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Synthesis and physico-chemical properties of highly conjugated azo-aromatic systems. 4-(azulen-1-yl)-pyridines with mono- and bis azo-aromatic moieties at C3-position of azulene

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ABSTRACT

Highly conjugated azo-aromatic systems have been prepared in high to moderate yields by linking mono- and bis-azo aromatic fragments to 4-(Rn-azulen-1-yl)-2,6-dimethyl-pyridine. The synthesized π-extended systems have been studied by NMR spectroscopy, UV–Vis and electrochemistry. Systematic increase of the conjugation along the azobenzene skeleton has affected the spectral properties of the azophenyl substituted 4-(azulen-1-yl)-pyridine. The synthesized compounds exhibit a bathochromic shift of the visible absorption maxima with the increase of the conjugating skeleton and introduction of an electron-withdrawing group. The electrochemical behavior revealed a high stability toward oxidation owing to the higher polarization induced by the azulenylpyridine moiety.

1. Introduction

Molecules with various functionalities possess peculiar properties, and their facile preparation is one of the most challenging goals for synthetic chemistry. The unusual electronic and optical properties of azulenes have led to a significant interest in the design and synthesis of new materials incorporating this aromatic system [1–7]. Azulene, isomer of naphthalene, is a nonbenzenoid aromatic hydrocarbon with a characteristic deep blue color. The color arises from the easy electronic transition from the highest occupied molecular orbital to the lowest unoccupied antibonding orbital. Substitution of the ring can alter the wavelength of the absorption bands resulting in different colors for different azulene derivatives. The electron drift from the seven-membered ring toward the five-membered ring forming an intrinsic dipolar structure makes this molecule versatile for designing a large variety of push–pull compounds with NLO properties [6,7]. Moreover, azulene-based compounds have found applications as molecular switchers [8,9], liquid crystals [10,11] or in optical data storage devices [12].

As part of our on going interest in developing methodologies for polyfunctionalization of azulenes, we have investigated the synthesis of series of 2,6-dimethyl-4-(azulen-1yl) pyranylium and pyridinium salts, as well as the corresponding pyridines [13,14]. These compounds represent valuable synthons for synthesis of highly conjugated aromatic systems with potential NLO properties and other technical applications. In addition, pyridylazulenes are useful for constructing novel analytical reagents with utility as colorimetric reaction indicators [1–4]. Therefore, we proposed to take advantage of the reactivity of the azulene moiety of these heteroarylazulene derivatives and to further extend the π electronic system by substitution of the azulenyl fragment with an azobenzene functionality. This azo chromophores possesses numerous spectroscopic and photophysical properties, in particular strong electronic absorption in the UV and Vis regions of the spectrum [15] and, because of the planarity of the azo bridge *versus* stilbenes or other similar systems, they contribute to larger π transmission effects

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leading to higher optical activity [16,17]. Therefore, we expect that, the obtained more complex chromophores possess interesting spectroscopic and photophysical properties, mainly strong electronic absorption in the visible region of the spectrum. Thus, we report herein the synthesis, spectroscopic investigation and solvatochromic behavior of new (2,6-dimethyl-pyridin-4-yl)-azulen-1-yl diazenes with azulen-1-yl moiety substituted in position 3.

2. Experimental

2.1. Materials and instrumentation

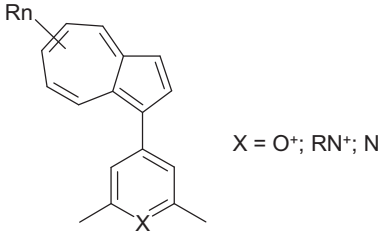
The azo-coupling was performed using commercially available aromatic amines. Dichloromethane (DCM) was dried over calcium hydride. Acetonitrile, spectroscopic purity for cyclic voltammetry was dried and kept over molecular sieves. For the column chromatography basic alumina (II–III Brockman grade) was used. 4-(Azulen-1-yl)-2,6-dimethyl-pyranylium perchlorate, 4-(4,6,8-trimethyl-azulen-1-yl)-2,6-dimethyl-pyranylium perchlorate and their corresponding pyridine derivatives were obtained as described in the literature [13]. The numbering of atom positions used for the characterization of the products is described in Scheme 2.

Melting points were determined with Koehler Automatic Melting Point Range Apparatus (K90190). Elemental analyses were performed with Perkin Elmer CHN 240B analyzer. UV–Vis spectra were recorded on Varian Cary 100 spectrophotometer. NMR spectra in $CDCl_3$ containing TMS as internal standard were recorded on Bruker Avance DRX4 (^{1}H: 400 MHz, ^{13}C: 100.62 MHz) spectrometer; chemical shifts (δ) are expressed in ppm, and J values are given in Hz. Mass spectra were recorded with Varian 1200L Quadrupole/MS/MS spectrometer by direct injection in ESI, positive mode. Electrochemical measurements were performed using a Princeton Applied Research model 273 potentiostat and CorrWare software (Scribner Associates). Cyclic voltammetry was performed in argon atmosphere in an undivided cell, using a platinum disk working electrode (2 mm in diameter), a platinum gauze auxiliary electrode and a silver–silver ion reference electrode. All potentials are reported against the Ag/Ag^+ 0.01 M reference electrode. Potentials were scanned independently from 0 to −2.5 V and from 0 to +2.5 V with 100 mV/s scan rate. The electrochemical measurements were carried out on 2 mM concentration using anhydrous acetonitrile containing 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte. HOMO and LUMO orbital energies were calculated with MOPAC-9 package using AM1 approach.

2.2. Synthesis and spectroscopic characterization

2.2.1. General procedure for the synthesis of mono-diazene, **3**–**6**

To a stirred suspension of aromatic amine (0.87 mmol) in water (10 ml) an aqueous solution of HCl (0.8 ml; 5 M) was added with heating until complete dissolution of the amine hydrochloride. The resulted solution was cooled at 0 °C on ice bath, while some solid started to precipitate. To this mixture, $NaNO_2$ (0.9 mmol, 60 mg) dissolved in a minimum amount of water was added slowly with vigorous stirring. The stirring was continued at low temperature for 15 min. Then, it has been added to an ice-cooled solution of 4-(Rn-azulen-1-yl)-2,6-dimethyl-pyridine (0.87 mmol) and potassium acetate (0.6 g) dissolved in methanol (50 ml). The solution was stirred on ice bath for 30 min and then was neutralized with NaOH, 10% aqueous solution and extracted with DCM. The organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography on alumina using as eluent hexane: DCM (3:1).



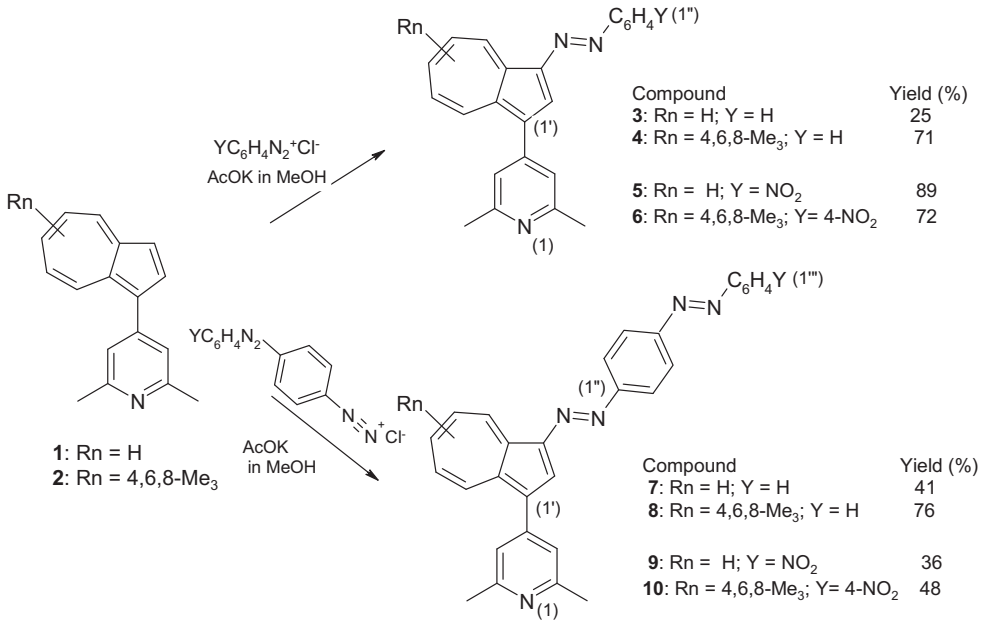
1: X = N; Rn = H
2: X = N; Rn = 4,6,8-Me_3

Scheme 1.

*2.2.1.1. (E)-[3-(2,6-dimethyl-pyridin-4-yl)azulen-1-yl]-phenyl-diazene **(3)**.* This compound was synthesized from 4-azulen-1-yl-2,6-dimethyl-pyridine (202 mg, 0.87 mmol) with diazonium salt of aniline (81 mg, 0.87 mmol) following the general procedure. It was obtained as greenish brown solid; mp 150–152 °C. UV–Vis (methanol): λ (log ε) 237 (4.40), 324 (4.39), 425 (4.32) 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; ^{13}C NMR ($CDCl_3$): δ 24.6 (Me-2,6), 121.0 (CH-3,5), 122.4 (CH-2″,6″), 124.6 (CH-2′), 125.3 (Cq), 127.1 (CH-5′), 127.3 (CH-7′), 129.1 (CH-3″,5″), 129.3 (CH-4″), 129.6 (Cq), 130.1 (Cq), 136.2 (CH-8′), 137.0 (CH-4′), 139.5 (Cq), 140.1 (Cq), 140.5 (CH-6′), 142.9 (Cq), 144.8 (Cq), 154.1 (Cq), 158.1 (Cq) ppm. ESI-MS: m/z (%) = 338 (100) [M+1]. Anal. Calcd. for $C_{23}H_{19}N_3$ (337.42): C, 81.87; H, 5.68; N, 12.45; found: C, 81.85; H, 5.62; N, 12.48.

*2.2.1.2. (E)-[3-(2,6-dimethyl-pyridin-4-yl)-4,6,8-trimethyl-azulen-1-yl]-phenyl-diazene, **(4)**.* This compound was synthesized from 2,6-dimethyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridine (240 mg, 0.87 mmol) with diazonium salt of aniline (81 mg, 0.87 mmol) following the general procedure. It was obtained as brown crystals; mp 213–214 °C. UV–Vis (methanol): λ (log ε) 253 (4.45), 326 (4.36), 433 (4.38) 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), 7.03 (s, 2H, 3-H, 5-H), 7.12 (s, 1H, 5′-H), 7.33 (s, 1H, 7′-H), 7.37 (t, 1H, J = 7.6 Hz, 4″-H), 7.49 (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; ^{13}C NMR ($CDCl_3$): δ 24.5 (Me-2,6), 28.2 (Me-8′), 29.6 (Me-6′), 30.4 (Me-4′), 121.7 (CH-3,5), 122.4 (CH-2″,6″), 125.5 (CH-2′), 128.9 (CH-4″), 129.0 (CH-3″,5″), 131.5 (Cq), 132.4 (CH-5′), 133.3 (CH-7′), 134.9 (Cq), 136.2 (Cq), 145.6 (Cq), 147.8 (Cq), 148.8 (Cq), 149.9 (Cq), 150.0 (Cq), 154.1 (Cq), 156.9 (Cq) ppm. ESI-MS: m/z (%) = 380 (100) [M]. Anal. Calcd for $C_{26}H_{25}N_3$ (379.50): C, 82.29; H, 6.64; N, 11.07; found: C, 82.26; H, 6.63; N, 11.10.

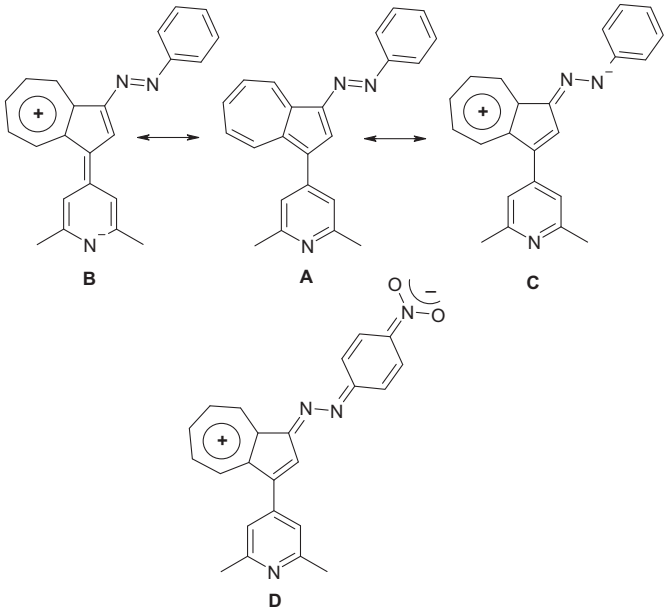
*2.2.1.3. (E)-[3-(2,6-dimethyl-pyridin-4-yl)azulen-1-yl]-(4-nitro-phenyl) diazene, **(5)**.* This compound was synthesized from 4-azulen-1-yl-2,6-dimethyl-pyridine (202 mg, 0.87 mmol) with diazonium salt of p-nitro-aniline (121 mg, 0.87 mmol) following the general procedure. It was obtained as dark brown crystals; mp 247 °C. UV–Vis (methanol): λ (log ε) 234 (4.65), 302 (4.57), 470 (4.60) nm. ^{1}H NMR ($CDCl_3$): δ 2.64 (s, 6H, 2-Me, 6-Me), 7.23 (s, 2H, 3-H, 5-H), 7.49 (t, 1H, J = 9.8 Hz, 5′-H), 7.62 (t, 1H, J = 9.6 Hz, 7′-H), 7.90 (t, 1H, J = 9.8 Hz, 6′-H), 8.06 (d_{AB}t, 2H, J = 8.8 Hz and 2 Hz, 2″-H, 6″-H), 8.35 (d_{AB}t, 2H, J = 8.8 Hz and 2 Hz, 3″-H, 5″-H), 8.39 (s, 1H, 2′-H), 8.61 (d, 1H, J = 9.6 Hz, 4′-H), 9.43 (d, 1H, J = 9.6 Hz, 8′-H) ppm; ^{13}C NMR ($CDCl_3$): δ 24.5 (Me-2,6), 120.9 (CH-3,5), 122.6 (CH-2″,6″), 124.6 (CH-2′), 124.8 (CH-3″,5″), 128.7 (CH-5′), 128.8 (CH-7′), 131.4 (Cq), 136.4 (CH-8′), 137.5 (CH-4′), 140.9 (Cq), 141.1 (CH-6′), 141.8 (Cq), 143.4 (Cq), 144.3 (Cq), 147.4 (Cq), 157.5 (Cq), 158.2 (Cq) ppm. ESI-



Scheme 2.

MS: *m/z* (%) = 383 (100) [M+1]. Anal. Calcd for $C_{23}H_{18}N_4O_2$ (382.41): C, 72.24; H, 4.74; N, 14.65; found: C, 72.21; H, 4.76; N, 14.61.

2.2.1.4. (E)-[3-(2,6-dimethyl-pyridin-4-yl)-4,6,8-trimethyl-azulen-1-yl]-(4-nitro-phenyl)diazene, ***(6)****.* This compound was synthesized from 2,6-dimethyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridine (240 mg, 0.87 mmol) with diazonium salt of p-nitro-aniline (121 mg, 0.87 mmol) following the general procedure. It was obtained as dark brown crystals; mp 255–256 °C. UV–Vis (methanol): λ (log ε) 251 (4.48), 320 (4.32), 477 (4.48) nm. ^{1}H NMR ($CDCl_3$): δ 2.49 (s, 3H, 6′-Me), 2.58 (s, 6H, 2-Me, 6-Me), 2.68 (s, 3H, 4′-Me), 3.41 (s, 3H, 8′-Me), 7.01 (s, 2H, 3-H, 5-H), 7.24 (s, 1H, 5′-H), 7.46 (s, 1H, 7′-H), 7.90 (d_{AB}, 1H, J = 8.8 Hz, 2″-H, 6″-H), 8.04 (s, 1H, 2′-H), 8.33 (d_{AB}, 2H, J = 9.2 Hz, 3″-H, 5″-H) ppm; ^{13}C NMR ($CDCl_3$): δ 24.5 (Me-2,6), 28.3 (Me-8′), 29.7 (Me-6′), 30.6 (Me-4′), 121.4 (CH-3,5), 122.5 (CH-2″,6″), 124.8 (CH-3″,5″), 125.5 (CH-2′), 132.8 (Cq), 134.2 (CH-5′), 135.0 (CH-7′), 136.9 (Cq), 138.2 (Cq), 146.5 (Cq), 146.8 (Cq), 148.7 (Cq), 149.5 (Cq), 149.6 (Cq), 150.3 (Cq), 157.1 (Cq), 157.8 (Cq) ppm. ESI-MS: *m/z* (%) = 425 (100) [M+1]. Anal. Calcd for $C_{26}H_{24}N_4O_2$ (424.49): C, 73.56; H, 5.70; N, 13.20; found: C, 73.52; H, 5.66; N, 13.15.



Scheme 3.

2.2.2. General procedure for the synthesis of bis-diazene, ***7–10***

To a stirred suspension of 4-phenylazo-phenylamine (1.0 mmol) in water (15 ml) an aqueous solution of HCl (1.15 ml; 10 M) was added with heating until the main amount of the amine salt was dissolved. The resulted slurry solution was cooled at 0 °C and a solution of $NaNO_2$ (70 mg, 1.0 mmol) dissolved in a minimum amount of water was added slowly with vigorous stirring. The stirring was continued at low temperature for 15 min. Then, the mixture has been added to an ice-cooled solution of 4-(Rn-azulen-1-yl)-2,6-dimethyl-pyridine (1.0 mmol) and potassium acetate (3.35 g) in methanol (50 ml). The mixture was stirred at the same temperature for 1 h, then neutralized with NaOH 10% aqueous solution and extracted with DCM. The organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography on alumina using as eluent hexane: DCM (3:1), with increasing the polarity of the eluting mixture. Due to the incomplete separation of the desired product from the starting amine, second chromatography using the same conditions was necessary for these compounds.

2.2.2.1. (E)-[3-(2,6-dimethyl-pyridin-4-yl)azulen-1-yl]-[4-[(Z)-phenylazo]phenyl]diazene, ***(7)****.* This compound was synthesized from 4-azulen-1-yl-2,6-dimethyl-pyridine (233 mg, 1.0 mmol) with diazonium salt of 4-phenylazo-phenylamine (197 mg, 1.0 mmol) following the general procedure. It was obtained as black crystals; mp 125–127 °C. UV–Vis (MeOH), λ (log ε): 235 (4.39), 307 (4.40), 353 (4.34), 471 (4.38) nm. ^{1}H NMR ($CDCl_3$): δ 2.63 (s, 6 H, 2-Me, 6-Me), 7.21 (s, 2H, 3-H, 5-H), 7.37 (t, 1H, J = 9.8 Hz, 5′-H), 7.53 (t, 2H, J = 6.9 Hz, 3‴-H, 5‴-H), 7.47-7.52 (m, 2H, 7′-H and 4‴-H), 7.79 (t, 1H, J = 9.8 Hz, 6′-H), 7.95 (d, 2H, J = 7.2 Hz, 2‴-H, 6‴-H), 8.07 (d_{AB},

2H, $J = 8.8$ Hz, 2″-H, 6″-H or 3″-H, 5″-H), 8.12 (d_{AB}, 2H, $J = 8.8$ Hz, 3″-H, 5″-H or 2″-H, 6″-H), 8.39 (s, 1H, 2′-H), 8.54 (d, 1H, $J = 9.6$ Hz, 4′-H), 9.40 (d, 1H, $J = 10.0$ Hz, 8′-H) ppm; ^{13}C NMR ($CDCl_3$): δ 24.6 (Me-2,6), 120.9 (CH-3,5), 122.9 (CH-2‴,6‴), 123.1 (CH-3″,5″), 123.9 (CH-2″,6″), 124.6 (CH-2′), 127.7 (CH-5′),127.8 (CH-7′), 129.1 (CH-3‴,5‴), 130.6 (Cq), 131.1 (CH-4‴), 136.3 (CH-8′), 137.1 (CH-4′), 140.1 (Cq), 140.7 (CH-6′), 143.3 (Cq), 144.5 (Cq), 152.7 (Cq), 152.8 (Cq), 155.4 (Cq), 158.1 (Cq) ppm. ESI-MS: m/z (%) = 442 (100) [M+1]. Anal. Calcd. for $C_{29}H_{23}N_5$ (441.53): C, 78.89; H, 5.25; N, 15.86; found: C, 78.84; H, 5.24; N, 15.81.

2.2.2.2. (E)-[3-(2,6-dimethyl-pyridin-4-yl)-4,6,8-trimethyl-azulen-1-yl]-[4-[(Z)-phenylazo]phenyl]diazene, ***(8)****.* This compound was synthesized from 2,6-dimethyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridine (275 mg, 1.0 mmol) with diazonium salt of 4-phenylazo-phenylamine (197 mg, 1.0 mmol) following the general procedure. It was obtained as black crystals; mp 196–198 °C. UV–Vis (MeOH), λ (log ε): 250 (4.58), 320 (4.42), 353 (sh), 478 (4.57) nm. ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H, 8′-Me), 2.57 (s, 6H, 2-Me, 6-Me), 2.63 (s, 3H, 6′-Me), 3.41 (s, 3H, 4′-Me), 7.02 (s, 2H, 3-H, 5-H), 7.14 (s, 1H, 5′-H), 7.35 (s, 1H, 7′-H), 7.45-7.54 (m, 3H, 3‴-H, 4‴-H, 5‴-H), 7.93-(d, 2H, $J = 7.6$ Hz, 2‴-H, 6‴-H), 7.95 (d, 2H, $J = 9.6$ Hz, 3″-H, 5″-H), 8.04 (d, 2H, $J = 9.6$ Hz, 2″-H, 6″-H) 8.05 (s, 1H, 2′-H) ppm; ^{13}C NMR ($CDCl_3$): δ 24.5 (Me-2,6), 28.3 (Me-6′), 29.6 (Me-4′), 30.5 (Me-8′), 121.6 (CH-3,5), 122.4 (Cq), 122.9 (CH-2‴,6‴), 123.1 (CH-3″,5″), 123.9 (CH-2″,6″), 125.1 (Cq), 125.6 (CH-2′), 129.1 (CH-4‴), 129.8 (CH-3‴,5‴), 131.0 (Cq), 132.1 (Cq), 133.1 (CH-5′),134.0 (CH-7′),135.8 (Cq), 137.1 (Cq), 146.3 (Cq), 148.1 (Cq), 149.0 (Cq), 149.9 (Cq), 150.1 (Cq), 152.3 (Cq), 152.9 (Cq), 155.6 (Cq), 157.0 (Cq) ppm. ESI-MS: m/z (%) = 484 (100) [M+1]. Anal. Calcd. for $C_{29}H_{29}N_5$ (483.61): C, 79.47; H, 6.04; N, 14.48; found: C, 79.44; H, 6.08; N, 14.52.

2.2.2.3. (E)-[3-(2,6-dimethyl-pyridin-4-yl)azulen-1-yl]-[4-[(Z)-(4-nitrophenyl)azo]phenyl]diazene, ***(9)****.* This compound was synthesized from 4-azulen-1-yl-2,6-dimethyl-pyridine (233 mg, 1.0 mmol) with diazonium salt of 4-(4-nitro-phenylazo)-phenylamine (242 mg, 1.0 mmol) following the general procedure. It was obtained as dark violet crystals; mp 294–295 °C. UV–Vis (MeOH), λ (log ε): 236 (4.41), 306 (4.44), 356 (4.33), 500 (4.48) nm. ^{1}H NMR ($CDCl_3$): δ 2.65 (s, 6H, 2-Me, 6-Me), 7.27 (s, 2H, 3-H, 5-H), 7.46 (t, 1H, $J = 9.8$ Hz, 5′-H), 7.59 (t, 1H, $J = 9.6$ Hz, 7′-H), 7.87 (t, 1H, $J = 10.0$ Hz, 6′-H), 8.08 (d_{AB}, 2H, $J = 9.2$ Hz, 2‴-H, 6‴-H), 8.15 (d_{AB}, 2H, $J = 8.8$ Hz, 2″-H, 3″-H or 5″-H, 6″-H), 8.16 (d_{AB}, 2H, $J = 8.8$ Hz, 5″-H, 6″-H or 2″-H, 3″-H), 8.41 (d_{AB}t, 2H, $J = 9.2$ Hz and 2.0 Hz, 3‴-H, 5‴-H), 8.45 (s, 1H, 2′-H), 8.61 (d, 1H, $J = 9.6$ Hz, 4′-H), 9.47 (d, 1H, $J = 9.2$ Hz, 8′-H) ppm; ^{13}C NMR ($CDCl_3$): δ 24.5 (Me-2,6), 121.0 (CH-3,5), 123.2 (CH-2‴,6‴), 123.5 (CH-2″,6″), 124.6 (CH-3″,5″), 124.7 (CH-2′), 124.8 (CH-3‴,5‴), 128.1 (CH-5′), 128.2 (CH-7′), 136.4 (CH-8′), 137.3 (CH-4′), 140.5 (Cq), 140.9 (CH-6′), 141.1 (Cq), 143.6 (Cq), 148.7 (Cq), 152.5 (Cq), 155.9 (Cq), 156.3 (Cq), 158.0 (Cq) ppm. ESI-MS: m/z (%) = 487 (100) [M+1]. Anal. Calcd. for $C_{29}H_{22}N_6O_2$ (486.52): C, 71.59; H, 4.56; N, 17.27; found: C, 71.62; H, 4.54; N, 17.24.

2.2.2.4. (E)-[3-(2,6-dimethyl-pyridin-4-yl)-4,6,8-trimethyl-azulen-1-yl]-[4-[(Z)-(4-nitrophenyl)azo]phenyl], ***(10)****.* This compound was synthesized from 2,6-dimethyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridine (275 mg, 1.0 mmol) with diazonium salt of 4-(4-nitro-phenylazo)-phenylamine (242 mg, 1.0 mmol) following the general procedure. It was obtained as dark violet crystals; mp 276–277 °C. UV–Vis (MeOH), λ (log ε): 250 (4.58), 320 (4.42), 353 (sh), 478 (4.57) nm. ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 3H, 6′-Me), 2.59 (s, 6H, 2-Me, 6-Me), 2.67 (s, 3H, 4′-Me), 3.44 (s, 3H, 8′-Me), 7.04 (s, 2H, 3-H, 5-H), 7.20 (s, 1H, 5′-H), 7.41 (s, 1H, 7′-H), 7.98 (d_{AB}, 2H, $J = 8.4$ Hz, 2‴-H, 6‴-H), 8.03 (d_{AB}, 2H, $J = 8.8$ Hz, 2″-H, 6″-H), 8.07 (s, 1H, 2′-H), 8.10 (d_{AB}, 2H, $J = 8.4$ Hz, 3″-H, 5″-H), 8.38 (d_{AB}, 2H, $J = 9.2$ Hz, 3‴-H, 5‴-H) ppm; ^{13}C NMR ($CDCl_3$): δ 24.3 (Me-2,6), 28.3 (Me-6′), 29.6 (Me-4′), 30.5 (Me-8′), 121.6 (CH-3,5), 123.2 (CH-2‴,6‴), 123.5 (CH-3″,5″), 124.7 (CH-2″,6″), 124.8 (CH-3‴,5‴), 125.6 (CH-2′), 128,8 (Cq), 130.9 (Cq), 133.6 (CH-5′), 134.4 (CH-7′), 136.3 (Cq), 137.6 (Cq), 146.6 (Cq), 148.4 (Cq), 148.7 (Cq), 149.3 (Cq), 150.3 (Cq), 152.1 (Cq), 156.0 (Cq), 156.6 (Cq), 156.9 (Cq) ppm. ESI-MS: m/z (%) = 529 (100) [M+1]. Anal. Calcd. for $C_{32}H_{28}N_6O_2$ (528.60): C, 72.71; H, 5.34; N, 15.90; found: C, 72.74; H, 5.38; N, 15.86.

3. Results and discussions

3.1. Synthesis

The ability of the azulene system to be involved in electrophile reactions is given by the enhanced electron density at C1(and/or C3)-position. Substitution with electron donor or releasing group increases the reactivity of the azulene moiety, whereas, the presence of an electron-acceptor group has an opposite effect. Recently, we have reported the synthesis and physico-chemical properties of azulenes substituted with heterocyclic rings at C1-position as described in Scheme 1 [13,14].

Substitution of azulene in 1-position with positive charged group, as for example 4-pyranylium or 4-pyridinium moiety, renders more difficult the electrophile substitution at C3-position. Therefore, we have used as starting materials for azo-coupling reactions the pyridines ***1*** and ***2*** which were generated in high yields from the corresponding pyranylium perchlorates [14]. The reaction routes are shown in Scheme 2.

The diazonium salts were generated in situ from the corresponding amine using equimolecular amounts of sodium azotite in acidic media. According with the used amine, hydrochloric acid of various concentrations has been used: 5 M aqueous solution for anilines and concentrated acid (~32%, ~10 M) for 4-phenylazo-phenylamines. The diazonium salts reacted with a solution of azulenylpyridine 1 or 2 in methanol, in the presence of potassium acetate. The electrophilicity of the diazonium salts increases in the following order of the starting amines: aniline < 4-phenylazo-phenylamine < 4-(4-nitro-phenylazo)-phenylamine < 4-nitro-aniline. Therefore, the coupling yield increases in the same order (Scheme 2) generating the azo derivatives **3** < **7** < **9** and **5**, respectively. Substitution of the azulenyl moiety with electron releasing group, i. e. methyl groups, generally enhances the nucleophilicity of the azulenyl system, the diazo-coupling reaction occurring in higher yields. A peculiar exception was observed in the case of compound **10** which was generated in low yield.

3.2. ^{1}H-NMR spectra

The comparison between the δ values of the heterocycle protons at C3(5) in the starting azulenylpyridines and in the herein described compounds shows that the introduction of the azophenyl group has no influence upon these protons. The azo group is too far away to have inductive influence and moreover, the conjugation is interrupt by a sequence of two single bonds. At the same time, the substitution of the azulenyl moiety with the 4-pyridyl group has no influence on the phenyl or phenylen protons. Instead, the azulenyl protons are strongly deshielded in both series of synthesized azo-compounds. These protons are influenced by both the pyridine ring and the azo-aryl moiety. Table 1 summarizes the chemical shifts of the azulenyl protons in the herein described azo compound, as compared with those in the starting azulenylpyridine **1** and azo-azulene compounds [6,18]. As it results from Table 1, the 2′-H proton is downfield shifted in compound **3** as compared with the same proton in the parent compound **1**. The deshielding effect of the 4′H–6′-H protons increases slowly in the order: compound

Table 1
Azulenyl protons (δ, ppm).

Entry	Compound	Protons					
		2′	4′	5′	6′	7′	8′
1	**1**	7.95	8.30	7.15	7.57	7.17	8.52
2	Az(1)N_2Ph[a]	8.30	8.39	7.37	7.80	7.45	9.36
3	**3**	8.44	8.59	7.39	7.82	7.51	9.44
4	**5**	8.39	8.61	7.49	7.90	7.62	9.43
5	4-PhN_2PhN_2Az[b]	8.35	8.33	7.34	7.75	7.51	9.36
6	**7**	8.39	8.54	7.37	7.79	7.49	9.40

[a] Reference [5].
[b] Reference [17].

1 < Az(1)N_2Ph (entry 2) < compound **3**. However, the shift toward a lower field is more pronounced for the 7′-H proton and especially for the 8′-H proton which is dramatically deshielded. It is notable that, close value of δ for the 7′-H and 8′-H protons were found for Az(1)N_2Ph and compound **3**. These results indicate a reduced conjugative contribution of the pyridine and phenyl-azo moieties upon the chemical shifts of the 4′-H–6′-H azulenyl protons. The high deshielding of the 2′-H, 7′-H and especially 8′-H protons for Az(1)N_2Ph [18] and compound **3** can be attributed to the anisotropy of the magnetic field generated by the phenylazo group. Introduction of an electron-withdrawing group in the phenylazo fragment, compound **5**, causes a very small shielding effect of the 2′-H proton as compared with compound **3**. From Table 1 it also results the similarity between the δ values of the protons belonging to the 1-azulenyl-2-[4-(phenyldiazenyl)phenyl]diazenes (entry 5) and the herein described compounds with 4-pyridyl attached to the azulene, for example compound **7**. One might also expect a little influence of the magnetic field of the pyridine ring on the protons 2′-H, 7′-H and 8′-H which differentiates the δ values of the compounds **1** and **3** from previously described Az(1)N_2Ph and 4-PhN_2PhN_2Az, respectively.

3.3. Electronic behavior

The absorption maxima of the low energy charge transfer transition, λ_{max}, for the compound **3**–**10**, recorded in different solvents, are reported in the Table 2. As expected, the λ_{max} for the parent compounds, **1** and **2**, (369 nm and 350 nm) [14] lies lower than that of the corresponding compounds with the phenyl-azo chromophores, **3** and **4** (425 nm and 433 nm). At the same time, substitution of the azulene in Az(1)N_2Ph and 4-PhN_2PhN_2Az with the 4-(2,6-dimethyl-pyridil) moiety, as in compounds **3** and **7**, enhances the values of λ_{max} with 10 nm [19] and 45 nm [18], respectively.

As it results from Table 2, the bathochromic shift increases in series **3** < **4** < **5** < **6** and **7** < **8** < **9** < **10**. In methanol solution, the $\Delta\lambda_{max}$ resulted by methyl substitution of the azulenyl moiety, compound **3** toward **4** and **7** toward **8**, is under 10 nm (Fig. 1, upper picture). However, the attachment of a nitro group in the *para*-position of the benzene ring, compound **3** toward **5** and **7** toward **9** causes a bathochromic shift of around 45 nm for the first pair of compounds and 29 nm for the last one (Fig. 1, down picture). Furthermore, a bathochromic shift is also observed when the *para*-phenyl-azo chromophore is inserted in the molecule. Thus, passing from compounds **3**–**6** to **7**–**10** the $\Delta\lambda_{max}$ values exceed 30 nm.

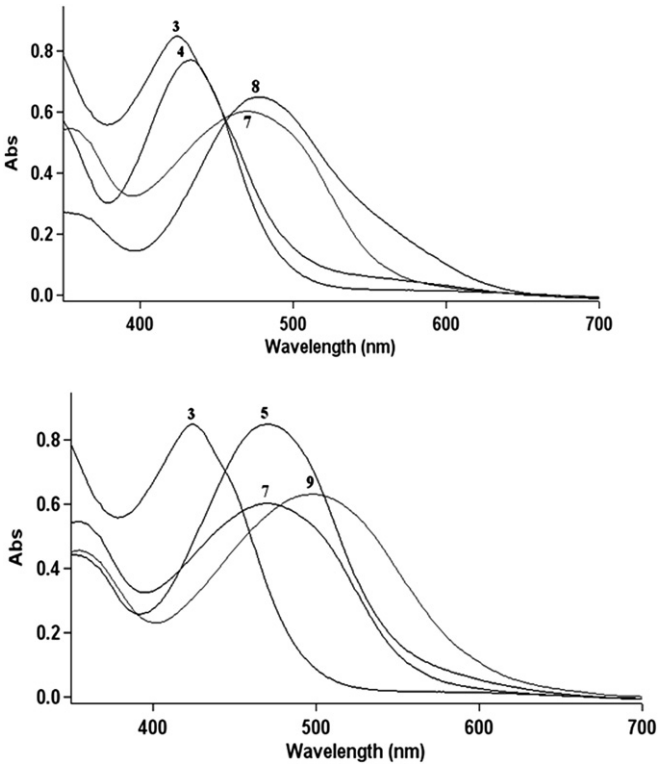


Fig. 1. Bathochromic shift of the visible absorption maxima owing to the methyl substitution of the azulenyl moiety (up) and the influence of the *para*-nitro substitution of the phenyl ring, respectively (down).

The structural analysis of compound **3** (Scheme 3) reveals that, beside the structures **A** and **C**, where **C** is also present in Az(1)N_2Ph, the herein described compound allows the conjugation between the π-electronic system of the azulenyl and heterocycle moieties as in structure **B**. Both structures **B** and **C** contribute to the extension of the electronic conjugation and produces the bathochromic shift of the λ_{max} in the case of compound **3** as compared with Az(1)N_2Ph. The conjugation is more extended in the case of the second azo group and this is reflected by the shift of the λ_{max} to higher wavelength in compounds **7**–**10** *versus* compounds **3**–**6**. The strong bathochromic shift observed in compounds with a nitro group **5**, **6**, **9** and **10** is explained by the high contribution of the structure of type **D**.

The MOPAC calculations for HOMO and LUMO orbital energy seem to confirm the observed experimental results. Thus, by

Table 2
Absorption maxima (λ_{max} in nm) in the visible region in solvents of different polarities.

Solvent	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Hexane	424	432	460	470	467	477	–	–
Dioxane	430	436	443	450	449	458	505	518
Ethyl acetate	427	434	443	450	446	455	501	515
Acetonitrile	428	434	447	453	448	451	498	508
Acetone	428	434	476	481	475	485	501	516
DMF	432	438	456	461	459	465	514	531
Methanol	425	433	470	477	471	478	500	512
Chloroform	431	437	481	490	479	491	511	529

Table 3
MOPAC calculations.

	Compounds							
	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**
HOMO (eV)	−8.21	−7.99	−8.53	−8.26	−8.02	−7.90	−8.14	−8.07
LUMO (eV)	−1.40	−1.33	−1.81	−1.76	−1.49	−1.40	−1.80	−1.77
Δ HOMO/LUMO[a]	6.81	6.66	6.72	6.50	6.53	6.50	6.34	6.30

[a] Absolute values.

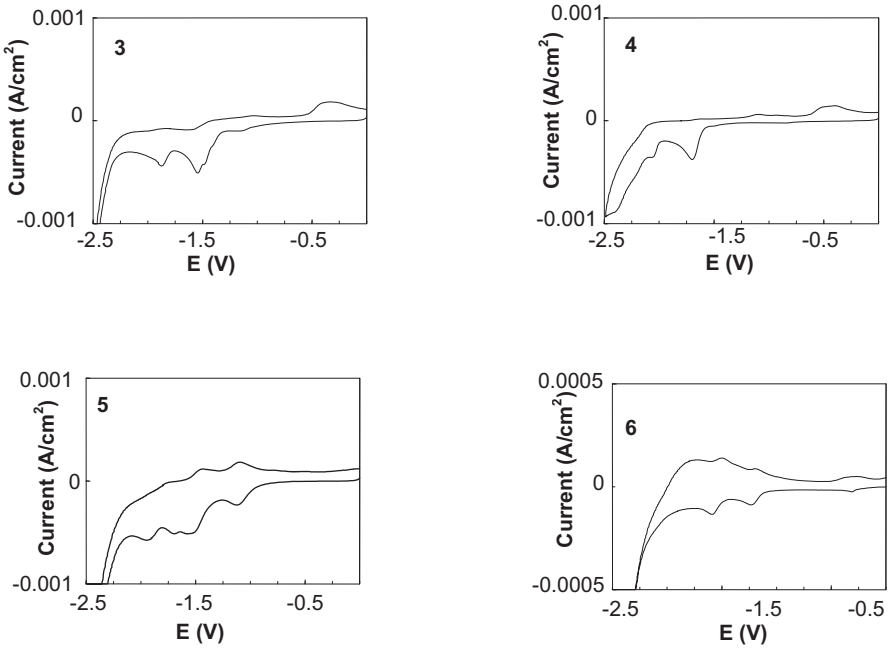


Fig. 2. Cyclic voltammograms showing the reduction potentials for compounds **3**–**6** (2 mM) in acetonitrile containing Bu_4NClO_4 (0.1 M) as supporting electrolyte.

extension of the electronic conjugation, the LUMO energy decreases, and in turn reduces the HOMO-LUMO gap (Table 3) and moves the absorption band at higher wavelengths. This fact is better reflected by the substitution with nitro groups.

Besides the structurally characteristics, for technical applications, the compounds must possess also other properties. Thus, in order to be used as NLO-materials, the compounds should exhibit good hyperpolarizability reflected by efficient solvatochromism. Several classes of azulenyl-containing compounds were already studied from this point of view [6,7]. Therefore, we were also interested on the solvatochromic behavior of the obtained compounds. Table 2 compares the values of λ_{max} for the mono- and bis-azo azulenylpyridines in solvents of different polarities. Slight effects on the absorption bands are to be seen between the solutions of the dyes **3**–**8**, which is consistent with the complex structure of the studied compounds. Thus, the influence of the solvent on the electronic molecular system is reduced due the presence of two moieties which can act as push–pull systems (see Scheme 3).

The redox behavior of the compounds represents another important feature toward mutual donor–acceptor electronic influence in the herein described compounds. With the aim to

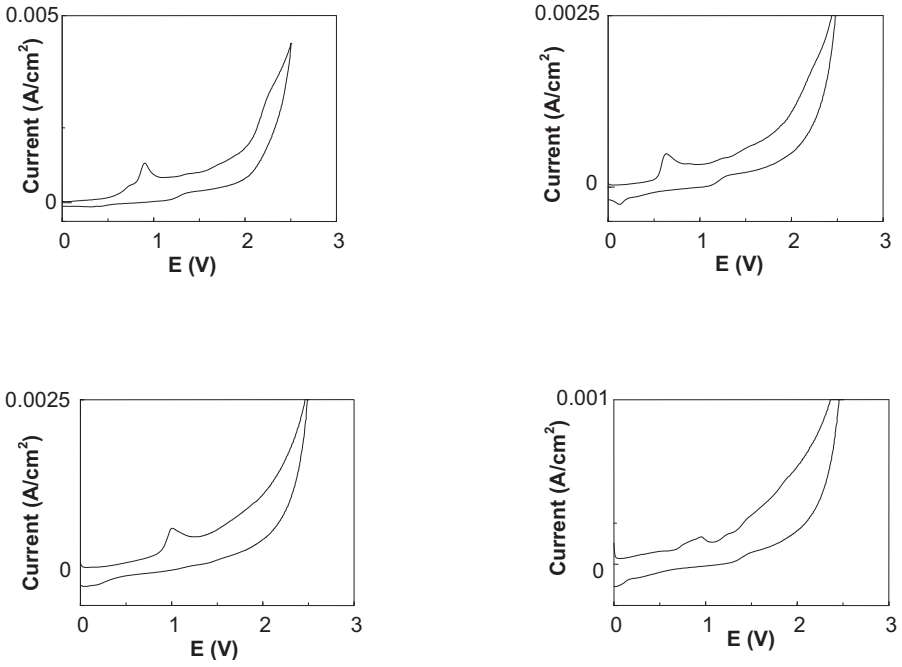


Fig. 3. Cyclic voltammograms showing the oxidation potentials for compounds **3**–**6** (2 mM) in acetonitrile containing Bu_4NClO_4 (0.1 M) as supporting electrolyte.

Table 4
Values of reduction and oxidation peak potentials (V) obtained by cyclic voltammetry.

Compound	E_{red}	E_{ox}
Az(1)N_2Ph	−1.54, −1.67	0.62
3	−1.54, −1.87	0.91
4	−1.71, −2.06	0.63
5	−1.12, −1.55, −1.70	1.00
6	−1.23, −1.58, −1.91	0.96

obtain information in this field we have studied the redox properties of the mono-azo derivatives, **3**–**6** by cyclic voltammetry (Fig. 2 and Fig. 3). The electrochemical behavior of the these compounds was studied on 2 mM acetonitrile solutions containing 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte. The obtained values for the reduction and oxidation potentials are summarized in Table 4.

The phenylazo-substituted azulenylpyridine, compounds **3** and **4**, show two reduction potentials with easier reduction processes in the case of 4,6,8-trimethyl-substituted azulenyl moiety (compound **4**) for which the reduction potentials are shifted to lower values (Fig. 2). The reduction of the azo functionality is very much influenced by the polarization effect induced by substitution. Compared with the reduction potential of the azulenyl azo derivatives of type Az(1)N_2Ph [20], the reduction of mono-azo azulenylpyridine **3** occurs at lower potential (Fig. 2, Table 4). Introduction of an electron-withdrawing group, i.e. NO_2 substituent, causes a higher polarization of the azo-bond, thus the higher anodic reduction potentials. Consequently, as found with other azulenyl-containing dyes [20,21], the electron-withdrawing nature of the substituent makes the compound harder to oxidize. Indeed, the cyclic voltammetry displays oxidation at more positive potentials for compounds **5** and **6** as compared to compound **3** and **4** (Fig. 3). Owing to higher polarization, azulenylpyridine diazene exhibit higher oxidation potential as compared with 1-azulenyl-azobenzene that showed an oxidation potential at 0.62 V [20]. Obviously, the electron-acceptor effect of the pyridine fragment makes the compounds more stable and therefore, harder to oxidize, in accordance with previous reported results for pyridylazulene derivatives [22]. Nevertheless, the electrochemical studies demonstrated the existence of the electronic communication and the delocalization of the π-electron cloud around the conjugated system.

4. Conclusions

Mono- and bis-azo azulenylpyridines were synthesized in good to moderate yields by diazo-coupling reaction of the corresponding azulenylpyridines with diazonium salts. The azo-coupling was facilitated by both, inductive effect of the grafted methyl groups of the azulenyl moiety and the conjugation effect of the nitro substituent with the aromatic ring in the diazonium intermediate. The structure of the compounds was assigned by spectroscopic and elemental analysis. Several considerations on the influence of the structure of the azo-dyes and the NMR and UV–Vis spectra were made. Thus, it was established that the azoic substituent has a higher participation in the electronic conjugation as compared with the contribution of the heterocycle. Due to the charge delocalization by substituting the azulenyl moiety in both 1′ and 3′ positions, an important deshielding of the azulenyl protons in both series of azo-compounds was observed showing a strong conjugation mainly along the azo-bridges. The solvatochromic behavior of both mono- and bis-azo diazene showed that by changing the solvent polarity, the λ_{max} value is less influenced. Owing to higher polarization, the azulenylpyridine diazene exhibit high oxidation potential.

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