Anexo

Publicações no âmbito deste trabalho:

Artigos em anexo

Faustino H, El-Shishtawy RM, Reis LV, Santos PF, Almeida P. 2-Nitrosobenzothiazoles: a useful synthon for new azobenzothiazole dyes. Tetrahedron Letters (submetido) (**2008**).

Faustino H, Reis LV, Santos PF, Almeida P. New Azobenzothiazoles Dyes from 2-Nitrosobenzothiazoles. Dyes Pigments (em fase de submissão).

ARTIGO 1

Faustino H, El-Shishtawy RM, Reis LV, Santos PF, Almeida P. 2-Nitrosobenzothiazoles: a useful synthon for new azobenzothiazole dyes. Tetrahedron Letters (submetido) (**2008**).

Pergamon

TETRAHEDRON LETTERS

2-Nitrosobenzothiazoles: useful synthons for new azobenzothiazole dyes

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Abstract— Novel azobenzothiazole dyes have been synthesized by condensation of 2-nitrosobenzothiazole and 6-nitro-2-nitrosobenzothiazole with aniline, anthranilic acid, 3-hydroxymethylaniline, 2-, 3- and 4-chloroaniline, 4-fluoraniline, 4-iodoaniline or 4-nitroaniline. The new synthetic approach described is advantageous over the classic diazotization process commonly used for the preparation of related disperse dyes, since the presence of an electron donating group at the *para* position, or equivalent, of the coupling component is no more a pre-requisite for the success of the condensation reaction.

Azo compounds constitute the largest class of compounds amongst all known families of dyes. The structural versatility inherent to the methodology of preparation and the application in a variety of fields, being the use as textile fiber dyestuff the most prominent one, are undoubtedly on the basis of their popularity. Despite the endless number of patents and papers describing the synthesis and dyeing properties of this group of dyes that can be found in the literature, the diazotization of an aromatic or heteroaromatic primary amine, followed by coupling with an electron donating aromatic compound are the two steps by which practically almost all azo dyes are prepared.[1]

Azo dyes based on heterocyclic amines, in particular, have found great success due to their higher tinctorial strength and brighter dyeing in relation to diazo dyes based uniquely on aniline.[2] Most disperse heterylazo and disazo dyes of technical interest for application to textiles are constituted by five-member rings containing one sulphur atom and a diazotable amino group. Additionally, this heterocyclic ring may possess one or two nitrogen atoms and be fused to an aromatic ring. Systems of this type, with emphasis on thiazoles, benzothiazoles, isothiazoles, benzoisothiazoles, thiadiazoles and thiophenes, have been well reviewed by Towns.[3]

Benzothiazole-based disperse dyes are considered to be the first example of the successful commercial exploitation of heterocyclic amines, by using the 2-aminobenzothiazole nucleus as diazonium component in the production of red dyes.[4] Due to their cheapness, brightness and dyeing performance, this type of dyes have become economically important, motivating a substantial research effort, both in industry and in academia.[5] Aside from the continuous interest on benzothiazole disperse dyes for textiles dying, a diverse range of non-textile applications have also emerged. As an example, thiazole and azobenzothiazole dyes have found application in liquid crystal technology,[6] reprography[7] and non-linear optics (NLO),[8] and more recently have been investigated as potential sensitizers for photodynamic therapy (PDT).[9] Nevertheless, the majority of the developments concerning azobenzothiazole dyes have tended to focus on series of compounds where the substitution pattern was varied and the color-structure relationship, as well as the effect of the solvent, temperature and acidity in the visible spectrum, were studied.

Some significant azobenzothiazole derivatives hitherto described are alcoxy,[6,8a,10] alkyl,[8a,11] (di and tri)chloro,[8a,11] dialkylamino,[12] (di)nitro,[2b,8a,c,10c-d,f,11a,c,13] methylsulphonyl,[11c] thiocyanates[12] and compounds

Keywords: Disperse dyes, Benzothiazole, Azo, Nitroso condensation

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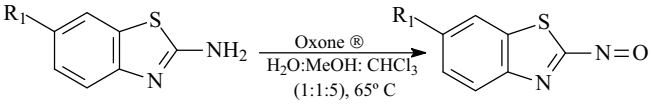
bearing multiple combinations of different substituents,[8a,11a,d] in addition to the unsubstituted one.[2b,8a,10a,c,f,12,13b] Of this group of dyes, molecules produced by the coupling of diazotized 2-aminobenzothiazole to aniline derivatives, are by far the most explored case. Other suitably substituted couplers less frequently used are alcoxybenzenes,[6] azulenes,[8a] benzopyranones,[2b] imidazoles,[11c] naphtalenes,[10d,13b] naphthalimides,[14] pyrazoles,[10a] pyrazolones,[10b] pyridones[10f] and thiophenes.[13a]

Invariably, azo- and disazobenzothiazole disperse dyes have been prepared by diazotization of an aminobenzothiazole, followed by coupling with an electron donating aromatic molecule. Consequently, the presence of an electron donating group or equivalent in the aromatic coupler is always a precondition for the success of the coupling reaction, being the location of the new bound limited to the *para*-position in relation to the donating group. To extend the access to new azobenzothioazole dyes, especially to those bearing electron withdrawing groups at the coupling component, we have envisioning an alternative synthetic route to this family of dyes based on the condensation of a reactive 2-nitrosobenzothiazole with an aromatic amine, for which a strong electron donating capability is dispensable.

Amongst the wide variety of available synthetic procedures for the oxidation of an aromatic primary amine to the nitroso group,[15] the use of a Caro's acid related oxidant, commercially available as Oxone®,[16] has revealed to be the most effective one. Other common oxidation reagents, such as peracetic acid[18] or *meta*-chloroperbenzoic acid,[19] have failed due to a lack of efficiency or to the production of very complex reaction mixtures. Therefore, the 2-nitrosobenzothiazoles **2a**,**b** were prepared by oxidation of the corresponding 2-aminobenzothiazoles **1a**,**b** with Oxone®, in a aqueous-organic system (H_2O/MeOH/$CHCl_3$ - 1/1/5).[17] In these conditions, the success of the reaction was found to critically depend on the solubility of the aniline in water, since the reaction occurs in the organic phase. In fact, 6-nitro-2-nitrosobenzothiazole (**2b**) was prepared in a much higher yield than the parent unsubstituted **2a**, due to the less solubility of 2-amino-6-nitrobenzothiazole (**1b)** in water when compared to that of **1a**. A large volume of organic solvents was also used to avoid undesirable condensation reactions.

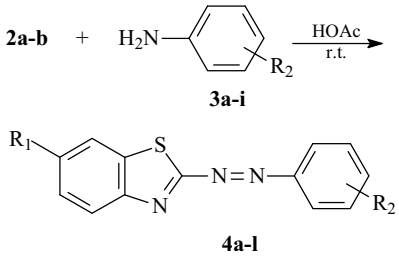


1a R_1 = H
b R_1 = NO_2

2a R_1 = H (16%)
b R_1 = NO_2 (68%)

Scheme 1. Synthesis of 2-nitrosobenzothiazoles **2a**,**b**.

To assess the generality of our methodology both 2-nitrosobenzothiazoles **2a**,**b** were condensed with aniline (**3a**), anthranilic acid (**3b**), 2-chloroaniline (**3c**), 3-chloroaniline (**3d**), 3-hydroxymethylaniline (**3e**), 4-chloroaniline (**3f**), 4-fluoraniline (**3g**), 4-iodoaniline (**3h**) or 4-nitroaniline (**3i**) (Scheme 2).[20] The condensation reaction was carried out at room temperature in glacial acetic acid for 0.5h to 3 days. The azobenzothiazole dyes **4a**-**m** precipitated from the reaction mixture and could be readily isolated by simple filtration in 8 to 82% non-optimized yield (Table 1).



Scheme 2. Synthesis of azobenzothiazoles **4a**-**l**.

Table 1. Yields, melting points and λ_{max} of azobenzothiazole dyes **4a**-**l**.

	Dye		Yield	M.p.	λ_{max} (nm)
	R_1	R_2	(%)	(ºC)	(MeOH)
4a	H	H	30	99-100	328
4b	H	2-Cl	10	105-107	332
4c	H	3-CH_2OH	16	87-89	328
4d	NO_2	H	53	137-139	340
4e	NO_2	2-CO_2H	63	188-190	340
4f	NO_2	2-Cl	58	194-196	340
4g	NO_2	3-Cl	63	138-140	336
4h	NO_2	3-CH_2OH	43	127-130	340
4i	NO_2	4-F	72	155-156	344
4j	NO_2	4-Cl	82	166-167	346
4k	NO_2	4-I	77	190-192	370
4l	NO_2	4-NO_2	33	173-175	332

As expected, the presence of the powerful electron withdrawing nitro substituent in the heteroaryl coupler has shown to increase the reactivity of the 2-nitroso group towards anilines. In fact, whereas 2-nitroso-6-nitrobenzothiazole (**2b**) afforded the corresponding azobenzothiazole dyes **4d**-**l** in 33-82% yield, being the lower yield obtained for the compound bearing the two push-pull nitro groups in both aromatic moieties, its unsubstituted analogue **2a** was only able to condense with the less electron withdrawing anilines **3a**,**d**,**e** in 10-30% yield. The corresponding azo dyes **4a**-**c** were obtained in poor yields, being compound **4a,** resulting from the coupling with the weakest electron withdrawing aniline, the one isolated with the higher yield.

The influence of the substitution pattern of azobenzothiazole disperse dyes possessing an aromatic amine coupler with typical push-groups on their absorption spectrum, based on conventional donor-acceptor interactions, is well documented.[3] However, the effect of substitution in the benzene ring acting as

coupling component, as in dyes **4a-l**, to the best of our knowledge has never been studied.

All the synthetized azobenzothiazole dyes displayed large absorption bands, with λ_{max} within the range 328-370 nm (Table 1). As expected, the presence of a nitro group in the benzothiazole moiety leads to a bathochromic shift due to the extension of conjugation. Accordingly, nitrobenzothiazoles **4d**,**f**,**h** have shown $\Delta\lambda$ 8-12 nm with respect to their parent non substituted analogues **4a-c**.

The influence of the substitution pattern of the aniline coupling moiety of the dyes in their visible absorption spectra seems to depend on a balance between the bathochromic electronic donating and hipsochromic electron withdrawing effects. Hence, while dyes **4c,h**, bearing the benzene ring substituted with alkyl-type groups, have λ_{max} identical to those of the correspondent non substituted counter-parts **4a,d**. The presence of a second strong electron withdrawing nitro group in **4l** induces an hipsochromic shift of 8 nm. Halogen substitution revealed to have a net bathochromic effect, resulting from the electron donating outcome by resonance, attenuated by the opposite inductive electron withdrawal. Thus, the halogen *para*-substituted dyes **4i-k** revealed $\Delta\lambda$ ranging from 4 to 30 nm, being the larger shift displayed by **4k**, which holds the less electronegative halogen atom, with the higher electronic density. Consistently, the absorption of 2- and 4-chloro dyes **4f**,**j**, which hold the halogen atom in a position directly conjugated with the pulling azobenzothiazole moiety, is more red-shifted than that of the 3-substituted parent **4g**. The crowding effect over the chlorine atom of the 2-substituted dye **4f**, being superior to that in the 4-substituted compound **4j**, probably explains the larger red shift of the later.

In conclusion, it can be claimed that 2-nitrosobenzothiazole (**2a**) and 6-nitro-2-nitrosobenzothiazole (**2b**), whose synthesis is disclosed herein, are useful synthons for the preparation of new azobenzothiazole dyes, extending the access to molecules possessing electron withdrawing groups in different positions of the aromatic coupler ring. This synthetic methodology presents the advantage of being a more general approach to the preparation of this class of azoheterocyclic dyes than the classic diazotization process used for the preparation of azo disperse dyes, since the presence of an activating electron donating group suitably located in the coupling component is no longer crucial.

Acknowledgements

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17. Synthesis of 6-nitro-2-nitrosobenzothiazole (**2b**). Typical procedure. Oxone® (23.16 g, 37.67 mmol) in water (130 mL) was added to a solution of **1b** (2.39g, 11.88 mmol) in MeOH/$CHCl_3$ (1/5) (670 mL) and the resulting mixture was heated under reflux for 24 h. After cooling, the reaction

mixture was filtrated under reduced pressure to remove the insoluble material. The organic layer was separated by decantation, washed with brine, dried over anydrous Na_2SO_4 and evaporated to dryness. The residue was subjected to c.c. (silica gel, CH_2Cl_2) to afford **2b** as green needles. Yield: 68%. M.p. 97-99ºC. Vis (MeOH) λ_{max} (nm): 392. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ: 8.61 (1H, dd, *J* = 8.5, 2.0 Hz, C*H*), 8.76 (1H, d, *J* = 2.0 Hz, C*H*), 9.14 (1H, d, *J* = 8.5 Hz, C*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ: 108.3 (*C*), 120.2 (*C*), 123.9 (*C*H), 124.0 (*C*H), 124.9 (*C*), 133.5 (*C*H), 159.3 (*C*). IR (KBr) ν_{max} (cm^{-1}): 3095 (w), 3070 (w), 1532 (s), 1483 (m), 1390 (m), 1353 (s), 1248 (m), 1165 (s), 1151 (m), 1107 (s), 897 (m), 846 (m), 829 (s), 743 (m). TOFHRMS: calc. for $C_7H_3N_3O_3S$ $[M]^+$: 208.9895; found 208.9894.

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20. Synthesis of (6-nitrobenzothiazole-2-yl)phenyldiazene (**4d**). Typical procedure. A solution of **2b** (0.21 g, 1.00 mmol) in glacial AcOH (1.5 mL), prepared in an ultrasound bath at 40ºC, was added dropwise (3 min.) to a solution of aniline (**3a**) (0.09 mL, 1.0 mmol) in the same solvent (0.5 mL) and the mixture was stirred at r.t. for 4 h. The resulting yellow-orange precipitate was collected by filtration under reduce pressure, washed with petroleum or diethyl ether and dried. Recrystallization from MeOH/CH_2Cl_2 afforded **4d** as orange needles. Yield: 53%. M.p. 137-139ºC. Vis (MeOH) λ_{max} (nm): 340. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ: 7.56 - 7.65 (3H, m), 7.98 (2H, d, *J* = 6.50Hz), 8.13 (1H, d, *J* = 8.50 Hz), 8.33 (1H, dd, *J* = 8.75 Hz, *J* = 1.75 Hz), 8.73 (1H, d, *J* = 1.50 Hz)^{13}C NMR (62.90 MHz, $CDCl_3$) δ: 109.8 (*C*), 123.3 (*C*H), 123.6 (*C*H), 123.7 (*C*H), 124.2 (*C*H), 127.4 (*C*), 129.6 (*C*H), 133.8 (*C*H), 148.9 (*C*), 150.5 (*C*), 151.2 (*C*). IR (KBr) ν (cm^{-1}): 3094 (w), 1525 (s), 1485 (m), 1469 (m), 1442 (m), 1345 (s), 1319 (m), 1310 (m), 882 (m), 774 (m), 708 (m), 683 (m). FABHRMS (3-NBA) calcd. for $C_{13}H_9N_4O_2S^+$ $[M+H]^+$: 285.0446; found 285.0435.

ARTIGO 2

Faustino H, Reis LV, Santos PF, Almeida P. New Azobenzothiazoles Dyes from 2-Nitrosobenzothiazoles. Dyes Pigments (em fase de submissão).

New Azobenzothiazoles Dyes from 2-Nitrosobenzothiazoles

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Abstract

Novel azobenzothiazole dyes derived from the condensation between 2-nitrosobenzothiazoles with several anilines possessing different electronic types of substituents in different positions, have been synthesized and fully characterized by ^{1}H and ^{13}C NMR, FTIR and Visible Spectroscopy and HRMS. Of special interest, *ortho*-substituted azobenzothiazole dyes with electron donor substituents were herein described. The relationship between the structures of the azobenzothiazoles in relation to the maximum absorption is briefly discussed.

Keywords: benzothiazole; azo; disperse dyes; nitroso condensation; spectroscopic characterization.

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1. Introduction

Azo compounds are by far the most important class of coloured compounds, accounting for over 50% of all commercial dyes, and having been studied more than any other class due to their most popular application as textile fiber dyestuff. Despite a few exceptions, azo dyes are made by diazotization of a primary aromatic amine followed by coupling of the resultant diazonium salt with an electron-rich nucleophile [1,2].

Within azo dyes, (benzo)thiazole-based disperse dyes have gained importance and have been the first example of the successful textile commercial exploitation of heterocyclic amines, by using the 2-aminobenzothiazole nucleus as diazonium component in the production of red dyes [3]. Recently, azobenzothiazole dyes have found a new interest as so-called functional dyes. Emerging examples of applications found recently in the literature 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 the benzothiazole diazonium salt with anilines bearing multiple combinations of different substituents. Other not so common substituted couplers are alcoxybenzenes, azulenes, benzopyranones, imidazoles, naphtalenes, naphthalimides, pyrazoles, pyrazolones, pyridines and thiophenes [4,5]. Nevertheless, with the azobenzothiazole dye, examples found are intrinsically limited to couplers with electrodonating groups in a *para* position or their equivalent in relation to the azo group.

To access new azobenzothioazole dyes, especially to those bearing electron withdrawing groups at the coupling component or to substituted ones in any other position than just the *para*, we have recently described an alternative synthetic route to this family of dyes [5]. This method is based on the condensation of new synthons 2-

nitrosobenzothiazoles with an aromatic amine, for which a strong electron donating capability is dispensable. Herein, in addition to the full spectroscopic description of the examples previously provided, we extend the generality of this method with several azobenzothiazole dyes possessing the electrodonating hydroxylmethyl, thiomethyl and *N*-acetamide in both *ortho* and *para* position as second coupler. Of special interest are the *ortho*-substituted dyes with electron dononating substituents that provided new push-pull systems.

2. Experimental

2.1. General

All reagents were of the highest purity available, purchased from Sigma-Aldrich, 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} (0.25mm) using chloroform or chloroform/ petroleum ether (1:1) and the spots have been examined under 254 nm UV light.

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ solutions on a Brücker 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 spectrometer. 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 intensive and/or characteristics bands are given in cm^{-1}.

Visible spectra (Vis) were recorded on a Perkin-Elmer Lambda 6 spectrophotometer using methanol as solvent. Wavelength of maximum absorption is reported in nm.

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 GCT spectrometer, operating in EI at 70 eV. Electrospray Ionisation High Resolution Mass Spectra (ESIMSHR) were determined on an ions ciclotropic resonance BRUKER APEXIII FT-MS. All new dyes were determined to be >95% pure by ^{1}H NMR.

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® (21.91 g, 35.64 mmol) in an acid acetic/ sodium acetate buffer (0.5 M) pH=5 (150 mL) to which was further added a 5% aqueous solution of sodium hydroxide (45 mL), was added to a solution of 2-aminobenzothiazole **1b** (1.78g, 11.88 mmol) in MeOH/$CHCl_3$ (1/5) (400 mL) followed by the addition of the acetic acid/sodium acetate (0.5 M) until the total dissolution of the precipitated material, and the resulting mixture was heated under reflux for 8 h. After cooling, the reaction mixture was filtrated 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 c.c. (silica gel, CH_2Cl_2) to afford **1a** as green needles. Yield: 44 %. M.p. 96-97 ºC. ^{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): 110.05 (*C*), 116.61 (*C*), 126.56 (*C*), 127.90 (*C*H), 128.80 (*C*H), 135.08 (*C*H), 136.49 (*C*H). IR (KBr) ν (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-N (NO)), 764 (s). Vis (MeOH): 384 nm. TOFHRMS ($[M]^+$, $C_7H_4N_2OS^+$): Calc: 164.0044; found: 164.0042.

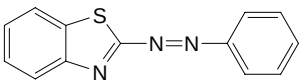
*2.2.1. 6-Nitro-2-Nitrosobenzothiazole (**1b**).*

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

*2.3. Synthesis of azobenzothiazoles dyes **3a-x***

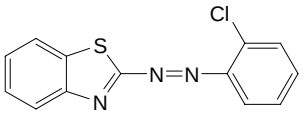
All azobenzothiazole dyes were prepared by the condensation of 2-nitroso- and 6-nitro-2-nitrosobenzothiazole **1a**,**b** with the appropriated anilines according to our previous communication [5].

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



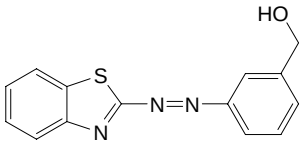
Obtained as yellow crystals after 48 h of reaction. Yield: 31 %. M.p. 99-100 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.50 -7.58 (5H, m, Ar*H*), 7.88 (1H, d, *J* = 8.25 Hz, Ar*H*), 7.91-7.95 (2H, m, Ar*H*), 8.01 (1H, dd, *J* = 2.00; 7.25. Ar*H*). ^{13}C NMR (62.90 MHz,

$CDCl_3$) δ (ppm): 111.39 (*C*), 123.08 (2*C*H), 124.01 (*C*H), 125.00 (*C*), 127.98 (*C*H), 128.40 (*C*H), 129.35 (2*C*H), 132.12 (*C*H), 132.24 (*C*H), 148.03 (*C*), 151.23 (*C*). IR (KBr) ν (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). Vis (MeOH): 328 nm. 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 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.37 (1H, dt, *J* = 1.33; 7.63 Hz, Ar*H*), 7.46 (1H, dt, *J* = 1.83; 7.63 Hz, Ar*H*), 7.52-7.62 (3H, m, Ar*H*), 7.77 (1H, dd, *J* = 1.75; 8.00 Hz, Ar*H*), 7.91 (1H, dd, *J* = 1.93; 7.76 Hz, Ar*H*), 8.10 (1H, dd, *J* = 2.00; 7.50 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 111.50 (*C*), 117.80 (*C*H), 123.83 (*C*), 126.62 (*C*H), 127.40 (*C*H), 128.15 (*C*H), 128.39 (*C*H), 131.01 (*C*H), 132.55 (*C*H), 132.87 (*C*H), 135.94 (*C*), 147.80 (*C*), 148.04 (*C*). IR (KBr) ν (cm^{-1}): 3069 (w, C-H_{arom}), 1589 (w, C-C_{arom}), 1562 (w), 1466 (w), 1441 (m), 1228 (w), 1120 (w), 1057 (m, *o*-C_{arom}-Cl), 955 (w), 762 (s), 723 (s), 636 (w), 575 (w), 554 (w), 466 (w). Vis (MeOH): 332 nm. FABHRMS ($[M+H]^+$, $C_{13}H_9ClN_3S^+$): Calc: 274.0206; found: 274.0218.

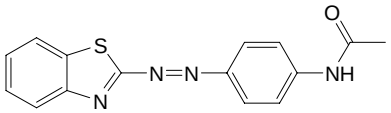


2.3.3. [3-(Benzothiazol-2-ylazo)phenyl]methanol ***3c***

Obtained as yellow crystals after 6 days of reaction. Yield: 16 %. M.p. 87-89 ºC. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 4.63 (2H, d, *J* = 5.50 Hz, CH_2OH, s in the presence of D_2O), 5.45 (1H, t, *J* = 5.75 Hz, CH_2O*H*, changed with D_2O), 7.57-7.59 (2H, m,

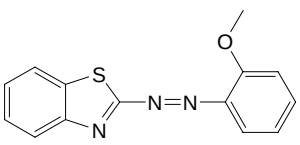
Ar*H*), 7.65 (1H, t, J = 7.50 Hz, Ar*H*), 7.74 (1H, t, J = 7.50 Hz, Ar*H*), 7.80-7.85 (2H, m, Ar*H*), 7.90 (1H, s, Ar*H*), 8.06 (1H, d, *J* = 7.50 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 63.25 (*C*H_2), 112.80 (*C*), 121.33 (*C*H), 122.49 (*C*H), 124.04 (*C*), 125.69 (*C*H), 129.10 (*C*H), 130.31 (*C*H), 130.61 (*C*H), 131.81 (*C*H), 133.80 (*C*H), 144.49 (*C*), 148.56 (*C*), 151.47 (*C*). IR (KBr) ν (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). Vis (MeOH): 328 nm. FABHRMS ($[M+H]^+$, $C_{14}H_{12}N_3OS^+$): Calc: 270.0701; found: 270.0704.

2.3.5. N-[4-(Benzothiazol-2-ylazo)phenyl]acetamide ***3d***



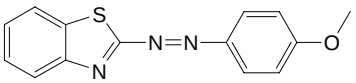
Obtained as yellow crystals after 20 h of reaction. Yield: 56 %. M.p. 172-174 ºC. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 2.11 (3H, s, CH_3), 7.61-7.68 (2H, m, Ar*H*), 7.78-7.98 (6H, m, Ar*H*), 10.40 (1H, s, N*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 24.16 (*C*H_3), 111.45 (*C*), 119.16 (2*C*H), 123.44 (*C*), 123.76 (*C*H), 124.06 (2*C*H), 127.89 (*C*H), 129.12 (*C*H), 132.36 (*C*H), 143.53 (*C*), 146.01 (*C*), 147.68 (*C*), 168.97 (*C*O). IR (KBr) ν (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). Vis (MeOH): 368 nm. FABHRMS ($[M+H]^+$, $C_{15}H_{13}N_4OS^+$): Calc: 297.0810; found: 297.0818.

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

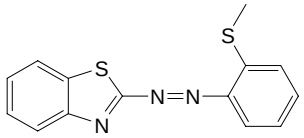


Obtained as yellow crystals after 15 h of reaction. Yield: 27 %. M.p. 82-84 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 4.05 (3H, s, C*H*$_3$), 7.03 (1H, t, *J* = 7.63 Hz, Ar*H*), 7.12 (1H, d, *J* = 8.50 Hz, Ar*H*), 7.48-7.50 (3H, m, Ar*H*), 7.75 (1H, d, *J* = 8.00 Hz, Ar*H*), 7.87-7.91 (1H, m, Ar*H*), 8.04-8.07 (1H, m, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 56.18 (*C*H$_3$), 112.45 (*C*), 112.80 (*C*H), 116.93 (*C*H), 120.76 (*C*H), 122.91 (*C*), 126.86 (*C*H), 128.02 (*C*H), 128.10 (*C*H), 131.48 (*C*H), 133.94 (*C*H), 140.39 (*C*), 148.48 (*C*), 157.64 (*C*). IR (KBr) ν (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, Carom-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). Vis (MeOH): 376 nm. FABHRMS ([M+H]$^+$, $C_{14}H_{12}N_3OS^+$): Calc: 270.0701; found: 270.0697.

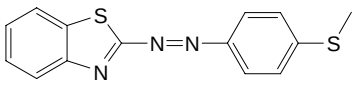
2.3.7. Benzothiazol-2-yl-(4-methoxyphenyl)diazene ***3f***



Obtained as orange crystals after 2 h of reaction. Yield: 33 %. M.p. 129-131 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 3.91 (3H, s, C*H*$_3$), 7.02 (2H, d, *J* = 9.00 Hz, Ar*H*), 7.45-7.50 (2H, m, Ar*H*), 7.82-7.86 (2H, m, Ar*H*), 7.91 (2H, d, *J* = 9.00 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 55.66 (*C*H$_3$), 111.59 (*C*), 114.49 (2*C*H), 123.21 (*C*H), 124.60 (*C*), 125.14 (2*C*H), 127.80 (*C*H), 128.32 (*C*H), 131.38 (*C*H), 145.66 (*C*), 148.12 (*C*), 163.07 (*C*). IR (KBr) ν (cm^{-1}): 3058 (w, C-H$_{arom}$), 1604 (m, C-C$_{arom}$), 1584 (m, C-C$_{arom}$), 1503 (m), 1257 (s, C-OCH$_3$), 1149 (m, C$_{arom}$-O-CH$_3$), 1025 (m), 835 (m), 757 (m). Vis (MeOH): 364 nm. FABHRMS ([M+H]$^+$, $C_{14}H_{12}N_3OS^+$): Calc: 270.0701; found: 270.0701.

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

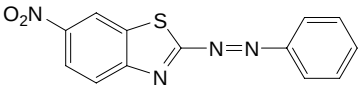
Obtained as yellow crystals after 3 days of reaction. Yield: 59 %. M.p. 155-157 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.54 (3H, s, C*H*$_3$), 7.21 (1H, t, *J* = 7.50 Hz, Ar*H*), 7.33 (1H, d, *J* = 8.00 Hz, Ar*H*), 7.43-7.56 (3H, m, Ar*H*), 7.74 (1H, d, *J* = 8.00 Hz, Ar*H*), 7.87 (1H, d, *J* = 7.50 Hz, Ar*H*), 8.00 (1H, d, *J* = 7.75 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 14.81 (*C*H$_3$), 111.36 (*C*), 118.30 (*C*H), 124.11 (*C*H + *C*), 124.59 (*C*H), 124.82 (*C*H), 127.85 (*C*H), 128.38 (*C*H), 132.12 (*CH*), 132.44 (*CH*), 141.53 (*C*), 147.99 (*2C*). IR (KBr) ν (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). Vis (MeOH): 420 nm. 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 ***3h*** 

Obtained as yellow crystals after 24 h of reaction. Yield: 68 %. M.p. 112-114 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 22.56 (3H, s, C*H*$_3$) 7.33 (2H, d, *J* = 8.25 Hz, Ar*H*), 7.46 (1H, t, *J* = 7.25 Hz, Ar*H*), 7.51 (1H, t, *J* = 7.00 Hz, Ar*H*), 7.85 (3H, d, *J* = 8.25 Hz, Ar*H*), 7.95 (1H, d, *J* = 7.75 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 15.03 (*C*H$_3$) 111.43 (*C*), 123.49 (3*C*H), 124.88 (*C*), 125.75 (2*C*H), 127.86 (*C*H), 128.36 (*C*H), 131.77 (*C*H), 145.05 (*C*), 148.07 (*C*), 148.47 (*C*). IR (KBr) ν (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),

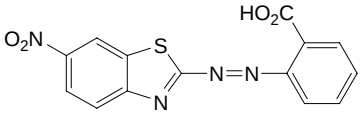
766 (s), 748 (m), 721 (m). Vis (MeOH): 396 nm. FABHRMS ($[M+H]^+$, $C_{14}H_{12}N_3S_2^+$): Calc: 286.0473; found: 286.0479.

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



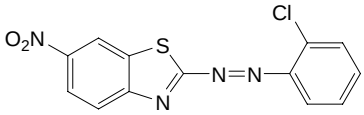
Yield: 53 %. M.p. 137-139 ºC [1].

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



Obtained as orange crystals after 3 days of reaction. Yield: 63 %. M.p. 188-190 ºC. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 7.65-7.87 (4H, m, Ar*H*), 8.13 (1H, d, *J* = 8.50 Hz, Ar*H*), 8.48 (1H, dd, *J* = 2.25; 8.50 Hz, Ar*H*), 8.55 (1H, d, *J* = 2.25 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 110.56 (*C*), 118.41 (*C*H), 123.40 (*C*H), 124.33 (*C*H), 124.63 (*C*H), 126.59 (*C*), 129.45 (*C*H), 131.47 (*C*H), 131.91 (*C*), 132.73 (*C*H), 148.96 (*C*), 149.36 (*C*), 150.07 (*C*), 167.88 (*C*O). IR (KBr) ν (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). Vis (MeOH): 340 nm. ESIMSHR ($[M+Na]^+$, $C_{14}H_8N_4NaO_4S^+$): Calc: 351.01585; found: 315.01653.

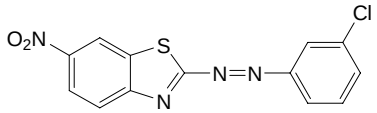
2.3.12. (2-Chlorophenyl)-(6-nitrobenzothiazol-2-yl)diazene ***3k***



Obtained as orange crystals after 6 h of reaction. Yield: 58 %. M.p. 194-196 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.42 (1H, t, *J* = 7.25 Hz, Ar*H*), 7.55 (1H, t, *J* = 7.50 Hz, Ar*H*), 7.66 (1H, d, *J* = 8.00 Hz, Ar*H*), 7.82 (1H, d, *J* = 8.25 Hz, Ar*H*), 8.25 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.37 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.79 (1H, d, *J* = 2.25 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 109.95 (*C*), 117.77 (*C*H), 123.49 (*C*H), 123.60 (*C*H),

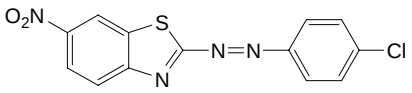
126.21 (*C*), 126.89 (*C*H), 127.61 (*C*H), 131.40 (*C*H), 134.46 (*C*H), 137.32 (*C*), 147.83 (*C*), 149.04 (*C*), 150.44 (*C*). IR (KBr) ν (cm^{-1}): 3094 (w, C-H_{arom}), 2360 (m), 2342 (m), 1583 (w, C-C_{arom}), 1573 (w, C-C_{arom}), 1525 (s, NO_2), 1347 (s, NO_2), 1058 (w, *o*-C_{arom}-Cl), 888 (w), 761 (w). Vis (MeOH): 340 nm. 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 ***3l***



Obtained as orange crystals after 6 h of reaction. Yield: 63 %. M.p. 138-140 ºC. ^{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* = 8.75 Hz, Ar*H*), 8.35 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.75 (1H, d, *J* = 2.25 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 109.43 (*C*), 122.49 (*C*H), 123.10 (*C*H), 123.46 (*C*H), 123.68 (*C*H), 124.25 (*C*H), 127.83 (*C*), 130.68 (*C*H), 133.38 (*C*H), 135.79 (*C*), 149.22 (*C*) 150.24 (*C*), 151.89 (*C*). IR (KBr) ν (cm^{-1}): 3083 (w, C-H_{arom}), 1571 (w, C-C_{arom}), 1525 (s, NO_2), 1346 (s, NO_2), 1061 (w, *m*-C_{arom}-Cl), 894 (w). Vis (MeOH): 336 nm. ESIMSHR ($[M+Na]^+$, $C_{13}H_7ClN_4NaO_2S^+$): Calc: 340.98704; found: 340.98547.

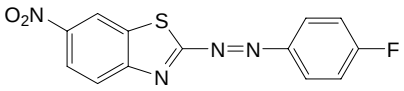
2.3.14. (4-Chlorophenyl)-(6-nitrobenzothiazol-2-yl)diazene ***3m***



Obtained as orange crystals after 1 h of reaction. Yield: 82 %. M.p. 166-167 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.56 (2H, d, *J* = 8.75 Hz, Ar*H*), 7.94 (2H, d, *J* = 8.75 Hz, Ar*H*), 8.12 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.34 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.74 (1H, d, *J* = 2.25 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 109.50 (*C*), 123.43 (*C*H), 123.69 (*C*H), 123.84 (*C*H), 124.90 (2*C*H), 127.75 (*C*), 130.00 (2*C*H), 140.17 (*C*), 149.07 (*C*), 149.63 (*C*), 150.39 (*C*). IR (KBr) ν (cm^{-1}): 3089 (w, C-H_{arom}), 1587 (w, C-C_{arom}),

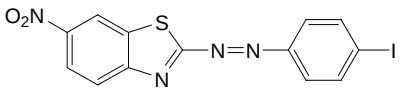
1573 (w, C-C_{arom}), 1531 (s, NO_2), 1483 (m), 1347 (s, NO_2), 1315 (m), 1087 (m, *p*-C_{arom}-Cl), 846 (m). Vis (MeOH): 344 nm. ESIMSHR ($[M+Na]^+$, $C_{13}H_7ClN_4NaO_2S^+$): Calc: 340.98704; found: 340.98632.

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



Obtained as orange crystals after 30 min of reaction. Yield: 72 %. M.p. 155-157 ºC. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 7.53 (2H, t, *J* = 8.50 Hz, Ar*H*), 8.05-8.11 (2H, m, Ar*H*), 8.19 (1H, d, *J* = 8.50 Hz, Ar*H*), 8.43 (1H, d, *J* = 8.50 Hz, Ar*H*), 8.51 (1H, d, *J* = 1.75 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 110.76 (*C*), 116.90 + 117.27 (2*C*H), 123.23 (*C*H), 124.40 (*C*H), 124.66 (*C*H), 125.90 + 126.06 (2*CH*), 126.18 (*C*), 147.50 (*C*), 147.55 (*C*), 148.52 (*C*), 150.16 (*C*). IR (KBr) ν (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). Vis (MeOH): 344 nm. FABHRMS ($[M+H]^+$, $C_{13}H_8FN_4O_2S^+$): Calc: 303.0352; found: 303.0352.

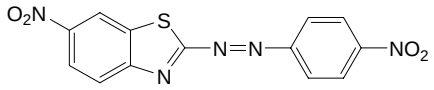
2.3.16. (4-Iodophenyl)-(6-nitrobenzothiazol-2-yl)diazene ***3o***



Obtained as orange crystals after 16 h of reaction. Yield: 77 %. M.p. 190-192 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 7.70 (2H, d, *J* = 8.75 Hz, Ar*H*), 7.95 (2H, d, *J* = 8.75 Hz, Ar*H*), 8.13 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.34 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.75 (1H, d, *J* = 2.25 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 101.69 (*C*), 109.51

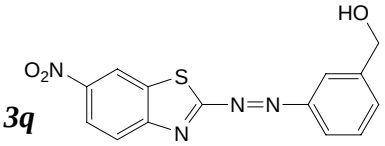
(*C*), 123.48 (*C*H), 123.71 (*C*H), 123.95 (*C*H), 124.94 (2*C*H), 127.77 (*C*), 139.05 (2*C*H), 149.11 (*C*), 149.41 (*C*), 150.54 (*C*). IR (KBr) ν (cm^{-1}): 3083 (w, C-H_{arom}), 1576 (w, C-C_{arom}), 1565 (w, C-C_{arom}), 1523 (s, NO_2), 1478 (w), 1342 (s, NO_2), 1315 (w), 1304 (w), 1149 (w, *p*-C_{arom}-I), 1005 (w), 842 (w). Vis (MeOH): 370 nm. 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 ***3p***



Obtained as orange crystals after 3 days of reaction. Yield: 33 %. M.p. 173-175 ºC. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 8.15 (2H, d, *J* = 8.50 Hz, Ar*H*), 8.25 (1H, d, *J* = 8.50 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): 110.56 (*C*), 123.40 (*C*H), 124.22 (2*C*H), 124.45 (*C*H), 125.29 (2*C*H), 125.54 (*C*H), 126.98 (*C*), 149.11 (*C*), 149.63 (*C*), 150.05 (*C*), 153.44 (*C*). IR (KBr) ν (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). Vis (MeOH): 332 nm. 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 ***3q***

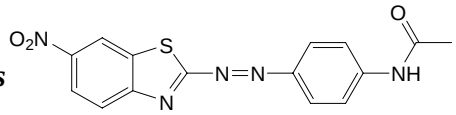


Obtained as orange crystals after 24 h of reaction. Yield: 43 %. M.p. 127-130 ºC. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 4.63 (2H, s, CH_2OH), 5.50 (1H, sl, CH_2O*H*, change with D_2O), 7.60-7.63 (2H, m, Ar*H*), 7.87 (1H, dd, *J* = 2.50; 6.50 Hz, Ar*H*), 7.93 (1H, s, Ar*H*), 8.22 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.41 (1H, dd, *J* = 2.25; 8.75. Ar*H*), 8.50 (1H, d, *J* = 2.25 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 62.18 (CH_2), 111.00 (*C*), 120.54 (*C*H), 122.20 (*C*H), 123.18 (*C*H), 124.37 (*C*H), 125.64 (C), 125.74 (*C*H),

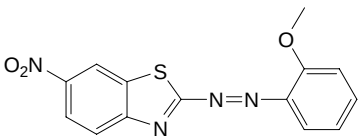
129.71 (*C*H), 131.95 (*C*H), 144.76 (C), 148.48 (C), 150.32 (C), 150.64 (C). IR (KBr) ν (cm^{-1}): 3555-3400 (m, O-H), 3099 (w, C-H_{arom}), 2927 (w), 2877 (w), 2360 (w), 2341 (w), 2149 (w), 1599 (w, C-C_{arom}), 1570 (w, C-C_{arom}), 1519 (s, NO_2), 1487 (w), 1474 (w), 1444 (m), 1345 (s, NO_2), 1311 (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). Vis (MeOH): 340 nm. 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 ***3r***

Obtained as orange crystals after 30 min of reaction. Yield: 60 %. M.p. 191-193 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$ + drop of DMSO-d_6) δ (ppm): 2.17 (3H, s, C*H*$_3$), 7.06 (1H, dt, *J* = 7.63 Hz, *J* = 1.17 Hz, Ar*H*), 7.46 (1H, dt, *J* = 1.75; 8.75 Hz, Ar*H*), 7.66 (1H, dd, *J* = 1.25; 8.25 Hz, Ar*H*), 7.95 (1H, d, *J* = 9.00 Hz, Ar*H*), 8.21 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.44 (1H, d, *J* = 8.00 Hz, Ar*H*), 8.57 (1H, d, *J* = 2.00 Hz, Ar*H*), 9.49 (1H, s, N*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$ + drop of DMSO-d_6) δ (ppm): 24.37 (*C*H$_3$), 108.58 (*C*), 117.87 (*C*H), 121.33 (*C*H), 121.47 (*C*H), 122.43 (*C*H), 123.36 (*2C*H), 127.58 (*C*), 135.04 (*C*H), 137.74 (*C*), 139.43 (*C*), 148.23 (*C*), 150.01 (*C*), 168.29 (*C*). IR (KBr) ν (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). Vis (MeOH): 372 nm. 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 ***3s*** 

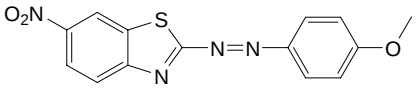
Obtained as orange crystals after 20 min of reaction. Yield: 72 %. M.p. 211-213 ºC. ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 2.12 (3H, s, C*H*$_3$), 7.86 (2H, d, *J* = 9.00 Hz, Ar*H*), 8.00 (2H, d, *J* = 9.00 Hz, Ar*H*), 8.17 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.42 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.53 (1H, d, *J* = 2.25 Hz, Ar*H*), 10.52 (1H, s, N*H*). ^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 24.25 (*C*H$_3$), 111.06 (*C*), 119.28 (2*C*H), 123.09 (*C*H), 124.39 (*C*H), 124.47 (*C*H), 125.05 (2*C*H), 125.58 (*C*), 144.83 (*C*), 146.25 (*C*), 148.11 (*C*), 161.09 (*C*), 161.74 (*C*), 169.29 (*C*). IR (KBr) ν (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). Vis (MeOH): 400 nm. 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 ***3t*** 

Obtained as orange crystals after 1 h of reaction. Yield: 54 %. M.p. 168-170 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 4.09 (3H, s, C*H*$_3$), 7.05 (1H, t, *J* = 7.50 Hz, Ar*H*), 7.16 (1H, d, *J* = 8.25 Hz, Ar*H*), 7.59 (1H, t, *J* = 7.50 Hz, Ar*H*), 7.78 (1H, d, *J* = 8.00 Hz, Ar*H*), 8.19 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.32 (1H, dd, *J* = 2.00; 8.75 Hz, Ar*H*), 8.76 (1H, d, *J* = 2.00 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 56.23 (*C*H$_3$), 111.15 (*C*), 113.06 (*C*H), 116.93 (*C*H), 120.91 (*C*H), 123.14 (*C*H), 123.45 (*C*H), 124.86 (*C*), 127.61 (*C*H), 135.89 (*C*H), 140.31 (*C*), 148.21 (*C*), 150.94 (*C*), 158.59 (*C*). IR (KBr) ν (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$_2$),

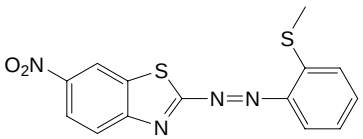
1484 (s), 1456 (w), 1437 (w), 1411 (w), 1344 (s, NO_2), 1312 (m), 1285 (m), 1248 (s, C_{arom}-OCH_3), 1184 (w), 1177 (w), 1157 (s), 1121 (w), 1108 (w), 1057 (w), 1039 (w), 1022 (m), 885 (m), 841 (m), 830 (m), 758 (s), 734 (m), 726 (w). Vis (MeOH): 404 nm. FABHRMS ($[M+H]^+$, $C_{14}H_{11}N_4O_3S^+$): Calc: 315.0552; found: 315.0545.

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



Obtained as orange crystals after 1 h of reaction. Yield: 57 %. M.p. 162-164 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 3.94 (3H, s, C*H*$_3$), 7.04 (2H, d, *J* = 9.00 Hz, Ar*H*), 7.94 (2H, d, *J* = 9.00 Hz, Ar*H*), 8.03 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.27 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.67 (1H, d, *J* = 2.25 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 55.84 (*C*H$_3$), 110.00 (*C*), 114.84 (2*C*H), 123.08 (*C*H), 123.16 (*C*H), 123.55 (*C*H), 126.14 (2*C*H), 126.96 (*C*), 145.80 (*C*), 148.33 (*C*), 150.78 (*C*), 164.50 (*C*). IR (KBr) ν (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, COMe), 1151 (m), 1139 (s), 1117 (m), 1023 (m), 845 (m). Vis (MeOH): 396 nm. FABHRMS ($[M+H]^+$, $C_{14}H_{11}N_4O_3S^+$): Calc: 315.0552; found: 315.0555.

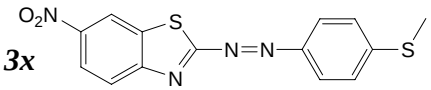
2.3.23. (6-Nitrobenzothiazol-2-yl)-(2-methylsulfanylphenyl)diazene ***3v***



Obtained as reddish-orange crystals after 17 h of reaction. Yield: 57 %. M.p. 184-186 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.57 (3H, s, C*H*$_3$), 7.25 (1H, t, *J* = 8.00 Hz, Ar*H*), 7.37 (1H, d, *J* = 8.25 Hz, Ar*H*), 7.53 (1H, t, *J* = 7.00 Hz, Ar*H*), 7.81 (1H, d, *J* = 7.25 Hz, Ar*H*), 8.12 (1H, d, *J* = 8.75 Hz, Ar*H*), 8.31 (1H, dd, *J* = 2.25; 8.75 Hz, Ar*H*), 8.74 (1H, d, *J* = 2.00 Hz, Ar*H*). ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 14.83 (*C*H$_3$), 109.80

(*C*), 119.64 (*C*H), 123.26 (*C*H), 123.56 (*C*H), 123.97 (*C*H), 124.71 (*C*H), 125.02 (*C*H), 127.21 (*C*), 133.94 (*C*H), 143.13 (*C*), 148.02 (*C*), 148.76 (*C*), 150.55 (*C*). IR (KBr) ν (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). Vis (MeOH): 456 nm. 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 ***3x***



Obtained as reddish-orange crystals after 17 h of reaction. Yield: 57 %. M.p. 153-155 ºC. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.60 (3H, s, C*H*$_3$), 7.50 (2H, d, *J* = 8.75 Hz, Ar*H*), 7.94 (2H, d, *J* = 8.75 Hz, Ar*H*), 8.18 (1H, d, *J* = 8.50 Hz, Ar*H*), 8.41 (1H, dd, *J* = 2.50; 8.75 Hz, Ar*H*), 8.52 (1H, d, *J* = 2.25 Hz, Ar*H*. ^{13}C NMR (62.90 MHz, $CDCl_3$) δ (ppm): 14.88 (*C*H$_3$), 109.88 (*C*), 123.26 (*C*H), 123.38 (*C*H), 123.60 (*C*H), 124.16 (2*C*H), 125.63 (2*C*H), 127.23 (*C*), 147.88 (*C*), 148.50 (*C*), 148.57 (*C*), 150.73 (*C*). IR (KBr) ν (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). Vis (MeOH): 424 nm. FABHRMS ($[M+H]^+$, $C_{14}H_{11}N_4O_2S_2^+$): Calc: 331.0323; found: 331.0332.

3. Results and discussion

Azobenzothiazole dyes **3a-x** were synthesized from the condensation of 2-nitroso- and 6-nitro-2-nitrosobenzothiazole **1a,b** with several anilines **2a-o** following the new

synthetic route previously developed (Scheme 1) [5]. In addition to the non-substituted anilines or substituted anilines with different types of electronic groups in the *ortho*-, *meta*- or *para*- positions, azobenzothiazole dyes with an electron donating hydroxylmethyl, thiomethyl and acetamide in both *ortho* and *para* positions in the phenyl moiety of the dye in relation to the azo group are also presented here.

(Scheme 1)

The condensation reaction was carried out at room temperature in glacial acetic acid for 0.5h to 6 days. The azobenzothiazole dyes **4a**-**x** precipitated from the reaction mixture and could be readily isolated by simple filtration in 10 to 82% non-optimized yield (Table 1). The presence of more powerful electron donating hydroxylmethyl, thiomethyl or acetamide groups has shown to increase the reactivity of the coupling anilines, increasing the yields from 10-30% for azobenzothiazoles **3a-c** to 27-68%. As previously observed, the additional presence of the electron withdrawing nitro group in 2-nitrosobenzothiazoles also increases the reactivity in relation to those without subtituents, but no so dramatically as the presence of electron donating groups in the aniline coupler mentioned above.

(Table 1)

Apart from 6-nitro-2-nitrosobenzothiazole **1b** and the azobenzothiazole **3i**, the nitroso precursor **1a** and remaining all dyes haven't hitherto been fully spectroscopically characterized. Therefore, our preliminary communication [5] was completed with all left over spectroscopic data, namely ^{1}H and ^{13}C NMR, FTIR and Visible Spectroscopy and HRMS (FAB, ESI or TOF).

The influence of the substitution pattern in azobenzothiazole disperse 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]

Recently, the influence of the substitution pattern of the aniline coupling moiety of the dyes in their visible absorption spectra was also described, in cases where the aniline is substituted with several types of electronic substituents and in different positions besides the *para* position in relation to the azo group. [5] In these cases the value of the absorption maximum seems to depend on a balance between the bathochromic electronic donating and hipsochromic electron withdrawing effects [2,5].

The new electron donating hydroxylmethyl, thiomethyl or acetamide benzothiazoles both in *ortho* and *para* position in relation to the azo group, to the best of our knowledge, allow for the first time, comparison of the difference of the maximum absorbance between azobenzothiazoles with pull groups in these two positions in a conventional donor-acceptor interactions electronic transitions pattern.

As expected, in both cases, the presence of a nitro group in the benzothiazole moiety leads to a bathochromic shift due to the extension of conjugation [6]. Accordingly, nitrobenzothiazoles **3s-x** have show $\Delta\lambda$ 28-36 nm with respect to their parent non-substituted analogues **3d-h** (table 1), a substantially more significant variation than the $\Delta\lambda$ 8-12 nm observed for non push-pull azobenzothiazoles dye analogues [5]. However, and contrary to what we would have expected with regards to the crowding effect [2], the *para*-substituted hydroxylmethyl- and thiomethylazobenzothiazoles have shown a hipsochromic effect of $\Delta\lambda$ 8-32 nm in relation to the *ortho*-substituted, this effect being more prominent with the thiomethyl substitution. However, the acetamide group in the para position induces a bathochromic shift of $\Delta\lambda$ 28 nm in relation to the *ortho* one, due to the well documented effect resulting from the acetamide hydrogen atom share with the non bound electron of the azo group which removes the electronic delocalization capacity of this group [2].

4. Conclusions

The use of new 2-nitrosobenzothiazoles synthons to access new azobenzothioazole dyes by condensation with aromatic amines, especially to those bearing electron withdrawing groups at the coupling component or to substitute ones in any other position other than the *para*, was extended here successfully. Therefore, six new azobenzothiazole dyes possessing the electrodonating hydroxylmethyl, thiomethyl and *N*-acetamide as second coupler were prepared in moderate to good yields. Of special interest were the *ortho*-substituted dyes with electron donor substituents that provided new push-pull systems.

Acknowledgements

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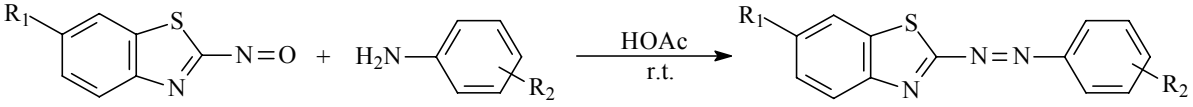

1a-b **2a-o** **3a-x**

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

Scheme 1. Synthesis of azobenzothiazole dyes **3a-x**.

Table 1. Yields and λ_{max} of azobenzothiazole dyes **3a-x**.

Dye			Yield	λ_{max} (nm)
	R_1	R_2	(%)	(MeOH)
3a	H	H	30	328
3b	H	2-Cl	10	332
3c	H	3-CH_2OH	16	328
3d	H	4-$NHCOCH_3$	56	368
3e	H	2-OCH_3	27	376
3f	H	4-OCH_3	33	364
3g	H	2-SCH_3	59	420
3h	H	4-SCH_3	68	396
3i	NO_2	H	53	340
3j	NO_2	2-CO_2H	63	340
3k	NO_2	2-Cl	58	340
3l	NO_2	3-Cl	63	336
3m	NO_2	4-Cl	82	346
3n	NO_2	4-F	72	344
3o	NO_2	4-I	77	370
3p	NO_2	4-NO_2	33	332
3q	NO_2	3-CH_2OH	43	340
3r	NO_2	2-$NHCOCH_3$	60	372
3s	NO_2	4-$NHCOCH_3$	72	400
3t	NO_2	2-OCH_3	54	404
3u	NO_2	4-OCH_3	57	396
3v	NO_2	2-SCH_3	57	456
3x	NO_2	4-SCH_3	65	424

Azobenzothiazoles **3a-c**,**i-q** were object of a previous communication [5]