Research Article

Synthesis and Photochromism of Quinolines and Benzo[h]quinolines of 1,3-Diazabicyclo[3.1.0]hex-3-ene

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1,3-Diazabicyclo[3.1.0]hex-3-ene systems represent a very interesting class of organic materials, possessing unique photochromic properties in the solid state. It has been demonstrated that these compounds form deeply colored, fairly stable materials under UV radiation. Here, for the first time we report synthesis of several 1,3-diazabicyclo[3.1.0]hex-3-enes with premade substituted quinoline and benzo[h]quinoline rings.

1. Introduction

Photochromism is defined as light-induced reversible transformation of a chemical species between two isomers having different absorption spectra [1–3]. During photoisomerization, along with absorption spectra, the chemical and physical properties of isomers such as refraction coefficient, dielectric constant, viscosity, and color apparently changed. Such change in the molecular properties may usefully be utilized in many optic devices such as removable optic memories and within components of light switching device [4, 5]. Although many types of photochromic compounds have been reported so far, crystals that show photochromic reactions in the crystal state are very rare [6, 7]. 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 of crystals, 1,3-diazabicyclo[3.1.0]hex-3-ene derivative turns yellow, pink, blue, or green upon UV irradiation. 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, and information storage. Typical examples include N-salicylideneanilines,

dinitrobenzylpyridines, diphenylmaleonitriles, triarylimidazole dimers, aziridines, diarylethenes, diarylperfluorocyclopentenes, and biindenylidenedione derivatives. Among them, 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives that are synthesized from aziridine moiety are a class of unique photochromic compounds, which generate bistable molecules and undergo photochromism in the crystalline state. This property allows us to consider bicyclic aziridines as possible candidates in the search for radiochromic materials [8–12]. Here, for the first time we report the synthesis of new 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives that possess quinoline and benzo[h]quinoline rings.

2. Experiments

2.1. General Procedure. All of the chemicals were purchased from Merck and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. All ¹H and ¹³C NMR data were recorded in CDCl₃ using a Bruker Avance 500-MHZ spectrometer, the chemical shifts are reported in ppm (δ) using deuterated solvents as internal references. UV spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Elemental analyses were performed with a Carlo-Erba

EA1110 CNNO-S analyzer. The IR spectra were recorded on a Shimadzu IR-470 spectrophotometer.

2.2. Synthesis. To the solution of synthesised aldehydes (1 mmol), ketoaziridine (1 mmol) in dry ethanol (5 mL) was added along with ammonium acetate (10 mmol) at rt. The reaction mixture was stirred for 2 days at rt. The precipitate was collected by filtration and washed with small portions of hot EtOH to furnish the desired products in 65–80% yields.

2-Chloro-3-[6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]quinoline (3). Yield is 75%. Melting point is 225–226°C. White solid was converted to blue after irradiation with UV light; IR (KBr, ν/cm^{-1}): 3080, 3060, 3020, 2800, 1610, 1590, 1540, 1520, 1490, 1450, 1340, 1050, 930, 705, 740, 730, 690. Closed-form, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.50 (s, 1H), 3.76 (s, 1H), 6.99 (s, 1H), 7.40 (d, $J = 8.3$ Hz, 2H), 7.53–7.57 (m, 3H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.73 (td, $J = 1.0, 8.2$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 8.01 (d, $J = 9.0$ Hz, 2H), 8.04 (d, $J = 7.3$ Hz, 2H), 8.08 (d, $J = 8.7$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 41.5, 57.8, 93.2, 124.1, 127.1, 127.8, 128.0, 128.2, 128.8, 129.1, 129.5, 130.7, 131.3, 131.6, 132.8, 138.4, 144.8, 147.8, 147.9, 150.3, 173.1. UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 208, 232, 316 before irradiation and 208, 232, 406 after irradiation. Anal. Calcd for $\text{C}_{25}\text{H}_{17}\text{ClN}_4\text{O}_2$; C, 68.11; H, 3.89; Cl, 8.04; N, 12.71; O, 7.26; found C, 68.12; H, 3.88; Cl, 8.05; N, 12.72; O, 7.24.

2-Chloro-3-[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]quinoline (4). White solid. Yield is 82%. Melting point 196–197°C; IR (KBr, ν/cm^{-1}): 3080, 3060, 3020, 2800, 1610, 1590, 1540, 1520, 1490, 1450, 1340, 1050, 930, 705, 740, 730, 690. Closed-form, **4A**: 57%, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.53 (s, 1H), 3.77 (t, $J = 1.8$ Hz, 1H), 6.99 (s, 1H), 7.42 (t, $J = 7.9$ Hz, 1H), 7.51–7.62 (m, 5H), 7.72–7.76 (m, 2H), 7.76 (d, $J = 8.13$ Hz, 1H), 8.00–8.06 (m, 4H), 8.09 (app t, $J = 1.9$ Hz, 1H), 8.16 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 41.3, 57.6, 93.2, 122.3, 123.0, 127.1, 127.8, 128.2, 128.8, 129.1, 129.2, 129.5, 129.9, 130.7, 131.3, 131.7, 132.7, 133.2, 138.4, 147.9, 148.7, 150.3, 173.1. After irradiation with UV light, it converted to pink; open-form, **4B**: 43%, ^1H NMR (500 MHz, CDCl_3): δ 3.00 (d, $J = 2.0$ Hz, 1H), 3.77 (t, $J = 2.3$ Hz, 1H), 6.67 (d, $J = 2.9$ Hz, 1H), 7.51–7.62 (m, 6H), 7.72–7.76 (m, 1H), 7.82 (d, $J = 6.4$ Hz, 1H), 8.00–8.06 (m, 4H), 8.16 (m, 1H), 8.26 (app t, $J = 1.9$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 48.6, 57.0, 94.7, 112.0, 123.2, 127.6, 127.8, 128.3, 128.8, 129.1, 129.2, 129.5, 130.0, 130.7, 131.2, 131.6, 132.6, 133.2, 139.7, 147.9, 148.9, 150.3, 169.0. UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 206, 236, 320 before irradiation and 221, 262, 376 after irradiation. Anal. Calcd for $\text{C}_{25}\text{H}_{17}\text{ClN}_4\text{O}_2$; C, 68.11; H, 3.89; Cl, 8.04; N, 12.71; O, 7.26; found C, 68.13; H, 3.88; Cl, 8.03; N, 12.73; O, 7.24.

2-Chloro-6-methyl-3-[6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]quinoline (5). Yield is 80%. Melting point is 218–219°C, as a pale green solid; IR (KBr, ν/cm^{-1}): 3100, 3080, 3030, 2950, 2900, 1600, 1560, 1510,

1490, 1445, 1380, 1345, 1300, 1285, 1260, 1200, 1180, 1105, 1055, 1022, 1010, 990, 960, 925, 860, 818, 770, 740, 690, 635. Closed-form, **5A**: 27%, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.56 (s, 4H), 3.80–3.82 (m, 1H), 7.04 (s, 1H), 7.45 (d, $J = 8.8$ Hz, 2H), 7.58–7.68 (m, 5H), 7.95–8.01 (m, 3H), 8.08–8.11 (m, 1H), 8.15 (d, $J = 8.8$ Hz, 2H). After irradiation with UV light it was converted to deep green; open-form, **5B**: 73%, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.57 (s, 3H), 3.05 (d, $J = 1.7$ Hz, 1H), 3.80–3.82 (m, 1H), 6.70 (d, $J = 2.8$ Hz, 1H), 7.58–7.68 (m, 7H), 8.08–8.11 (m, 4H), 8.28 (d, $J = 8.8$ Hz, 2H). UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 208, 239 before irradiation and 207, 241, 404 after irradiation. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{ClN}_4\text{O}_2$; C, 68.65; H, 4.21; Cl, 7.79; N, 12.32; O, 7.03; found C, 68.64; H, 4.20; Cl, 7.77; N, 12.33; O, 7.01.

2-Chloro-6-methyl-3-[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]quinoline (6). Yield is 76%. Melting point is 189–190°C, as a white solid; IR (KBr, ν/cm^{-1}): 3080, 3040, 2980, 2910, 2850, 1600, 1570, 1520, 1490, 1450, 1342, 1300, 1270, 1180, 1060, 1025, 980, 920, 820, 770, 730, 690. Closed-form, **6A**: 59%, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.55 (s, 4H), 3.80 (d, $J = 1.3$ Hz, 1H), 7.03 (s, 1H), 7.47 (t, $J = 7.9$ Hz, 1H), 7.57–7.67 (m, 5H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.97 (s, 1H), 8.07–8.13 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 22.0, 41.2, 57.6, 93.2, 122.4, 123.0, 127.1, 127.2, 128.4, 129.1, 129.5, 130.5, 131.7, 132.7, 133.2, 133.6, 136.8, 137.7, 137.9, 139.7, 146.4, 148.6, 149.4, 173.0. After irradiation with UV light it was converted to yellow; open-form, **6B**: 41%, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.56 (s, 3H), 3.04 (s, 1H), 3.84 (d, $J = 2.0$ Hz, 1H), 6.69 (d, $J = 2.5$ Hz, 1H), 7.57–7.67 (m, 8H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.99 (s, 1H), 8.07–8.13 (m, 1H), 8.21 (d, $J = 8.1$ Hz, 1H), 8.30 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 22.0, 48.6, 57.0, 94.8, 122.0, 123.2, 127.2, 127.3, 128.4, 129.2, 129.9, 130.0, 131.6, 132.6, 133.2, 133.4, 136.8, 137.6, 137.9, 140.2, 146.4, 148.9, 149.4, 171.9. UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 213, 238 before irradiation and 211, 239, 361 after irradiation. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{ClN}_4\text{O}_2$; C, 68.65; H, 4.21; Cl, 7.79; N, 12.32; O, 7.03; found C, 68.66; H, 4.22; Cl, 7.80; N, 12.34; O, 7.00.

2-Chloro-6-methoxy-3-[6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]quinoline (7). Yield is 61%. Melting point is 226–227°C, as a pale green solid; IR (KBr, ν/cm^{-1}): 3100, 3070, 3000, 2940, 2830, 1620, 1590, 1510, 1495, 1442, 1340, 1230, 1182, 1060, 1020, 1000, 920, 825, 770, 740, 690, 535. Closed-form, **7A**: ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.55 (s, 1H), 3.81 (s, 1H), 3.94 (s, 3H), 7.02 (s, 1H), 7.20 (s, 1H), 7.43–7.49 (m, 3H), 7.58–7.66 (m, 3H), 7.95–8.09 (m, 4H), 8.15 (d, $J = 8.4$ Hz, 2H). After irradiation with UV light it was converted to deep green; open-form, **7B**: ^1H NMR (500 MHz, CDCl_3 , ppm): δ 3.03 (s, 1H), 3.94 (s, 1H), 3.96 (s, 3H), 6.68 (s, 1H), 7.24 (s, 1H), 7.43–7.49 (m, 1H), 7.58–7.66 (m, 5H), 7.95–8.09 (m, 4H), 8.27 (d, $J = 8.3$ Hz, 2H). UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 212, 246 before irradiation and 211, 248, 303 after irradiation. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{ClN}_4\text{O}_3$; C, 66.31; H, 4.07; Cl, 7.53; N, 11.90; O, 10.19; found C, 66.32; H, 4.06; Cl, 7.55; N, 11.92; O, 10.18.

2-Chloro-6-methoxy-3-[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]-quinoline (8). Yield is 79%. Melting point is 214–215°C, as a white solid, which after irradiation with UV light converted to pink. IR (KBr, ν/cm^{-1}): 3080, 3030, 3000, 2950, 2930, 2910, 1620, 1595, 1520, 1495, 1450, 1380, 1340, 1305, 1285, 1230, 1180, 1160, 1060, 1045, 1025, 980, 920, 830, 775, 730, 695. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.58 (s, 1H), 3.80 (s, 1H), 3.93 (s, 3H), 7.02 (s, 1H), 7.11 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 7.3 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.93–7.96 (m, 2H), 8.10 (d, J = 7.3 Hz, 3H), 8.13 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 41.2, 56.0, 57.6, 93.2, 105.8, 122.4, 123.0, 123.9, 128.2, 129.1, 129.5, 129.9, 130.1, 130.8, 131.7, 132.7, 133.2, 137.2, 139.7, 143.9, 147.6, 148.6, 158.8, 173.0. UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 213, 242 before irradiation and 214, 245, 366 after irradiation. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{ClN}_4\text{O}_3$; C, 66.31; H, 4.07; Cl, 7.53; N, 11.90; O, 10.19; found C, 66.32; H, 4.08; Cl, 7.55; N, 11.91; O, 10.17.

2-Chloro-3-[6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]-benzo[h]quinoline (9). Yield is 78%. Melting point is 202–203°C, as a pale green solid; IR (KBr, ν/cm^{-1}): 3050, 1595, 1560, 1505, 1475, 1445, 1430, 1400, 1370, 1340, 1300, 1275, 1180, 1110, 1060, 1015, 925, 860, 820, 800, 770, 745, 690. Closed-form, **9A**: 70%, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.59 (s, 1H), 3.82 (s, 1H), 7.10 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.59–7.77 (m, 6H), 7.87 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 8.08–8.13 (m, 5H), 9.23 (d, J = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 41.5, 57.4, 96.3, 124.1, 124.9, 125.1, 125.3, 127.9, 127.91, 128.0, 128.2, 129.1, 129.3, 129.5, 130.6, 131.0, 131.7, 132.8, 134.4, 138.0, 144.8, 146.6, 147.8, 149.4, 173.1. After irradiation with UV light, it converted to deep blue; open-form, **9B**: 41%, ^1H NMR (500 MHz, CDCl_3): δ 3.06 (s, 1H), 3.86 (s, 1H), 6.77 (d, J = 2.2 Hz, 1H), 7.59–7.77 (m, 7H), 7.87 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 8.08–8.13 (m, 3H), 8.20 (s, 1H), 8.25 (d, J = 8.4 Hz, 2H), 9.29 (d, J = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 48.4, 57.7, 94.8, 124.3, 124.9, 125.1, 125.3, 127.8, 127.91, 128.0, 128.2, 128.8, 129.0, 129.4, 130.6, 131.0, 131.7, 132.7, 134.4, 137.1, 145.2, 146.5, 147.7, 149.2, 173.1. UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 204, 235, 276 before irradiation and 203, 277, 403 after irradiation. Anal. Calcd for $\text{C}_{29}\text{H}_{19}\text{ClN}_4\text{O}_2$; C, 70.95; H, 3.90; Cl, 7.22; N, 11.41; O, 6.52; found C, 70.96; H, 3.92; Cl, 7.21; N, 11.40; O, 6.51.

2-Chloro-3-[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl]-benzo[h]quinoline (10). Yield is 73%. Melting point is 191–192°C, as a white solid, IR (KBr, ν/cm^{-1}): 3080, 3050, 3020, 2970, 1605, 1570, 1525, 1400, 1370, 1345, 1180, 1060, 1020, 910, 810, 730, 690. Closed-form, **10A**: 51%, ^1H NMR (500 MHz, CDCl_3 , ppm): δ 2.60 (s, 1H), 3.84 (s, 1H), 7.12 (s, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.59–7.79 (m, 5H), 7.83 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.94 (t, J = 6.8 Hz, 2H), 8.09–8.15 (m, 4H), 8.22 (s, 1H), 9.24 (d, J = 7.3 Hz, 1H). After irradiation with UV light there was no change in color;

open-form, **10B**: 41%, ^1H NMR (500 MHz, CDCl_3): δ 3.08 (s, 1H), 3.89 (s, 1H), 6.78 (d, J = 2.5 Hz, 1H), 7.59–7.79 (m, 8H), 7.83 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 8.09–8.15 (m, 3H), 8.23 (s, 1H), 8.33 (s, 1H), 9.30 (d, J = 7.6 Hz, 1H). UV-Vis (EtOH) $\lambda_{\text{max}}/\text{nm}$: 212, 237 before irradiation and 211, 280, 379 after irradiation. Anal. Calcd for $\text{C}_{29}\text{H}_{19}\text{ClN}_4\text{O}_2$; C, 70.95; H, 3.90; Cl, 7.22; N, 11.41; O, 6.52; found C, 70.94; H, 3.91; Cl, 7.23; N, 11.40; O, 6.51.

3. Results and Discussion

Ketoaziridines **1** and **2** were prepared starting from corresponding chalcones, which were brominated at the double bond utilizing bromine in chloroform, followed by aziridination with solution of ammonia in ethanol at room temperature [8, 10, 12]. Quinoline and benzo[h]quinoline aldehydes were prepared starting from acylation of aromatic amines in the presence of acetic anhydride and glacial acetic acid and refluxing for 2–3 h followed by formylation with POCl_3 and DMF for 16–18 h at 70–80°C [13, 14]. The general preparation of photochromic compound **3–10** is depicted in Scheme 1. All of these compounds all except compound **10** showed photochromic behavior in the crystalline state. However the UV spectra for all of these synthesis compounds **3–10** in the solution of ethanol confirmed their photochromic properties.

These 1,3-diazabicyclo[3.1.0]hex-3-enes photochromic compounds can undergo reversible photocyclization between their closed-ring isomer (c) and open-ring isomer (o) under irradiation using a light source of appropriate wavelength. Photoisomerization of these photochromic compounds via nitrile ylides is illustrated in Scheme 2.

All synthesized 1,3-diazabicyclo[3.1.0]hex-3-enes **3A–10A** undergoes reversible photochromic reactions in cyclohexane, ethanol, acetone, and ethyl acetate by irradiation with 254 nm UV-Vis light. However in the solvent phase undergo reversible photochromic reaction with a shorter half-life compared to the solid phase with more than 10000 turnovers. By interpreting the ^1H and ^{13}C NMR of several 1,3-diazabicyclo[3.1.0]hex-3-ene systems in CDCl_3 , we found that all of them except **3** and **8** undergo reversible photochromic reaction. However in the crystalline state and in the presence of sun light, all of them except **10** involve 2 + 2 ring opening process, and their color after ~5–20 sec was changed, see Experiments. Both the c-isomer (colorless) and the photogenerated isomer (o-form, colored) are stable at the ambient condition and the coloration/decoloration cycles could be repeated without destruction of the crystals. By rising the duration of irradiation, the population of the o-form in the colored crystals increases resulting in deeper color of photochromic crystals. The changes of absorption for **3–10** in ethanol at 254 nm are shown in Table 1.

The changes of absorption for **3** and **4** in ethanol at 254 nm are shown in Figure 1. In general, the absorption of the closed-ring form appears at a shorter wavelength, while the absorption of the open-ring form takes place at a longer wavelength. When **3A** was irradiated, three new absorption

SCHEME 1: Synthetic route for the preparation of compounds.

SCHEME 2: Photochromic reactions of **3** and **4** before and after irradiation with UV light.

TABLE 1: The absorption changes for **3–10** in ethanol at 254 nm. Spectra and $\lambda_{\max}^A$, $\lambda_{\max}^B$, λ_{ex} , ϵ , and percent yield of **3–10**.

Entry	λ_{ex} (nm)	$\lambda_{\max}^A$ (nm)	$\lambda_{\max}^B$ (nm)	ϵ (cm ⁻¹ M ⁻¹)/EtoH	Yield (%)
3	236	208, 232, 316	208, 232, 406	3.91	75
4	241	206, 236, 320	221, 262, 376	8.31	82
5	245	208, 239	207, 241, 404	3.75	80
6	249	213, 238	211, 239, 361	8.02	76
7	253	212, 246	211, 248, 403	3.31	61
8	254	213, 242	214, 245, 366	10.67	79
9	271	204, 235, 276	203, 277, 403	6.40	78
10	272	212, 237	211, 280, 379	4.94	73

FIGURE 1: Change in the UV-Vis absorption spectra of **3–4** upon irradiation with 254 nm light. Irradiation periods are 0, 5, 30, 60, 120, 180, 240, 300, and 600 s for **3** and 0, 5, 10, 25, 60, 120, and 240 s for **4**. All spectra were recorded in ethanol solutions at 2×10^{-4} M. FIGURE 2: Examination of MM2 model of **9A**.

bands appeared at 208 and 232 nm, respectively, corresponding to open-form **3B**. A similar result was obtained from Figure 2 when **4A** was irradiated at 254 nm, and the three new absorption bands appeared at 221, 262 and 376 nm, respectively, which were ascribed to the open form isomer **4B**. Both figures showed the typical absorption spectral changes of 1,3-diazabicyclo [3.1.0]hex-3-ene derivatives in solvents. From the figures it could also be seen clearly that an isobestic point appeared in both absorption spectra. Only two isomers exist when the compound underwent the photoisomerization reaction. Color faded slowly when the samples in solid state were left in the dark at room temperature.

This behavior is similar to that observed in solution and indicates obviously that 1,3-diazabicyclo[3.1.0]hex-3-enes are photochromic in the crystalline state. Examination of MM2 model of **9A** together with the small steric course of the reaction leaves no doubt that the 2-chlorobenzo[h]quinolines at C2 lies above the plane of the imidazoline ring (Figure 2).

4. Conclusion

A facile and efficient protocol for the synthesis of 1,3-diazabicyclo[3.1.0]hex-3-ene photochromic compounds with premade substituted quinoline and benzo[h]quinoline

ring has been developed. This method is readily accessible to a variety of these intelligent compounds. These compounds show photochromic behavior in solid state and as well in the solution state. Although this system undergoes reversible photochromic reaction in the solvent phase, the major photochromic activity is practical in solid phase with more than 10000 turnovers.

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