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Novel azobenzothiazole dyes from 2-nitrosobenzothiazoles

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ABSTRACT

Novel azobenzothiazole dyes obtained by condensation of 2-nitrosobenzothiazoles with several substituted anilines were synthesized and characterized. The influence of solvent polarity on absorption spectra was examined, as was the relationship between dye structures and absorption in the UV–visible region. Azobenzothiazole dyes possessing an anilino unit which possessed an o-electron donating group, displayed unique absorption properties as revealed by a second, long wavelength absorption band.

1. Introduction

Azo compounds are by far the most important class of colored compounds, accounting for more than 50% of all commercial dyes. They have been studied more than any other class of dyes due to their popular application as textile fiber dyestuffs. Excluding exceptions, azo dyes are prepared by diazotization of a primary aromatic amine followed by coupling the resulting diazonium salt with an electron donating aromatic compound [1,2].

Of the azo dyes, (benzo)thiazole-based disperse dyes have gained importance and constitute the first example of the successful textile commercial exploitation of heterocyclic amines, using the 2-aminobenzothiazole nucleus as the diazonium component in the production of red dyes [3]. Recently, azobenzothiazoles have found a new use as functional dyes. The emerging applications that have been recently reported are in liquid crystal technology, reprography, non-linear optics and as potential sensitizers for photodynamic therapy [4,5].

Most of the azobenzothiazole derivatives hitherto described result from the condensation of a benzothiazole diazonium salt with anilines. Other less common substituted couplers are alkoxybenzenes, azulenes, benzopyranones, imidazoles, naphthalenes, naphthalimides, pyrazoles, pyrazolones, pyridines and thiophenes [4,5]. All examples found in the literature are intrinsically limited to couplers with electron donating groups in the *para* position relative to the azo group or its equivalent.

To produce novel azobenzothiazole dyes, especially those bearing electron withdrawing groups at the coupling component or those substituted in any position of the phenyl moiety including the *ortho* and the *meta* positions, the authors recently developed an alternative synthetic route to this family of dyes based on the condensation of 2-nitrosobenzothiazoles with an aromatic amine, for which a strong electron donating capability is dispensable [5]. In addition to the full spectroscopic description of the examples reported in our previous communication, the generality of the method was extended to several azobenzothiazole dyes possessing electron donating methoxy, methylmercapto and acetamide groups located at the *ortho* or *para* positions of the aniline coupler. The new azobenzothiazole push–pull systems possessing electron donating *ortho* substituents in the phenyl moiety are of particular interest.

2. Experimental

2.1. General

All reagents were of the highest purity available, purchased from Sigma–Aldrich Company, and used as received; solvents were of analytical grade.

All reactions were monitored by thin-layer chromatography (tlc) on aluminum plates precoated with Merck silica gel 60 F_{254} (0.25 mm) using chloroform or chloroform/petroleum ether (1:1) and the spots were examined under 254 nm UV light.

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^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ solutions on a Bruker ACP 250 (250.13 and 62.90 MHz) spectrometer. Chemical shifts are reported in ppm relative to residual solvent signals or Me_4Si and coupling constants (J) are given in Hz.

Infrared spectra (IR) were performed on a Mattson 5000-FTS FTIR spectrophotometer. All samples were prepared by mixing FTIR-grade KBr with 1% (w/w) compound and grinding to a fine powder. Spectra were recorded over the 400–4000 cm^{-1} range without baseline corrections. More intense and/or characteristic bands are given in cm^{-1}.

Visible spectra (Vis) were recorded on a Perkin–Elmer Lambda 6 spectrophotometer in various solvents of increasing polarities, namely dichloromethane (DCM), acetone, dimethylsulfoxide (DMSO), acetonitrile and methanol at a concentration of 1.36×10^{-5} to 5.86×10^{-4} M. Wavelength of maximum absorption (λ_{max}) is reported in nm and the molar extinction coefficient (ε) in M^{-1} cm^{-1}.

Fast Atom Bombardment High Resolution Mass Spectra (FABHRMS) were determined on a Micromass AutoSpec M spectrometer, operating at 70 eV, using a matrix of 3-nitrobenzyl alcohol (3-NBA). Time-of-Flight High Resolution Mass Spectra (TOFHRMS) were recorded in a Waters Micromass GC-TOF spectrometer, operating in EI at 70 eV. Electrospray Ionisation High Resolution Mass Spectra (ESIMSHR) were determined on an ion cyclotropic resonance Bruker FTMS APEXIII spectrometer.

All new dyes were recrystallized from methanol/dichloromethane until a unique spot was observable by tlc.

Melting points were determined in open capillary tubes in a Büchi 530 melting point apparatus and are uncorrected.

2.2. Synthesis of 2-nitrosobenzothiazoles **1a–b**

2.2.1. 2-Nitrosobenzothiazole (**1a**). Modified procedure [5]

A solution of *Oxone* (Du Pont; ed note: monopersulfate based oxidant that requires caution in storage, handling and use) (21.91 g, 35.64 mmol) in a pH 5 acetic acid/sodium acetate buffer (0.5 M) (150 mL) and 5% aqueous sodium hydroxide (45 mL), were added to a solution of 2-aminobenzothiazole **1b** (1.78 g, 11.9 mmol) in MeOH/$CHCl_3$ [1/5 (v/v)] (400 mL), followed by the addition of the acetic acid/sodium acetate buffer (0.5 M) until total dissolution of the precipitated material. The resulting mixture was heated under reflux for 8 h. After cooling, the reaction mixture was filtered under reduced pressure to remove the insoluble material. The organic layer was separated by decantation, washed with brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was subjected to column chromatography (c.c.) (silica gel, CH_2Cl_2) to afford **1a** as green needles. Yield: 44%. M.p. 96–97 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.80–7.91 (3H, m, Ar*H*), 9.04–9.08 (1H, m, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 110.1 (*C*), 116.6 (*C*), 126.6 (*C*), 127.9 (*C*H), 128.8 (*C*H), 135.1 (*C*H), 136.5 (*C*H). IR (KBr) ν_{max} (cm^{-1}): 3086 (w, C–H_{arom}), 3068 (w, C–H_{arom}), 1584 (m, C–C_{arom}), 1565 (m, C–C_{arom}), 1471 (s, N=O), 1443 (m) 1398 (m), 1320 (m), 1263 (m), 1179 (s), 1167 (s), 1104 (s, C–NO), 764 (s). UV–Vis (MeOH) λ_{max} (nm) (ε): 312 nm (0.81×10^4); 384 nm (0.31×10^4). (TOFHRMS $[M]^+$, $C_7H_4N_2OS^+$): Calc: 164.0044; found: 164.0042.

2.2.2. 6-Nitro-2-nitrosobenzothiazole (**1b**)

Prepared by oxidation of the corresponding 2-amino-6-nitrobenzothiazole with Oxone, according to our previous communication [5].

2.3. Synthesis of azobenzothiazole dyes **3a–y**

All azobenzothiazole dyes were prepared by condensation of 2-nitrosobenzothiazole **1a** and 6-nitro-2-nitrosobenzothiazole **1b** with the appropriate anilines according to our previous communication [5].

2.3.1. Benzothiazol-2-yl-phenyldiazene (**3a**)

Obtained as yellow crystals after 48 h of reaction. Yield: 31%. M.p. 99–100 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.50–7.58 (5H, m, Ar*H*), 7.88 (1H, d, J = 8.3 Hz, Ar*H*), 7.91–7.95 (2H, m, Ar*H*), 8.01 (1H, dd, J = 2.0; 7.3, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 111.4 (*C*), 123.1 (2*C*H), 124.0 (*C*H), 125.0 (*C*), 128.0 (*C*H), 128.4 (*C*H), 129.4 (2*C*H), 132.1 (*C*H), 132.2 (*C*H), 148.0 (*C*), 151.2 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3461 (w), 3056 (w, C–H_{arom}), 2148 (w), 1581 (w, C–C_{arom}), 1560 (w), 1474 (w), 1452 (m), 1300 (w), 1269 (w), 1299 (w), 1061 (w), 1033 (w), 920 (w), 767 (s), 711 (m), 683 (s), 623 (w), 502 (w). FABHRMS ($[M + H]^+$, $C_{13}H_{10}N_4O_2S^+$): Calc: 240.0595; found: 240.0591.

2.3.2. Benzothiazol-2-yl-(2-chlorophenyl)diazene (**3b**)

Obtained as yellow crystals after 7 days of reaction. Yield: 10%. M.p. 105–107 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.37 (1H, dt, J = 1.3; 7.6 Hz, Ar*H*), 7.46 (1H, dt, J = 1.8; 7.6 Hz, Ar*H*), 7.52–7.62 (3H, m, Ar*H*), 7.77 (1H, dd, J = 1.8; 8.0 Hz, Ar*H*), 7.91 (1H, dd, J = 1.9; 7.8 Hz, Ar*H*), 8.10 (1H, dd, J = 2.0; 7.5 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 111.5 (*C*), 117.8 (*C*H), 123.8 (*C*), 126.6 (*C*H), 127.4 (*C*H), 128.2 (*C*H), 128.4 (*C*H), 131.0 (*C*H), 132.6 (*C*H), 132.9 (*C*H), 135.9 (*C*), 147.8 (*C*), 148.0 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3069 (w, C–H_{arom}), 1589 (w, C–C_{arom}), 1562 (w), 1466 (w), 1441 (m), 1228 (w), 1120 (w), 1057 (m, C_{arom}–Cl), 955 (w), 762 (s), 723 (s), 636 (w), 575 (w), 554 (w), 466 (w). FABHRMS ($[M + H]^+$, $C_{13}H_9ClN_3S^+$): Calc: 274.0206; found: 274.0218.

2.3.3. [3-(Benzothiazol-2-ylazo)phenyl]methanol (**3c**)

Obtained as yellow crystals after 6 days of reaction. Yield: 16%. M.p. 87–89 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 4.63 (2H, d, J = 5.5 Hz, CH_2OH, collapses to s with D_2O), 5.45 (1H, t, J = 5.8 Hz, broad s, CH_2OH, exchangeable D_2O), 7.57–7.59 (2H, m, Ar*H*), 7.65 (1H, t, J = 7.5 Hz, Ar*H*), 7.74 (1H, t, J = 7.5 Hz, Ar*H*), 7.80–7.85 (2H, m, Ar*H*), 7.90 (1H, s, Ar*H*), 8.06 (1H, d, J = 7.5 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 63.3 (CH_2), 112.8 (*C*), 121.3 (*C*H), 122.5 (*C*H), 124.0 (*C*), 125.7 (*C*H), 129.1 (*C*H), 130.3 (*C*H), 130.6 (*C*H), 131.8 (*C*H), 133.8 (*C*H), 144.5 (*C*), 148.6 (*C*), 151.5 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3265–3140 (m, O–H), 3103–3050 (w, C-H_{arom}), 2916 (w), 2853 (w), 2156 (m), 1729 (w), 1725 (w), 1588 (w, C–C_{arom}), 1480 (m), 1444 (s), 1368 (w), 1304 (w), 1241 (m), 1200 (w), 1129 (w), 1037 (s, C–OH), 786 (s), 765 (s), 715 (s), 681 (s), 511 (s). FABHRMS ($[M + H]^+$, $C_{14}H_{12}N_3OS^+$): Calc: 270.0701; found: 270.0704.

2.3.4. N-[2-(benzothiazol-2-ylazo)phenyl]acetamide (**3d**)

Obtained as yellow crystals after 60 h of reaction. Yield: 18%. M.p. 174–176 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 2.18 (3H, s, CH_3), 7.26 (1H, t, J = 7.8 Hz, Ar*H*), 7.59 (1H, dt, J = 1.5; 8.5 Hz, Ar*H*), 7.63–7.69 (2H, m, Ar*H*), 7.75 (1H, dt, J = 1.2 Hz; J = 7.4 Hz, Ar*H*), 7.85 (1H, d, J = 8.0 Hz, Ar*H*), 8.17 (2H, d, J = 7.8 Hz, Ar*H*), 10.08 (1H, s, N*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 24.1 (CH_3), 111.1 (*C*), 116.2 (*C*H), 122.9 (*C*H), 123.4 (*C*H), 124.4 (*C*H), 125.1 (*C*), 128.0 (*C*H), 129.3 (*C*H), 133.2 (*C*H), 133.5 (*C*H), 137.6 (*C*), 141.2 (*C*), 147.9 (*C*), 168.9 (*C*O). IR (KBr) ν_{max} (cm^{-1}): 3312 (s, N–H), 3182–3010 (w, C–H_{arom}), 1668 (s, C=O), 1591 (m, C–C_{arom}), 1526 (s, –HNCO–), 1483 (w), 1444 (m), 1372 (w), 1322 (m), 773 (m). ESIMSHR ($[M + Na]^+$, $C_{15}H_{12}N_4NaOS^+$): Calc: 319.06240; found: 319.06265.

2.3.5. N-[4-(benzothiazol-2-ylazo)phenyl]acetamide (**3e**)

Obtained as yellow crystals after 20 h of reaction. Yield: 56%. M.p. 172–174 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 2.11 (3H, s, CH_3), 7.61–7.68 (2H, m, Ar*H*), 7.88–7.98 (6H, m, Ar*H*), 10.40 (1H, s, N*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 24.2 (CH_3), 111.5 (*C*), 119.2 (2*C*H), 123.4 (*C*), 123.8 (*C*H), 124.1 (2*C*H), 127.9 (*C*H), 129.1 (*C*H), 132.4 (*C*H), 143.5 (*C*), 146.0 (*C*), 147.7 (*C*), 169.0 (*C*O). IR (KBr) ν_{max} (cm^{-1}): 3300 (w, N–H), 3262 (w, N–H), 3065 (w, C–H_{arom}), 1671 (s, C=O), 1595 (s, C–C_{arom}), 1543 (s, –HNCO–), 1502 (s), 1406 (m), 1370

(m), 1319 (m), 1307 (m), 1262 (m, C–N), 1147 (m). FABHRMS ($[M + H]^+$, $C_{15}H_{13}N_4OS^+$): Calc: 297.0810; found: 297.0818.

*2.3.6. Benzothiazol-2-yl-(2-methoxyphenyl)diazene (**3f**)*

Obtained as yellow crystals after 15 h of reaction. Yield: 27%. M.p. 82–84 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 4.05 (3H, s, C*H*$_3$), 7.03 (1H, t, $J = 7.6$ Hz, Ar*H*), 7.12 (1H, d, $J = 8.5$ Hz, Ar*H*), 7.48–7.50 (3H, m, Ar*H*), 7.75 (1H, d, $J = 8.0$ Hz, Ar*H*), 7.87–7.91 (1H, m, Ar*H*), 8.04–8.07 (1H, m, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 56.2 (*C*H$_3$), 112.5 (*C*), 112.8 (*C*H), 116.9 (*C*H), 120.8 (*C*H), 122.9 (*C*), 126.9 (*C*H), 128.0 (*C*H), 128.1 (*C*H), 131.5 (*C*H), 133.9 (*C*H), 140.4 (*C*), 148.5 (*C*), 157.6 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3078 (w, C–H$_{arom}$), 3061 (w, C–H$_{arom}$), 3011 (w), 2978 (w), 2943 (w), 2840 (w), 2148 (m), 1595 (m, C–C$_{arom}$), 1585 (m, C–C$_{arom}$), 1487 (s), 1460 (m), 1440 (m), 1316 (w), 1306 (w), 1282 (m), 1268 (w), 1249 (s, C$_{arom}$–O–CH$_3$), 1231 (m), 1184 (m), 1154 (w), 1109 (m), 1045 (w), 1024 (m), 939 (w), 781 (w), 763 (s), 753 (s), 711 (w), 630 (w), 571 (w), 537 (w), 502 (m), 488 (w). FABHRMS ($[M + H]^+$, $C_{14}H_{12}N_3OS^+$): Calc: 270.0701; found: 270.0697.

*2.3.7. Benzothiazol-2-yl-(4-methoxyphenyl)diazene (**3g**)*

Obtained as orange crystals after 2 h of reaction. Yield: 33%. M.p. 129–131 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 3.91 (3H, s, C*H*$_3$), 7.02 (2H, d, $J = 9.0$ Hz, Ar*H*), 7.45–7.50 (2H, m, Ar*H*), 7.82–7.86 (2H, m, Ar*H*), 7.91 (2H, d, $J = 9.0$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 55.7 (*C*H$_3$), 111.6 (*C*), 114.5 (2*C*H), 123.2 (*C*H), 124.6 (*C*), 125.1 (2*C*H), 127.8 (*C*H), 128.3 (*C*H), 131.4 (*C*H), 145.7 (*C*), 148.1 (*C*), 163.1 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3058 (w, C–H$_{arom}$), 1604 (m, C–C$_{arom}$), 1584 (m, C–C$_{arom}$), 1503 (m), 1257 (s, C$_{arom}$–O–CH$_3$), 1149 (m), 1025 (m), 835 (m), 757 (m). FABHRMS ($[M + H]^+$, $C_{14}H_{12}N_3OS^+$): Calc: 270.0701; found: 270.0701.

*2.3.8. Benzothiazol-2-yl-(2-methylsulfanylphenyl)diazene (**3h**)*

Obtained as yellow crystals after 3 days of reaction. Yield: 59%. M.p. 155–157 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.54 (3H, s, C*H*$_3$), 7.21 (1H, t, $J = 7.5$ Hz, Ar*H*), 7.33 (1H, d, $J = 8.0$ Hz, Ar*H*), 7.43–7.56 (3H, m, Ar*H*), 7.74 (1H, d, $J = 8.0$ Hz, Ar*H*), 7.87 (1H, d, $J = 7.5$ Hz, Ar*H*), 8.00 (1H, d, $J = 7.8$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 14.8 (*C*H$_3$), 111.4 (*C*), 118.3 (*C*H), 124.1 (*C*H + *C*), 124.6 (*C*H), 124.8 (*C*H), 127.9 (*C*H), 128.4 (*C*H), 132.1 (*CH*), 132.4 (*CH*), 141.5 (*C*), 148.0 (*2C*). IR (KBr) ν_{max} (cm^{-1}): 3062 (w, C–H$_{arom}$), 2976 (w), 2916 (w), 2151 (m), 1576 (w, C–C$_{arom}$), 1565 (w, C–C$_{arom}$), 1460 (m), 1438 (m), 1254 (w), 1224 (w), 1070 (w), 1056 (w), 1040 (w), 1029 (w), 955 (w), 760 (s), 747 (m), 723 (s), 553 (w), 506 (s), 497 (m). FABHRMS ($[M + H]^+$, $C_{14}H_{12}N_3S_2^+$): Calc: 286.0473; found: 286.0466.

*2.3.9. Benzothiazol-2-yl-(4-methylsulfanylphenyl)diazene (**3i**)*

Obtained as yellow crystals after 24 h of reaction. Yield: 68%. M.p. 112–114 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.56 (3H, s, C*H*$_3$) 7.33 (2H, d, $J = 8.3$ Hz, Ar*H*), 7.46 (1H, t, $J = 7.3$ Hz, Ar*H*), 7.51 (1H, t, $J = 7.0$ Hz, Ar*H*), 7.85 (3H, d, $J = 8.3$ Hz, Ar*H*), 7.95 (1H, d, $J = 7.8$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 15.0 (*C*H$_3$) 111.4 (*C*), 123.5 (3*C*H), 124.9 (*C*), 125.8 (2*C*H), 127.9 (*C*H), 128.4 (*C*H), 131.8 (*C*H), 145.1 (*C*), 148.1 (*C*), 148.5 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3057 (w, C–H$_{arom}$), 2914 (w), 2156 (m), 1585 (s, C–C$_{arom}$), 1565 (m, C–C$_{arom}$), 1512 (w), 1482 (m), 1457 (w), 1433 (w), 1422 (w), 1397 (m), 1256 (w), 1235 (w), 1150 (m), 1089 (s), 825 (m), 814 (w), 766 (s), 748 (m), 721 (m). FABHRMS ($[M + H]^+$, $C_{14}H_{12}N_3S_2^+$): Calc: 286.0473; found: 286.0479.

*2.3.10. (6-Nitrobenzothiazol-2-yl)phenyldiazene (**3j**)*

For experimental details as well as spectroscopic data see Ref. [5]

*2.3.11. 2-(6-Nitrobenzothiazol-2-ylazo)benzoic acid (**3k**)*

Obtained as orange crystals after 3 days of reaction. Yield: 63%. M.p. 188–190 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 7.65–7.87 (4H, m, Ar*H*), 8.13 (1H, d, $J = 8.5$ Hz, Ar*H*), 8.48 (1H, dd, $J = 2.3$; 8.5 Hz, Ar*H*), 8.55 (1H, d, $J = 2.3$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 110.6 (*C*), 118.4 (*C*H), 123.4 (*C*H), 124.3 (*C*H), 124.6 (*C*H), 126.6 (*C*), 129.5 (*C*H), 131.5 (*C*H), 131.9 (*C*), 132.7 (*C*H), 149.0 (*C*), 149.4 (*C*), 150.1 (*C*), 167.9 (*C*O). IR (KBr) ν_{max} (cm^{-1}): 3456 (w, COO–H), 3101 (w, C–H$_{arom}$), 1695 (s, C=O), 1593 (w, C–C$_{arom}$), 1525 (m, NO$_2$), 1485 (w), 1426 (w) 1349 (s, NO$_2$), 1310 (m), 1295 (m), 887 (w), 760 (w). ESIMSHR ($[M + Na]^+$, $C_{14}H_8N_4NaO_4S^+$): Calc: 351.01585; found: 315.01653.

*2.3.12. (2-Chlorophenyl)-(6-nitrobenzothiazol-2-yl)diazene (**3l**)*

Obtained as orange crystals after 6 h of reaction. Yield: 58%. M.p. 194–196 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.42 (1H, t, $J = 7.3$ Hz, Ar*H*), 7.55 (1H, t, $J = 7.5$ Hz, Ar*H*), 7.66 (1H, d, $J = 8.0$ Hz, Ar*H*), 7.82 (1H, d, $J = 8.3$ Hz, Ar*H*), 8.25 (1H, d, $J = 8.8$ Hz, Ar*H*), 8.37 (1H, dd, $J = 2.3$; 8.8 Hz, Ar*H*), 8.79 (1H, d, $J = 2.3$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 110.0 (*C*), 117.8 (*C*H), 123.5 (*C*H), 123.6 (*C*H), 126.2 (*C*), 126.9 (*C*H), 127.6 (*C*H), 131.4 (*C*H), 134.5 (*C*H), 137.3 (*C*), 147.8 (*C*), 149.0 (*C*), 150.4 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3094 (w, C–H$_{arom}$), 2360 (m), 2342 (m), 1583 (w, C–C$_{arom}$), 1573 (w, C–C$_{arom}$), 1525 (s, NO$_2$), 1347 (s, NO$_2$), 1058 (w, C$_{arom}$–Cl), 888 (w), 761 (w). ESIMSHR ($[M + Na]^+$, $C_{13}H_7ClN_4NaO_2S^+$): Calc: 340.98704; found: 340.98720.

*2.3.13. (3-Chlorophenyl)-(6-nitrobenzothiazol-2-yl)diazene (**3m**)*

Obtained as orange crystals after 6 h of reaction. Yield: 63%. M.p. 138–140 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.51–7.62 (2H, m, Ar*H*), 7.89–7.94 (2H, m, Ar*H*), 8.14 (1H, d, $J = 8.8$ Hz, Ar*H*), 8.35 (1H, dd, $J = 2.3$; 8.8 Hz, Ar*H*), 8.75 (1H, d, $J = 2.3$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 109.4 (*C*), 122.5 (*C*H), 123.1 (*C*H), 123.5 (*C*H), 123.7 (*C*H), 124.3 (*C*H), 127.8 (*C*), 130.7 (*C*H), 133.4 (*C*H), 135.8 (*C*), 149.2 (*C*) 150.2 (*C*), 151.9 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3083 (w, C–H$_{arom}$), 1571 (w, C–C$_{arom}$), 1525 (s, NO$_2$), 1346 (s, NO$_2$), 1061 (w, C$_{arom}$–Cl), 894 (w). ESIMSHR ($[M + Na]^+$, $C_{13}H_7ClN_4NaO_2S^+$): Calc: 340.98704; found: 340.98547.

*2.3.14. (4-Chlorophenyl)-(6-nitrobenzothiazol-2-yl)diazene (**3n**)*

Obtained as orange crystals after 1 h of reaction. Yield: 82%. M.p. 166–167 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.56 (2H, d, $J = 8.8$ Hz, Ar*H*), 7.94 (2H, d, $J = 8.8$ Hz, Ar*H*), 8.12 (1H, d, $J = 8.8$ Hz, Ar*H*), 8.34 (1H, dd, $J = 2.3$; 8.8 Hz, Ar*H*), 8.74 (1H, d, $J = 2.3$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 109.5 (*C*), 123.4 (*C*H), 123.7 (*C*H), 123.8 (*C*H), 124.9 (2*C*H), 127.8 (*C*), 130.0 (2*C*H), 140.2 (*C*), 149.1 (*C*), 149.6 (*C*), 150.4 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3089 (w, C–H$_{arom}$), 1587 (w, C–C$_{arom}$), 1573 (w, C–C$_{arom}$), 1531 (s, NO$_2$), 1483 (m), 1347 (s, NO$_2$), 1315 (m), 1087 (m, C$_{arom}$–Cl), 846 (m). ESIMSHR ($[M + Na]^+$, $C_{13}H_7ClN_4NaO_2S^+$): Calc: 340.98704; found: 340.98632.

*2.3.15. (4-Fluorophenyl)-(6-nitrobenzothiazol-2-yl)diazene (**3o**)*

Obtained as orange crystals after 30 min of reaction. Yield: 72%. M.p. 155–157 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 7.53 (2H, t, $J = 8.5$ Hz, Ar*H*), 8.05–8.11 (2H, m, Ar*H*), 8.19 (1H, d, $J = 8.5$ Hz, Ar*H*), 8.43 (1H, d, $J = 8.5$ Hz, Ar*H*), 8.51 (1H, d, $J = 1.8$ Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 110.8 (*C*), 116.9 + 117.3 (*C*H), 123.3 (*C*H), 124.4 (*C*H), 124.7 (*C*H), 125.9 + 126.1 (*CH*), 126.2 (*C*), 147.5 (*C*), 147.6 (*C*), 148.5 (*C*), 150.2 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3479–3380 (w), 3078 (w, C–H$_{arom}$), 2360 (w), 2342 (w), 2164 (w), 1591 (s, C–C$_{arom}$), 1543 (m, NO$_2$), 1495 (m), 1449 (w), 1433 (w), 1410 (w), 1393 (w), 1346 (s, NO$_2$), 1313 (m), 1237 (s, C$_{arom}$–F), 1172 (w), 1137 (s, C$_{arom}$–F), 1095 (w), 1047 (w), 899 (w), 884 (w), 851 (m), 836 (w), 746 (w), 720 (w), 544 (w). FABHRMS ($[M + H]^+$, $C_{13}H_8FN_4O_2S^+$): Calc: 303.0352; found: 303.0352.

*2.3.16. (4-Iodophenyl)-(6-nitrobenzothiazol-2-yl)diazene (**3p**)*

Obtained as orange crystals after 16 h of reaction. Yield: 77%. M.p. 190–192 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.70 (2H, d,

J = 8.8 Hz, Ar*H*), 7.95 (2H, d, J = 8.8 Hz, Ar*H*), 8.13 (1H, d, J = 8.8 Hz, Ar*H*), 8.34 (1H, dd, J = 2.3; 8.8 Hz, Ar*H*), 8.75 (1H, d, J = 2.3 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 101.7 (*C*), 109.5 (*C*), 123.5 (*C*H), 123.7 (*C*H), 124.0 (*C*H), 125.0 (2*C*H), 127.8 (*C*), 139.1 (2*C*H), 149.1 (*C*), 149.4 (*C*), 150.5 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3083 (w, C–H_{arom}), 1576 (w, C–C_{arom}), 1565 (w, C–C_{arom}), 1523 (s, NO_2), 1478 (w), 1342 (s, NO_2), 1315 (w), 1304 (w), 1149 (w, C_{arom}–I), 1005 (w), 842 (w). ESIMSHR ($[M + Na]^+$, $C_{13}H_7IN_4NaO_2S^+$): Calc: 432.92266; found: 432.92153.

*2.3.17. (6-Nitrobenzothiazol-2-yl)-(4-nitrophenyl)diazene (**3q**)*

Obtained as orange crystals after 3 days of reaction. Yield: 33%. M.p. 173–175 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 8.15 (2H, d, J = 8.5 Hz, Ar*H*), 8.25 (1H, d, J = 8.5 Hz, Ar*H*), 8.44–8.47 (3H, m, Ar*H*), 8.51 (1H, s, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 110.6 (*C*), 123.4 (*C*H), 124.2 (2*C*H), 124.5 (*C*H), 125.3 (2*C*H), 125.5 (*C*H), 127.0 (*C*), 149.1 (*C*), 149.6 (*C*), 150.1 (*C*), 153.4 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3099 (w, C–C_{arom}), 1606 (w, C–C_{arom}), 1526 (s, NO_2), 1347 (s, NO_2), 1312 (w), 884 (w), 867 (w), 812 (w). ESIMSHR ($[M + Na]^+$, $C_{13}H_7N_5NaO_4S^+$): Calc: 352.01110; found: 352.01253.

*2.3.18. [3-(6-Nitrobenzothiazol-2-ylazo)phenyl]methanol (**3r**)*

Obtained as orange crystals after 24 h of reaction. Yield: 43%. M.p. 127–130 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 4.63 (2H, s, CH_2OH), 5.50 (1H, broad s, CH_2O*H,* exchangeable D_2O), 7.60–7.63 (2H, m, Ar*H*), 7.87 (1H, dd, J = 2.5; 6.5 Hz, Ar*H*), 7.93 (1H, s, Ar*H*), 8.22 (1H, d, J = 8.8 Hz, Ar*H*), 8.41 (1H, dd, J = 2.3; 8.8 Hz, Ar*H*), 8.50 (1H, d, J = 2.3 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 62.2 (*C*H_2), 111.0 (*C*), 120.5 (*C*H), 122.2 (*C*H), 123.2 (*C*H), 124.4 (*C*H), 125.6 (C), 125.7 (*C*H), 129.7 (*C*H), 132.0 (*C*H), 144.8 (C), 148.5 (C), 150.3 (C), 150.6 (C). IR (KBr) ν_{max} (cm^{-1}): 3555–3400 (m, O–H), 3099 (w, C–H_{arom}), 2927 (w), 2877 (w), 2360 (w), 2341 (w), 2149 (w), 1599 (w, C–C_{arom}), 1570 (w, C–C_{arom}), 1519 (s, NO_2), 1487 (w), 1474 (w), 1444 (m), 1345 (s, NO_2), 1311 (m), 1260 (w), 1241 (m), 1191 (w), 1133 (w), 1120 (m), 1046 (m, C–OH), 1024 (m, C–OH), 889 (m), 853 (w), 839 (m), 808 (w), 800 (w), 745 (m), 709 (m), 686 (m). FABHRMS ($[M + H]^+$, $C_{14}H_{11}N_4O_3S^+$): Calc: 315.0552; found: 315.0552.

*2.3.19. N-[2-(6-nitrobenzothiazol-2-ylazo)phenyl]acetamide (**3s**)*

Obtained as orange crystals after 30 min of reaction. Yield: 60%. M.p. 191–193 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$/DMSO-d_6 – 0.5%) δ (ppm): 2.17 (3H, s, CH_3), 7.06 (1H, dt, J = 7.6 Hz, J = 1.2 Hz, Ar*H*), 7.46 (1H, dt, J = 1.8; 8.8 Hz, Ar*H*), 7.66 (1H, dd, J = 1.3; 8.3 Hz, Ar*H*), 7.95 (1H, d, J = 9.0 Hz, Ar*H*), 8.21 (1H, dd, J = 2.3; 8.8 Hz, Ar*H*), 8.44 (1H, d, J = 8.0 Hz, Ar*H*), 8.57 (1H, d, J = 2.0 Hz, Ar*H*), 9.49 (1H, s, N*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$/DMSO-d_6 – 0.5%) δ (ppm): 24.4 (*C*H_3), 108.6 (*C*), 117.9 (*C*H), 121.3 (*C*H), 121.5 (*C*H), 122.4 (*C*H), 123.4 (2*C*H), 127.6 (*C*), 135.0 (*C*H), 137.7 (*C*), 139.4 (*C*), 148.2 (*C*), 150.0 (*C*), 168.3 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3485–3367 (w, N–H), 3299 (m, N–H), 3094 (w, C–H_{arom}), 2360–2332 (w), 2162 (w), 1674 (s, C═O), 1645 (w), 1638 (w), 1586 (m, C–C_{arom}), 1531 (s, NO_2), 1520 (s), 1476 (m), 1462 (m), 1432 (m) 1392 (w), 1369 (w), 1344 (s, NO_2), 1314 (m), 1295 (m, C–N), 1251 (m), 1231 (m), 1176 (w), 1154 (m), 1125 (w), 1117 (w) 1051 (w), 890 (w), 883 (w), 767 (m), 740 (w), 731 (w), 667 (w), 659 (w), 647 (w). FABHRMS ($[M + H]^+$, $C_{15}H_{12}N_5O_3S^+$): Calc: 342.0661; found: 342.0658.

*2.3.20. N-[4-(6-nitrobenzothiazol-2-ylazo)phenyl]acetamide (**3t**)*

Obtained as orange crystals after 20 min of reaction. Yield: 72%. M.p. 211–213 °C. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 2.12 (3H, s, CH_3), 7.86 (2H, d, J = 9.0 Hz, Ar*H*), 8.00 (2H, d, J = 9.0 Hz, Ar*H*), 8.17 (1H, d, J = 8.8 Hz, Ar*H*), 8.42 (1H, dd, J = 2.3; 8.8 Hz, Ar*H*), 8.53 (1H, d, J = 2.3 Hz, Ar*H*), 10.52 (1H, s, N*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 24.3 (*C*H_3), 111.1 (*C*), 119.3 (2*C*H), 123.1 (*C*H), 124.4 (*C*H), 124.5 (*C*H), 125.1 (2*C*H), 125.6 (*C*), 144.8 (*C*), 146.3 (*C*), 148.1 (*C*), 161.1 (*C*), 161.7 (*C*), 169.3 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3340 (w, N–H), 3291 (w, N–H), 3093 (w, C–H_{arom}), 2360 (m), 2342 (w), 2171 (w), 1706 (s, C═O), 1599 (s, C–C_{arom}) 1540 (m, –HNCO–), 1526 (s, NO_2), 1501 (w), 1438 (w), 1427 (w), 1405 (w), 1367 (w), 1347 (s, NO_2), 1312 (w), 1268–1259 (m, C–N), 1150 (m), 884 (w), 867 (w), 812 (w). FABHRMS ($[M + H]^+$, $C_{15}H_{12}N_5O_3S^+$): Calc: 342.0661; found: 342.0658.

*2.3.21. (6-Nitrobenzothiazol-2-yl)-(2-methoxyphenyl)diazene (**3u**)*

Obtained as orange crystals after 1 h of reaction. Yield: 54%. M.p. 168–170 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 4.09 (3H, s, CH_3), 7.05 (1H, t, J = 7.5 Hz, Ar*H*), 7.16 (1H, d, J = 8.3 Hz, Ar*H*), 7.59 (1H, t, J = 7.5 Hz, Ar*H*), 7.78 (1H, d, J = 8.0 Hz, Ar*H*), 8.19 (1H, d, J = 8.8 Hz, Ar*H*), 8.32 (1H, dd, J = 2.0; 8.8 Hz, Ar*H*), 8.76 (1H, d, J = 2.0 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 56.2 (*C*H_3), 111.2 (*C*), 113.1 (*C*H), 116.9 (*C*H), 120.9 (*C*H), 123.1 (*C*H), 123.5 (*C*H), 124.9 (*C*), 127.6 (*C*H), 135.9 (*C*H), 140.3 (*C*), 148.2 (*C*), 150.9 (*C*), 158.6 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3101 (w, C–H_{arom}), 2942 (w), 2842 (w), 2146 (w), 1592 (m, C–C_{arom}), 1581 (m, C–C_{arom}), 1522 (s, NO_2), 1484 (s), 1456 (w), 1437 (w), 1411 (w), 1344 (s, NO_2), 1312 (m), 1285 (m), 1248 (s, C_{arom}–O–CH_3), 1184 (w), 1177 (w), 1157 (s), 1121 (w), 1108 (w), 1057 (w), 1039 (w), 1022 (m), 885 (m), 841 (m), 830 (m), 758 (s), 734 (m), 726 (w). FABHRMS ($[M + H]^+$, $C_{14}H_{11}N_4O_3S^+$): Calc: 315.0552; found: 315.0545.

*2.3.22. (6-Nitrobenzothiazol-2-yl)-(4-methoxyphenyl)diazene (**3v**)*

Obtained as orange crystals after 1 h of reaction. Yield: 57%. M.p. 162–164 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 3.94 (3H, s, CH_3), 7.04 (2H, d, J = 9.0 Hz, Ar*H*), 7.94 (2H, d, J = 9.0 Hz, Ar*H*), 8.03 (1H, d, J = 8.8 Hz, Ar*H*), 8.27 (1H, dd, J = 2.3; 8.8 Hz, Ar*H*), 8.67 (1H, d, J = 2.3 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 55.8 (*C*H_3), 110.0 (*C*), 114.8 (2*C*H), 123.1 (*C*H), 123.2 (*C*H), 123.6 (*C*H), 126.1 (2*C*H), 127.0 (*C*), 145.9 (*C*), 148.3 (*C*), 150.8 (*C*), 164.5 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3098 (w, C–H_{arom}), 3075 (w), 1597 (s, C–C_{arom}), 1581 (m, C–C_{arom}), 1522 (s, NO_2), 1501 (m), 1341 (s, NO_2), 1313 (m), 1260 (s, C_{arom}–O–CH_3), 1247 (s), 1151 (m), 1139 (s), 1117 (m), 1023 (m), 845 (m). FABHRMS ($[M + H]^+$, $C_{14}H_{11}N_4O_3S^+$): Calc: 315.0552; found: 315.0555.

*2.3.23. (6-Nitrobenzothiazol-2-yl)-(2-methylsulfanylphenyl)diazene (**3x**)*

Obtained as reddish-orange crystals after 17 h of reaction. Yield: 57%. M.p. 184–186 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.57 (3H, s, CH_3), 7.25 (1H, t, J = 8.0 Hz, Ar*H*), 7.37 (1H, d, J = 8.3 Hz, Ar*H*), 7.53 (1H, t, J = 7.0 Hz, Ar*H*), 7.81 (1H, d, J = 7.3 Hz, Ar*H*), 8.12 (1H, d, J = 8.8 Hz, Ar*H*), 8.31 (1H, dd, J = 2.3; 8.8 Hz, Ar*H*), 8.74 (1H, d, J = 2.0 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 14.8 (*C*H_3), 109.8 (*C*), 119.6 (*C*H), 123.3 (*C*H), 123.6 (*C*H), 124.0 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 127.2 (*C*), 133.9 (*C*H), 143.1 (*C*), 148.0 (*C*), 148.8 (*C*), 150.6 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3456 (w), 3419 (w), 3099 (w, C–H_{arom}), 2923 (w), 2160 (w), 1579 (m, C–C_{arom}), 1525 (s, NO_2), 1465 (m), 1434 (m), 1425 (m), 1390 (m), 1344 (s, NO_2) 1258 (m), 1318 (m), 1304 (m), 1258 (w), 1178 (w), 1117 (m), 1108 (m), 1070 (w), 1047 (w), 883 (m), 766 (m), 719 (m). ESIMSHR ($[M + Na]^+$, $C_{14}H_{10}N_4NaO_2S_2^+$): Calc: 353.01374; found: 353.01356.

*2.3.24. (6-Nitrobenzothiazol-2-yl)-(4-methylsulfanylphenyl)diazene (**3y**)*

Obtained as reddish-orange crystals after 17 h of reaction. Yield: 57%. M.p. 153–155 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.60 (3H, s, CH_3), 7.50 (2H, d, J = 8.8 Hz, Ar*H*), 7.94 (2H, d, J = 8.8 Hz, Ar*H*), 8.18 (1H, d, J = 8.5 Hz, Ar*H*), 8.41 (1H, dd, J = 2.5; 8.8 Hz, Ar*H*), 8.52 (1H, d, J = 2.3 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 14.9 (*C*H_3), 109.9 (*C*), 123.3 (*C*H), 123.4 (*C*H), 123.6 (*C*H), 124.2 (2*C*H), 125.6 (2*C*H), 127.2 (*C*), 147.9 (*C*), 148.5 (*C*), 148.6 (*C*), 150.7 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3466–3378 (w), 3093 (w, C–H_{arom}), 3080 (w), 3006 (w), 2926 (w), 2152 (w), 1583 (s, C–C_{arom}), 1558 (w), 1524 (s, NO_2), 1483 (m), 1433 (m), 1399 (w), 1383 (w), 1341 (s, NO_2), 1246

(w), 1152 (m), 1119 (w), 1087 (s), 883 (m), 837 (m). FABHRMS ($[M + H]^+$, $C_{14}H_{11}N_4O_2S_2^+$): Calc: 331.0323; found: 331.0332.

3. Results and discussion

Azobenzothiazole dyes **3a**–**y** were synthesized by the condensation of 2-nitrosobenzothiazole (**1a**) and 6-nitro-2-nitrosobenzothiazole (**1b**) with aniline (**2a**), anthranilic acid (**2b**), 2-chloroaniline (**2c**), 3-chloroaniline (**2d**), 4-chloroaniline (**2e**), 4-fluororoaniline (**2f**), 4-iodoaniline (**2g**), 3-aminobenzyl alcohol (**2h**), 4-nitroaniline (**2i**), 2′-aminoacetanilide (**2j**), 4′-aminoacetanilide (**2k**), *o*-anisidine (**2l**), *p*-anisidine (**2m**), (2-methylmercapto)aniline (**2n**) and (4-methylmercapto)aniline (**2o**), following a new synthetic route recently developed by our group (Scheme 1) [5]. In addition to the non-substituted anilines **3a**,**j** and substituted anilines **3b**–**c**,**k**–**r** with different types of electronic groups in the *ortho*, *meta* or *para* positions, azobenzothiazole dyes **3d**–**i**,**s**–**y** bearing an electron donating methoxy, methylmercapto or acetamide group in either *ortho*- or *para*-positions of the phenyl moiety of the dye in relation to the azo group are also presented.

The condensation reaction was carried out at room temperature in glacial acetic acid for 0.5 h to 7 days until tlc showed complete consumption of the starting materials. The azobenzothiazole dyes **3a**–**y** precipitated from the reaction mixture and could be isolated in pure form by simple filtration with non-optimized yields, after recrystallization from methanol/dichloromethane, ranging from 10 to 82% (Table 1). In general, the presence of powerful electron donating groups (methoxy, methylmercapto or acetamide) in the aniline coupler was shown to increase the reaction yields. For example, azobenzothiazoles **3a**–**c** and their analogues **3d**–**i** were obtained in yields of 10–30% and 18–68%, respectively. As previously observed [5], the presence of the electron withdrawing nitro group in 2-nitrosobenzothiazole also increases the reactivity, but not so dramatically as the presence of electron donating groups in the aniline coupler as mentioned above. In these cases, an increased yield is obtained when there is an electron withdrawing substituent in the aniline coupler. This is seen in *ortho* substituted **3b** and **3l**, where the nitro group induces a 48% increase in yield between the 2-Cl analogues and similarly in 3-CH_2OH (**3c** and **3r**) where the yield increases from 16 to 43%. This effect is even more pronounced when an electron donating substituent such as acetamide (**3d**–**e** and **3s**–**t**), methoxy (**3f**–**g** and **3u**–**v**) or methylmercapto (**3h**–**i** and **3x**–**y**), is present. Attempts to prepare the azobenzothiazole dyes **3a**,**j** from the condensation of 2-aminobenzothiazoles with 2-nitrosobenzene were unsuccessful.

The spectroscopic characterization of the new dyes **3d**–**i**,**s**–**y** together with those reported in our preliminary communication [5] using ^1H and ^{13}C NMR, FTIR and UV–Vis Spectroscopy and HRMS (FAB, ESI or TOF) is discussed.

The influence of the substitution pattern in azobenzothiazole dyes possessing an aromatic amine coupler with typical push-groups on their absorption spectrum, based on conventional donor–acceptor interactions, is well documented [2,4,6,7]. The influence of the substitution pattern of the unsubstituted aniline coupling moiety or those bearing different types of electronic substituents in positions other than *para* to the azo group was demonstrated by the UV–Vis absorption spectra for that type of dyes [5]. In these cases, the wavelength of maximum absorption seems to depend on a balance between the bathochromic effects induced by the electron donating substituents on the phenyl ring or by the electron withdrawing substituents on the benzothiazole moiety and the hypsochromic effects due to electron withdrawing phenyl substituents [2,5].

However, and to the best of our knowledge, the new azobenzothiazoles possessing electron donating methoxy, methylmercapto or acetamide substituents in the *ortho* position to the azo group has not yet been described and therefore allows, for the first time, a comparison of the UV–Vis absorption between azobenzothiazole dyes with push groups in the *ortho* position in relation to the analogues in *para* position, as in a conventional donor–acceptor interaction electronic transitions pattern.

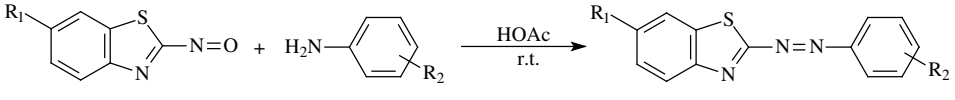
The UV–Vis absorption spectra of benzothiazole dyes **3a**–**y** were recorded in various solvents of increasing polarities [8], namely DCM ($E_T(30) = 40.7$), acetone ($E_T(30) = 42.2$), DMSO ($E_T(30) = 45.1$), acetonitrile ($E_T(30) = 45.6$) and methanol ($E_T(30) = 55.4$) and the results are summarized in Table 1.

Contrary to what has been observed with some azo(benzo)thiazole dyes [9–13], the polarity of the solvent does not seems to show any meaningful solvatochromic effects. Even acetamide dyes **3d**,**e**,**s**,**t** that can undergo a solvent-dependent tautomeric equilibrium due to the interaction of the amido hydrogen atom with polar solvents, did not show any regular bathochromic shift as the polarity of the solvent increased.

As expected, the absorption band of azobenzothiazoles is affected by steric as well as electronic effects whatever the solvent. In general, bathochromicity is promoted by the incorporation of an electron withdrawing group into the benzothiazole acceptor ring and/or an electron releasing group into the phenyl moiety, in a position that extends conjugation between the two aromatic rings in a typical donor–acceptor chromogen [2,6,7].

Therefore, the presence of a nitro group in the benzothiazole moiety invariably leads to a bathochromic shift due to the extension of conjugation [14–17] and above all to its electron-withdrawing nature. Accordingly, nitrobenzothiazoles **3t**,**v**,**y** with acetamide, methoxy or methylmercapto or acetamide groups in the *para* position have shown values of λ_{max} 25–38 nm higher than those of their parent non-substituted analogues **3e**,**g**,**i**. These differences are more significant than that observed between the non push–pull nitroazobenzothiazole dyes **3j**,**l**,**r** in relation to the non nitro analogues **3a**–**c** (λ_{max} 0–17 nm) (Table 1).

Azobenzothiazole dye **3m** substituted in the *meta* position exhibits a hypsochromic shift in relation to both *ortho* and *para* isomers **3l**,**n** ($\Delta\lambda_{max}$ = 3–10 nm and 10–16 nm, respectively) due to a lack of conjugation. Despite the electron-withdrawing nature of



1a-b **2a-o** **3a-y**

R_1 = H, NO_2
R_2 = H, 2-CO_2H, (2-, 3-, 4-)Cl, 4-F, 4-I, 3-CH_2OH, 4-NO_2, (2-, 4-)$NHCOCH_3$, (2-, 4-)OCH_3, (2-, 4-)SCH_3

Scheme 1. Synthesis of azobenzothiazole dyes **3a**–**y**.

Table 1
λ_{max} (nm) and ε_{max} (M^{-1} cm^{-1}) of azobenzothiazole dyes **3a**–**y**.

Dye			DCM		Acetone		DMSO		Acetonitrile		Methanol	
	R_1	R_2	λ_{max}	$\varepsilon_{max} \times 10^4$	λ_{max}	$\varepsilon_{max} \times 10^4$	λ_{max}	$\varepsilon_{max} \times 10^4$	λ_{max}	$\varepsilon_{max} \times 10^4$	λ_{max}	$\varepsilon_{max} \times 10^4$
3a	H	H	328	2.53	332	2.04	332	1.97	328	1.84	328	1.74
3b	H	2-Cl	348	0.85	342	0.76	344	0.54	335	0.67	332	2.07
3c	H	3-CH_2OH	330	1.60	334	1.28	335	2.15	328	2.50	328	1.92
3d	H	2-$NHCOCH_3$	334	1.83	335	1.53	332	0.81	331	2.54	331	1.45
3e	H	4-$NHCOCH_3$	371	2.13	371	7.31	385	1.73	371	1.81	368	2.08
3f	H	2-OCH_3	325	1.48	332	0.95	331	1.13	325	1.09	325	0.70
			370	1.59	376	1.04	382	1.16	376	1.12	376	0.70
3g	H	4-OCH_3	368	1.30	366	0.16	370	1.80	361	1.47	365	1.59
3h	H	2-SCH_3	330	0.68	333	1.19	332	1.75	328	1.31	328	1.08
			420	0.29	420	0.48	428	0.73	418	0.53	420	0.44
3i	H	4-SCH_3	397	2.50	396	1.94	403	1.98	392	2.03	396	1.89
3j	NO_2	H	343	2.53	341	2.25	349	2.80	340	2.32	340	2.32
3k	NO_2	2-CO_2H	347	1.59	339	1.65	342	1.54	335	3.54	340	1.58
3l	NO_2	2-Cl	347	1.72	342	1.92	352	2.07	343	1.81	340	2.00
3m	NO_2	3-Cl	337	2.49	339	1.86	343	2.61	334	4.44	336	2.08
3n	NO_2	4-Cl	353	2.41	349	3.14	355	1.70	346	2.55	346	2.43
3o	NO_2	4-F	348	2.45	343	8.51	352	1.97	342	2.31	344	2.11
3p	NO_2	4-I	369	2.61	366	3.68	371	2.54	368	4.81	370	2.25
3q	NO_2	4-NO_2	334	2.29	338	2.16	338	1.28	332	2.70	332	2.72
3r	NO_2	3-CH_2OH	346	1.58	343	0.35	352	4.16	341	4.43	340	3.10
3s	NO_2	2-$NHCOCH_3$	353	1.71	344	0.19	352	1.32	346	1.41	345	1.56
3t	NO_2	4-$NHCOCH_3$	405	2.94	409	2.95	419	2.56	406	2.50	401	2.51
3u	NO_2	2-OCH_3	341	1.27	339	2.83	342	1.37	337	1.39	337	1.18
			412	1.30	405	2.76	414	1.43	403	1.48	403	1.14
3v	NO_2	4-OCH_3	404	2.83	400	5.27	407	2.39	399	2.53	399	2.75
3x	NO_2	2-SCH_3	346	1.70	342	0.62	353	1.40	340	1.50	343	2.23
			462	0.65	456	0.24	466	0.58	455	0.56	452	0.81
3y	NO_2	4-SCH_3	431	2.32	421	2.25	437	2.11	421	2.42	421	2.55

Dyes **3a**–**c**,**j**–**r** were object of a previous communication [5].

the chloro substituent, the expected hypsochromic shift is compensated by electron releasing resonance effects, especially in both *ortho* and *para* positions.

Furthermore, a bathochromic shift was generally observed for *para*-substituted dyes in relation to those substituted at the *ortho* position. One possible explanation for this difference is that steric congestion on an *ortho* isomer forces the molecule to adopt a non-planar conformation, while its *para* congener is mainly planar. This is due to the unfavorable interaction between the substituent on the *ortho* position and the lone pair of electrons on one of the azo nitrogen atoms, which forces the rotation into a non-planar conformation with a concomitant destabilization of the first excited state of the dye and reduction of the expected bathochromic effect [2]. However, steric hindrance effects caused by *ortho*-substitution in azo derivatives are generally only notable when both *ortho*-positions adjacent to an azo bridge are substituted and therefore other effects must be taken in consideration [18].

Chloroazonitrobenzothiazoles **3l**,**n** showed a $\Delta\lambda_{max} = 3$–7 nm, for benzothiazoles **3d**–**i** and nitrobenzothiazoles **3s**–**y**, with the more powerful electron releasing groups methoxy, methylmercapto or acetamide $\Delta\lambda_{max} = 34$–71 nm and 52–85 nm, respectively.

Surprisingly, benzothiazoles **3f**,**h**,**u**,**x** bearing methoxy and methylmercapto groups in the *ortho* position, exhibit a second absorption band of longer wavelength, whose intensity, in the case of methoxybenzothiazoles **3f**,**u**, was very similar to that of the main one, and sometimes even slightly higher. Since azo-hydrazo tautomerism is not expected to occur given the absence of a necessary hydroxyl or similar group in the amine moiety, we suspect that the appearance of two bands on the spectra could be due to the presence of both *cis* and *trans* azo isomers, which are frequently found in some azo dyes [19]. It is known that the more thermodynamically stable *trans* isomer is converted into the *cis* isomer upon exposure to UV light [20]. Thus, a methanolic solution of the methoxyazobenzothiazole dye **3f** was exposed to UV light and the UV–Vis spectra recorded at intervals of 30 min. After the first half hour of irradiation a slight inversion of the relative intensity of the two bands was observed, followed by a proportional and gradual decrease of the intensity of both bands until total decolourisation due to photobleaching, leading to inconclusive results.

Alternatively, the appearance of two bands may result merely from the bathochromic shift of the longest wavelength band by the introduction of the *ortho* donor group whilst also shifting the second longest wavelength band from <300 nm into the near UV region, apparently given the emergence of a new band. However, this less elaborate explanation is not completely satisfactory since there are no observable bands below or near 300 nm in the UV–Vis spectra of the remaining azobenzothiazole dyes studied and the corresponding *para* isomers have displayed similar bathochromicity in relation to the longest wavelength band without the appearance of a second band at lower wavelength.

4. Conclusions

The use of new 2-nitrosobenzothiazoles as synthons to access new azobenzothioazole dyes by condensation with aromatic amines, particularly those bearing electron withdrawing groups at the coupling component or those substituents in other positions than *para*, was extended successfully. Therefore, six new azobenzothiazole dyes possessing electron donating methoxy, methylmercapto and acetamide groups at the aniline coupler were prepared in moderate to good yields.

Inspection of the UV–Vis spectral data showed that the stronger the electron-releasing effect of the substituent in the *para* position, the greater the bathochromic shift and that this effect is more pronounced when there is an electron withdrawing group on the benzothiazole ring and an electron-donating group on the aniline moiety, due to the typical donor–acceptor chromogen relationship. However, this effect is meaningless for the corresponding isomeric

azobenzothiazoles substituted in the o*rtho* position of the aniline group.

Of special interest are dyes with electron donating *ortho* substituents on the aniline coupler that provide new push–pull systems, presenting a second longer wavelength absorption band in the UV–Visible.

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