Dyes and Pigments 80 (2009) 337–342

Contents lists available at ScienceDirect

Dyes and Pigments

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

Novel mono- and bis-azo dyes containing the azulen-1-yl moiety: Synthesis, characterization, electronic spectra and basicity

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ARTICLE INFO

Article history:
Received 10 June 2008
Received in revised form 24 July 2008
Accepted 11 August 2008
Available online 3 September 2008

Keywords:
Azulene
Azo
Diazene
Electronic spectra
Basicity

ABSTRACT

3- and 4-[(Azulen-1-yl)-azo]-azo-benzenes were obtained in good yields using the buffered coupling reaction between several alkyl-substituted azulenes and diazotized phenylazo-phenylamines in dichloroacetic acid. The coupling products were characterized and the recorded electronic spectra are discussed. The isosbestic points obtained by protonation enabled the determination of their pK_a values.

1. Introduction

The applications of azo derivatives in several important technical purposes explain the continuous interest for the study of synthesis and properties of this large class of compounds.

The mobility of the extended azo-azulene electronic system allots these derivatives with valuable technical utilities such as photoconductor films [1], positive dichroic dyes used in guest–host (GH) liquid crystal displays (LCDs) [2] or second-order non-linear optical chromophores [3]. The syntheses of azo-azulenes and their properties, mainly the behavior in UV–vis light, were studied by several research groups [4], as well as, by our group [5]. As a non-benzenoid aromatic hydrocarbon, azulene can couple with an active diazonium salt due to its remarkable permanent polarizability that enhances the electron density on the five-membered ring favoring the electrophilic attack at the positions 1 and/or 3. Now, we consider interesting to ascertain if the azulenic bis-azo derivatives possess more favorable optical properties and therefore, we report here the synthesis of azo-benzene derivatives, substituted with (azulene-1-yl)-azo group. Further, we compare some properties of the synthesized compounds with those of the corresponding derivatives that contain only phenyl and phenylene moieties.

2. Experimental section

2.1. Materials and instrumentations

Melting points are uncorrected: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV spectra in methanol: Varian Cary 100 spectrophotometer. ^{1}H and ^{13}C NMR: 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; COSY and HETCOR correlation experiments were used for the structure assignment. Mass spectra: Varian 1200L Quadrupole/MS/MS spectrometer by direct injection in ESI or APCI. For the column chromatography alumina [II–III Brockmann grade, 70–230 mesh ASTM] was used. Dichloromethane (DCM) was distilled over CaH_2.

2.2. Coupling reactions

(a) *In aqueous hydrochloric medium*. A mixture of phenylazo-phenylamines, **1** (2 mmol), 2.3 ml solution HCl 32% and 2 ml of water (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 **3**Rn (2 mmol), and

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0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.08.011

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 aqueous sodium hydroxide (10%). The products **4** were repeatedly extracted with DCM, the organic layers were washed with water, dried on sodium sulfate and the solvent was removed in vacuum. The residue was chromatographed on alumina with a mixture of *n*-hexane and DCM as eluent (with gradient from 2:1 to 1:2). The small eluted amount of unreacted azulene was followed by the starting amine (brown colored). Finally the desired product was eluted from the column as brown or violet colored compound depending on the isomer. Due to the incomplete separation from the starting amine, for purification the product needed sometimes a second chromatography on silica gel.

(b) *In dichloroacetic acid*. To stirred solution of phenylazo-phenylamines, **1** or **2** (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 **3**Rn (1.6 mmol) and potassium acetate 12 g in 100 ml methanol. If potassium acetate was not completely dissolved, the yields decrease significantly. The mixture was stirred at 0 °C for 1 h after which an aqueous sodium hydroxide solution (10%) was carefully added to bring the pH of the mixture to neutral. The neutrality of the reaction mixture was important for the quantitative extraction of the products and for avoiding the emulsification at the extraction. The products **4** or **5** were extracted with DCM. From this point, the work-up is similar to one that has been already reported.

2.3. Product characterization

2.3.1. 1-Azulen-1-yl-2-[3-(phenyldiazenyl)phenyl]diazene, ***4(H)***

Brown crystals, m.p. 100 °C. UV–vis (MeOH), λ_{max} (log ε): 231 (4.20), 278 (4.09), 344 (4.05), 469 (4.33); UV–vis (*n*-hexane), λ_{max} (log ε): 234 (4.16), 275 (4.07), 344 (4.06), 459 (4.34). ^{1}H NMR δ (ppm): 7.60 (t, $^3J = 9.6$ Hz, 1H, 5-H), 7.71 (d, $^3J = 4.5$ Hz, 1H, 3-H), 7.74 (t, $^3J = 9.7$ Hz, 1H, 7-H), 7.74–7.85 (m, 3H, 3″-H, 4″-H, 5″-H), 7.92 (t, $^3J = 8.0$ Hz, 1H, 5′-H), 8.02 (t, $^3J = 9.8$ Hz, 1H, 6-H), 8.24 (ddd, $^3J = 8.0$ Hz, $^4J = 2.0$ Hz, $^5J = 1.1$ Hz, 1H, 4′-H), 8.26 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 2H, 2″-H, 6″-H), 8.38 (ddd, $^3J = 7.9$ Hz, $^4J = 2.0$ Hz, $^5J = 1.1$ Hz, 1H, 6′-H), 8.60 (d, $^3J = 9.3$ Hz, 1H, 4-H), 8.63 (d, $^3J = 4.5$ Hz, 1H, 2-H), 8.80 (t, $^4J = 1.9$ Hz, $^4J = 1.1$ Hz, 1H, 2′-H), 9.66 (d, $^3J = 10.0$ Hz, 1H, 8-H). ^{13}C NMR δ (ppm): 116.3, 120.4, 123.2, 123.3, 125.4, 125.6, 127.1, 129.3, 129.7, 131.3, 135.8, 138.8, 139.3, 139.8, 144.3, 144.4, 152.9, 153.7, 155.2. MS [ESI]: 337 [M + 1]. Element Anal. Calcd for $C_{22}H_{16}N_4$: C, 78.55%; H, 4.79%; N, 16.65%. Found: C, 78.53%; H, 4.79%; N, 16.68%.

2.3.2. 1-(4,6,8-Trimethyl)azulen-1-yl-2-[3-(phenyldiazenyl)phenyl]diazene, ***4(4,6,8-Me$_3$)***

Brown crystals, m.p. 110 °C. UV–vis (MeOH), λ_{max} (log ε): 238 (4.30), 258 (4.25), 305 (4.12), 347 (4.15), 484 (4.40); UV–vis (*n*-hexane), λ_{max} (log ε): 244 (4.31), 306 (4.15), 348 (4.24), 352 (4.23), 471 (4.43). ^{1}H NMR δ (ppm): 2.58 (s, 3H, Me(6)), 2.82 (s, 3H, Me(4)), 3.35 (s, 3H, Me(8)), 7.12 (s, 1H, 5-H), 7.25 (s, 3H, 7-H), 7.33 (d, $^3J = 5.0$ Hz, 1H, 3-H), 7.53 (dt, $^3J = 7.6$ Hz, $^4J = 1.0$ Hz, 1H, 4″-H), 7.57 (dt, $^3J = 7.5$ Hz, $^4J = 1.1$ Hz, 2H, 3″-H, 5″-H), 7.62 (t, $^3J = 7.8$ Hz, 1H, 5′-H), 7.88 (br dd, $^3J = 7.8$ Hz, $^4J = 1.1$ Hz, 2H, 2″-H, 6″-H), 7.98 (d, $^3J = 8.0$ Hz, $^4J = 1.1$ Hz, 1H, 4′-H), 8.01 (d, $^3J = 8.3$ Hz, 1H, 6′-H), 8.18 (d, $^3J = 4.8$ Hz, 1H, 2-H), 8.42 (br s, 1H, 2′-H). ^{13}C NMR δ (ppm): 25.40, 28.61, 29.80, 116.7, 118.3, 122.1, 122.7, 123.1, 124.6, 128.9, 129.2, 129.4, 131.0, 131.1, 134.2, 141.0, 147.2, 147.5, 149.8, 152.8, 153.6, 155.2. MS [ESI]: 379 [M + 1]. Element Anal. Calcd for $C_{25}H_{22}N_4$: C, 79.34%; H, 5.86%; N, 14.80%. Found: C, 79.27%; H, 5.95%; N, 14.78%.

2.3.3. 1-(4,8-Dimethyl-6-tert-butyl)azulen-1-yl-2-[3-(phenyldiazenyl)phenyl]diazene, ***4(4,8-Me$_2$-6-tBu)***

Brown crystals, m.p. 72 °C. UV–vis (MeOH), λ_{max} (log ε): 235 (4.10), 308 (4.14), 348 (4.14), 486 (4.39); UV–vis (*n*-hexane), λ_{max} (log ε): 232 (4.30), 301 (4.10), 347 (4.14), 481 (4.36). ^{1}H NMR δ (ppm): 1.55 (s, 9H, Me(*t*Bu)), 2.95 (s, 3H, Me(4)), 3.52 (s, 3H, Me(8)), 7.41 (d, $^3J = 5.0$ Hz, 1H, 3-H), 7.49 (d, $^4J = 1.5$ Hz, 1H, 5-H), 7.55–7.64 (m, 3H, 3″-H, 4″-H, 5″-H), 7.66 (d, $^4J = 1.5$ Hz, 3H, 7-H), 7.69 (t, $^3J = 7.9$ Hz, 1H, 5′-H), 8.00 (br dd, $^3J = 8.0$ Hz, $^4J = 1.4$ Hz, 1H, 6′-H), 8.06–8.09 (m, 3H, 4′-H, 2″-H, 6″-H), 8.30 (d, $^3J = 4.9$ Hz, 1H, 2-H), 8.53 (t, $^4J = 1.9$ Hz, 1-H, 2′-H). ^{13}C NMR δ (ppm): 26.05, 30.42, 32.01, 38.78, 116.6, 118.1, 122.8, 123.1, 124.6, 127.8, 129.1, 129.4, 130.4, 131.1, 134.5, 141.3, 147.0, 147.2, 149.5, 152.7, 153.6, 155.3, 159.8. MS [ESI]: 421 [M + 1]. Element Anal. Calcd for $C_{28}H_{28}N_4$: C, 79.96%; H, 6.72%; N, 13.33%. Found: C, 79.93%; H, 6.80%; N, 13.27%.

2.3.4. 1-(3,8-Dimethyl-5-isopropyl)azulen-1-yl-2-[3-(phenyldiazenyl)phenyl]diazene, ***4(3,8-Me$_2$-5-iPr)***

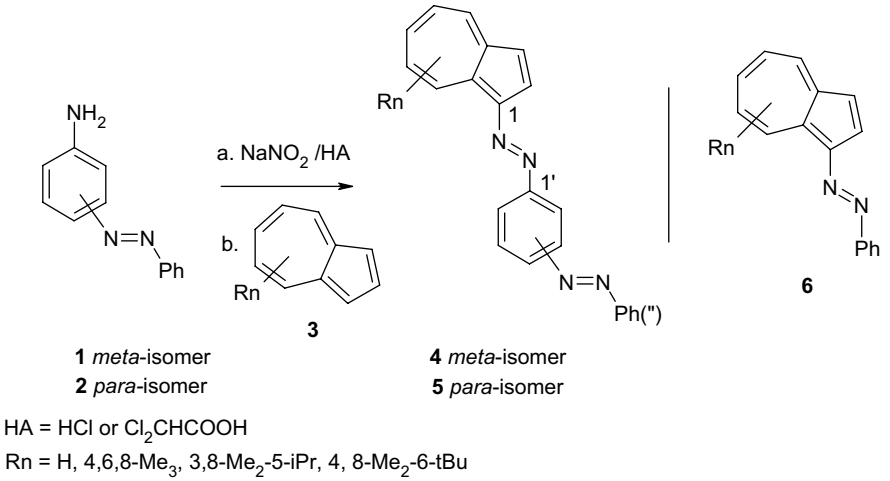
Brown crystals, m.p. 70 °C. UV–vis (MeOH), λ_{max} (log ε): 245 (4.30), 303 (4.13), 358 (4.14), 368sh (4.12), 517 (4.46); UV–vis (*n*-hexane), λ_{max} (log ε): 247 (4.40), 301 (4.24), 358 (4.31), 493 (4.57). ^{1}H NMR δ (ppm): 1.40 (d, $^3J = 6.9$ Hz, 6H, CH*Me*), 2.63 (s, 3H, Me(3)), 3.11 (heptet, 1H, $^3J = 6.9$ Hz, C*H*Me), 3.38 (s, 3H, Me(8)), 7.31 (d, $^3J = 10.8$ Hz, 1H, 7-H), 7.48–7.58 (m, 3H, 3″-H, 4″-H, 5″-H), 7.46 (d, $^3J = 10.8$ Hz, 1H, 6-H), 7.62 (dt, $^3J = 7.8$ Hz, $^4J = 0.5$ Hz, 1H, 5′-H), 7.91 (d, $^3J = 7.8$ Hz, $^4J = 2.0$ Hz, $^5J = 1.1$ Hz, 1H, 4′-H), 7.97–8.00 (m, 3H, 6′-H, 2″-H, 6″-H), 8.18 (s, 1H, 2-H), 8.16 (d, $^4J = 2.1$ Hz, 1H, 4-H), 8.41 (dt, $^4J = 1.9$ Hz, $^5J = 0.5$ Hz, 1H, 2′-H). ^{13}C NMR δ (ppm): 13.20, 24.55, 28.84, 38.23, 116.6, 123.1, 124.6, 125.7, 128.8, 129.2, 129.5, 131.2, 132.0, 135.0, 136.0, 143.0, 145.1, 145.7, 148.7, 152.8, 153.7, 155.6. MS [ESI]: 407 [M + 1]. Element Anal. Calcd for $C_{27}H_{26}N_4$: C, 79.77%; H, 6.45%; N, 13.78%. Found: C, 79.64%; H, 6.54%; N, 13.82%.

2.3.5. 1-Azulen-1-yl-2-[4-(phenyldiazenyl)phenyl]diazene, ***5(H)***

Brown crystals, m.p. 185 °C. UV–vis (MeOH), λ_{max} (log ε): 231 (4.49), 283 (4.45), 323 (4.48), 428 (4.50); UV–vis (*n*-hexane), λ_{max} (log ε): 231 (4.49), 281 (4.44), 323 (4.49), 422 (4.52). ^{1}H NMR δ (ppm): 7.34 (t, $^3J = 9.8$ Hz, 1H, 5-H), 7.44 (d, $^3J = 4.7$ Hz, 1H, 3-H), 7.51 (t, $^3J = 9.8$ Hz, 1H, 7-H), 7.52 (t, $^3J = 7.8$ Hz, 1H, 4″-H), 7.54 (t, $^3J = 7.3$ Hz, 2H, 3″-H, 5″-H), 7.75 (t, $^3J = 9.8$ Hz, 1H, 6-H), 7.96 (dd, $^3J = 7.4$ Hz, $^4J = 1.0$ Hz, 2H, 2″-H, 6″-H), 8.08 (d_{AB}, $^3J = 9.1$ Hz, 2H, 2′-H, 6′-H), 8.13 (d_{AB}, $^3J = 9.1$ Hz, 2H, 3′-H, 5′-H), 8.33 (d, $^3J = 9.2$ Hz, 1H, 4-H), 8.35 (d, $^3J = 4.8$ Hz, 1H, 2-H), 9.36 (d, $^3J = 9.8$ Hz, 1H, 8-H). ^{13}C NMR δ (ppm): 120.9, 122.9, 123.0, 124.2, 125.7, 127.5, 129.2, 129.5, 131.2, 131.4, 136.0, 139.0, 140.1, 144.4, 144.9, 152.9, 153.3, 156.0. MS [ESI]: 337 [M + 1]. Element Anal. Calcd for $C_{22}H_{16}N_4$: C, 78.55%; H, 4.79%; N, 16.65%. Found: C, 78.50%; H, 4.85%; N, 16.65%.

2.3.6. 1-(4,6,8-Trimethyl)azulen-1-yl-2-[4-(phenyldiazenyl)phenyl]diazene, ***5(4,6,8-Me$_3$)***

Brown crystals, m.p. 198 °C. UV–vis (MeOH), λ_{max} (log ε): 231 (4.34), 317 (4.31), 438 (4.30). UV–vis (*n*-hexane), λ_{max} (log ε): 231 (4.36), 317 (4.33), 433 (4.35). ^{1}H NMR δ (ppm): 2.63 (s, 3H, Me(6)), 2.86 (s, 3H, Me(4)), 3.38 (s, 3H, Me(8)), 7.04 (d, $^3J = 5.0$ Hz, 1H, 3-H), 7.20 (s, 1H, 5-H), 7.33 (s, 3H, 7-H), 7.48–7.57 (m, 3H, 3″-H, 4″-H, 5″-H), 7.96 (dd_{AB}, $^3J = 8.4$ Hz, $^4J = 1.2$ Hz, 2H, 2′-H, 6′-H), 7.99 (d_{AB}, $^3J = 9.1$ Hz, 2H, 2′-H, 6′-H), 8.07 (d_{AB}, $^3J = 8.9$ Hz, 1H, 3′-H, 5′-H), 8.18 (d, $^3J = 5.0$ Hz, 1H, 2-H). ^{13}C NMR δ (ppm): 25.30, 28.47, 29.69, 118.6, 122.0, 122.9, 123.9, 124.3, 129.7, 130.8, 131.4, 133.7, 145.4, 147.3, 148.0, 149.5, 152.8, 153.0, 155.8. MS [ESI]: 379 [M + 1]. Element Anal. Calcd for $C_{25}H_{22}N_4$: C, 79.34%; H, 5.86%; N, 14.80%. Found: C, 79.28%; H, 5.88%; N, 14.84%.



Scheme 1.

*2.3.7. 1-(4,8-Dimethyl-6-*tert*-butyl)azulen-1-yl-2-[4-(phenyldiazenyl)phenyl]diazene,* ***5(4,8-Me$_2$-6-tBu)***

Brown crystals, m.p. 230 °C. UV–vis (MeOH), λ_{max} (log ε): 232 (4.65), 316 (4.56), 439 (4.57); UV–vis (*n*-hexane), λ_{max} (log ε): 235 (4.48), 316 (4.39), 438 (4.50). ^{1}H NMR δ (ppm): 1.51 (s, 9H, Me(tBu)), 2.94 (s, 3H, Me(4)), 3.45 (s, 3H, Me(8)), 7.38 (d, ^3J = 4.8 Hz, 1H, 3-H), 7.48–7.50 (m, 3H, 3″-H, 4″-H, 5″-H), 7.50 (s, 1H, 5-H), 7.63 (s, 3H, 7-H), 7.90 (d_{AB}, ^3J = 8.7 Hz, 2H, 2″-H, 6″-H), 7.99 (d_{AB}, ^3J = 8.9 Hz, 2H, 2′-H, 6′-H), 8.05 (d_{AB}, ^3J = 8.9 Hz, 1H, 3′-H, 5′-H), 8.21 (d, ^3J = 4.9 Hz, 1H, 2-H). ^{13}C NMR δ (ppm): 26.16, 30.46, 32.07, 38.93, 118.6, 122.9, 123.1, 124.2, 124.3, 128.5, 128.9, 129.5, 130.9, 135.1, 141.9, 147.3, 148.1, 151.4, 152.0, 156.3, 160.3. MS [ESI]: 421 [M + 1]. Element Anal. Calcd for $C_{28}H_{28}N_4$: C, 79.97%; H, 6.71%; N, 13.32%. Found: C, 79.98%; H, 6.75%; N, 13.27%.

2.3.8. 1-(3,8-Dimethyl-5-isopropyl)azulen-1-yl-2-[4-(phenyldiazenyl)phenyl]diazene, ***5(3,8-Me$_2$-5-iPr)***

Brown crystals, m.p. 138 °C. UV–vis (MeOH), λ_{max} (log ε): 230 (4.46), 314 (4.43), 459 (4.38); UV–vis (*n*-hexane), λ_{max} (log ε): 233 (4.49), 246 (4.48), 309 (4.46), 452 (4.54). ^{1}H NMR δ (ppm): 1.39 (d, ^3J = 6.9 Hz, 6H, CH*Me*), 2.61 (s, 3H, Me(3)), 3.16 (heptet, 1H, ^3J = 6.8 Hz, C*H*Me), 3.96 (s, 3H, Me(8)), 7.33 (d, ^3J = 10.7 Hz, 1H, 7-H), 7.45–7.55 (m, 4H, 6-H, 3″-H, 4″-H, 5″-H), 7.95 (dd, ^3J = 9.9 Hz, ^4J = 1.2 Hz, 2H, 2″-H, 6″-H), 7.98 (d_{AB}, ^3J = 8.8 Hz, 2H, 3′-H, 5′-H), 8.06 (d_{AB}, ^3J = 8.8 Hz, 2H, 2′-H, 6′-H), 8.15 (d, ^4J = 2.2 Hz, 1H, 4-H), 8.16 (s, 1H, 2-H). ^{13}C NMR δ (ppm): 13.43, 24.76, 29.04, 38.48, 122.7, 123.2, 124.3, 125.9, 129.4, 130.1, 131.2, 132.7, 135.3, 136.4, 143.7, 146.0, 146.5, 149.2, 152.3, 153.3, 156.4. MS [ESI]: 407 [M + 1]. Element Anal. Calcd for $C_{27}H_{26}N_4$: C, 79.77%; H, 6.54%; N, 13.78%. Found: C, 79.62%; H, 6.62%; N, 13.76%.

3. Results and discussion

The synthesis of the target products started with the diazotization of readily available phenylazo-phenylamines: **1** is obtained by the condensation of *meta*-nitroaniline with nitrosobenzene followed by the product reduction with sodium sulfide [6] and **2** is commercially available. The obtained diazonium salt was then coupled with azulene or its alkyl derivatives, **3**, as shown in Scheme 1.

There are two difficulties in the diazotization process, namely the low water solubility of the phenylazo-phenylamine hydrochlorides and the reactivity of the amino group that depends on the used isomers. Thus, starting from amino derivative **1**, the reactions occurred with moderate yields (25–40% for *meta*-isomer and 60–70% for *para*) when the diazotizations were performed in aqueous hydrochloric acid. The replacement of aqueous medium with dichloroacetic acid and the use of diazonium salt in excess (25%) improved significantly the reaction yields for both amino derivatives, **1** and **2** (Table 1). The neighborhood of the amino and the azo groups in 2-phenylazo-phenylamine promoted secondary undesired reactions, preventing the formation of the normal coupling products.

3.1. The electronic spectra of bis-azo derivatives

The absorption maxima of the low energy charge transfer transitions for bis-azo derivatives **4** and **5** both in polar and non-polar media are summarized in Table 2. The visible absorption maximum is well defined and has a high molar extinction coefficient (L4 band); the values for the other bands are included in

Table 1
Yields of diazotization and coupling reactions between diazonium salts and azulenes

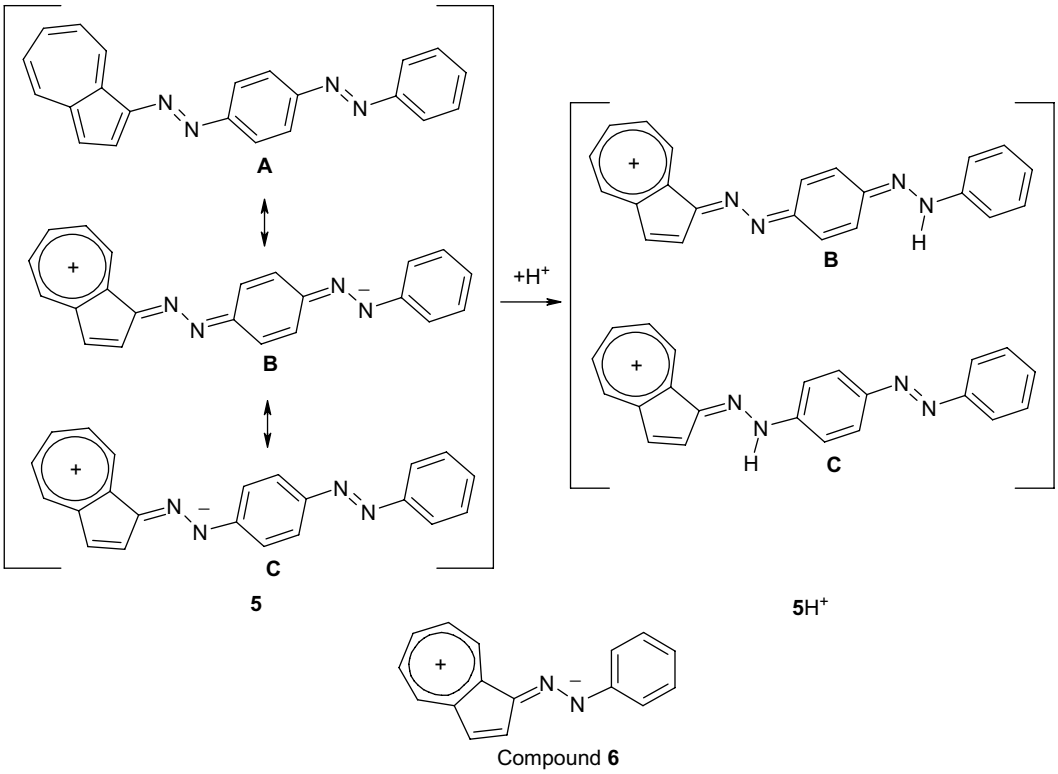
Product	Rn	Yield[a]/%	
		HCl	Cl_2CHCO_2H
4	H	40[b]	60
	4,6,8-Me_3	35	92
	3,8-Me_2-5-*i*Pr	29	90
	4,8-Me_2-6-*t*Bu	25	94
5	H	59	72
	4,6,8-Me_3	55	92
	3,8-Me_2-5-*i*Pr	69	76
	4,8-Me_2-6-*t*Bu	65	95

[a] Calculated toward azulene.
[b] The yield reaches 56% using $NaNO_2$ in excess (~25%).

Table 2
λ_{max} in visible for azo and bis-azo derivatives

Compound	Solvent	λ_{max}/nm (log ε)			
		Rn			
		H	4,6,8-Me_3	3,8-Me_2-5-*i*Pr	4,8-Me_2-6-*t*Bu
4	*n*-Hexane	422 (4.52)	433 (4.52)	452 (4.54)	438 (4.54)
	Methanol	428 (4.50)	438 (4.30)	459 (4.38)	439 (4.57)
5	*n*-Hexane	459 (4.34)	471 (4.43)	493 (4.57)	481 (4.36)
	Methanol	469 (4.33)	484 (4.40)	517 (4.46)	486 (4.39)
6	Cyclohexane	417 (4.16)	–	445 (4.52)	–
	Methanol	421 (4.72)	–	–	–

PhN = NPh, 442; *m*(PhN=N)$_2$C$_6$H$_4$, (**7**), 435 (3.16)[a] and *p*(PhN=N)$_2$C$_6$H$_4$ (**8**), 445 (3.48)[a].
[a] Spectra for **7** and **8** in ethanol [7].



Scheme 2.

Section 2. For comparison, in Table 2 are included the values of the same band for phenylazo-azulene, **6** [3,4b,4c].

The substitution of azo-benzene with phenylazo moiety in 3- or 4-position, as in compounds **7** and **8**, has a small influence on the electronic spectra; for compound **7** a hipsochromic shift of 7 nm was reported and, for both azo-benzene and compound **8** almost the same λ_{max} values can be observed.

When the phenyl moiety in (azulene-1-yl)-azo-benzenes, **6**, is substituted with a phenylazo group in position 3, as in compounds **4**, a small bathochromic shift of only 5–7 nm takes place in both solvents. However, the bathochromic effect in the case of compounds **5**, in which the substitution is in position 4, surpasses 35 nm. Two features of the last compound could explain this behavior. Generally, the azulene derivatives are good electron donors due to the possibility of the seven-membered ring to stabilize the positive charge as tropylium cation (structure **5B** and **5C** in Scheme 2). According to the well-known and widely used "two-levels model" [8], this stabilization acts very efficient on the charge transfer from the ground state of compound **5** to the excited state with dipolar structure. The quinoidal character of the structure **B** contributes also to the bathochromic shift observed for compound **5**, as compared to its isomer **4**. The general increase of the bathochromic displacement in substituted azulene is due to the inductive effect of the alkyl groups that stabilize the positive charge.

At protonation, a bathochromic effect can be signaled, both for compounds **4** and **5** as well as for **6** (Table 3). The $\Delta\lambda_{max}$ between acidic and neutral forms however, is high for compounds **4** and **6** and it is moderate for **5**. It seems that the protonation modifies only a little the electron distribution in the ground state form of compound **5** where the contribution of the structure **5B** is important. When compounds **4** and **6** are protonated the tropylium structure becomes, however, important and the difference between HOMO and LUMO decreases appreciably.

The differences in color of compounds **4** and **5** as compared to compounds **7** and **8** are determined by a multitude of bands in the visible range at ca. 600–700 nm belonging to the azulene moiety, despite their very low molar extension coefficient (azulene finger print) (Table 4). The color of compounds **4** and **5** shifts toward red in acidic medium as it occurs in general for azulene azo derivatives.

The change in color with the pH modification suggested us to investigate the acid–base equilibrium for compounds **4** and **5** in order to determine the pK_a values of their conjugated acids. The experiments were accomplished in ethanol 96% as solvent due to the good solubility of the compounds in this solvent and due to the reproducibility of the pH measurements. The obtained results are shown in

Table 3
λ_{max} in visible for azo and bis-azo derivatives, **4**–**6**, in neutral and acidic methanol (n and ac, respectively) and the isosbestic point (is)

Compound	n/nm	ac/nm	$\Delta\lambda_{max}$ (ac − n)/nm	is/nm
4 (Rn = H)	428	517	89	469
5 (Rn = H)	469	527	58	509
6 (Rn = H)	421	522	101	459

Table 4
The change in color of compounds **4** and **5** in neutral or acid methanol

Compound	Rn	The color in		Obtained pK_a
		Neutral MeOH	Acidic MeOH	
4	H	Yellow	Red	1.33
	4,6,8-Me_3	Yellow	Red	1.84
	4,8-Me_2-6-*t*Bu	Yellow	Red	1.80
	3,8-Me_2-5-*i*Pr	Yellow	Bluish red	2.73
5	H	Orange-yellow	Bluish red	1.76
	4,6,8-Me_3	Orange	Bluish red	2.95
	4,8-Me_2-6-*t*Bu	Orange	Bluish red	3.00
	3,8-Me_2-5-*i*Pr	Red	Violet	4.10
6	H	Green-yellow	Red-purple	1.78

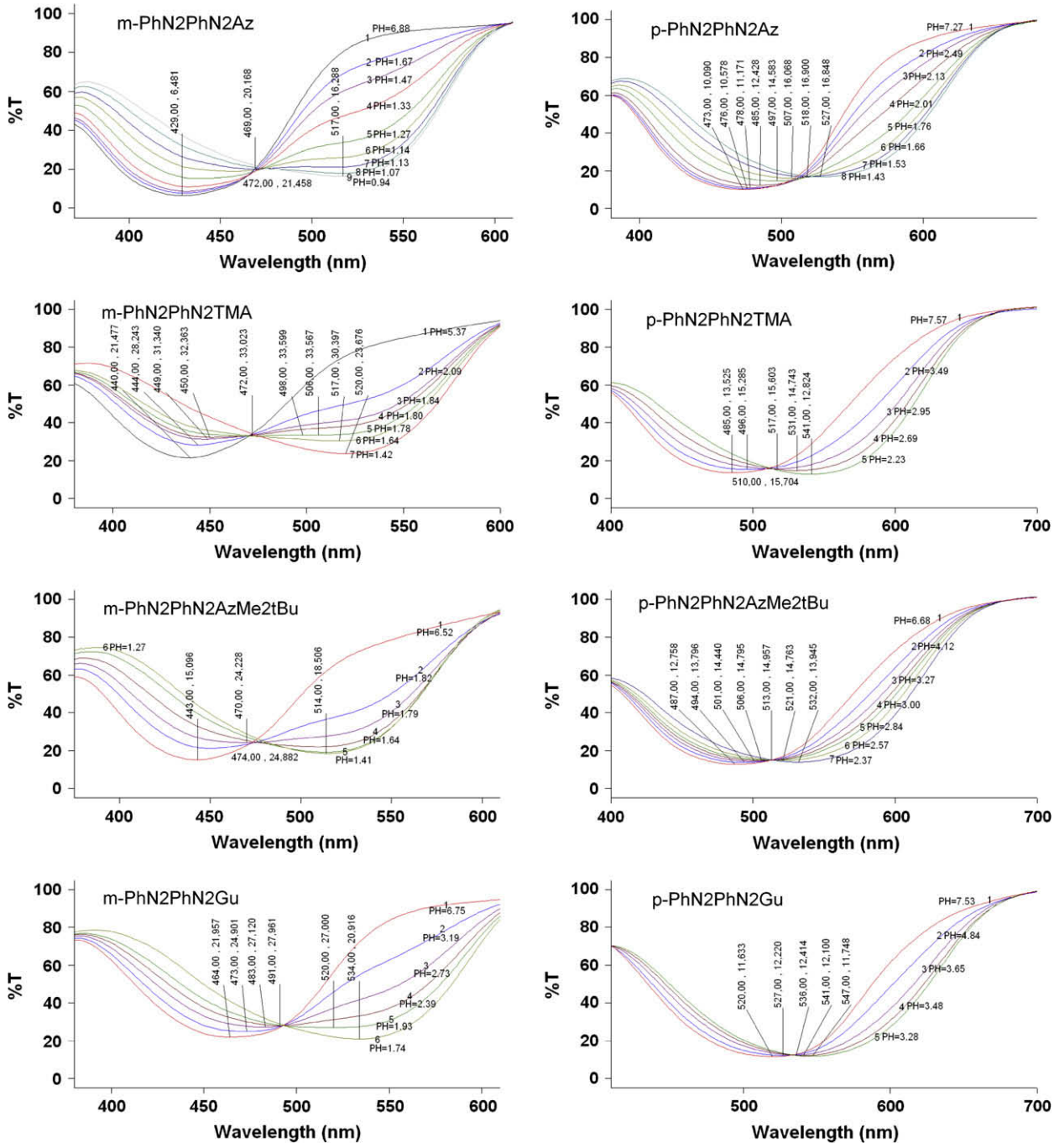


Fig. 1. The influence of the pH on the UV–vis spectra of compounds **4** and **5**.

Table 3. It is well known that the pK_a value can be considered equal to the pH value where the absorptions of the base and conjugated acid of the dyes are 50% of the maximum values of the bands. The UV–vis spectra were recorded by adding aqueous hydrochloric acid to ethanolic solutions of compounds **4** and **5** (Fig. 1).

For compounds **4**, the pK_a values are close to the value of compound **6** and increase smoothly with the azulenyl alkylation, as it is expected, due to the inductive effect. The conjugated acids of the dyes belonging to series **5** are weaker as compared with the corresponding compounds **4**. This is a consequence of the strong conjugation between the azulene moiety and other part of the molecule that increases significantly the electron densities at the nitrogen atoms increasing their basicity (see structures **5B** and **5C** in Scheme 2).

These results are in concordance with the variation of the absorption maxima in function of the azulene substituents presented in Table 2. Derivatives **4** and **5** (Rn = 3,8-Me_2-5-*i*Pr), possessing the strongest electron releasing guaiazulene moiety, present the highest values of the visible wavelength absorption, while the smallest values are observed for pattern compounds (Rn = H). The azo derivatives (Rn = 4,6,8-Me_3), containing alkyl substituents at 4, 6 and 8 positions, are placed on an intermediary position due to combination of two effects: one is the azulene peculiarity to move hypsochromic by alkyl substitution at 4,6,8-positions [9] and the second is the intensification of the push–pull conjugation generated by the inductive effect of the alkyl groups.

4. Conclusions

In summary, we have reported the synthesis of the azo dyes with two azo bonds and one azulene moiety in the molecule. The behavior in UV–vis light was analyzed comparing with the corresponding compounds only with phenyl and phenylene moieties. The acid–base properties were studied using electronic spectra. The influence of alkyl substitution on pK_a values was compared with that observed on the variation of the visible absorption maxima. The research is in progress on the compounds with two or more azulenyl moieties in bis or tris azo compounds.

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