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Novel azobenzothiazole dyes from 2-nitrosobenzothiazoles

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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, C*H*$_2$OH, collapses to s with D_2O), 5.45 (1H, t, $J = 5.8$ Hz, broad s, CH_2O*H,* 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 (*C*H$_2$), 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, C*H*$_3$), 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 (*C*H$_3$), 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, C*H*$_3$), 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 (*C*H$_3$), 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