Dyes and Pigments 82 (2009) 216–225

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Aromatic diazenes containing azulen-1-yl moieties Part 2: The synthesis, characterization, electronic spectra and basicity of novel, bis aromatic diazenes containing two azulen-1-yl moieties

Alexandru C. Razus, Liviu Birzan*, Mihaela Cristea, Bogdan Popa

Synthesis, Institute of Organic Chemistry "C. D. Nenitzescu" of Romanian Academy, Spl. Independentei 202 B, P.O. Box 35–108, 060023 Bucharest, Romania

ARTICLE INFO

Article history:
Received 23 September 2008
Received in revised form
5 January 2009
Accepted 7 January 2009
Available online 17 January 2009

Keywords:
Azulene
Azo
Diazene
Electronic spectra
Basicity

ABSTRACT

Bis aromatic diazenes which possess either two identical or two different azulene-1-yl groups substituted at either 1,3 or 1,4-positions in the bridging phenylene moiety were synthesized in good yield via diazotization of the 3- or 4-azulen-1-ylazo-phenylamines followed by coupling with azulene in a buffered medium. The electronic spectra of the synthesized compounds were analyzed by comparison with those of previously published compounds. The isosbestic points obtained by protonation of the compounds enabled their pK_a values to be determined.

1. Introduction

Despite the very large number of studies on azo chromophores, the research interest for this class of compounds remains unaltered due to their various technical applications. One of the important and, more recently investigated azo-dye classes is represented by the push pull systems with *an* azo double bond between various electron acceptor groups and azulene-1-yl as a donor moiety. Several such systems present enhanced hyperpolarizability and can be used as NLO chromophores [1–7], molecular switches [8], liquid crystals displays [9], holographic surface relief gratings [10] or for optical storage devices [11]. The hyperpolarizability of the push pull chromophores is well described in terms of a ground and an excited state having charge transfer character and, therefore, is related to the energy of the optical transitions. In the previous article [12], hereafter referred to as part 1, we have developed research on the synthesis and properties of bis azo derivatives with a single azulenyl group in their structure, **1**(***m***) and **1**(***p***) (Scheme 1). We have showed that, by replacement of one phenyl group in compound **3**(***m***) with azulenyl moiety, as in compound **1**(***m***), only a small hypsochromic shift was observed in the electronic spectra. However, the same substitution in the case of compound **3(*p*)** produced a bathochromic effect of 24 nm observed for compound **1**(***p***). This behavior is determined by the stabilizing effect of the positive charge by the tropylium structure of the seven-membered ring. This structure is very efficient in the charge transfer from the ground state of compound **1(*p*)** to the excited state with a dipolar structure [13]. Moreover, only compound **1(*p*)** can adopt a quinoidal structure with separated charges.

As expected, the phenyl substitution in azulene-azobenzene, **2** [1], by the chromophore phenylazo produced a small bathochromic shift when the chromophore is substituted in the 3-position. However, this effect surpasses 40 nm when phenylazo was substituted in position 4. These findings are consistent with the important contribution brought both by azulenyl moiety and the relative position of the substituents on the properties of bis azo compounds. In the present article, we turn our attention to the isolation of bis azo derivatives which contain two azulenyl moieties with the aim to evaluate the effect of this modification towards the synthesis, structure and electronic properties of the obtained compounds.

2. Experimental section

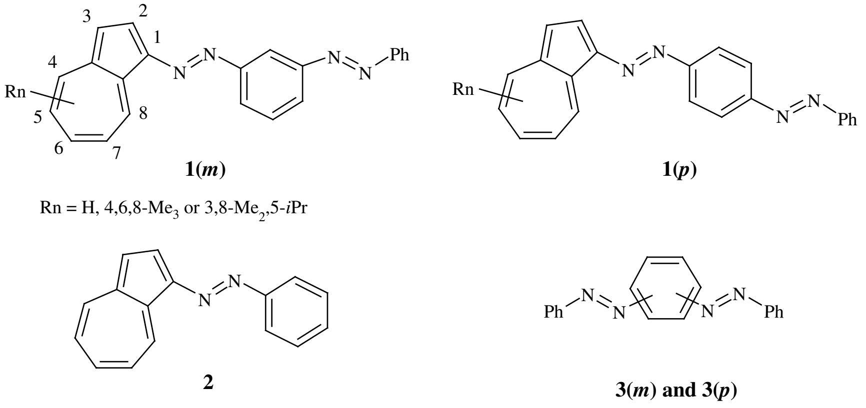
2.1. Materials and instrumentations

Melting points are uncorrected: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV spectra

---

* Corresponding author. Tel.: +40 0213167900; fax: +40 0213121601.
E-mail address: lbirzan@cco.ro (L. Birzan).

0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.01.005



Scheme 1.

in methanol: Varian Cary 100 spectrophotometer. ^{1}H- and ^{13}C-NMR: Bruker ARX 500 (^{1}H: 500 MHz, ^{13}C: 125.75 MHz), Bruker Avance DRX4 (^{1}H: 400 MHz, ^{13}C: 100.62 MHz) and Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz), *J* values are given in hertz, TMS was used as internal standard in $CDCl_3$ as solvent; mass spectra: Varian 1200L Quadrupole/MS/MS spectrometer by direct injection in ESI or APCI. For the column chromatography silica gel 60 and alumina [II–III Brockmann grade, 70–230 mesh ASTM] were used. Dichloromethane (DCM) was distilled over CaH_2. The pH values were measured with an Orion 3 Star pH-meter. The nomenclature was obtained using ACD/I-Lab Web service (ACD/IUPAC Name free 7.06).

2.2. Synthetic routes

2.2.1. Diazotization of acetylamino-phenylamines (step I in Scheme 2) + coupling of the obtained salt, with azulenes (step II) + hydrolysis of amides **4** and **5** (step III) + diazotization of amines **6** and **7** + coupling with azulenes (step IV)

(a) *Diazotization in aqueous hydrochloric medium.* A mixture of aromatic amines (2 mmol), 2.3 ml solution HCl 32% and 2 ml of water (generally, the amine was incompletely dissolved) was magnetically stirred and cooled at 0 °C. To this mixture a solution of sodium nitrite 140 mg (2 mmol) dissolved in 2 ml water was added slowly maintaining the temperature under 5 °C. After 10 min, the mixture was added under stirring to the solution of the azulene (1 mmol), and potassium acetate 6.7 g in 50 ml methanol, cooled at 0 °C. The mixture was stirred at 0 °C for 1 h and then neutralized with sodium hydroxide. The products were repeatedly extracted with DCM. The organic layers were washed with water, dried over sodium sulfate and the solvent was removed in vacuum. The residue was chromatographed on silica gel with *n*-hexane for recovery of the unreacted azulene and the starting amine, then with DCM for azo derivatives. Due to the incomplete separation from the starting amine, sometimes for the product purification a second chromatography on silica gel was necessary. This diazotization and coupling protocol were used for all anilines (e.g. 3-nitroaniline and compounds **6** and **7**).

(b) *Diazotization in dichloroacetic acid.* To a stirred solution of aromatic amines (2 mmol) in dichloroacetic acid (8 ml, 12.4 g) at 0 °C, a solution of sodium nitrite, 140 mg (2 mmol), dissolved in 1 ml water was added slowly, maintaining the temperature below 5 °C. After 10 min, the mixture was added at 0 °C to the very well stirred solution of azulene (2 mmol) and potassium acetate (12 g) in 100 ml methanol. If the potassium acetate was not completely dissolved, the yields decrease significantly. The mixture was stirred at 0 °C for 1 h. The pH of the mixture was adjusted to neutral with a sodium hydroxide solution which was carefully added. This work-up of the reaction mixture was important for the quantitative extraction of the products and for avoiding the generation of an emulsion by extraction. The products were extracted with DCM. From this point, the work-up is similar to one that has been reported above.

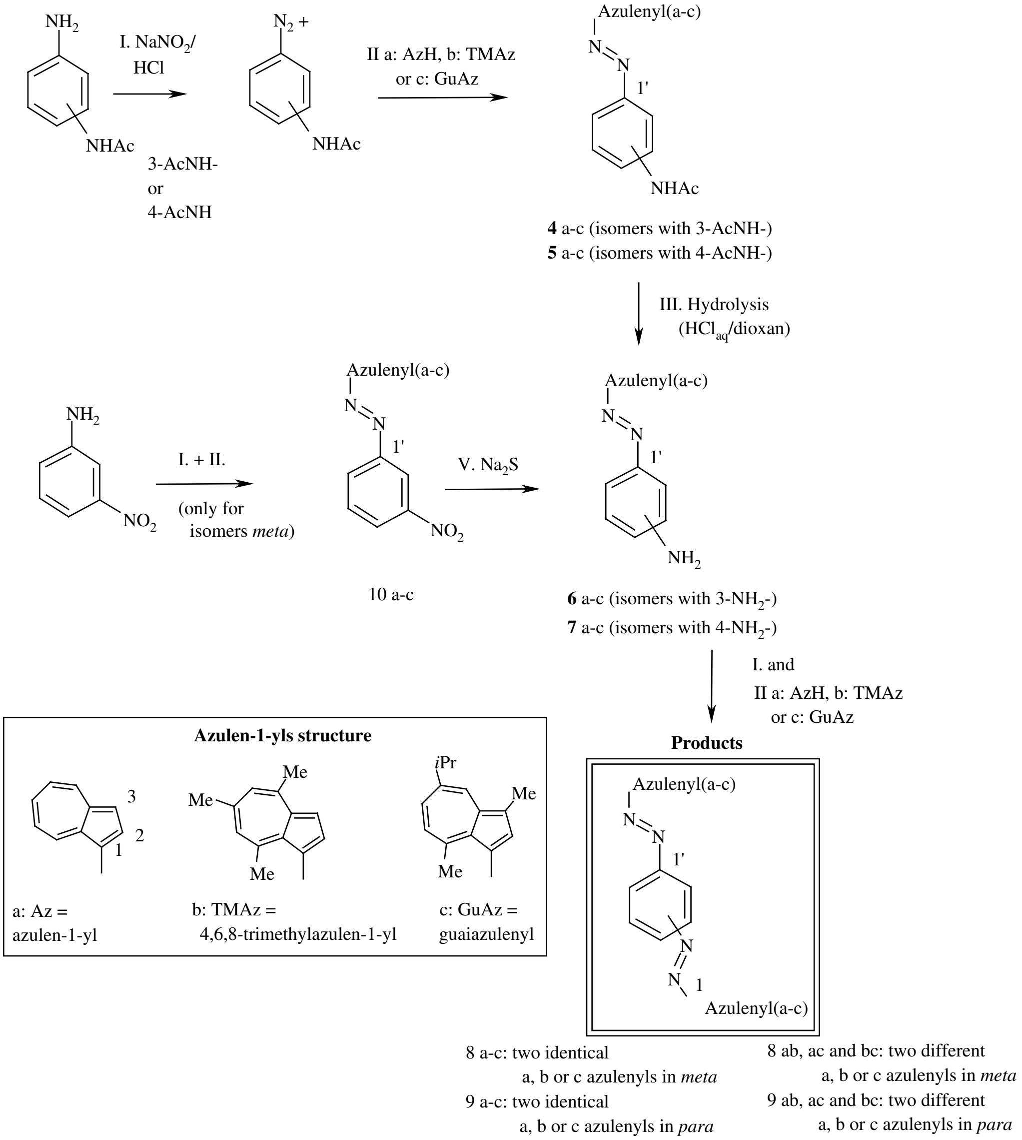
(c) *Hydrolysis reaction.* The acylated amine **4** or **5** (3 mmol) was dissolved in a mixture of dioxane (16 ml) and hydrochloric acid 32% (4 ml). The resulting solution was heated under stirring for 3 h at 80 °C. After cooling at room temperature, the reaction mixture was neutralized with aqueous sodium hydroxide (10%). The resulting mixture was treated with ethyl acetate and two layers were separated. The lower aqueous layer was extracted with DCM to recover all the organic material. The organic extracts were washed with water and dried over sodium sulfate. The solvents were removed in vacuum and the residue was chromatographed on alumina using DCM as eluent for the first fraction containing unidentified compounds and DCM:ethyl acetate (9:1) for the elution of product **6** or **7** (brown colored).

2.2.2. Diazotization of 3-nitro-phenylamine + coupling of the obtained salt with azulenes + reduction of nitro group in compound **10** (step IV) to compounds

Because most of the reactions are already discussed in this section only the reduction reaction is reported. A solution of $Na_2S \cdot 9H_2O$ (9.1 g, 37.9 mmol) in water (9.5 ml) was added in small portions, under stirring and in nitrogen atmosphere to the nitro derivative **10** (25 mmol) dissolved in boiling alcohol (20 ml). The reaction mixture was refluxed for 45 min and then was cooled and the alcohol was removed in vacuum. The residue was dissolved in DCM and the solution was washed with water, dried over sodium sulfate and the solvent was removed in vacuum. By chromatography on alumina using an eluent mixture of petroleum ether and DCM (with concentration gradient) the nitro derivative was first eluted and then the amine **6**.

2.3. Determination of isosbestic points and the pK_a values

The bis aromatic diazenes containing two identical or different azulenyl moieties, **8**a–c and **9**a–c or **8**ab, ac or bc and **9**ab, ac or bc, respectively were dissolved in ethanol 96% obtaining an $\sim 3 \times 10^{-5}$ mol/l solution. Then an aqueous 0.1 N hydrochloric solution was added with a syringe and the pH values were



Scheme 2.

measured (4 × 25 µl, 150 µl, 250 µl, 500 µl, 1000 µl). The double protonation was realized adding 1 ml of concentrated sulfuric acid.

2.4. Intermediates and product characterization

N-[3-(azulen-1-ylazo)-phenyl]-acetamide (**4a**), brown crystals, m.p. 168 °C, UV–vis (MeOH), λ_{max} (log ε): 234 (4.59), 280 (4.31), 331 (4.08), 424 (4.37). ^{1}H-NMR δ (ppm): 2.23 (s, 3H, Me), 7.34 (t, ^{3}J = 10.0 Hz, 1H, 5′-H), 7.39 (s, 1H, NH), 7.39 (d, ^{3}J = 4.7 Hz, 1H, 3′-H), 7.44 (t, ^{3}J = 9.9 Hz, 1H, 7′-H), 7.46 (t, ^{3}J = 7.7 Hz, 1H, 5-H), 7.75 (t, ^{3}J = 9.6 Hz, 1H, 6′-H), 7.67 (br d, ^{3}J = 9.3 Hz, 1H. 6-H), 7.72–7.74 (m, 1H, 4-H), 8.31 (d, ^{3}J = 4.7 Hz, 1H, 2′-H), 8.34 (d, ^{3}J = 9.4 Hz, 1H, 4′-H), 8.03 (t, ^{4}J = 2.0 Hz, 1H, 2-H), 9.34 (d, ^{3}J = 9.9 Hz, 1H, 8′-H). ^{13}C-NMR δ (ppm): 24.72; 112.3; 119.3; 120.1; 120.6; 125.4; 126.7; 129.5; 135.5; 138.5; 138.6; 143.9; 144.1; 154.8; 168.4. MS (ESI): 290 [M + 1]. Element Anal. Calcd. for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.60; H, 5.29; N, 14.50.

N-[3-(4,6,8-trimethylazulen-1-ylazo)-phenyl]-acetamide (**4b**), brown crystals, m.p. 232 °C. UV–vis (MeOH), λ_{max} (log ε): 238 (4.59), 291 (4.11), 314 (4.11), 434 (4.34). ^{1}H-NMR δ (ppm): 2.22 (s, 3H, COMe), 2.65 (s, 3H, Me(6)), 2.88 (s, 3H, Me(4)), 3.39 (s, 3H, Me(8)), 7.21 (s, 1H, 5′-H), 7.32 (s, 1H, 7′-H), 7.37 (d, ^{3}J = 5.0 Hz, 1H, 3′-H), 7.43 (t, ^{3}J = 8.0 Hz, 1H, 5-H), 7.61 (d, ^{3}J = 8.8 Hz, 1H, 6-H), 7.64 (d, ^{3}J = 8.8 Hz, 1H, 4-H), 8.13 (d, ^{3}J = 5.0 Hz, 1H, 2′-H), 7.92 (t, ^{4}J = 1.8 Hz, 1H, 2-H). MS (ESI): 332 [M + 1]. Element Anal. Calcd. for $C_{21}H_{19}N_3O$: C, 76.11; H, 6.39; N, 12.68. Found: C, 76.12; H, 6.42; N, 12.59.

N-[3-(3,8-dimethyl-5-isopropylazulen-1-ylazo)-phenyl]-acetamide (**4c**), brown crystals, m.p. 193 °C. UV–vis (MeOH), λ_{max} (log ε): 239 (4.65), 291 (4.23), 342 (4.13), 455 (4.47). ^{1}H-NMR δ (ppm): 1.38 (d, ^{3}J = 6.9 Hz, 6H, Me_2CH), 2.21 (s, 3H, CH_3CO), 2.60 (s, 3H, Me(3)), 3.09 (hept, 1H, Me_2CH), 3.34 (s, 3H, Me(8)), 7.29 (t, ^{3}J = 10.4 Hz, 1H, 7′-H), 7.42 (t, ^{3}J = 8.0 Hz, 1H, 5-H), 7.45 (dd, ^{3}J = 10.4 Hz, ^{4}J = 1.9 Hz, 1H, 6′-H), 7.58 (d, ^{3}J = 8.2 Hz, 1H, 6-H), 7.62 (d, ^{3}J = 8.2 Hz, 1H, 4-H), 7.92 (t, ^{4}J = 2.1 Hz, 1H, 2-H), 8.11 (s, 1H, 2′-H), 8.14 (d, ^{4}J = 1.9 Hz, 1H, 4′-H). MS (ESI): 360 [M + 1]. Element Anal. Calcd. for $C_{23}H_{25}N_3O$: C, 76.85; H, 7.01; N, 11.69. Found: C, 76.87; H, 7.08; N, 11.65.

N-[4-(azulen-1-ylazo)-phenyl]-acetamide (**5a**), brown crystals, m.p. 169 °C, UV–vis (MeOH), λ_{max} (log ε): 228 (4.32), 279 (4.31), 338 (4.12), 432 (4.49). ^{1}H-NMR δ (ppm): 2,24 (s, 3H, Me), 7.70 (d_{AB}, ^{3}J = 8.8 Hz, 2H, 3-H, 5-H), 7.34 (t, ^{3}J = 9.8 Hz, 1H, 5′-H), 7.44 (t, ^{3}J = 9.6 Hz, 1H, 7′-H), 7.45 (d, ^{3}J = 4.4 Hz, 1H, 3′-H), 7.53 (s, 1H,

Table 1
The yields of compounds **4** and **5** starting from corresponding anilines.

Azulen-1-yl	Compound, yield (%)	
	4a–c	**5a–c**
a	56	55
b	62 (74)[a]	51
c	73 (90)[a]	50

[a] In dichloroacetic acid.

NH), 7.76 (t, $^{3}J = 9.8$ Hz, 1H, 6′-H), 8.00 (d_{AB}, $^{3}J = 8.8$ Hz, 2H, 2-H, 6-H), 8.34 (d, $^{3}J = 4.6$ Hz, 1H, 2′-H), 8.35 (d, $^{3}J = 8.8$ Hz, 1H, 4′-H), 9.34 (d, $^{3}J = 9.6$ Hz, 1H, 8′-H). MS (ESI): 290 [M + 1]. Element Anal. Calcd. for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.65; H, 5.28; N, 14.47.

N-[4-(4,6,8-trimethylazulen-1-ylazo)-phenyl]-acetamide (**5b**), brown crystals, m.p. 197 °C, UV–vis (MeOH), λ_{max} (log ε): 234 (4.47), 297 (4.27), 341 (4.26), 441 (4.57). ^{1}H-NMR δ (ppm): 2.20 (s, 3H, MeCO), 2.62 (s, 3H, Me(6)), 2.86 (s, 3H, Me(4)), 3.34 (s, 3H, Me(8)), 7.16 (s, 1H, 5′-H), 7.35 (d, $^{3}J = 5.0$ Hz, 1H, 3′-H), 7.38 (s, 1H, 7′-H), 7.62 (d, $^{3}J = 8.8$ Hz, 2H, 3-H, 5-H), 7.84 (d, $^{3}J = 8.8$ Hz, 2H, 2-H, 6-H), 8.12 (d, $^{3}J = 4.9$ Hz, 1H, 2′-H). ^{13}C-NMR δ (ppm): 25.06; 25.64; 28.86; 30.00; 118.3; 120.3; 122.2; 123.4; 130.9; 133.2; 138.5; 147.4; 148.0; 150.0. MS (ESI): 332 [M + 1]. Element Anal. Calcd. for $C_{21}H_{19}N_3O$: C, 76.11; H, 6.39; N, 12.68. Found: C, 76.05; H, 6.31; N, 12.64.

N-[4-(3,8-dimethyl-5-isopropylazulen-1-ylazo)-phenyl]-acetamide (**5c**), brown crystals, m.p. 183 °C. UV–vis (MeOH), λ_{max} (log ε): 233 (4.45), 250 (4.44), 296 (4.29), 347 (4.12), 467 (4.60). ^{1}H-NMR δ (ppm): 1.36 (d, $^{3}J = 6.9$ Hz, 6H, *Me*$_2$CH), 2.18 (s, 3H, MeCO), 2.58 (s, 3H, Me(3)), 3.06 (hept, 1H, $^{3}J = 6.8$ Hz, Me$_2$*CH*), 3.28 (s, 3H, Me(8)), 7.21 (d, $^{3}J = 10.6$ Hz, 1H, 7′-H), 7.39 (dd, $^{3}J = 10.7$ Hz, $^{4}J = 2.0$ Hz, 1H, 6′-H), 7.61 (d_{AB}, $^{3}J = 8.8$ Hz, 2H, 3-H, 5-H), 7.81 (d_{AB}, $^{3}J = 9.0$ Hz, 2H, 2-H, 6-H), 8.09 (s, 1H, 2′-H), 8.10 (d, $^{4}J = 2.2$ Hz, 1H, 4′-H). ^{13}C-NMR δ (ppm): 13.35; 24.73; 24.96; 28.93; 38.36; 120.4; 123.2; 125.7; 128.7; 131.7; 135.1; 136.1; 138.4; 142.8; 145.4; 148.8; 151.2; 168.76. MS (ESI): 360 [M + 1]. Element Anal. Calcd. for $C_{23}H_{25}N_3O$: C, 76.85; H, 7.01; N, 11.69. Found: C, 76.76; H, 7.11; N, 11.58.

3-(Azulen-1-ylazo)-phenylamine (**6a**), dark green oil, UV–vis (MeOH), λ_{max} (log ε): 227 (4.59), 282 (4.36), 327 (4.20), 421 (4.47). ^{1}H-NMR δ (ppm): 6.76 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 2.4$ Hz, $^{4}J = 1.0$ Hz, 1H, 4-H), 7.29 (t, $^{3}J = 7.8$ Hz, 1H, 5-H), 7.31 (t, $^{3}J = 9.7$ Hz, 1H, 5′-H), 7.32–7.33 (m, 1H, 6-H), 7.39–7.41 (m, 1H, 2-H), 7.40 (d, $^{3}J = 4.7$ Hz, 1H, 3′-H), 7.42 (t, $^{3}J = 9.9$ Hz, 1H, 7′-H), 7.73 (t, $^{3}J = 10.0$ Hz, 1H, 6′-H), 8.31 (d, $^{3}J = 4.3$ Hz, 1H, 2′-H), 8.32 (d, $^{3}J = 10.2$ Hz, 1H, 4′-H), 9.39 (d, $^{3}J = 9.7$ Hz, 1H, 8′-H). ^{13}C-NMR δ (ppm): 107.7; 114.6; 116.6; 116.7; 120.2; 125.6; 126.7; 126.8; 130.0; 135.8; 138.7; 139.8; 144.0; 147.7. MS (ESI): 248 [M + 1]. Element Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.69; H, 5.35; N, 16.96.

Table 2
The yields of bis aromatic diazenes **8** and **9** starting from compounds **6** and **7**.

Azulen-1-yl	Compound, yield (%)	
	8	**9**
a	68	70
b	73	68
c	77	93
a,**b**/**b**,**a**[a]	75/73	87/71
a,**c**/**c**,**a**[b]	70/75	70/75
b,**c**/**c**,**a**[c]	64/78	64/84

[a] Starting from amine **6a** and 4,6,8-trimethylazulene/starting from amine **6b** and azulene.
[b] Starting from amine **6a** and guaiazulene/starting from amine **6c** and azulene.
[c] Starting from amine **6b** and guaiazulene/starting from amine **6c** and 4,6,8-trimethylazulene.

Table 3
Yields of the diazotization + coupling of 3-nitroanilines and of the reduction of the reaction products to the corresponding amino derivatives.

Reaction	Yield (%) of **10a–c** and of **6a–c**		
	a	**b**	**c**
3-Nitroaniline → → **10a–c**[a]	80	79	88
10a–c → **6a–c**[b]	49	45	48

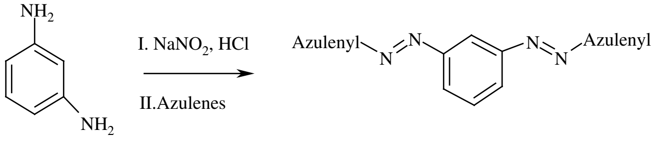
[a] When an excess of 25% sodium nitrite was used the yields overpass 90%.
[b] Without the recovery of the intermediate **10**. The recovery of **10** enhances the yields to 70–75%.

3-(4,6,8-Trimethylazulen-1-ylazo)-phenylamine (**6b**), dark green crystals, m.p. 162 °C. UV–vis (MeOH), λ_{max} (log ε): 233 (4.51), 295 (4.16), 317 (4.21), 332 (4.19), 429 (4.46). ^{1}H-NMR δ (ppm): 2.63 (s, 6H, Me(6)), 2.86 (s, 6H, Me(4)), 3.36 (s, 6H, Me(8)), 6.71 (ddd, $^{3}J = 7.5$ Hz, $^{4}J = 2.4$ Hz, $^{4}J = 1.4$ Hz, 1H, 4-H), 7.17 (s, 1H, 5′-H), 7.20 (t, $^{4}J = 2.0$ Hz, 1H, 2-H), 7.28 (s, 1H, 7′-H), 7.29 (t, $^{3}J = 8.0$ Hz, 1H, 5-H), 7.34 (dt, $^{3}J = 8.0$ Hz, $^{4}J = 1.6$ Hz, 1H, 6-H), 7.35 (d, $^{3}J = 4.9$ Hz, 1H, 3′-H), 8.13 (d, $^{3}J = 4.7$ Hz, 1H, 2′-H). ^{13}C-NMR δ (ppm): 12.49; 28.71; 29.87; 108.3; 114.1; 115.9; 118.1; 122.2; 129.8; 130.8; 133.0; 133.8; 140.6; 147.2; 147.5; 147.8; 149.8; 155.6. MS (ESI): 290 [M + 1]. Element Anal. Calcd. for $C_{21}H_{23}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.78; H, 6.70; N, 14.52.

3-(3,8-Dimethyl-5-isopropylazulen-1-ylazo)-phenylamine (**6c**), dark green oil. UV–vis (MeOH), λ_{max} (log ε): 234 (4.59), 294 (4.25), 342 (4.18), 452 (4.48). ^{1}H-NMR δ (ppm): 1.37 (d, $^{3}J = 6.9$ Hz, 6H, *Me*$_2$CH), 2.60 (s, 3H, Me(3)), 3.09 (hept, 1H, Me$_2$*CH*), 3.32 (s, 3H, Me(8)), 6.68 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 2.4$ Hz, $^{4}J = 1.0$ Hz, 1H, 4-H), 7.19 (t, $^{4}J = 1.9$ Hz, 1H, 2-H), 7.25 (t, $^{3}J = 11.0$ Hz, 1H, 7′-H), 7.26 (t, $^{3}J = 7.6$ Hz, 1H, 5-H), 7.32 (dt, $^{3}J = 8.0$ Hz, $^{4}J = 1.6$ Hz, 1H, 6-H), 7.43 (dd, $^{3}J = 10.6$ Hz, $^{4}J = 1.9$ Hz, 1H, 6′-H), 8.11 (s, 1H, 2′-H), 8.12 (d, $^{4}J = 2.2$ Hz, 1H, 4′-H). ^{13}C-NMR δ (ppm): 13.20; 24.60; 28.81; 38.24; 108.1; 114.1; 115.7; 125.7; 128.4; 129.8; 131.4; 134.9; 135.2; 135.9; 142.6; 145.0; 145.2; 147.2; 148.6; 155.7. MS (ESI): 318 [M + 1]. Element Anal. Calcd. for $C_{21}H_{23}N_3$: C, 79.46; H, 7.30; N, 13.24. Found: C, 79.45; H, 7.42; N, 13.13.

4-(Azulen-1-ylazo)-phenylamine (**7a**), dark green crystals, m.p. 128 °C. UV–vis (MeOH), λ_{max} (log ε): 229 (4.18), 286 (4.21), 338 (3.87), 464 (4.34). ^{1}H-NMR δ (ppm): 3.92 (s, 2H, NH), 6.76 (dd, $^{3}J = 6.9$ Hz, $^{4}J = 1.8$ Hz, 2H, 3-H, 5-H), 7.22 (t, $^{3}J = 9.8$ Hz, 1H, 5′-H), 7.33 (t, $^{3}J = 9.8$ Hz, 1H, 7′-H), 7.40 (d, $^{3}J = 4.6$ Hz, 1H, 3′-H), 7.66 (t, $^{3}J = 9.8$ Hz, 1H, 6′-H), 7.88 (dd, $^{3}J = 6.9$ Hz, $^{4}J = 1.9$ Hz, 2H, 2-H, 6-H), 8.26 (d, $^{3}J = 9.3$ Hz, 1H, 4′-H), 8.31 (d, $^{3}J = 4.4$ Hz, 1H, 2′-H), 9.27 (d, $^{3}J = 9.9$ Hz, 1H, 8′-H). ^{13}C-NMR δ (ppm): 115.1; 115.2; 119.7; 124.4; 125.4; 125.5; 125.7; 125.9; 135.6; 137.5; 138.4; 139.4; 143.6; 144.4; 147.5; 148.4. MS (ESI): 248 [M + 1]. Element Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.64; H, 5.39; N, 16.97.

4-(4,6,8-Trimethylazulen-1-ylazo)-phenylamine (**7b**), dark green crystals, m.p. 98 °C. UV–vis (MeOH), λ_{max} (log ε): 236 (4.41), 299 (4.30), 345 (4.12), 454 (4.47), 472(4.46). ^{1}H-NMR δ (ppm): 2.60 (s, 3H, Me(6)), 2.85 (s, 3H, Me(4)), 3.36 (s, 3H, Me(8)), 6.76 (d, $^{3}J = 8.9$ Hz, 2H, 3-H, 5-H), 7.15 (s, 1H, 5-H), 7.21 (s, 1H, 7-H), 7.36 (d, $^{3}J = 4.8$ Hz, 1H, 3′-H), 7.77 (d, $^{3}J = 8.8$ Hz, 2H, 2-H, 6-H), 8.14 (d, $^{3}J = 4.9$ Hz, 1H, 2′-H). ^{13}C-NMR δ (ppm): 25.85; 29.12; 30.19;



11 **8** a-c

Scheme 3.

Table 4
λ_{max} (log ε) in visible for azo and bis azo derivatives[a] and the difference $\Delta\lambda_{max}$ between λ_{max} (CH_3OH) and λ_{max} (nC_6H_{14}).

Compound	Solvent	λ_{max} and $\Delta\lambda_{max}$ (in nm)					
		Azulen-1-yl substituents					
		a	$\Delta\lambda_{max}$	**b**	$\Delta\lambda_{max}$	**c**	$\Delta\lambda_{max}$
1(*m*)	nC_6H_{14}	422 (4.52)		433 (4.52)		452 (4.54)	
	CH_3OH	428 (4.50)	6	438 (4.30)	5	459 (4.38)	7
8	nC_6H_{14}	433 (4.47)		444 (4.53)		464 (4.62)	
	CH_3OH	442 (4.49)	9	450 (4.54)	6	493 (4.60)	29
1(*p*)	nC_6H_{14}	459 (4.34)		471 (4.43)		493 (4.57)	
	CH_3OH	469 (4.33)	10	484 (4.40)	13	517 (4.46)	26
9	nC_6H_{14}	503 (4.62)		–[b]		545 (4.77)[c]	
	CH_3OH	520 (4.60)	17	546 (4.70)	–	569 (4.75)	24

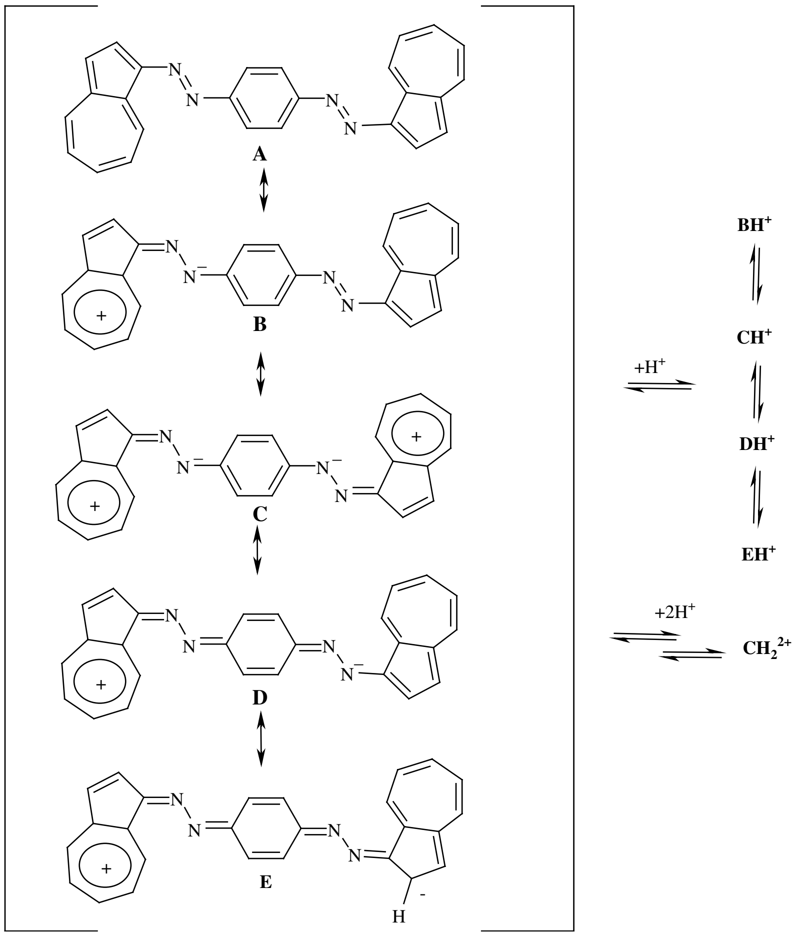
[a] λ_{max} (in nm) in ethanol for **3(*m*)**: 435 (3.16) and for **3(*p*)**: 445 (3.48) [16].
[b] Insoluble in nC_6H_{14}.
[c] One shoulder is also present at 514 (4.70).

115.6; 118.2; 122.5; 124.7; 130.4; 132.6; 147.3; 147.9; 148.0; 148.1; 150.0. MS (ESI): 290 [M + 1]. Element Anal. Calcd. for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.76; H, 6.54; N, 14.70.

4-(3,8-Dimethyl-5-isopropylazulen-1-ylazo)-phenylamine (**7c**), dark green crystals. m.p. 180 °C. UV–vis (MeOH), λ_{max} (log ε): 235 (4.42), 252 (4.38), 297 (4.32), 347 (4.11), 358 (4.10), 475 (4.58), 490 (4.60). ^{1}H-NMR δ (ppm): 1.37 (d, $^3J = 7.0$ Hz, 6H, *Me*$_2$CH), 2.61 (s, 3H, Me(3)), 3.06 (hept, 1H, $^3J = 6.8$ Hz, Me$_2$C*H*), 3.31 (s, 3H, Me(8)), 6.75 (d$_{AB}$, $^3J = 8.9$ Hz, 2H, 3-H, 5-H), 7.16 (d, $^3J = 10.7$ Hz, 1H, 7′-H), 7.37 (dd, $^3J = 10.4$ Hz, $^4J = 2.1$ Hz, 1H, 6′-H), 7.74 (d$_{AB}$, $^3J = 8.9$ Hz, 2H, 2-H, 6-H), 8.09 (d, $^4J = 2.0$ Hz, 1H, 4′-H), 8.12 (s, 1H, 2′-H). ^{13}C-NMR δ (ppm): 13.00; 24.40; 28.51; 37.96; 115.0; 123.9; 125.5; 127.8; 130.2; 133.6; 134.5; 135.4; 141.7; 143.9; 144.7; 147.3; 147.5; 148.2. MS (ESI): 318 [M + 1]. Element Anal. Calcd. for $C_{21}H_{23}N_3$: C, 79.46; H, 7.30; N, 13.24. Found: C, 79.38; H, 7.38; N, 13.24.

Azulen-1-yl-(3-nitro-phenyl)-diazene (**10a**), brown crystals, m.p. 183 °C (lit [14] 183 °C). UV–vis (MeOH), λ_{max} (log ε): 234 (4.29), 278 (4.10), 337 (3.95), 433 (4.30). ^{1}H-NMR δ (ppm): 7.42 (t, $^3J = 9.8$ Hz, 1H, 5′-H), 7.46 (d, $^3J = 4.4$ Hz, 1H, 3′-H), 7.56 (t, $^3J = 9.8$ Hz, 1H, 7′-H), 7.66 (t, $^3J = 8.1$ Hz, 1H, 5-H), 7.83 (t, $^3J = 9.9$ Hz, 1H, 6′-H), 8.22 (ddd, $^3J = 8.2$ Hz, $^4J = 1.7$ Hz, $^4J = 1.1$ Hz, 1H, 4-H or 6-H), 8.27 (ddd, $^3J = 8.0$ Hz, $^4J = 2.0$ Hz, $^4J = 1.0$ Hz, 1H, 6-H or 4-H), 8.32 (d, $^3J = 4.6$ Hz, 1H, 2′-H), 8.38 (d, $^3J = 9.4$ Hz, 1H, 4′-H), 8.78 (t, $^4J = 2.0$ Hz, 1H, 2-H), 9.37 (d, $^3J = 9.9$ Hz, 1H, 8′-H). ^{13}C-NMR δ (ppm): 115.9; 121.1; 123.6; 125.7; 128.0; 129.5; 130.0; 136.0; 139.2; 140.3; 155.1. MS (ESI): 278 [M + 1]. Element Anal. Calcd. for $C_{16}H_{11}N_3O_2$: C, 69.31; H, 4.00; N, 15.15. Found: C, 69.35; H, 4.12; N, 15.08.

4,6,8-Trimethylazulen-1-yl-(3-nitro-phenyl)-diazene (**10b**), brown crystals, m.p. 197 °C, lit [15] (196–197 °C). UV–vis (MeOH), λ_{max} (log ε): 234 (4.36), 312 (4.02), 340 (3.96), 443 (4.30). ^{1}H-NMR δ (ppm): 2.67 (s, 3H, Me(6)), 2.89 (s, 3H, Me(4)), 3.37 (s, 3H, Me(8)), 7.25 (s, 1H, 5′-H), 7.38 (s, 1H, 7′-H), 7.37 (d, $^3J = 5.0$ Hz, 1H, 3′-H), 7.61 (t, $^3J = 8.1$ Hz, 1H, 5-H), 8.12–8.16 (m, 2H, 4-H, 6-H), 8.14 (d, $^3J = 4.6$ Hz, 1H, 2′-H), 8.62 (t, $^4J = 1.9$ Hz, $^4J = 1.6$ Hz, 1H, 2-H).



Scheme 4.

^{13}C-NMR δ (ppm): 25.58; 28.73; 29.85; 116.4; 118.9; 122.3; 128.6; 129.7; 132.1; 134.4; 135.2; 141.9; 147.6; 147.9; 148.5; 149.3; 150.1; 155.1. MS (ESI): 320 [M + 1]. Element Anal. Calcd. for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.42; H, 5.41; N, 13.15.

3,8-Dimethyl-5-isopropylazulen-1-yl-(3-nitro-phenyl)-diazene (**10c**), brown crystals, m.p. 155 °C (dec). UV–vis (MeOH), λ_{max} (log ε): 233 (4.48), 353 (4.01), 473 (4.33). ^{1}H-NMR δ (ppm): 1.40 (d, ^3J = 6.9 Hz, 6H, *Me*$_2$CH), 2.61 (s, 3H, Me(3′)), 3.13 (hept, 1H, Me$_2$*CH*), 3.35 (s, 3H, Me(8′)), 7.40 (t, ^3J = 10.7 Hz, 1H, 7′-H), 7.60 (t, ^3J = 8.1 Hz, 1H, 5-H), 7.53 (dd, ^3J = 10.7 Hz, ^4J = 1.9 Hz, 1H, 6′-H), 8.11–8.14 (m, 3H, 6-H, 4-H, 2′-H), 8.18 (d, ^4J = 1.9 Hz, 1H, 4′-H), 8.62 (t, ^4J = 2.1 Hz, 1H, 2-H). ^{13}C-NMR δ (ppm): 13.32; 24.64; 28.94; 38.40; 116.1; 121.9; 125.5; 128.3; 129.5; 129.6; 133.0; 135.2; 136.3; 136.5; 143.8; 145.1; 147.4; 149.2; 155.2. MS (ESI): 348 [M + 1]. Element Anal. Calcd. for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.09. Found: C, 72.56; H, 6.11; N, 12.13.

1,3-Bis [(E)-1-azulen-1-yl-2-diazenyl]benzene (**8a**), brown crystals, m.p. 180 °C. UV–vis (MeOH), λ_{max} (log ε): 232 (4.43), 279 (4.32), 334 (4.23), 442 (4.49). UV–vis (*n*-hexane), λ_{max} (log ε): 238 (4.38), 277 (4.40), 329 (4.22), 433 (4.47). ^{1}H-NMR δ (ppm): 7.34 (t, ^3J = 9.8 Hz, 2H, 5′-H, 5″-H), 7.46 (d, ^3J = 4.6 Hz, 2H, 3′-H, 3″-H), 7.48 (t, ^3J = 9.8 Hz, 2H, 7′-H, 7″-H), 7.65 (t, ^3J = 7.8 Hz, 1H, 5-H), 7.76 (t, ^3J = 9.8 Hz, 2H, 6′-H, 6″-H), 8.04 (dd, ^3J = 7.8 Hz, ^4J = 2.0 Hz, 2H, 4-H, 6-H), 8.35 (d, ^3J = 9.3 Hz, 2H, 4′-H, 4″-H), 8.40 (d, ^3J = 4.7 Hz, 2H, 2′-H, 2″-H), 8.58 (t, ^4J = 2.0 Hz, 1H, 2-H), 9.43 (d, ^3J = 9.9 Hz, 2H, 8′-H, 8″-H). ^{13}C-NMR δ (ppm): 115.9; 120.0; 122.9; 125.3; 126.7; 129.3; 135.6; 138.5; 138.9; 139.5; 144.0; 155.0. MS [ESI]: 387 [M + 1]. Element Anal. Calcd. for $C_{26}H_{18}N_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.68; H, 4.78; N, 14.54.

1,3-Bis [(E)-1-(4,6,8-trimethylazulen-1-yl)-2-diazenyl]benzene (**8b**), brown crystals, m.p. 178 °C. UV–vis (MeOH), λ_{max} (log ε): 233 (4.64), 307 (4.43), 331 (4.39), 358 (4.23), 370 (4.11), 450 (4.54). UV–vis (DME), λ_{max} (log ε): 236 (4.68), 309 (4.43), 350 (4.44), 417sh (4.50), 449 (4.56). UV–vis (DCM), λ_{max} (log ε): 231 (4.82), 280 (4.52), 346 (4.31), 458 (4.55). UV–vis (*n*-hexane), λ_{max} (log ε): 231 (4.82), 280 (4.52), 346 (4.31), 458 (4.55). UV–vis (*n*-hexane), λ_{max} (log ε): 246 (4.52), 312 (4.34), 336 (4.33), 444 (4.53). ^{1}H-NMR δ (ppm): 2.66 (s, 6H, Me(6)), 2.89 (s, 6H, Me(4)), 3.44 (s, 6H, Me(8)), 7.21 (s, 2H, 5′-H, 5″-H), 7.34 (s, 2H, 7′-H, 7″-H), 7.39 (d, ^3J = 4.8 Hz, 2H, 3′-H, 3″-H), 7.60 (t, ^3J = 7.8 Hz, 1H, 5-H), 7.90 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 2H, 4-H, 6-H), 8.20 (d, ^3J = 4.9 Hz, 2H, 2′-H, 2″-H), 8.31 (t, ^4J = 1.9 Hz, ^4J = 1.6 Hz, 1H, 2-H). MS [ESI]: 527 [M + 1]. Element Anal. Calcd. for $C_{36}H_{38}N_4$: C, 82.09; H, 7.27; N, 10.64. Found: C, 82.05; H, 7.37; N, 10.68.

1,3-Bis [(E)-1-(3,8-dimethyl-5-isopropylazulen-1-yl)-2-diazenyl]benzene (**8c**), brown crystals, m.p. 298 °C. UV–vis (MeOH), λ_{max} (log ε): 236 (4.55), 248 (4.56), 300 (4.32), 346 (4.29), 438sh (4.51), 493 (4.60). UV–vis (*n*-hexane), λ_{max} (log ε): 235 (4.53), 249 (4.56), 296 (4.36), 346 (4.36), 428 (4.54), 464 (4.62). UV–vis (DCM), λ_{max} (log ε): 249 (4.83), 299 (4.50), 347 (4.37), 489 (4.63). ^{1}H-NMR δ (ppm): 1.40 (d, ^3J = 6.9 Hz, 12H, *Me*$_2$CH), 2.64 (s, 6H, Me(3)), 3.10 (hept, ^3J = 6.9 Hz, 2H, Me$_2$*CH*), 3.39 (s, 6H, Me(8)), 7.29 (d, ^3J = 10.6 Hz, 2H, 7′-H, 7″-H), 7.45 (dd, ^3J = 10.6 Hz, ^4J = 2.0 Hz, 2H, 6′-H, 6″-H), 7.61 (t, ^3J = 7.8 Hz, 1H, 5-H), 7.89 (dd, ^3J = 7.8 Hz, ^4J = 2.0 Hz, 2H, 4-H, 6-H), 8.15 (d, ^4J = 2.0 Hz, 2H, 4′-H, 4″-H), 8.18 (s, 2H, 2′-H, 2″-H), 8.32 (t, ^4J = 1.9 Hz, 1H, 2-H). ^{13}C-NMR δ (ppm): 13.44; 24.80; 29.22; 38.43; 113.54; 123.9; 126.1; 128.7; 129.6; 131.8; 135.1; 135.5; 136.1; 143.0; 145.5; 148.9; 155.6. MS [ESI]: 527 [M + 1]. Element Anal. Calcd. for $C_{36}H_{38}N_4$: C, 82.09; H, 7.27; N, 10.64. Found: C, 82.00; H, 7.35; N, 10.65.

(E)-1-azulen-1-yl-2-{3-[(E)-(4,6,8-trimethylazulen-1-yl)-diazenyl]-phenyl}-diazene (**8ab**), brown crystals, m.p. 178 °C. UV–vis (MeOH), λ_{max} (log ε): 234 (4.53), 281 (4.29), 325 (4.30), 331 (4.30), 334 (4.30), 446 (4.53). UV–vis (*n*-hexane), λ_{max} (log ε): 240 (4.51), 276 (4.31), 324 (4.47), 327 (4.47), 331 (4.47), 437 (4.57). ^{1}H-NMR δ (ppm): 2.59 (s, 3H, Me(6)), 2.83 (s, 3H, Me(4)), 3.40 (s, 3H, Me(8)), 7.13 (s, 1H, 5(b)-H), 7.26 (s, 1H, 7(b)-H), 7.21–7.31 (m, 1H, 5(a)-H), 7.36–7.44 (m, 2H, 3(a)-H, 7(a)-H), 7.34 (d, ^3J = 4.8 Hz, 1H, 3(b)-H), 7.52 (t, ^3J = 7.8 Hz, 1H, 5-H), 7.68 (t, ^3J = 9.8 Hz, 1H, 6(a)-H), 7.91 (bd, ^3J = 7.8 Hz, 1H, 4-H or 6-H), 7.99 (br d, ^3J = 7.8 Hz, 1H, 6-H or 4-H), 8.18 (d, ^3J = 4.8 Hz, 1H, 2(b)-H), 8.29 (d, ^3J = 9.3 Hz, 1H, 4(a)-H), 8.30 (d, ^3J = 4.8 Hz, 1H, 2(a)-H), 8.46 (t, ^4J = 1.9 Hz, 1H, 2-H), 9.36 (d, ^3J = 9.8 Hz, 1H, 8(a)-H). ^{13}C-NMR δ (ppm): 25.70; 28.91; 30.12; 114.8; 118.5; 120.4; 122.4; 123.6; 123.9; 125.5; 126.8; 126.9; 129.7; 131.3; 133.6; 135.9; 138.8; 139.4; 139.9; 141.1; 144.3; 147.5; 148.1; 150.1; 155.4. MS [ESI]: 429 [M + 1]. Element Anal. Calcd. for $C_{29}H_{24}N_4$: C, 81.28; H, 5.65; N, 13.07. Found: C, 81.22; H, 5.70; N, 13.08.

(E)-1-azulen-1-yl-2-{3-[(E)-(5-isopropyl-3,8-trimethylazulen-1-yl)-diazenyl]phenyl}-diazene (**8ac**), brown crystals, m.p. 140 °C. UV–vis (MeOH), λ_{max} (log ε): 234 (4.52), 280 (4.32), 337 (4.26), 339 (4.26), 322sh (4.45), 470 (4.52). UV–vis (*n*-hexane), λ_{max} (log ε): 241 (4.34), 276 (4.26), 334 (4.15), 413 (4.28), 452 (4.57). ^{1}H-NMR δ (ppm): 1.37 (d, ^3J = 6.9 Hz, 6H, *Me2*CH), 2.63 (s, 3H, Me(3)), 3.08 (hept, ^3J = 6.8 Hz, 1H, Me$_3$*CH*), 3.42 (s, 3H, Me(8)), 7.23 (t, ^3J = 9.5 Hz, 1H, 5(a)-H), 7.28 (d, ^3J = 10.7 Hz, 1H, 7(c)-H), 7.42 (d, ^3J = 4.4 Hz, 1H, 3(a)-H), 7.43 (t, ^3J = 9.7 Hz, 1H, 7(a)-H), 7.45 (d, ^3J = 10.0 Hz, 1H, 6(c)-H), 7.60 (t, ^3J = 7.8 Hz, 1H, 5-H), 7.73 (t, ^3J = 9.1 Hz, 1H, 6(a)-H), 7.92 (ddd, ^3J = 7.9 Hz, ^4J = 1.0 Hz, ^4J = 1.0 Hz, 1H, 4-H or 6-H), 7.98 (ddd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, ^4J = 1.0 Hz, 1H, 6-H or 4-H), 8.14 (d, ^4J = 1.7 Hz, 1H, 4(c)-H), 8.20 (s, 1H, 2(c)-H), 8.31 (d, ^3J = 9.4 Hz, 1H, 4(a)-H), 8.37 (d, ^3J = 4.5 Hz, 1H, 2(a)-H), 8.49 (t, ^4J = 1.5 Hz, 1H, 2-H), 9.38 (d, ^3J = 9.9 Hz, 1H, 8(a)-H). ^{13}C-NMR δ (ppm): 13.05; 24.44; 28.88; 37.95; 114.2; 120.0; 123.1; 123.3; 125.1; 125.5; 126.5; 126.6; 128.5; 129.3; 131.7; 134.8; 135.5; 135.8; 138.4; 139.0; 139.5; 142.7; 143.9; 144.9; 145.3; 148.5; 155.0; 155.2. MS [ESI]: 457 [M + 1]. Element Anal. Calcd. for $C_{31}H_{28}N_4$: C, 81.55; H, 6.18; N, 12.27. Found: C, 81.43; H, 6.27; N, 12.30.

(E)-1-(4,6,8-trimethylazulen-1-yl)-2-{3-[(E)-(5-isopropyl-3,8-trimethylazulen-1-yl)-diazenyl]phenyl}-diazene (**8bc**), brown crystals, m.p. 202 °C. UV–vis (MeOH), λ_{max} (log ε): 231 (4.52), 307 (4.35), 342 (4.31), 430sh (4.51), 474 (4.57). UV–vis (*n*-hexane), λ_{max} (log ε): 248 (4.49), 305 (4.34), 343 (4.34), 420 (4.50), 454 (4.57). ^{1}H-NMR δ (ppm): 1.39 (d, ^3J = 6.9 Hz, 6H, *Me*$_2$CH), 2.63 (s, 3H, Me-6(b)), 2.66 (s, 3H, Me-3(c)), 2.89 (s, 3H, Me-4(b)), 3.11 (hept, ^3J = 6.8 Hz, 1H, Me$_2$*CH*), 3.40 (s, 3H, Me-8(b or c)), 3.44 (s, 3H, Me-8(c or b)), 7.20 (s, 1H, 5(b)-H), 7.29 (d, ^3J = 10.0 Hz, 1H, 7(c)-H), 7.33 (s, 1H, 7(b)-H), 7.39 (d, ^3J = 4.9 Hz, 1H, 3(b)-H), 7.46 (dd, ^3J = 10.6 Hz, ^4J = 1.8 Hz, 1H, 6(c)-H), 7.60 (t, ^3J = 7.8 Hz, 1H, 5-H), 7.88 (d, ^3J = 8.0 Hz, 1H, 4-H or 6-H), 7.89 (d, ^3J = 8.0 Hz, 1H, 6-H or 4-H), 8.16 (d, ^4J = 1.9 Hz, 1H, 4(c)-H), 8.19 (s, 1H, 2(c)-H), 8.20 (d, ^3J = 4.9 Hz, 1H, 2(b)-H), 8.30 (t, ^4J = 1.9 Hz, 1H, 2-H). ^{13}C-NMR δ (ppm): 13.07; 24.45; 25.37; 28.56; 28.86; 29.92; 38.11; 113.2; 118.0; 122.2; 123.6; 123.7; 125.7; 128.4; 129.2; 130.7; 131.5; 131.8; 134.8; 135.5; 138.9; 135.8; 140.6; 142.6; 145.2; 147.1; 147.7; 148.6; 148.9 149.8; 155.1; 155.2. MS [ESI]: 499 [M + 1]. Element Anal. Calcd. for $C_{34}H_{34}N_4$: C, 81.89; H, 6.87; N, 11.24. Found: C, 81.83; H, 6.89; N, 11.28.

1,4-Bis [(E)-1-azulen-1-yl-2-diazenyl]benzene (**9a**), brown crystals, m. p. 201 °C. UV–vis (MeOH), λ_{max} (log ε): 230 (4.54), 281 (4.49), 408 (4.12), 520 (4.60). UV–vis (*n*-hexane), λ_{max} (log ε): 232 (4.49), 279 (4.52), 342 (4.10), 400 (4.12), 479 (4.59), 503 (4.62). ^{1}H-NMR δ (ppm): 7.34 (t, ^3J = 9.7 Hz, 2H, 5′-H and 5″-H), 7.45 (d, ^3J = 4.8 Hz, 2H, 3′-H and 3″-H), 7.48 (t, ^3J = 9.4 Hz, 2H, 7′-H and 7″-H), 7.76 (t, ^3J = 9.9 Hz, 2H, 6′-H and 6″-H), 8.10 (s, 4H, phenyl H), 8.34 (d, ^3J = 9.7 Hz, 1H, 4′-H and 4″-H), 8.36 (d, ^3J = 4.6 Hz, 1H, 2′-H and 2″-H), 9.38 (d, ^3J = 9.7 Hz, 1H, 8′-H and 8″-H). ^{13}C-NMR δ (ppm): 120.7; 123.4; 125.6; 127.1; 127.2; 136.0; 138.9; 139.3; 140.0; 144.6; 154.8. MS [ESI]: 387 [M + 1]. Element Anal. Calcd. for $C_{26}H_{18}N_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.73; H, 4.75; N, 14.52.

1,4-Bis [(E)-1-(4,6,8-trimethylazulen-1-yl)-2-diazenyl]benzene (**9b**), brown crystals, m.p. 324 °C. UV–vis (MeOH), λ_{max} (log ε): 236 (4.58), 283 (4.42), 352 (4.09), 420 (4.07), 546 (4.70). UV–vis (DCM), λ_{max} (log ε): 239 (4.62), 306 (4.41), 354 (4.10), 420 (4.08), 546 (4.68). UV–vis (DME), λ_{max} (log ε): 231 (4.94), 283 (4.53), 353 (4.19), 419 (4.21), 546 (4.72). ^{1}H-NMR δ (ppm): 2.66 (s, 6H, Me(6)), 2.87 (s, 6H, Me(4)), 3.43 (s, 6H, Me(8)), 7.19 (s, 2H, $5'$-H and $5''$-H), 7.32 (s, 2H, $7'$-H and $7''$-H), 7.38 (d, $^3J = 4.8$ Hz, 2H, $3'$-H and $3''$-H), 7.98 (s, 4H, phenyl H), 8.18 (d, $^3J = 5.0$ Hz, 2H, $2'$-H and $2''$-H). MS [ESI]: 471 [M + 1]. Element Anal. Calcd. for $C_{32}H_{30}N_4$: C, 81.76; H, 6.43; N, 11.90. Found: C, 81.68; H, 6.50; N, 11.82.

1,4-Bis [(E)-1-(3,8-dimethyl-5-isopropylazulen-1-yl)-2-diazenyl]benzene (**9c**), brown crystals, m.p. 330 °C. UV–vis (MeOH), λ_{max} (log ε): 244 (4.53), 297 (4.37), 347 (4.11), 359 (4.06), 441 (4.17), 569 (4.75). UV–vis (*n*-hexane), λ_{max} (log ε): 241 (4.60), 296 (4.45), 348 (4.14), 359 (4.44), 429 (4.21), 514 (4.70), 545 (4.77), 581 (4.78). ^{1}H-NMR δ (ppm): 1.39 (d, $^3J = 6.8$ Hz, 12H, *Me*$_2$CH), 2.61 (s, 6H, Me(3)), 3.08 (hept, 2H, $^3J = 6.8$ Hz, Me$_2$*CH*), 3.36 (s, 6H, Me(8)), 7.29 (d, $^3J = 9.9$ Hz, 2H, $7'$-H and $7''$-H), 7.45 (d, $^3J = 9.9$ Hz, 2H, $6'$-H and $6''$-H), 7.96 (s, 4H, phenyl H), 8.12 (s, 2H, $2'$-H and $2''$-H), 8.16 (s, 2H, $4'$-H and $4''$-H). ^{13}C-NMR δ (ppm): 13.05; 24.40; 28.68; 38.09; 123.0; 125.6; 128.8; 131.6; 134.8; 135.4; 135.8; 142.9; 145.7; 148.7; 154.2. MS [ESI]: 527 [M + 1]. Element Anal. Calcd. for $C_{36}H_{38}N_4$: C, 82.09; H, 7.27; N, 10.64. Found: C, 81.96; H, 7.37; N, 10.67.

(E)-1-azulen-1-yl-2-{4-[(E)-(4,6,8-trimethylazulen-1-yl)-diazenyl]phenyl}-diazene (**9ab**), brown crystals, m.p. 195 °C. UV–vis (MeOH), λ_{max} (log ε): 233 (4.56), 284 (4.43), 411 (4.14), 531 (4.65). UV–vis (*n*-hexane), λ_{max} (log ε): 236 (4.52), 284 (4.45), 342 (4.15), 368 (3.96), 405 (4.16), 513 (4.65). ^{1}H-NMR δ (ppm): 2.66 (s, 3H, Me(6)), 2.88 (s, 3H, Me(4)), 3.42 (s, 3H, Me(8)), 7.21 (s, 1H, 5(b)-H), 7.33 (t, $^3J = 9.6$ Hz, 1H, 5(a)-H), 7.34 (s, 1H, 7(b)-H), 7.39 (d, $^3J = 4.9$ Hz, 1H, 3(b)-H), 7.45 (d, $^3J = 4.3$ Hz, 1H, 3(a)-H), 7.46 (t, $^3J = 9.9$ Hz, 1H, 7(a)-H), 7.76 (t, $^3J = 9.8$ Hz, 1H, 6(a)-H), 8.02 (d$_{AB}$, $^3J = 7.8$ Hz, 2H, *m*-phenyl H), 8.12 (d$_{AB}$, $^3J = 7.8$ Hz, 2H, *m*-phenyl H), 8.19 (d, $^3J = 4.9$ Hz, 1H, 2(b)-H), 8.34 (d, $^3J = 9.8$ Hz, 1H, 4(a)-H), 8.36 (d, $^3J = 4.7$ Hz, 1H, 2(a)-H), 9.37 (d, $^3J = 9.9$ Hz, 1H, 8(a)-H). ^{13}C-NMR δ (ppm): 25.78; 30.19; 118.9; 120.7; 122.4; 123.5; 125.6; 127.0; 127.1; 131.5; 133.8; 136.0; 138.8; 140.0; 144.5; 147.6; 148.3; 150.3; 154.4; 155.0; 155.9. MS [ESI]: 429 [M + 1]. Element Anal. Calcd. for $C_{29}H_{24}N_4$: C, 81.28; H, 5.65; N, 13.07. Found: C, 81.22; H, 5.70; N, 13.08.

(E)-1-azulen-1-yl-2-{4-[(E)-(5-isopropyl-3,8-trimethylazulen-1-yl)-diazenyl]phenyl}-diazene (**9ac**) brown crystals, m.p. 192 °C. UV–vis (MeOH), λ_{max} (log ε): 234 (4.65), 284 (4.55), 419 (4.26), 549 (4.79). UV–vis (*n*-hexane), λ_{max} (log ε): 236 (4.63), 284 (4.56), 345 (4.21), 368 (4.04), 413 (4.30), 528 (4.80). ^{1}H-NMR δ (ppm): 1.39 (d, $^3J = 6.9$ Hz, 6H, *Me*$_2$CH), 2.62 (s, 3H, Me(3)), 3.09 (hept, $^3J = 6.9$ Hz, 1H, Me$_2$*CH*), 3.36 (s, 3H, Me(8)), 7.28 (t, $^3J = 9.5$ Hz, 1H, 5(a)-H), 7.29 (d, $^3J = 10.8$ Hz, 1H, 7(c)-H), 7.42 (t, $^3J = 9.2$ Hz, 1H, 7(a)-H), 7.43 (d, $^3J = 4.8$ Hz, 1H, 3(a)-H), 7.44 (d, $^3J = 10.2$ Hz, 1H, 6(c)-H), 7.71 (t, $^3J = 10.0$ Hz, 1H, 6(a)-H), 8.01 (d$_{AB}$, $^3J = 8.8$ Hz, 2H, *m*-phenyl H), 8.12 (s, 1H, 4(c)-H), 8.14 (d$_{AB}$, $^3J = 8.8$ Hz, 2H, *m*-phenyl H), 8.17 (s, 1H, 2(c)-H), 8.29 (d, $^3J = 9.2$ Hz, 1H, 4(a)-H), 8.36 (d, $^3J = 4.5$ Hz, 1H, 2(a)-H), 9.34 (d, $^3J = 9.6$ Hz, 1H, 8(a)-H). ^{13}C-NMR δ (ppm): 13.41; 24.78; 29.05; 38.43; 120.6; 123.3; 123.5; 125.5; 125.9; 126.9; 129.3; 131.3; 132.3; 135.2; 135.9; 136.0; 136.3; 138.7; 139.1; 139.9; 143.4; 144.4; 144.5; 146.0; 149.1; 154.2; 155.2. MS [ESI]: 457 [M + 1]. Element Anal. Calcd. for $C_{31}H_{28}N_4$: C, 81.55; H, 6.18; N, 12.27. Found: C, 81.52; H, 6.22; N, 12.26.

Table 5
λ_{max} in the visible region for the bis azo derivatives with two identical or different azulenyl moieties (in nC_6H_{14}/CH_3OH).

Compound	**8a**	**8b**	**8c**	**8ab**	**8ac**	**8bc**
λ_{max} (nm)	433/442	444/450	464/491	437/446	452/470	454/474
Compound	**9a**	**9b**	**9c**	**9ab**	**9ac**	**9bc**
λ_{max} (nm)	503/520	–/546	545/569	513/531	528/549	550/566

The values of log ε are reported in Section 2.

Table 6
λ^*_{max} in visible for the neutral, mono-protonated and di-protonated bis azo derivatives in ethanol and their isosbestic point (IP).

Compound	**8a**/[**8a**H]$^+$	**8b**/[**8b**H]$^+$	**8c**/[**8c**H]$^+$	**8ab**/[**8ab**H]$^+$	**8ac**/[**8ac**H]$^+$	**8bc**/[**8bc**H]$^+$
λ_{max} (nm)	442/554	450/533	493/570	446/529	471/544	474/566
IP	480	484	512	485	503	504
Compound	**9a**/[**9a**H]$^+$/[**9a**H$_2$]$^{2+}$	**9b**/[**9b**H]$^+$	**9c**/[**9c**H]$^+$/[**9c**H$_2$]$^{2+}$	**9ab**/[**9ab**H]$^+$	**9ac**/[**9ac**H]$^+$/[**9ac**H$_2$]$^{2+}$	**9bc**/[**9bc**H]$^+$
λ_{max} (nm)	520/644/690	546/656	567/682/719	532/640	549/659/707	567/682/719
IP	580	592	633	583	598	606

(E)-1-(4,6,8-trimethylazulen-1-yl)-2-{4-[(E)-(5-isopropyl-3,8-trimethylazulen-1-yl)-diazenyl]phenyl}-diazene (**9bc**), brown crystals, m.p. 225 °C. UV–vis (MeOH), λ_{max} (log ε): 239 (4.61), 297 (4.42), 354 (4.14), 430 (4.24), 433 (4.24), 555 (4.70). UV–vis (*n*-hexane), λ_{max} (log ε): 244 (4.69), 295 (4.54), 353 (4.24), 421 (4.32), 509 (4.75), 534 (4.78), 566 (4.70). ^{1}H-NMR δ (ppm): 1.39 (d, $^3J = 7.1$ Hz, 6H, *Me*$_2$CH), 2.62 (s, 3H, Me(3) or Me(6c)), 2.64 (s, 3H, Me(6c) or Me(3)), 2.86 (s, 3H, Me(4c)), 3.09 (hept, $^3J = 7.0$ Hz, 1H, Me$_2$*CH*), 3.37 (s, 3H, Me(8b) or Me(8c)), 3,41 (s, 3H, Me(8c) or Me(8b)), 7.18 (s, 1H, 5(b)-H), 7.29 (d, $^3J = 10.7$ Hz, 1H, 7(c)-H), 7.30 (s, 1H, 7(b)-H), 7.37 (d, $^3J = 4.8$ Hz, 1H, 3(b)-H), 7.44 (dd, $^3J = 10.2$ Hz, $^4J = 2.0$ Hz, 1H, 6(c)-H), 7.97 (s, 4H, phenyl H), 8.13 (d, $^4J = 2.0$ Hz, 1H, 4(c)-H), 8.17 (s, 1H, 2(c)-H), 8.18 (d, $^3J = 4.8$ Hz, 1H, 2(b)-H). ^{13}C-NMR δ (ppm): 13.06; 24.41; 25.32; 28.53; 29.75; 38.09; 118.3; 122.1; 123.0; 123.1; 125.6; 128.8; 130.9; 131.7; 133.9; 134.8; 135.4; 135.9; 140.8; 142.9; 145.5; 145.7; 147.1; 147.8; 148.1; 148.7; 149.9; 154.1; 154.4. MS [ESI]: 499 [M + 1]. Element Anal. Calcd. for $C_{34}H_{34}N_4$: C, 81.89; H, 6.87; N, 11.24. Found: C, 81.86; H, 6.88; N, 11.26.

3. Results and discussion

3.1. Diazene synthesis

The bis aromatic diazenes with only one azulene-1-yl moiety were readily prepared using commercially or easily available 3- and 4-phenylazo-phenylamine which were diazotized and coupled with azulenes in good yields [1]. Unfortunately, both corresponding 3- and 4-azulen-1-ylazo-phenylamines must be synthesized and

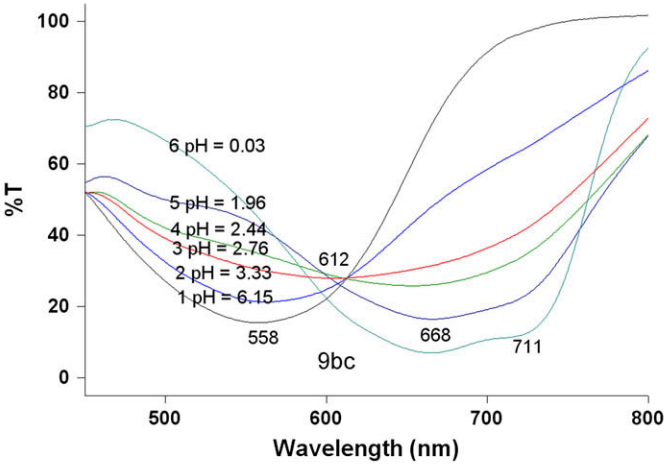


Fig. 1. Mono- and di-protonation of compound **9bc**.

their syntheses raised some problems. It is well known that azulene is an aromatic hydrocarbon with a reduced nucleophilic reactivity compared with the benzenoid derivatives. Therefore, these compounds are smoothly coupled with normal diazonium salts. However, the reaction does not take place when less reactive diazonium salts are used, for example amino-benzenediazonium salts. Two routes were used in order to substitute two azulene-1-ylazo moieties at the benzene ring.

The first synthesis started from the more reactive 3- and 4-acetylamino-benzenediazonium salts, (Scheme 2) which were able to couple with azulenes. As described in Table 1, moderate to good yields of intermediates **4** and **5** after diazotizion (step I) and coupling (step II) are obtained. Predictably, the *meta*-isomers, **4**, are obtained in higher yields.

The acylated amines **4** and **5** were hydrolyzed in almost quantitative yields to the corresponding anilines **6** and **7** (step III in Scheme 2) with aqueous hydrochloric acid in dioxane (3 h at 80 °C). The resulting anilines were diazotized and coupled with azulene derivatives (step IV) to obtain the bis aromatic diazenes containing two either identical or different azulenyl moieties, **8a**–**c** and **9a**–**c** or **8ab**, **ac** or **bc** and **9ab**, **ac** or **bc**, respectively. As expected, this second azo coupling occurred in good yields (Table 2) due to the presence in the diazonium salts of the activating azulenylazo group with electron withdrawing effect. Small amounts (less than 5%) of

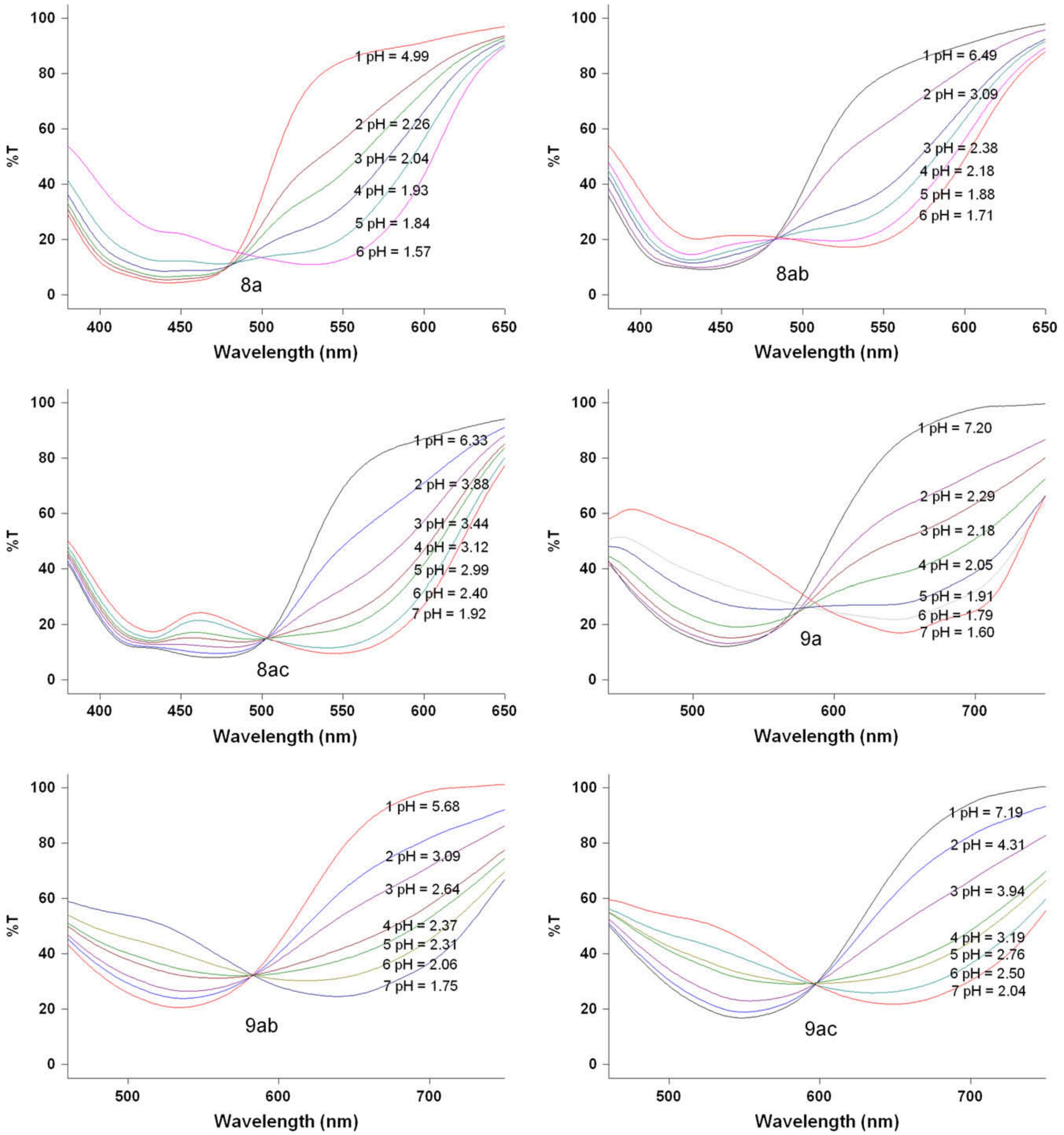


Fig. 2. Isosbestic curves of some compounds **8** and **9**.

(azulen-1-yl)-azobenzenes are produced as by-product in this synthesis probably because of the reducing character of azulenes which is capable of reducing the diazonium group of the intermediate salt.

The diazotization of 3-nitroaniline and the coupling of the corresponding reactive diazonium salts with azulenes represents the first step of the second route for the syntheses of bis aromatic diazenes **8** (Scheme 1). 3-Nitroaniline was normally diazotized with sodium nitrite in the presence of hydrochloric acid and then coupled with azulenes which were dissolved in methanol using potassium acetate as a buffer. The 3-nitrophenylazo-1-azulenes, **10**, were reduced with sodium sulfide to the corresponding amines **6** (step V in Scheme 1). Whereas the coupling occurred in good yields, only moderate yields are obtained for the reduction (Table 3). The amines **6** followed the steps I and IV for the generation of compounds **8**.

We also attempted the one-step coupling reaction of one mole of bis diazonium salt (Scheme 3) with two mole of azulenes. Unfortunately, the resulting yields were not reproducible and the reaction occurred only for the *meta* isomer but, even in this case with low yields (under 20%). Besides, together with compounds **8a** high amount of tar resulted from this reaction.

3.2. UV-vis spectra interpretation

In order to study the influence of azulene moiety on the electronic spectra for these compounds, we have compared the absorption maxima of the low energy charge transfer transitions of the synthesized compounds **8** and **9** with those of bis azo derivatives **1(*m*)** and **1(*p*)** which contain only one azulene moiety in the molecule. In the aim to establish if a solvatochromic effect can be encountered for these compounds, the absorption maxima, both in polar and non-polar media, were determined (Table 4). The visible absorption maximum for the compounds mentioned above is well defined and it has a high molar extinction coefficient (L4 band); the values for the other bands of the compounds **8** and **9** are included in Section 2.

From Table 4 it is apparent that there are not any significant differences between the absorption bands in the visible region for *meta*-substituted derivatives, **3(*m*)**, **1(*m*)** and **8a**. This means that only the presence of the new chromophore in the molecule, namely azulene, does not induce the proposed bathochromic shift. However, the magnitude of the bathochromic displacement by introduction of azulene in the molecule is very high for the *para*-derivatives. Thus, this displacement increases in series **3(*p*)**: 445 nm, **1(*p*)**: 469 nm, **9a**: 520 nm. We have already explained the difference of 24 nm observed between compounds **3(*p*)** and **1(*p*)**, therefore it remains to understand how the structure of bis azo compound **9a** determines the dramatic bathocromic shift of 52 nm as compared to compounds **1(*p*)** and of 75 nm comparing to **3(*p*)**.

The *para*-substitution contributes to an extended conjugation which involves the phenyl moiety and, it also implies the contribution of the quinoidal structures of type **D** (Scheme 4; the represented compound is **9a**) which is important in the ground state (also structure **E** can be taken into account). Supplementary to this, the presence of two azulenyl groups in the molecule favors the structure **C** with two tropylium moieties in the same molecule which fails in the case of the compounds **1(*p*)**. Additionally, the pairs of structures **B**, **D** and **E** (as an alternative to the structures described in Scheme 4 with the negative charge placed at the nitrogen near the other azulenyl group) contribute to the ground state of compounds **9**. All of these structural features contribute to the dramatic bathochromic effect encountered for these compounds.

The increase in bathochromic displacement in series **9a**, **9b** and **9c** is produced by the inductive effect of the alkyl groups that stabilize the positive tropylium charge. Generally, in all compounds, the bathochromic influence of guaiazulenyl group(s) is substantially higher than that of trimethylazulenyl(s).

It is interesting to remark that the λ_{max} in the visible region for the bis azo derivatives which contain two different azulenyl moieties (Table 5) is placed between the values observed for compounds with the same azulenyl moieties, e.g. 433/442 for **8a**, 437/446 for **8ab** and 444/450 for **8b** or 503/520 for **9a**, 528/549 for **9ac** and 545/569 for **9c**.

Comparing the values of λ_{max} for the electronic spectra recorded in *n*-hexane and in methanol, for both compounds **8** and **9**, only a small solvatochromic response was observed (Table 4). Despite the extended conjugation for the *para* isomers, the expected high solvatochromic effect was not observed. An explanation of this can be given by the strong contribution of the symmetrical structures **C** (Scheme 4) to the ground state that is only little influenced by increasing the medium polarity.

The bathochromic effect shown by compounds **1(*m*)** upon protonation exceeds the effect presented for compounds **1(*p*)**. We have explained this difference by the important contribution of the electronic structure **B** or **D** (see Scheme 4) which changes only a little upon protonation. Conversely, upon protonation, the bathocromism of compounds **9** surpasses that of compounds **8**. That seems also to confirm the important contribution of the structure **C** on the ground state of the compounds **9**. Thus, after protonation, the structure **CH**$^+$ (Scheme 4) remains with an electronic distribution with a dipolar structure comparable with either **B** or **D**, with a tropylium moiety. According to two level model [3], this structure decreases the gap between the HOMO and LUMO. In strong acidic media, obtained by addition of concentrated sulfuric acid, the second protonation take places leading to blue dyes.

Table 7 contains the color of the compounds **8** and **9** in neutral and in acidic media as well as the pK_a values.

The obtained isosbestic points (Table 6 and Figs. 1 and 2) offered the possibility to calculate the pK_a values [17] for the synthesized compounds shown in Table 7. It is difficult to establish a rule for the interdependency between the obtained pK_a values and the structure of the investigated compounds. It is possible that numerous factors contribute to the basicity of the neutral bis aromatic diazenes with two azulenyl moieties.

Table 7
Colors of the azulenic dyes in ethanol 96% and the pK_a values.

Compound	Color		pK_a
	In neutral medium	In acidic medium	
8a	Yellow	Brick red color	1.99
8b	Yellow	Brick red color	2.35
8c	Yellow-orange	Purple	2.96
8ab	Yellow-orange	Brick red color	2.50
8ac	Yellow-orange	Dark purple	3.12
8bc	Yellow	Dark violet	2.77
9a	Red-violet	Green-blue	1.91
9b	Violet	Green-blue	2.35
9c	Violet	Green-blue	3.03
9ab	Red-violet	Green-blue	2.51
9ac	Light violet	Green-blue	3.19
9bc	Violet	Light blue	2.88

4. Conclusions

The syntheses of 1,3- and 1,4-bis (azulen-1-yl-azo)benzenes, **8** and **9**, were accomplished in good yields by the coupling reaction between 3- or 4-(azulen-1-ylazo)-phenylamines and another azulene. The two azulene units in the molecules were unsubstituted or substituted with alkyl groups and were either identical or different. Both the influence of the location of the azulene unit in the molecule and of the substitution of these groups on the electronic spectra was compared with the influence of these factors on the monoazulenyl bis azo derivatives. Examination of the visible spectra of compounds **8** and **9** in solvents with different polarities showed that these compounds display only minor solvatochromism. The isosbestic points were recorded and the resulting p*K*a of their conjugated acid proved the weak basicity of bis (azulen-1-ylazo)benzenes. Our results also indicated that on using concentrated sulfuric acid double protonation of the compounds **8** and **9** takes place.

Acknowledgements

The financial support of this research, received from the Ministry of Education and Research, Romania, PN-II No. 115/2007, is gratefully acknowledged.

References

[1] Lacroix PG, Malfant I, Iftime G, Razus AC, Nakatani K, Delaire JA. Chem Eur J 2000:2599–608.
[2] Schilling ML, Katz HE, Cox DJ. J Org Chem 1988;53:5538–40.
[3] Moylan CR, McNelis BJ, Nathan LC, Morques MA, Harmstad EL, Brichler BA. J Org Chem 2004;69:8239–43.
[4] Figueiredo LJO, Koscheres C. J Org Chem 1997;62:1164–7.
[5] Burland DM, Miller RD, Walsh CA. Chem Rev 1994;94:31–85.
[6] Natanshon A, Rochon P. Chem Rev 2002;102:4136–76.
[7] Tuuttila T, Lipsonen J, Huuskonen J, Rissansen K. Dyes Pigments 2009;80:34–40.
[8] Wen G, Zhang D, Huang Y, Zhao R, Zhu L, Shuai Z, et al. J Org Chem 2007;72:6247–50.
[9] Tomasulo M, Sortino S, White AJP, Rayno FM. J Org Chem 2006;71:744–53.
[10] Constantino CJL, Aroca RF, Mendonça CR, Mello SV, Balogh DT, Zilio SC, et al. Adv Funct Mater 2001;11:65–8.
[11] Rainer H, Thomas B. Adv Mater 2001;13:1805–10.
[12] Razus AC, Birzan L, Cristea M, Tecuceanu V, Blanariu L, Enache C. Dyes Pigments 2009;80:337–42.
[13] Oudar JL. J Chem Phys 1977;67:446–57;
Oudar JL, Chemla J. J Chem Phys 1977;66:2664–8.
[14] Gerson F, Heilbronner E. Helv Chim Acta 1958;41:1444–63.
[15] Porshinev YN, Erikhov VI, Cherkashin MI. Izv Akad Nauk SSSR Ser Khim 1980:1145–7.
[16] Dahn Hv, Castelmur H. Helv Chim Acta 1953;80:638–45.
[17] The pK_a value was considered equal with pH where the absorption of the base and conjugated acid of dyes are 50% of the maximum values of bands.