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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-fluoroaniline, 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 heteroarylazo and disazo dyes of technical interest for application to textiles are constituted by five-membered rings containing one sulfur atom and a diazotizable 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 has 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, was studied.

Some significant azobenzothiazole derivatives hitherto described are alkoxy,[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] methylsulfonyl,[11c] thiocyanates,[12] and compounds 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 alkoxybenzenes,[6] azulenes,[8a] benzopyranones,[2b] imidazoles,[11c] naphthalenes,[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 bond limited to the *para*-position in relation to the donating group. To extend the access to new azobenzothioazole dyes,

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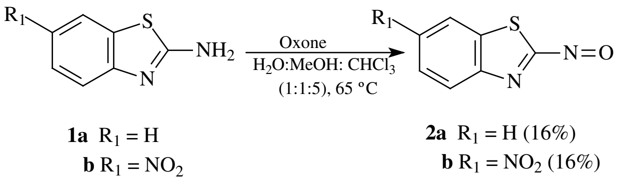
especially to those bearing electron-withdrawing groups at the coupling component, we have envisioned an alternative synthetic route to this family of dyes based on the condensation of a reactive 2-nitrosobenzothiazole with an aromatic amine, for which a strong electron-donating capability is dispensable.

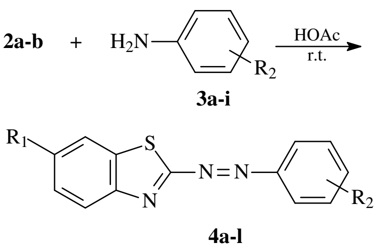
Amongst the wide variety of available synthetic procedures for the oxidation of an aromatic primary amine to the nitroso group,[15] the use of Caro's acid related oxidant, commercially available as Oxone®,[16] has revealed to be the most effective one. Other common oxidation reagents, such as peracetic acid[17] or *meta*-chloroperbenzoic acid,[18] have failed due to a lack of efficiency or to the production of very complex reaction mixtures. Therefore, 2-nitrosobenzothiazoles **2a**,**b** were prepared by oxidation of the corresponding 2-aminobenzothiazoles **1a**,**b** with Oxone®, in an aqueous–organic system ($H_2O/MeOH/CHCl_3$—1:1:5).[19] 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 (Scheme 1).

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-fluoroaniline (**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 0.5 h to 3 days. The azobenzothiazole dyes **4a**–**l** are precipitated from the reaction mixture, and could be readily isolated by simple filtration in 10–82% non-optimized yield (Table 1).

As expected, the presence of the powerful electron-withdrawing nitro substituent in the heteroaryl coupler has shown to increase the reactivity of the nitroso component toward 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 pull nitro groups in both aromatic moieties, its unsubstituted analogue **2a** was only able to condense with the less electron-withdrawing anilines **3a**,**c**,**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.



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



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

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

Dye			Yield (%)	Mp (°C)	λ_{max} (nm) (MeOH)
	R_1	R_2			
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

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 synthesized 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 $\Delta\lambda$ ranging from 8 to 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 electron donating and hypsochromic 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 hypsochromic 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, the larger shift being 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 latter.

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 coupling component. 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.

Acknowledgments

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19. *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** (2.39 g, 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 anhydrous 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%. Mp 97–99 °C. Vis (MeOH) λ_{max} (nm): 392. ^1H 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: calcd for $C_7H_3N_3O_3S$ $[M]^+$: 208.9895; found 208.9894.
20. *Synthesis of (6-nitrobenzothiazol-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 40 °C, 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 rt 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%. Mp 137–139 °C. Vis (MeOH) λ_{max} (nm): 340. ^1H NMR (250.13 MHz, $CDCl_3$): δ 7.56–7.65 (3H, m), 7.98 (2H, d, *J* = 6.50 Hz), 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.