



Structural characterization of a pyrazolone-based heterocyclic dye and its acid-base adduct



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ARTICLE INFO

Article history:

Received 3 February 2014

Received in revised form

18 June 2014

Accepted 19 June 2014

Available online 25 June 2014

Keywords:

Heterocyclic dye

Pyrazolone

Benzo-thiazole

Acid-base adduct

Hydrogen bonding

Azo-hydrazone tautomerism

ABSTRACT

The first structural report of an S-containing heterocycle based pyrazolone dye, 3-methyl-4-((6'-methylbenzo[d]thiazol-2'-yl)hydrazono)-1-phenyl-5-pyrazolone (**1**), is presented. The compound exhibits the hydrazone-tautomeric form. Treatment of **1** with a mixture of ammonia and acetone results in the formation of an acid-base adduct, **2**, consisting of the deprotonated dye as anion and *in-situ* formed 2,2,6,6-tetramethylpiperidone as the cation. This acid-base adduct was investigated by crystal structure determination. Comparison of the related bonds in both compounds, **1** and **2**, confirmed the formation of the anion.

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1. Introduction

Pyrazolone based heterocyclic compounds, like pyridine-2,4-dione and quinoline-2,4-dione based ones, are one type of important dyes and pigments [1–4]. In 2009, the crystal structures of several pyrazolone based Ca²⁺ complexes, i.e., Pigment Yellow 183 and Pigment Yellow 191, have been reported from X-ray powder and single-crystal data [5,6]. To date, there have been three structural reports on pyrazolone based the dye-metal complexes using aniline derivatives as the diazonium components [7–9]. On the other hand, isomeric benzisothiazole and benzothiazole based aromatic heterocyclic compounds are very useful intermediates for preparing a large amount of disperse dyes with great market demands [10–17].

In our previous work, several pyridine-2,4-dione and quinoline-2,4-dione based disperse dyes crystallizing in the hydrazone form and their azo-hydrazone tautomerism driven by pH titration and metal-ion complexation have been investigated [18–21]. As an extensive study in this area, we report herein the first structural examples for two dyes having pyrazolone and benzothiazole coupling components simultaneously, namely, a neutral pyrazolone/benzothiazole based heterocyclic dye **1** in the hydrazone-tautomeric form and its organic acid-base adduct **2** in the

deprotonated form countered by *in situ* formed 2,2,6,6-tetramethyl-4-oxopiperidinium cation in the mixture of acetone and aqueous ammonia. To the best of our knowledge, this is the first structural report involving S-containing heterocycle based pyrazolone dyes.

2. Experimental section

2.1. Materials and measurements

Melting point was measured without corrections. 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. Infrared (IR) spectra (4000–400 cm⁻¹) were recorded using a Nicolet FT-IR 170X spectrophotometer on KBr disks. ¹H NMR spectra were measured with a Bruker dmx500 MHz NMR spectrometer at room temperature.

2.2. Preparation of 3-methyl-4-((6'-methylbenzo[d]thiazol-2'-yl)hydrazono)-1-phenyl-5-pyrazolone (**1**) and its 2,2,6,6-tetramethyl-4-oxopiperidinium salt (**2**)

2-Amino-6-methylbenzothiazole (1.64 g, 10.0 mmol) was dissolved in a mixture of concentrated sulfuric acid (2 mL) and glacial

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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 vigorous stirring. The diazonium salt was obtained and used for the next coupling reaction. 5-Methyl-2-phenyl-1H-pyrazol-3-one (1.74 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 ($0-5^{\circ}\text{C}$). After additional stirring for 1.5 h, the mixture was neutralized with aqueous ammonia to pH 5–6. The precipitate was filtered and dried after thorough washing with acetone and ethanol. The crude product was recrystallized and the microcrystals of **1** were obtained in a yield of 2.53 g (72%). M.p. 224–226 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3 , ppm, TMS): $\delta = 7.96$ (d, 2H, $J = 8.1$ Hz, phenyl), 7.72 (d, 1H, $J = 8.2$ Hz, benzothiazole), 7.59 (s, 1H, benzothiazole), 7.46 (t, 2H, phenyl), 7.26 (t, 2H, benzothiazole and phenyl), 2.49 (s, 3H, CH_3 -benzothiazole), 2.39 (s, 3H, CH_3 -pyrazolone); Main FT-IR absorptions (KBr pellets, ν , cm^{-1}): 3440 (vs), 1660 (s), 1548 (vs), 1498 (s), 1226 (s), 1155 (s), 1043 (m), 1002 (m). ESI-TOF-MS (negative): m/z 348.1 (100%), $[\text{M}-\text{H}]^-$; Elemental analysis: calcd (%) for $\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_2\text{S}$: C, 61.87; H, 4.33; N, 20.04; found: C, 61.62; H, 4.19; N, 20.23. Orange single crystals of **1** suitable for X-ray diffraction measurement were grown from acetonitrile by slow evaporation in air at room temperature for two weeks, while red single crystals of acid-base adduct **2** were obtained from a mixture of acetone and aqueous ammonia by slow evaporation in air at room temperature for one week.

2.3. X-ray data collection and solution

Single-crystal samples of **1** and **2** were covered with glue and mounted on glass fibers for data collection on a Bruker SMART 1K CCD area detector at 291(2) K, using graphite mono-chromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data were reduced by using the program SAINT [22] and empirical absorption corrections were done by SADABS [23] 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 by full-matrix least-squares procedure using anisotropic displacement parameters. The two hydrazone protons in **1** and two quaternary amine protons in **2** were located in the difference synthesis and were refined isotropically in order to examine exactly the hydrogen bonding interactions. All the other hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times of the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. All calculations were carried out with the SHELXTL PC program package [24]. The summary of the crystal data, experimental details and refinement results for **1** and **2** is listed in Table 1. Selected bond distances and bond angles of **1** and **2** are given in Table 2, while intermolecular hydrogen bonding interactions are listed in Table 3.

3. Results and discussion

3.1. Synthesis and spectral characterizations of compounds **1** and **2**

Dye **1** can be easily prepared by the classical diazotization reaction in a satisfactory yield, where aromatic heterocyclic compounds 2-amino-6-methylbenzothiazole and 5-methyl-2-phenyl-1H-pyrazol-3-one serve as the diazonium and coupling components, respectively. Although this compound was firstly mentioned by Nermin Ertan in 2000 [25], its ^1H NMR spectrum was in very low

Table 1
Crystal and structural refinement data for compounds **1** and **2**.

Compound	1	2
Empirical formula	$\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_2\text{S}$	$\text{C}_{27}\text{H}_{32}\text{N}_6\text{O}_2\text{S}$
Formula weight	349.41	504.65
Temperature/K	291(2)	291(2)
Wavelength/Å	0.71073	0.71073
Crystal Size (mm)	$0.10 \times 0.12 \times 0.14$	$0.10 \times 0.12 \times 0.12$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	7.995(8)	7.695(1)
$b/\text{Å}$	12.014(1)	13.314(2)
$c/\text{Å}$	17.751(2)	14.677(2)
$\alpha/^\circ$	102.118(2)	111.549(2)
$\beta/^\circ$	99.332(2)	92.603(2)
$\gamma/^\circ$	93.516(2)	103.614(2)
$V/\text{Å}^3$	1639.9(3)	1344.7(3)
$Z/D_{\text{calcd}}(\text{g}/\text{cm}^3)$	4/1.418	2/1.246
$F(000)$	728	536
μ/mm^{-1}	0.215	0.155
$h_{\text{min}}/h_{\text{max}}$	–9/9	–8/9
$k_{\text{min}}/k_{\text{max}}$	–21/17	–15/15
$l_{\text{min}}/l_{\text{max}}$	–9/9	–17/13
Data/parameters	5747/463	4695/339
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$ $wR_2 = 0.1107$	$R_1 = 0.0385$ $wR_2 = 0.1067$
R indices(all data)	$R_1 = 0.0953$ $wR_2 = 0.1245$	$R_1 = 0.0469$ $wR_2 = 0.1108$
S	0.973	1.082
Max./min. $\Delta\rho/e \cdot \text{Å}^{-3}$	0.197/–0.209	0.237/–0.214

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{[\sum w(F_o^2)^2]}^{1/2}.$$

resolution and no mass spectrum was included. In addition, a wrong formula of $\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_2\text{S}$ was used for the elemental analysis. So we reported herein the full characterizations of this compound again.

It is interesting to mention that a remarkable acid-base salt **2** can be produced from dye **1** in the mixture of ammonium hydroxide and acetone. The pyrazolone/benzothiazole based heterocyclic dye moiety in **2** is in the deprotonation form, which is countered by an *in situ* formed 2,2,6,6-tetramethyl-4-oxopiperidinium cation. The formation of 2,2,6,6-tetramethylpiperidin-4-one molecule undergoes amination of ammonium hydroxide to a diol arising from the trimerization of acetone, and then the dehydration and ring-closing processes [26], as illustrated in Scheme 1. As a result, a weak acid-base adduct of **1** is *in situ* formed in the case of **2**.

UV–vis spectra are carried out in both acetone and methanol for compounds **1** and **2** at the same concentration of 3.0×10^{-5} mol L^{-1} . As can be seen from Fig. 1, the maximum UV–vis absorption wavelength dye **1** in its acetone solution (pH = 6.1) is centered at 406 nm, which is different from the previously reported 421 nm [25]. In contrast, it is significantly red-shifted to 463 nm in methanol ($\xi = 28,267$ L cm^{-1} mol $^{-1}$), indicative of typical solvatochromic property of this dye molecule. It is also noted that no obvious discrepancy of the maximum absorption wavelength can be observed for ion-pair compound **2** in comparison with dye **1** in methanol (462 nm), indicating that **2** does not exist as an ion pair in solution, but a mixture of neutral **1** and neutral tetramethylpiperidinone instead. However, a remarkable red shift of the maximum absorption wavelength from 406 to 470 nm can be found in acetone after forming the acid-base adduct, mainly owing to the ionization of compound **2** and the following stabilization in acetone. That is to say, compounds **1** and **2** can be distinguished by their UV–vis spectra in the non-protic acetone solvent although they cannot be discriminated in the protic methanol solvent.

3.2. Structural description of compounds **1** and **2**

The molecular structures of compounds **1** and **2** with the atom-numbering scheme are shown in Figs. 2 and 4, respectively. X-ray

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