New (azulen-1-yldiazenyl)-heteroaromatic Compounds Containing 1,2,5-oxadiazol-3-yl Moieties

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Several new azulenyl diazenes containing furazans or furoxans heterocycles were prepared. Despite both the diazotation and azo coupling reactions were conditioned by the poor basicity and stability of these heterocyclic moieties the reaction yields are fair. Some of the compounds properties as UV-Vis, NMR and MS, are discussed insisting on the peculiarities induced by the presence of these high-energy heterocycles in the molecules. The acido-basic properties and the redox properties have been also investigated and correlated with frontier orbital energies.

Keywords: azulene, furazans, furoxans, azo coupling, diazenes

A large number of recent studies have demonstrated the possible use of diazenes in technical purposes as: molecular photo-oscillators based on highly accelerated heterocyclic azo dyes in nematic liquid crystals [1], compounds with optical limiting property and enhancement mechanism [2], photoresponsive materials with various lengths of flexible spacers [3], push-pull chromophores [4], photoswitching compounds in vivo with red light [5] and electrowetting-based reflective display with potential for use in the field of electronic paper [6]. At the same time, some calculations were performed for DFT/TDDFT modeling for optoelectronic applications [7].

In our previous researches, we dealt with some azulen-1-yl diazenes taking into account the ability of azulen-1yl system to transfer an electron toward an acceptor group to build push-pull molecules with possible technical applications [8]. As acceptors in these push-pull molecules aromatic, as well as heteroaromatic systems, were introduced and spacers as azo group, carbon, carbon double bond, or even favorable disubstituted aryl were used for the charge expansion.

Investigations already carried out by us on the azulen-1-yl diazenes with heteroaromatic moieties in their structure were focused on the (azulen-1-yldiazenyl) pyridines [9, 10], 2-(azulen-1-yldiazenyl) thiazoles [11] and 2-(azulen-1-yldiazenyl) benzothiazols [12]. There were detailed the synthesis route and several properties of the obtained compound classes as the UV, NMR and mass spectra as well as the derivatives acidity or the redox behavior [13, 14]. We now turn our attention on the furazan (trivial name of 1,2,5-oxadiazole) and furoxan moieties as hetero-aromatic system. A challenge for us was both the extremely poor basicity of 3-aminofurazans [15] (for example for 3-amino-4-aminofurazan pK_a = -2.14 whereas for 3-amino-4-methylfuroxan this parameter drops to -3.01) and the low stability of 3-furazandiazonium salts which can decompose before the coupling reaction. There are known the diazotization of aminofurazans followed by coupling only with very good coupling reagents as naphthols or anisols [16]. On the other hand, some furazan diazenes have been of interest for its biological usage as guanylate cyclase inhibitior [17].

Experimental part

Melting points (uncorrected) were measured with a Koehler Automatic Melting Point Range Apparatus (K90190). Elemental analyses were performed using Perkin Elmer CHN 240B. UV spectra were obtained using Varian Cary 100 spectrophotometer (λ values are given in nm and the molar extinction, ε, in M^{-1} cm^{-1}). For ^1H- and ^{13}C-NMR: Gemini 300 spectrometer (^1H: 300 MHz, ^{13}C: 75 MHz) was used, with TMS as internal standard in $CDCl_3$; several signals were assigned on the basis of COSY, HETCOR and HMBC experiments. Mass spectra were obtained with Varian 1200L Triple Quadrupole LC/MS/MS spectrometer by direct injection in ESI. For the column chromatography, silica gel 60 or alumina [II-III Brockmann grade, 70e230 mesh ASTM] were used. Acetonitrile (Rathburn, HPLC grade), tetra-n-butylammonium perchlorate (TBAP) and tetra-n-butylammonium fluoro-borate (TBABF4) from Fluka were used as received like solvent and supporting electrolytes, respectively. The DCM was distilled over CaH_2 and the ether was preserved on sodium. The compounds nomenclature was obtained by the CambridgeSoft package of structure-to-name algorithm included with ChemBioDraw Ultra 11.0.

Reaction of azulenes with diazotized aminofurazans and aminofuroxans

Nitrosyl sulfate was prepared by adding sodium nitrite (69 mg, 1 mmol) in sulfuric acid (0.8 mL) cooled at 0-2 °C followed by the addition of phosphoric acid (0.8 mL). Then aminofurazan or aminofuroxan (1 mmol) was added in portions to avoid temperature rises. The reaction mixture was stirred at 0°C for one hour and then to this mixture, a solution of azulene (1 mmol) in pyridine (7 mL) was added slowly; in this time, the solution became very viscous and a vigorous stirring was required. The solution was stirred at room temperature for 10 min and then poured into water when precipitated a dark brown compound. DCM was added in order to obtain two immiscible layers: the organic layer was separated and then washed with water to eliminate the pyridine. In some cases, the entire aqueous extract retained an important amount of the desired compounds being relatively strong coloured. Therefore, it

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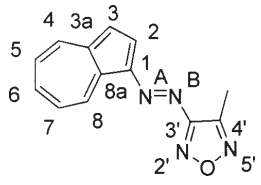
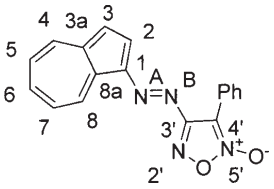
was extracted with small amounts of DCM, and the resulted organic layer was added to the main organic layer. The organic layer was dried on sodium sulfate, filtered and the solvent was evaporated. The residue was chromatographed on silica gel with petroleum ether:DCM = 1:1 for the elution of the starting material followed by DCM for the desired products.

Product characterization





For the sake of simplicity, the atom numbers in NMR spectra are indicated above despite the ChemBioDraw Ultra 11.0 nomenclature used for the name of compounds **6** and **7** (see below).

(E)-3-(azulen-1-yldiazenyl)-4-methyl-1,2,5-oxadiazole, **3a,** brown crystals; yield 40%; m. p. 158 °C (dec); UV-Vis (MeOH), λmax (log ε): 225 (4.23), 287 (4.07), 337 (3.98), 429 (4.34) nm; ^{1}H-NMR ($CDCl_3$): δ = 2.75 (s, 3 H, Me), 7.48 (d, ^{3}J = 4.7 Hz, 1 H, 3-H), 7.54 (t, ^{3}J =9.7 Hz, 1 H, 5-H), 7.64 (t, ^{3}J =9.8 Hz, 1 H, 7-H), 7.90 (t, ^{3}J =9.9 Hz, 1 H, 6-H), 8.35 (d, ^{3}J =4.7 Hz, 1 H, 2-H), 8.44 (d, ^{3}J =9.4 Hz, 1 H, 4-H), 9.16 (d, ^{3}J =9.8 Hz, 1 H, 8-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 11.23 (Me), 122.0 (C3), 125.7 (C2), 129.3 (C5), 129.4 (C7), 135.6 (C8), 139.5 (C4), 140.5 (C6), 141.7 (C1), 144.3 (C8a), 145.8 (C3a), 146.2 (C3'), 163.8 (C4') ppm; MS [ESI]: 239 [M+1]; Found: C, 65.52; H, 4.25; N, 23.51; Molecular formula: $C_{13}H_{10}N_4O$ requires: C, 65.54; H, 4.23; N, 23.52; O, 6.71.

(E)-3-(3-tert-butylazulen-1-yldiazenyl)-4-methyl-1,2,5-oxadiazole, **3b,** brown crystals; yield 40%; m. p. 204 °C (strongly fumigation form 134 °C); UV-Vis (MeOH), λmax (log ε): 223 (4.15), 225 (4.15), 235 (4.14), 239 (4.15), 294 (4.00), 320 (3.86), 343 (4.01), 345 (4.00), 454 (4.31) nm; ^{1}H-NMR ($CDCl_3$): δ = 1.61 (s, 9 H, tBu), 2.75 (s, 3 H, 4'-Me), 7.47 (t, ^{3}J =10.0 Hz, 1 H, 5-H), 7.55 (t, ^{3}J =9.7 Hz, 1 H, 7-H), 7.84 (t, ^{3}J =9.8 Hz, 1 H, 6-H), 8.27 (s, 1 H, 2-H), 8.78 (d, ^{3}J =9.7 Hz, 1 H, 4-H), 9.15 (d, ^{3}J =9.9 Hz, 1 H, 8-H); ^{13}C-NMR ($CDCl_3$): δ = 11.25 (Me_f), 31.70 (C*Me*), 33.67 (*C*Me), 123.4 (C2), 127.8 (C5), 129.0 (C7), 135.1 (C8), 138.3 (C4), 140.3 (C6), 142.6 (C3), 143.5 (C8a), 144.4 (C1), 145.8 (C4'), 155.2 (C3a), 164.0 (C3'); MS [ESI]: 295 [M+1]; Found: C, 69.36; H, 6.18; N, 19.03; Molecular formula: $C_{17}H_{18}N_4O$ requires: C, 69.37; H, 6.16; N, 19.03; O, 5.44.

(E)-3-(4,8-dimethylazulen-1-yldiazenyl)-4-methyl-1,2,5-oxadiazole, **3c,** brown crystals; yield 42%; m. p. 107 °C (dec); UV-Vis (MeOH), λmax (log ε): 237 (4.33), 310 (4.09), 339 (4.01), 341 (4.02), 434 (4.38) nm; ^{1}H-NMR ($CDCl_3$): δ = 2.59 (s, 3 H, 4'-Me), 2.92 (s, 3 H, Me_4), 3.29 (s, 3 H, Me_8), 7.40 (d, ^{3}J = 10.1 Hz, 1 H, 5-H), 7.41 (d, ^{3}J = 5.0 Hz, 1 H, 3-H), 7.48 (d, ^{3}J = 10.1 Hz, 1 H, 7-H), 7.58 (t, ^{3}J = 10.1 Hz, 1 H, 6-H), 8.27 (d, ^{3}J = 5.0 Hz, 1 H, 2-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 10.48 (4'-Me), 25.37 (Me_4), 29.32 (Me_8), 119.7 (C3), 124.2 (C2), 132.0 (C5), 133.6 (C7), 137.4 (C6), 137.7 (C1), 144.7 (C8a), 145.8 (C3a), 149.0 (C4'), 149.7(C8), 151.5 (C8), 163.8 (C3') ppm; MS [ESI]: 267 [M+1]; Found: C, 67.63; H, 5.32; N, 21.03; Molecular formula: $C_{15}H_{14}N_4O$ requires: C, 67.65; H, 5.30; N, 21.04; O, 6.01.

(E)-3-(4,6,8-trimethylazulen-1-yldiazenyl)-4-methyl-1,2,5-oxadiazole, **3d,** brown crystals; yield 41%; m. p. 207 °C (dec); UV-Vis (MeOH), λmax (log ε): 236 (4.28), 314 (4.08), 341 (3.98), 344 (3.98), 438 (4.35) nm; ^{1}H-NMR ($CDCl_3$): d = 2.61 (s, 3 H, 4'-Me), 2.69 (s, 3 H, Me_6), 2.89 (s, 3 H, Me_4), 3.28 (s, 3 H, Me_8), 7.37 (d, ^{3}J = 5.1 Hz, 1H, 3-H), 7.38 (s, 1H, 5-H), 7.45 (s, 1 H, 7-H), 8.19 (d, ^{3}J = 5.0 Hz, 1H, 2-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 10.44 (4'-Me), 25.71(Me_4), 28.68 (Me_6), 29.82 (Me_8), 119.8 (C3), 122.9 (C2), 133.4 (C5), 135.5 (C7), 136.5 (C1), 143.3 (C8a), 145.9 (C3a), 148.5 (C8), 149.2 (C4), 149.3 (C4'), 150.3 (C6), 163.9 (C3') ppm; MS [ESI]: 281 [M+1]; Found: C, 68.56; H, 5.77; N, 19.98; Molecular formula: $C_{16}H_{16}N_4O$ requires: C, 68.55; H, 5.75; N, 19.99; O, 5.71.

(E)-3-(4,8-dimethyl-6-tert-butylazulen-1-yldiazenyl)-4-methyl-1,2,5-oxadiazole, **3e,** brown crystals; yield 42%; m.p. 135 °C; UV-Vis (MeOH), λmax (log ε): 237 (4.34) , 313 (4.19), 334 (4.08), 337 (4.08), 341 (4.08), 346 (4.08), 354 (4.02), 439 (4.45) nm; ^{1}H-NMR ($CDCl_3$): δ = 1.50 (s, 9 H, tBu), 2.59 (s, 3 H, 4'-Me), 2.93 (s, 3 H, Me_4), 3.32 (s, 3 H, Me_8), 7.34 (d, ^{3}J = 5.1 Hz, 1 H, 3-H), 7.61 (d, ^{4}J = 1.4 Hz, 1 H, 5-H), 7.71 (d, ^{4}J = 1.4 Hz, 1 H, 7-H), 8.20 (d, ^{3}J = 5.1 Hz, 1 H, 2-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 10.42 (4'-Me), 26.30 (Me_4), 30.14 (Me_8), 31.98 (C*Me*), 39.03 (*C*Me), 119.5 (C3), 123.4 (C2), 130.2 (C5), 132.4 (C7), 136.8 (C1), 143.6 (C8a), 145.8 (C3a), 148.2 (C8), 149.0 (C4'), 150.0 (C4), 161.3 (C6), 163.9 (C3'); MS [ESI]: 323 [M+1]; Found: C, 70.76; H, 6.88; N, 17.39. Molecular formula: $C_{19}H_{22}N_4O$ requires: C, 70.78; H, 6.88; N, 17.38; O, 4.96.

(E)-3-(3,8-Dimethyl-5-isopropylazulen-1-yldiazenyl)-4-methyl-1,2,5-oxadiazole, **3f,** brown crystals; yield 45%; m. p. 159 °C (dec); UV-Vis (MeOH), λmax (log ε): 231 (4.31), 254 (4.26), 308 (4.05), 348 (3.99), 350 (3.97), 352 (3.97), 472 (4.43) nm; ^{1}H-NMR ($CDCl_3$): δ= 1.41 (d, ^{3}J = 6.9 Hz, 6 H, CH*Me*), 2.58 (s, 3 H, Me_3), 2.61 (s, 3 H, 4'-Me), 3.15 (hept, ^{3}J = 6.9 Hz, 1 H, *CH*Me), 3.25 (s, 3 H, Me_8), 7.47 (d, ^{3}J = 10.7 Hz, 1 H, 5-H), 7.59 (dd, ^{3}J = 10.7 Hz, ^{4}J = 1.8 Hz, 1 H, 6-H), 8.16 (s, 1 H, 2-H), 8.20 (d, ^{4}J = 1.8 Hz, 1 H, 4-H). ^{13}C-NMR ($CDCl_3$): δ= 10.58 (4'-Me), 13.21 (Me_3), 24.49 (CH*Me*), 28.59 (*CH*Me), 38.39 (Me_8), 126.1 (C2), 130.5 (C3), 134.5 (C7), 135.7 (C4), 137.0 (C6), 138.5 (C1), 145.3 (C5), 145.9 (C3a), 147.0 (C8a), 148.9 (C8), 149.2 (C4'), 164.0 (C3'); MS [ESI]: 309 [M+1]; Found: C, 70.10; H, 6.56; N, 18.16. Molecular formula: $C_{18}H_{20}N_4O$ requires: C, 70.11; H, 6.54; N, 18.17; O, 5.18.

(E)-3-(azulen-1-yldiazenyl)-4-phenyl-1,2,5-oxadiazole, **4a,** brown crystals; yield 35%; m. p. 138 °C (dec); UV-Vis (MeOH), λmax (log ε): 229 (4.33), 293 (4.05), 337 (3.95), 340 (395), 438 (4.35) nm; ^{1}H-NMR ($CDCl_3$): δ = 7.46 (d, ^{3}J = 4.7 Hz, 1 H, 3-H), 7.51 (t, ^{3}J =9.8 Hz, 1 H, 5-H), 7.52-7.55 (m, 3 H, m,p-Ph), 7.55 (t, ^{3}J =9.8 Hz, 1 H, 7-H), 8.05-8.10 (m, 2 H, o-Ph), 7.86 (t, ^{3}J =9.9 Hz, 1 H, 6-H), 8.30 (d, ^{3}J =4.7 Hz, 1 H, 2-H), 8.41 (d, ^{3}J =9.4 Hz, 1 H, 4-H), 9.08 (d, ^{3}J =9.8 Hz, 1 H, 8-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 122.2 (C3), 125.6 (C2), 126.6 (C1'-Ph), 128.9 (m-Ph), 129.2 (o-Ph), 129.5 (C5), 129.8 (C7), 130.5 (p-Ph), 136.5 (C8), 139.5 (C4), 140.7 (C6), 142.4 (C1), 145.6 (C8a), 146.4 (C3a), 150.7 (C4"), 162.9 (C3") ppm; MS [ESI]: 301 [M+1]; Found: C, 71.99; H, 4.03; N, 18.66. Molecular formula: $C_{18}H_{12}N_4O$ requires: C, 71.99; H, 4.03; N, 18.66; O, 5.32.

(E)-3-(3-tert-butylazulen-1-yldiazenyl)-4-phenyl-1,2,5-oxadiazole, **4b,** brown crystals; yield 31%; m. p. 108 °C (dec); UV-Vis (MeOH), λmax (log ε): 228 (4.37), 232 (4.37), 234 (4.37), 298 (4.10), 343 (4.02), 345 (4.02), 457 (4.36) nm; ^{1}H-NMR ($CDCl_3$): δ = 1.59 (s, 9 H, tBu), 7.42 (t, ^{3}J =9.3 Hz, 1 H, 5-H), 7.44 (t, ^{3}J =9.4 Hz, 1 H, 7-H), 7.48-7.55 (m, 3 H, m,p-Ph), 7.79 (t, ^{3}J = 9.8 Hz, 1 H, 6-H), 8.00-8.03 (m, 2 H, Ph), 8.18 (s, 1 H, 2-H), 8.74 (d, ^{3}J =9.5 Hz, 1 H, 4-H), 8.94 (dd, ^{3}J =10.0 Hz, ^{4}J = 1.0 Hz, 1 H, 8-H) ppm; ^{13}C-NMR ($CDCl_3$): λ = 31.55 (Me), 33.55 (C), 123.0 (C2), 126.7 (C1-Ph), 128.2 (C7), 128.8 (m-Ph), 129.2 (o-Ph), 129.5 (C5), 130.3 (p-Ph), 136.0 (C8), 138.4 (C4), 140.5 (C6), 142.9 (C3), 143.6 (C8a), 144.5 (C3a), 144.6 (C1), 150.4 (C4'), 163.1

(C3'); MS [ESI]: 349 [M+1]; Found: C, 74.14; H, 5.66; N, 15.72. Molecular formula: $C_{22}H_{20}N_4O$ requires: C, 74.14; H, 5.66; N, 15.72; O, 4.48.

(E)-3-(4,8-dimethylazulen-1-yldiazenyl)-4-phenyl-1,2,5-oxadiazole, **4c,** brown crystals; yield 20%; m. p. 157 °C (dec); UV-Vis (MeOH), λmax (log ε): 206 (4.21), 209 (4.21), 213 (4.21), 238 (4.37), 309 (4.04), 442 (4.37) nm; ^{1}H-NMR ($CDCl_3$): δ = 2.93 (s, 3 H, Me_4), 3.17 (s, 3 H, Me_8), 7.42 (d, ^{3}J = 9.9 Hz, 1 H, 5-H), 7.45 (d, ^{3}J = 5.2 Hz, 1 H, 3-H), 7.47 (d, ^{3}J = 10.1 Hz, 1 H, 7-H), 7.48-7.52 (m. 3 H, m,p-Ph), 7.58 (t, ^{3}J = 10.0 Hz, 1 H, 6-H), 8.07-8.12 (m, 2 H, o-Ph), 8.24 (d, ^{3}J = 5.1 Hz, 1 H, 2-H) ppm; ^{13}C-NMR ($CDCl_3$): δ= 25.32 (Me_4), 28.82 (Me_8), 120.0 (C3), 123.6 (C2), 126.5 (C1-Ph), 128.9 (m-Ph), 129.0 (o-Ph), 130.5 (p-Ph), 132.2 (C5), 134.3 (C7), 137.5 (C6), 138.5 (C1), 145.1 (C8a), 149.1 (C3a), 149.7 (C8), 150.8 (C4'), 153.2 (C4), 163.0 (C3') ppm; MS [ESI]: 329 [M+1]; Found: C, 73.15; H, 4.90; N, 17.07. Molecular formula: $C_{20}H_{16}N_4O$ requires: C, 73.15; H, 4.91; N, 17.06; O, 4.88.

(E)-3-(4,6,8-trimethylazulen-1-yldiazenyl)-4-phenyl-1,2,5-oxadiazole, **4d,** brown crystals; yield 27%; m. p. 108 °C (dec); UV-Vis (MeOH), λmax (log ε): 205 (4.29), 238 (4.43), 314 (4.14), 446 (4.41) nm; ^{1}H-NMR ($CDCl_3$): δ = 2.62 (s, 3 H, Me_6), 2.84 (s, 3 H, Me_4), 3.09 (s, 3 H, Me_8), 7.31 (s, 1H, 5-H), 7.32 (d, ^{3}J = 4.9 Hz, 1H, 3-H), 7.40 (s, 1 H, 7-H), 7.47-7.51 (m, 3 H, m,p-Ph), 8.08 (d, ^{3}J = 5.0 Hz, 1H, 2-H), 8.08-8.11 (m, 2 H, o-Ph) ppm; ^{13}C-NMR ($CDCl_3$): δ= 25.60 (Me_4), 28.67 (Me_6), 29.08 (Me_8), 120.1 (C3), 122.2 (C2), 126.6 (C1-Ph), 128.9 (m-Ph), 129.0 (o-Ph), 130.4 (p-Ph), 133.8 (C5), 136.3 (C7), 137.3 (C1), 143.7 (C8a), 148.5 (C8), 149.3 (C3a), 149.4 (C4), 150.8 (C4'), 151.8 (C6), 163.0 (C3') ppm; MS [ESI]: 343 [M+1]; Found: C, 73.68; H, 5.31; N, 16.35. Molecular formula: $C_{21}H_{18}N_4O$ requires: C, 73.67; H, 5.30; N, 16.36; O, 4.67.

(E)-3-(4,8-dimethyl-6-tert-butylazulen-1-yldiazenyl)-4-phenyl-1,2,5-oxadiazole, **4e,** brown crystals; yield 24%; m. p. 132 °C; UV-Vis (MeOH), λmax (log ε): 206 (4.27), 238 (4.43), 314 (4.17), 446 (4.43) nm; ^{1}H-NMR ($CDCl_3$): δ = 1.49 (s, 9 H, tBu), 2.94 (s, 3 H, Me_4), 3.19 (s, 3 H, Me_8), 7.37 (d, ^{3}J = 5.1 Hz, 1 H, 3-H), 7.49-7.51 (m, 3 H, m,p-Ph), 7.62 (d, ^{4}J = 1.3 Hz, 1 H, 5-H), 7.72 (d, ^{4}J = 1.3 Hz, 1 H, 7-H), 8.09-8.13 (m, 2 H, o-Ph), 8.17 (d, ^{3}J = 5.1 Hz, 1 H, 2-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 26.30 (Me_4), 29.68 (Me_8), 32.01 (C*Me*$_3$), 39.10 (*C*Me_3), 119.9 (C3), 122.9 (C2), 126.6 (C1-Ph), 128.9 (m-Ph), 129.0 (oh), 130.4 (p-Ph), 130.6 (C5), 133.2 (C7), 137.6 (C1), 144.0 (C8a), 148.3 (C8), 149.2 (C3a), 150.8 (C4'), 151.6 (C4), 161.5 (C6), 163.0 (C3') ppm; MS [ESI]: 385 [M+1]; Found: C, 74.98; H, 6.30; N, 14.57. Molecular formula: $C_{24}H_{24}N_4O$ requires: C, 74.97; H, 6.29; N, 14.57; O, 4.17.

(E)-3-(3,8-Dimethyl-5-isopropylazulen-1-yldiazenyl)-4-phenyl-1,2,5-oxadiazole, **4f,** brown crystals; yield 40%; m. p. 138 °C (dec); UV-Vis (MeOH), λmax (log ε): 206 (4.29), 232 (4.41), 313 (4.09), 345 (3.98), 350 (3.95), 354 (3.95), 472 (4.45) nm; ^{1}H-NMR ($CDCl_3$): δ = 1.38 (d, ^{3}J = 6.9 Hz, 6 H, iPr), 2.57 (s, 3 H, Me_3), 3.08 (s, 3 H, Me_8), 3.12 (hept, ^{3}J = 6.9 Hz, iPr), 7.45 (d, ^{3}J = 10.8 Hz, 1 H, 5-H), 7.47-7.51 (m, 3 H, m,p-Ph), 7.55 (dd, ^{3}J = 10.7 Hz, ^{4}J = 1.8 Hz, 1 H, 6-H), 8.06 (s, 1 H, 2-H), 8.08-8.12 (m, 2 H, o-Ph), 8.18 (d, ^{4}J = 1.9 Hz, 1 H, 4-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 13.23 (Me_3), 24.43 (*Me*CH*)*, 27.96 (Me_8), 38.39 (Me*CH)*, 125.4 (C2), 126.7 (C1-Ph), 128.9 (m-Ph), 129.0 (o-Ph), 130.3 (p-Ph), 131.0 (C3), 135.3 (C7), 135.6 (C4), 137.1 (C6), 139.4 (C1), 145.6 (C8a), 147.1 (C3a), 149.4 (C5), 150.7 (C8), 150.8 (C4'), 163.1 (C3') ppm; MS [ESI]: 371 [M+1]; Found: C, 74.56; H, 6.01; N, 15.13. Molecular formula: $C_{23}H_{22}N_4O$ requires: C, 74.57; H, 5.99; N, 15.12; O, 4.32.

(E)-4-(azulen-1-yldiazenyl)-3-phenyl-1,2,5-oxadiazole 2-oxide, **6,** redish-brow crystals; yield 11%; m.p. 139 °C; UV-Vis (MeOH), λmax (log ε): 206 (4.03), 225 (4.15), 250 (4.10), 288 (4.00), 458 (4.30) nm; ^{1}H-NMR ($CDCl_3$): δ = 7.46 (d, ^{3}J = 4.6 Hz, 1 H, 3-H), 7.52 (t, ^{3}J =9.7 Hz, 1 H, 5-H), 7.55 (t, ^{3}J = 8.5 Hz, 1 H, 4'-H), 7.55 (t, ^{3}J = 8.5 Hz, 2 H, 3'-H, 5'-H), 7.57 (t, ^{3}J = 9.7 Hz, 1 H, 7-H), 7.85 (t, ^{3}J =9.8 Hz, 1 H, 6-H), 8.10 (dd, ^{3}J = 7.9 Hz, 2 H, 2'-H, 6'-H), 8.22 (d, ^{3}J =4.7 Hz, 1 H, 2-H), 8.37 (d, ^{3}J =9.4 Hz, 1 H, 4-H), 9.01 (d, ^{3}J =9.7 Hz, 1 H, 8-H) ppm; ^{13}C-NMR ($CDCl_3$): δ = 110.2 (C4'), 122.3 (C3), 125.0 (C2), 127.4 (C1-Ph), 128.5 (m-Ph), 128.8 (o-Ph), 129.5 (C5), 129.8 (C7), 130.9 (p-Ph), 136.6 (C8), 139.4 (C4), 140.8 (C6), 141.9 (C1), 146.1 (C8a), 146.4 (C3a), 153.5 (C3') ppm; MS [ESI]: 317 [M+1]. Found: C, 68.35; H, 3.81; N, 17.72. Molecular formula: $C_{18}H_{12}N_4O_2$ requires: C, 68.35; H, 3.82; N, 17.71; O, 10.12.

(E)-4-(4,6,8-trimethylazulen-1-yldiazenyl)-3-phenyl-1,2,5-oxadiazole 2-oxide, **7,** 2-oxide, redish-brow crystals; yield 13%; m.p. 150 °C; UV-Vis (MeOH), λmax (log ε): 218 (4.00), 234 (4.18), 306 (4.07), 466 (4.31) nm; ^{1}H-NMR ($CDCl_3$): δ = 2.65 (Me_6), 2.85 (Me_4), 3.23 (Me_8), 7.31(s, 1 H, 5-H), 7.35 (d, ^{3}J = 5.0 Hz, 1 H, 3-H), 7.42 (s, 1 H, 7-H), 7.51-7.54 (m, 3 H, m,p-Ph), 8.02 (d, ^{3}J = 5.0 Hz, 1 H, 2-H), 8.14-8.17 (m, 2 H, o-Ph) ppm; ^{13}C-NMR ($CDCl_3$): δ= 25.59 (Me_4), 28.71 (Me_6), 29.36 (Me_8), 114.2 (C3'), 120.6 (C3), 121.8 (C2), 127.5 (C1-Ph); 128.2 (m-Ph), 128.9 (o-Ph), 130.9 (p-Ph), 133.7 (C5), 136.3 (C7), 136.9 (C1), 143.6 (C8a), 148.4 (C8), 149.5 (C4), 149.9 (C3a), 152.6 (C6), 153.7 (C3') ppm; [ESI]: 359 [M+1]; Found: C, 70.39; H, 5.07; N, 15.62. Molecular formula: $C_{21}H_{18}N_4O_2$ requires: C, 70.38; H, 5.06; N, 15.63; O, 8.93.

Electrochemical experiments

Electrochemical experiments were performed by cyclic voltammetry, as well as differential pulse voltammetry in a conventional three-electrode cell under argon atmosphere at 20 °C using a LPG603-Potentiostat Bank E potentiostat. The CV was conducted at 0.1 V/s and the DPV curves were recorded at 10 mV/s with a pulse height of 25 mV and a step time of 0.2 s. The working electrode was a glassy carbon disk (2 mm in diameter) polished with 200 mm diamond paste before each experiment. The Ag/AgCl system was used as reference electrode. All the potentials were referred to the potential of ferrocene/ferricinium (Fc/Fct) couple, which in our experimental conditions was 0.442 V.

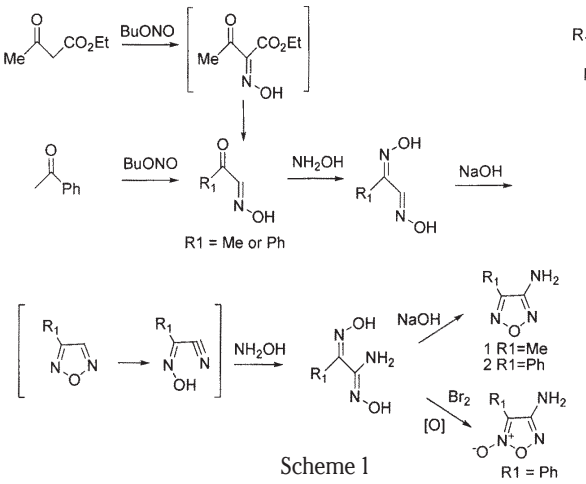
Results and discussions

Diazene synthesis

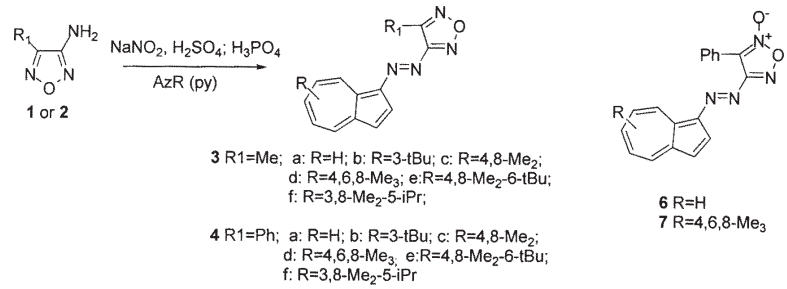
3-aminofurazans being not commercially available, must be prepared; their synthesis of was reviewed by Andrianov and Eremeev [18]. The derivatives substituted at 4 position were obtained by the heterocycle building as described in Scheme 1 for 3-aminofurazan with methyl or phenyl in this position, compounds **1** and **2**. 3-Aminofuroxanes have been also obtained as described in literature [2] (scheme 1).

Because of the low basicity of 3-aminofurazans and 3-aminofuroxanes and due to instability of their diazonium salts, the diazotization was carried out in a mixture of sulfuric and phosphoric acids, using nitrosyl sulfate [16], [19, 20]. Then, the diazonium salts coupling with azulenes was achieved by adding a solution of azulene in pyridine for the buffering of the reaction medium, scheme 2. The diazenes were obtained as dark brown solid in the yields reported in table 1.

As results from table 1, the yields are higher starting from 3-aminofurazan that contains the methyl group, richer



Scheme 1



Scheme 2

Compound	a	b	c	d	e	f
3	40	40	42	41	42	45
4	35	31	20	27	24	40

Table 1
THE DIAZOTIZATION AND COUPLING YIELDS (IN % TOWARD USED AZULENES)

Atom No	3a	3c	3d	3e	3b	3f
1 (C)	-0.1548	-0.1561	-0.1575	-0.1577	-0.1564	-0.1548
2 (C)	-0.0472	-0.0547	-0.0598	-0.0745	-0.0472	-0.0534
3 (C)	-0.2185	-0.2241	-0.2226	-0.2145	-0.1448	-0.1667
3a (C)	-0.0133	-0.0303	-0.0399	-0.0567	-0.0190	-0.0277
4 (C)	-0.0024	0.0340	0.0456	0.0560	-0.0367	-0.0333
5 (C)	-0.1478	-0.1541	-0.1605	-0.1617	-0.1472	-0.0796
6 (C)	-0.0562	-0.0483	0.0248	0.0339	-0.0561	-0.0490
7 (C)	-0.1434	-0.1609	-0.1690	-0.1572	-0.1483	-0.1546
8 (C)	-0.0355	0.0798	0.0804	0.0484	-0.0055	0.0720
8a (C)	-0.0314	-0.0166	-0.0130	0.0190	-0.0137	-0.0080
A (N)	-0.0080	-0.0099	-0.0108	-0.0094	-0.0091	-0.0116
B (N)	-0.0752	-0.0813	-0.0836	-0.0833	-0.0748	-0.0819
1' (O)	-0.0265	-0.0256	-0.0280	-0.0282	-0.0299	-0.0299
2' (N)	-0.0008	-0.0096	-0.0102	-0.0100	0.0023	-0.0062
3' (C)	-0.0947	-0.0905	-0.0892	-0.0889	-0.0947	-0.0894
4' (C)	-0.0881	-0.0888	-0.0899	-0.0907	-0.0906	-0.0930
5' (N)	-0.0230	-0.0256	-0.0251	-0.0250	-0.0299	-0.0207
Me-4' (C)	-0.1569	-0.1563	-0.1565	-0.1562	-0.1579	-0.1576

Table 2
NET ATOM CHARGES OF DIAZENES **3**

in electron density, than from the corresponding amine with a phenyl substituent. If the work-up of the products was carried out by precipitation, as described in the literature, higher yields were obtained. However, the NMR spectra of the products showed the presence of impurities (probably nitrosated azulene and azulenic polymers). Therefore, it was necessary a further purification by column chromatography although the product could be partially destroyed decreasing the obtained yields.

We have also tested the diazotization of the 3-amino-4-phenylfuroxan, **5**, and its coupling with azulene and 4,6,8-trimethylazulene. The overall yields for the resulted diazenes **6** and **7**, shown in scheme 2 (11 and 13 % respectively), were far below the yields obtained for the corresponding furazan diazenes, **4a** or **4d**. It should be noted that, together with the obtained products, were also generated in a low extent correspondent deoxygenated compounds, namely the furazan diazenes **4a** or **4d**.

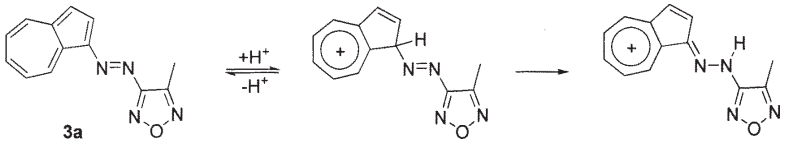
Properties of diazenes

Net atom charges and energies of frontier orbitals

In the aim to predict or to explain some of the diazenes properties we have undertaken calculations of the net atom charges and of frontier orbitals energies using a semiempirical molecular orbital package – MOPAC v9.0

	3		4	
	HOMO (eV)	LUMO (eV)	HOMO (eV)	LUMO (eV)
a	-8.300	-1.605	-8.340	-1.599
b	-8.226	-1.578	-8.257	-1.567
c	-8.175	-1.591	-8.213	-1.542
d	-8.120	-1.540	-8.175	-1.530
e	-8.103	-1.534	-8.116	-1.480
f	-8.013	-1.576	-8.021	-1.471

Table 3
THE ENERGIES OF THE FRONTIER ORBITALS FOR DIAZENES **3** AND **4**



Scheme 3

Compound	**a**	**c**	**d**	**e**	**b**	**f**
3	429	434	438	439	454	471
4	438	442	446	457	457	472
6	458	-	466	-	-	-

Table 4
THE ABSORPTION MAXIMA IN VISIBLE FOR COMPOUNDS **3**, **4** AND **6** (in nm)

Solv	nC_5	Dioxane	Benzene	$CHCl_3$	DCM	MeOH	DMF	MeCN	DMSO
ε*	2.02	2.25	2.27	4.81	8.93	32.7	36.7	37.5	46.7
3d	427	434	437	440	439	439	441	436	445
4d	436	443	447	448	449	446	451	447	453
7	457	463	465	469	469	466	471	465	474

* Dielectric constants for the used solvents.

Table 5
SOLVATOCHROMIC EFFECT OF **3d**, **4d** AND **7**

program with a semiempirical Hamiltonian-AM1 method and the results are detailed in the tables 2 and 3.

Analyzing data contained in table 2, it can be concluded that the nitrogen atoms possess low net charges, which prevent their easily protonation. In acidic medium, the proton rather attacks reversibly the azulenic moiety at the most negative charged position 1 or 3 with the generation of stable tropylium system, scheme 3. When it binds at 1-position, the furazandiazonium ion can be eliminated as an electrophilic leaving group, making these compounds unstable at very low *p*H values, as it was observed during our researches. From the calculated data results a significant acidity of methyl in 4-position of furazane. This fact creates premise to use this property in condensation reactions.

To further understand the electrochemical properties of the molecular synthesized materials, the frontier orbitals energies of compounds **3** and **4** were calculated as is described in table 3.

Electronic spectra

The described compounds are brown solids and their solutions are yellow colored. As in all azulenic derivatives, the alkyl substitution of the azulene moiety generated a bathochromic effect (table 4) due to increase of the molecules polarization. The gap of the absorption maxima in visible region deepens with both the number of alkyl substituents and their bulk.

The electronic effect of the methylfurazan moiety in diazene **3a** is close to that exerted by the 4-chlorophenyl group in the similar (azulen-1-yl) diazene (λ= 424 nm), being a less electron withdrawing group than 4-nitrophenyl (λ = 454 nm) [21]. Replacing the methyl group belonging to the furazan ring with phenyl, a bathochromic gap of 9 nm was observed possible due to the expansion of the π-electrons conjugation.

The higher polarization of furoxan derivatives **6**, produced by the higher electron withdrawing properties of this group, increases the absorption maxima of the visible wavelength, which value becomes similar with that observed for the 4-nitrophenyl group.

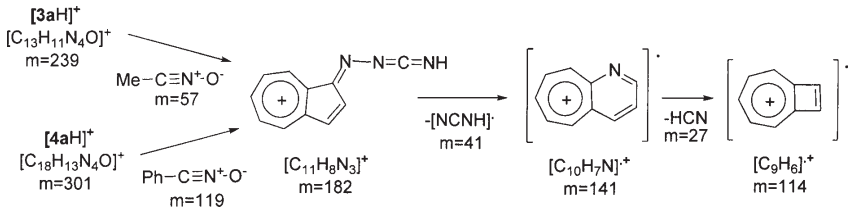
The structurally characteristics of the studied compounds suggested the hyperpolarizability of their electronic charges and thus the possibility to use them as NLO-materials. Several classes of azulenyl-containing compounds have already been studied from this point of view [10]. Because the hyperpolarizability can be reflected by an efficient solvatochromism, we have studied this latter property of the obtained compounds. Although it is clear that they present a positive solvatochromic effect, the change in the visible absorption maxima are rather modest varying between 424-447 nm according to the used solvent (the data provided in table 5 are for the compounds **3d**, **4d** and **7** with satisfactory solubility). A similar behaviour is observed also for the corresponding furoxans.

As already noted, the azulenyl-diazenyl furazans **3** and **4** are very weak bases with the higher electronic density at the azulenic C1 or C3, which can be protonated only at the *p*H < 0. However, the protonation at C1 or C3 destroys the azulenic chromophore, the main band from visible (472

Compound	H2	H3	H4	H5	H6	H7	H8
AzN_2thi^*	8.36	7.41	8.31	7.40	7.78	7.52	9.19
3a	8.35	7.48	8.44	7.54	7.90	7.64	9.16
4a	8.30	7.46	8.41	7.51	7.86	7.55	9.08
6	8.22	7.46	8.37	7.49	7.85	7.55	9.01

*2-(Azulen-1-yldiazenyl)-thiazole.

Table 6
CHEMICAL SHIFTS FOR PROTONS OF THE MAIN COMPOUNDS **3a, 4a** AND **6** AND OF THIAZOLE DIAZENE



Scheme 4

nm for **3f**) moving into near ultraviolet region (362 nm). This could be a sign that in thermodynamic conditions, the proton jumps on nitrogen near heterocycle stabilizing the hydrazone tautomeric form of the generated ion (scheme 3).

NMR spectra

The chemical shifts of the azulenyl protons and the carbon atoms in compounds **3** and **4** show similarities with those of the corresponding atoms in other azulen-1-yl diazenes, for example with 2-(azulen-1-yldiazenyl)-thiazole [11]. The deshielding effect of the heteroaromatic moiety on the protons bounded to the largest azulenic ring is higher for furazan than for thiazole (table 6). The substitution of the methyl group with a phenyl in the furazan or furoxan moieties induces a very slight shielding of the azulenic protons.

More interesting seems to be the position of carbon atoms signals of the heterocycle ring in the ^{13}C-NMR spectra. The signals attribution was realized using the coupling constants between the protons belonging to furazan methyl group and furazan carbon atoms. Their chemical shifts are very close to those already reported for other aryldiazenyl furazans, namely 163.8 ppm for C3' and 148.6 ppm for C4' (for positions assignment see Cap. 2.2) [22]. The presence of a phenyl group in 4-position does not disturb significantly the chemical shifts of atoms C3' or C4' (162.9 and 150.7 ppm, respectively).

More complicated becomes the attribution of ^{13}C signals in the case of the furoxan moiety in compound **6**. There is no information on the ^{13}C-NMR spectra of arylazofuroxans substituted with methyl or phenyl groups at the heterocycle, the characterization of these compounds being made only based on the ^{1}H-NMR spectra [20]. However, it is known that in diarylfuroxans the chemical shift of the carbon atom next to $N^+ \rightarrow O$ group is shielded with 42 ppm if compared with that of the corresponding furazan carbon atom. The same observation is right for the nitro-arylfuroxans being, thus, general for all substituted furoxans [23]. The chemical shift of C4' drops with almost 41 ppm passing from furazan dye, **4a** to furoxan **6a**, while the value for C3' decreases from 162.9 ppm for **4a** only to 153.5 ppm for **6a.** This is an evidence that C4' has the close position to $N^+ \rightarrow O$.

Mass spectra

Usually, the fragmentation of molecular protonated ions of the azulen-1-yl diazenes, occurs between the azo group and one of the azo group substituents, as well as, between the two nitrogen atoms [24]. As a peculiarity of the corresponding furazan derivatives, the first splitting of protonated molecular ion affects the furazan ring (fig. 1) due to its instability and also due to the low charge density at the nitrogen atoms in molecules. Thus, as described in Scheme 4 for the compounds **3a** and **4a**, the fragmentation at 20 eV starts with the heterocycle splitting and elimination of Me-Ca≡N→ O (57) respectively Ph-Ca≡N→ O (119) [18], [25]. Form the cation thus obtained, the following fragmentation of radical [NCNH]· (41) generates the radical cation $[C_{10}H_7N]^{\cdot +}$**.** It should be emphasized the occurrence of radical cation $[AzN]^{\cdot +}$ for all fragmentation of compounds **3** and **4** as well as in the mass spectra of other azulen-1-yl diazenes [25]. Finally, the radical cation eliminates HCN (27) as can be seen in scheme 4 and figure 1. When the compound contains alkylated azulene some dealkylations can interfere with the second fragmentation step.

Electrochemical behaviour

Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) experiments were performed in acetonitrile containing tetrabutylammonium perchlorate (TBAP). The general feature of all studied compounds consists in the irreversibility of redox processes despite

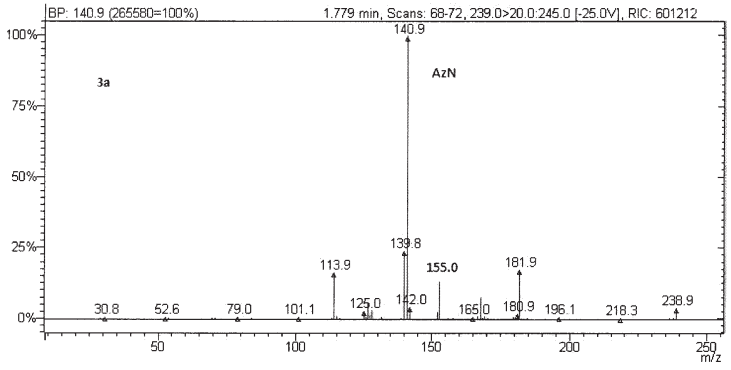
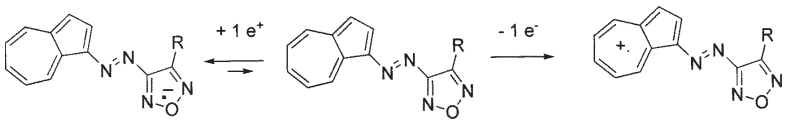


Fig. 1. Fragmentation of molecular ion for diazene **3a**



Scheme 5

Compound	Oxidation potentials	Reduction potentials
3a	0.793; 1.055; 1.580	-1.285; -1.450; -1.545; -2.258
3c	0.730; 0.967; 1.280sh; 1.643	-1.290; -1.482; -2.208; -2.258
3d	0.668; 0.905; 1.705; 1.930	-1.325; -1.495; -2.183; -2.345; -3.108
3e	0.655; 0.768; 0.905; 1.193; 1.718; 1.917	-1.330; -1.520; -2.145; -2.370; -2.970
3b	0.767; 1.093	-1.300; -1.445; -2.195; -2.433; -2.970
3f	0.605; 1.105; 1.293; 1.530; 1.868	-1.345; -1.830; -2.230; -2.285
4a	0.815; 0.930; 1.095	-1.256; -2.145; -2.445; -2.645; -2.770
4c	0.730; 1.130; 1.530	-1.287; -2.158; -2.270; -2.633; -2.858
4d	0.701; 0.868; 0.955; 1.105; 1.718; 1.918	-1.295; -1.420; -2.133; -2.345; -2.683; -2.795
4e	0.655; 0.992; 1.117; 1.217; 1.292; 1.705; 1.930	-1.308; -2.295; -2.408; -2.670; -2.833
4b	0.768; 0.993; 1.218; 1.293; 1.605	-1.270; -1.670; -2.158; -2.557; -2.783
4f	0.592; 0.780; 1.355; 2.018	-1.320; -2.215; -2.320; -2.358; -2.808
6a	0.715; 0.870; 1.230; 1.605	-1.283; -1.858; -2.183; -2.458

Table 7
REDOX POTENTIALS (DPV) OF THE COMPOUNDS **3, 4, 6** DETERMINED TOWARD Fc/Fc^+

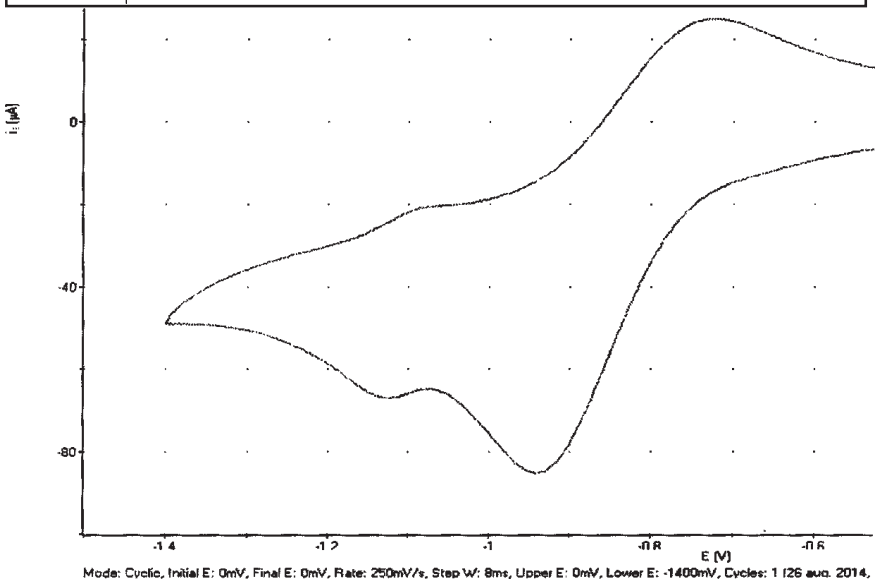


Fig. 2. CV for the quasireversible first electron reduction of azuleneazofurazan, **3**e

the quite reversibility of the first reduction step mainly at low current speeds (5-10 mV/s). The more substituted with alkyl group is the azulenyl moiety the faster is the compound oxidized and the hardest it is reduced.

The oxidation takes place at azulenyl moiety and occurs faster, at 1.1-1.2 V, with the generation of radical cation and then of dication. At higher potentials, the molecules are destroyed with the formation of polyoxygenated oligomers. Because the numerous decay products formed as intermediates, these potentials are distributed randomly.

On contrary, the reduction is more probable to take place at furazanic moiety, the first reduction potential being quasi reversible, especially at low rates (fig. 2). In addition, in this case the upper reduction peaks are not well defined because of the multitude of possibilities for reductive decomposition of compounds.

The replace of furazan ring with furoxan should decrease the reduction potential and increase the oxidation ones, however the lower stability of the last moiety lowered both first potentials for the compounds **6** as compared with **3** despite the values are not very different.

All furazan compounds **3** and **4** show quite good correlations between the values of the frontier orbitals and those of the reduction and oxidation potentials, as can be seen in figure 3.

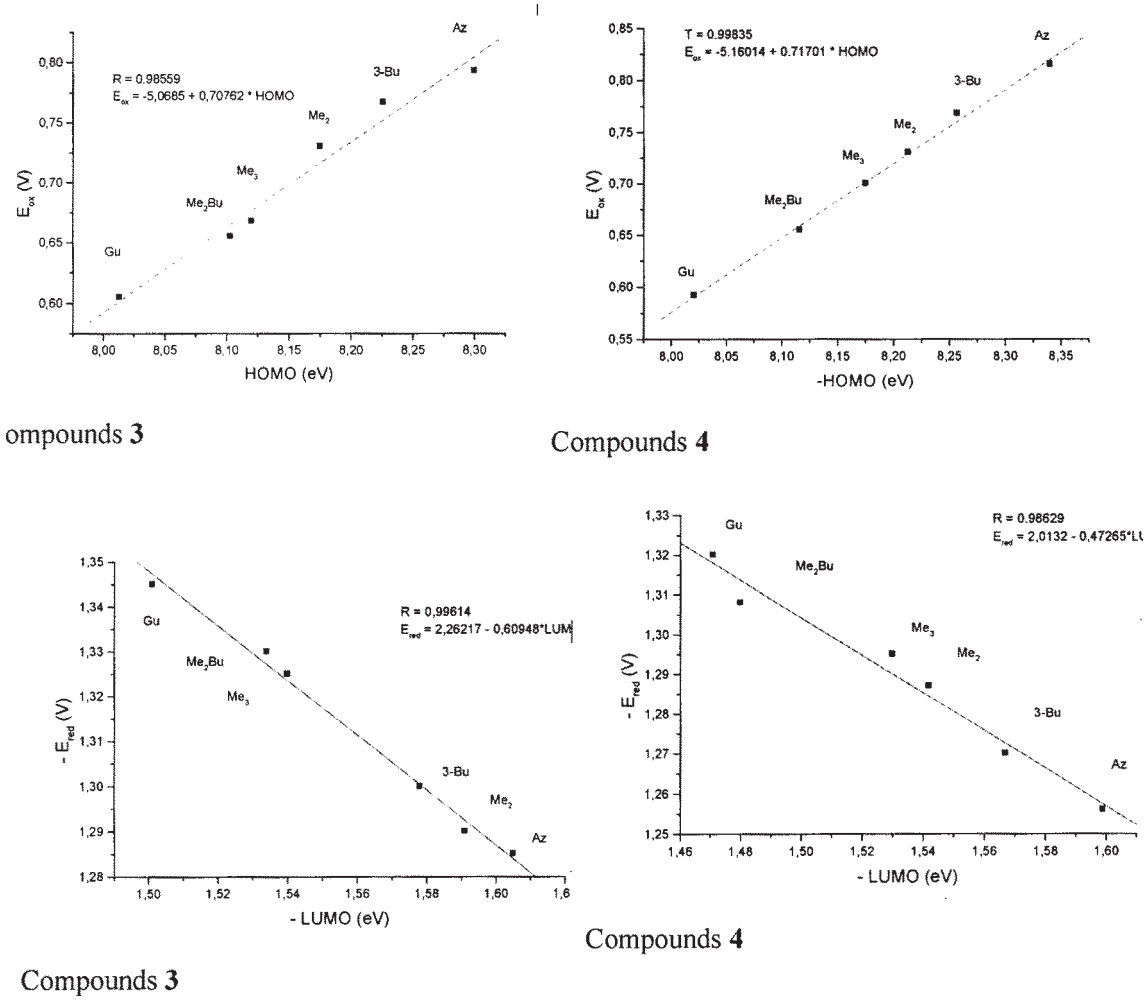


Fig. 3. The correlation between frontier orbital energies and the experimental oxidation (A) and reduction (B) peak potentials (obtained by DPV) of the compounds **3** and **4**

Conclusions

The unknown (azulen-1-yldiazenyl)-heteroaromatic compounds classes with furazan and furoxan moieties as heterocycle partners were studied. The peculiarity of the investigated compounds consists in the reduced stability of the heterocycle, which can be easily destroyed during the diazotization and coupling sequence. Nevertheless the azulenes are enough reactive to couple with their diazonium salts before the decomposition. The synthesis yields of (azulen-1-yldiazenyl)-furazans **3** and **4** are satisfactory; however, for the furoxan diazenes **6** and **7** poor yields were obtained. The methyl substitution of furazan stabilizes better the intermediate diazonium salt affording higher coupling yields than those obtained for phenyl substituent. The sensibility of the diazotized furoxanamines in the presence of reducible systems dramatically decreases the yields of diazotization-coupling sequence as compared with the compounds with furazane moiety. The reduced stability of heterocycle ring in all compounds studied was reflected also in the peculiar compounds fragmentation in the mass spectrometer where the heterocycle split represents the first molecular ion fragmentation. At the same time, all compounds are thermally instable and their melting occurred with decomposition, violent in some cases. Like other (azulen-1-yl diazenyl) heteroaromatic compounds, these combinations are extremely poor bases being protonated at electron rich azulenic carbon atoms with the dramatic modification of the chromophore. The oxidation and reduction potentials were investigated, especially as DPV experiments and their values were successfully correlated with the frontier orbital energies.

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