



# Synthesis and spectral properties of some azo disperse dyes containing a benzothiazole moiety<sup>☆</sup>



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## ABSTRACT

A known method was employed for the preparation of four substituted benzothiazole amines **I–IV** in moderate yields. These heterocyclic amines were diazotized with nitrosyl sulfuric acid and subsequently coupled with *N,N*-diethyl aniline and *N*-phenyl-2, 2'-iminodiethanol to afford heteroarylazo amine dyes **1–8** in satisfactory yields. These dyes were characterized by UV–Visible, FT-IR, <sup>1</sup>H NMR, and elemental analysis techniques. The solvatochromism behavior of the azo compounds is investigated by studying their spectra in pure and mixed organic solvents of different characteristics. The color of the dyes is discussed with respect to the nature of the heterocyclic ring and substituent present therein. In addition, effects of acid and base on the visible absorption maxima of the dyes are also reported.

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## 1. Introduction

Azo dyes with heterocyclic diazo components have been intensively investigated to produce bright and strong color shades ranging from red to greenish blue on synthetic fabrics [1,2]. These results led to commercial products to replace the conventional anthraquinone dyes [3]. Additionally, particularly bathochromic azo dyes that are structurally analogous to the azo benzenes may be obtained by replacement of the carbocyclic acceptor ring with a thiazole or benzothiazole ring [4–6]. These sulfur or sulfur–nitrogen containing heterocyclic azo dyes provide bright and strong shades that range from red through green and blue, which complement the yellow–orange colors of the nitrogen heterocyclic azo dyes to provide a complete coverage of the entire shade range [7–14]. It is also well known that azo dyes including thiazolyl components have been hugely utilized in the fields of nonlinear optics and optical data storage and have shown excellent optical properties in comparison with azo dyes derived from substituted anilines [15–19]. Derivatives of 2-aminobenzothiazole have a long history of use as heterocyclic diazo components for disperse dyes [20]. Some of the best-known representatives of coupling components for thiazole and benzothiazole diazo components are *N,N*-disubstituted anilines and their derivatives which are among the most widely used compounds for the synthesis of a vast variety of azo dyes and pigments [21–24]. In the present study, we report the synthesis of the four

substituted 2-aminobenzothiazoles **I–IV** as diazo components (Scheme 1) and the subsequent monoazo disperse dyes **1–8**, starting from *N,N*-diethylaniline and *N*-phenyl-2,2'-imino diethanol (Scheme 2). The spectral properties of the prepared dyes were also evaluated in pure and mixed organic solvents of various polarities. The pH effect is also included with the aim of elucidating the absorption behaviors of the compounds under investigation.

## 2. Experimental

### 2.1. General

All starting materials were obtained from Merck and Aldrich chemical companies and were used without further purification. IR spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were obtained by FT-NMR 400 MHz Bruker apparatus in DMSO-*d*<sub>6</sub> using TMS as internal standard. The absorption spectra of the compounds were run on a Cary UV–Vis double-beam spectrophotometer (Model 100). Mass spectra were recorded on a Micromass Agilent Technology (HP) spectrometer, operating at 70 eV. The elemental analysis was determined on a Leco CHNS-900 analyzer. Melting points were recorded with an Electro-thermal apparatus and uncorrected.

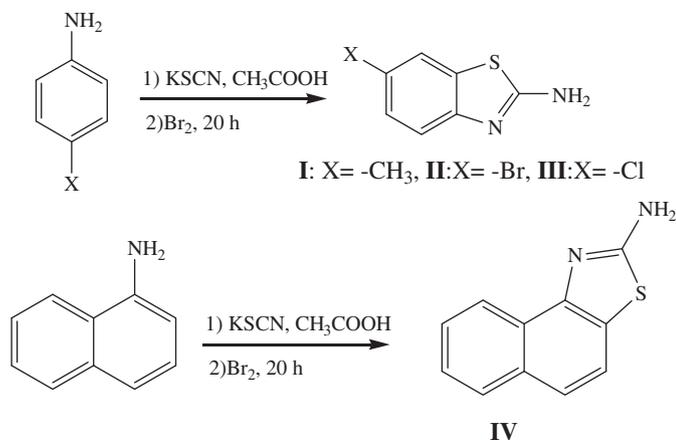
### 2.2. Synthesis of 2-aminobenzothiazoles **I–IV**

A solution of bromine (0.26 mL, 10.0 mmol) in acetic acid (5.0 mL) was added over about 30 min to a mixture of aromatic amine (10.0 mmol) and potassium thiocyanate (1.07 g, 11.0 mmol) in acetic acid (20 mL), the temperature being kept between 25 and 35 °C. The

<sup>☆</sup> This paper is dedicated to Prof. M.R. Yazdanbakhsh on the occasion of his 70th birthday.

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**Scheme 1.** Synthetic routes for the prepared 2-aminobenzothiazoles.

slurry was then stirred for 20 h at room temperature. The precipitate was filtered, washed with a little acetic acid, slurried in water, made neutral with aqueous ammonia, and filtered again. The residue was boiled for 20 min with excess of hydrochloric acid (15% v/v) and the hot mixture was filtered from impurities. The filtrate, cooled to 10 °C, was made alkaline with aqueous ammonia and the precipitate was filtered, washed, and dried. The crude product was recrystallized from ethanol–water to afford **I–IV**, respectively. The physical and spectral data of the purified dyes are as follows.

#### 2.2.1. 2-Amino-6-methyl benzothiazole **I**

White pearly crystals (0.80 g, 49%), m.p. 118–120 °C (reported 137 °C [25]); FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>): 3370 and 3212 (NH<sub>2</sub>), 3075 (Aro.-H), 2950 (Aliph.-H), <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  ppm: 7.45 (1H, d, J = 8.2 Hz), 7.42 (1H, s), 7.15 (1H, dd, J = 1.1, 8.2 Hz), 5.55 (2H, br, NH<sub>2</sub>), 2.41 (1H, s, -CH<sub>3</sub>).

#### 2.2.2. 2-Amino-6-bromo benzothiazole **II**

Yellow crystals (1.50 g, 65.5%), m.p. 187–190 °C; FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>): 3375 and 3188 (NH<sub>2</sub>), 3070 (Aro.-H), <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  ppm: 7.34 (1H, d, J = 7.9 Hz), 7.18 (1H, s), 7.03 (1H, dd, J = 2.0, 7.9 Hz), 5.45 (2H, br, NH<sub>2</sub>).

#### 2.2.3. 2-Amino-6-chloro benzothiazole **III**

White crystals (0.77 g, 42%), m.p. 208–211 °C (reported 209 °C [25]); FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>): 3394 and 3218 (NH<sub>2</sub>), 3050 (Aro.-H), <sup>1</sup>H NMR

(400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  ppm: 8.10 (1H, s), 7.97 (1H, d, J = 8.0 Hz), 7.48 (1H, dd, J = 2.1, 8.0 Hz), 5.15 (2H, br, NH<sub>2</sub>).

#### 2.2.4. Naphtho [1,2-*d*]thiazol-2-amine **IV**

Pale brown crystals (1.23 g, 61.5%), mp > 350 °C; FT-IR (KBr):  $\nu$  (cm<sup>-1</sup>): 3414 and 3225 (NH<sub>2</sub>), 3075 (Aro.-H), <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  ppm: 8.48 (1H, d, J = 8.4 Hz), 8.46 (1H, s), 8.29 (1H, d, J = 8.4 Hz), 8.05 (1H, s), 7.45 (1H, t, J = 7.0 Hz), 7.70 (1H, t, J = 7.0 Hz), 6.25 (2H, br, NH<sub>2</sub>), MS: Calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>S (M<sup>+</sup>) m/e 200.04. Found: 200.30.

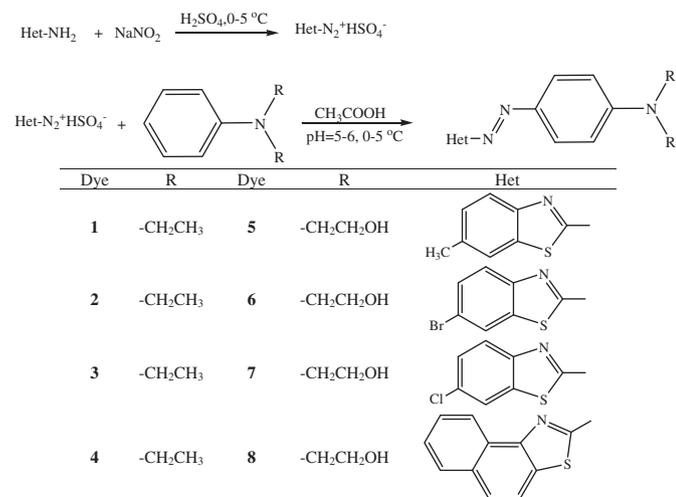
#### 2.3. Preparation of benzothiazoleazo dyes **1–8**

2-Aminobenzothiazoles (2.0 mmol) were dissolved in glacial acetic acid: propionic acid mixture (2:1, 6.0 mL) and was quickly cooled in an ice-salt bath to 0–5 °C. The liquor was then added in portions during 15 min to a cold solution of nitrosyl sulfuric acid (prepared from sodium nitrite (2.2 mmol, 0.15 g) and concentrated sulfuric acid (3 mL at 60 °C)). The mixture was stirred for an additional 3 h at the same temperature. After completion of diazotization procedure, the diazonium salt solution was added dropwise to the solution of coupler compounds (2.0 mmol) in acetic acid. The resulting solution was vigorously stirred at 0–4 °C for 2 h, while the pH of the reaction mixture was maintained at 5–6 by simultaneous addition of sodium hydroxide solution (0.5 M). The progress of the reaction was evaluated by thin layer chromatography (TLC) and then crude dyes were filtered, washed with cold ethanol and purified by recrystallization method. The physical and spectral data of the purified dyes are shown in Table 1.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

As depicted in Scheme 1, a known method was modified and then employed for the preparation of substituted 2-aminobenzothiazoles **I–IV**. The known 2-aminobenzothiazoles (**I–III**) and the new one (**IV**) were obtained by allowing one-pot reaction of the appropriate aniline derivatives with thiocyanogen generated from bromine and potassium thiocyanate. The crude products were obtained in the satisfactory yields and purified by crystallization from ethanol–water. In addition to comparison with authentic samples, all of the known and new prepared compounds were characterized by the FT-IR and <sup>1</sup>H NMR spectral analysis. For compound **IV**, the Mass spectrum was measured and confirmed the desired structure. <sup>1</sup>H NMR spectra recorded for the prepared



**Scheme 2.** Synthetic routes for the preparation of azo dyes **1–8**.

**Table 1**

The physical properties of the dyes prepared in this study.

Dye	Color	mp (°C)	Recrystallization	%C		%H		%N		Yield (%)
				Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	Purple	170–171	DMF/H <sub>2</sub> O	66.63	67.15	6.21	6.19	17.27	17.88	72
2	Dark red	>250	DMF/H <sub>2</sub> O	52.45	52.11	4.40	4.47	14.39	14.73	75
3	Bright red	160–161	DMF/H <sub>2</sub> O	59.21	59.92	4.97	4.91	16.25	16.87	74
4	Clear red	160–162	DMF/H <sub>2</sub> O	69.97	69.21	5.59	5.69	15.54	15.74	65
5	Dark red	187–189	DMF/H <sub>2</sub> O	60.65	60.89	5.66	5.61	15.72	15.25	69
6	Dark red	232–234	DMF/H <sub>2</sub> O	48.46	48.91	4.07	4.14	13.30	13.02	81
7	Clear red	183–184	DMF/H <sub>2</sub> O	54.18	54.92	4.55	4.58	14.87	15.23	63
8	Dark red	179–180	DMF/H <sub>2</sub> O	64.27	63.92	5.14	5.19	14.28	13.05	71

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