe$, $R^5 = OH$
5 $R^1 = NO_2$, $R^2 = R^3 = R^5 = H$, $R^4 = OH$

6 $R^1 = H$, $R^2 = NO_2$
7 $R^1 = NO_2$, $R^2 = H$

Figure 1

between their closed-closed ring isomer (cc), closed-open ring isomer (co) and open-open ring isomer (oo) forms (Scheme 3). The pale orange **AA6** after 15 s exposure to sunlight converted to deep orange **BB6**, while colourless **AA7** changes to yellow **BB7** (Scheme 3). Irradiation of the EtOH solution of **1A**–**5A**, **6AA** and **7AA** at 254 nm generated the coloured open forms **1B**–**5B**, **6BB** and **7BB**, which reverted to the original species upon heating at 80–90 °C for 4–5 min.

The pronounced photochromic behaviour of **2** over **5** can be attributed to the electron-withdrawing effect of *para*-NO_2 substitution (Scheme 2). The nitrile ylide of photoisomer **2B** with a *para*-NO_2 group is more highly stabilized than photoisomer **5B** with *meta*-NO_2 substitution. 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.[8–11,17,18]



Scheme 2 Photochromic reactions of 1,3-diazabicyclo[3,1,0]hex-3-enes **1**–**5**.

The photochromic behaviour of **1**–**7** in ethanol induced by photoirradiation at room temperature was also studied. Mono- and bis-1,3-diazabicyclo[3.1.0]hex-3-enes showed good photochromic properties and could be switched between their colourless closed-ring isomers [**1A**–**5A**, **6AA** (pale orange) and **7AA**] and coloured open-ring isomers (**1B**–**5B**, **6BB** and **7BB**) (Schemes 2 and 3).

Figure 2 shows the UV-visible spectra of **3** in EtOH (c = $= 1.0\times10^{-4}$ mol dm^{-3}). Compound **3** exhibits absorption maxima at 205 and 262 nm at 0 s (closed form), UV irradiation causes

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[†] Melting points were measured on a Mettler Fp5 apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu IR-470 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker 500 MHz instrument using solvent as an internal standard ($CDCl_3$ at 7.26 ppm, [$^2H_6$]DMSO at 2.50 ppm). The absorption spectra in the range 200–800 nm (EtOH, c 1.0×10^{-4} mol dm^{-3}), as well as the positions of absorption band maxima for initial **A** ($\lambda^{\mathrm{A}}_{\max}$/nm) and photoinduced **B** ($\lambda^{\mathrm{B}}_{\max}$/nm) forms were measured with a Shimadzu UV-2100 spectrophotometer. The photoinduced (open) form **B** was formed upon UV irradiation (Hg lamp DRSh-260+ UV-transmitting glass filters). Reversion to the initial form **A** was achieved upon either storage in the dark for 1–7 days or by heating at 80–90 °C for 4–5 min. TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300).

General procedure for the synthesis of mono and bis 1,3-diazabicyclo-[3.1.0]hex-3-ene derivatives **1**–**7**. A mixture of ketoaziridine **8** or **9** (268 mg, 1 mmol), hydroxy aldehyde (1 mmol), and ammonium acetate (750 mg, 10 mmol) in absolute ethanol (7 ml) was vigorously stirred at room temperature for 2–4 days. The colour of the reaction mixture gradually changed, and after completion of reaction solid compounds precipitated. The reaction mixture was filtered, solids washed with EtOH (3×15 ml), purified by column chromatography (ethyl acetate/light petroleum, 3:1) to yield the desired compounds. Bis-1,3-diazabicyclo[3.1.0]hex-3-ene **6** and **7** were prepared analogously using bis-aldehyde **10** instead of hydroxy aldehydes.

2-{6-(4-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl}-phenol **1**: yield 75%, mp 167–168 °C, colourless solid, after irradiation with UV light converted to pale pinkish. IR (KBr, ν/cm^{-1}): 3400, 3010, 1600, 1515, 1325. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.51 (s, 1H), 3.81 (s, 1H), 6.69 (s, 1H), 6.75 (t, 1H, J 7.5 Hz), 6.85 (d, 1H, J 8.1 Hz), 7.14 (t, 1H, J 7.7 Hz), 7.28 (d, 1H, J 7.7 Hz), 7.42–7.46 (m, 4H), 7.53 (t, 1H, J 7.5 Hz), 7.87 (d, 2H, J 7.4 Hz), 8.16 (d, 2H, J 8.6 Hz), 9.40 (s, 1H). UV-Vis (EtOH, $\lambda_{\max}$/nm): 205, 245, 256, 276 (sh.) before irradiation and 205, 245, 262, 405 after irradiation.

4-{6-(4-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl}-phenol **3**: yield 75%, mp 180–181 °C, colourless solid, after irradiation with UV light converted to blue. IR (KBr, ν/cm^{-1}): 3400, 3010, 1605, 1520, 1340. Closed form, **3A**: 61%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.43 (s, 1H), 3.59 (s, 1H), 6.55 (s, 1H), 6.65 (d, 2H, J 8.5 Hz), 7.15 (d, 2H, J 8.4 Hz), 7.24 (d, 2H, J 8.6 Hz), 7.33 (t, 2H, J 3.5 and 7.6 Hz), 7.37 (t, 1H, J 4.2 and 7.4 Hz), 7.80 (d, 2H, J 8.2 Hz), 7.98 (d, 2H, J 8.6 Hz), 8.50 (s, 1H). Open form, **3B**: 39%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.60 (d, 1H, J 1.3 Hz), 3.57 (d, 1H, J 2.1 Hz), 6.02 (d, 1H, J 2.6 Hz), 6.72 (d, 2H, J 8.4 Hz), 7.15 (d, 2H, J 8.4 Hz), 7.33 (t, 2H, J 3.5 and 7.6 Hz), 7.38 (t, 1H, J 4.2 and 7.4 Hz), 7.38 (d, 2H, J 8.7 Hz), 7.80 (d, 2H, J 8.2 Hz), 8.03 (d, 2H, J 8.6 Hz), 8.53 (s, 1H). UV-Vis (EtOH, $\lambda_{\max}$/nm): 205, 240, 262, 278 (sh.) before irradiation and 205, 240, 280, 415 after irradiation.

2-Methoxy-4-{6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl}phenol **4**: yield 80%, mp 189–190 °C, colourless solid, after irradiation with UV light converted to deep blue. IR (KBr, ν/cm^{-1}): 3400, 3020, 1595, 1510, 1340, 1264. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.50 (s, 1H), 3.79 (s, 1H), 3.84 (s, 3H), 6.73 (s, 1H), 6.87 (d, 1H, J 8.2 Hz), 7.00 (d, 1H, J 8.0 Hz), 7.10 (s, 1H), 7.42 (d, 2H, J 8.6 Hz), 7.51 (d, 2H, J 7.26 Hz), 7.58 (t, 1H, J 7.5 Hz), 8.02 (d, 2H, J 7.3 Hz), 8.18 (d, 2H, J 8.6 Hz). UV-Vis (EtOH, $\lambda_{\max}$/nm): 220, 280 before irradiation and 220, 280, 420 after irradiation.

4-{3-Methoxy-4-[4-(2-methoxy-4-{6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl}phenoxy)butoxy]phenyl}-6-(4-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene **6**: yield 72%, mp 195–196 °C, pale orange solid, after irradiation with UV light converted to deep orange. IR (KBr, ν/cm^{-1}): 3010, 2880, 1600, 1520, 1340, 1260. Closed form, **6AA**: 58%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.94–1.96 (q, 4H, J 2.8 and 6.0 Hz), 2.44 (s, 2H), 3.69 (s, 6H), 3.80 (s, 2H), 4.02 (t, 4H, J 6.7 Hz), 6.67 (s, 2H), 6.76 (d, 2H, J 8.5 Hz), 6.95 (d, 2H, J 7.2 Hz), 6.98–7.02 (m, 2H), 7.33 (dd, 4H, J 1.6 and 8.6 Hz), 7.41–7.44 (m, 4H), 7.48 (d, 4H, J 7.9 Hz), 7.91 (d, 4H, J 7.2 Hz), 8.09 (d, 4H, J 8.6 Hz). Open form, **6BB**: 42%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.94–1.96 (q, 4H, J 2.8 and 6.0 Hz), 2.70 (d, 2H, J 1.2 Hz), 3.71 (s, 6H), 3.82 (s, 6H), 4.04 (t, 4H, J 6.8 Hz), 6.13 (d, 2H, J 2.7 Hz), 6.85 (d, 2H, J 8.5 Hz), 6.98–7.02 (m, 4H), 7.41–7.44 (m, 4H), 7.48 (d, 4H, J 7.9 Hz), 7.91 (d, 4H, J 7.2 Hz), 8.14 (d, 4H, J 8.6 Hz). UV-Vis (EtOH, $\lambda_{\max}$/nm): 206, 240 before irradiation and 206, 230, 275, 315, 390 after irradiation.

4-{3-Methoxy-4-[4-(2-methoxy-4-{6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl}phenoxy)butoxy]phenyl}-6-(3-nitrophenyl)-2-phenyl-3,5-diazabicyclo[3.1.0]hex-2-ene **7**: yield 68%, mp 175–176 °C, colourless (almost white) solid, after irradiation with UV light converted to yellow. IR (KBr, ν/cm^{-1}): 3010, 2900, 1600, 1515, 1340, 1260. Closed form, **7AA**: 52%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.94–1.96 (m, 4H), 2.46 (s, 2H), 3.70 (s, 6H), 3.80 (s, 2H), 4.01 (t, 4H, J 6.7 Hz), 6.67 (d, 2H, J 4.2 Hz), 6.68 (s, 2H), 6.77 (d, 2H, J 8.5 Hz), 6.95 (d, 2H, J 6.7 Hz), 6.98–7.02 (m, 2H), 7.37–7.49 (m, 9H), 7.92 (d, 4H, J 7.3 Hz), 8.03–8.09 (m, 4H), 8.17 (s, 2H). Open form, **7BB**: 48%, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.94–1.96 (m, 4H), 2.71 (d, 2H, J 1.3 Hz), 3.73 (s, 6H), 3.82 (s, 2H), 4.04 (t, 4H, J 7.5 Hz), 6.13 (d, 2H, J 2.8 Hz), 6.85 (d, 2H, J 8.5 Hz), 6.98–7.02 (m, 4H), 7.37–7.49 (m, 9H), 7.92 (d, 4H, J 7.3 Hz), 8.03–8.09 (m, 4H). UV-Vis (EtOH, $\lambda_{\max}$/nm): 205, 242 before irradiation and 205, 280, 320, 420 after irradiation.

For characteristics of compounds **2** and **5**, see Online Supplementary Materials.

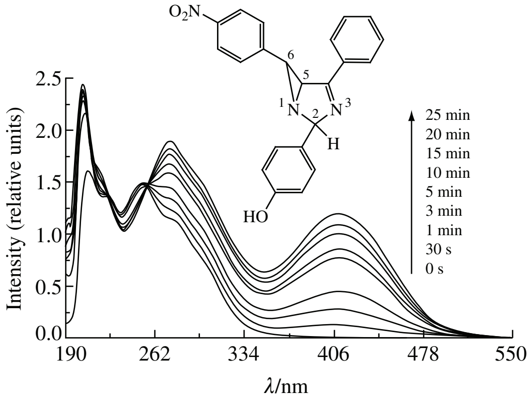

Figure 2 UV-Vis absorption spectra of **3** upon irradiation under 254 nm light in EtOH ($c = 1.0\times10^{-4}$) before and after successive UV irradiation (λ_{max} = 205, 262 nm for **3A** and 205, 280, 415 nm for **3B**).

absorption at 280, 415 nm for **3B** due to the formation of zwitterionic double charged imine ylide (open form).

At different irradiation times between 0–25 min, a well-defined isosbestic point at 258 nm is observed, which indicates that clean photochemical transformations occur (Figure 2).

3B was also converted to **3A** either by stirring in the dark for two days or after being held at 90 °C for 4–5 min. Compounds **1**, **2** and **4**–**7** showed photochromic behaviour both in solid form and EtOH solution comparable to **3**.

The ^{1}H NMR spectrum of compound **3** in $CDCl_3$ solution indicates the equilibrium ratio for **3A**:**3B** isomers at steady state to be 61:39 upon exposure to room light. The identity of the two isomers was easily assigned based on an analysis of the integration of four characteristic signals for each isomer: 2-H, 5-H, 6-H and phenolic OH. Thus, the ratio of the combined integral for the peaks at δ 6.55 (s, 2-H), 3.59 (s, 5-H), 2.43 (s, 6-H) and 8.50 (s, OH) for **3A** to corresponding peaks **3B** λ_{max} = 205, 262 nm for **3A**, and 205, 280, 415 nm for **3B** at δ 6.02 (d, 2-H), 3.57 (d, 5-H), 2.60 (d, 6-H) and 8.53 (s, OH) was *ca.* 1.12 to 2.86 for **3B**:**3A**, ~39:61% at equilibrium. This ratio for bis-photochromic **6BB**:**6AA** or **7BB**:**7AA** was 42:58 or 48:52, respectively (**6AB** and **7AB** are not distinguishable by this method). The presence of an *ortho*-hydroxyphenyl group at the 2-position of the imidazoline ring was found to induce large chemical shifts in either the closed or open-ring forms of **1** due to hydrogen bonding with N1 or N3 [δ 9.40 (OH) instead of 8.5 for **2**, **3**, **5** and 7.1 for **4**].

In conclusion, bicyclic aziridines represent a very interesting class of organic compounds possessing unique photochromic properties. These compounds form deeply coloured, fairly stable materials under UV radiation. This property allows us to consider them as candidates in the search for intelligent photochromic materials.

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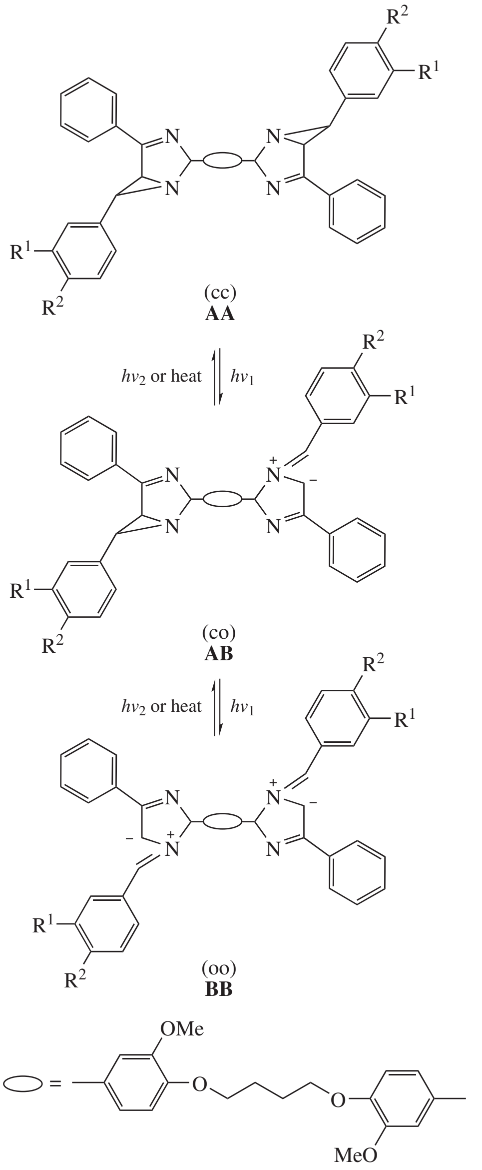
Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.07.010.



Scheme 3 Photochromic reactions of bis 1,3-diazabicyclo[3,1,0]hex-3-enes **6** and **7**.

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