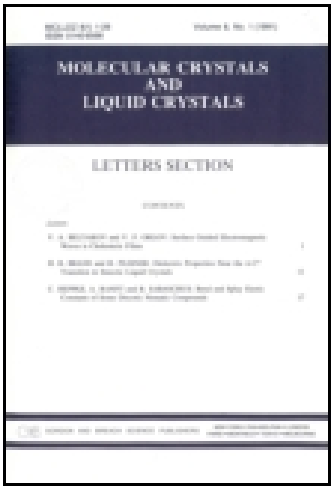

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photochemistry of Fluorescent Azobenzenes Substituted with Azulenylpyridine Moiety

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Published online: 15 Dec 2014.

Mol. Cryst. Liq. Cryst., Vol. 604: pp. 41–51, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.967653

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Photochemistry of Fluorescent Azobenzenes Substituted with Azulenylpyridine Moiety

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Fluorescent properties and the photoisomerization behaviour of 4-azulenylpyridine-substituted azobenzenes were investigated. All studied compounds have shown fluorescent emission in solution, originating from excited singlet state $S_2 \rightarrow S_0$ of azulene moiety. The substitution of the azobenzene chromophore has affected the preservation of the fluorescence emission in thin films prepared in PMMA matrix. Correlation of absorption spectra with ^{1}H–NMR spectroscopy revealed that for all compounds the E → Z *isomerization takes place upon exposure to UV light.*

Keywords Azobenzene; azulenylpyridine; fluorescence; photoisomerization.

Introduction

Azo compounds are versatile molecules, and have received considerable attention in both fundamental and applied research areas. One of the most intriguing properties of these compounds is the reversible photoisomerization process between the E and Z isomers of different stability [1–4]. This property has been exploited in numerous applications such as switchable sensors [5–7], ion channels [8–10], catalysts [11–13], liquid crystals [14–16], or enhanced by their successful incorporation in various polymeric matrixes, both through covalent linkage and/or host/guest doping providing systems with direct application in biochemistry and optical devices [17–20]. In general, azo compounds show strong electronic absorption bands which can be shifted from UV to the visible region by chemical modification, thus allowing for the fine-tuning of color. When the appropriate electron donor/acceptor ring substitution was chosen, the azo chromophores yielded high optical nonlinearity with application in the field of optoelectronics and photonics [21–25].

The photoisomerization of azobenzene has been used to drive functional changes in biomolecules like for example the photo-control of coiled coil proteins in cell culture and ion channels on extracellular surfaces *in vivo*. [26, 27] In order to function as tools for controlling molecular events in complex living systems however, the photoswitching

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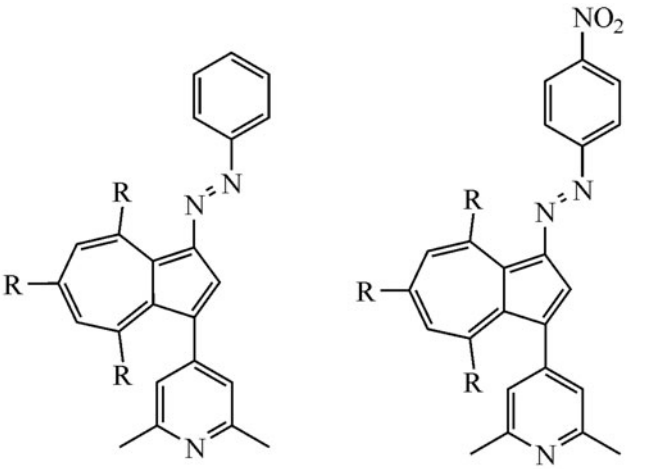
properties of the azobenzene chromophore must involve non-destructive external stimuli for the biological environment. Investigations into azobenzenes chemistry showed that these molecules can be modified such as that, new properties may be achieved making them appropriate for applications in biological systems. Azobenzenes are known to be non-fluorescent in solutions owing to their ability to undergo fast $E \rightarrow Z$ isomerization [9]. Hence, it would be very useful to have photoswitching azobenzenes that include fluorescent readout to monitor their activity in complex structures. Modification of the chromophore skeleton with electron donating/accepting groups at *para*-positions can yield derivatives emitting green, yellow, orange and red fluorescence with high quantum yields when the azo-bond is successfully "locked" in the excited state [29, 30].

Among various types of electron donating/accepting groups, azulene derivatives can play an important role. Azulene is a non-bezenoid aromatic hydrocarbon with unique redox properties [31–33], reason why has been used to prepare semiconductive materials [34, 35]. This aromatic hydrocarbon is a bicyclo[5.3.0]decapentene with five- and seven-membered rings carrying negative and positive charges, respectively. Therefore, azulene can react both with electrophile and nucleophile, being versatile fragment for the design of organic materials [36]. Moreover, azulene and its derivatives exhibit fluorescent emission originating from excited singlet state $S_2 \rightarrow S_0$ with relatively high fluorescence quantum yield, and $S_1 \rightarrow S_0$ fluorescence with extremely low fluorescence quantum yield [37, 38]. In this context, the use of azulene in the design of fluorescent azobenzenes is quite promising.

Owing to our continuing interests related to π-conjugated azulene derivatives [39–42], we have recently reported the synthesis, optical and electrochemical properties of azophenyl substituted 4-(azulen-1-yl)-pyridines **1–4** (Scheme 1) [43]. The aim of the present work is to investigate the fluorescence properties of these compounds both in solution and poly(methyl methacrylate) (PMMA) thin films, as well as their photochemical $E \rightarrow Z$ isomerization in solution.



1: R = H

2: R = CH_3

3: R = H

4: R = CH_3

Scheme 1. Chemical structure of the compounds under investigation.

Experimental Techniques and Characterization

The azo coupling reactions for isolation of compounds **1** – **4** (Scheme 1) was recently reported [43]. The numbering of atom positions used for the characterization of the compounds is described in Figure 7. The fluorescence measurements were performed on Jasco FP 6500 fluorimeter using solvent of fluorescence grade. The UV-Vis spectra were recorded on Varian Cary 100 spectrophotometer. Thin films were obtained using spin-coating technique on Laurell –WS– 400B – 6NPP/LITE apparatus. The photoisomerization reaction was performed in the dark by using a Micro photochemical reaction assembly with quartz well and UV lamp of 5.5 W, equipped with a water jacket. The monitoring of the E → Z reaction progress was followed spectroscopically in a quartz cell with pass length of 1.0 cm. The thin films were prepared using PMMA (purchased from Sigma Aldrich). The concentration of the 4-azulenylpyridine-substituted azobenzene films were made by mixing the indicated concentration of dye with PMMA in TCE as solvent. The NMR spectra in $CDCl_3$ containing TMS as internal standard were recorded on Bruker Avance DRX400 spectrometer; chemical shifts (δ) are expressed in ppm, and J values are given in Hz. The full characterization of the stable E – isomers of the herein investigated compounds was previously reported [43]. The ^{1}H-NMR data of the two E and Z isomers (obtained after 30 minutes of irradiation with a UV lamp of 254 nm (5.5 W)) are presented here.

(E)-[3-(2,6-dimethyl-pyridin-4-yl)azulen-1-yl]-phenyl-diazene **(1)**. UV-Vis (chloroform): λ_{max} (log ε) 247 (4.35), 327 (4.40), 430 (4.47) nm. ^{1}H NMR ($CDCl_3$): δ 2.66 (s, 6H, 2-Me, 6-Me), 7.24 (s, 2H, 3-H, 5-H), 7.39 (t, 1H, J = 9.6 Hz, 5′-H), 7.41 (t, J = 7.5 Hz, 1H, 4″-H), 7.48 (t, 1H, J = 10.0 Hz, 7′-H), 7.56 (t, 2H, J = 7.6 Hz, 3″-H, 5″-H), 7.82 (t, 1H, J = 10.0 Hz, 6′-H), 8.03 (d_{AB}, 2H, J = 7.6 Hz, 2″-H, 6″-H), 8.44 (s, 1H, 2′-H), 8.59 (d, 1H, J = 9.6 Hz, 4′-H), 9.44 (d, 1H, J = 9.6 Hz, 8′-H) ppm. *(Z)*- **1**: ^{1}H NMR ($CDCl_3$): δ 2.93 (s, 6H, 2-Me, 6-Me), 7.36 (t, 1H, J = 9.6 Hz, 5′-H), 7.46 (t, 3 H, J = 10.0 Hz, 7′-H, 3″-H, 5″-H), 7.57 (s, 2H, 3-H, 5-H), 7.64 (t, J = 8.4 Hz, 1H, 4″-H), 7.73 (t, 1H, J = 10.0 Hz, 6′-H), 8.01 (d_{AB}, 2H, J = 7.6 Hz, 2″-H, 6″-H), 8.61 (d, 1H, J = 9.8 Hz, 4′-H), 8.85 (s, 1H, 2′-H), 9.45 (d, 1H, J = 9.6 Hz, 8′-H) ppm.

(E)-[3-(2,6-dimethyl-pyridin-4-yl)-4,6,8-trimethyl-azulen-1-yl]-phenyl-diazene, **(2)**. UV-Vis (chloroform): λ_{max} (log ε) 252 (4.61), 324 (4.44), 438 (4.46) nm. ^{1}H NMR ($CDCl_3$): δ 2.47 (s, 3H, 6′-Me), 2.57 (s, 6H, 2-Me, 6-Me), 2.64 (s, 3H, 4′-Me), 3.41 (s, 3H, 4′-Me), 7.02 (s, 2H, 3-H, 5-H), 7.12 (s, 1H, 5′-H), 7.32 (s, 1H, 7′-H), 7.36 (t, 1H, J = 7.6 Hz, 4″-H), 7.48 (t, 2H, J = 7.2 Hz, 3″-H, 5″-H), 7.85 (d_{AB}, 2H, J = 7.6 Hz, 2″-H, 6″-H), 8.04 (s, 1H, 2′-H) ppm. *(Z)*- **2**: ^{1}H NMR ($CDCl_3$): δ 2.47 (s, 3H, 6′-Me), 2.67 (s, 3H, 4′-Me), 2.94 (s, 6H, 2-Me, 6-Me), 3.38 (s, 3H, 4′-Me), 7.22 (s, 1H, 5′-H), 7.32 (s, 2H, 3-H, 5-H), 7.37 (t, 1H, J = 7.2 Hz, 4″-H), 7.45 (s, 1H, 7′-H), 7.48 (d, 2H, J = 7.6 Hz, 3″-H, 5″-H), 7.82 (d_{AB}, 2H, J = 7.6 Hz, 2″-H, 6″-H), 8.12 (s, 1H, 2′-H) ppm.

(E)-[3-(2,6-dimethyl-pyridin-4-yl)azulen-1-yl]-(4-nitro-phenyl)diazene, **(3)**. UV-Vis (chloroform): λ_{max} (log ε) 247 (4.44), 301 (4.46), 480 (4.42) nm. ^{1}H NMR ($CDCl_3$): δ 2.66 (s, 6H, 2-Me, 6-Me), 7.29 (s, 2H, 3-H, 5-H), 7.53 (t, 1H, J = 9.8 Hz, 5′-H), 7.65 (t, 1H, J = 9.8 Hz, 7′-H), 7.93 (t, 1H, J = 9.8 Hz, 6′-H), 8.09 (d_{AB}, 2H, J = 9.2 Hz, 2″-H, 6″-H), 8.39 (d_{AB}, 2H, J = 8.8 Hz, 3″-H, 5″-H), 8.43 (s, 1H, 2′-H), 8.64 (d, 1H, J = 9.6 Hz, 4′-H), 9.46 (d, 1H, J = 10.0 Hz, 8′-H) ppm. *(Z)* -**3**: ^{1}H NMR ($CDCl_3$): δ 2.77 (s, 6H, 2-Me, 6-Me), 7.35 (s, 2H, 3-H, 5-H), 7.56 (t, 1H, J = 9.8 Hz, 5′-H), 7.68 (t, 1H, J = 9.8 Hz, 7′-H), 7.96 (t, 1H, J = 10.0 Hz, 6′-H), 8.08 (d_{AB}, 2H, J = 8.8 Hz, 2″-H, 6″-H), 8.38 (d_{AB}, 2H, J = 9.2 Hz, 3″-H, 5″-H), 8.44 (s, 1H, 2′-H), 8.64 (d, 1H, J = 9.6 Hz, 4′-H), 9.48 (d, 1H, J = 10.0 Hz, 8′-H) ppm.

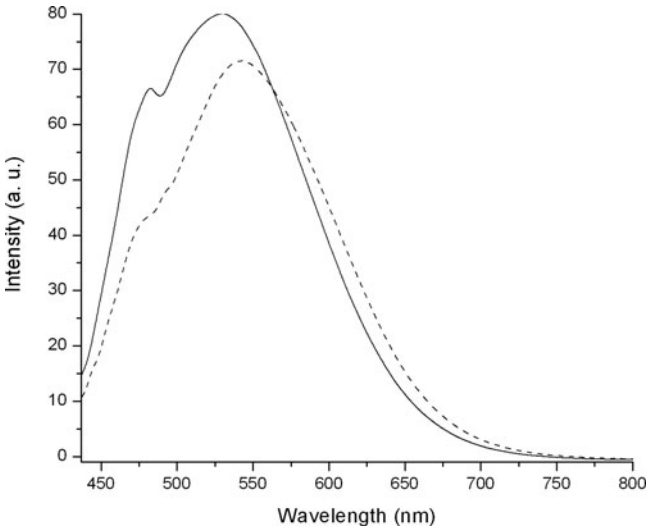


Figure 1. Fluorescent spectra of **1** (solid line) and **2** (dashed line) in 1,1,2-trichloroethane (conc. $1.3 \cdot 10^{-5}$ M, excitation wavelength = 420 nm).

(E)-[3-(2,6-dimethyl-pyridin-4-yl)-4,6,8-trimethyl-azulen-1-yl]-(4-nitro-phenyl)diazene, (**4**). UV-Vis (chloroform): λ_{max} (log ε) 254 (4.49), 323 (4.37), 486 (4.52) nm. ^{1}H NMR ($CDCl_3$): δ 2.49 (s, 3H, 6′-Me), 2.59 (s, 6H, 2-Me, 6-Me), 2.68 (s, 3H, 4′-Me), 3.41 (s, 3H, 8′-Me), 7.03 (s, 2H, 3-H, 5-H), 7.26 (s, 1H, 5′-H), 7.46 (s, 1H, 7′-H), 7.90 (d_{AB}, 1H, J = 8.8 Hz, 2″-H, 6″-H), 8.05 (s, 1H, 2′-H), 8.34 (d_{AB}, 2H, J = 9.2 Hz, 3″-H, 5″-H) ppm. *(Z)*- **4**: ^{1}H NMR ($CDCl_3$): δ 2.51 (s, 3H, 6′-Me), 2.73 (s, 6H, 2-Me, 6-Me), 2.95 (s, 3H, 4′-Me), 3.42 (s, 3H, 8′-Me), 7.33 (s, 2H, 3-H, 5-H), 7.38 (s, 1H,

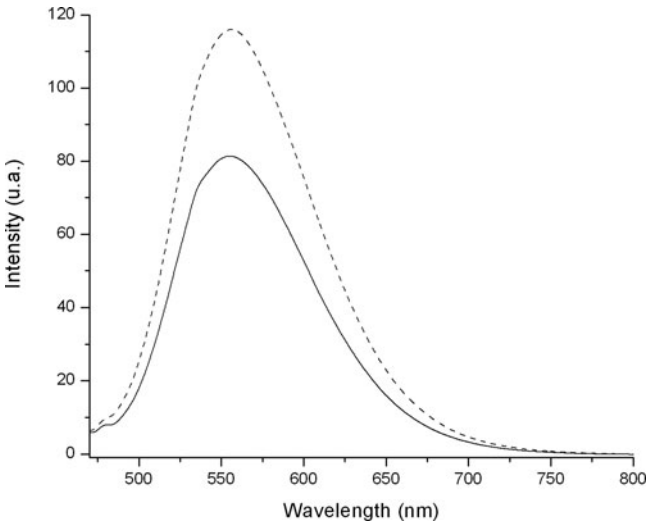


Figure 2. Fluorescent spectra of **3** (solid line) and **4** (dashed line) in 1,1,2-trichloroethane (conc. $0.6 \cdot 10^{-5}$ M, excitation wavelength = 460 nm).

5′-H), 7.58 (s, 1H, 7′-H), 7.92 (d_{AB}, 1H, $J = 9.2$ Hz, 2″-H, 6″-H), 8.14 (s, 1H, 2′-H), 8.36 (d_{AB}, 2H, $J = 8.8$ Hz, 3″-H, 5″-H) ppm.

Results and Discussion

Synthesis

The synthesis of compounds **1–4** (Scheme 1) was previously reported and involves the azo coupling reaction of 4-azulenylpyridines with the diazonium salts of aniline and p-nitroaniline, respectively, in potassium acetate buffer [43]. The reaction proceed in mild conditions with moderate to high yields, making the compounds easily accessible.

Fluorescence Investigations

Azobenzene molecules are in general not fluorescent. The attachement of the azulenyl moiety has induced fluorescent properties of the herein described compounds. The fluorescence measurements were performed in 1,1,2-trichloroethane (TCE) solutions. Differences in the intensity and position of the emission peaks have been observed. The main fluorescence emission was the usual $S_2 \rightarrow S_0$ azulene transition. The position of the visible absorption bands was influenced by the functional groups grafted to the azobenzene skeleton and, to a lesser extent, by the alkyl substituents of the azulene moiety. Thus, the nitro-substituted dyes **3** and **4** displayed intense absorption maxima at 465 and 480 nm, respectively, while the unsubstituted azobenzene dyes **1** and **2** showed visible maxima at lower wavelengths of 423 and 426 nm, respectively, therefore the fluorescence spectra were recorded using different excitation wavelength. The emission spectra of TCE solutions are shown in Figures 1 and 2. First, excitation of compounds **1** and **2** at the related wavelength (420 nm) gave the emission spectra with λ at 531 nm for compound **1** and 540 nm for compounds **2**, respectively, with shoulder like maximum around 480 nm in both cases. The electron-withdrawing

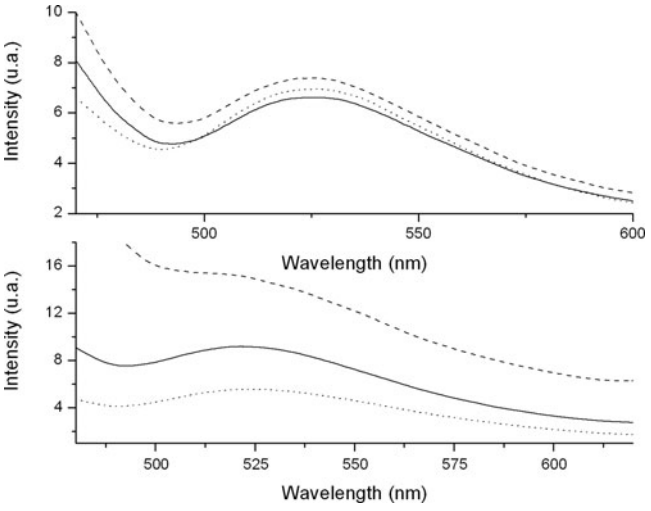


Figure 3. Fluorescent spectra of PMMA thin films containing compound **1** (up) and compound **2** (down) of different loadings: 2% (solid line), 5% (dashed line) and 10% (dotted line).

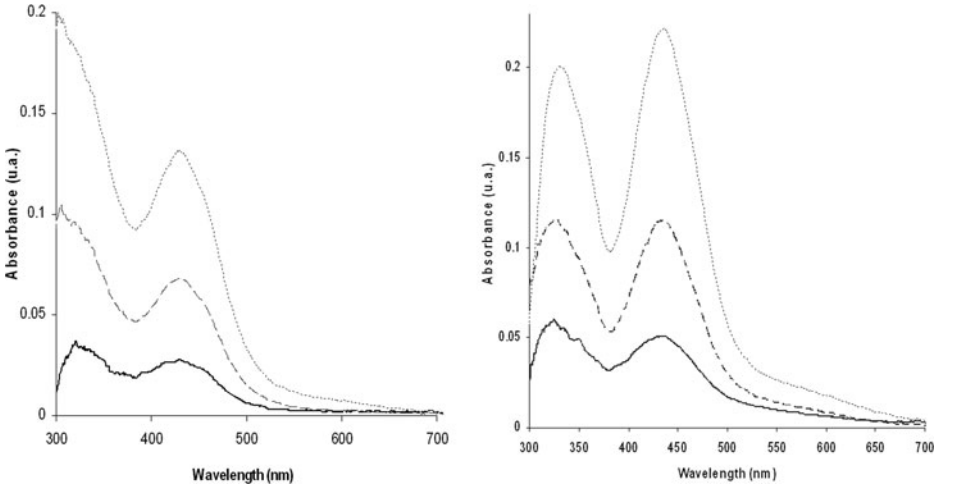


Figure 4. UV-Vis spectra of PMMA thin films containing compound **1** (left side) and compound **2** (right side) of different loadings: 2% (solid line), 5% (dashed line) and 10% (dotted line).

effect of the methyl groups in compound **2** caused a red shift of the emission wavelength accompanied by a small decrease of the intensity value.

The electron-donating ability of the nitro-substituent has influenced the λ_{Ex} of compounds **3** and **4**. The emission spectra are shown in Figure 2. The absorption maximum appeared at long wave position, with emission spectra showing maximum peaks at 554 and 556 nm, for **3** and **4**, respectively. Most likely the electronic effect of the nitro-group decreases the HOMO-LUMO gap and makes λ_{Em} shift to red direction. Indeed, MOPAC calculations for HOMO and LUMO orbital energy showed that through extension of the electronic conjugation, the LUMO energy decreases, and in turn reduces the HOMO-LUMO gap, moving the absorption band at higher wavelengths [43].

Fluorescence measurements were also performed in thin films in order to monitor the assembly process of the azulenyl-pyridine substituted azobenzenes. Only for the unsubstituted azobenzene compounds **1** and **2**, could be recorded the fluorescence spectra of the PMMA thin films containing different chromophore loadings (2%, 5% and 10%) (Fig. 3). The visible absorption peaks in thin films (∼430 nm) are well preserved, being close to the absorption maxima recorded in solutions (Fig. 4) with a linear increase of intensity with the dye loading. For these compounds, characteristic emission peaks are observed at 525 nm, close to emission position in the corresponding TCE solutions. This indicates that, the characteristic emission of the 4-azulenylpyridine azobenzene molecules preserve after incorporation in polymeric matrix.

The stable growth of these assemblies yields an increase of the fluorescence intensity with the amount of azulene-based dye incorporated in the PMMA matrix for the first two concentrations, 2% and 5% respectively. Further loading (10% dye) causes a decrease of the fluorescence intensity. This partial quenching effect is a consequence of strong π-π contacts established between azulenyl moieties, in agreement with the well-known polarization of the azulene in solid state [44].

In the case of PMMA thin films containing dye-compounds **3** and **4**, the fluorescence spectra exhibit no measurable emission peaks when excited at wavelengths longer than 400 nm. This is in accordance with the observed red shift of the visible absorption maxima

Table 1. UV-Vis spectra of compounds **1–4** before irradiation, in $CHCl_3$ solution

Compound	λ_1 (ε)	λ_2 (ε)	λ_3 (ε)
1	247 (22291)	327 (25129)	430 (29318)
2	252 (40760)	324 (27480)	438 (29150)
3	247 (27432)	301 (29066)	480 (26381)
4	254 (31405)	323 (23500)	486 (33081)

in solutions. The recorded bathochromic shift is caused by strong π-conjugation induced through electron-donating nitro substitution. As previously reported, planar molecules with long electron conjugation path show negligible fluorescence due to the fact that close $\pi - \pi$ stacking in the solid state is promoted, which in turns quenches the fluorescence [45, 46].

Photoisomerization Investigations

The photochemical $E \rightarrow Z$ isomerization of the azo bond of compounds **1–4** was investigated by UV-Vis and NMR spectroscopy in chloroform solutions. When the compounds were in the thermally stable *E* configuration, the absorption spectra showed two strong bands in the UV region (see Table 1) and one in the visible region with molar absorptivities ranging from 26381 to 33081 $M^{-1}cm^{-1}$ and not much effect of solvent polarity. Thus, unsubstituted azobenzene dyes **1** and **2** showed visible maxima at lower wavelengths of 430 and 438 nm while the, nitro-substituted dyes **3** and **4** displayed intense absorption maxima at 480 and 486 nm, respectively.

The photochromic behaviour of compounds **1–4** was spectrophotometrically monitored by following the changes in the absorption spectra while irradiating at 254 nm (5.5 W UV lamp, at room temperature). As expected, all compounds displayed $E \rightarrow Z$ isomerization upon exposure to UV light. In the first 30 seconds of irradiation, both the nitro-substituted and the unsubstituted dyes showed a hypsochromic shift of the visible band (Figs. 5 and 6), while upon prolonged irradiation they displayed different absorption profiles. Thus,

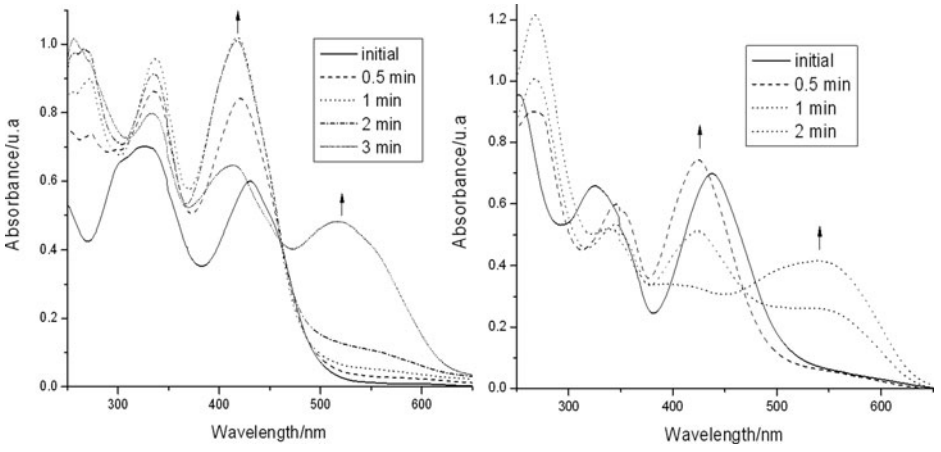


Figure 5. Absorption spectra of compounds **1** and **2** in $CHCl_3$ solutions under 254 nm irradiation. The exposure time is shown in the inset legends.

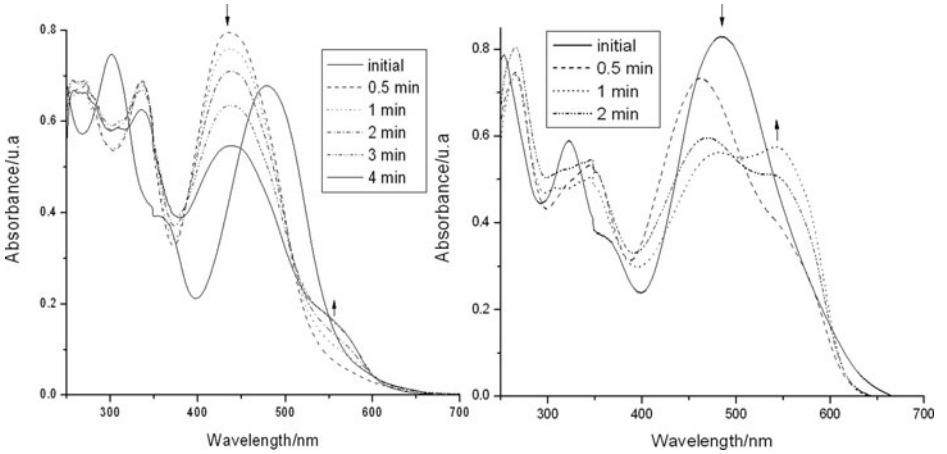


Figure 6. Absorption spectra of compounds **3** and **4** in $CHCl_3$ solutions under 254 nm irradiation. The exposure time is shown in the inset legends.

the unsubstituted dyes **1** and **2** showed an increase in the absorption at around 400 nm accompanied by the appearance of a new absorption band in the visible region at 514 and 534 nm, respectively (Fig. 5). On the other hand, prolonged irradiation of the nitro-substituted dyes **3** and **4** produced the same hypsochromic shift of the absorption maximum, whereas the appearance of the new visible band was not as clear (Fig. 5). However, for all four compounds, the photochemical $E \rightarrow Z$ isomerization proceeded to approximately the same extent, with the absorbance variation after UV irradiation ranging between 0.43 and 0.53 absorbance units. Exposure of the irradiated solutions to sunlight for a day caused the disappearance of the newly formed visible band and the partial recovery of the UV-Vis spectra recorded after 30 seconds of UV irradiation.

Correlation of absorption spectra with ^{1}H–NMR data elucidated the spectral assignments. Examination of the NMR data for the pre-irradiated solutions of all azobenzenes in $CDCl_3$ (around 5 mM for NMR experiments, but diluted to 0.025 mM for absorption spectra) revealed the absence of the *Z* isomer. In contrast, the NMR spectra of the samples after 30 minutes of UV irradiation (5.5 W, UV lamp) were comprised of peaks corresponding only to the *Z* stereoisomer, thus demonstrating that the E → Z isomerization occurred.

The differences in chemical shifts between the *E* and *Z* isomers are more pronounced for the pyridyl protons and less for the azulenyl moiety. A summary of the NMR data and spectral assignments for the *E* and *Z* isomers of compounds **1–4** is given in Table 2. The spectral changes occurring after the $E \rightarrow Z$ isomerization can be summarized as follows:

1. The pyridyl protons, both aromatic and methyl protons, are consistently more deshielded in the *Z* than in the *E* isomer.
2. The protons at the 2′-position of the azulene ring (see Fig. 7 for atom numbering) resonate at significantly different chemical shifts in the two isomers, depending on the substitution of both the azobenzene core and the azulene moiety.

For the sake of clarity, the NMR spectral changes induced by irradiation will be detailed for compound **2** in which the alkyl substitution of the azulene moiety simplifies the assignment of aromatic protons. Thus, the ^{1}H-NMR spectrum of the pre-irradiated solution of **2** showed singlet peaks at 2.57 and 7.02 ppm, corresponding to the protons at the 2/6- and

Table 2. Relevant chemical shifts of pyridinium ring and azulen protons for compounds **1–4**

Entry	Compound	$\delta_{CH3-2.6}$ (ppm)	$\delta_{H-3.5}$ (ppm)	$\delta_{H-2'}$ (ppm)
1	1–E	2.66	7.24	8.44
	1–Z	2.93	7.57	8.61
2	2–E	2.57	7.02	8.04
	2–Z	2.94	7.32	8.12
3	3–E	2.66	7.29	8.43
	3–Z	2.77	7.35	8.44
4	4–E	2.59	7.03	8.05
	4–Z	2.73	7.33	8.14

3/5-positions of the pyridyl moiety. Upon UV irradiation, these two peaks shifted downfield to 2.94 and 7.32 ppm, respectively (Figure 7). This significant downfield chemical shift is in accordance with the proposed photoisomerization reaction and can be correlated with the loss of symmetry in the resulting *Z* isomer. Furthermore, the proton at the 2′-position of azulene also shifted downfield by 0.08 ppm because of the deshielding effect of the phenyl group which is located closer to the azulenyl moiety in the *Z* than in the *E* isomer.

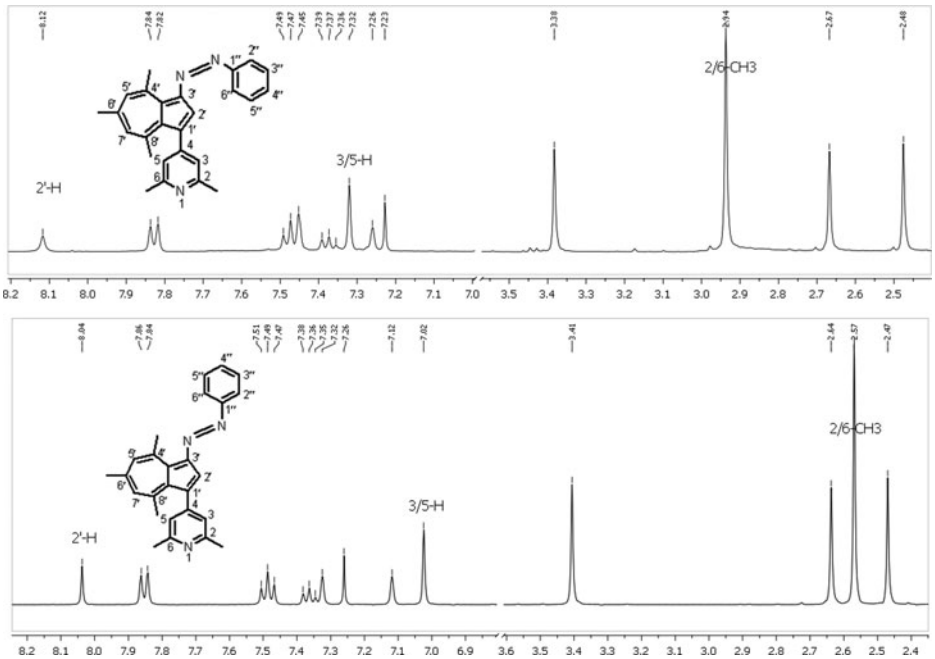


Figure 7. ^{1}H-NMR spectra of **2** in CDCl3, before (down) and after UV irradiation (top). The NMR scale is truncated for better comparison.

Conclusions

Azobenzene molecules substituted with 4-azulenylpyridine moiety showed strong fluorescent properties in solution. It has been showed that, the attachment of the azulenyl fragment to the non fluorescent azobenzene chromophore has induced fluorescent properties of the herein described compounds. Differences in the intensity and position of the emission peaks have been observed. For all compounds, photochemical $E \rightarrow Z$ isomerization of the azo bond proceeded when UV wavelength of 254 nm was used. This was confirmed by UV-Vis and NMR spectrsoscopy with differences in the position of the maximum absorption and in chemical shifts between the E and Z isomers. The fluorescence data and the photoisomerization behaviour provide supporting evidence of the possible practical use of these molecules in material science. Further investigation of their non linear optical properties is in progress.

Funding

I.R., F.K. and A.T. acknowledge the financial support of Romanian Ministry of Education, Research, Youth and Sports, through the UEFISCDI organism, under Contract Number 279/7.10.2011, Code Project PN-II-ID-PCE-2011-3-0505.

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