



# Structural and spectral comparisons between isomeric benzisothiazole and benzothiazole based aromatic heterocyclic dyes



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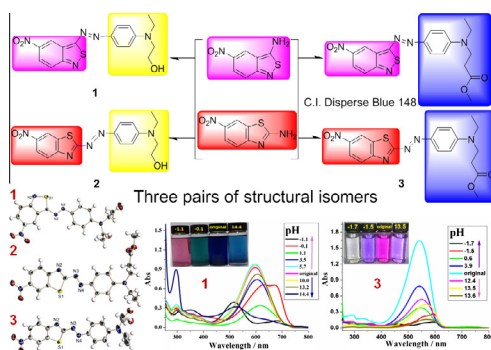
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## HIGHLIGHTS

- Two pairs of isomeric benzothiazole and benzisothiazole based dyes are described.
- Single-crystal structures of three heterocyclic dyes 1–3 are included.
- Solvatochromism and acid–base discoloration of these dyes are studied.
- Benzisothiazole based dyes show higher thermal stability and larger  $\lambda_{\text{max}}$ .

## GRAPHICAL ABSTRACT

Single-crystal structures, UV–vis spectra, solvatochromism and reversible acid–base discoloration have been done for two pairs of isomeric heterocyclic dyes.



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## ABSTRACT

A pair of isomeric heterocyclic compounds, namely 3-amino-5-nitro-[2,1]-benzisothiazole and 2-amino-6-nitrobenzothiazole, are used as the diazonium components to couple with two *N*-substituted 4-aminobenzene derivatives. As a result, two pairs of isomeric aromatic heterocyclic azo dyes have been produced and they are structurally and spectrally characterized and compared including single-crystal structures, electronic spectra, solvatochromism and reversible acid–base discoloration, thermal stability and theoretical calculations. It is concluded that both benzisothiazole and benzothiazole based dyes show planar molecular structures and offset  $\pi$ – $\pi$  stacking interactions, solvatochromism and reversible acid–base discoloration. Furthermore, benzisothiazole based aromatic heterocyclic dyes exhibit higher thermal stability, larger solvatochromic effects and maximum absorption wavelengths than corresponding benzothiazole based ones, which can be explained successfully by the differences of their calculated isomerization energy, dipole moment and molecular band gaps.

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## Introduction

Aromatic heterocyclic groups as the diazo components of azo dyes have long been noted and studied [1]. Heterocyclic azo dyes have attracted great interests in recent years because of their good performance on optical data storage [2], dye-sensitized solar cells [3,4], organic semiconducting materials [5], and even in the biological area as probes for metal-ion detection [6]. The design and development of new heterocyclic azo-functionalized dyes have caught the attention of dye chemists in modern textile chemistry based on their large molar extinction, brilliant color and high chromophoric strength [7–13].

3-Amino-5-nitro-[2,1]-benzothiazole and 2-amino-6-nitrobenzothiazole are a pair of isomeric heterocyclic compounds, and both of them are useful intermediates in organic synthesis for preparing many drugs, pesticides and dyes [14–16]. Furthermore, azo-benzothiazole and its derivatives are important functional materials with wide applications in the nonlinear optical, electroluminescence and photochromic materials owing to their high molecular polarizability and sensitive response to the external field [17–19]. In addition, 2-aminobenzothiazole has been used as the important intermediates in the synthesis of chromophoric polyureas [20]. 3-Amino-5-nitro-[2,1]-benzothiazole is also highly important as the diazo component for the production of disperse dyes with great market demand, for example, the best high-temperature trichromatic blue azo dye C.I. Disperse Blue 148 (B148) [21]. However, systematic comparisons for isomeric benzothiazole and benzothiazole based aromatic heterocyclic dyes, including single-crystal structures, UV-vis spectra, solvatochromism and acid-base discoloration, thermal stability, band gaps and isomerization energy, have not been reported yet.

In our previous work, a series of disperse yellow heterocyclic azo dyes crystallizing in the hydrazone form in the solid state and their azo-hydrazone tautomerism driven by the pH titration and metal-ion complexation have been investigated [22–28]. Recently, we have reported the first crystal structure of a benzothiazole based azo dye B148, and revealed the existence of a new crystalline form which is obviously different from all the known  $\alpha$ ,  $\beta$ , and  $\gamma$  forms [21]. As an extensive study in this area, we have reported herein the structural and spectral comparisons between two pairs of isomeric benzothiazole and benzothiazole based aromatic heterocyclic dyes (1–3 and B148), where X-ray single-crystal structures, solvatochromism and reversible acid-base discoloration, thermal stability and density function theory (DFT) computational investigations have been included. The aim of systematic comparisons is to further reveal the structure–function relationship between these two pairs of isomeric azo dyes, which is very important for the rational design, extension, screening and possible applications of high-performance disperse dyes.

## Experimental section

### Materials and measurements

Melting point was measured without corrections. Dyes 2 and B148 were synthesized by previously reported methods [21,29]. The reagents of analytical grade were purchased from commercial sources and used without any further purification. UV-vis spectra were recorded with a Shimadzu UV-2700 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm. All pH measurements were made with a pH-10C digital pH meter. Infrared (IR) spectra (4000–400  $\text{cm}^{-1}$ ) were recorded using a Nicolet FT-IR 170X spectrophotometer on KBr disks.  $^1\text{H}$  NMR spectra were measured with a Bruker dmx500 MHz NMR spectrometer at room temperature. Thermogravimetry analysis-

differential scanning calorimeter (TGA–DSC) experiments were carried out by a NETZSCH STA449C thermogravimetric analyzer instrument in the nitrogen flow from 10 to 600 °C at a heating rate of 10.0 °C/min.

### Synthesis

#### Preparation of dye 1

3-Amino-5-nitro-[2,1]-benzothiazole (1.95 g, 10.0 mmol) was dissolved in a mixture of concentrated sulfuric acid (2 mL) and glacial acetic acid (10 mL) at  $-5$  °C in an ice-salt bath. Sodium nitrite (0.76 g, 11.0 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stirring. The diazonium salt was obtained and used for the next coupling reaction. *N*-Ethyl-*N'*-phenylethanolamine (2.07 g, 10.0 mmol) was added to a mixture of methanol/water (90 mL, 2:1, v/v) solution in a three-necked flask immersed in an ice bath. Freshly prepared diazonium salt was added dropwise for 1 h to the reaction mixture under vigorous mechanical stirring (0–5 °C). After additional stirring for 1.5 h, the mixture was neutralized with aqueous ammonia to pH 5–6, and the precipitate was filtered and dried after thorough washing with ethanol and water. The crude product was recrystallized by acetonitrile and water (v/v = 5:1), and the microcrystals of dye 1 were finally obtained. Yield, 2.12 g (57%). M.p. 206–208 °C; Main FT-IR absorptions (KBr pellets,  $\nu$ ,  $\text{cm}^{-1}$ ): 3344 (w), 1736 (s), 1660 (s), 1597 (vs), 1519 (s), 1410 (vs), 1255 (vs), and 1122 (vs).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  9.23 (s, 1H, benzothiazole), 8.23 (dd, 1H,  $J = 2.2$  and 9.6 Hz, benzothiazole), 8.00 (d, 2H,  $J = 9.2$  Hz, phenyl), 7.79 (d, 1H,  $J = 9.6$  Hz, benzothiazole), 6.88 (d, 2H,  $J = 9.2$  Hz, phenyl), 3.97 (t, 2H,  $\text{CH}_2\text{OH}$ ), 3.71 (t, 2H,  $\text{NCH}_2$ ), 3.66 (q, 2H,  $\text{NCH}_2$ ), 1.33 (t, 3H,  $\text{CH}_3$ ). Blue single crystals of dye 1 suitable for X-ray diffraction measurement were obtained from a mixture of acetonitrile and ethanol (v:v = 1:1) by slow evaporation in air at room temperature for one week.

#### Preparation of dye 3

The preparation of dye 3 was identical to that of dye 1 except that 6-nitro-2-benzothiazolamine (1.95 g, 10.0 mmol) was used to prepare the diazonium component and *N*-ethyl-*N'*-2-(methoxycarbonyl)ethylaniline (2.07 g, 10.0 mmol) was used as the coupling component. The crude product was recrystallized by acetonitrile and water (v/v = 5:1), and the microcrystals of dye 3 were obtained in a yield of 2.96 g (71%). M.p. 157–159 °C. Main FT-IR absorptions (KBr pellets,  $\nu$ ,  $\text{cm}^{-1}$ ): 3441 (s), 1730 (s), 1600 (vs), 1513 (s), 1333 (vs), 1270 (vs), and 1150 (vs).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , ppm):  $\delta$  8.85 (s, 1H, benzothiazole), 8.32 (d, 1H,  $J = 2.1$  and 8.9 Hz, benzothiazole), 8.11 (d, 1H,  $J = 9.0$  Hz, benzothiazole), 7.94 (d, 2H,  $J = 9.0$  Hz, phenyl), 6.93 (d, 2H,  $J = 9.0$  Hz, phenyl), 3.82 (t, 2H,  $\text{NCH}_2$ ), 3.69 (s, 3H,  $\text{OCH}_3$ ), 3.61 (q, 2H,  $\text{NCH}_2$ ), 2.72 (t, 2H,  $\text{CH}_2$ ) and 1.25 (t, 3H,  $\text{CH}_3$ ). Violet single crystals of dye 3 suitable for X-ray diffraction measurement were obtained from a mixture of acetonitrile and acetone (v:v = 1:2) by slow evaporation in air at room temperature for one week.

### X-ray data collection and solution

Single-crystal samples of 1, 2 and 3 were covered in glue and mounted on glass fibers for data collection on a Bruker SMART 1 K CCD area detector at 291(2)K, respectively, using graphite mono-chromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The collected data were reduced by using the program SAINT [30] and empirical absorption corrections were done by SADABS [31] program. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences by using XPREP. The structures were solved by direct method and refined by least-squares method. All non-hydrogen atoms were refined on  $F^2$

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