New (azulen-1-yldiazenyl)-heteroaromatic Compounds Containing 1,3,4-thiadiazole -3-yl Moieties

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*(E)-2-(Azulen-1-yldiazenyl)-1,3,4-thiadiazoles, unsubstituted or substituted either at azulen-1-yl moiety or at 5-position of thiadiazole ring were synthesized. Among the acids used as diazotization medium, dichloroacetic acid was the best choice. In several cases the by-products such as thioether **9** were isolated along with the normal coupling derivatives. The generated products were characterized and their MS and UV-vis spectra discussed. A computational study on (E)-2-(azulen-1-yldiazenyl)-1,3,4-thiadiazoles was undertaken based on density functional theory (DFT) to determine frontier orbital energies and other physical properties. The absorption maxima and the basicity of the new compounds are close to those of the corresponding diazenes containing thiazole, previously described. They have brick color in neutral medium and violet in strong acidic solutions. The redox potentials were also determined remarking the influence of the substituents on these potentials.*

Keywords: Azulene; diazene; thiadiazoles; azo coupling; isosbestic point; reduction and oxidation potentials

Numerous diazenes containing heterocycles have been prepared due to their easy availability and to their promising technical properties as dyes. Another important aspect is represented by the higher stability and lack of the toxicity of the compounds. Therefore, some of the obtained diazenes were studied for their biological properties as: anti-bacterial, anti-viral, anti-inflammatory or analgesic activities. An important heterocycle system largely used in diazenes structure was 1,3,4-thiadiazole, which can be readily obtained and is stable [1]. The building of numerous derivatives of this heterocycle with various arylazo substituents was reported [2,3] as well as their use as dyes [4-10] or in biological purposes [11,12] (antimicrobial and antifungal) [13], cytotoxicity against ascites carcinoma tumor cells [14]. Some cationic dyes were obtained by alkylation of the dyes containing strong electron donating groups (EDGs), like R_2N on the thiadiazole ring [15]. The introduction of azulene-1-yl moiety as the second component of heteroaryl diazenes significantly extends the molecular electronic system. An important number of (azulen-1-yl)-azo derivatives containing heterocycles have been prepared by our group in the aim to study their synthesis, physical and chemical properties and to find possible technical applications. Thus were investigated azulene-1-azopyridines and azopyranylium salts [16], azulene-1-azopyridine 1'-oxides [17], azulene-1-azo-2-thiazoles [18,19], azulene-1-azo-2-benzothiazol [20,21] and azulene-1-azo-1,2,5-oxadiazol [22]. On the other hand, the electron donor property of azulene-1-yl moiety can be used to afford push-pull systems especially when at the other end of nitrogen double bond there is an acceptor as a positive charged heterocycle [23]. The large use of diazenes containing 1,3,4-thiadiazole group together with the extended interest on azulene derivatives stimulated us to turn our attention to build diazenes with both these moieties and to examine some of their properties.

Experimental part

Materials and instrumentation

Melting points (uncorrected) were measured with Kofler apparatus (Reichert Austria). Elemental analyses were performed using Perkin Elmer CHN 240B. UV-Vis 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 ^{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) spectrometers were 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. The DCM was distilled over CaH_2 and the ether was preserved on sodium. Acetonitrile (Rathburn, HPLC grade), tetra-n-butylammonium perchlorate (TBAP) and tetra-n-butylammonium fluoroborate (TBABF4) from Fluka were used as received like solvent and supporting electrolytes, respectively. All potentials were referred to the potential of ferrocene/ferrocenium (Fc/Fc^+), which was 0.424 V vs Ag+/AgCl(std). Anodic and cathodic DPV curves were recorded individually, starting from the stationary potential. Concentration of diazenes was 10^{-3} Min acetonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (i.d. 1.6 mm), scan rate = 100 mVs^{-1}. The starting 5-substituted 1,3,4-thiadiazoles-2-amines, **1**Q, where Q is described in scheme 1 were commercially available. The known amine 1(Nf) with 1-naphthyl in position 5 [24] was obtained on the route described in scheme 1 from the corresponding carboxylic acids and thiosemicarbazide (1-(aminomethyl)thiourea), **2**, in the presence of dehydrating agent. The compounds nomenclature was obtained by the CambridgeSoft package of structure-to-name algorithm included with ChemBioDraw Ultra 11.0.

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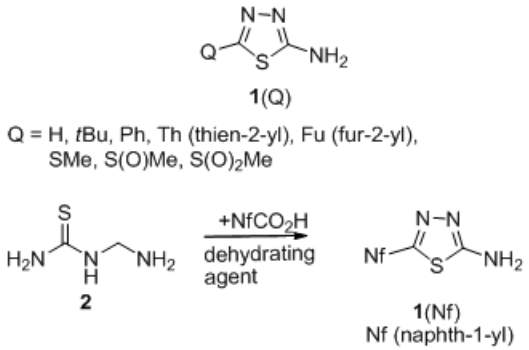


Scheme 1. Starting 5-substituted 1,3,4-thiadiazoles-2-amines

Diazotization and coupling of 2-amino-5-substituted-1,3,4-thiadizole, ***1(Q)***

Synthesis of compounds **5**(Ph) - **7**(Ph)

To a stirred mixture of phosphoric acid 85% (0.4 mL) and nitric acid 63% (0.4 mL), cooled to 0 °C, 2-amino-5-phenyl-1,3,4-thiadiazole, **1**(Ph) (177 mg, 1 mmol) was added at such a rate as to avoid overheating. The diazonium salt, orange colored, was obtained by the addition of solid sodium nitrite (69 mg, 1 mmol). After stirring at 0 °C for 10 minutes the viscous mixture was poured into a well stirred solution of azulene, **4**a-c, (1 mmol) and a large excess of sodium acetate (5.5 g, 67 mmol) in methanol (20 mL) also cooled to 0 °C. The coupling reaction takes place in 30-40 minutes the color of reaction mixture changing from blue to red. After reaching room temperature DCM (50 mL) and water (50 mL) were added. The organic layer was separated and washed two times with water and then dried on sodium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel obtaining diazene **5**(Ph) - **7**(Ph) in yields shown in Table 1. Generally, at the chromatography of resulted mixture in this reaction, as well as in the following synthesis, the first collected fraction contained unreacted azulene.

Synthesis of compounds ***5****(SMe)* - **7***(SMe)*

To a stirred solution of 2-amino-5-methylthio-1,3,4-tiadiazole, **1**(SMe) (147 mg, 1 mmol) in dichloroacetic acid (1.2 mL), cooled to 0 °C, solid sodium nitrite (69 mg, 1 mmol) was added and the diazonium salt was kept for 5-10 minutes at 0 °C. The diazonium salt was added to a well stirred solution of azulene, **4**a-c, (1 mmol) and sodium acetate (3.0 g, 36 mmol) in methanol (20 mL) cooled at 0 °C. The work up was similar with that previously described and the yields of resulted diazenes **5**(SMe) - **7**(SMe) are shown in table 1.

Synthesis of compounds ***5****(Th)* and ***5****(Fu)*

To a stirred solution of phosphoric acid 85% (0.75 mL), cooled to 0 °C, 2-aminothiadiazole, **1**(Th) or **1**(Fu) (1 mmol), was added at such a rate as to avoid overheating. The diazonium salt was generated by the addition of solid sodium nitrite (69 mg, 1 mmol). After manually stirring at 0 °C for 10 minutes, the viscous mixture was poured under strong magnetically stirring into the solution of azulene, **4**a, (128 mg, 1 mmol) and sodium acetate (5.6 g, 68 mmol) in methanol (20 mL) also cooled to 0 °C. The coupling reaction takes place in 30-40 minutes in which the reaction mixture turns from blue to red. Then it was let to reach the room temperature and DCM (50 mL) and water (50 mL) are added. The organic layer was separated and washed two times with water and then dried on sodium sulfate. The solvent was evaporated and the residue chromatographed on silica gel using DCM for azulene elution and a mixture DCM-AcOEt (with ester gradient from 5 to 20%) for next fractions. The third, brown band, represented the desired product (the other bands contained unknown mixtures in very small amounts). The yields in products **5**(Th) and **5**(Fu) are shown in table 1.

Synthesis of compounds ***5****(t-Bu)*

To a stirred solution of 2-amino-5-*tert*-butyl-1,3,4-tiadizole, **1**(*t*-Bu) (157 mg, 1 mmol) in dichloroacetic acid (1.2 mL), cooled to 0 °C, solid sodium nitrite (138 mg, 2 mmol) was added. The mixture was kept for 5-10 min at this temperature and added to a solution of azulene (128 mg, 1 mmol) and sodium acetate (3.0 g, 36 mmol) in methanol (20 mL) cooled 0 °C and strongly stirred. After stirring for 30-40 min at 0 °C the work up was similar with that previously described but alumina was used for chromatography. Azulene was recovered from the column followed by diazene **5**(*t*-Bu) as a brown band in the yield shown in table 1.

Synthesis of compounds ***5****(H)*

Working in the same reaction conditions as above, the chromatography of reaction mixture gave 73% recovered azulene followed by (*E*)-2-(azulen-1-yldiazenyl)-1,3,4-thiadiazole, **5**(H), 23%.

Synthesis of compounds **5(**S(O)Me) by coupling

5-(Methylsulfinyl)-1,3,4-thiadiazol-2-amine, **1**(S(O)Me), (163 mg, 1 mmol) was suspended in phosphoric acid 85% (1.19 g, 0.69 mL, 11.9 mmol) and cooled to 0° C. Then solid sodium nitrite (69 mg,1 mmol) was added portion wise with stirring to the milky suspension and keep 15 min at 0° C. The color turned from pale yellow to orange. This viscous material was added portion wise to a solution of azulene (128 mg, 1 mmol) and sodium acetate (3.0 g, 36 mmol) in methanol (20 mL) during 5 min under vigorous stirring. The color of the solution turns from blue to violet. After 1 hour of stirring the solution was diluted with water and the product was extracted in DCM. The organic phase was washed with water, dried on sodium sulfate, filtered and the solvent was evaporated. The residue was chromatographed on silica gel column and DCM was used for the elution of unreacted azulene (93 mg, 75%) and DCM-EtOAc (ester gradient from 5 to 100%) for the next fractions. The desired product, **5(**S(O)Me), resulted in 60 mg, yield 20%.

Synthesis of compounds **5(**S(O)Me) by oxidation

The diazene **5**(SMe) 143 mg (0.5 mmol) and sodium periodate 428 mg (2 mmol) in methanol (26 mL) and water (16 mL) were refluxed for 3 h. Then the methanol was partially evaporated and DCM (50 mL) and water (50 mL) are added. After layers separation, the organic solution was washed again with water (50 mL) and dried on sodium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel and eluted with a mixture DCM-AcOEt in increasing amounts, then AcOEt and AcOEt-MeOH (9:1 in %). The first collected fraction, brown colored, 81 mg (57%), was the starting material, **5**(SMe) and the second reddish-brown fraction, 54 mg (36%), represented the desired product **5(**S(O)Me).

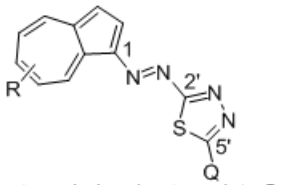
Synthesis of compounds **5(**$S(O)_2$Me) by oxidation

The diazene **5**(SMe) 143 mg (0.5 mmol) and sodium periodate 428 mg (2 mmol) in dioxane (8 mL) and water (5 mL) were refluxed for 5 h. Then the solvent partially evaporated and DCM (50 mL) and water (50 mL) were added. After layers separation, the organic solution was washed again with water (50 mL) and dried on sodium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel and eluted with a mixture

DCM-AcOEt in increasing amounts, then AcOEt and AcOEt-MeOH (9:1 in %). The first collected fraction, brown colored, 68 mg (48%) was **5**(S(O)$_2$Me) and the second, reddish-brown fraction, 68 mg (45%) was the compound **5**(S(O)Me).

Products characterization

The atoms numbering were assigned as in scheme 2.



The atoms belonging to moiety Q receive the indicative Q"

Scheme 2. Atoms numbering

*(E)-2-(Azulen-1-yldiazenyl)-1,3,4-thiadiazole, **5**(H)*

Brown crystals, m. p. 77 ºC. UV-vis (MeOH) λ_{max} (log ε): 223 (4.22), 281 (4.05), 346 (3.80), 476 (4.35) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, ^{3}J = 4.7 Hz, 1 H, 3-H), 7.52 (t, ^{3}J = 9.7 Hz, 1 H, 5-H), 7.66 (t, ^{3}J = 9.8 Hz, 1 H, 7-H), 7.89 (t, ^{3}J = 9.8 Hz, 1 H, 6-H), 8.36 (d, ^{3}J = 4.7 Hz, 1 H, 2-H), 8.40 (d, ^{3}J = 9.4 Hz, 1 H, 4-H), 9.00 (s, 1 H, 5'-H), 9.19 (d, ^{3}J = 9.8 Hz, 1 H, 8-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 122.9 (C-3), 127.1 (C-2), 130.1 (C-1, C-5), 130.2 (C-7), 136.0 (C-8), 139.5 (C-4), 140.8 (C-6), 144.3 (C-8a), 146.9 (C-3a), 150.6 (C-5'), 181.2 (C-2') ppm. IR (neat): 750, 847, 1188, 1228, 1266, 1315, 1343, 1460, 1484, 1570, 2358, 2849, 2917, 3075 cm^{-1}. MS [ESI]: 241 [M+1]. Calcd. for $C_{12}H_8N_4S$: C, 59.98; H, 3.36; N, 23.32. Found: C, 60.01; H, 3.39; N, 23.30.

*(E)-2-(Azulen-1-yldiazenyl)-5-phenyl-1,3,4-thiadiazole, **5**(Ph)*

Brown crystals, m. p. 258 ºC. UV-vis (MeOH), λ_{max} (log ε): 228 (5.06), 290 (4.07), 343 (3.82), 345 (3.82), 347 (3.82), 356 (3.77), 498 (4.41) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.46-7.51 (m, 4 H, 3-H, 3"-H and 4"-H), 7.54 (t, ^{3}J = 9.7 Hz, 1 H, 5-H), 7.66 (t, ^{3}J = 9.9 Hz, 1 H, 7-H), 7.89 (t, ^{3}J = 9.9 Hz, 1 H, 6-H), 8.04-8.09 (m, 2 H, 2"-H), 8.38 (d, ^{3}J = 4.8 Hz, 1 H, 2-H), 8.39 (d, ^{3}J = 9.2 Hz, 1 H, 4-H), 9.22 (d, ^{3}J = 9.5 Hz, 1 H, 8-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 123.1 (C-3), 127.2 (C-2), 128.0 (C-2" and C-6"), 129.2 (C-3" and C-5"), 130.0 (C-5), 130.1 (C-7), 131.0 (C-1"), 131.3 (C-4"), 136.2 (C-8), 139.6 (C-4), 140.9 (C-6), 144.7 (C-8a), 146.9 (C-3a), 166.8 (C-5'), 181.7 (C-2') ppm. IR (neat): 680, 750, 778, 859, 1198, 1240, 1268, 1317, 1410, 1455, 1491, 1573, 2360, 2849, 2917, 2955, 3026 cm^{-1}. MS [ESI]: 317 [M+1].Calcd. for: $C_{18}H_{12}N_4S$: C, 68.33; H, 3.82; N, 17.71. Found: C, 68.35; H, 3.84; N, 17.70.

*(E)-2-(4,6,8-Trimethyl-azulen-1-yldiazenyl)-5-phenyl-1,3,4-thiadiazole, **6**(Ph)*

Brown crystals, m. p. 236 ºC. UV-vis (MeOH), λ_{max} (log ε): 203 (4.45), 236 (4.49), 261 (4.31), 307 (4.13), 310 (4.13), 312 (4.13), 512 (4.53) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 2.70 (s, 3 H, Me_6), 2.88 (s, 3 H, Me_4), 3.27 (s, 3 H, Me_8), 7.40 (d, ^{3}J = 5.0 Hz, 1 H, 3-H), 7.40 (s, 1 H, 5-H), 7.48-7.50 (m, 3 H, 3"-H and 4"-H), 7.52 (s, 1 H, 7-H), 8.04-8.07 (m, 2 H, 2"-H), 8.26 (d, ^{3}J = 5.1 Hz, 1 H, 2-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 25.71 (Me_4), 28.79 (Me_8), 29.87 (Me_6), 121.3 (C-3), 124.1(C-2), 127.9 (C-2"-C-6"), 129.2 (C-3"-C-5"), 134.6 (C-5), 136.9 (C-7), 131.1 (C-4"), 131.2 (C-1"), 148.8 (C-8), 149.7 (C-4), 151.0 (C-6), 144.6 (C-8a), 148.4 (C-3a), 166.1 (C-5'), 181.7 (C-2') ppm. IR (neat): 688, 725, 760, 792, 847, 995, 1068, 1111, 1188, 1204, 1227, 1267, 1285, 1351, 1368, 1407, 1441, 1498, 1574, 2340, 2361, 2957 cm^{-1}. MS [ESI]: 359 [M+1].]. Calcd. for $C_{21}H_{18}N_4S$: C, 70.36; H, 5.06; N, 15.63. Found: C, 70.32; H, 5.08; N, 15.64.

*(E)-2-(3,8-Dimethyl-5-isopropyl-azulen-1-yldiazenyl)-5-phenyl-1,3,4-thiadiazole, **7**(Ph)*

Brown crystals, m. p. 210 ºC. UV-vis (MeOH), λ_{max} (log ε): 205(4.39), 236 (4.38), 289 (4.22), 291 (4.22), 368 (3.85), 536 (4.41) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ1.41 (d, ^{3}J = 6.9 Hz, 6 H, Me_{iPr}), 2.58 (s, 3 H, Me_3), 3.16 (hept, ^{3}J = 6.9 Hz, 1 H, CH_{iPr}), 3.28 (s, 3 H, Me_8), 7.48 (m, 3 H, 3"-H and 4"-H), 7.57 (d, ^{3}J = 10.8 Hz, 1 H, 7-H), 7.63 (d, ^{3}J = 10.8 Hz, 1 H, 6-H), 8.05-8.07 (m, 2 H, 2"-H), 8.21 (s, 1 H, 2-H), 8.23 (s, 1 H, 4-H). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.19 (Me_3), 24.32 (Me_{iPr}), 29.66 (Me_8), 38.41 (*C*$(Me)_2$), 132.0 (C-1),127.0 (C-2), 127.7 (C-2"-C-6"), 129.0 (C-3"-C-5"), 130.8 ((C-4"), 131.2 (C-1"), 135.6 (C-7), 135.9 (C-4), 137.2 (C-6), 139.2 (C-3), 146.2 (C-5), 146.6 (C-8a), 150.0 (C-3a), 150.3 (C-8), 165.6 (C-5'), 182.3 (C-2'). IR (neat): 685, 760, 819, 854, 913, 961, 1035, 1089, 1163, 1206, 1241, 1265, 1293, 1398, 1415, 1456, 1546, 1696, 2043, 2191, 2339, 2361, 2852, 2920, 2959, 3379 cm^{-1}. MS [ESI]: 387 [M+1].Calcd. for $C_{23}H_{22}N_4S$: C, 71.47; H, 5.73; N, 14.49. Found: C, 71.45; H, 5.79; N, 14.50.

*(E)-2-(Azulen-1-yldiazenyl)-5-(methylthio)-1,3,4-thiadiazole, **5**(SMe)*

Brown crystals, m. p. 197 ºC. UV-vis (MeOH), λ_{max} (log ε): 224 (4.31), 291 (4.10), 342 (3.84), 348 (3.85), 351 (3.81), 492 (4.50) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 2.86 (s, 3 H, Me), 7.47 (t, ^{3}J = 4.7 Hz, 1 H, 3-H), 7.54 (t, ^{3}J = 9.6 Hz, 1 H, 5-H), 7.64 (t, ^{3}J = 9.8 Hz, 1 H, 7-H), 7.89 (t, ^{3}J = 9.9 Hz, 1 H, 6-H), 8.36 (d, ^{3}J = 4.7 Hz, 1 H, 2-H), 8.40 (d, ^{3}J = 9.3 Hz, 1 H, 4-H), 9.16 (d, ^{3}J = 9.9 Hz, 1 H, 8-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 16.09 (Me), 122.9 (C-3), 127.0 (C-2), 128.9 (C-1), 129.8 (C-5), 129.9 (C-7), 136.1 (C-8), 139.6 (C-4), 140.8 (C-6), 144.4 (C-8a), 146.8 (C-3a), 166.4 (C-5'), 181.7 (C-2') ppm. IR (neat): 574, 635, 674, 750, 769, 791, 852, 958, 1013, 1042, 1077, 1187, 1222, 1262, 1307, 1344, 1408, 1427, 1460, 1482, 1534, 1568, 1587, 2358, 2851, 2917, 2921, 2955 cm^{-1}. MS [ESI]: 287 [M+1].Calcd. for $C_{13}H_{10}N_4S_2$: C, 54.52; H, 3.52; N, 19.56. Found: C, 54.50; H, 3.58; N, 19.50.

*(E)-5-(Methylthio)-2-(4,6,8-trimethylazulen-1-yldiazenyl)-1,3,4-thiadiazole, **6**(SMe)*

Brown crystals, m. p. 175 ºC. UV-vis (MeOH), λ_{max} (log ε): 235 (4.36), 264 (4.20), 307 (3.99), 310 (3.99), 503 (4.38) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 2.70 (s, 3 H, MeS), 2.85 (s, 3 H, Me_6), 2.89 (s, 3 H, Me_4), 3.20 (s, 3 H, Me_8), 7.39 (d, ^{3}J = 5.1 Hz, 1 H, 3-H), 7.40 (s, 1 H, 5-H), 7.49 (s, 1 H, 7-H), 8.21 (d, ^{3}J = 5.2 Hz, 1 H, 2-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 15.98 (MeS), 25.71 (Me_4), 28.78 (Me_8), 29.84 (Me_6), 121.1 (C-3), 124.0 (C-2), 129.8 (C-1), 134.4 (C-5), 136.8 (C-7), 148.7 (C-8), 149.7 (C-4), 150.9 (C-6), 144.4 (C-8a), 148.1 (C-3a), 165.2 (C-5'), 182.2 (C-2') ppm. IR (neat): 651, 690, 797, 850, 1034, 1052, 1068, 102, 1112, 1186, 1205, 1227 1289, 1363, 1384, 1431, 1457, 1496, 1519, 1551, 1579, 1703, 1817, 2006, 2334, 2925, 2973, 3858 cm^{-1}. MS [ESI]: 329 [M+1].Calcd. for $C_{16}H_{16}N_4S_2$: C, 58.51; H, 4.91; N, 17.06. Found: C, 58.50; H, 4.93; N, 17.08.

*(E)-2-(3,8-Dimethyl-5-isopropylazulen-1-yldiazenyl)-5-(methylthio)-1,3,4-thiadiazole, **7**(SMe)*

Brown crystals, m. p. 142 ºC. UV-vis (MeOH), λ_{max} (log ε): 233 (4.31), 260 (4.18), 292 (4.04), 307 (4.01), 356 (3.84), 358 (3.85), 360 (3.84), 527 (4.30) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.40 (d, ^{3}J = 6.9 Hz, 6 H, Me_{iPr}), 2.56 (s, 3 H, Me_3), 2.83 (s, 3 H, MeS), 3.16 (hept, ^{3}J = 6.9 Hz, 1 H, CH_{iPr}), 3.18 (s, 3 H, Me_8), 7.52 (t, ^{3}J = 10.8 Hz, 1 H, 7-H), 7.61 (t, ^{3}J = 10.8 Hz, ^{4}J = 1.4 Hz, 1 H, 6-H), 8.15 (s, 1 H, 2-H), 8.18 (d, ^{4}J = 1.4 Hz, 1 H, 4-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.31 (Me_3), 15.97 (MeS), 24.45 (Me_{iPr}), 29.82 (Me_8), 38.49

(*C*(Me)$_2$), 126.7 (C-1), 126.9 (C-2), 135.7 (C-7), 135.9 (C-4), 137.3 (C-6), 139.1 (C-3), 146.0 (C-5), 146.5 (C-8a), 150.0 (C-3a), 150.3 (C-8), 164.7 (C-5'), 182.4 (C-2') ppm. IR (neat): 961, 1035, 1089, 1099, 1194, 1246, 1265, 1287, 1403, 1415, 1456, 1554, 1696, 1868, 1949, 1982, 2000, 2026, 2057, 2119, 2149, 2199, 2226, 2259, 2362, 2852, 2923, 2959, 3329 cm^{-1}. MS [ESI]: 357 [M+1]. Calcd. for $C_{18}H_{20}N_4S_2$: C, 60.64; H, 5.65; N, 15.72. Found: C, 60.65; H, 5.68; N, 15.71.

(E)-2-(Azulen-1-yldiazenyl)-5-(tert-butyl)-1,3,4-thiadiazole, ***5****(t-Bu)*

Brown crystals, m. p. 151 °C. UV-vis (MeOH), λ_{max} (log ε): 225 (4.22), 281 (4.05), 347 (3.80), 478 (4.45) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.48 (s, 9 H, Me), 7.46 (t, ^{3}J = 4.7 Hz, 1 H, 3-H), 7.53 (t, ^{3}J = 9.7 Hz, 1 H, 5-H), 7.64 (t, ^{3}J = 9.8 Hz, 1 H, 7-H), 7.88 (t, ^{3}J = 9.9 Hz, 1 H, 6-H), 8.38 (d, ^{3}J = 4.7 Hz, 1 H, 2-H), 8.40 (d, ^{3}J = 9.6 Hz, 1 H, 4-H), 9.21 (d, ^{3}J = 9.6 Hz, 1 H, 8-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ31.06 (Me), 36.92 (C_{tBu}), 122.6 (C-3), 127.1 (C-2), 128.6 (C-1), 129.6 (C-5), 129.7 (C-7), 136.0 (C-8), 139.5 (C-4), 140.7 (C-6), 144.4 (C-8a), 146.6 (C-3a), 179.2 (C-5'), 181.7 (C-2') ppm. IR (neat): 571, 636, 689, 749, 768, 792, 855, 958, 1012, 1046, 1091, 1180, 1228, 1256, 1318, 1346, 1367, 1405, 1431, 1460, 1484, 1567, 1733, 2339, 2361, 2851, 2920, 2954, 3080 cm^{-1}. MS [ESI]: 297 [M+1].Calcd. for $C_{16}H_{16}N_4S$: C, 64.84; H, 5.44; N, 18.90. Found: C, 64.83; H, 5.47; N, 18.92.

(E)-2-(Azulen-1-yldiazenyl)-5-(1-naphthyl)-1,3,4-thiadiazole, ***5****(Nf)*

Brown crystals, m. p. 99 °C (with dec.). UV-vis (MeOH), λ_{max} (log ε): 221 (4.22), 283 (4.16), 344 (3.80), 496 (4.39) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.52 (t, ^{3}J = 4.7 Hz, 1 H, 3-H), 7.56 (t, ^{3}J = 9.7 Hz, 1 H, 5-H), 7.59 (t, ^{3}J = 8.0 Hz, 2 H, 6"-H, 7"H), 7.65 (d, ^{3}J = 7.4 Hz, 1 H, 3"-H), 7.67 (t, ^{3}J = 9.8 Hz, 1 H, 7-H), 7.88 (t, ^{3}J = 9.9 Hz, 1 H, 6-H), 7.94 (d, ^{3}J = 8.1 Hz, 1 H, 5"'-H), 7.95 (d, ^{3}J = 7.0 Hz, 1 H, 2"-H), 8.01 (d, ^{3}J = 8.2 Hz, 1 H, 4"-H), 8.42 (d, ^{3}J = 9.6 Hz, 1 H, 4-H), 8.45 (d, ^{3}J = 4.7 Hz, 1 H, 2-H), 8.93 (d, ^{3}J = 8.5 Hz, 1 H, 8"-H), 9.27 (d, ^{3}J = 9.6 Hz, 1 H, 8-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 123.0 (C-3), 125.0 (C-2"), 125.1 (C-7"), 125.6 (C-3"), 126.0 (C-6"), 126.7 (C-2), 127.8 (C-8"), 128.5 (C-1), 129.8 (C-7), 129.9 (C-5), 130.1 (C-5"), 130.6 (C-8a"), 131.5 (C-4"), 134.0 (C-4a"), 136.1 (C-8), 139.5 (C-4), 140.8 (C-6), 144.7 (C-8a), 146.9 (C-3a), 166.1 (C-5'), 182.0 (C-2') ppm. IR (neat): 666, 692, 744, 768, 795, 860, 940, 1017, 1050, 1196, 1238, 1266, 1314, 1347, 1388, 1410, 1460, 1491, 1575, 1674, 2340, 2361, 2849, 2917, 2955, 3043 cm^{-1}. MS [ESI]: 367. Calcd. for $C_{22}H_{14}N_4S$: C, 72.11; H, 3.85; N, 15.29. Found: C, 72.09; H, 3.88; N, 15.28.

(E)-2-(Azulen-1-yldiazenyl)-5-(2-thienyl)-1,3,4-thiadiazole, ***5****(Th)*

Brown crystals, m. p. 212 °C. UV-vis (MeOH), λ_{max} (log ε): 228 (4.39), 275 (4.18), 346 (3.96), 507 (4.51) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.15 (dd, ^{3}J = 5.1, 3.7 Hz, 1 H, 4"-H), 7.48 (t, ^{3}J = 4.7 Hz, 1 H, 3-H), 7.51 (d, ^{3}J = 5.1 Hz, 1 H, 5"-H), 7.54 (t, ^{3}J = 9.7 Hz, 1 H, 5-H), 7.64 (d, ^{3}J = 3.7 Hz, 1 H, 3"-H), 7.67 (t, ^{3}J = 9.8 Hz, 1 H, 7-H), 7.89 (t, ^{3}J = 9.9 Hz, 1 H, 6-H), 8.38 (d, ^{3}J = 4.7 Hz, 1 H, 2-H), 8.39 (d, ^{3}J = 9.6 Hz, 1 H, 4-H), 9.21 (d, ^{3}J = 9.6 Hz, 1 H, 8-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 123.0 (C-3), 127.1 (C-2), 128.1 (C-4"), 129.5 (C-3"), 129.6 (C-1), 129.7 (C-2"), 129.9 (C-5), 130.0 (C-7), 133.6 (C-5"), 136.1 (C-8), 139.4 (C-4), 140.8 (C-6), 144.6 (C-8a), 146.9 (C-3a), 160.6 (C-5'), 181.0 (C-2') ppm. IR (neat): 714, 742, 783, 839, 915, 1013, 1049, 1078, 1165, 1196, 1238, 1264, 1314, 1405, 1436, 1489, 1531, 1589, 1981, 2056, 2169, 2196, 2360, 2849, 2917, 2955, 3095 cm^{-1}. MS [ESI]: 323 [M+1].Calcd. for $C_{16}H_{10}N_4S_2$: C, 59.61; H, 3.13; N, 17.38. Found: C, 59.60; H, 3.15; N, 17.37.

(E)-2-(azulen-1-yldiazenyl)-5-(2-furyl)-1,3,4-thiadiazole, ***5****(Fu)*

Brown crystals, m. p. 210 °C, UV-vis (MeOH), λ_{max} (log ε): 223 (4.42), 272 (4.23), 275 (4.23), 277 (4.23), 343 (3.95), 346 (3.96), 350 (3.95), 506 (4.50) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 6.61, (dd, ^{3}J = 3.3, 1.6 Hz, 1 H, 4"-H), 7.51 (t, ^{3}J = 4.6 Hz, 1 H, 3-H), 7.28 (d, ^{3}J = 3.3 Hz, 1 H, 3"-H), 7.56 (t, ^{3}J = 9.7 Hz, 1 H, 5-H),7.62 (d, ^{3}J = 1.7 Hz, 1 H, 5"-H),7.67 (t, ^{3}J = 9.8 Hz, 1 H, 7-H), 7.91 (t, ^{3}J = 9.9 Hz, 1 H, 6-H), 8.40 (d, ^{3}J = 4.6 Hz, 1 H, 2-H), 8.41 (d, ^{3}J = 9.6 Hz, 1 H, 4-H), 9.26 (d, ^{3}J = 9.6 Hz, 1 H, 8-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 123.0 (C-3), 127.1 (C-2), 112.0 (C-4"), 112.7 (C-3"), 129.9 (C-1), 129.9 (C-5), 130.0 (C-7), 136.1 (C-8), 139.5 (C-4), 140.7 (C-6), 144.6 (C-8a), 145.1 (C-5"), 146.4 (C-2"), 146.9 (C-3a),176.8 (C-5'),181.1 (C-2') ppm. IR (neat): 589, 744, 856, 886, 999, 1020, 1066, 1066, 1127, 1155, 1199, 1232, 1260, 1316, 1363, 1409, 1431, 1488, 1531, 1560, 1603, 1627, 1667, 1976, 2063, 2158, 2185, 2206, 2360, 2851, 2920, 3338 cm^{-1}. MS [ESI]: 307 [M+1].Calcd. for $C_{16}H_{10}N_4OS$: C, 62.73; H, 3.29; N, 18.29. Found: C, 62.70; H, 3.31; N, 18.28.

(E)-2-(Azulen-1-yldiazenyl)-5-(methylsulfinyl)-1,3,4-thiadiazole, ***5****(S(O)Me)*

Brown crystals, m. p. 213 °C. UV-vis (MeOH), λ_{max} (log ε): 221 (4.31), 278 (4.10), 354 (3.84), 357 (3.85), 360 (3.81), 498 (4.50) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 3.16 (s, 3 H, Me), 7.53 (t, ^{3}J = 4.2 Hz, 1 H, 3-H), 7.65 (t, ^{3}J = 9.6 Hz, 1 H, 5-H), 7.76 (t, ^{3}J = 9.7 Hz, 1 H, 7-H), 7.98 (t, ^{3}J = 9.6 Hz, 1 H, 6-H), 8.40 (d, ^{3}J = 4.2 Hz, 1 H, 2-H), 8.46 (d, ^{3}J = 9.3 Hz, 1 H, 4-H), 9.24 (d, ^{3}J = 9.9 Hz, 1 H, 8-H) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 43.19 (Me), 123.9 (C-3), 126.9 (C-2), 128.9 (C-1), 131.1 (C-5), 131.3 (C-7), 136.3 (C-8), 139.8 (C-4), 141.3 (C-6), 144.8 (C-8a), 147.9 (C-3a), 176.8 (C5'), 185.1 (C2') ppm. IR (neat): 680, 754, 776, 794, 858, 965, 1017, 1060, 1078, 1165, 1199, 1240, 1255, 1304, 1333, 1408, 1429, 1472, 1494, 1573, 2359, 2850, 2919, 2956, 2996 cm^{-1}. MS [ESI]: 303 [M+1]. Calcd. for $C_{13}H_{10}N_4OS_2$: C, 51.64; H, 3.33; N, 18.53. Found: C, 51.62; H, 3.35; N, 18.52.

(E)-2-(Azulen-1-yldiazenyl)-5-(methylsulfonyl)-1,3,4-thiadiazole, 5(S(O$_2$)Me)

Brown crystals, m.p. 225 °C. UV-vis (MeOH), λ_{max} (log ε): 223 (4.27), 251 (4.09), 278 (4.10), 348 (3.84), 353 (3.85), 502 (4.48) nm. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 3.63 (s, 3 H, Me), 7.76 (t, ^{3}J = 4.8 Hz, 1 H, 3-H), 7.95 (t, ^{3}J = 9.7 Hz, 1 H, 5-H), 8.04 (t, ^{3}J = 9.8 Hz, 1 H, 7-H), 8.26 (t, ^{3}J = 9.8 Hz, 1 H, 6-H), 8.26 (d, ^{3}J = 4.8 Hz, 1 H, 2-H), 8.79 (d, ^{3}J = 9.4 Hz, 1 H, 4-H), 9.27 (d, ^{3}J = 9.6 Hz, 1 H, 8-H) ppm. ^{13}C-NMR (DMSO-d_6, 125 MHz) δ 43.31 (Me), 126.3 (C-2, C-3), 132.0 (C-1), 134.4(C-5), 134.5 (C-7), 137.3 (C-8), 142.0 (C-4), 143.7 (C-6), 144.8 (C-8a), 149.3 (C-3a), 165.8(C5'), 186.0 (C2') ppm. IR (neat): 497, 529, 547, 576, 623, 647, 688, 759, 790, 860, 886, 967, 1019, 1082, 1145, 1205, 1241, 1269, 1302, 1317, 1380, 1405, 1428, 1496, 1531, 1574, 2101, 2343, 2851, 2919, 3001 cm^{-1}. MS [ESI]: 319 [M+1]. Calcd. for $C_{13}H_{10}N_4O_2S_2$: C, 49.04; H, 3.17; N, 17.60. Found: C, 49.06; H, 3.20; N, 17.58.

(E)-2-(3,8-Dimethyl-5-isopropylazulen-1-yldiazenyl)-5-(mercapto)-1,3,4-thiadiazole, ***7****(SH)*

Green-brown crystals, dec. without melt. UV-vis (MeOH) λ_{max} (log ε): 240 (4.31), 292 (4.04), 365 (3.84), 348 (3.85), 363(3.84), 365 (3.84), 368 (3.84), 536 (4.30) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.35 (d, ^{3}J = 6.9 Hz, 6 H, Me_{iPr}), 2.50 (s, 3 H, Me), 3.11 (hept, ^{3}J = 6.9 Hz, 1 H, CH_{iPr}), 3.11 (s, 3 H, Me), 7.56 (t, ^{3}J = 10.8 Hz, 1 H, 7-H), 7.62 (t, ^{3}J = 10.8 Hz, ^{4}J

= 1.4 Hz , 1 H, 6-H), 8.05 (s, 1 H, 2-H), 8.15 (d, ^4J = 1.4 Hz, 1 H, 4-H) ppm.^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.31 (Me), 24.45 (Me_{iPr}), 29.82 (Me), 38.49 ($C(Me)_2$), 126.7 (C-1), 126.9 (C-2), 135.7 (C-7), 135.9 (C-4), 137.3 (C-6), 139.1 (C-3), 146.0 (C-5), 146.5 (C-8a), 150.0 (C-3a), 150.3 (C-8), 164.7 (C-5'), 182.4 (C-2') ppm. IR (neat): 471, 600, 627, 656, 686, 720, 762, 845, 892, 922, 965, 1035, 1068, 1088, 1103, 1191, 1237, 1292, 1363, 1415, 1445, 1471, 1519, 1552, 1686, 2852, 2959, 3060 cm^{-1}. MS [-ESI]: 341 [M-1]. Calcd. for $C_{17}H_{18}N_4S_2$: C, 59.62; H, 5.30; N, 16.36. Found: C, 59.60; H, 5.32; N, 16.39.

(E)-2-(3,8-Dimethyl-5-isopropylazulen-1-yldiazenyl)-5-[(3,8-dimethyl-5-isopropylazulen-1-yl)thio)-1,3,4-thiadiazole, ***9***

Green-brown crystals, dec. without melt. UV-vis (MeOH) λ_{max} (log ε): 237 (4.22), 294 (4.13), 368 (3.86), 373 (3.86), 534 (3.75) nm. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.31 (d, ^3J = 6.9 Hz, 6 H, $Me_{iPr''}$), 1.34 (d, ^3J = 6.9 Hz, 6 H, Me_{iPr}), 2.47 (s, 3 H, $Me_{3''}$), 2.58 (s, 3 H, Me_3), 3.09 (sept, ^3J = 6.9 Hz, 1 H, $CH_{iPr''}$), 3.16 (sept, ^3J = 6.9 Hz, 1 H, CH_{iPr}), 2.83 (s, 3 H, $Me_{8''}$), 3.18 (s, 3 H, Me_8), 7.10 (t, ^3J = 10.8 Hz, 1 H, 7"-H), 7.35 (t, ^3J = 11.0 Hz, 1 H, 7-H), 7.45 (t, ^3J = 10.8 Hz, ^4J = 1.9 Hz , 1 H, 6"-H), 7.50 (t, ^3J = 11.0 Hz, ^4J = 2.2 Hz , 1 H, 6-H), 7.74 (s, 1 H, 2"-H), 8.06 (s, 1 H, 2-H), 8.08 (d, ^4J = 1.9 Hz, 1 H, 4"-H), 8.20 (d, ^4J = 2.2 Hz, 1 H, 4-H) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 13.14 ($Me_{3''}$), 13.22 (Me_3), 24.29 ($CH_{iPr''}$), 24.61 (CH_{iPr}), 29.66 ($Me_{8''}$), 29.69 (Me_8), 37.97 ($C''(Me)_2$), 38.35 ($C(Me)_2$), 123.5 (C-1"), 125.8 (C-2"), 126.7 (C-2), 130.5 (C-7"), 132.0 (C-1), 133.5 (C-3"), 134.5 (C-4"), 134.5 (C-8a"), 135.2 (C-7), 135.5 (C-8a), 136.2 (C-4), 136.2 (C-6"), 137.3 (C-6), 139.1 (C-3), 143.0 (C-3a"), 144.7 (C-5"), 144.7 (C-3a), 145.0 (C-5), 149.8 (C-8"), 151.9 (C-8), 164.7 (C-5'), 182.4 (C-2') ppm. IR (neat): 486, 607, 642, 658, 686, 738, 813, 853, 919, 965, 997, 1025, 1066, 1099, 1160, 1187, 1245, 1281, 1365, 1387, 1461, 1547, 1919, 2118, 2360, 2921, 29550 3060 cm^{-1}. MS [ESI]: 539 [M+1]. Calcd. for$C_{27}H_{34}N_4S_2$: C, 67.74; H, 7.16; N, 11.70. Found: C,67.71 ; H, 7.18; N, 11.34.

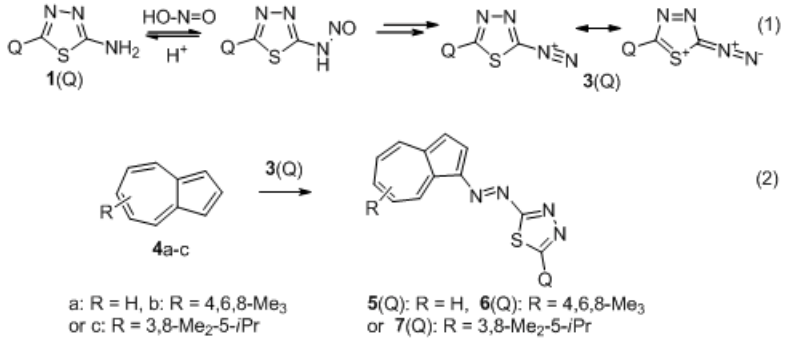
Results and discussions

Synthesis

The proposed diazenes were achieved starting from the 5-substituted 1,3,4-thiadiazoles-2-amines, **1**Q, where Q is described in Scheme 3. To obtain a fair yield of the diazonium salts at diazotization of amines **1**Q, generally, nitrososulfuric acid was used at low temperatures mainly in acetic acid [25], or a mixture of propionic acid-acetic acid [6,26] (eq. 1 in Scheme 3). The diazotization of **1**(SH) was realized with $NaNO_2$ in the water solution of HCl [27]. However it must be noted that the diazonium salts **3**(Q) is not very stable as, for example, the pyridine or thiazole correspondents. The subsequent azo coupling of **3**(Q) was described as arising in good yields in the presence of urea in the aim to nitroso cation elimination or, in the same purpose, adding different bases to buffered medium [6, 25-27].

The coupling with azulenes (eq. 2 in scheme 3), occurred with modest yields and low azulenes conversions as results from Table 1. Because the azulene is a strongly polarized aromatic hydrocarbon which has a relatively weak nucleophilicity, coupling with diazonium salts are at the limit of the azulene system reactivity. Therefore an efficient azo electrophilic substitution in position 1 takes place with parent azulene or with azulenes activated by the inductive effect of alkyl groups. Supplementary, the weak electrophiles as, for example 4-dimethylamino-phenyldiazonium ion, are not able to substitute the proton in 1-position of azulene [28]. It seems that the diazonium salts generated from aminothiadiazoles, **1**(Q), are also quite weak electrophiles (see the limit structures described in scheme 3 for salt **3**(Q)) leading to low azulenes conversions and, therefore, to their damage prior to the coupling reaction. The particular reaction conditions and the yields for each diazotization-coupling sequence are shown in table 1.

More difficulties are encountered when the SH group is present as in starting compounds **1**(SH) and in coupling products. Presumably, this group can be oxidized by the nitrosyl ion present in medium giving the reactive radical sulfur. Thus **1**(SH), besides the providing of diazenes **5** or **7**, can be substituted at sulfur atom giving the compounds **8**. These last products, due to the amino group can be again diazotized and coupled with a new azulene. Therefore, the composition of the generated reaction mixture became very complex and a high amount of polymer accompanies the products (scheme 4). The attempts to separate

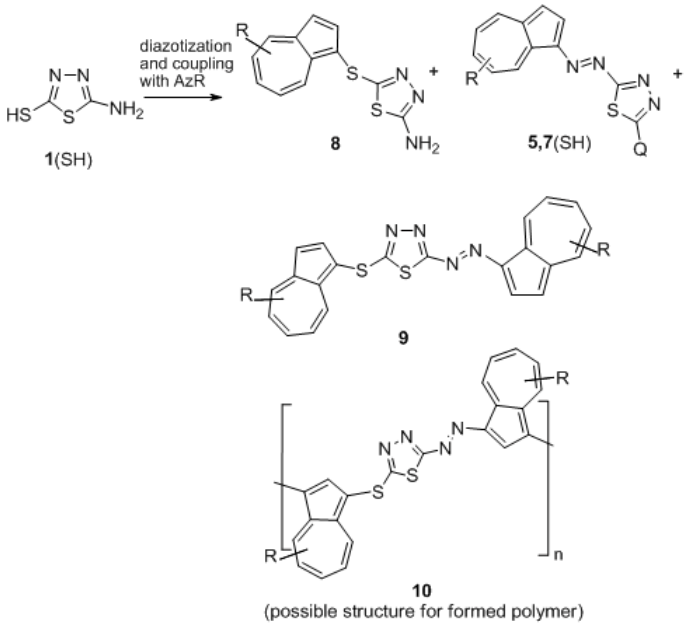


Scheme 3. Diazotization and coupling reactions

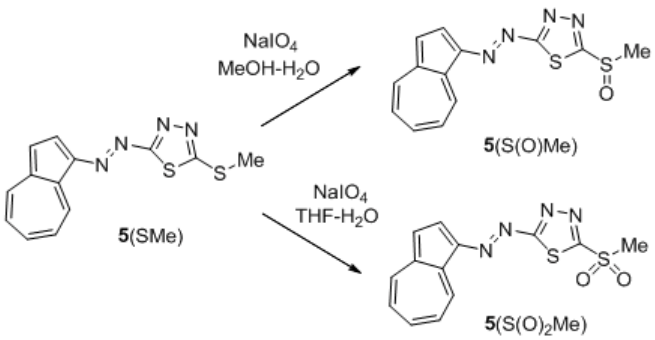
Q	Diazotization medium	5	6	7
SMe	$CHCl_2COOH$	51(92)/brown	46(94)/ brown	52(88)/ brown
	HCl 36%	16(95)	18(93)	28(93)
	H_2SO_4 98%	15(90)	-	-
	H_3PO_4 85%	26(88)	-	-
Ph	H_3PO_4/HNO_3	30(96)/brown	18(94)/brown	25(94)/ brown
	$CHCl_2COOH$	20(93)	-	-
Th	H_3PO_4/HNO_3	34(85)/ brown	-	-
	H_3PO_4 85%	31(87)		
Fu	H_3PO_4 85%	5(69)/ brown	-	-
Nf	$CHCl_2COOH$	15(77)/ brown	-	-
*t*Bu	$CHCl_2COOH$	72(98)/ brown	-	-
H	$CHCl_2COOH$	23(73)/brown		

Table 1
DIAZOTIZATION-COUPLING SEQUENCE: YIELDS IN % Q (YIELDS WITH AZULENES RECOVERY IN %)/ COLORS OF DCM SOLUTION

samples containing pure compounds have succeeded only starting from guaiazulene, **4**c. Their higher reactivity accelerates the reaction with the diazonium group in position 1 together with the attack of sulfur radical avoiding to a good extent the polymerization. In this way were separated and characterized the normal coupling product **7**(SH) alongside the product with guaiazulene moieties both at sulfur as well as at azo group, **9**(R=3,7-Me_2-5-*i*Pr) (based only on the molar peak present in mass spectrum of reaction mixture can be also suggested the generation of amine **8**(R=3,8-Me_2-5-*i*Pr)). Several products starting from azulene, **4**a, as compounds **8**(R=H) or **5**(SH), were highlighted by mass spectrometry and ^{1}H-NMR spectra of the mixtures enriched in one of the component.



Scheme 4. Diazotization and coupling of amine 1(SH) and of product 8



Scheme 5. Oxidation of diazene **5**(SMe)

Diazene **5**(SMe) can be oxidized selectively at the sulfur atom in the presence of sodium periodate. While in methanol-water, at reflux the reaction stops at the stage of sulfoxide, **5**(S(O)Me), in THF-water it gives a mixture of sulfone and sulfoxide. Trying to increase the conversions, the reaction becomes non selective and the system is destroyed.

Semiempirical molecular orbital calculation

A computational study on (*E*)-2-(azulen-1-yldiazenyl)-1,3,4-thiadiazoles was undertaken based on density functional theory (DFT) using Spartan 14 software Wavefunction, Inc. Irvine CA USA on Intel(R) Core i5 at 3. 2 Ghz CPU PC. Calculations of molecular properties and topological descriptors has been carried out using software algorithm hybrid B3LYP model (the Becke's three parameter hybrid exchange functional with the Lee-Yang-Parr correlation functional) and polarization basis set 6-31G* vacuum, for equilibrium geometry at ground state. A series of molecular descriptors and properties of their optimized geometries (natural charges, molecular frontier orbitals energies, etc.) were calculated. Thermodynamic properties (dipole moments, polarizability, log P, solvation energies) have been also computed proving their lipophilic and strong polar character. Reduction and oxidation potentials have been correlated to their calculated energy levels for LUMO and HOMO orbitals.

The HOMO energies decrease when EWG-s are attached to the 5-position of the heterocyclic system making the compounds more stable. Contrary, aryl and donor groups increase these values what destabilize the molecules but the effect is modest. At the same time, LUMO energies

Atom	Natural charges								
	Az-C3	Az-C1	N1azo	N2azo	Het-N3'	Het-N4'	Het-S	Het-C2'	Het-C5'
5(Ph)	-0.252	0.082	-0.173	-0.288	-0.257	-0.260	0.395	0.170	0.018
6(Ph)	-0.264	0.081	-0.180	-0.298	-0.268	-0.260	0.390	0.175	0.016
7(Ph)	-0.050	0.089	-0.183	-0.301	-0.268	-0.260	0.388	0.175	0.016
5(SMe)	-0.253	0.081	-0.173	-0.288	-0.255	-0.308	0.405	0.171	-0.199
6(SMe)	-0.264	0.080	-0.180	-0.298	-0.266	-0.309	0.400	0.176	-0.199
7(SMe)	-0.050	0.088	-0.183	-0.302	-0.267	-0.309	0.398	0.177	-0.198
5(*t*Bu)	-0.253	0.080	-0.171	-0.286	-0.263	-0.273	0.385	0.169	0.042
5(H)	-0.252	0.081	-0.169	-0.289	-0.268	-0.255	0.394	0.167	-0.255
5(Nf)	-0.252	0.082	-0.173	-0.287	-0.259	-0.268	0.398	0.166	-0.025
5(Th)	-0.252	0.083	-0.174	-0.289	-0.254	-0.254	0.401	0.169	-0.10
5(Fu)	-0.252	0.083	-0.174	-0.289	-0.257	-0.252	0.419	0.164	-0.037
5(S(O)Me)	-0.251	0.082	-0.168	-0.293	-0.267	-0.273	0.458	0.168	-0.266
5(S(O)$_2$Me)	-0.252	0.081	-0.172	-0.291	-0.255	-0.294	0.409	0.173	-0.186

Table 2
THE HIGHEST NATURAL CHARGES OF THE MOST REACTIVE ATOMS OF THE SYNTHESIZED DIAZENES

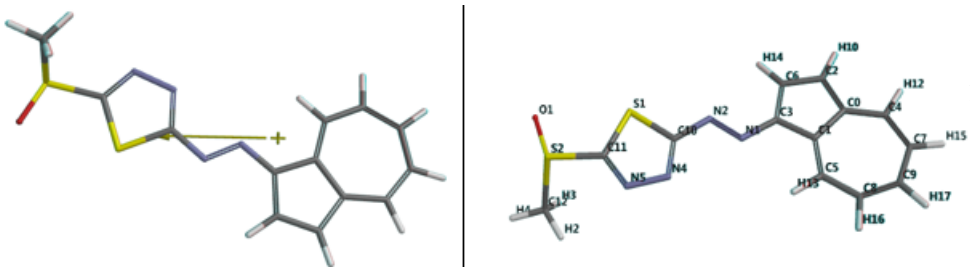


Fig. 1. Dipole moment and geometry of **5**(S(O)Me)

decrease when the EWG-s are present and increase in the presence of aryls or donor group. As a result, in the first case the molecules are less stable to reduction and in last one they are more resistant. Azulene alkylation increases both values of HOMO and LUMO energies, making the compounds more sensitive to oxidation and more stable to reduction. Polarizability is increased by substitution with EWGs on the heterocyclic moiety due to the intensification of the pull-push effect.

The natural charges explain the polarization vector with the positive pole in the tropylium moiety and the negative pole toward the thiadiazole system. However, the negative charges are disseminated on more nitrogen atoms and azulenic C3 and therefore the system does not interact strongly with metal cations or electrophiles. For example it is methylated only in traces by MeI, while the corresponding thiadiazolamines react in high yields (fig. 2 gives the mass spectrum of methylated diazene **5**(SMe) separated in very small amount and incompletely characterized).

At the same time, the metal complexation at nitrogen atoms is disadvantaged and also the protonation is observed at very low *p*H units in ethanol 96% (*p*H = ~ 0 units). The most reactive site to soft electrophiles attack is at azulene C3 atom (scheme 6).

As expected, the alkyl groups substituted at azulene seven ring increases the molecule polarity and polarizability (table 3). The most polarizable molecule contains 1-naphthyl group at position 5 of thiadiazole moieties. Log P is the lowest for the patern compound and the highest for the naphthyl substituted thiadiazole derivative. It is obvious that while nonpolar substituents increase this parameter those polar decrease its value (table 3).

Mass and UV-Vis spectra

All the diazenes **5** - **7** have a similar behavior in the mass spectrometer and the figure 3 is an example. The molecular ion is present but it is not very stable. He generates the diazonium ion of azulene, also instable, which further split to azulene fragment after nitrogen elimination. It is interesting that the thiadiazole moiety or its diazonium salt are not present between the obtained fragments, which proves a selective split between the heterocycle and the azo group.

The replace of aryl group in 2-aryldiazenyl-5-phenyl-1,3,4-thiadiazoles, already described [29], with azulene chromophores as in diazenes **5** - **7** is expected to modify the electronic spectra. Besides this, the study of solvatochromic behavior as well as that of acid-basic equilibrium of the last compounds can highlight some particular features for these compounds.

In UV region 2-aryldiazenyl-5-phenyl-1,3,4-thiadiazoles generally shows bands between 204-238 nm attributed to the π-π^* transition belonging to aryl moiety and between 273-313 nm from the same transition at heterocyclic system. In visible region there are present the bands

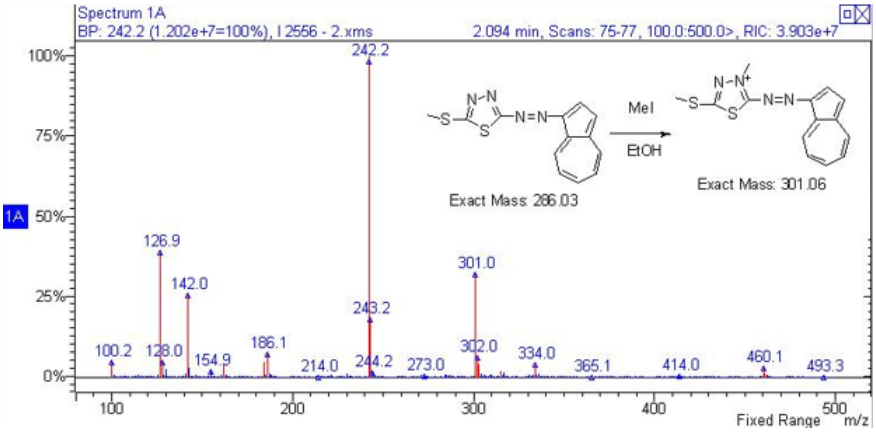
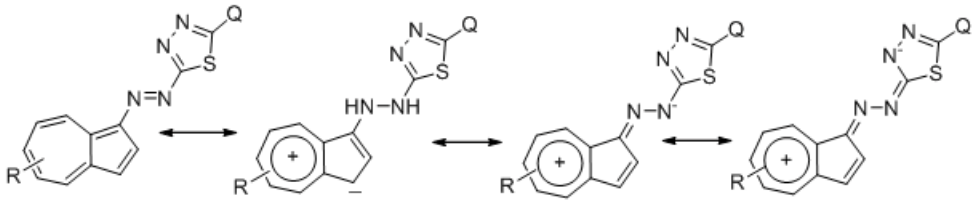


Fig. 2. Mass spectrum of the alkylated product of **5**(SMe)



Scheme 6. Charge distribution over more significant hybrid structures of compounds **5**

Table 3

MOLECULAR PROPERTIES OF THE SYNTHESIZED DIAZENES

Substituents	-HOMO (eV)	-LUMO (eV)	Dipole moments (Debye)	Solvation (Kj/mol)	Polarizability	Log P
5(Ph)	5.42	2.50	4.14	53.01	66.08	5.01
6(Ph)	5.26	2.49	5.32	47.72	70.44	5.54
7(Ph)	5.17	2.47	5.60	44.53	73.45	6.29
5(SMe)	5.41	2.54	4.52	61.14	62.31	4.27
6(SMe)	5.25	2.46	5.72	55.91	66.68	4.70
7(SMe)	5.16	2.42	5.84	52.77	69.69	5.54
5(*t*Bu)	5.48	2.49	4.06	45.84	65.14	5.04
5(H)	5.59	2.60	5.35	52.78	59.23	2.85
5(Nf)	5.38	2.50	4.26	56.13	70.22	6.01
5(Th)	5.35	2.60	3.75	63.89	65.10	3.71
5(Fu)	5.31	2.56	3.35	59.22	64.37	2.98
5(S(O)Me)	5.68	2.76	7.47	107.35	62.94	3.01
5($S(O)_2$Me)	5.89	2.96	9.89	118.55	63.50	3.06

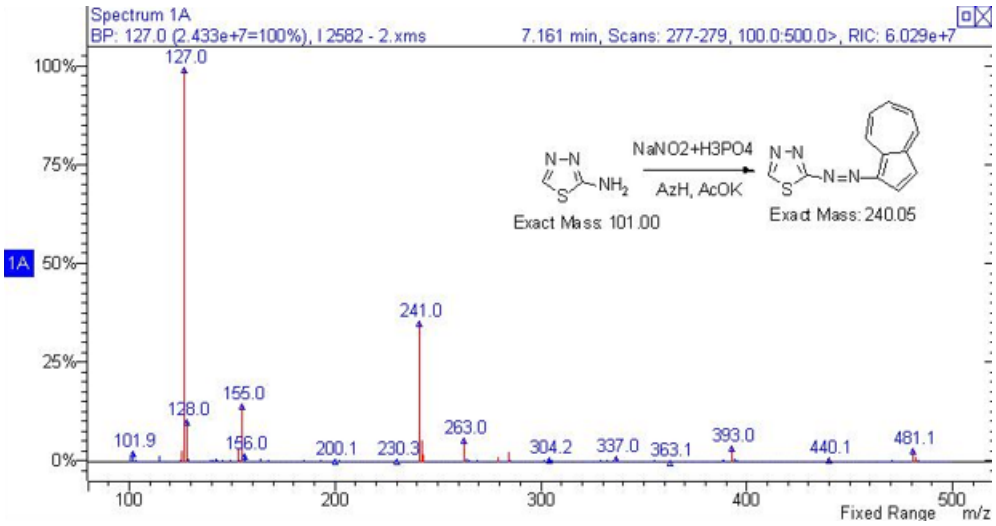
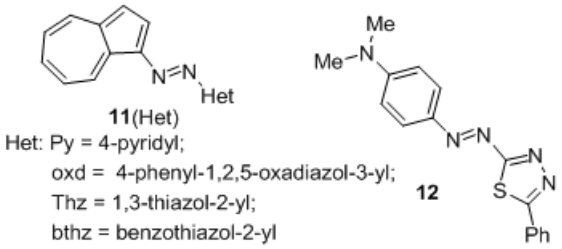


Fig. 3. Mass spectrum of compound **5**(H)

generated by the aromatic groups bounded to the azo bond. Accordingly, in UV region of the 2-(azulen-1-yldiazenyl)-5-phenyl-1,3,4-thiadiazole, **5**(Ph), a band at λ_{max} = 228 nm (ε 5.06) and several less intense bands between 343 and 356 nm are present.

The possible use of obtained compounds as coloring materials justify a more detailed discussion on their recorded visible region of electronic spectra compared to other 1-heteroaryldiazenyl azulene, **11**(Het) or with the compound **12**, with 4-dimethylaminophenyl [19] instead of azulen-1-yl moiety (scheme 7 and table 4). From the beginning it must emphasis the electron donating character of the azulen-1-yl moiety and the resulted push-pull systems by connection with various heterocycles as acceptors. This polarizability of electronic system induces a bathochromic shift in visible range. A similarity can be observed when (azulen-1-yl)diazenyl is substituted with other efficient electron donor, e.g. 4-dimethylaminophenyl group as in compound **12;** the bathochromic effect induced by this group is even more pronounced (table 4, row 1,2). The bathochromism of diazenes **11**(Het) increase with change of heterocycle in order: **11**(Py) [16] ≈ **11**(oxd) [22] < **11**(Thz) [18,19] < **8**(bthz) [27] ≈ **5**(Ph) (scheme 7). Our system looks similar to that possessing 2-thiazolyl or 2-benzothiadiazolyl, **11**(Thz) or **8**(bthz), respectively and is more polarized than those with 4-pyridyl, **11**(Py). Therefore the strongest visible bands are shifted to red for the compounds **5**(Ph), **11**(Thz) or **11**(bthz).

Both, the nature of substituents at 5-position in heterocycle as well as the presence of alkyl substituents at azulen-1-yl moiety influences the signal shift in visible. Thus, the substitution of 5-position by *t*Bu does not alter the signal recorded for compound **5**(H). The presence of aryl group in this position exerts a bathochromic shift more pronounced for the thienyl and furyl groups. The influence of aryl is due to the charge extension of the π-electronic



Scheme 7. Heteroaryldiazenes with azulene-1-yl and 4-dimethylaminophenyl moiety

system and supplementary, this groups increase the substantivity of the dyes. The SMe group in compound **5** has an intermediate effect. The increase in polarity produced by the azulen-1-yl substitution with the repulsive electron alkyls, in series **5**, **6**, **7**, has as result a bathochromic shift more pronounced for the last compounds (table 4, row 5,6).

The solvatochromism of these compounds is positive, the highest values of the absorption being observed in polar solvents as results from figure 4 (in dioxan: 485 nm; acetone: 488 nm; THF: 489 nm; DCM: 491 nm; methanol: 493 nm; DMSO: 500 nm; DMF: 496 nm; nitromethane: 568 nm). The observed strong shift in nitromethane, signaled also for other systems, can be explained by an intermolecular electron transfer. Therefore, all the solutions of **5**(SMe) have brownish color with the exception of that in nitromethane which is violet.

Consideration on the acid-base properties of (azulen-1-yldiazenyl) heteroaryls seems to be troublesome due to their extremely weak basicity (pK_a values are around 0) which is situated at the limit for registration capacity of the common pH-meters. The absorption maxima of some 2-(azulen-1-yldiazenyl)-1,3,4-thiadiazoles in ethanol both in neutral and in strong acid medium are presented in table 5.

Table 4

MAXIMA OF THE WAVELENGTH OF THE MAIN VISIBLE ABSORPTION FOR (AZULEN-1-YL)DIAZENYL HETEROCYCLES IN METHANOl (λ_{max}(IN nm) / (log ε) (IN $dm^3mol^{-1}cm^{-1}$))

1	Compd.	**11**(Ph)	**11**(Py)	**11**(oxd)	**11**(Thz)	**11**(bthz)	**5**(Ph)	**12**
2	λ_{max} (log ε)	415 (4.30)	439 (4.39)	438 (4.35)	472 (4.36)	494 (4.36)	498 (4.41)	512 (4.02)
3	Compd.	**5**(H)	**5**(*t*Bu)	**5**(Ph)	**5**(Th)	**5**(Fu)		
4	λ_{max} (log ε)	476 (4.35)	478 (4.45)	498 (4.41)	507 4.51	506 4.50		
5	Compd.	**5** (Ph)	**6**(Ph)	**7**(Ph)	**5** (SMe)	**6**(SMe)		
6	λ_{max} (log ε)	498 (4.41)	512 4.53	536 4.41	492 4.50	503 4.38		

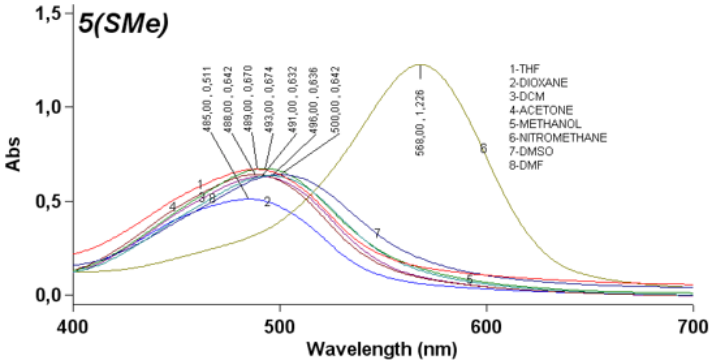
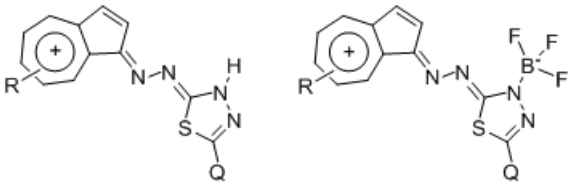


Fig.4. Solvatochromic behavior of compound **5**(SMe)

Compound	Maximum absorption in base (%)	Isosbestic point	Maximum absorption in acid medium (%)
5(*t*Bu)	479	501	552
5(SMe)	493	525	562
5(S(O)Me)	498	519	547
5(Ph)	499	529	567
5($S(O)_2$Me)	505	537	-
5(Th)	509	542	575

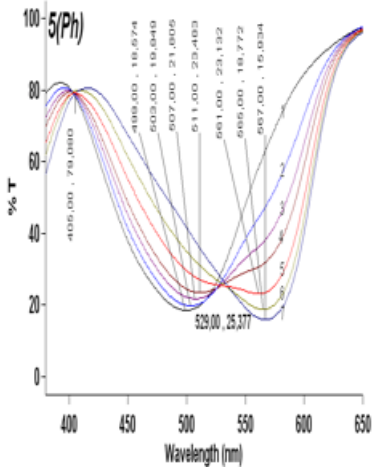
Table 5
MAXIMA OF ABSORPTION OF SOME 2-(AZULEN-1-YLDIAZENYL)-1,3,4-THIADIAZOLES DEPENDING ON *p*H

The protonation of the (azulen-1-yldiazenyl)-thiadiazoles moves the absorption maxima of the main visible band (S_2-S_0) toward higher wavelengths (bathochromically) (fig. 5). This can be explained by the intensification of the push-pull effect by heterocycle protonation (scheme 8). Because in basic medium the compounds **5** are yellow-brown or brick colored and in acidic medium becomes orange they can be used as *p*H indicator.



Scheme 8. (Azulen-1-yldiazenyl)-thiadiazoles protonation and coordination with BF_3

The very low basicity of the studied compounds also hinders the complex generation with metals ions as these of Ni or Fe in ethanol; our attempt to obtain complexes remains unsuccessful. However, they formed complexes with BF_3, a Lewis acid (fig. 6), which was highlighted by UV-vis spectroscopy. In alcoholic solutions they are red-violet, very similar with the protonated species of compounds. As can be seen in figure 6-A the main visible bond belonging to compound **5**(SMe) was bathochromic shifted from 494 nm to 561 nm by interaction with BF_3-Et_2O in ethanol 96%. Another salt possessing Lewis acid properties is $SnCl_4$, which has a similar reactivity toward the ligand **5**(SMe) (fig.6-B).



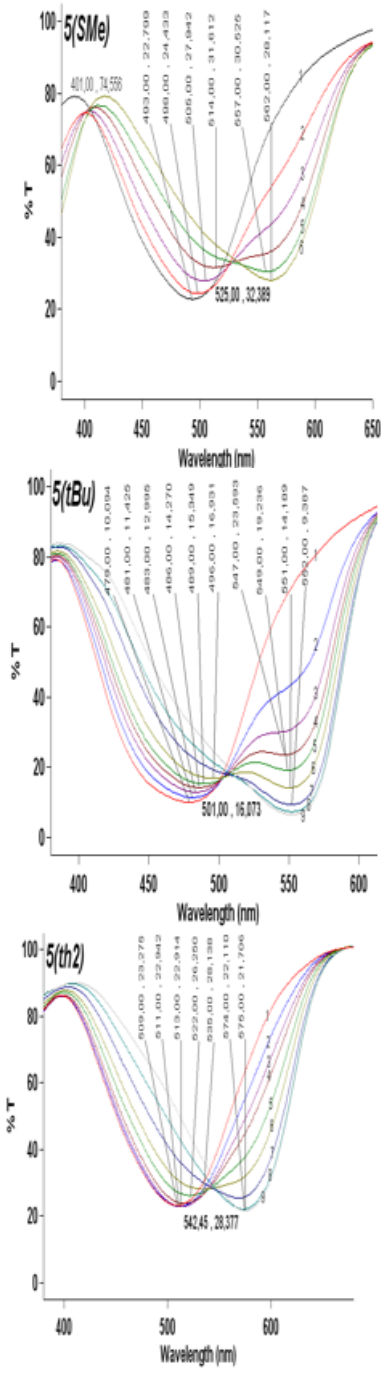


Fig.5a. Isosbestic curves of **5**(Ph), **5**(SMe), **5**(*t*Bu), **5**(Th) in ethanol 96% with HCl 37%

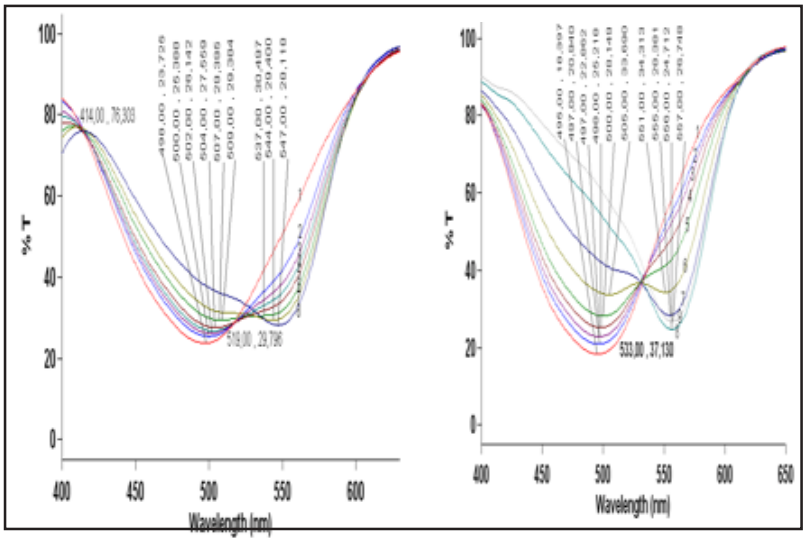


Fig.5b. Isosbestic curves of **5**(S(O)Me), in ethanol 96% and DCM with HCl 37%

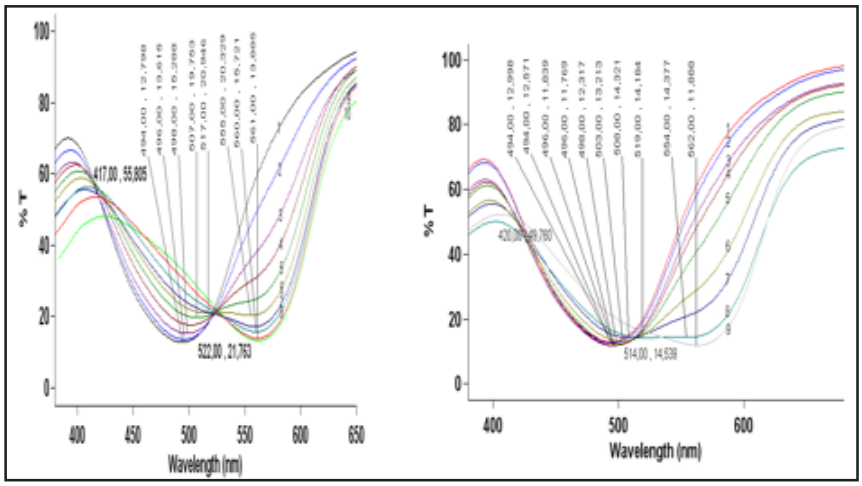


Fig. 6. Complexation of ligand (E)-2-(azulen-1-yldiazenyl)-5-(methylthio)-1,3,4-thiadiazole, (L), (A) with BF_3-Et_2O and (B) with $SnCl_4$ in EtOH 96%. A) Curve 1-ligand; curve 2- L+2 mL etherate; curve 3- L+3 mL etherate; curve 4- L+4 mL etherate; curve 5- L+5mL etherate; curve 6- L+6 mL etherate; curve 7-L+7 mL etherate; curve 8- L+8 mL etherate; curve 9-L+10 mL etherate; curve 10-L+14 mL etherate; B) Curve 1-ligand; curve 2- L+0.1 mL $SnCl_4$; curve 3-L+0.5 mL $SnCl_4$; curve 4-L+1 mL $SnCl_4$; curve 5-L+2 mL $SnCl_4$; curve 6-L+3 mL $SnCl_4$; curve 7-L+4 mL $SnCl_4$; curve 8-L+5 mL $SnCl_4$; curve 9-L+6 mL $SnCl_4$

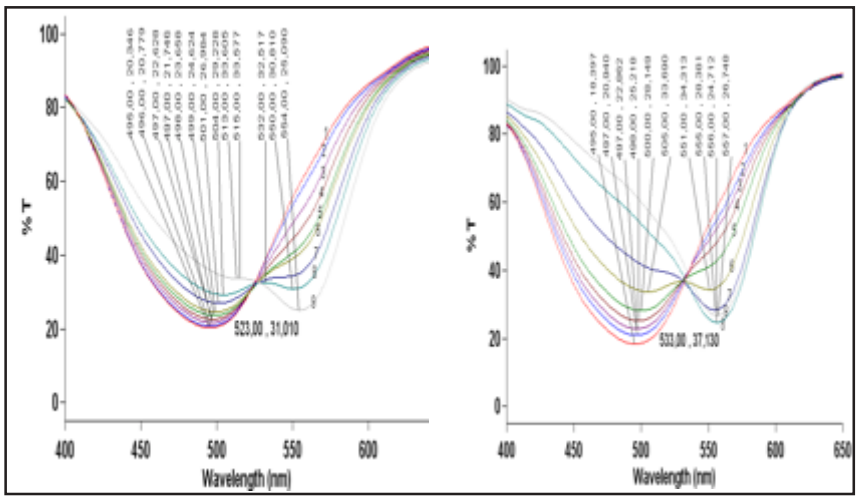


Fig. 7. Complexation of ligand (E)-2-(azulen-1-yldiazenyl)-5-(methylsulfinyl)-1,3,4-thiadiazole, (L), (A) with $Fe(ClO_4)_2 * H_2O$ and (B) with $Fe(ClO_4)_3 * 9\ H_2O$, in DCM A) Curve 1-ligand; curve 2- L+l Eq.salt; curve 3- L+ 2 Eq. salt; curve 4- L+3Eq. salt; curve 5- L+4 Eq. salt; curve 6- L+5 Eq. salt; curve 7-L+8 Eq. salt; curve 8- L+10 Eq. salt; curve 9-L+15 Eq. salt;
(B) Curve 1-ligand; curve 2- L+l Eq.salt; curve 3- L+ 2 Eq. salt; curve 4- L+3Eq. salt; curve 5- L+4 Eq. salt; curve 6- L+5 Eq. salt; curve 7-L+8 Eq. salt; curve 8- L+9 Eq. salt; curve 9-L+12 Eq. salt

A better complexing capacity was found when solvents, as alcohol, were replaced by non-nucleophilic, DCM. Thus treating the ligand (*E*)-2-(azulen-1-yldiazenyl)-5-(methylsulfinyl)-1,3,4-thiadiazole, (L), **5**(S(O)Me) with iron (II) or (III) perchlorates (fig. 7) the most important maxima of absorption in visible is shifted bathochromically from 495 nm to 556 nm. Moreover, the complexing effect is observed only in the presence of non-nucleophilic counter ions such as perchlorate. Solvents as alcohols or, anions such as acetates prevent the maxima of absorption shift. Therefore, the modification of the absorption maxima of the main visible band could be the result of binding either of iron ions or of protons resulted by the hydrolysis of the iron perchlorates hydrates. However, the maximum gap is proportional with the amount of the salt added and can be used to link salts concentration with the gap of the wavelength (fig. 8).

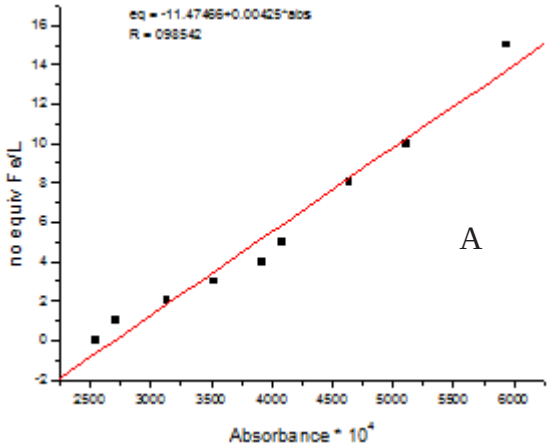


Fig. 8. Correlation between absorbance and ratio Fe(II)/L

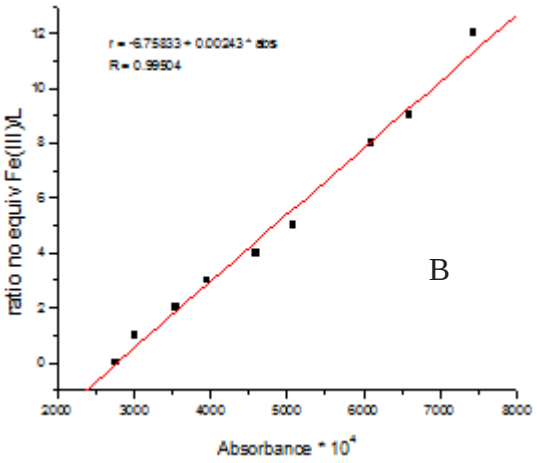


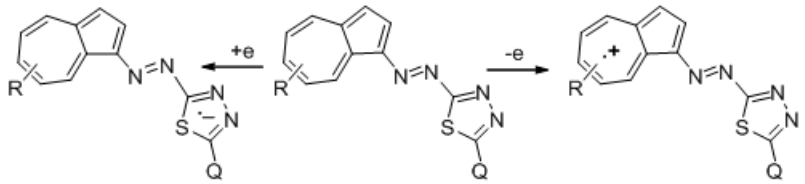
Fig. 8. Correlation between absorbance and ratio Fe(III)/L

Electrochemical behavior

We have previously mentioned that, usually, the oxidation of (azulen-1-yldiazenyl)-heteroaryls takes place at azulenyl moiety with the generation of the stabilized structure as radical cation whereas for the reduction the heteroaryl group is responsible (scheme 9) [22,30].

The electrochemical [31] data in table 6 show that the (azulen-1-yldiazenyl)-thiadiazoles prove a good stability in redox reactions. Though if these date are compared with those for 3-(azulen-1-yldiazenyl)-1,2,5-oxadiazoles, it can be seen that the diazenes with thiadiazole moiety are easier oxidized and hardly reduced. In Table 6 there are compared the data for the first oxidation and reduction potentials of compound **5** - **7** with these for **11**(oxd = 4-methyl-1,2,5-oxadiazol-3-yl) (scheme 9).

As expected, the electron rich substituents at heteroaryls moiety, Q, decrease the oxidation potential. Thus, the potential for compound **5**(SMe) is lower by 84 mV as compared with **5(**H). The inductive effect of *t*Bu destabilizes the molecules toward oxidation but only with 60 eV. Contrary, the electron withdrawing group S(O)Me deeply increases this potential by 32 mV. The conjugation extension due to the presence of the Q = aryl group decreases the oxidation potential in order ((Nf) with 105 mV) < ((Th) with 125 mV). The inductive effect of alkyl groups at azulenyl moiety decrease significantly these potentials: the three Me groups in 4,6,8 positions decrease the oxidation potential with around 95 mV and the alkyls belonging to guaiazulenyl moiety decrease this potential even more, till 150 mV. As expected, the reduction potentials vary in reverse. The CV experiments revealed that all the processes are irreversible. However, as can be seen in figure 9, the first cathodic process is partially reversible.



Scheme 9. Redox reactions of 2-(azulen-1-yldiazenyl)-1,3,4-thiadiazoles

Table 6

FIRST OXIDATION AND REDUCTION POTENTIALS FOR 2-(AZULEN-1-YLDIAZENYL)-1,3,4-THIADIAZOLES

Q	5		6		7r	
	ox	red	ox	red	Ox	red
Ph	0.740	-1.226	0.645	-1.284	0.590	-1.315
11(oxd)[a]	0.815[b]	-1.256[b]	0.70[c]	-1.295[c]	0.592[d]	-1.320[d]
SMe	0.731	-1.225	0.520	-1.115	0.560	-1.250
S(O)Me	0.847	-1.095				
S(O$_2$)Me	0.932	-1.006				
H	0.815	-1.207	-	-	-	-
Th	0.690	-1.210	-	-	-	-
1-Nf	0.710	-1.235	-	-	-	-
t-Bu	0.755	-1.260	-	-	-	-

[a]oxd = 4-methyl-1,2,5-oxadiazoles; [b] with H in position 4 of heteroaryl; [c]4,6,8-Me$_3$ in this position; [d]3,8-Me$_2$-5-iPr in this position.

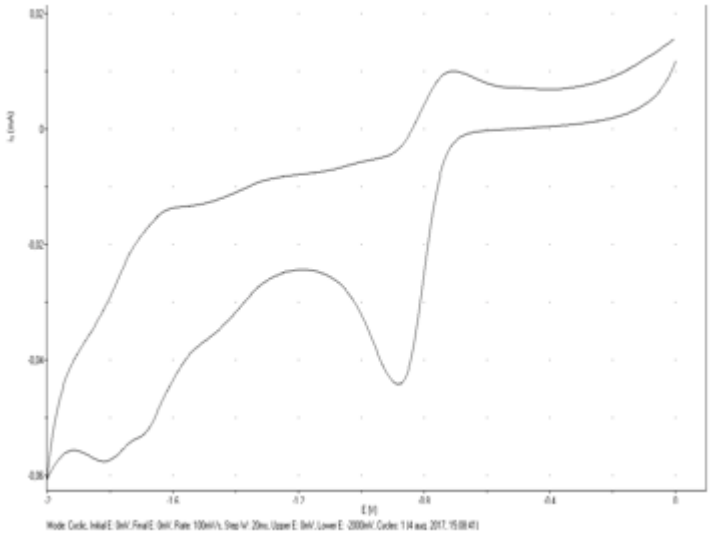


Fig. 9. CV (0.1 V/s) - glassy carbon electrode for 5(H) 1mM in 0.1M TBAP/CH3CN–cathodic side. The potential is measured toward Ag/AgCl(std)

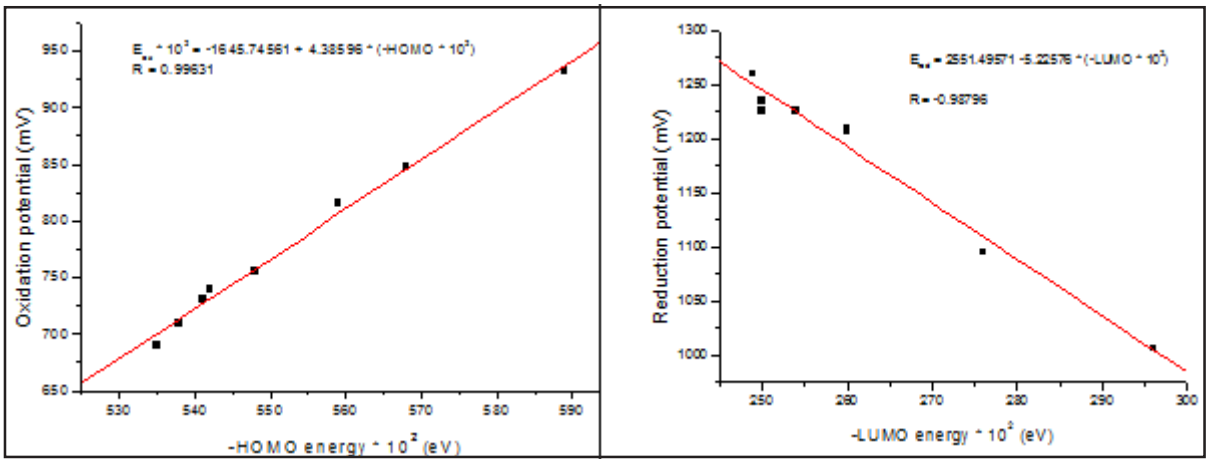


Fig. 10. Correlation between the experimental redox potentials and calculated energies of the frontier orbitals

A very good correlation between the experimental redox potentials and calculated energies of the frontier orbitals was observed in figure 10.

Conclusions

As a continuation of our studies regarding the preparation of azulen-1-yldiazenyl heteroaryl compounds several 2-(azulen-1-yldiazenyl)-1,3,4-thiadiazols were synthesized and characterized. Both the weak azulene nucleophilicity and the low reactivity of the diazonium salts arising from thiadiazolamines prevented the obtaining of high yields. Supplementary, the salts show a low selectivity, generating undesired compounds. Due to the oxidizing character toward the thiadiazole system of nitric acid, usually used for other diazotizations (e.g. for pyridines and thiazoles), this reaction was carried out in dichloroacetic acid. Starting from the compounds substituted at the diazonium position 5 of the thiadiazole moiety with Q = SH, some azulenic azulen-1-ylthioethers are generated.

All products were characterized and their spectra discussed. It must be noted that the protonated compounds splitting in mass spectrometer produces azulenediazonium ion and the unionized heterocycle. This peculiar decomposition could be the result of the low stability of diazonium salts arising from thiadiazole, which has also a higher oxidation capacity. The absorption maxima of the new compounds are close to those of the corresponding diazenes containing thiazole. They have brick-brown color in neutral medium and violet in strong acidic solutions. However, their nuances differ in neutral solvents with substituents: EDGs make them brownish and EWGs make them reddish-brown.

The redox potentials of products were also recorded noticing the influence of the substituents on the potentials. Linear correlations have been found for their oxidation and reduction potentials.

Acknowledgments: The authors are grateful to UEFISCDI - Exploratory Research Projects: PN-II-PT-PCCA-2013-4-2151, ID 15/2011 and 236/2014.

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Manuscript received: 25.04.2018