Photochromism of several synthesised 1,3-diazabicyclo[3,1,0]hex-3-ene derivatives

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Several 1,3-diazabicyclo[3,1,0]hex-3-ene derivatives with varying substitutions such as 9H-fluorenyl, 4-(cyclohexyl-phenyl)-2-methyl, 4-cyclohexyl phenyl, 2-phenyl-2-methyl, and 2-cyclohexyl-2-phenyl that behave as 'intelligent material' are reported.

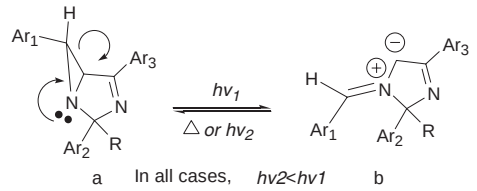
Keywords: photochromism; aziridine ring, imine ylide; 9H-fluorenyl; 1,3-diazabicyclo[3,1,0]hex-3-ene derivatives; intelligent material

Phtochromism is a vast field encompassing well-known phenomena associated with reversible transformations upon irradiation with UV and visible light. In this chemical process, a compound undergoes a reversible change between two states having separate absorption spectra, *i.e.* different colours. Photochromic materials has have significant application in optical data storage, holographic storage, solar cells, and sensitises. Typical photochromic optical switching devices include ophthalmic and sunglass lenses.[1-3] Various photochromic dyes have been developed to improve major photochromic properties such as reversibility and stability. Most photochromic dyes fail to show photoisomerisation in the crystalline state, therefore photochromic properties have been studied in the solution phase. Even the preparation of high-quality thin film appears to be difficult in many cases.[4]

Recently we became interested in the photochromism and photoreproduction of 1,3-diazabicyclo [3,1,0]hex-3-ene derivatives with varying substituents.[5] The synthesis of several fluorescence emission-producer bases on symmetrical and unsymmetrical trisannelated benzene constructions in addition were attempted.[6,7]

We herein present the synthesis of the 1,3-diazabicyclo [3,1,0]hex-3-enes **1**–**6** (Fig. 1) as intelligent materials, prepared by a slight modification of an accessible procedure.[8] The molecular cause of the colour produced upon exposure of the light is quite remarkable. Irradiation after 20 min with 254nm light in ethanol of colourless **1a**–**6a** with UV light presumably causes heterolytic cleavage of the aziridine ring in a conrotatory fashion and opening to form a zwiterionic (double charged imine ylide) highly coloured, highly conjugated species **1b**–**6b** (Schemes 1 and 2).

The structures of **1b–6b** were assigned based upon their UV-Visible absorption spectra in ethanol solution. Santagio and Becker[9] presented persuasive evidence that the typical photochemical reaction arose from an intramolecular rearrangement of chemical bonds. A reversible change in colour is not the only alteration in physical properties; there are also changes in refractive index, dielectric constant and oxidation/reduction potentials.[10]



a In all cases, *hv2<hv1* b

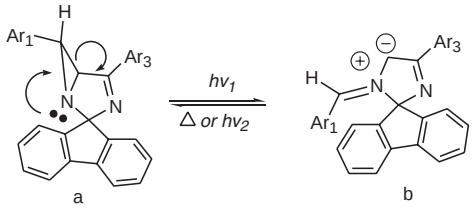
1) Ar_1 = 4-nitrophenyl Ar_2 = phenyl, Ar_3 = phenyl, R =CH3

2) Ar_1 = 4-nitrophenyl Ar_2 = phenyl, Ar_3 = phenyl, R = Cyclohexyl

3) Ar_1 = 3-nitrophenyl Ar_2 = phenyl, Ar_3 = phenyl, R = Cyclohexyl

4) Ar_1 = 4-nitrophenyl Ar_2 = 4-(cyclohexyl)-phenyl , Ar_3 = phenyl, R = CH3

Scheme 1



a b

5) Ar_1 = 4-nitrophenyl Ar_3 = phenyl,

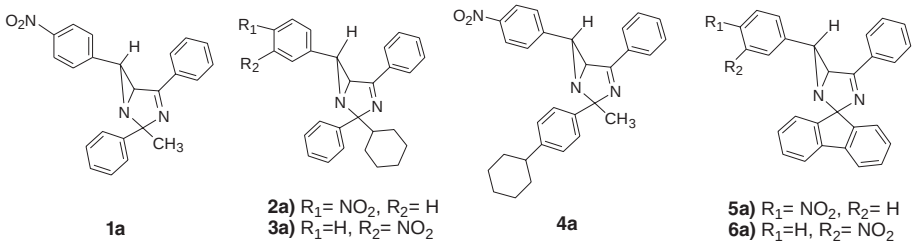
6) Ar_1 = 3-nitrophenyl Ar_3 = phenyl,

Scheme 2

The aziridine **9** was prepared starting with electrophilic addition of bromide to the double bond of trans-chalcone **7** (Scheme 3).[11] Presumably the stereochemistry of the addition is anti, based on $J_{H2\text{-}H3} \sim 11$ Hz.

Treatment of the dibromide **8** with a saturated solution of ammonia in ethanol initiates a series of three consequence reactions which ultimately lead to the *in situ* formation of aziridine **9** via intermediates of the 1,2-E_2 reaction of HBr from dibromide **8** and a Michael type addition of NH_3, followed by an intramolecular nucleophilic substitution.[12] A subsequent

Addition of ammonia to the carbonyl group of **9** yielded the desired **1a**–**6a**. In the typical procedure for preparation of



1a **2a)** R_1= NO_2, R_2= H **3a)** R_1=H, R_2= NO_2 **4a** **5a)** R_1= NO_2, R_2= H **6a)** R_1=H, R_2= NO_2

Fig. 1

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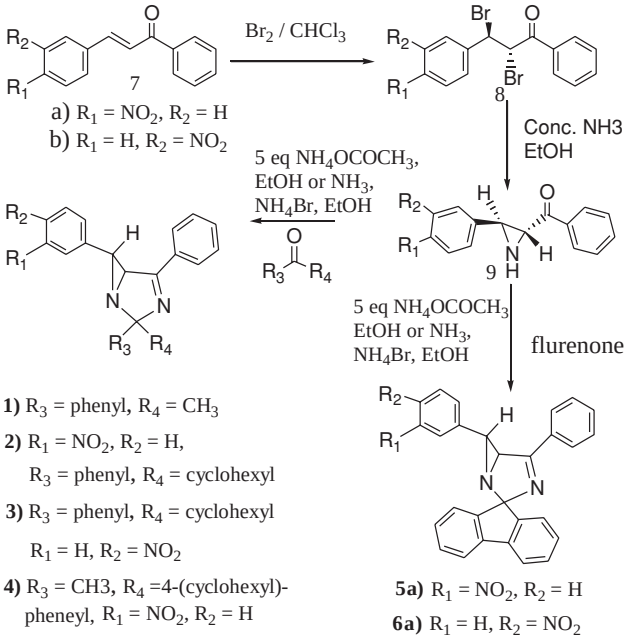


Scheme 3

1a–6a, instead of the more traditional 1 mmol gaseous ammonia and 1mmol NH_4Br in absolute ethanol, we found that 5 mmol NH_4OOCCH_3 and 1mmol NH_4Br in absolute ethanol also work very well; in this case the reaction was completed after 4 days instead of 1 week. The synthesis of **1a** has been reported by using 1 mmol gaseous ammonia and 1 mmol NH4Br in absolute EtOH.[8] However, this published yield of conversion for crude **1a** is 37%. In our hands, the yield of conversion for pure **1a** has been increased to 65.5%.

Several alternative mechanisms can be proposed for the formation of the **1a–6a**, among the possibilities, the proposed methylenamine aziridine intermediate could react with the corresponding ketone to form an iminohydrin that undergoes cyclisation to target molecules **1a–6a**.[13] The UV-visible spectrum of **1–6**, after 20 min irradiation under UV light in ethanol solution exhibits absorption maxima at 295 nm for **1a**, 283 nm for **2a**, 284 nm for **3a**, 280 nm for **4a**, 298 nm for **5a** and 275 nm for **6a**, respectively. By comparison, for the zwiterionic double charged imine ylide, UV irradiation causes absorption in the visible range maximum at 300, 420 for **1b**, maximum at 415, 283 nm and shoulder at 300 nm for **2b**, maximum at 275, 385 nm for **3b**, 283, 420 nm for **4b**, 298, 420 nm and shoulder at 310 nm for **5b**, and 362, 280 nm for **6b**, respectively, due to the breaking of the aziridine ring and forming a conjugated system. Absorption spectra changes of colorless of **1a–6a** ($1.4x10^{-4}$ mol^{-1} dm^{-3} in EtOH; cell length 1 cm), irradiation time/min, 0, 0.5, 1, 5, 10, 15, and 20 were obtained immediately after 254-nm light irradiation, respectively. All spectra afforded the photostationary states, respectively.

The ^{13}C NMR of recrystallised **2a** and **5a** showed 21 and 24 peaks, respectively. Considering the ^1H NMR spectra of **1a–6a**

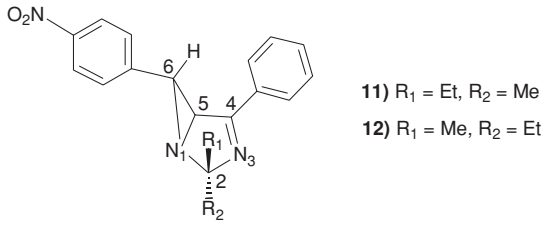
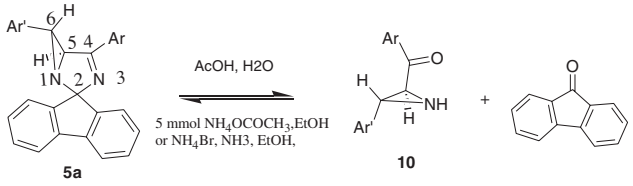


Fig. 2



Scheme 4

the proton-proton coupling between hydrogens on C_5 and C_6 in the aziridine ring in such a rigid system is about 0 Hz (in accord with the vicinal Karplus correlation, presumably the ϕ –90°. However, direct "reading off" of the angle from the magnitude of the *J* value is risky) (Scheme 4). In acetic acid the 1,3-diazabicyclo [3.1.0]hex-3-ene **5a** in wet acetic acid for ~3 days at room temperature contracts to trans-[3-(4-nitro-phenyl)-aziridin-2-yl]-phenyl-methanone **10**. As a result, separation of the starting *trans*-aziridine **10** designates that the hydrogens at C_5 and C_6 in the related 1,3-diazabicyclo[3.1.0]hex-3-ene **5a** were also *trans* to each other and that no epimerization occurred in the synthesis of the bicyclic aziridines (Scheme 4).

In the upfield region of the ^1H NMR for all compounds **1a–6a** just two singlets for C_5 and C_6 protons were observed. We have also synthesised 2-ethyl-2-methyl-6-(4-nitrophenyl)-4-phenyl-1,3-diazbicyclo[3.1.0]hex-3-en (Fig. 2). The ^{1}HNMR of this compound shows two well-resolved triplets at 1.04 ppm, *J* = 7.5 Hz and 1.12 ppm, *J* = 7.5 Hz corresponding to the terminal methyl protons attached to C_2 for isomers **11** and **12**, respectively. This is best ascertained by monitoring the integral for two characteristic triplets for **11** and **12**. Thus the ratio of the integral for the triplet peaks was *ca* 2:1.

In contrast to the ^1H NMR of **11** and **12** isomers, the ^1H NMR of **1a** for the methyl group at C_2 shows one singlet at 1.87 ppm with integration for three protons. The chemical shifts of 2.88 and 3.58 ppm were assigned to methine protons at C_6 and C_5 of **1a**, respectively.

Examination of the AM1 model of **1a** together with the small steric course of the reaction, *i.e.*, preparation of **11** and **12** mixture (*ca* 2:1), leaves little doubt that the methyl proton at C_2 lies below the plane of the imidazoline ring (Fig. 3).

Experimental

Chemicals were purchased from Fluka, Merck, and Aldrich. Products were characterised by comparison with authentic samples (IR, NMR, GC, TLC, and m.p.). Yields refer to isolated pure centre cut from column chromatography or for material scratched from preparative TLC plates. Melting points are uncorrected and were determined on a Mettler Fp5 melting point apparatus. IR spectra were obtained on a Shimadzu IR-470 instrument. All NMR data were recorded in $CDCl_3$ on a Brucker FT-500 MHz spectrometer, using *TMS* as internal reference. The UV/Vis spectra were recorded on a Shimadzu UV-2100 spectometer. The 4-nitrochalcone **7a** was prepared according to a standard procedure.[11] The structure of the intermediates and the final products were consistent with their spectral properties.

Synthesis of 2,3–dibromo-4-nitrochalcone (**8**; $C_{15}H_{11}NO_3Br_2$): The 4-nitrochalcone **7a** was prepared according to a standard procedure.[11] 4-Nitrochalcone (0.413g, 1mmol) was dissolved in ~

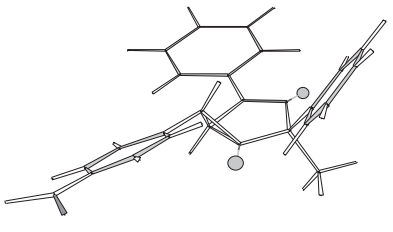


Fig. 3

12 cm^3 $CHCl_3$ in the hood. Then, 5 cm^3 bromine – $CHCl_3$ was added dropwise to the cooled homogenous 4-nitrochalcone solutions with stirring at room temperature. After 5–10 min, the bromine colour discharged and a lemon yellow solution remained. At this point, an additional 0.5–1cm^3 of the bromine-$CHCl_3$ solution was added. When the bromine colour persisted for longer than 30 min., the reaction was completed. The solution was evaporated under vacuum. The solid residue was purified by silica gel column chromatography and recrystallised from CH_2Cl_2/ hexane to afford a white solid 0.493g (98%) m.p. = 137–139 °C. IR(KBr): 3050, 1680, 1590, 1522, 1342, 1265, 1220, 1100, 980, 844, 775, 720, 484, 620, 570 cm^{-1}; ^{1}HNMR($CHCl_3$): δ; 5.72 (d, *J* = 11.23Hz, 1H), 5.81 (d, *J* = 11.51Hz, 1H), 7.58–7.61 (t, *J* = 7.7 Hz, 1H), 7.70–7.74 (m, 3H), 8.12 (d, *J* = 7.7Hz, 2H), 8.32 (d, 8.5Hz, 2H) ppm.

Synthesis of 2-benzoyl-3- (4-nitrophenyl) aziridine (**10**; $C_{15}H_{12}N_2O_3$): A total of 3 cm^3 solution of concentrated ammonia was added to a solution of 2,3-dibromo-4-nitrochalcone (0.413g, 1mmol) in 6 cm^3 of 96% EtOH with stirring at room temperature. After 4 days, the reaction mixture was filtered, the solid was washed with methanol and dried in the air and the resulting residue was purified with silica gel column and recrystallised from ethanol to give orange solid 0.196g (73%) m.p. = 139–140°C lit[12] = 136.8–137°C. IR(KBr): 3260, 3050, 1662, 1600, 1512, 1445, 1343, 1265, 1230, 1020, 825, 747, 710 cm^{-1}; ^{1}H NMR($CHCl_3$): δ; 2.8 (br, t, *J* = 8.5 Hz, 1H), 3.28 (dd, *J* = 2.0, 9.2Hz, 1H), 3.54 (dd, *J* = 2.1, 8.1 Hz, 1H), 7.52–7.58 (m, 4H), 7.65–7.68 (t, *J* = 7.4Hz, 1H), 8.01 (d, *J* = 7.5Hz, 2H), 8.24 (d, *J* = 8.6 Hz, 2H) ppm.

Preparation of 2-methyl-6-(4-nitro-phenyl)-2,4-diphenyl-1,3-diaza bicyclo[3,1,0]hex-3-ene: *a typical procedure* (**1a**; $C_{23}H_{19}N_3O_2$): 2-benzoyl-3-(4-nitrophenyl)-aziridine **8** (0.268g, 1mmol), NH_4Br (0.1g, 1mmol) and the appropriate ketone (1mmol) were dissolved in 6 cm^3 of absolute ethanol and stirred at room temperature. Anhydrous gaseous ammonia is gently blown into reaction mixture for several hours. Alternatively, instead of gaseous ammonia, 5 mmol NH_4OOCCH_3 was used. In this case, the reaction was completed after 4 days instead of 1 week. A colour change in the reaction mixture from orange into blue or greenish blue is characteristic for product formation. The reaction mixture was filtered, washed with ethanol, dried in the air and the resulting solid recovered 0.36 g (97.45), purified by silica gel column chromatography and recrystallised from ethanol (65.5%), methanol or some other suitable solvent. The colour of **1a** changed from colourless to **1b** gray. M.p. =186–187 °C. IR (KBr): 3060, 3020, 3000, 2910, 1600, 1565, 1517, 1440, 1340, 1238, 1140, 1100, 930, 855, 760, 740, 695, 595, 505cm^{-1} ^{1}H NMR ($CDCl_3$) δ: 1.97 (s, 3H), 2.88 (s, 1H), 3.58 (s, 1H) 7.32 (t, 1H, *J* = 6.78, 7.15Hz), 7.4–7.48 (m, 4H), 7.5–7.54 (t, 1H, *J* = 6.83Hz), 7.63 (d, 2H, *J* = 8.4Hz), 7.89 (d, 2H, *J* = 8Hz), 7.94 (d, 2H, *J* = 7.95Hz), 8.24 (d, 2H, *J* = 8.02) ppm.

Synthesis of 2-cyclohexyl-6-(4-nitro-phenyl)-2,4-diphenyl-1, 3-diazabicyclo[3,1,0]hex-3-ene (**2a**; $C_{28}H_{27}N_3O_2$): A similar procedure to that used for **1a** was applied. The resulting solid was recovered 0.325g (74.28%) and then recrystallised from ethanol. The colour of **2a** changed from pale yellow to deep green **2b**. IR (KBr) cm^{-1}: 3050, 2900, 2850, 1600,1510,1440, 1340, 1100, 1040, 1010, 840, 830, 760, 710, 695; ^{1}H NMR ($CDCl_3$) δ: 0.88–0.99 (m, 2H), 1.11–1.29 (m, 3H), 1.55–1.58 (d, 1H, *J* = 12.4Hz), 1.66–1.74 (m, 3H), 1.95 (d, 1H, *J* = 7Hz), 2.26–2.29 (d, 1H, *J*=12.31Hz), 2.94 (s, 1H), 3.49 (s, 1H), 7.3–7.33 (t, 1H, *J* = 7.1, 7.3 Hz), 7.39–7.42 (t, 2H, *J* = 7.5, 7.6 Hz), 7.44–7.47 (t, 2H, *J* = 7.0, 7.5 Hz), 7.49–7.51 (t, 1H, *J* = 6.9, 6.8 Hz), 7.93–7.96 (t, 4H, *J* = 7.3 Hz), 8.28 (d, 2H, *J* = 8.5 Hz) ppm; ^{13}C NMR: 26.73, 27, 27.14, 28.92, 30.61, 42.74, 47.01, 56.527, 104.47, 124.38, 127.68, 127.92, 128.53, 129.03, 129.25, 131.94, 132.55, 143.97, 146.6, 147.95, 168.15; m.p. = 214–215 °C, yield (63.2 %).

Synthesis of 2-cyclohexyl-6-(3-nitro-phenyl)-2,4-diaza-bicyclo [3.1.0] hex-3-ene (**3a**; $C_{28}H_{27}N_3O_2$): A similar procedure as used for **1a** was applied, the resulting solid recovered, 0.30g (86.10%), was recrystallised from ethanol (yield 56.69 %) m.p. = 206–207 °C. The colour of **3a** changed from colourless to pink **3b**. IR (KBr): 3050, 3010, 2900, 2830, 1600, 1565, 6951525, 1480, 1440, 1345, 1305, 1040, 1020, 760, 725, 705, 690, 520 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ:0.9–0.97(q, 2H, J_1 = 11.8, J_2 = 11.7 Hz), 1.16–1.29 (m, 3H), 1.57 (d, 1H *J* = 12.2 Hz), 1.66–1.74 (dd, 3H, *J* = 8.7 Hz), 1.97 (s, 1H), 2.38 (d, 1H), 2.96 (s, 1H), 4.49 (s, 1H), 7.32 (t, 1H, J_1 = 7.02 Hz, J_2 = 7.4 Hz), 7.39–7.49 (m, 5H), 7.85 (d, 4H, *J* = 7.2 Hz), 8.19 (d, 1H, *J* = 7.9 Hz), 8.36 (s, 1H) ppm.

Synthesis of 2-(4-cyclohexyl-phenyl)-2-methyl-6-(4-nitro-phenyl)-2,4-diphenyl-1,3-diaza bicyclo [3,1,0]hex-3-ene (**4a**; $C_{29}H_{29}N_3O_2$): A similar procedure as used for **1a** was applied; the resulting solid recovered, 0.325g (88.26%) m.p. = 186–187 °C, was recrystallised from ethanol (56.59 % yield). The colour of **4a** changed from colourless to blue. **4a;** IR (KBr): 3050, 2905, 2850, 1600, 1510, 1440, 1340, 1240, 1100, 1010, 930, 820, 850, 765, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.25–1.28 (m, 1H), 1.39–1.48 (m, 4H), 1.76 (d, 1H, *J* = 11.4 Hz), 1.84–1.9 (m, 7H), 2.52–2.54 (m, 1H), 2.87 (s. 1H), 3.58 (s, 1H), 7.25 (d, 2H, *J* = 8.2 Hz), 7.44–7.47 (t, 2H, *J* = 7.2, 7.7Hz), 7.5–7.53 (t, 1H, *J* = 7.2, 7.3 Hz), 7.62 (d, 2H, *J* = 8.7 Hz), 7.77 (d, 2H, *J* = 8.2 Hz), 7.94 (d, 2H, *J* = 7.3 Hz), 8.24 (d, 2H, *J* = 8.7 Hz) ppm.

Synthesis of 2-(9H-fluorenyl)-2-6-(4-nitro-phenyl)-4-phenyl-1, 3-diazabicyclo[3,1,0]hex-3-ene (**5a**; $C_{28}H_{19}N_3O_2$): A similar procedure to that used for **1a** was applied, the resulting solid recovered 0.30g (82.89%), was recrystallised from ethanol (59.6 % yield), m.p. = 210–211 °C. The colour of **5a** changed from colourless to **5b** deep blue. IR (KBr): 3010,1590,1505, 1440,1340, 1100, 1040, 1010, 850, 810, 760,740, 695, 500 cm^{-1}; ^{1}H NMR & ^{13}C NMR ($CDCl_3$) δ: 3.43 (s, 1H), 4.01(s, 1H), 7.23 (d, 1H, *J* = 7.5 Hz), 7.23–7.30 (t, 1H, *J*= 7.4 Hz), 7.32–7.35 (t, 1H, *J* =7.4 Hz), 7.43–7.54 (m, 7H), 7.58–7.61 (t, 1H, *J* = 7.3Hz), 7.73–7.76 (t, 2H, *J* = 8.7, 8.2Hz), 8.05 (d, 2H, *J* = 7.35Hz), 8.12 (d, 2H, *J* = 8.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ: 44.27, 56.78, 103.52, 120.83. 121.16, 124.1, 124.16, 125.24, 128.22, 128.52, 128.84, 129.24, 129.52, 130.34, 130.50, 131.93, 132.66, 139.7, 142.6, 143.79, 145.3, 147.07, 147.93, 173.47 ppm.

Synthesis of 2-(9H-fluorenyl)-2-6-(3-nitro-phenyl)-4-phenyl-1, 3-diazabicyclo[3,1,0]hex-3-ene (**6a**; $C_{28}H_{19}N_3O_2$): A similar procedure to that used for **1a** was applied, the resulting solid recovered, 0.30g (79.24%), was recrystallised from ethanol (57.2 % yield) m.p. = 191–192 °C. The colour of **6a** changes from colourless to **6b** orange pink; IR (KBr): 3090, 3060, 1595, 1560, 1520, 1460, 1440, 1345, 1295, 1050, 1020, 748, 730, 695, 525 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 3.45 (s, 1H), 4.04 (s, 1H), 7.25 (d, 1H, *J* = 7.4 Hz), 7.28–7.31 (t, 1H, J_1 = 7.5), 7.33–7.36 (t, 1H, *J* = 7.5 Hz), 7.41–7.46 (m, 4H), 7.50–7.53 (t, 2H, J_1 = 7.6, J_2 = 7.3Hz), 7.57–7.60 (t, 1H, *J* = 7.2, J_2 = 7.2Hz), 7.65–7.67 (d, *J* = 7.7 Hz), 8.05–8.07 (d, 2H, *J* = 7.1 Hz), 8.08 (t, 1H, *J* = 1Hz), 8.19 (s, 2H, *J* = 8.6 Hz) δ ppm.

Synthesis of (mixture of **11** and **12**; $C_{19}H_{19}N_3O_2$) *2-Ethyl-2-methyl-6-(4-nitro-phenyl)-4-phenyl-1,3-diaza-bicyclo[3,1,0]hex-3-ene:* A similar procedure to that used for **1a** was applied, the resulting solid recovered, 0.273g (85%), was recrystallised from ethanol (59 % yield) mixture of *ca*, 2/1 of **11**:**12**. m.p. = 136–137 °C; IR (KBr): 3100, 3080, 2980, 2920, 1600, 1570, 1510, 1450, 1340, 1160, 1100, 930, 860, 820, 770, 740, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.02–1.05 (t, *J* = 7.5Hz, 3H), 1.1–1.14 (t, *J* = 7.5 Hz, 3H), 1.56 (s, 6H), 1.69–1.74 (m, 1H), 1.87–2.02 (m, 3H), 2.62 (s, 2H), 3.52(d, *J* = 1.42 Hz, 1H), 3.6 (d, *J* = 1.24 Hz, 1H), 7.44–7.53 (m, 10H), 7.88 (d, *J* = 7.2 Hz, 4H), 8.2 (d, 2H, *J* = 8.6, 4H) ppm. UV-Vis (EtOH): λmax = 280, 405 nm

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