



# 1-[(5-Benzyl-1,3-thiazol-2-yl)diazenyl]naphthalene-2-ol: X-ray structure, spectroscopic characterization, dissociation studies and application in mercury(II) detection

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## ABSTRACT

A new thiazolylazo reagent, 1-[(5-benzyl-1,3-thiazol-2-yl)diazenyl]naphthalene-2-ol, has been synthesized for the first time. Single crystals of the azo dye were grown from a saturated solution by the vapour diffusion technique. The compound was analyzed using the single-crystal X-ray diffraction technique, and the chemical structure was also confirmed by ATR-IR, <sup>1</sup>H, <sup>13</sup>C, COSY and HSQC NMR spectra. The pK<sub>a</sub> dissociation constant of the substance was determined in volumes of methanol (MeOH), dioxane and acetonitrile (MeCN) by means of the potentiometric method. The Yasuda–Shedlovsky extrapolation procedure was employed to obtain the value of pK<sub>a</sub> in aqueous solution. The chelate complex of the azo dye with mercury(II) was studied spectrophotometrically. A method for Hg(II) ion determination with the new reagent was elaborated and the limit of detection calculated.

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## 1. Introduction

Thiazolylazo dyes are a group of organic compounds that have found numerous applications in industry and everyday life [1]. They offer a wide spectrum of colours from red to blue with a great colour fastness for a comparatively low price. Today, such thiazolylazo dyes as 1-(2-thiazolylazo)-2-naphthol are used in the preparation of chromatography columns [2,3], data storage devices (CD, DVD and Blue-ray discs [4–6]), clothes, leather, food, cosmetics, plastics, toys and other consumer goods [7].

Thiazolylazo dyes are obtained from 2-aminothiazoles, which have great synthetic capabilities as potential biologically active compounds as evidenced in the synthesis of 2-[(1,3-thiazol-2-yl)imino]-1,3-thiazolidin-4-ones [8]. In chemistry a large number of azo dyes that are prepared by diazotization of 2-aminothiazole and its derivatives and subsequently coupled to the corresponding

product with phenolic or other aromatic substances have been prepared, mainly to serve as sensitive and selective organic analytical reagents in the analysis of transition metals [9–23] and even some lanthanides and actinides [24–26].

The concern about contamination of the environment by transition metals like mercury has been changed dramatically over the last 60 years. Mercury is recognized as a global pollutant and one of the most toxic elements known for its accumulative and persistent character in the environment. It has many unique properties that make it useful in a large number of industrial applications, however. It is used in thermometers, batteries and fluorescent lamps and also in chemical industry as a heat transfer agent, catalyst, electrode, fungicide and bactericide [27]. In 1956 more than 100 citizens of Minamata, Japan, were poisoned and died from consuming fish which contained methylmercury [28]. After this tragedy, the whole world began to ban the dumping of mercury into the rivers, lakes and seas. Nevertheless, mercury contamination of the environment still remains a significant problem.

Thiazolylazo dyes have been successfully used in the analysis of the mercuric ion for decades [29,30]. In addition, azo derivatives of

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2-naphthol have proven to be more sensitive than derivatives of phenol [31]. The simplest thiazolylazo dye, 1-(2-thiazolylazo)-2-naphthol (TAN), is applied most commonly despite the lack of selectivity. In this case a new azo dye should be synthesized with better analytical characteristics than TAN.

Although UV/Vis spectrophotometry is considered to be a traditional classical analytical method, its value for monitoring mercury in the environment is still considerable. Spectrophotometry is usually combined with some preconcentration and separation techniques (e.g. extraction [32], the application of adsorbents [33], thin layers [34] or surfactants [35]). On the other hand, the number of methods of direct spectrophotometric determination of Hg(II) in water samples is comparatively small.

In this work the structure and properties of a novel thiazolylazo reagent are characterized and the possibility of Hg<sup>2+</sup> ions determination as a chelate complex with this agent directly in aqueous solutions is reviewed. Because of the high toxicity of mercury(II), it is necessary to develop a sensitive method for detecting trace amounts of this transition metal in various environmental samples. It was also important to determine the dissociation constant of the new reagent in order to evaluate the optimal conditions for mercury(II) determination and to suggest a possible new indicator for acid-base titrations.

## 2. Experimental

### 2.1. Materials and instrumentation

All chemicals and solvents used in the synthesis were of analytical reagent grade or the best quality available and were obtained from commercial sources and used without further purification.

The HCl (0.5 mol dm<sup>-3</sup> ± 0.045%) and KOH (0.5 mol dm<sup>-3</sup> ± 0.13%) stock solutions were purchased from Merck KGaA (Germany) as concentrates for the preparation of standard solutions. The appropriate KOH solutions were obtained by dilution of the concentrate and were then standardized with a potassium hydrogen phthalate standard. The concentrations of HCl solutions were determined by potentiometric titrations using Gran's method. The potassium hydrogen phthalate (purity ≥ 99.5%) and KCl (purity ≥ 99.5%) were obtained from POCh Gliwice (Poland). The potassium hydrogen phthalate was dried at 110 °C before use. The methanol, acetonitrile, dioxane, and toluene were purchased from Merck and were of HPLC grade (purity ≥ 99.9%).

The melting point was determined on a Mettler Toledo differential scanning calorimeter DSC822e equipped with a Haake EK90/MT intercooler. UV/Vis spectra were recorded on a Jasco UV-Vis-NIR V-670 double beam spectrophotometer in 1.00 cm quartz cells. IR spectra were obtained by a Bruker Alpha-P IR spectrometer in KBr pellets in the range of 4000–400 cm<sup>-1</sup>. The <sup>1</sup>H, <sup>13</sup>C, COSY and HSQC NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer. Elemental analysis (C, H, N and S) was performed with the elemental analyzer Vario EL III, manufactured by Elementar. The single-crystal X-ray diffraction data were collected at 293.15 K on an Oxford Diffraction Gemini A Ultra diffractometer.

Potentiometric titrations were carried out using the automatic titrator T70 (Mettler Toledo), equipped with the combined glass electrode DG114-SC (E ± 0.2 mV). All potentiometric titrations were performed in a thermostated double-walled vessel of 100 cm<sup>3</sup> at 25.0 ± 0.1 °C under nitrogen atmosphere. The constant temperature in the vessel during the titration was ensured by a thermostat (P5 E1 Funke Medingen) equipped with a water bath (0.15 M KCl). All titrations were performed in solutions of constant ionic strength, maintained by KCl (0.1 mol dm<sup>-3</sup>).

### 2.2. Synthesis, growth and characterization of 1-[(5-benzyl-1,3-thiazol-2-yl)diazenyl]naphthalene-2-ol

In the first step the acrolein was chloroarylated by diazonium salt under Meerwein reaction conditions (Fig. 1). A three-necked flask equipped with a dropping funnel, a stirrer and a gas-outlet tube attached to a bubble counter was charged with acrolein (0.2 mol or 13.5 cm<sup>3</sup>), CuCl<sub>2</sub>·2H<sub>2</sub>O (10 g) and acetone (50 cm<sup>3</sup>). Then a cold aqueous solution of arenediazonium chloride **1** prepared by diazotization of aniline (0.2 mol) was added dropwise to the flask under vigorous stirring. The temperature of the mixture was kept within 10–30 °C. The organic phase was separated when the reaction was complete and the aqueous phase was extracted with chloroform. The extract was combined with the previous organic phase, dried over magnesium sulfate, evaporated and the residue was distilled under reduced pressure.

A mixture of 8 g of thiourea and 0.1 mol of 3-phenyl-2-chloropropanal **2** in 50 cm<sup>3</sup> of ethanol was heated for 2 h under reflux. It was then cooled, diluted with 300 cm<sup>3</sup> of water, and made alkaline by adding aqueous ammonia. The precipitate was filtered off and recrystallized from carbon tetrachloride. The 3-phenyl-2-chloropropanal **2** reacted with thiourea in ethanol, forming 2-amino-5-benzyl-1,3-thiazole **3** with a good yield [38].

1.9 g (10 mmol) of 2-amino-5-benzyl-1,3-thiazole **3** was dissolved in 5.2 cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> at –5 °C. The solution was diluted with 4 cm<sup>3</sup> of water. The suspension was warmed until a clear solution was formed. The mixture was cooled to –10 °C, and 0.83 g (12 mmol) of sodium nitrite in a minimal quantity of water was added dropwise while keeping the temperature below –5 °C. When the resinous sediment was formed after 10 min, it was filtered, and the clear solution was added slowly with intensive stirring to a mixture of 1.44 g (10 mmol) of naphthalen-2-ol, 0.4 g (10 mmol) of NaOH, 20 g of Na<sub>2</sub>CO<sub>3</sub> and 20 cm<sup>3</sup> of water. The temperature was maintained below 5 °C. After the addition of diazonium salt, the mixture was left for 2 h at the room temperature and diluted with water (100 cm<sup>3</sup>). The precipitate was filtered off and recrystallized from DMF-ethanol. 5-Benzyl-1,3-thiazole-2-diazonium salt reacts in a diazocoupling reaction with naphthalen-2-ol under alkaline conditions, efficiently forming 1-[(5-benzyl-1,3-thiazol-2-yl)diazenyl]naphthalen-2-ol **5** (BnTAN) with high yield.

A saturated solution of BnTAN was prepared from the pure synthesized material, using DMF as the solvent, and was put into the desiccator with a small beaker containing pure ethanol. The solutions were allowed to diffuse at room temperature in order to enhance the purity of the material and to obtain single crystals of BnTAN suitable for structural studies. The red-coloured needle-shaped crystals suitable for single-crystal diffraction study were isolated after six weeks.

Data for BnTAN: M.p. 159.7 °C; Anal. Calcd for C<sub>20</sub>H<sub>15</sub>N<sub>3</sub>OS (345.42): C, 69.54; H, 4.38; N, 12.17; S, 9.28. Found: C, 69.31; H, 4.13; N, 11.83; S, 9.53; ATR-IR (cm<sup>-1</sup>): 3063, 3000, 1667, 1618, 1596, 1568, 1508, 1492, 1469, 1451, 1426, 1303, 1245, 1186, 1144, 1092, 1026, 982, 865, 830, 746, 696, 649, 622, 537, 511; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 14.88 (br.s, 1H, N(O)H), 8.44 (d, J = 8.2 Hz, 1H, C1), 7.78 (d, J = 9.3 Hz, 1H, C7), 7.63 (d, J = 7.8 Hz, 1H, C4), 7.59–7.55 (m, 1H, C2), 7.54–7.50 (m, 1H, C3), 7.46–7.43 (m, 1H, C23), 7.40–7.35 (m, 2H, C22 + C24), 7.32–7.29 (m, 2H, C21 + C25), 7.28 (s, 1H, C15), 6.95 (d, J = 9.3 Hz, 1H, C8), 4.17 (s, 2H, C18) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 172.2 (C9), 166.4 (C13), 141.2 (C7), 138.4 (C20), 137.9 (C16), 136.7 (C3), 132.4 (C5), 131.8 (C6), 130.7 (10), 129.5 (C2), 129.2 (C22 + C24), 129.0 (C4), 128.7 (C21 + C25), 127.5 (C15), 127.0 (C23), 122.8 (C8), 122.7 (C1), 34.1 (C18) ppm; UV-Vis (C<sub>2</sub>H<sub>5</sub>OH): λ<sub>max</sub> (nm) 495, ε × 10<sup>-4</sup> (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) 2.9.

The solubility of the compounds in ethanol (96%) at 20 °C is 2.12 · 10<sup>-3</sup> mol dm<sup>-3</sup> (0.073 g/100 g soln.).

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