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Extended aromatic π-electron conjugated dyes with three azo bonds and either one or two azulen-1-yl moieties in molecule. Synthesis and basicity

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Azo dyes with either one or two identical or different azulen-1-yl moieties attached to the structure -N_2-C_6H_4-N_2-C_6H_4-N_2- were prepared, the phenylene ring being either 1,3-1′,3′ or 1,4-1′,4′ disubstituted. The syntheses were accomplished in good yields via mono or bis diazotization of the corresponding anilines followed by the coupling with unsubstituted or alkyl substituted azulenes in acetic/acetate medium. The recorded electronic spectra of the synthesized compounds were analyzed and were compared with those of related compounds. The isosbestic points resulting from protonation of the azo compounds enabled pK_a values to be determined. From these pK_a values it is apparent that all studied compounds are very weak bases. The high solvatochromic property of the compounds with *para,para*-substituted phenylene groups reflects the hyperpolarizability of these compounds.

1. Introduction

The long history of azoaryl dyes, the large diversity of their possible structure, as well as the important technical applications of these chromophores has ensured continued interest in these compounds. For example, they have been investigated as NLO materials [1–9], optical limiting materials [10], molecular switches [11], NIR absorbing dyes [12] and as colorimetric sensors [13]. Their mesomorphic properties [14], solvatochromic behavior [15–17], electrochemical behavior [18] and surface-relief-grating (SRG) formation of azo polymer films [19] have also been studied. Various aromatic or heteroaromatic moieties have been attached to the azo bond. One aromatic system investigated was the azulen-1-yl group [20–22]. The interest shown in this group results from its electron donor strength. Upon attachment at the position 1 in azulene of an electron acceptor, a push–pull system is obtained stabilized by the generation of tropylium cation at the seven-membered azulene ring. This peculiarity enables the use of the azulen-1-yl moiety in electronic push–pull systems [23], as well as for other molecular structures with valuable technical purposes, such as photoconductor films [24] or in positive dichroic dyes used in guest-host (GH) liquid crystal displays (LCD's) [25]. After the investigations of the azulene-1-yl diazenes with one azo bond [26–29], we have synthesized and studied the bis azo derivative with one or two azulen-1-yl moieties in the molecule, $AzN_2C_6H_4N_2C_6H_5$ [30] and $AzN_2C_6H_4N_2Az$ [31] (phenylene ring was *meta* or *para* disubstituted and Az represents substituted or unsubstituted azulen-1-yl group). The interesting physico-chemical properties of the obtained compounds and the possibility to use them for technical purposes encouraged us to extend our investigation into azulene compounds containing poly azophenyl groups such as **1**–**4** (Scheme 1).

2. Experimental

2.1. Materials and instrumentations

Melting points are uncorrected: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV spectra in methanol and dioxane: Varian Cary 100 spectrophotometer; λ values are given in nm, while log ε has no dimension; the molar extinction, ε, is expressed in $M^{-1}\,cm^{-1}$ units. ^{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 Hz, TMS was used as internal standard in $CDCl_3$ as solvent. Mass spectra: Varian 1200L Triple Quadrupole LC/MS/MS spectrometer by direct injection in ESI. For the column chromatography silica gel 60 and alumina [II-III Brockmann grade, 70–230 mesh ASTM] were used.

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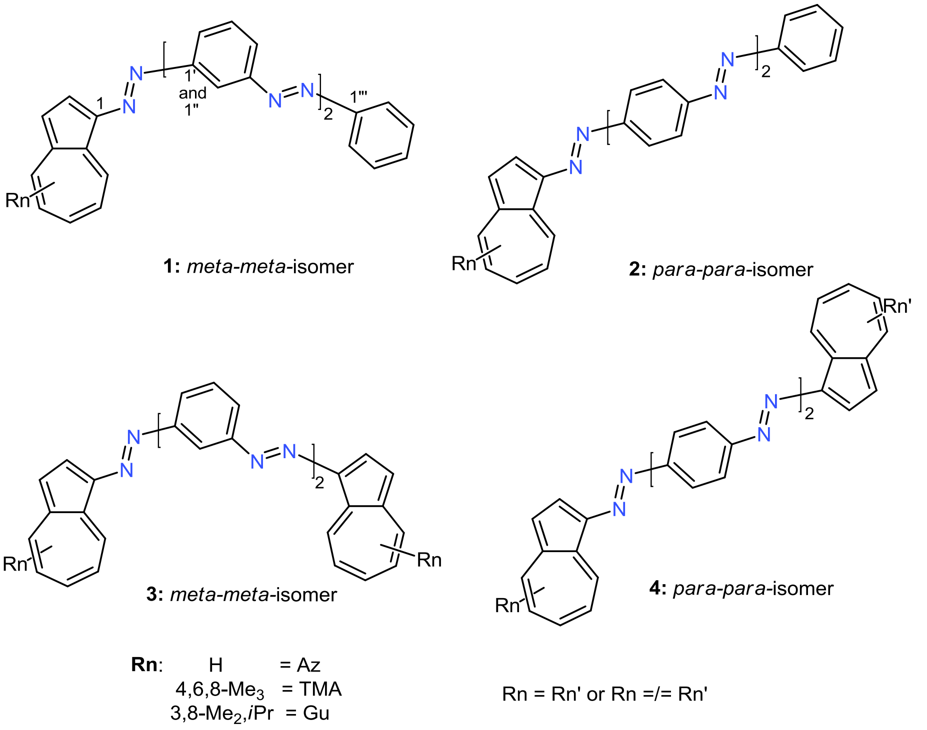


Scheme 1. The structures of the mono- and bis-azulenyl tris azo compounds.

The dichloromethane (DCM) was distilled over CaH_2. The pH values were measured with an Orion 3 Star pH-meter.

2.2. Syntheses routes

(a) *Diazotization in aqueous hydrochloric medium.* A mixture of the aromatic amines, (2 mmol), HCl (32% aq. 2.3 mL) and water (2 mL) was magnetically stirred and cooled at 0 °C (generally, the amine was incompletely dissolved). To this mixture a solution of sodium nitrite (140 mg, 2 mmol) dissolved in water (2 mL) was added slowly maintaining the temperature under 5 °C. After 10 min, the mixture was added under stirring to the solution of the azulene (2 mmol), and potassium acetate (6.7 g) in methanol (50 mL), cooled at 0 °C. The mixture was stirred at 0 °C for 1 h and then neutralized with sodium hydroxide or carbonate (10%). The solution was diluted with water (100 ml) and the products were repeatedly extracted with DCM (typically 3 × 100 mL). 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 as eluent 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. For the bis amino compounds, two equivalents of sodium nitrite, azulenes and potassium acetate were used.

(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 water (1 mL) 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 methanol (100 mL). 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 at the extraction. The products were extracted with DCM. From this point, the work-up was similar to the above reported procedure.

2.3. Reduction of nitro group

A solution of $Na_2S \cdot 9H_2O$ (9.1 g, 37.9 mmol) in water (9.5 mL) was added in small portions to a stirred solution of the nitro derivative (25 mmol) dissolved in hot ethanol (20 mL) under N_2. The reaction mixture was heated under reflux 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 as eluent mixture of *n*-hexane and DCM (with concentration gradient), the nitro derivative was first eluted and then the amine.

2.4. Determination of isosbestic points and the pK_a values

The bis aromatic diazenes containing two identical or different azulenyl moieties were dissolved in dioxane–water: 3-1, obtaining a ~3 × 10^{-5} mol/L solution. Then HCl (0.1 N, aq.) solution was added with a syringe and the pH values were recorded (4 × 25 μL, 150 μL, 250 μL, 500 μL, 1000 μL). The double protonation was realized adding concentrated sulfuric acid (1 mL). The pK_a values were considered the pH values for which the absorbance gap of the main visible band between the neutral and the protonated forms of the compound, Δ*A* represents 50% of its initial value measured in basic medium [21].

2.5. Product characterization

(*E*)-azulen-1-yl-[3-(3-phenylazophenyl)azophenyl]diazene, **1**Az, dark brown crystals, m.p. 160 °C. UV–Vis (MeOH): 229 (4.52), 285sh (4.71), 323 (4.65), 429 (4.48). ^{1}H-NMR (CDCl$_3$): 7.36 (t, $^{3}J = 9.7$ Hz, 1 H, 5-H), 7.46 (d, $^{3}J = 4.5$ Hz, 1 H, 3-H), 7.51 (t, $^{3}J = 9.9$ Hz, 1 H, 7-H), 7.78 (t, $^{3}J = 9.8$ Hz, 1 H, 6-H), 7.53–7.54 (m, 1 H, 4‴-H), 7.56 (t, $^{3}J = 6.8$ Hz, 2 H, 3‴-H, 5‴-H), 7.68 (t, $^{3}J = 7.9$ Hz, 1 H, 5″-H), 7.70 (t, $^{3}J = 7.9$ Hz, 1 H, 5′-H), 7.99 (d, $^{3}J = 7.0$ Hz, 3 H, 4′-H, 2‴-H, 6‴-H), 8.08 (d, $^{3}J = 7.8$ Hz, 1 H, 4″-H), 8.12 (d, $^{3}J = 6.6$ Hz, 1 H, 6″-H), 8.13 (d, $^{3}J = 6.9$ Hz, 1 H, 6′-H), 8.37 (d, $^{3}J = 9.0$ Hz, 1 H, 4-H), 8.38 (d, $^{3}J = 4.8$ Hz, 1 H, 2-H), 8.52 (s, 1 H, 2″-H), 8.57 (s, 1 H, 2′-H), 9.42 (d, $^{3}J = 9.9$ Hz, 1 H, 8-H). ^{13}C-NMR (CDCl$_3$): 116.0, 116.6, 120.2, 123.0, 123.1, 125.4, 125.6, 126.8, 126.9, 129.2, 129.6, 129.7, 131.3, 135.7, 138.6, 139.2, 139.6, 144.0, 144.2, 152.6, 153.4, 153.5, 155.1. MS [ESI]: 441 [M + 1]. Calcd for C$_{28}$H$_{20}$N$_6$: C, 76.35; H, 4.58; N, 19.08. Found: C, 76.34; H, 4.59; N, 19.07.

(*E*)-[3-(3-phenylazophenyl)azophenyl]-(4,6,8-trimethylazulen-1-yl)diazene, **1**TMA, dark brown crystals, m.p. 113 °C. UV–Vis (MeOH): 227(4.55), 253sh (4.71), 316 (4.79), 438 (4.58). ^{1}H-NMR: 2.64 (s, 3 H, Me$_6$), 2.87 (s, 3 H, Me$_4$), 3.41 (s, 3 H, Me$_8$), 7.20 (s, 1 H, 5-H), 7.33 (t, $^{3}J = 9.8$ Hz, 1 H, 7-H), 7.38 (d, $^{3}J = 4.9$ Hz, 1 H, 3-H), 7.53 (t, $^{3}J = 7.5$ Hz, 2 H, 3‴-H, 5‴-H), 7.55 (t, $^{3}J = 7.8$ Hz, 1 H, 4‴-H), 7.63 (t, $^{3}J = 7.9$ Hz, 1 H, 5′-H), 7.69 (t, $^{3}J = 7.9$ Hz, 1 H, 5″-H), 7.95 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 1.1$ Hz, $^{4}J = 1.8$ Hz, 1 H, 4′-H), 7.98 (dd, $^{3}J = 8.0$ Hz, $^{4}J = 1.5$ Hz, 2 H, 2‴-H, 6‴-H), 8.01 (ddd, $^{3}J = 7.9$ Hz, $^{4}J = 1.1$ Hz, $^{4}J = 1.8$ Hz, 1 H, 6′H), 8.06 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 1.1$ Hz, $^{4}J = 1.8$ Hz, 1 H, 4″-H), 8.09 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 1.1$ Hz, $^{4}J = 1.8$ Hz, 1 H, 6″-H), 8.19 (d, $^{3}J = 4.9$ Hz, 1 H, 2-H), 8.44 (t, $^{4}J = 1.9$ Hz, 1 H, 2′-H), 8.49 (t, $^{4}J = 1.9$ Hz, 1 H, 2″-H). ^{13}C-NMR (CDCl$_3$): 25.39, 28.58, 29.81, 116.7, 116.8, 118.3, 122.1, 122.8, 123.1, 124.9, 125.2, 125.5, 129.2, 129.5, 129.7, 131.1, 131.6, 133.4, 134.2, 141.0, 147.3, 147.5, 147.9, 149.9, 152.7, 153.5, 155.2. MS [ESI]: 483 [M + 1]. Calcd for C$_{31}$H$_{26}$N$_6$: C, 77.16; H, 5.43; N, 17.41. Found: C, 77.13; H, 5.47; N, 17.40.

(*E*)-(5-isopropyl-3,8-dimethylazulen-1-yl)-[3-(3-phenylazophenyl)azophenyl]diazene, **1**Gu, dark brown crystals, m.p. 212 °C. UV–Vis (MeOH): 229 (4.56), 319 (4.71), 458 (4.59). ^{1}H-NMR (CDCl$_3$): 1.38 (d, $^{3}J = 6.8$ Hz, 6 H, CH*Me*), 2.64 (s, 3 H, Me$_3$), 3.12 (hept, $^{3}J = 6.9$ Hz, 1 H, *CH*Me), 3.41 (s, 3 H, Me$_8$), 7.35 (d, $^{3}J = 10.3$ Hz, 2 H, 7-H), 7.49 (dd, $^{3}J = 10.5$ Hz, $^{4}J = 1.7$ Hz, 1 H, 6-H), 7.51–7.58 (m, 3 H, 4‴-H, 3‴-H, 5‴-H), 7.64 (t, $^{3}J = 7.8$ Hz, 1 H, 5′-H), 7.70 (t, $^{3}J = 7.8$ Hz, 1 H, 5″-H), 7.95 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 1.8$ Hz, $^{4}J = 1.0$ Hz, 1 H, 4′-H), 7.99 (dd, $^{3}J = 7.4$ Hz, $^{4}J = 1.6$ Hz, 2 H, 2‴-H, 6‴-H), 8.01 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 1.8$ Hz, $^{4}J = 1.1.$ Hz, 1 H, 6′-H), 8.07 (ddd, $^{3}J = 7.9$ Hz, $^{4}J = 1.8$ Hz, $^{4}J = 1.1$ Hz, 1 H, 4″-H), 8.11 (ddd, $^{3}J = 7.8$ Hz, $^{4}J = 1.8$ Hz, $^{4}J = 1.1$ Hz, 1 H, 6″-H), 8.18 (d, $^{4}J = 2.0$ Hz, 1 H, 4-H), 8.19 (s, 1 H, 2-H), 8.44 (t, $^{4}J = 1.8$ Hz, 1 H, 2′-H), 8.50 (t, $^{4}J = 1.8$ Hz, 1 H, 2″-H). ^{13}C-NMR (CDCl$_3$): 13.09, 24.43, 28.69, 38.19, 116.5, 116.8, 122.6, 123.1, 125.5, 125.6, 128.8, 129.2, 129.5, 129.7, 131.3, 132.0, 135.0, 135.9, 136.3, 143.0, 144.5, 145.7, 148.7, 152.6, 153.5, 155.3. MS [ESI]: 511 [M + 1]. Calcd for C$_{33}$H$_{30}$N$_6$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.56; H, 5.97; N, 16.47.

(*E*)-azulen-1-yl-[4-(4-phenylazophenyl)azophenyl]diazene, **2**Az, dark brown crystals, m.p. 217 °C. UV–Vis (MeOH): 228 (4.32), 286 (4.19), 363 (4.34), 368 (4.34), 374sh (4.32), 494 (4.52). UV–Vis (dioxane): 242 (4.26), 288 (4.18), 365 (4.34), 368 (4.34), 379sh (4.30), 494 (4.58). ^{1}H-NMR (CDCl$_3$): 7.39 (t, $^{3}J = 9.6$ Hz, 1 H, 5-H), 7.48 (d, $^{3}J = 4.5$ Hz, 1 H, 3-H), 7.52 (t, $^{3}J = 10.0$ Hz, 1 H, 7-H), 7.52 (t, $^{3}J = 6.5$ Hz, 1 H, 4‴-H), 7.55 (t, $^{3}J = 7.2$ Hz, 2 H, 3‴-H, 5‴-H), 7.80 (t, $^{3}J = 9.8$ Hz, 1 H, 6-H), 7.98 (d, $^{3}J = 7.3$ Hz, 2 H, 2‴-H, 6‴-H), 8.08 (d$_{AB}$, $^{3}J = 9.0$ Hz, 2 H, 3″-H, 5″-H), 8.10 (d$_{AB}$, $^{3}J = 9.0$ Hz, 2 H, 2″-H, 6″-H), 8.13 (d$_{AB}$, $^{3}J = 9.0$ Hz, 2 H, 3′-H, 5′-H), 8.15 (d$_{AB}$, $^{3}J = 9.0$ Hz, 2 H, 2′-H, 6′-H), 8.36 (d, $^{3}J = 4.8$ Hz, 1 H, 2-H), 8.37 (d, $^{3}J = 9.0$ Hz, 1 H, 4-H), 9.40 (d, $^{3}J = 9.9$ Hz, 1 H, 8-H). ^{13}C-NMR (CDCl$_3$): 120.7, 123.1, 123.9, 124.2, 125.4, 127.3, 129.2, 131.4, 135.7, 138.7, 139.6, 139.8, 144.6, 144.7, 152.1, 152.8, 153.7, 154.0, 155.9. MS [ESI]: 441 [M + 1]. Calcd for C$_{28}$H$_{20}$N$_6$: C, 76.35; H, 4.58; N, 19.08. Found: C, 76.30; H, 4.62; N, 19.11.

(*E*)-[4-(4-phenylazophenyl)azophenyl]-(4,6,8-trimethylazulen-1-yl)diazene, **2**TMA, dark brown crystals, m.p. 218 °C. UV–Vis (dioxane): 237 (4.59), 257 (4.47), 300sh (4.60), 364 (4.58), 368 (4.58), 382sh (4.50), 511 (4.75). ^{1}H-NMR (CDCl$_3$): 2.67 (s, 3 H, Me$_6$), 2.90 (s, 3 H, Me$_4$), 3.42 (s, 3 H, Me$_8$), 7.26 (s, 1 H, 5-H), 7.39 (s, 1 H, 7-H), 7.41 (d, $^{3}J = 4.9$ Hz, 1 H, 3-H), 7.52 (t, $^{3}J = 7.6$ Hz, 1 H, 4‴-H), 7.55 (t, $^{3}J = 7.6$ Hz, 2 H, 3‴-H, 5‴-H), 7.97 (d, $^{3}J = 7.6$ Hz, 2 H, 2‴-H, 6‴-H), 8.02 (d$_{AB}$, $^{3}J = 8.8$ Hz, 2 H, 2′-H, 6′-H), 8.10 (s, 4 H, 3′-H, 3″-H, 5″-H, 5′-H), 8.11 (d$_{AB}$, $^{3}J = 8.8$ Hz, 2 H, 2″-H, 6″-H), 8.20 (d, $^{3}J = 5.0$ Hz, 1 H, 2-H). ^{13}C-NMR (CDCl$_3$): 25.44, 28.61, 29.81, 118.8, 122.2, 122.9, 123.1, 123.2, 123.9, 124.3, 129.2, 131.4, 131.6, 133.9, 134.8, 141.6, 143.8, 147.5, 148.2, 149.1, 152.4, 152.9, 153.7, 154.2, 156.3. MS [ESI]: 483 [M + 1]. Calcd for C$_{31}$H$_{26}$N$_6$: C, 77.16; H, 5.43; N, 17.41. Found: C, 77.14; H, 5.51; N, 17.35.

(*E*)-(5-isopropyl-3,8-dimethylazulen-1-yl)-[4-(4-phenylazophenyl)azophenyl]diazene, **2**Gu, dark brown crystals, m.p. 212 °C. UV–Vis (dioxane): 245 (4.65), 303 (4.48), 368 (4.60), 388sh (4.53), 540 (4.82). ^{1}H-NMR (CDCl$_3$): 1.39 (d, $^{3}J = 6.9$ Hz, 6 H, CH*Me*), 2.61 (s, 3 H, Me$_3$), 3.10 (hept, $^{3}J = 6.9$ Hz, 1 H, *CH*Me), 3.37 (s, 3 H, Me$_8$), 7.35 (d, $^{3}J = 10.7$ Hz, 2 H, 7-H), 7.48 (dd, $^{3}J = 10.5$ Hz, 2 H, 6-H), 7.51 (t, $^{3}J = 7.6$ Hz, 1 H, 4‴-H), 7.54 (t, $^{3}J = 7.6$ Hz, 2 H, 3‴-H, 5‴-H), 7.94 (d, $^{3}J = 8.2$ Hz, 2 H, 2′-H, 6′-H), 7.98 (d, $^{3}J = 8.3$ Hz, 2 H, 2‴-H, 6‴-H), 8.08 (s, 4 H, 2″-H, 3″-H, 5″-H, 6″-H), 8.09 (d, $^{3}J = 8.8$ Hz, 3′-H, 5′-H), 8.15 (s, 1 H, 4-H), 8.16 (s, 1 H, 2-H). ^{13}C-NMR (CDCl$_3$): 13.09, 24.43, 28.69, 38.19, 122.9, 123.1, 123.8, 124.2, 125.6, 129.2, 129.3, 131.3, 132.5, 135.0, 136.1, 136.4, 143.6, 145.9, 146.4, 148.9, 152.1, 152.8, 153.7, 154.1, 156.4. MS [ESI]: 511 [M + 1]. Calcd for C$_{33}$H$_{30}$N$_6$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.58; H, 5.96; N, 16.46.

(*E*)-azulen-1-yl-[3-(3-azulen-1-ylazophenyl)azophenyl] diazene, **3**Az, dark green crystals, m.p. 171 °C. UV–Vis (dioxane): 234 (5.15), 271 (4.95), 336 (4.68), 434 (4.98). ^{1}H-NMR (CDCl$_3$): 7.42 (t, $^{3}J = 9.8$ Hz, 2 H, 5-H), 7.45 (d, $^{3}J = 4.5$ Hz, 2 H, 3-H), 7.56 (t, $^{3}J = 9.7$ Hz, 2 H, 7-H), 7.66 (t, $^{3}J = 8.0$ Hz, 2 H, 5′-H), 7.83 (t, $^{3}J = 9.9$ Hz, 2 H, 6-H), 8.20 (d, $^{3}J = 8.0$ Hz, 2 H, 4′-H), 8.26 (d, $^{3}J = 7.8$ Hz, 2 H, 6′-H), 8.32 (d, $^{3}J = 4.5$ Hz, 2 H, 2-H), 8.38 (d, $^{3}J = 9.3$ Hz, 2 H, 4-H), 8.78 (s, 2 H, 2′-H), 9.38 (d, $^{3}J = 9.9$ Hz, 2 H, 8-H). ^{13}C-NMR (CDCl$_3$): 115.6, 120.8, 122.9, 125.4, 127.6, 127.7, 129.1, 129.7, 135.7, 138.9, 140.0, 143.9, 144.8, 149.2, 154.8. MS [ESI]: 491 [M + 1]. Calcd. for C$_{32}$H$_{22}$N$_6$: C, 78.35; H, 4.52; N, 17.13. Found: C, 78.34; H, 4.56; N, 17.10.

(*E*)-(4,6,8-trimethylazulen-1-yl)-[3-[3-(4,6,8-trimethylazulen-1-yl)azophenyl] azophenyl]diazene, **3**TMA, dark green crystals, m.p. 234 °C. UV–Vis (dioxane): 233 (5.40), 250sh (4.76), 307 (4.58), 312 (4.58), 321 (4.58), 438 (4.71). ^{1}H-NMR (CDCl$_3$): 2.67 (s, 6 H, Me$_6$), 2.90 (s, 6 H, Me$_4$), 3.45 (s, 6 H, Me$_8$), 7.23 (s, 2 H, 5-H), 7.37 (s, 2 H, 7-H), 7.41 (d, $^{3}J = 4.8$ Hz, 2 H, 3-H), 7.65 (t, $^{3}J = 7.8$ Hz, 2 H, 5′-H), 7.97 (d, $^{3}J = 7.6$ Hz, 2 H, 4′-H), 8.02 (d, $^{3}J = 7.8$ Hz, 2 H, 6′-H), 8.21 (d, $^{3}J = 4.8$ Hz, 2 H, 2-H), 8.46 (bs, 2 H, 3′-H). ^{13}C-NMR (CDCl$_3$): 25.43, 28.59, 29.76, 116.3, 118.8, 122.2, 125.5, 125.7, 129.6, 131.9, 134.3, 135.1, 141.8, 147.5, 147.7, 148.4, 149.2, 150.0, 155.1. MS [ESI]: 575 [M + 1]. Calcd for C$_{38}$H$_{34}$N$_6$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.41; H, 5.98; N, 14.61.

(*E*)-(5-isopropyl-3,8-dimethylazulen-1-yl)-[3-[3-(5-isopropyl-3,8-dimethylazulen-1-yl)azophenyl]azophenyl]diazene, **3**Gu, dark green crystals, m.p. 335 °C. UV–Vis (dioxane): 232 (5.04), 246 (4.93), 248 (4.93), 251 (4.93), 295 (4.76), 339 (4.66), 341 (4.66), 458 (4.84). ^{1}H-NMR (CDCl$_3$): 1.41 (d, $^{3}J = 6.9$ Hz, 12 H, CH*Me*), 2.64 (s, 6 H, Me$_3$), 3.12 (hept, $^{3}J = 6.9$ Hz, 2 H, *CH*Me), 3.42 (s, 3 H, Me$_8$), 7.35 (d, $^{3}J = 10.7$ Hz, 2 H, 7-H), 7.48 (dd, $^{3}J = 10.5$ Hz, $^{4}J = 1.8$ Hz, 2 H, 6-H), 7.64 (t, $^{3}J = 7.8$ Hz, 2 H, 5′-H), 7.95 (bd, $^{3}J = 7.8$ Hz, 2 H, 4′-H), 8.00 (bd, $^{3}J = 7.8$ Hz, 2 H, 6′-H), 8.17 (d, $^{4}J = 1.9$ Hz, 2 H, 4-H), 8.20 (s, 2 H, 2-H), 8.45 (t, $^{4}J = 1.8$ Hz, 2 H, 2′-H). ^{13}C-NMR (CDCl$_3$): 13.11, 24.47, 28.80, 38.15, 116.3, 122.6, 124.9, 125.6, 128.7, 129.4, 131.9, 135.0, 135.7, 135.9, 142.9, 145.0, 145.6, 148.7, 153.6, 155.3. MS [ESI]: 631 [M + 1]. Calcd for C$_{42}$H$_{42}$N$_6$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.98; H, 6.72; N, 13.30.

(*E*)-azulen-1-yl-[4-(4-azulen-1-ylazophenyl)azophenyl]diazene, **4**Az, dark green crystals, m.p. 212 °C. UV–Vis (dioxane): 230 (4.88), 259 (4.67), 277 (4.64), 332 (4.29), 518 (4.73). ^{1}H-NMR (CDCl$_3$): 7.38 (t,

$^3J = 9.6$ Hz, 2 H, 5-H), 7.47 (d, $^3J = 4.4$ Hz, 2 H, 3-H), 7.52 (t, $^3J = 9.7$ Hz, 2 H, 7-H), 7.80 (t, $^3J = 9.8$ Hz, 2 H, 6-H), 8.12 (d$_{AB}$, $^3J = 9.2$ Hz, 4 H, 3′-H, 5′-H), 8.15 (d$_{AB}$, $^3J = 9.2$ Hz, 4 H, 2′-H, 6′-H), 8.36 (d, $^3J = 9.3$ Hz, 2 H, 4-H), 8.37 (d, $^3J = 4.8$ Hz, 2 H, 2-H), 9.40 (d, $^3J = 9.8$ Hz, 2 H, 8-H). ^{13}C-NMR ($CDCl_3$): 120.6, 123.0, 124.0, 125.3, 127.1, 135.7, 138.6, 139.5, 139.7, 144.5, 144.6, 152.9, 155.7. MS [ESI]: 491 [M + 1]. Calcd. for: $C_{32}H_{22}N_6$: C, 78.35; H, 4.52; N, 17.13. Found: C, 78.32; H, 4.57; N, 17.11.

(*E*)-(4,6,8-trimethylazulen-1-yl)-[4-[4-(4,6,8-trimethylazulen-1-yl)azophenyl]azophenyl]diazene, **4**TMA, brown crystals, m.p. 264 °C. UV–Vis (dioxane): 241 (4.96), 301 (4.87), 332sh (4.67), 514(4.96). ^{1}H-NMR ($CDCl_3$): 2.68 (s, 6 H, Me$_6$), 2.90 (s, 6 H, Me$_4$), 3.43 (s, 6 H, Me$_8$), 7.23 (s, 2 H, 5-H), 7.36 (s, 2 H, 7-H), 7.39 (d, $^3J = 5.6$ Hz, 2 H, 3-H), 8.01 (d, $^3J = 8.7$ Hz, 4 H, 2′-H, 6′-H), 8.09 (d, $^3J = 8.4$ Hz, 4 H, 3′-H, 5′-H), 8.20 (d, $^3J = 5.6$ Hz, 2 H, 2-H). MS [ESI]: 575 [M + 1]. Calcd for $C_{38}H_{34}N_6$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.43; H, 5.99; N, 14.58.

(*E*)-(5-isopropyl-3,8-dimethylazulen-1-yl)-[4-[4-(5-isopropyl-3,8-dimethylazulen-1-yl) azophenyl]azophenyl]diazene, **4**Gu, dark green crystals, m.p. 284 °C. UV–Vis (dioxane): 232 (5.13), 256 (4.99), 287sh (4.78), 337 (4.40), 342 (4.40), 345 (4.40), 353 (4.36), 359 (4.35), 365 (4.31), 565 (4.95). ^{1}H-NMR ($CDCl_3$): 1.40 (d, $^3J = 6.9$ Hz, 12 H, CH*Me*), 2.63 (s, 6 H, Me$_3$), 3.12 (hept, $^3J = 6.9$ Hz, 2 H, *CH*Me), 3.38 (s, 3 H, Me$_8$), 7.35 (d, $^3J = 10.8$ Hz, 2 H, 7-H), 7.49 (dd, $^3J = 10.6$ Hz, $^4J = 1.5$ Hz, 2 H, 6-H), 7.99 (d$_{AB}$, $^3J = 8.7$ Hz, 4 H, 2′-H, 6′-H), 8.08 (d$_{AB}$, $^3J = 8.7$ Hz, 4 H, 3′-H, 5′-H), 8.16 (d, $^4J = 1.7$ Hz, 2 H, 4-H), 8.18 (s, 2 H, 2-H). ^{13}C-NMR ($CDCl_3$): 13.09, 24.43, 28.69, 38.19, 122.9, 124.0, 125.6, 129.2, 132.3, 135.0, 136.1, 136.2, 143.4, 145.9, 146.0, 148.9, 152.4, 156.1. MS [ESI]: 631 [M + 1]. Calcd for $C_{42}H_{42}N_6$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.95; H, 6.73; N, 13.32.

(*E*)-azulen-1-yl-[4-[4-(4,6,8-trimethylazulen-1-yl)azophenyl] azophenyl]diazene, **4**AzTMA, dark green crystals, m.p. 235 °C. UV–Vis (dioxane): 244 (4.56), 262 (4.51), 280sh (4.47), 334 (4.30), 534 (4.79). ^{1}H-NMR ($CDCl_3$): 2.67 (s, 3 H, Me$_{6'}$), 2.90 (s, 3 H, Me$_{4'}$), 3.46 (s, 3 H, Me$_{8'}$), 7.23 (s, 2 H, 5′-H), 7.36 (s, 2 H, 7′-H), 7.36 (t, $^3J = 9.9$ Hz, 1 H, 5-H), 7.41 (d, $^3J = 4.8$ Hz, 1 H, 3′-H), 7.44 (d, $^3J = 4.6$ Hz, 1 H, 3-H), 7.49 (t, $^3J = 9.7$ Hz, 1 H, 7-H), 7.77 (t, $^3J = 9.8$ Hz, 1 H, 6-H), 7.97 (d$_{AB}$, $^3J = 8.7$ Hz, 2 H, 2‴-H, 6‴-H; phenylene attached to -N$_2$-TMA), 8.06 (d$_{AB}$, $^3J = 9.3$ Hz, 4 H, 3″-H, 5″-H, 3‴-H, 5‴-H), 8.10 (d$_{AB}$, $^3J = 8.7$ Hz, 2 H, 2″-H, 6″-H; phenylene attached to -N$_2$-Az), 8.14 (d, $^3J = 4.6$ Hz, 1 H, 2′-H), 8.32 (d, $^3J = 4.7$ Hz, 1 H, 2-H), 8.34 (d, $^3J = 9.4$ Hz, 1 H, 4-H), 9.35 (d, $^3J = 9.7$ Hz, 1 H, 8-H). ^{13}C-NMR ($CDCl_3$): 25.37, 28.56, 29.74, 118.7, 120.6, 123.0, 123.9, 124.0, 125.2, 125.4, 127.1, 131.4, 133.7, 134.6, 135.6, 138.6, 139.4, 139.6, 141.4, 144.5, 144.6, 147.4, 148.2, 148.1, 150.0, 152.5, 152.9, 155.6, 155.9. MS [ESI]: 533 [M + 1]. Calcd. for $C_{35}H_{28}N_6$: C, 78.92; H, 5.30; N, 15.78. Found: C, 78.89; H, 5.34; N, 15.77.

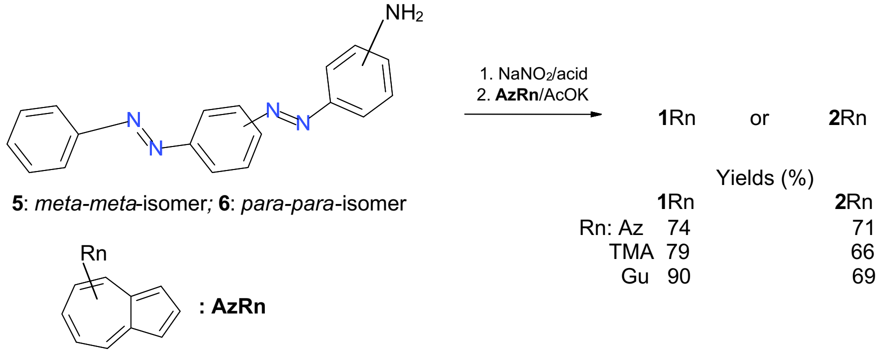
(*E*)-azulen-1-yl-[4-[4-(5-isopropyl-3,8-dimethylazulen-1-yl) azophenyl] azophenyl]diazene, **4**AzGu, dark green crystals, m.p. 189 °C. UV–Vis (dioxane): 244 (4.56), 262 (4.51), 280sh (4.47), 334 (4.30), 534 (4.79). ^{1}H-NMR ($CDCl_3$): 1.39 (d, $^3J = 6.9$ Hz, 6 H, MeCH), 2.62 (s, 3 H, Me$_{3'}$), 3.09 (hept, $^3J = 6.9$ Hz, 1 H, *C*HMe), 3.37 (s, 3 H, Me$_{8'}$), 7.35 (d, $^3J = 10.2$ Hz, 1 H, 7′-H), 7.36 (t, $^3J = 9.8$ Hz, 1 H, 5-H), 7.46 (d, $^3J = 4.5$ Hz, 1 H, 3-H), 7.50 (t, $^3J = 9.8$ Hz, 1 H, 7-H), 7.51 (d, $^3J = 10.2$ Hz, 1 H, 6′-H), 7.77 (t, $^3J = 9.9$ Hz, 1 H, 6-H), 7.99 (d$_{AB}$, $^3J = 8.7$ Hz, 2 H, 2‴-H, 6‴-H), 8.09 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 3‴-H, 5‴-H; phenylene attached to -N$_2$-Gu), 8.09 (d$_{AB}$, $^3J = 9.2$ Hz, 2 H, 3″-H, 5″-H; phenylene attached to -N$_2$-Az), 8.13 (d$_{AB}$, $^3J = 9.0$ Hz, 2 H, 2″-H, 6″-H), 8.16 (d, $^4J = 1.8$ Hz, 1 H, 4′-H), 8.17 (s, 1 H, 2′-H), 8.34 (d, $^3J = 9.7$ Hz, 1 H, 4-H), 8.36 (d, $^3J = 4.2$ Hz, 1 H, 2-H), 9.38 (d, $^3J = 9.9$ Hz, 2 H, 8-H). ^{13}C-NMR ($CDCl_3$): 13.09, 24.42, 28.70, 38.17, 120.5, 122.8, 123.1, 123.9, 124.1, 125.4, 125.6, 127.1, 129.2, 132.4, 135.0, 135.7, 136.1, 136.2, 138.6, 139.4, 139.7, 143.5, 144.5, 144.6, 145.9, 146.2, 148.9, 152.3, 153.0, 155.6, 156.1. MS [ESI]: 561 [M + 1]. Calcd. for $C_{37}H_{32}N_6$: C, 79.26; H, 5.75; N, 14.99. Found: C, 79.24; H, 5.78; N, 14.98.

(*E*)-[4-(5-isopropyl-3,8-dimethylazulen-1-yl)]-[4-[4-(4,6,8-trimethylazulen-1-yl) azophenyl]azophenyl]diazene, **4**TMAGu, dark green crystals, m.p. 320 °C. UV–Vis (dioxane): 241 (4.35), 301(4.11), 335 (3.98), 337 (3.98), 341 (3.98), 347 (3.98), 353 (3.95), 558 (4.49). ^{1}H-NMR ($CDCl_3$): 1.40 (d, $^3J = 6.9$ Hz, 6 H, CH*Me*), 2.63 (s, 3 H, Me$_{3'}$), 2.68 (s, 3 H, Me$_6$), 2.90 (s, 3 H, Me$_4$), 3.12 (hept, $^3J = 6.9$ Hz, 1 H, *CH*Me), 3.39 (s, 3 H, Me$_{8'}$), 3.49 (s, 3 H, Me$_8$), 7.23 (s, 1 H, 5-H), 7.37 (d, $^3J = 10.6$ Hz, 1 H, 7′-H), 7.38 (s, 1 H, 7-H), 7.41 (d, $^3J = 4.9$ Hz, 1 H, 3-H), 7.50 (dd, $^3J = 10.6$ Hz, $^4J = 1.4$ Hz, 2 H, 6′-H), 7.99 (d$_{AB}$, $^3J = 8.4$ Hz, 2 H, 2‴-H, 6‴-H; phenylene attached to -N$_2$-Gu), 8.01 (d$_{AB}$, $^3J = 8.5$ Hz, 2 H, 2″-H, 6″-H; phenylene attached to -N$_2$-TMA), 8.09 (d$_{AB}$, $^3J = 8.3$ Hz, 4 H, 3″-H, 5″-H, 3‴-H, 5‴-H), 8.17 (d, $^4J = 1.4$ Hz, 2 H, 4′-H), 8.18 (s, 2 H, 2′-H), 8.20 (d, $^3J = 5.0$ Hz, 1 H, 2-H). ^{13}C-NMR ($CDCl_3$): 13.09, 24.43, 25.44, 28.69, 28.60, 29.77, 38.19, 118.6, 122.9, 123.0, 123.9, 124.0, 125.4, 125.6, 129.1, 131.3, 132.1, 133.6, 134.6, 134.9, 136.0, 141.3, 143.4, 146.0, 147.3, 148.0, 148.2, 148.9, 150.0, 152.3, 152.5, 155.8. MS [ESI]: 603 [M + 1]. Calcd. for $C_{40}H_{38}N_6$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.68; H, 6.38; N, 13.94.

(*E*)-azulen-1-yl-[3-(3-azulen-1-ylazophenyl)azophenyl] diazene N-oxide, or (*Z*)-(4-azulen-1-ylazophenyl)-(4-azulen-1-ylazophenyl)imino-oxido-ammonium (IUPAC), **10**Az, brown crystals, m.p. 238 °C. UV–Vis (dioxane): 232 (5.16), 280 (5.01), 327 (4.86), 430 (5.00). ^{1}H-NMR ($CDCl_3$): 7.35 (t, $^3J = 9.7$ Hz, 1 H, 5′-H), 7.38 (t, $^3J = 9.7$ Hz, 1 H, 5-H), 7.46 (d, $^3J = 4.6$ Hz, 1 H, 3′-H), 7.47 (d, $^3J = 4.6$ Hz, 1 H, 3-H), 7.49 (t, $^3J = 9.7$ Hz, 1 H, 7′-H), 7.52 (t, $^3J = 9.7$ Hz, 1 H, 7-H), 7.65 (t, $^3J = 7.8$ Hz, 1 H, 5″-H), 7.67 (t, $^3J = 7.8$ Hz, 1 H, 5‴-H), 7.76 (t, $^3J = 10.0$ Hz, 1 H, 6′-H), 7.79 (t, $^3J = 10.0$ Hz, 1 H, 6-H), 8.06 (d, $^3J = 8.0$ Hz, 1 H, 4″-H), 8.19 (d, $^3J = 8.0$ Hz, 1 H, 4‴-H), 8.28 (d, $^3J = 8.0$ Hz, 1 H, 6″-H), 8.35 (d, $^3J = 8.0$ Hz, 1 H, 6‴-H), 8.36 (d, $^3J = 9.3$ Hz, 1 H, 4′-H), 8.37 (d, $^3J = 9.3$ Hz, 1 H, 4-H), 8.37 (d, $^3J = 4.2$ Hz, 2 H, 2-H, 2′-H), 8.79 (t, $^4J = 1.7$ Hz, 1 H, 2″-H), 8.94 (d, $^4J = 1.9$ Hz, 1 H, 2‴-H), 9.41 (d, $^3J = 9.9$ Hz, 2 H, 8-H, 8′-H). ^{13}C-NMR ($CDCl_3$): 115.4, 119.0, 120.2, 120.5, 122.4, 123.9, 125.4, 125.9, 126.1, 126.8, 126.9, 127.2, 127.3, 129.1, 129.3, 135.7, 138.6, 138.7, 139.6, 139.8, 144.0, 144.5, 144.9, 149.4, 154.7. MS [ESI]: 507 [M + 1]. Calcd. for $C_{32}H_{22}N_6O$: C, 75.87; H, 4.38; N, 16.59. Found: C, 75.79; H, 4.42; N, 16.62.

(*E*)-(4,6,8-trimethylazulen-1-yl)-[3-[3-(4,6,8-trimethylazulen-1-yl)azophenyl] azophenyl]diazene *N*-oxide or **(*Z*)-oxido-[4-(4,6,8-trimethylazulen-1-yl)azophenyl]-[4-(4,6,8-trimethylazulen-1-yl) azophenyl]imino-ammonium** (IUPAC), **10**TMA, green crystals, m.p. 192 °C. UV–Vis (dioxane): 232 (5.15), 250 (4.99), 306 (4.60), 315 (4.58), 445 (4.65). ^{1}H-NMR ($CDCl_3$): 2.67 (s, 6 H, Me$_6$ and Me$_{6'}$), 2.89 (s, 6 H, Me$_4$ and Me$_{4'}$), 3.43 (s, 6 H, Me$_8$ and Me$_{8'}$), 7.23 (s, 1 H, 5-H), 7.26 (s, 2 H, 5′-H), 7.35 (s, 1 H, 7-H), 7.38 (s, 1 H, 7′-H), 7.39 (d, $^3J = 4.7$ Hz, 1 H, 3-H), 7.40 (d, $^3J = 4.7$ Hz, 1 H, 3′-H), 7.61 (t, $^3J = 7.8$ Hz, 1 H, 5″-H), 7.63 (t, $^3J = 7.8$ Hz, 1 H, 5‴-H), 7.95 (d, $^3J = 8.0$ Hz, 1 H, 4″-H), 8.07 (d, $^3J = 7.7$ Hz, 1 H, 4‴-H), 8.19 (d, $^3J = 7.9$ Hz, 1 H, 6″-H), 8.20 (d, $^3J = 4.7$ Hz, 2 H, 2-H, 2′-H), 8.32 (d, $^3J = 7.6$ Hz, 1 H, 6‴), 8.71 (s, 1 H, 2″-H), 8.83 (s, 1 H, 2‴-H). ^{13}C-NMR ($CDCl_3$): 25.33, 25.36, 28.53, 29.77, 29.82, 115.4, 119.0, 118.2, 118.5, 121.7, 123.4, 122.1, 122.2, 125.4, 125.7, 130.8, 131.4, 133.3, 133.8, 129.0, 129.1, 134.8, 141.6, 144.8, 147.4, 147.5, 148.1, 149.3, 149.4, 150.0, 154.8. MS [ESI]: 591 [M + 1]. Calcd for $C_{38}H_{34}N_6O$: C, 77.26; H, 5.80; N, 14.23. Found: C, 77.22; H, 5.85; N, 14.26.

(*E*)-(5-isopropyl-3,8-dimethylazulen-1-yl)-[3-[3-(5-isopropyl-3,8-dimethylazulen-1-yl) azophenyl]azophenyl]diazene N-oxide, or (Z)-[4-(5-isopropyl-3,8-dimethylazulen-1-yl)azophenyl]-[4-(5-isopropyl-3,8-dimethylazulen-1-yl) azophenyl]imino-oxido-ammonium (IUPAC), **10**Gu, brown crystals, dec. without melting. UV–Vis (dioxane): 234 (4.97), 252sh (4.93), 291 (4.60), 298 (4.60), 351 (4.49), 467 (4.88). ^{1}H-NMR ($CDCl_3$): 1.41 (d, $^3J = 6.9$ Hz, 12 H, CH*Me*), 2.63 (s, 6 H, Me$_3$ and Me$_{3'}$), 3.11 (hept, $^3J = 6.9$ Hz, 1 H, *CH*Me), 3.12 (hept, $^3J = 6.9$ Hz, 1 H, *CH*Me′), 3.41 (s, 6 H, Me$_8$ and Me$_{8'}$), 7.32 (d, $^3J = 10.7$ Hz, 1 H, 7-H), 7.37 (d, $^3J = 10.7$ Hz, 1 H, 7′-H),



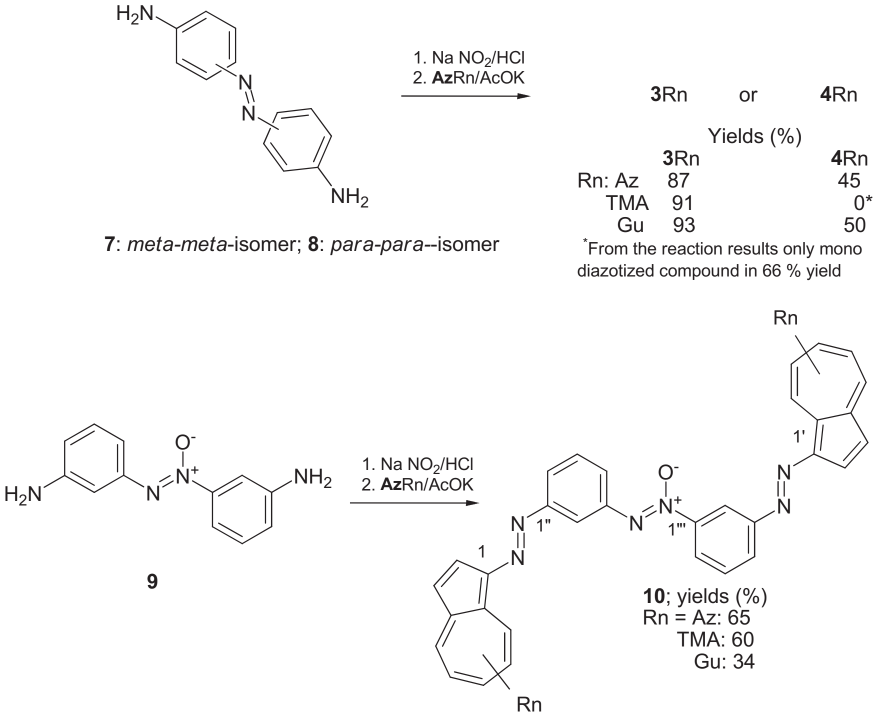
Scheme 2. Azo coupling of diazotized amines, **5** and **6**.

7.48 (d, ^3J = 10.6 Hz, 1 H, 6-H), 7.50 (d, ^3J = 10.6 Hz, 1 H, 6′-H), 7.60 (t, ^3J = 7.9 Hz, 1 H, 5″-H), 7.62 (t, ^3J = 8.0 Hz, 1 H, 5‴-H), 7.92 (d, ^3J = 8.1 Hz, 2 H, 4″-H), 8.05 (d, ^3J = 7.7 Hz, 2 H, 4‴-H), 8.14–8.20 (m, 5 H, 2-H, 2′-H, 4-H, 4′-H, 6″-H), 8.30 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1 H, 6‴-H), 8.70 (s, 1 H, 2″-H), 8.82 (t, ^4J = 1.9 Hz, 1 H, 2‴-H). ^{13}C-NMR ($CDCl_3$): 13.07, 24.47, 28.74, 28.80, 38.13, 38.16, 115.6, 119.1, 121.5, 123.4, 125.2, 125.5, 125.6, 128.5, 128.6, 129.0, 129.1, 131.8, 132.4, 134.9, 135.0, 135.7, 135.8, 136.0, 136.3, 142.8, 143.3, 144.9, 145.0, 145.4, 146.1, 148.8, 149.4, 153.6, 154.8, 155.0. MS [ESI]: 647 [M + 1]. Calcd. for $C_{42}H_{42}N_6O$: C, 77.99; H, 6.54; N, 12.99. Found: C, 78.02; H, 6.60; N, 12.95.

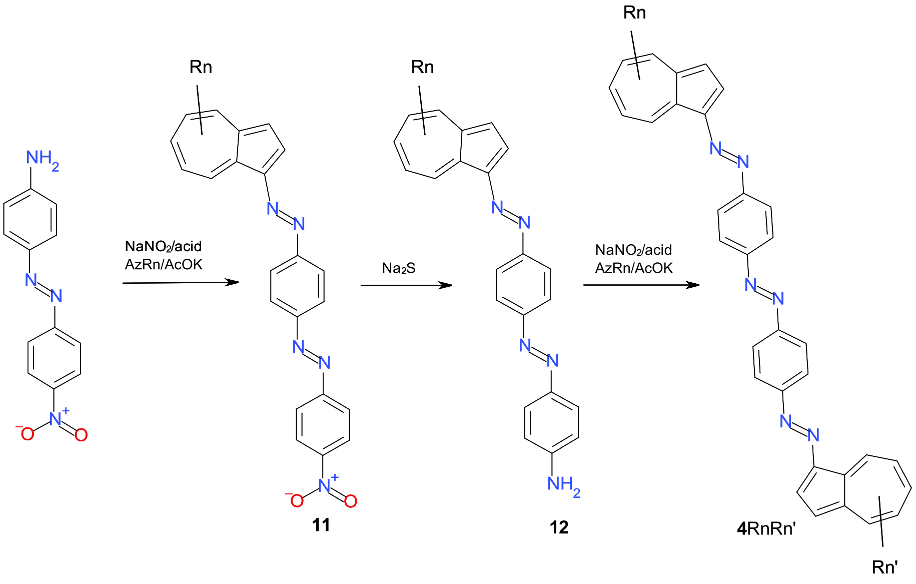
(*E*)-azulen-1-yl-[4-(4-nitrophenyl)azophenyl]diazene, **11**Az, green crystals, m.p. 252 °C. UV–Vis (MeOH): 228 (4.32), 278 (4.32), 346 (4.20), 497 (4.53). ^{1}H-NMR ($CDCl_3$): 7.41 (t, ^3J = 9.8 Hz, 1 H, 5-H), 7.48 (d, ^3J = 4.5 Hz, 1 H, 3-H), 7.54 (t, ^3J = 9.8 Hz, 1 H, 7-H), 7.81 (t, ^3J = 9.9 Hz, 1 H, 6-H), 8.08 (d_{AB}, ^3J = 9.1 Hz, 2 H, 3″-H, 5″-H), 8.14 (bs, 4 H, 2′-H, 3′-H, 5′-H, 6′-H), 8.36 (d, ^3J = 4.7 Hz, 1 H, 2-H), 8.45 (d, ^3J = 9.8 Hz, 1 H, 4-H), 8.55 (d_{AB}, ^3J = 7.0 Hz, 2 H, 2″-H, 6″-H), 9.40 (d, ^3J = 9.8 Hz, 1 H, 8-H). ^{13}C-NMR ($CDCl_3$): 120.9, 123.2, 123.5, 124.6, 124.8, 125.5, 127.6, 135.7, 138.8, 139.9, 151.4, 151.9, 156.7, 160.4. MS [ESI]: 382 [M + 1]. Calcd for $C_{22}H_{15}N_5O_2$: C, 69.28; H, 3.96; N, 18.36. Found: C, 69.25; H, 3.98; N, 18.38.

(*E*)-[4-(4-nitrophenyl)azophenyl]-(4,6,8-trimethylazulen-1-yl)diazene, **11**TMA, green crystals, m.p. 262 °C (dec). UV–Vis (MeOH): 237 (4.32), 264 (4.28), 310 (4.25), 340 (4.24), 506 (4.54). ^{1}H-NMR ($CDCl_3$): 2.68 (s, 3 H, Me_6), 2.90 (s, 3 H, Me_4), 3.42 (s, 3 H, Me_8), 7.28 (s, 1 H, 5-H), 7.40 (s, 1 H, 7-H), 7.41 (d, ^3J = 4.9 Hz, 1 H, 3-H), 8.01 (d, ^3J = 8.6 Hz, 2 H, 3′-H, 5′-H), 8.06 (d, ^3J = 8.8 Hz, 2 H, 3″-H, 5″-H), 8.11 (d, ^3J = 8.6 Hz, 2 H, 2′-H, 6′-H), 8.18 (d, ^3J = 4.7 Hz, 1 H, 2-H), 8.40 (d, ^3J = 8.7 Hz, 2 H, 2″-H, 6″-H). ^{13}C-NMR ($CDCl_3$): 25.41, 28.58, 29.75, 119.0, 122.2, 123.1, 123.4, 124.7, 124.8, 131.9, 134.1, 134.7, 141.1, 147.6, 149.9, 151.9, 154.6, 157.2. MS [ESI]: 424 [M + 1]. Calcd for $C_{25}H_{21}N_5O_2$: C, 70.91; H, 5.00; N, 16.54. Found: C, 70.90; H, 5.02; N, 16.55.

(*E*)-(5-isopropyl-3,8-dimethylazulen-1-yl)-[4-(4-nitrophenyl)azophenyl]diazene, **11**Gu, green crystals, m.p. 221 °C. UV–Vis (MeOH): 237 (4.32), 295 (4.25), 297 (4.25), 299 (4.25), 350 (4.14), 352 (4.14), 355 (4.14), 547 (4.52). ^{1}H-NMR ($CDCl_3$): 1.40 (d, ^3J = 6.8 Hz, 6 H,



Scheme 3. Azo coupling of diazotized **7**, **8** and **9**.



Scheme 4. Stepwise preparation of the *para-para* diphenylene bis-azulenyl tris azo compounds.

CH*Me*), 2.61 (s, 3 H, Me$_3$), 3.12 (hept, $^3J = 6.9$ Hz, 1 H, *CH*Me), 3.36 (s, 3 H, Me$_8$), 7.38 (d, $^3J = 10.8$ Hz, 2 H, 7-H), 7.51 (d, $^3J = 10.4$ Hz, 1 H, 6-H), 7.97 (d$_{AB}$, $^3J = 8.6$ Hz, 2 H, 2′-H, 6′-H), 8.03 (d, $^3J = 8.8$ Hz, 2 H, 3″-H, 5″-H), 8.08 (d$_{AB}$, $^3J = 8.6$ Hz, 2 H, 3′-H, 5′-H), 8.15 (bs, 1 H, 2-H), 8.16 (bs, 1 H, 4-H), 8.36 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 2″-H, 6″-H). ^{13}C-NMR (CDCl$_3$): 13.09, 24.40, 28.68, 38.21, 122.9, 123.4, 124.7, 125.6, 129.6, 132.9, 135.1, 136.3, 136.8, 143.9, 146.1, 146.9, 148.5, 149.0, 151.7, 156.1, 157.1. MS [ESI]: 452 [M + 1]. Calcd for $C_{27}H_{25}N_5O_2$: C, 71.82; H, 5.58; N, 15.51. Found: C, 71.80; H, 5.59; N, 15.54.

4-(4-azulen-1-ylazophenyl)azoaniline, **12**Az, dark green crystals, m.p. 210 °C. UV–Vis (MeOH): 228 (4.40), 280 (4.23), 396sh (4.00), 495 (4.54). ^{1}H-NMR (CDCl$_3$): 6.77 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 2″-H, 6″-H), 7.35 (t, $^3J = 9.8$ Hz, 1 H, 5-H), 7.45 (d, $^3J = 4.7$ Hz, 1 H, 3-H), 7.48 (t, $^3J = 9.8$ Hz, 1 H, 7-H), 7.77 (t, $^3J = 9.9$ Hz, 1 H, 6-H), 7.86 (d$_{AB}$, $^3J = 8.7$ Hz, 2 H, 3″-H, 5″-H), 8.00 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 3′-H, 5′-H), 8.10 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 2′-H, 6′-H), 8.35 (d, $^3J = 9.5$ Hz, 1 H, 4-H), 8.36 (d, $^3J = 4.7$ Hz, 1 H, 2-H), 9.38 (d, $^3J = 9.7$ Hz, 1 H, 8-H). ^{13}C-NMR (CDCl$_3$): 114.2, 119.9, 122.5, 122.8, 124.8, 124.9, 126.4, 135.2, 138.1, 138.6, 139.2, 143.8, 144.1, 146.5, 149.2, 152.6, 154.4. MS [ESI]: 352 [M + 1]. Calcd for $C_{22}H_{25}N_5$: C, 75.19; H, 4.88; N, 19.93. Found: C, 75.15; H, 4.91; N, 19.94.

4-[4-(4,6,8-trimethylazulen-1-yl)azophenyl]azoaniline, **12**TMA, dark green crystals, dec. without melting. UV–Vis (MeOH): 235 (4.43), 297 (4.18), 368 (4.16), 498 (4.58). ^{1}H-NMR (CDCl$_3$): 2.58 (s, 3 H, Me$_6$), 2.66 (s, 3 H, Me$_4$), 3.41 (s, 3 H, Me$_8$), 6.75 (d$_{AB,}$ $^3J = 8.8$ Hz, 2 H, 2″-H, 6″-H), 7.21 (s, 1 H, 5-H), 7.34 (s, 1 H, 7-H), 7.38 (d, $^3J = 4.9$ Hz, 1 H, 3-H), 7.84 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 3″-H, 5″-H), 7.97 (bs, 4 H, 2′-H, 3′-H, 5′-H, 6′-H), 8.17 (d, $^3J = 4.9$ Hz, 1 H, 2-H). ^{13}C-NMR (CDCl$_3$): 25.36, 28.57, 29.73, 114.7, 118.5, 122.1, 123.0, 123.3, 125.2, 131.2, 133.4, 134.3, 141.1, 146.0, 147.3, 147.9, 148.1, 149.6, 149.9, 152.7, 155.1. MS [ESI]: 394 [M + 1]. Calcd for $C_{25}H_{23}N_5$: C, 76.31; H, 5.89; N, 17.80. Found: C, 76.30; H, 5.88; N, 17.82.

4-[4-(5-isopropyl-3,8-dimethylazulen-1-yl)azophenyl]azoaniline, **12**Gu, dark green crystals, dec. without melting. UV–Vis (MeOH): 230 (4.65), 250 (4.56), 294 (4.29), 400 (4.33), 520 (4.71). ^{1}H-NMR (CDCl$_3$): 1.39 (d, $^3J = 6.8$ Hz, 6 H, CH*Me*), 2.61 (s, 3 H, Me$_3$), 3.10 (hept, $^3J = 6.9$ Hz, 1 H, *CH*Me), 3.36 (s, 3 H, Me$_8$), 6.75 (d$_{AB}$, $^3J = 8.0$ Hz, 2 H, 2″-H, 6″-H), 7.32 (d, $^3J = 10.8$ Hz, 2 H, 7-H), 7.46 (d, $^3J = 10.4$ Hz, 1 H, 6-H), 7.83 (d, $^3J = 8.0$ Hz, 2 H, 3″-H, 5″-H), 7.95 (d$_{AB}$, $^3J = 10.0$ Hz, 2 H, 2′-H, 6′-H), 7.97 (d$_{AB}$, $^3J = 10.0$ Hz, 2 H, 3′-H, 5′-H), 8.14 (bs, 1 H, 4-H), 8.16 (bs, 1 H, 2-H). ^{13}C-NMR (CDCl$_3$): 13.07, 24.41, 28.66, 38.14, 114.7, 122.8, 123.3, 125.2, 125.6, 129.0, 132.1, 134.9, 136.0, 136.8, 143.2, 145.6, 146.0, 148.8, 149.5, 152.5, 155.3. MS [ESI]: 422 [M + 1]. Calcd for $C_{27}H_{27}N_5$: C, 76.93; H, 6.46; N, 16.61. Found: C, 76.94; H, 6.44; N, 16.62.

(*Z*)-[4-(4-azulen-1-ylazophenyl)azophenyl]-(4-azulen-1-ylazophenyl)imino-oxido-ammonium, **15**Az, brown crystals, dec. without melting. UV–Vis (dioxane): 211 (5.13), 229 (5.15), 256sh (4.87), 277 (4.75), 346 (4.47), 365 (4.43), 507 (4.86). ^{1}H-NMR (CDCl$_3$): 7.38 (t, $^3J = 9.5$ Hz, 1 H, 5-H), 7.40 (t, $^3J = 9.6$ Hz, 1 H, 5′-H), 7.46 (d, $^3J = 3.6$ Hz, 1 H, 3-H), 7.47 (d, $^3J = 3.9$ Hz, 1 H, 3′-H), 7.51 (t, $^3J = 9.7$ Hz, 1 H, 7-H), 7.53 (t, $^3J = 9.7$ Hz, 1 H, 7′-H), 7.79 (t, $^3J = 9.7$ Hz, 1 H, 6-H), 7.80 (t, $^3J = 9.7$ Hz, 1 H, 6′-H), 8.10 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 2″-H, 6″-H), 8.12 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 3‴-H, 5‴-H), 8.14 (s, 4 H, 2⁗-H, 3⁗-H, 5⁗-H, 6⁗-H), 8.36 (d, $^3J = 9.3$ Hz, 1 H, 4-H), 8.37 (d, $^3J = 4.1$ Hz, 2 H, 2-H, 2′-H), 8.38 (d, $^3J = 9.3$ Hz, 1 H, 4′-H), 8.46 (d$_{AB}$, $^3J = 8.8$ Hz, 2 H, 3″-H, 5″-H), 8.53 (d$_{AB}$, $^3J = 8.9$ Hz, 2 H, 2‴-H, 6‴-H), 9.39 (d, $^3J = 9.8$ Hz, 2 H, 8-H), 9.40 (d, $^3J = 9.7$ Hz, 2 H, 8′-H). ^{13}C-NMR (CDCl$_3$): 120.6, 120.8, 122.6, 123.1, 123.3, 123.5, 124.3, 125.4, 125.8, 127.1, 127.2, 127.4, 135.7, 138.7, 138.8, 139.4, 139.8, 139.9, 144.4, 144.6, 144.7, 149.4, 152.5, 154.3, 155.7, 156.2, 159.6. MS [ESI]: 611 [M + 1]. Calcd for $C_{38}H_{26}N_8O$: C, 74.74; H, 4.29; N, 18.35. Found: C, 74.80; H, 4.35; N, 18.30.

(*Z*)-[4-[4-(5-isopropyl-3,8-dimethylazulen-1-yl)azophenyl]azophenyl]-[4-(5-isopropyl-3,8-dimethylazulen-1-yl)azophenyl]imino-oxido-ammonium, **15**Gu, brown crystals, dec. without melting. UV–Vis (dioxane): 250 (4.66), 302 (4.51), 364 (4.43), 366 (4.43), 368 (4.43), 548 (4.91). ^{1}H-NMR (CDCl$_3$): 1.40 (d, $^3J = 6.9$ Hz, 12 H, CH*Me*, CH*Me*′), 2.62 (s, 6 H, Me$_3$, Me$_{3'}$), 3.11 (hept, $^3J = 6.9$ Hz, 1 H, C*H*Me), 3.12 (hept, $^3J = 6.9$ Hz, 1 H, C*H*Me′), 3.38 (s, 3 H, Me$_8$), 3.39 (s, 3 H, Me$_{8'}$), 7.36 (d, $^3J = 10.6$ Hz, 1 H, 7-H), 7.38 (d, $^3J = 10.6$ Hz, 1 H, 7′-H), 7.51 (t, $^3J = 9.6$ Hz, $^4J = 1.7$ Hz, 1 H, 6-H), 7.55

Table 1
Diazotization of 4-(4-nitrophenyl)azoaniline, coupling with azulene and reduction of nitro-derivatives **11** to amine **12** (yields in %).

Compounds	Rn		
	Az	TMA	Gu
Diazotization of 4-(4-nitrophenyl)azoaniline and coupling with AzH	83	75	94
Reduction of compounds **11** to amine **12**	56	60	65

Table 2
Diazotization of amines **12** and azo coupling with azulenes to compounds **4**RnRn′ (yields in %).

Rn′	Rn		
	Az	TMA	Gu
Az	70	76	25
TMA	65	15	25
Gu	90	56	22

(dd, $^{3}J = 10.6$ Hz, $^{4}J = 1.7$ Hz, 1 H, 6′-H), 7.97 (d_{AB}, $^{3}J = 8.9$ Hz, 2 H, 2⁗-H, 6⁗-H), 8.00 (d_{AB}, $^{3}J = 8.8$ Hz, 2 H, 3⁗-H, 5⁗-H), 8.07 (d_{AB}, $^{3}J = 8.9$ Hz, 2 H, 2″-H, 6″-H), 8.10 (d_{AB}, $^{3}J = 8.7$ Hz, 2 H, 3‴-H, 5‴-H), 8.16 (d, $^{4}J = 1.9$ Hz, 1 H, 4-H), 8.17 (d, $^{4}J = 1.9$ Hz, 1 H, 4′-H) 8.17 (bs, 2-H, 2-H, 2′-H), 8.44 (d_{AB}, $^{3}J = 8.8$ Hz, 2 H, 3″-H, 5″-H), 8.51 (d_{AB}, $^{3}J = 8.8$ Hz, 2 H, 2‴-H, 6‴-H). ^{13}C-NMR ($CDCl_3$): 13.10, 24.42, 28.70, 38.19, 122.5, 122.9, 123.2, 123.4, 124.4, 125.6, 127.0, 127.1, 129.1, 132.6, 135.0, 135.1, 136.1, 136.3, 137.2, 143.3, 143.7, 145.9, 146.3, 149.0, 149.2, 151.8, 154.2, 154.8, 156.6, 158.2. MS [ESI]: 751 [M + 1]. Calcd for $C_{48}H_{46}N_8O$: C, 76.77; H, 6.17; N, 14.92. Found: C, 76.75; H, 6.21; N, 14.94.

3. Results and discussion

The syntheses of diazenes **1**–**4** (Scheme 1) are based on the nucleophilic character of the 1-position in azulene compounds, which allows the electrophilic coupling of these non-benzenoid aromatic hydrocarbons with the desired diazonium salts.

3.1. Syntheses of the compounds **1** and **2** with three azo bonds and one azulene-1-yl moiety

Compounds **1** and **2** were prepared by the coupling of azulenes with diazonium salts obtained from 3-(3-phenylazophenyl)azoaniline, **5**, and 4-(4-phenylazophenyl)azoaniline, **6** (Disperse Orange 3, Aldrich catalog) (Scheme 2). Because the amine **5** is not commercially available, it was synthesized using the protocols described in the literature for this compound [32,33].

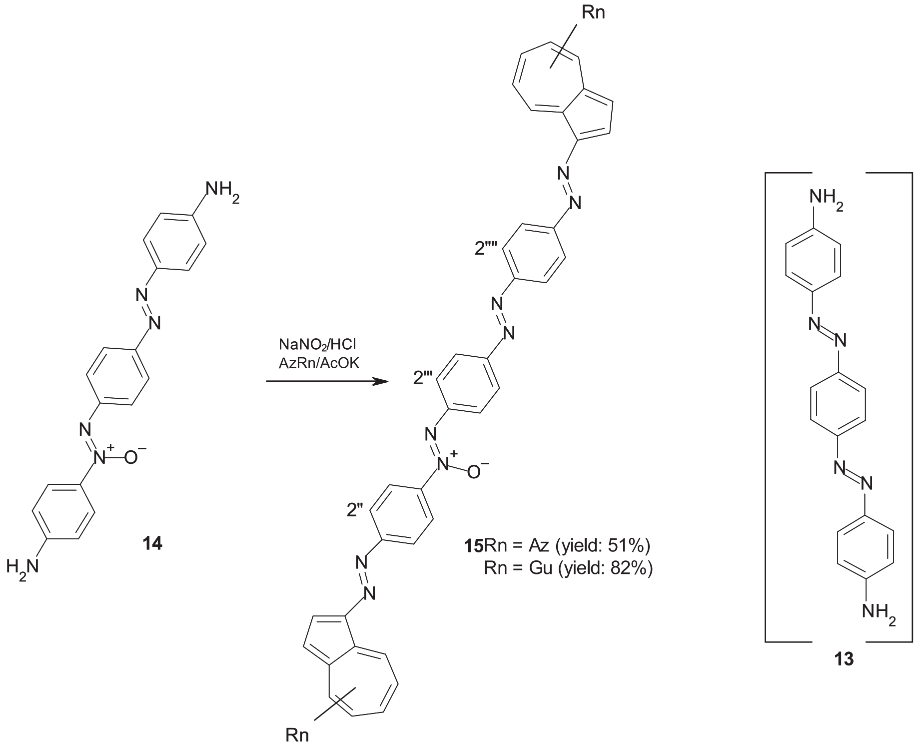
The diazotization of amine **6** was performed in the presence of hydrochloric acid, while dichloroacetic acid was more appropriate starting from the amine **5** [31]. The coupling with azulene occurred *in situ* without the diazonium salt separation. The yields obtained starting from the aniline with azo groups in the *para*-position has always been lower as compared with those for the *meta* isomer, due to the mesomeric effect exerted by azo group in diazonium salts. This effect decreases the positive charge at the diazonium group in *para*-position and, therefore, decreases the electrophilic activity of diazotized amine **6**. Nevertheless, yields between 66% and 90% were obtained for the compounds **1** and **2** (Scheme 2). The coupling reactions were always accompanied by anilines deamination in yields ranging from 3 to 5%.

It must be emphasized that our attempts to obtain and to couple the diazonium salt starting from the aniline with azo bonds in *ortho*-position toward amino group failed due to the generation of benzotriazoles before coupling could occur.

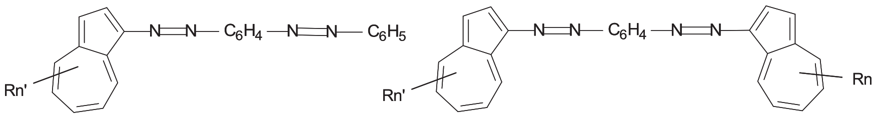
3.2. Syntheses of **3** and **4** with three azo bonds and two azulene-1-yl moieties

The presence of the second azulen-1-yl moiety in the molecules, as in the compounds **3** and **4**, necessitates more complicated synthetic routes. These routes are chosen in function of the symmetry of the synthesized azo compounds, if they possess either identical or different terminal azulen-1-yl groups (Scheme 3).

For symmetrical molecules, compounds **3**Rn and **4**Rn, the synthesis started from the already known 3-(3-aminophenyl)azoaniline, **7** [34], and 4-(4-aminophenyl)azoaniline, **8** [35] (Scheme 3). The preparation of diamine **7** occurred simultaneously with the generation of some amount of corresponding azoxy derivative, **9**. This by-product was separated using column chromatography and it



Scheme 5. Diazotization and coupling of compound **14**.



16Rn: phenylen *m*-disubstituted
17Rn: phenylen *p*-disubstituted

18RnRn': phenylen *m*-disubstituted
19RnRn': phenylen *p*-disubstituted

Scheme 6. The structures of bis azo compounds containing one or two azulenyl moieties in the molecule.

can be further reduced with Zn/NaOH to 3,3′-diaminohydrazobenzene, which, exposed to the air, yielded compound **8**.

The azoxy compound **9** was used as a starting diamine for the preparation of the new azoxy dyes **10** (Scheme 3). The azoxy group did not interfere in the coupling process and also it was compatible with the azulene moiety, known as very sensitive to common oxidants.

As emphasized, the coupling of amines with azo group in *meta*-position occurred readily, as compared with the *para* isomer. It is notable that, contrary to what was observed for *para*-phenylenediamine, which could not be diazotized and coupled with azulenes at both amino groups [31], this reaction sequence took place starting from diamine **8**. Another peculiarity of the reaction was the mono coupling of diamine **8** when the diazonium salt was reacted with 4,6,8-trimethylazulene and the lack of the disubstituted product from the experiment.

For the compounds possessing two different azulen-1-yl moieties, two consecutive coupling reactions were used, as depicted in Scheme 4. Thus, the diazotization of 4-(4-nitrophenyl)azoaniline, followed by the coupling with azulene generated the compounds **11**. These nitro-derivatives were reduced to the corresponding amines and the sequence diazotization-coupling was performed to afford the compounds **4**RnRn′ (Table 1 and 2).

The diazotization of amine **12**(Rn = Az) occurred in the hydrochloric acid medium. The amine **12**(Rn = TMA) is much less soluble in this acid, therefore for diazotization a mixture of phosphoric acid (85%):nitric acid (62%) (3:2 vol) was used [36]. Unfortunately, the guaiazulenyl moiety present in the structure of amine **12**(Rn = Gu) was oxidized by nitric acid leading to a tarry reaction mixture. Therefore only phosphoric acid was used but the coupling yields were significantly lower than it was observed in previous cases. This protocol was also used for the preparation of the diazenes **4** with Rn = Rn′. By this method, the yields of the compounds **4**Az and **4**Gu were increased and this route allowed the preparation of **4**TMA. Nevertheless, the more advantageous protocol described in Scheme 3 was used for the synthesis of the dyes **4**Az and **4**Gu.

3.3. Attempts to synthesize compounds with four azo bonds and two azulene-1-yl moieties

The attempts to directly obtain bis azo diamine **13**, the required starting reagent for the synthesis of tetra azo derivatives, failed. When *para*-di nitrosobenzene was condensed with *para*-acetylaminoaniline, instead of the expected compound **13**, the (mono azo)-(mono azoxy) derivative **14** was obtained [37]. Nevertheless, we have synthesized the tris azo azoxy compounds, **15**Rn to prove once more the compatibility between the azoxy group with an oxidant aptitude and the azulenyl moiety deactivated by an azo group (Scheme 5).

Table 3
Absorption maxima of the main visible band of mono azulenic diazenes, Rn = Az (λ_{max} in nm in methanol).

	AzN_2Ph[a]	Bis azo derivatives	Tris azo derivatives
para (or *p*,*p*)	422	Comp. **17**Az/469	Comp. **2**Az/494
		Comp. **17**TMA/484	Comp. **2**TMA/514
		Comp. **17**Gu/517	Comp. **2**Gu/540
meta (or *m*,*m*)		Comp. **16**Az/428	Comp. **1**Az/429
		Comp. **16**TMA/438	Comp. **1**TMA/438
		Comp. **16**Gu/459	Comp. **1**Gu/458

[a] Az = azulen-1-yl.

3.4. The electronic spectra of aromatic dyes 1–4 with three azo bonds and with one or two azulen-1-yl moieties in molecule; comparison with the corresponding compounds 16–19 with two azo bonds

The important effect produced on the electronic spectra by the presence of (azulen-1-yl)azo moiety as an extended conjugated π-electron system has already been studied for the molecules with one or two such moieties attached to one phenylene group, compounds **16**–**19** in Scheme 6 [30,31]. The enhancement in π-electron conjugation of azulen-1-yl-phenyl diazene by the supplementary introduction into the molecule of phenylene and azo groups, as in dyes **1**–**4**, induces an important bathochromic shift for the λ_{max} of the main visible band (Table 3). These results indicated that it would be of interest to build dyes with more extend conjugated π-electron system as in the new compounds **1**–**4**, **10** and **15** and to investigate their electronic spectra in comparison with the spectra of the previously reported compounds **16**–**17** (Table 3 and 4).

Generally, the bathochromic effect for the compounds with one azulen-1-yl moiety, **1** and **2** is more intense for the *para*-substituted phenylene isomers as for *meta* ones (Table 3) due to the more extended π-electron conjugation for the first compounds. At the same time, the data in Table 3 outlined that the red shift effect increases with the number of the 1,4-phenyleneazo groups present

Table 4
λ_{max} of the main visible band (in nm) for the synthesized dyes **1**–**4** in dioxane:water 3:1 (vol) at pH neutral and acid, as well as at isosbestic point (IP) and the obtained pK_a.

Compd.	Rn or Rn/Rn′	λ_{max}			Color in solution		$pK_a = pH_{eq}$
		Neutral	IP	Acid	Neutral	Acid	
1	Az	435	465	515	Yellow	Red	0.50
	TMA	435	477	517	Yellow	Red-brick	0.75
	Gu	458	492	538	Yellow	Red	1.34
2	Az	506	515	556	Red	Violet	0.96
	TMA	–	519	560	Red	Violet	0.98
	Gu	546	536	576	Violet	Indigo	1.21
3	Az	438	464	511	Yellow	Red-brick	0.31
	TMA	439	470	518	Yellow	Cyclamen	1.58
	Gu	463	495	542	Yellow	Cyclamen	1.45
4	Az/Az	528	553	604	Red	Blue	0.74
	Az/TMA	550	561	607	Red	Blue	1.23
	Az/Gu	564	576	617	Violet	Blue	1.36
	TMA/TMA	540	557	586	Violet	Violet	1.71
	TMA/Gu	559	597	615	Violet	Blue	1.46
	Gu/Gu	566	596	624	Violet	Blue	1.29
10	Az	434	468	528	Yellow	Red	0.74
	TMA	441	470	519	Yellow	Red	1.56
	Gu	464	493	539	Yellow	Red	1.47

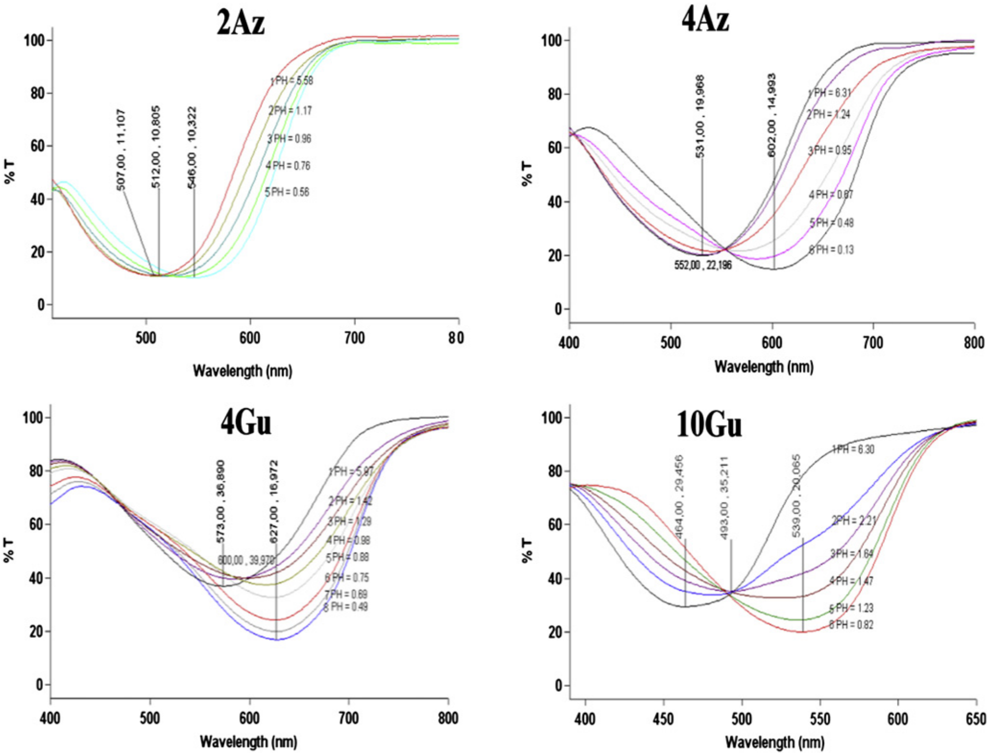


Fig. 1. The isosbestic points of several synthesized dyes.

in the molecule. Thus, the bathochromic shift of ca. 25 nm was found for λ_{max} of the main visible band when **17** is compared with **2**, whereas for the compounds **16** and **1** the values of λ_{max} remained unchanged.

The inductive effect of the alkyl substituents on azulenyl moiety enhances the electron density and mobility along the molecule. Therefore, the bathochromic effect increases with the number of alkyl groups (Table 3). The alkyl substitution was more effective for the *para* isomers, but their effect has also been observed for the *meta* isomers.

It is not surprising that for the symmetric bis (azulen-1-yl)azo systems, **3** and **4** with Rn = Rn′, no significant difference in the λ_{max} of the main visible band was detected due to the decrease in the charge polarization, which takes place in **1** and **2**. The alkyl substituents on azulen-1-yl moieties produce a bathochromic shift for all compounds being more pronounced for the *para*–*para* isomers and for the guaiazulenyl group.

There are no significant differences in λ_{max} of the main visible band between the compounds that contains an azoxy group, **10** and **15**, and the corresponding compounds only with azo groups, **4**. For the compounds containing one azo or azoxy bond the difference between the values of the main visible band of these groups is significant (azobenzene has a $\lambda_{max} = 314$ nm, while azoxybenzene has a $\lambda_{max} = 322$ nm in ethanol) [38]. However, this gap decreases with the increase of the number of azo groups. This behavior can be explained by an extended conjugation between azo and azoxy groups when the extra oxygen atom acquires a lower influence on the whole chromophores.

The very low solubility (at least at some pH values) of several polyazoazulenes in standard solvents, e.g. water or alcohol–water mixtures, forced us to choose a solvent mixture which dissolves all the compounds in both basic and acidic media and, at the same time, allows an easy recording of pH values. Therefore, the acid–base properties of the dyes **1**–**4** were studied in dioxane–water

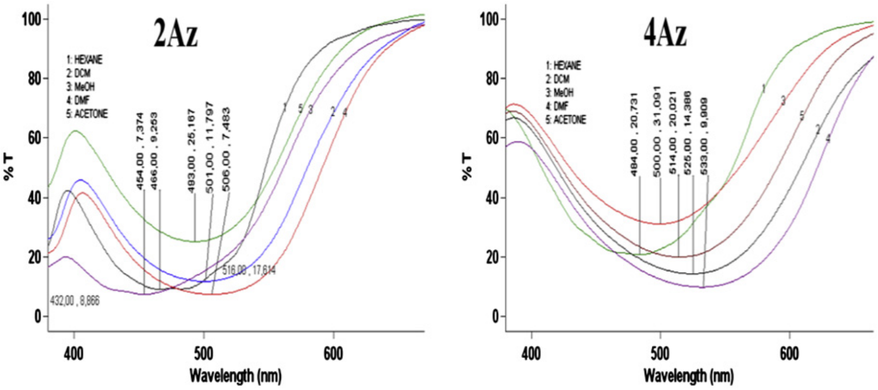


Fig. 2. The shift of the main visible band with the solvent for the compounds **2**Az and **4**Az.

solution 3:1 (vol). The values for λ_{max} of the main visible band in the neutral and acid medium, as well as at the isosbestic point (IP), are described in Table 4. As a rule, the obtained pK_a values (Table 4) indicate that all the compounds are very weak bases. Usually, only the single protonation of dyes **1**–**4** is observed in relatively strong acidic medium. However, electron rich azulenes, such as guaiazulene, increase the basicity of the azo compounds, allowing a double protonation. Therefore, in these cases, at lower pH, the protonation curves do not cross each other anymore at the initial isosbestic point. The basicity of *meta*–*meta* isomers **1**Az and **3**Az are lower than that of the *para*–*para* isomers, **2**Az and **4**Az. This fact can be explained by the more extended conjugation for the latter compounds, which increases the electron density at the nitrogen atoms. However, at substituted azulenes, some inversions are observed, presumably due to the steric effects produced by these substituents. Upon protonation, the λ_{max} of the main visible band of all the compounds is significantly bathochromic shifted. The absorption gap between the neutral and strong acid form is higher in the case of the *meta* isomers (ca. 80 nm) and lower for *para* (ca. 55 nm). The azoxy groups behave similarly with the azo groups even the differences of pK_a values of their conjugated acids are low (Fig. 1).

The high polarizability of *para*–*para* compounds **2** or **4** produces a strong positive solvatochromic effect. Thus, a bathochromic shift over 50 nm of the main visible band is obtained for the solutions in nonpolar solvents, e.g. hexane, as compared with the aprotic polar solvent, DMF. As results from Fig. 2, intermediate values for the λ_{max} in dichloromethane, methanol and acetone are obtained.

4. Conclusions

The syntheses of *meta,meta*- and *para,para*-tris azo compounds, **1**–**4** was accomplished in good yields by coupling reaction between corresponding mono- or di-arylamino moieties and azulenes. When two azulene-1-yl moieties are present in the molecules, they can be either identically or differently substituted. In our attempt to synthesize dyes with four azo bonds only the corresponding azoxy compounds **15** were obtained. The importance of the relative positions of substituents on phenylene rings, as well as the influence exerted by the nature of the azulene-1-yl(s) moiety on the electronic spectra of the investigate dyes, were discussed and compared with the behavior of the already studied bis azo derivatives. The isosbestic points of the main visible band belonging to the investigated tris azoic compounds were recorded. The resulted pK_a values of their conjugated acids proved their very weak basicity. Our results also suggest the possibility of the double protonation of some of these compounds. The high solvatochromic behavior of the compounds **2** and **4** enables us to expect also their molecular hyperpolarizability.

Acknowledgments

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