Two 1,3-Diazabicyclo[3.1.0]hex-3-enes with a 'Tripod' Core

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The photochromic 1,3-diazabiclyclo[3.1.0]hex-3-enes **5** and **6** were synthesized from two premade tris-aldehydes and two premade aziridinyl ketones and characterized (*Scheme 1*). Their spectra showed structure–photochromic behavior relationships (SPBR), which were analyzed.

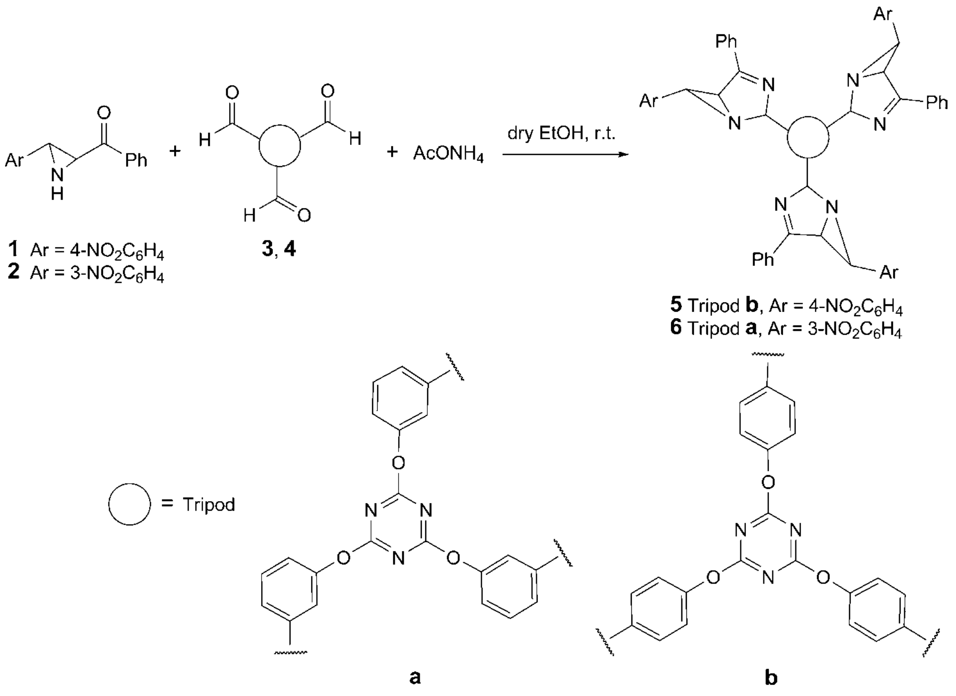
Introduction. – Photochromism is a vast field encompassing well known phenomena associated with reversible transformations of photoisomers having different absorptions upon irradiation with UV and VIS light. This phenomena is not limited to the color or absorption spectra, as the changes are based on two different molecules with different physical and chemical properties [1][2].

Although many types of photochromic compounds have been reported so far, crystals that show photochromic reactions in the crystalline state are very rare [2]. Bicyclic aziridines represent a very interesting class of organic compounds, possessing unique photochromic properties. It has been demonstrated that these compounds form deeply colored, fairly stable materials under UV radiation. This property allows us to consider bicyclic aziridines as possible candidates in the search for photochromic materials [3][4]. Recently, we used a novel type of potentiometry with membrane sensors based on 6-(4-nitrophenyl)-2,4-diphenyl-3,5-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 Sn^{II} [5] and Sr^{II} ions [6] at trace levels in real samples, respectively.

Results and Discussion. – In continuation of prior attempts [3] in the field of 1,3-diazabicyclo[3.1.0]hex-3-ene systems and their applications in photochromism [3][4], we present here the photochromism and synthesis of two novel 1,3-diazabicyclo[3.1.0]-hex-3-enes **5** and **6** from two tris-aldehydes and two aziridinyl ketones as starting materials (*Scheme 1*).

Both synthesized 1,3-diazabicyclo[3.1.0]hex-3-enes **5** and **6** undergo reversible photochromic reactions in cyclohexane, EtOH, Me_2CO, and AcOEt by irradiation with 254 nm UV light and VIS light. We have also found that 'tripod'-connected 1,3-diazabicyclo[3.1.0]hex-3-ene systems undergo reversible photochromic reaction in the crystalline state where also ring opening takes place. Both the **AAA** isomer as well as its photogenerated **BBB** form possess a threefold axis of symmetry and are stable under ambient condition, in addition the photochromic reaction could be repeated without destruction of the crystal structures (*Scheme 2*).

Scheme 1. *Synthetic Route to* **5** *and* **6**

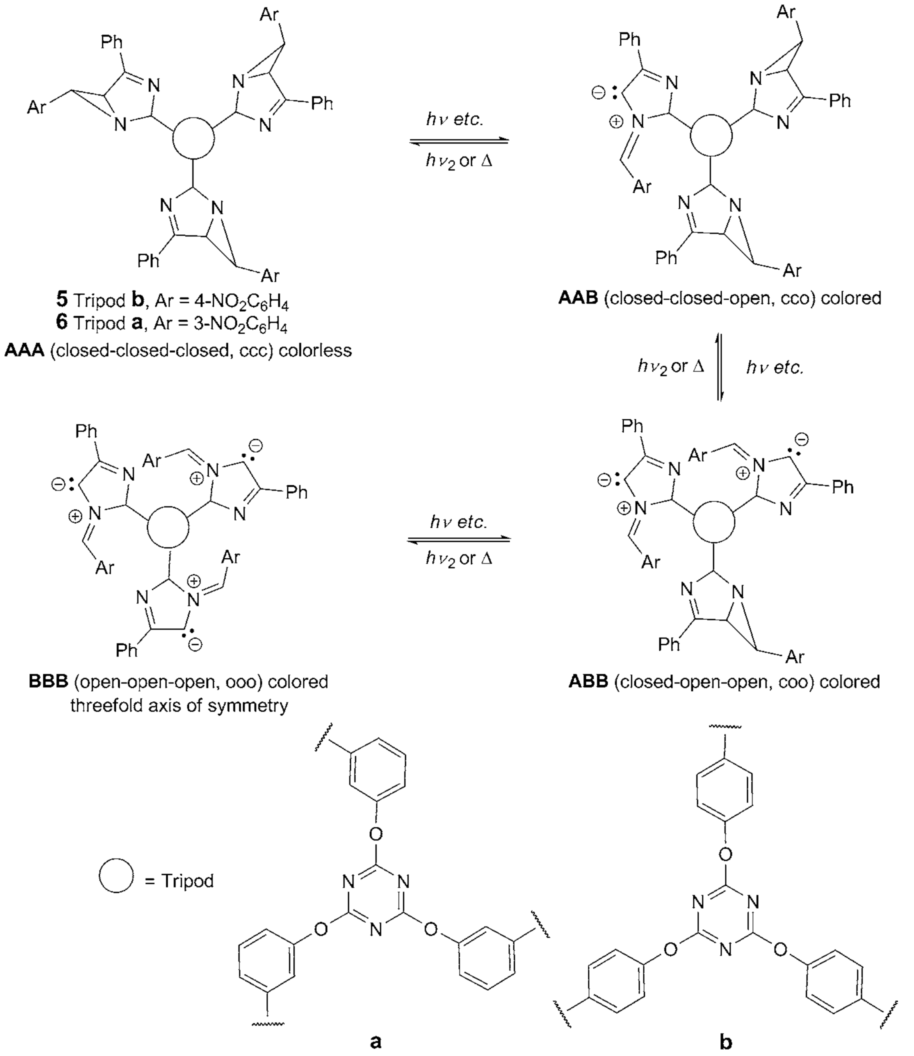


The changes in the absorption spectra of 'tripod'-linked 1,3-diazabicyclo[3.1.0]hex-3-enes **5** and **6** in EtOH under irradiation with 254 nm light are shown in *Fig. 1*. In general, the absorption of the ring-closed form appears at a shorter wavelength, while the absorption of the ring-open form takes place at a longer wavelength. When **AAA-5** was irradiated, two new absorption bands appeared at 258 and 410 nm, respectively, corresponding to **BBB-5**. A similar result was obtained when **AAA-6** was irradiated at 254 nm; the two new absorption bands appeared at 251and 375 nm, respectively, which are ascribed to **BBB-6**. When solid state samples were left in the dark at room temperature, the color faded slowly. This behavior is similar to that observed in solution and indicates clearly that 'tripod'-linked 1,3-diazabicyclo[3.1.0]hex-3-enes also behave similar in the crystalline state on irradiation.

In other attempts, we synthesized for the first time 1,3-diazabicyclo[3.1.0]hex-3-ene **7a**–**7m** under solvent-free conditions in much shorter reaction times. In this case, the reaction was completed after 1–12 h instead of 4–7 d as reported previously (*Fig. 2*, *Table*) [3c–3g]. A color change in the reaction mixture from orange to blue or greenish blue was characteristic for product formation.

Our studies indicate that compounds **5**–**7** in their solid state undergo very low fatigue on irradiation (they can be recycled many times without loss of performance) as compared to their behavior in solution. The described solvent-free procedure for the synthesis of **7** provides a ready access to a variety of these compounds. The colorless isomers **8A** and **9A**, after remaining for 0–15 s under ordinary room light, changed

Scheme 2. *Photochromic Reactions of 1,3-Diazabicyclo[3.1.0]hex-3-enes* **5** *and* **6** *with a Tripod Core*



color. Compound **8A** with a pyridin-2-yl group changed from colorless to deep green (**8B** photoisomer), while compound **9A** with a pyridin-3-yl group changed from colorless to deep blue (**9B** photoisomer; *Fig. 3*). There are principally two isomers possible for either **8B** or **9B**, the depicted (*E*)-form being more stable than its isomeric (*Z*)-form with a pendant arm (*Fig. 4*) [7].

The authors thank the Research Council of the University of Guilan for support of this study.

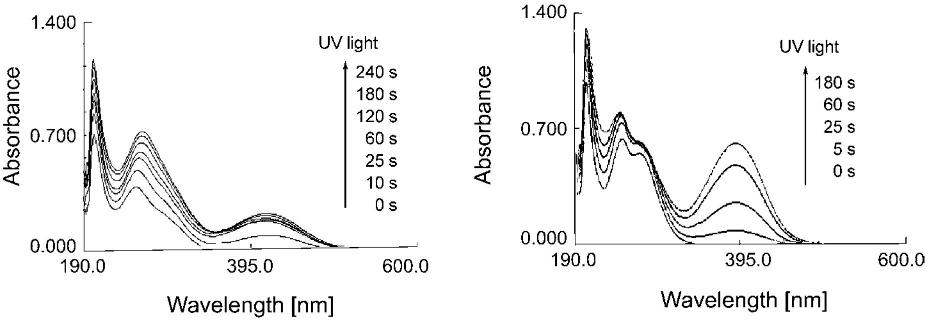
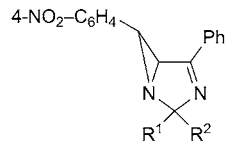


Fig. 1. *Change in the UV/VIS absorption spectra of* **5** (left) *and* **6** (right) *upon irradiation with 254 nm light in EtOH solutions* ($c = 2 \cdot 10^{-5}$ M)



	R^1	R^2		R^1	R^2
7a	Me	Me	**7h**	thiophen-2-yl	H
7b	^{i}Pr	^{i}Pr	**7i**	furan-2-yl	H
7c	Et	Me	**7j**	2-OHC_6H_4	H
7d	Me	^{i}Bu	**7k**	3-OHC_6H_4	H
7e	$(CH_2)_4$		**7l**	4-OHC_6H_4	H
7f	$(CH_2)_5$		**7m**	4-OH,3-$MeOC_6H_3$	H
7g	Ph	H			

Fig. 2. *1,3-Diazobicyclo[3.1.0]hex-3-enes* **7a**–**7m**, *synthesized under solvent-free conditions*

Table. *Synthesis of 1,3-Diazabicyclo[3.1.0]hex-3-enes* **7** *under Solvent-Free Conditions*

7[a])	R^1	R^2	Time [h]	Yield [%][b])	M.p. [°]
a	Me	Me	0.5	97	181–182
b	^{i}Pr	^{i}Pr	2	93	136–137
c	Et	Me	4	94	140–138
d	Me	^{i}Bu	4	90	148–147
e	$(CH_2)_4$		5	88	165–164
f	$(CH_2)_5$		4	95	153–152
g	Ph	H	2	96	172–170
h	2-thienyl	H	14	95	141–140
i	furan-2-yl	H	11	87	170–169
j	2-OHC_6H_4	H	13	85	168–167
k	3-OHC_6H_4	H	11	89	170–171
l	4-OHC_6H_4	H	9	94	180–181
m	4-OH,3-$MeOC_6H_3$	H	12	88	189–190

[a]) Compounds (**A** form) determined by IR and ^{1}H- and ^{13}C-NMR spectroscopy. [b]) Yield of isolated product.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; mesh 200–300). TLC: SiO_2 plates. M.p.: *Mettler-Fpc5* apparatus; uncorrected. Absorption spectra: spectra in the range 200–800 nm (EtOH, $c = 1.0 \cdot 10^{-4}$ mol dm^{-3}) as well as the positions of $\lambda^{\mathbf{A}}_{\max}$ (in nm) for the initial **A** form and of $\lambda^{\mathbf{B}}_{\max}$ (in nm) for the photoinduced **B** form were measured with a *Shimadzu-UV-2100* spectrophotometer; the photo-

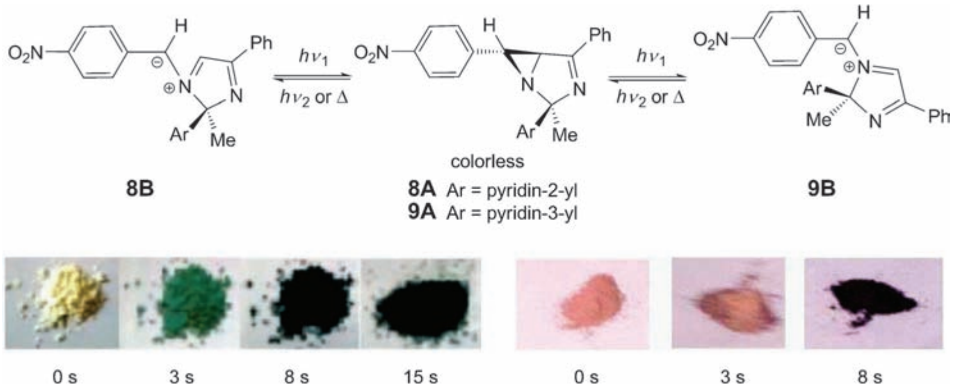


Fig. 3. *Colorless isomers* **8A** (left) *and* **9A** (right) *after remaining for 0–15 s under ordinary room light*

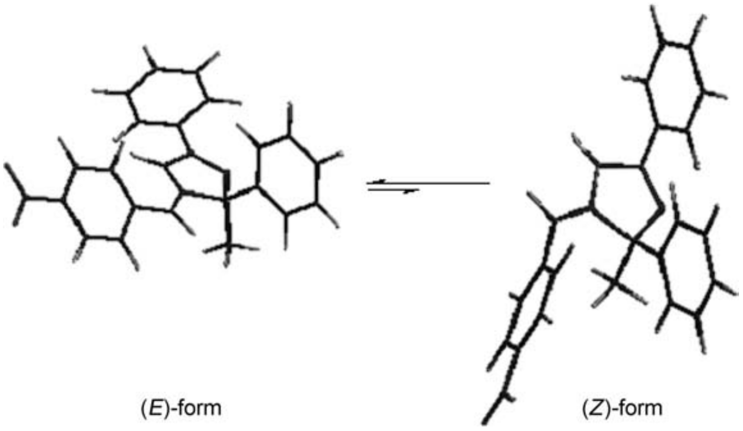


Fig. 4. *The MOPAC drawing for either* **8B** *or* **9B** *indicates* the *(*E*)-form as a more stable isomer compared to the (*Z*)-form*

induced open form **B** was generated upon UV irradiation (Hg low-pressure lamp (*DRSh-260*) + UV-transmitting glass filters), and reversion to the initial **A** form was achieved upon either storage in the dark for 1–7 d or by heating at 80–90° for 4–5 min. IR Spectra (KBr): *Shimadzu-IR-470* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker-DRX* 500 MHz (^{1}H) instrument and *Bruker-DRX-125-Avance* (^{13}C) spectrometer; δ in ppm with the solvent as internal standard (CDCl$_3$ at δ 7.26, (D$_6$)DMSO at δ 2.50), J in Hz.

4,4′,4″-[1,3,5-Triazine-2,4,6-triyltris(oxy)]tris[benzaldehyde] (**3**) was synthesized according to [8]. Yield 69.5%. White solid. M.p. 175–176°. IR: 3090*w*, 2850*m*, 1718v*s*, 1600*s*, 1570v*s*, 1370v*s*, 1210*s*, 1180*m*, 1100*w*, 810*s*, 760*m*, 690*m*. ^{1}H-NMR (CDCl$_3$): 7.30 (*d*, J = 8.5, 6 H); 7.90 (*d*, J = 8.6, 6 H); 9.98 (*s*, 3 H).

2,2′,2″-[1,3,5-Triazine-2,4,6-triyltris(oxy-4,1-phenylene)]tris[6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene] (**5**). To the soln. of **3** (1 mmol, 0.44 g) and aziridinyl ketone **1** (3 mmol, 0.81 g) in dry EtOH (7 ml) was added NH$_4$OAc (14 mmol, 1.08 g) at r.t. The mixture was stirred for 4 d at r.t. On cooling in a refrigerator, a precipitate was formed. The precipitate was collected by filtration, washed with small portions of EtOH, and dried. CC (SiO$_2$, hexane/AcOEt 5 : 1) gave **5** (72%). Yellow solid. Closed form 48%. M.p. 186–187°. IR: 3080*w*, 3020*w*, 1600*m*, 1560*s*, 1520*s*, 1480*m*, 1440*m*, 1370v*s*, 1340*s*, 1260*m*, 1230*m*, 1160*m*, 1080*m*, 1040*m*, 1020*w*, 765*m*, 740*m*, 690*s*. ^{1}H-NMR ($CDCl_3$; closed form 48%): 2.47 (*s*, 3 H); 3.77 (*s*, 3 H); 6.72 (*s*, 3 H); 7.05 – 7.14 (*m*, 6 H); 7.16 – 7.22 (*m*, 6 H); 7.40 (*d*, *J* = 7.3, 6 H); 7.46 – 7.59 (*m*, 9 H); 7.95 (br. *s*, 6 H); 8.16 (*d*, *J* = 8.0, 6 H). ^{13}C-NMR ($CDCl_3$): 42.2; 58.2; 96.1; 121.9; 124.1; 127.8; 128.6; 128.9; 129.3; 131.9; 132.3; 139.3; 145.7; 147.8; 151.5; 171.0; 174.0.

Irradiation of the EtOH soln. of **5** with UV light converted it to the open green form (open form 52%). UV/VIS (EtOH): 210 and 250 before irradiation, and 210, 255 and 415 after irradiation. ^{1}H-NMR ($CDCl_3$; open form **BBB-5**): 2.72 (*s*, 3 H); 3.72 (*s*, 3 H); 6.20 (*s*, 3 H); 7.46 – 7.59 (*m*, 27 H); 7.95 (br. *s*, 6 H); 8.20 (*d*, *J* = 8.2, 6 H). ^{13}C-NMR ($CDCl_3$): 48.3; 57.3; 97.2; 121.9; 124.2; 127.7; 128.5; 129.1; 129.34; 131.7; 132.4; 137.0; 145.8; 147.9; 151.8; 170.4; 174.0.

3,3′,3″-[1,3,5-Triazine-2,4,6-triyltris(oxy)]tris[benzaldehyde] (**4**) was synthesized according to [8]. Yield 78%. White solid. M.p. 225 – 226°. IR: 3390*w*, 3080*w*, 3020*w*, 2820*m*, 2710*m*, 1695*s*, 1590*s*, 1560*vs*, 1480*m*, 1450*m*, 1370*vs*, 1270*m*, 1220*vs*, 1150*m*, 1130*m*, 1080*m*, 805*s*, 760*m*, 690*m*, 640*m*. ^{1}H-NMR ($CDCl_3$): 7.34 (*d*, *J* = 7.4, 3 H); 7.48 (*t*, *J* = 7.3, 3 H); 7.58 (*s*, 3 H); 7.69 (*d*, *J* = 6.93, 3 H); 9.93 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 122.0; 127.7; 128.3; 129.2; 130.7; 138.1; 152.3; 173.7; 191.2.

2,2′,2″-[1,3,5-Triazine-2,4,6-triyltris(oxy-3,1-phenylene)]tris[6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene] (**6**). As described for **5**, with **4** and aziridinyl ketone **2**: 70% of **6**. Yellow solid. Closed form 46%. M.p. 181 – 182°. IR: 3080*w*, 3020*w*, 1595*m*, 1560*s*, 1518*s*, 1480*m*, 1440*m*, 1370*vs*, 1340*s*, 1260*m*, 1225*s*, 1150*m*, 1080*m*, 1040*m*, 1020*m*, 765*m*, 740*m*, 690*m*. ^{1}H-NMR ($CDCl_3$; closed form 46%): 2.48 (*s*, 3 H); 3.71 (*s*, 3 H); 6.72 (*s*, 3 H); 7.05 – 7.13 (*m*, 6 H); 7.29 – 7.53 (*m*, 24 H); 7.94 (br. *s*, 6 H); 8.02 – 8.07 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 41.9; 57.9; 95.9; 121.1; 121.7; 121.9; 122.9; 125.5; 128.9; 129.1; 129.3; 129.8; 129.9; 131.9; 133.0; 133.3; 140.7; 148.9; 152.1; 170.9; 174.0.

Irradiation of the EtOH soln. of **6** with UV light converted it to the open pale green form (open form 54%). UV/VIS (EtOH): 210, 246 and 272 before irradiation, and 210, 252 and 382 after irradiation. ^{1}H-NMR ($CDCl_3$): 2.77 (*s*, 3 H); 3.71 (*s*, 3 H); 6.20 (*s*, 3 H); 7.29 – 7.53 (*m*, 21 H); 7.94 (br. *s*, 6 H); 8.13 (*s*, 3 H); 8.19 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 48.0; 57.0; 97.1; 121.2; 121.8; 121.9; 123.1; 125.0; 128.9; 129.1; 129.3; 129.9; 130.1; 131.8; 132.3; 133.3; 140.5; 148.9; 152.1; 171.2; 174.0.

Synthesis of **7a – 7m**: *General Procedure.* A mixture of aziridinyl ketone **1** or **2** (268 mg, 1 mmol), aldehyde or ketone (1 mmol), and NH_4OAc (750 mg, 10 mmol) was vigorously stirred at r.t. for 1 – 12 h. During this time, the color of the mixture gradually changed. After completion of the reaction, the solid compounds were purified by either prep. TLC or CC (AcOEt/petroleum ether 3 : 1) and recrystallized from 96% EtOH yielding the desired compounds. In some cases (**7a – 7j**), the final product was recrystallized from 96% EtOH without preceding chromatography.

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Received August 21, 2011