Synthesis and Photochromic Properties of New Heterocyclic Derivatives of 1,3-diazabicyclo[3.1.0]hex-3-ene

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The facile synthesis of several 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives with varying substitutions such as 2-methyl-6-(4-nitrophenyl)-2,4-diphenyl-(**1**), 2-methyl-6-(4-nitrophenyl)-4-phenyl-2-(pyridin-3-yl)-(**2**), 2-(furan-2-yl)-6-(4-nitrophenyl)-4-phenyl-(**3**), 2-(furan-2-yl)-6-(3-nitrophenyl)-4-phenyl-(**4**), 6-(3-nitrophenyl)-2,4-diphenyl-(**5**) and 6-(4-chlorophenyl)-4-(3-nitrophenyl)-2-phenyl-(**6**) that all behave as "intelligent materials" are reported.

Keywords: Aziridine ring; Imine ylide; 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives; Intelligent material; Photochromism.

INTRODUCTION

Photochromism is a vast field encompassing well-known phenomena associated with reversible transformations a and b, having different absorptions upon irradiation with UV and visible light (Fig. 1).

Functionalized aziridines are an extremely important class of compounds; as they are precursors of new biologically active compounds, they are very useful synthetic intermediates.[1]

Study of photochromic materials has drawn great attention to their significant application in optical data storage, holographic storage, solar cells, and as sensitizers. In this chemical process, a compound undergoes a reversible change between two states having separate absorption spectra, i.e. different colors. Typical photochromic optical switching devices include ophthalmic and sunglass lenses.[2,3] Various photochromic dyes have been developed to improve major photochromic properties such as reversibility and stability. Examination of new methods of the synthesis of aziridine derivatives has therefore attracted considerable attention, and the search for a means of rapid access to these heterocycles and their diverse biological properties is well documented in the literature.[4]

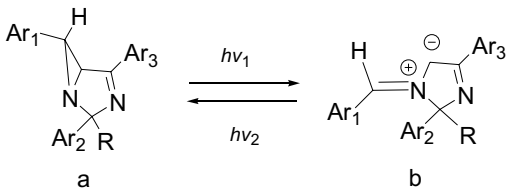

Fig. 1

RESULTS AND DISCUSSION

Our research in this area has been concerned with the synthesis of 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives with varying substitutions and their application as photochromics and in photoreproduction.[5] The synthesis of several fluorescence emission producers based on symmetrical and unsymmetrical trisannelated benzene constructions and several related photochromic compounds was attempted.[6,7] Here we describe an effiecient approach to the synthesis of stereodefined bridgehead aziridines **1**-**6** (Fig. 2) with varying heterocyclic substitutions at the 2-position. According to the recorded UV-Vis spectra all are considered as positive photochromism compounds and behave as intelligent materials.[8]

Currently, there are no published data available on the synthesis of **1**-**4** with the heterocyclic moieties at the 2 position of imidazol (d ring, Fig. 3). Synthesis of compound **6** with substitution on the b ring for the first time is reported. A synthesis sequence for the preparation of the precursor aziridine **12c** has not been previously reported (Scheme II). In our approach to aziridine **12c**, the dibromination of **8**

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was made practical by the addition of $Br_2/CHCl_3$ to a solution of chalcone **8**. Employment of the same brominating procedure to the other 4,4′-disubstitutedchalcone with substitutions such as ($R_1 = OCH_3$, $R_2 = NO_2$; $R_1 = NO_2$, $R_2 = OCH_3$ and $R_1 = OCH_3$, $R_2 = OCH_3$) failed. The molecular creation of the color produced upon contact of the light is quite notable. Irradiation after 20 min with 254 nm light in ethanol of colorless **1a**-**6a** with UV light causes heterolytic cleavage of the aziridine ring in a conrotatory fashion (σ2s + n2s) and opens to form a double charged imine ylide mainly colored highly conjugated species **1b**-**6b** (Scheme I). Upon UV irradiation, a solution of colorless or weakly colored solid **1a**-**6a** becomes colored.

The photochromic properties of solutions of **1b**-**6b** were assigned based upon their UV-visible absorption spectra in ethanol, toluene, ether, ketone and ester solutions. In our procedure the ethanol mostly works well. Irradiation of the powder of **5a** in an electric field produced a significant increase (~1.13%) of the total capacitance which we ascribe to the formation of the dipolar intermediate. The back reaction usually occurred thermally (photochromism of type T) or photochemically (photochromism of type P) in the solid phase. The key for success of this typical photochemical reaction arose from an intramolecular rearrangement of chemical bonds. The internal reflection ir spectrum of the irradiated solid of **5a** discovered new bands at 1450, 1320, and 1270 cm^{-1}; the latter two bands may be ascribed to an extensively conjugated nitro group in the colored intermediate. The IR (KBr) spectrum of other solids **1**-**4** and **6** remained almost identical for a-b isomers.

Diffuse reflectance spectra of solid-state **5a**-Al-MCM-41 after five min irradiation with UV indicate a maximum at 594 and 668 nm.[9] The two possible ylides derived from **1a** are *syn*- and *anti*- (Scheme I). The *syn* structure appears to involve a conrotation which is a symmetry-allowed concerted process.

Treatment of the dibromides **10a**-**10c** with a saturated solution of ammonia in ethanol initiates a series of three consequence reactions which ultimately lead to the *in situ* formation of aziridines **13** via intermediates of **11** and **12** ((1,2-E_2 reaction of HBr) and (Michael addition of NH_3)), followed by an intramolecular nucleophilic substitution.[12] A subsequent addition of ammonia to either the carbonyl groups of **14** (path a) or alternatively, to the carbonyl of aldehydes or ketones and formation of aldimine (path b) yielded the desired **1a**-**8a**. In the typical procedure for preparation of **1a**-**8a**, instead of the more traditional 1 mmol gaseous ammonia and 1 mmol NH_4Br in absolute ethanol, 5 mmol NH_4OOCCH_3 and 1 mmol NH_4Br in absolute ethanol also work very well; in this case, the reaction was completed after 4 days instead of 1 week.

The UV-visible spectrum of **1**-**6** in ethanol solution exhibits absorption maximums at 282 nm for **1a**, 270 nm

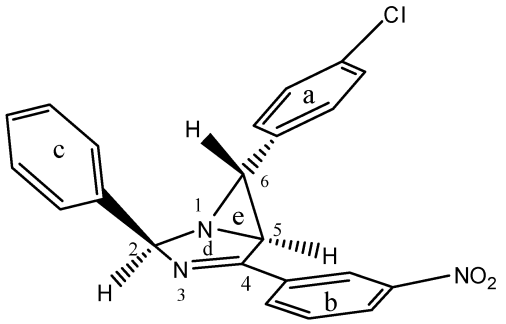
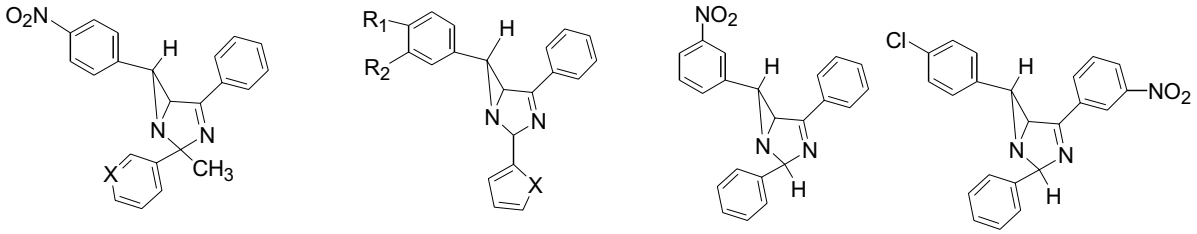


Fig. 3. Compounds **6** with three stereocenters are created and only one of the possible diastereoisomers is produced as a racemic mixture of (2R,5R,6S) and (2S,5S,6R)-6-(4-chlorophenyl)-4-(3-nitrophenyl)-2-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene.



1 = X = CH
2 = X = N

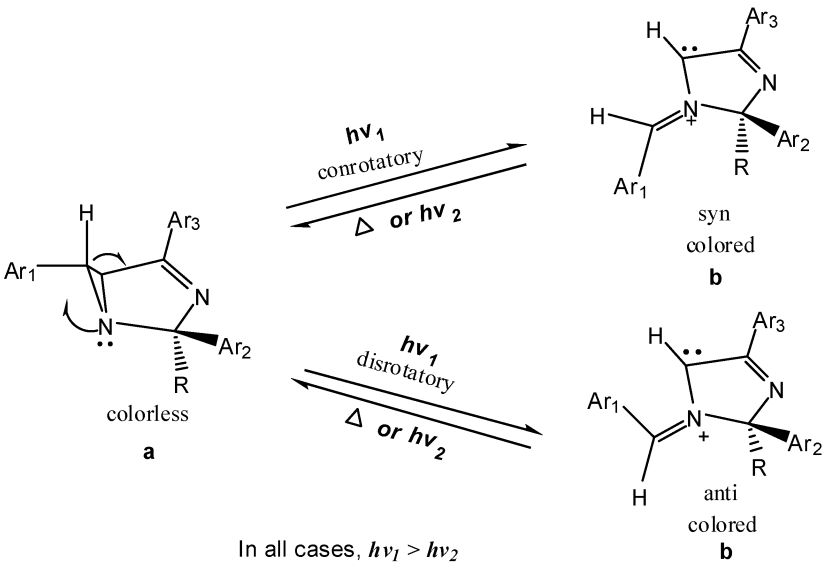
3) $R_1 = NO_2$, R_2 = H, X = O
4) R_1 = H, $R_2 = NO_2$, X = O

5

6

Fig. 2

Scheme I



1) Ar_1 = 4-nitrophenyl Ar_2 = phenyl, Ar_3 = phenyl, R = CH3
2) Ar_1 = 4-nitrophenyl Ar_2 = 3-pyridinyl, Ar_3 = phenyl, R = CH3
3) Ar_1 = 4-nitrophenyl Ar_2 = 2-furyl, Ar_3 = phenyl, R = H
4) Ar_1 = 3-nitrophenyl Ar_2 = 2-furyl, Ar_3 = phenyl, R = H
5) Ar_1 = 3-nitrophenyl Ar_2 = phenyl, Ar_3 = phenyl, R = H
6) Ar_1 = 3-nitrophenyl Ar_2 = phenyl, Ar_3 = 4-chloro phenyl, R = H

Scheme II

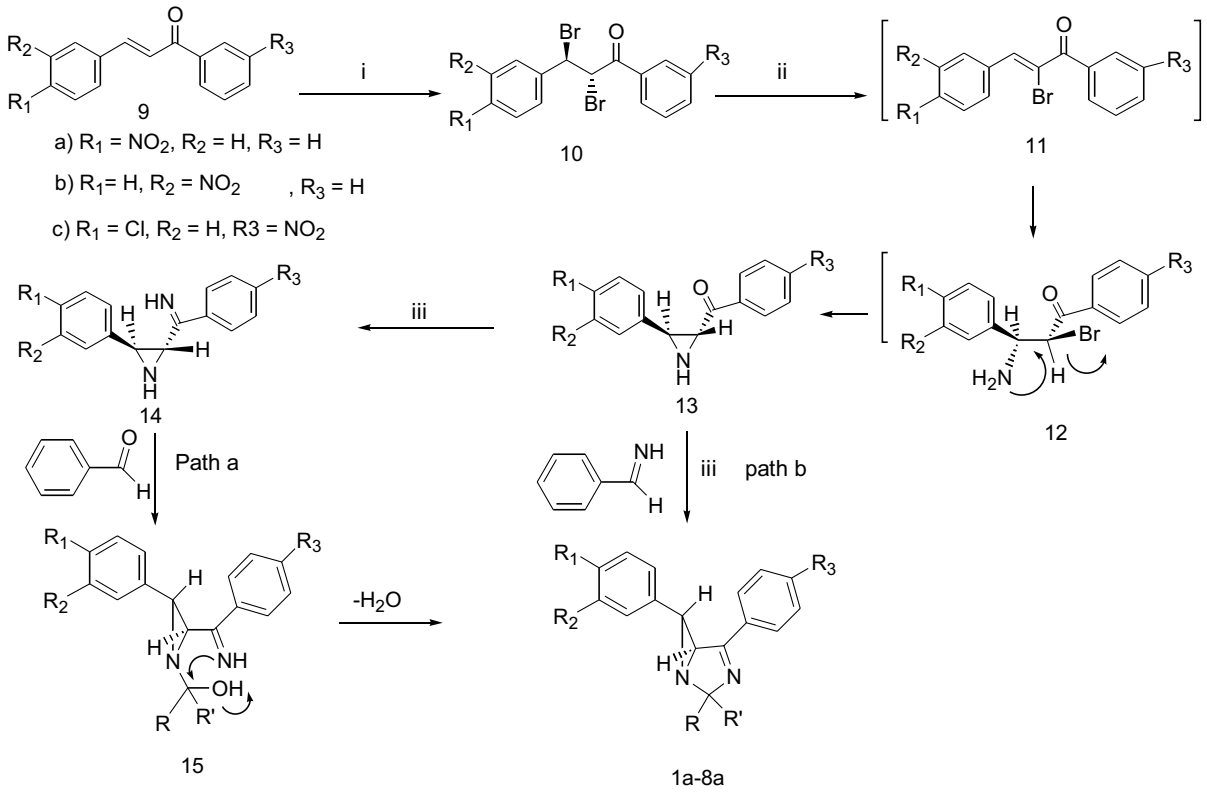


Table 1. Physical properties of all synthesized compounds

No	IR (KBr) cm^{-1} Ms spectra	^1H NMR (500 MHz) & ^{13}C NMR (125 MHz) ($CDCl_3$) δ ppm	m.p °C	Yield %
1a	3100, 3060, 3990, 2940, 2850, 1595, 1515, 1440, 1340, 1240, 1140, 760, 590; MS: (M^+): (EI); exact mass: calcd for $C_{23}H_{19}N_3O_2$, 369.1477; Found 369.1476.	1.9 (s, 3H), 2.9 (s, 1H), 3.6 (s, 1H), 7.3 (t, 1H, *J* = 6.9, 7.1 Hz), 7.4-7.5 (m, 4H), 7.5 (t, 1H, *J* = 6.9 Hz), 7.6 (d, 2H, *J* = 8.4 Hz), 7.9 (d, 1H, *J* = 8.0 Hz), 7.9 (d, 2H, *J* = 8.0 Hz), 8.3 (d, 2H, *J* = 8.0 Hz,); ^{13}C NMR, 42.3, 58.3, 93.4, 122.1, 123.1, 126.3, 127.7, 129.4, 129.5, 130.0, 131.4, 132.7, 133.3, 140.6, 141.1, 148.9, 171.8.	186-187	65.5 (EtOH)
2a	3100, 3050, 3000, 2980, 1600, 1510, 1445, 1340, 925; MS: (M^+): (EI); exact mass: calcd for: $C_{22}H_{18}N_4O_2$, 370.1430; Found 370.1430.	1.9 (s, 3H), 2.9 (s, 1H), 3.6 (s, 1H), 7.3 (t, 1H, *J* = 4.8, 7.9 Hz), 7.5 (t, 2H, *J* = 7.6 Hz), 7.6 (d, 2H, *J* = 8.5 Hz), 7.9 (d, 2H, *J* = 7.6 Hz), 8.2 (d, 1H, *J* = 7.9 Hz), 8.2 (d, 2H, *J* = 8.5 Hz), 8.6 (d, 1H, *J* = 4.3 Hz), 9.1 (s, 1H); 26.8, 44.3, 57.3, 97.8, 123.7, 124.3, 128.0, 129.1, 129.4, 131.8, 132.5, 134.2, 143.0, 145.9, 148.2, 148.8, 149.0, 169.9.	194-195	56 (EtOH)
3a	3100, 3050, 2890, 1600 (C=N), 1575, 1510 (N=O), 1345 (N=O), 1280, 1100, 740, 690; MS: (M^+): (EI); exact mass: calcd for $C_{20}H_{16}N_2O$. Exact Mass: 345.1113; Found 345: 345.3514.	2.9 (s, 1H), 3.8 (s, 1H), 6.3 (dd, *J* = 3.0, 1.55, 2.9 Hz, 1H), 6.7 (s, 1H), 7.5 (d, 2H, *J* = 8.8 Hz), 7.5 (d, 1H, *J* = 4.8 Hz), 7.5 (d, 2H, *J* = 7.6 Hz), 7.5 (d, 2H, *J* = 7.6 Hz), 8.0 (d, 2H, *J* = 7.3 Hz), 8.2 (d, 2H, *J* = 8.6 Hz); 42.9, 58.3, 93.4, 122.1, 123.6, 126.5, 127.0, 127.8, 129.0, 129.4, 129.9, 131.8, 132.5, 133.3, 140.6, 141.0, 149.0, 171.6.	169-170	75 (EtOH) blue
4a	3100, 3050, 2890, 1600 (C=N), 1575, 1510 (N=O), 1345 (N=O), 1280, 1100, 740, 690; (EI); exact mass: calcd for $C_{20}H_{15}N_3O_3$. Exact Mass: 345.1113; Found 345.1113.	2.7 (s, 1H), 3.8 (d, 1H, *J* = 0.6 Hz), 6.9 (s, 1H), 7.00 (dd, 1H, *J* = 3.6, 3.7 Hz), 7.2 (dd, 1H, *J* = 0.8, 1.3 Hz), 7.3 (d, 1H, *J* = 5.4 Hz), 7.5 (d, 1H, *J* = 3.5), 7.5 (d, 1H, *J* = 2.8 Hz), 7.5 (d, 1H, *J* = 2.4 Hz), 7.6 (t, 1H, *J* = 7.5 Hz), 7.62 (d, 1H, *J* = 7.6 Hz), 8 (d, 2H, *J* = 7.6 Hz), 8.1 (dd, 1H, *J* = 1.3, 0.9 Hz), 8.2 (s, 1H), 42.7, 58.4, 93.5, 122.2, 123.1, 126.1, 126.4, 127.5, 129.1, 129.4, 129.9, 133.3, 140.6, 141.0, 149.0, 171.6.	176-177	33 (MeOH)
5a	3050, 3020, 2900, 1610, 1570, 1525, 1480, 1440, 1340, 1040, 790, 690; MS: (M^+): (EI); exact mass: $C_{22}H_{17}N_3O_2$, 355.1321; Found, 355.1323.	2.5 (s, 1H), 3.8 (s, 1H), 6.8 (s, 1H), 7.3 (t, 1H, *J* = 7.4 Hz), 7.4 (t, 2H, *J* = 7.5 Hz), 7.4-7.6 (m, 7H), 8.00 (d, 1H, *J* = 8 Hz), 8.12 (s, 1H), 42.1, 58.3, 96.7, 124.2, 127.8, 128.09, 128.4, 129.0, 129.1, 129.4, 132.2, 132.4, 139.2, 141.9, 142.6 146.1, 147.8, 171.0.	139-140	68 (EtOH)
6a	3010, 3020, 2900, 1605, 1575, 1510, 1490, 1440, 1340, 1040, 780, 695; MS: (M^+): (EI); exact mass: calcd for $C_{22}H_{16}ClN_3O_2$: 389.0931, Found; 389.0930.	2.5 (s, 1H), 3.7 (s, 1H), 6.8 (s, 1H), 7.18 (d, 2H, *J* = 8.4 Hz), 7.3 (s, 1H), 7.31 (t, 2H, *J* = 7.0 Hz), 7.4 (t, 2H, *J* = 7.6 Hz), 7.5 (d, 2H, *J* = 7.4 Hz), 7.7 (t, 1H, *J* = 8.0 Hz), 8.3 (d, 1H, *J* = 7.7 Hz), 8.4 (dd, 1H, *J* = 1.2 Hz), 8.8 (s, 1H), 42.1, 52.9, 96.4, 123.2, 126.0, 127.4, 127.1, 127.1, 128.6, 128.7, 129.9, 133.5, 133.7, 134.0, 135.1, 138.3, 148.6, 168.9.	202-206	65 (EtOH) blue

for **2a**, 284 nm for **3a**, 284 nm for **4a**, 277 nm for **5a** and 275 nm for **6a**, respectively. By comparison, for the zwiterionic double charged imine ylide, 20 min UV irradiation causes absorption in the visible range maximum at 300, 420 for **1b**, maximum at 400, 260, 230 nm for **2b**, maximum at 284, 405 nm for **3b**, 283, 420 nm for **4b**, 278, 370 nm for **5b**, and 362, 280 nm for **6b**, respectively, due to the breaking of the aziridine ring and formation of a conjugation system. Absorption spectra changes of colorless **1a**-**6a** (1.4×10^{-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 quantum yields for the formation of **1b**-**6b** after 20 min irradiation with 254 nm light in EtOH on parallel irradiation of samples of identical volumes and concentrations have been determined (Table 2).

The ^{13}C NMR of recrystallized **2a** and **6a** both showed 18 peaks, correspondingly. Considering the ^1H NMR spectra of **1a**-**6a** 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 $\phi \sim 90°$).

In the upfield region of ^1H NMR for all compounds

Table 2. Quantum yields for photochromic conversion of **1a**-**8a** to **1b**-**8b**

Entry	Φ_a	Φ_b	Φ_c	Φ_d	Φ_{ss}
1a	0.11	0.23	0.06	0.01	0.42
2a	0.27	0.22	0.25	0.01	0.75
3a	0.38	0.27	0.09	0.10	0.85
4a	0.35	0.26	0.04	0.10	0.75
5a	0.23	0.40	0.01	0.01	0.65
6a	0.16	0.28	0.05	0.01	0.50
7a	0.40	0.07	0.04	0.02	0.54
8a	0.33	0.04	0.03	0.02	0.42

0.10 *M* EtOH solutions irradiated at 254 nm Uv-Vis. [ss] Total quantum yield for conversion of isomer **a** to isomer **b** in EtOH at stationary states (~ after 20 min); [a] Maximum quantum yields obtained upon 0-5 min; [b] Maximum quantum yields obtained upon 5-10 min; [c] Maximum quantum yields obtained upon 10-15 min; [d] Maximum quantum yields obtained upon 15-20; the convergent after 20 min is insignificant and was ignored.

1a-**6a** just two singlets for C_5 and C_6 protons were observed. Spectroscopic data for all compounds are shown in (Table 1).

^{1}H NMR of **7** and **8** with 4-NO_2-Ph-, and 4-CH_3-Ph-, substitutions at the carbon-2 of imidazole rings, both indicate the equilibrium ratio between **7a**:**7b** and **8a**:**8b** isomers at steady states upon exposure to room light. The ^{1}H NMR of compound **7** consists of a virtually pure mixture of **7a** and **7b**. This is best ascertained by monitoring the total integral for the two characteristic singlets for each isomer, e.g. 4-Me and 2-H. Thus, the ratio of the combined integral for the peaks at δ = s, 2.4 (4-Me) and s, 6.3 (C2-H) for **7a** to corresponding peaks **7b** at δ = s, 2.3 and s, 6.8 was 1.95 to 1.33 ca for **7a**:**7b**, ~60:40% in equilibrium (Scheme III). For **8a**:**8b** this ratio at steady state was found to be ~67:33. Therefore, the a-b percentage is the upper limit of the quantum yield at room temperature compared to **1a**-**6a**.

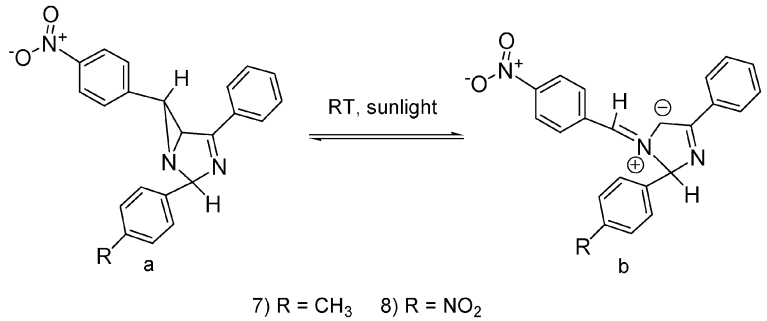
EXPERIMENTAL SECTION

Chemicals were purchased from Fluka, Merck, and Aldrich. Melting points are uncorrected and determined by a Mettler Fp5 melting point apparatus. IR spectra were obtained on a Shimadzu IR-470. Products were characterized by IR, NMR, GC-MS, TLC, and m.p.). All NMR data were recorded in $CDCl_3$ using a Bruker Avance 500-MHz spectrometer. Chemical shifts are reported in ppm (δ) using TMS as internal reference. Mass spectra were obtained from a GC-MS Agilent Technologies QP-5973N MSD instrument. The UV/Vis spectra were recorded on a Shimadzu UV-2100. The 4-nitrochalcone and 2,3-dibromo-4-nitrochalcone were prepared according to a standard procedure.[12]

Synthesis of 2,3-dibromo-4-nitrochalcone (10a; $C_{15}H_{11}NO_3Br_2$)

The 4-nitrochalcone **9a** was prepared according to a standard procedure.[11] 4-Nitrochalcone (0.413 g, 1 mmol) was dissolved in 12 mL $CHCl_3$ inside a hood. Then, 5 mL bromine-$CHCl_3$ was added dropwise to the cooled homogenous 4-nitochalcone solution with stirring at room temperature. After 5-10 minutes, the bromine color was discharged and a lemon yellow solution remained. At this point, an additional 0.5-1 mL of the bromine-$CHCl_3$ solution was added. When the bromine color persists for longer than 30 min., the reaction is completed. The solution was evaporated under vacuum. The solid residue was purified by silicagel column chromatography and recrystallized from CH_2Cl_2/hexane to afford a white solid 0.493 g (98% yield) 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}H NMR ($CDCl_3$) δ: 5.7 (d, *J* = 11.2 Hz, 1H), 5.8 (d, *J* = 11.5 Hz, 1H), 7.6 (t, *J* = 7.7 Hz, 1H), 7.8 (m, 3H),

Scheme III



7) R = CH_3 8) R = NO_2

8.1 (d, J = 7.7 Hz, 2H), 8.3 (d, 8.5 Hz, 2H) ppm.

Synthesis of 2,3-dibromo-3-nitrochalcone (10b; $C_{15}H_{11}NO_3Br_2$)

A similar procedure as used for **10a** was applied. The solid residue was purified by silicagel column chromatography and recrystallized from CH_2Cl_2/hexane to afford a white solid 0.388 g (94% yield) m.p. = 126-129 °C. IR (KBr): 3050, 3000, 1680, 1570, 1520, 1440, 1344, 1270, 1220, 980, 840, 810, 720, 680, 580 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.7 (d, J = 11.3 Hz, 1H), 5.8 (d, J = 11.2 Hz, 1H), 7.6 (t, J = 7.7 Hz, 2H), 7.7 (t, J = 7.9 Hz, 1H), 7.8 (t, J = 7.3 Hz, 1H), 7.9 (d, J = 7.7 Hz, 1H), 8.1 (d, J = 7.6 Hz, 2H), 8.3 (dd, J = 0.7, 8.1 Hz, 1H), 8.5 (s, 1H) ppm.

Synthesis of (3-(4-nitrophenyl)aziridin-2-yl)(phenyl)-methanone (13a; $C_{15}H_{12}N_2O_3$)

A total of 3 mL solution of concentrated ammonia was added to a solution of 2,3-dibromo-4-nitrochalcone (0.413 g, 1 mmol) in 6 mL 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 a silica gel column and recrystallized from ethanol to give an orange solid 0.196 g (73% yield) m.p = 139-140 °C lit[13] 136.8-137 °C. IR (KBr): 3260, 3050, 1662, 1600, 1512, 1445, 1343, 1265, 1230, 1020, 825, 747, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.8 (br, t, J = 8.5 Hz, 1H), 3.3 (dd, J = 2.0, 9.2 Hz, 1H), 3.5 (dd, J = 2.1, 8.1 Hz, 1H), 7.5-7.6 (m, 4H), 7.66 (t, J = 7.4 Hz, 1H), 8.0 (d, J = 7.5 Hz, 2H), 8.2 (d, J = 8.6 Hz, 2H) ppm. MS: (M^+): (EI); exact mass: calcd for $C_{15}H_{12}N_2O_3$ 268.2674, Found 268.2673.

Synthesis of (3-(3-nitrophenyl)aziridin-2-yl)(phenyl)-methanone (13b; $C_{15}H_{12}N_2O_3$)

A similar procedure as used for **13a** was applied. The solid residue was purified by silicagel column chromatography and recrystallized from CH_2Cl_2/hexane to afford a white solid 0.185 g (69% yield) m.p. = 97-98 °C. IR (KBr): 3260, 3050, 1660, 1590, 1520, 1350, 1260, 1220, 1080, 1010, 920, 840, 770, 730, 705, 680 cm^{-1}; ^1H NMR($CDCl_3$) δ: 2.8-2.8 (br, t, J = 8.6 Hz, 1H), 3.3 (dd, J = 2, 9.3 Hz, 1H), 3.6 (dd, J = 2.1, 8.1 Hz, 1H), 7.5-7.6 (m, 3H), 7.7 (t, J = 7.4 Hz, 1H), 7.7 (d, J = 7.7 Hz, 1H), 8.0 (d, J = 7.6 Hz, 1H), 8.2 (d, J = 8.6 Hz, 1H), 8.3 (s, 1H) ppm. MS: (M^+): (EI); exact mass: calcd for $C_{15}H_{12}N_2O_3$ 268.2674; Found 268.2671.

Synthesis of (3-(3-chlorophenyl)aziridin-2-yl)(3-nitro-phenyl)methanone (13c; $C_{15}H_{11}ClN_2O_3$)

A similar procedure as used for **13a** was applied. The solid residue was purified by silicagel column chromatography and recrystallized from CH_2Cl_2/hexane to afford a white solid 0.201 g (73% yield) m.p. = 150-153 °C. IR (KBr): 3250, 3050, 1675, 1590, 1520, 1350, 1255, 1220, 1100, 1010, 930, 845, 770, 730, 705, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.7 (br, 1H), 3.2 (s, 1H), 3.5 (s, 1H), 7.3 (t, J = 8.44, 2H), 7.4 (d, J = 2.2, 2H), 7.7 (t, J = 8.0 Hz, 1H), 8.3 (dd, J = 1.0 Hz, 1H), 8.5 (dddd, J = 1.0 Hz, 1H), 8.8 (t, J = 1.43 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ; 43.8, 44.2, 123.2, 127.6, 128.1, 128,9, 130.2, 133.7, 134.1, 136.3, 137.1, 148.6. MS: (M^+): (EI); exact mass: calcd for $C_{15}H_{11}ClN_2O_3$, 302.0458; Found 302.0456.

Preparation of 4-methyl-6-(4-nitrophenyl)-2,4-diphen-yl-3,5-diazabicyclo[3.1.0]hex-3-ene: A Typical Procedure (1a; $C_{23}H_{19}N_3O_2$)

(3-(4-Nitrophenyl)aziridin-2-yl)(phenyl)methanone **13a** (0.268 g, 1 mmol), NH_4Br (0.1 g, 1 mmol) and the appropriate ketone (1 mmol) were dissolved in 6 mL of absolute ethanol and stirred at room temperature. Anhydrous gaseous ammonia is gently blown into the 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 color 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 recrystallized by ethanol (65.5% yield), methanol or some other suitable solvent. The color of **1a** changes from colorless to **1b** gray m.p. = 186-187 °C. Spectroscopic data and yield for all of compounds **1a-6a** are shown in (Table 1).

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8. The linear dichroism of a sample is defined as the difference in absorbance between two linearly polarized beams of light possessing electric vectors perpendicular to each other. If a system has uniaxial symmetry, such as a nematic, the absorbances are conveniently measured parallel and perpendicular to the long molecular axis (director). In this case, the dichroic ratio R is defined as $R = A_{\|}/A_{\perp}$ where $A_{\|}$ and $A_{\perp}$ are the absorbance for light polarized parallel and perpendicular to the director, respectively. As it was measured, $A_{\|}$-$A_{\perp}$ is positive for absorption bands for these photochromic compounds and may be considered as a parallel transition (i.e π-π^*), provided that the photochromic $\mathbf{A}_{\|}$ molecule has the best orientation along the long axis of the aromatic skeleton.
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