



Visualized fabric discoloration of bi-heterocyclic hydrazone dyes



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ABSTRACT

A series of bi-heterocyclic hydrazone dyes have been synthesized by classic diazotization reactions between 2-amino-3-cyano-4-chloro-5-formylthiophene and five pyridine-2,6-dione based coupling components, including two acetal products undergoing dimethylacetalization of aldehyde group in the presence of methanol and glacial acetic acid. ¹H NMR spectral and single-crystal X-ray diffraction studies reveal the presence of hydrazone tautomeric form for this family of dyes both in solution and in the solid state. More interestingly, visualized fabric discoloration has been firstly observed for this family of dyes on five representative fibers (Polyester, Nylon, Silk, Wool and Cotton) under different pH values. It is believed that the proton transfer originated from the azo-hydrazone tautomerism is responsible for the above-mentioned solvatochromism and fabric discoloration.

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1. Introduction

Azo-functionalized compounds are the oldest and most important class of industrial synthesized dyes because of their various applications such as laser, ink-jet printers, optical data storage, dye-sensitized solar cells, non-linear optics and biological systems [1–6]. In addition, some azo dyes have been permitted to be used in cosmetics and drugs [7]. The design and development of azo dyes containing heterocyclic moieties become popular in recent years, because they have better tinctorial strength and brightness in comparison with analogues aromatic dyes [8]. In particular, thiophene-containing heterocyclic dyes have many advantages such as color-deepening effects and excellent sublimation fastness on fabrics [9,10].

Pyridine-2,6-dione based dyes are regarded as one important type of heterocyclic dyes which have a hydroxyl group in conjunction with the azo chromophore showing azo-hydrazone tautomerism [11–15]. Study on the proton transfer between oxygen and nitrogen atoms appears to be quite interesting from both the experimental and theoretical viewpoints, since tautomers in

different isomeric forms are believed to affect the basic properties of pyridine-2,6-dione derivatives such as color, tone and photostability [16]. In our previous work, several nitrogen-containing disperse heterocyclic dyes, such as pyridine-2,4-dione, quinoline-2,4-dione and pyrazolone derivatives crystallizing in the same hydrazone form in the solid state, have been systematically investigated on their azo-hydrazone tautomerisms driven by pH control and meta-ion complexation [17–23].

Fabric discoloration is an interesting phenomenon which means one dye can display distinct color on different kinds of fibers in the dyeing process. Traditional strategies for the fabric identification, such as microscopic observation, fiber burning and coloring test, have considerable limitations including low resolution, complicated procedures and vulnerable to outside conditions [24]. In this work, we have described seven new bi-heterocyclic hydrazone dyes **2–8**, where 2-amino-3-cyano-4-chloro-5-formylthiophene diazo component and a series of N-substituted pyridine-2,6-dione based coupling components are firstly combined in order to achieve some high performance disperse dyes. Single-crystal structures of dyes **4**, **7**·CH₃OH and **8** in the hydrazone form have been included in this work to give an intuitive proof. Solvatochromic behavior of synthesized dyes in various solvents as well as azo-hydrazone tautomerism by pH control has been fully investigated, too. More interestingly, dyes **2–6** are found to display distinct color on five conventional fibers (Polyester, Nylon, Silk, Wool and Cotton), and the simplicity of this method means that fabrics can be identified

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quickly and efficiently. Furthermore, UV–Vis reflection spectra of these dyed fabrics, obtained by performing the standard dyeing protocols under different pH values, have been determined with different K/S values (K : scattering coefficient; S : absorption coefficient). It is suggested that these dyes could serve as practical and efficient fiber identification reagents in dyestuff industry.

2. Experimental

2.1. Materials and physical measurements

All melting points were measured without corrections. The reagents of analytical grade were purchased from commercial sources and used without any further purification. Elemental analyses (EA) for carbon, hydrogen and nitrogen were performed on a Perkin–Elmer 1400C analyzer. Infrared (IR) spectra (4000–400 cm^{-1}) were recorded using a Nicolet FT–IR 170X spectrophotometer on KBr disks. Electrospray ionization mass spectra (ESI–MS) were recorded on a Finnigan MAT S50 mass spectrometer in a scan range of 200–2000 amu. ^1H NMR spectra were measured with a Bruker DMX500 MHz NMR spectrometer at room temperature in CDCl_3 or CD_3CN with tetramethylsilane as the internal reference. UV–Vis spectra were recorded with a Shimadzu UV–3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm.

2.1.1. Synthesis of dye 2

Compound **1** (1.87 g, 10.0 mmol) was dissolved in a mixture of concentrated sulfuric acid (6 mL) and phosphate (4.2 mL) at -5°C in an ice bath. Sodium nitrite (0.76 g, 7.0 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. 1,4-Dimethyl-3-cyano-6-hydroxy-2-pyridone (1.64 g, 10.0 mmol) was added to a mixture of methanol/water (90 mL, $v/v = 2:1$) solution in a three-necked flask immersed in an ice bath. Freshly prepared diazonium salt was added dropwise to the reaction mixture under vigorous mechanical stirring for 1 h ($0-5^\circ\text{C}$). The precipitate was filtered and dried after thorough washing with distilled water. The crude product was purified by recrystallization from acetonitrile, and compound **2** was finally obtained in a yield of 2.93 g (81%). Mp: $> 250^\circ\text{C}$. ^1H NMR (500 MHz, CD_3CN) δ : 9.91 (s, 1H), 3.28 (s, 1H), 2.51 (s, 3H). Main FT–IR absorptions (KBr pellets, cm^{-1}): 3427 (w), 2229 (m), 1641 (vs), 1496 (s), 793 (m), 1097 (m). Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{ClN}_5\text{O}_3\text{S}$: C, 46.48; H, 2.23; N, 19.36%. Found: C, 46.66; H, 2.34; N, 19.47%. Negative ESI–MS in acetonitrile: $m/z = 360.25$ (100%), $[\text{M}-\text{H}]^-$.

2.1.2. Preparation of dyes 3–6

Syntheses of **3–6** were similar to that described for **2**. Dye **3**: 3.30 g (Yield: 88%). Mp: $> 250^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ : 15.44 (s, 1H), 9.97 (s, 1H), 4.08 (m, 2H), 2.58 (s, 3H), 1.27 (m, 3H). Main FT–IR absorptions (KBr pellets, cm^{-1}): 3428(w), 2227 (m), 1691 (m), 1639 (vs), 158 (s), 1452 (s), 1901 (m). Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{ClN}_5\text{O}_3\text{S}$: C, 47.94; H, 2.68; N, 18.64%. Found: C, 48.11; H, 2.72; N, 18.87%. Negative ESI–MS in acetonitrile: $m/z = 374.17$ (100%), $[\text{M}-\text{H}]^-$. Dye **4**: 3.64 g (Yield: 86%). Mp: $> 250^\circ\text{C}$. ^1H NMR (500 MHz, CD_3CN) δ : 10.21 (s, 1H), 7.32 (m, 2H), 7.29 (m, 1H), 7.21 (m, 2H), 2.90 (s, 3H). Main FT–IR absorptions (KBr pellets, cm^{-1}): 3442 (m), 2233 (m), 1645 (vs), 1510 (s), 1440 (m), 1371 (m), 790 (m). Anal. Calcd. for $\text{C}_{19}\text{H}_{10}\text{ClN}_5\text{O}_3\text{S}$: C, 53.84; H, 2.38; N, 16.52%. Found: C, 53.64; H, 2.51; N, 16.38%. Negative ESI–MS in acetonitrile: $m/z = 436.25$ (100%), $[\text{M}-\text{H}]^-$. Single crystals of **4** suitable for X-ray diffraction measurement were grown from the acetonitrile by slow evaporation in air at room temperature for 3 weeks. Dye **5**: 3.33 g (Yield: 85%). Mp: $> 250^\circ\text{C}$. ^1H NMR (500 MHz, CD_3CN) δ : 9.94 (s,

Table 1
Crystal data and structural refinements for dyes **4**, **7**- CH_3OH and **8**.

Compound	4	7 - CH_3OH	8
Empirical formula	$\text{C}_{20}\text{H}_{12}\text{ClN}_5\text{O}_3\text{S}$	$\text{C}_{18}\text{H}_{20}\text{ClN}_5\text{O}_6\text{S}$	$\text{C}_{21}\text{H}_{24}\text{ClN}_5\text{O}_5\text{S}$
Formula weight	437.87	469.90	493.96
Temperature/K	291(2)	291(2)	291(2)
Wavelength/ \AA	0.71073	0.71073	0.71073
Crystal Size (mm)	$0.12 \times 0.10 \times 0.10$	$0.10 \times 0.08 \times 0.08$	$0.10 \times 0.10 \times 0.10$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	9.708(1)	7.727(1)	7.762(4)
$b/\text{\AA}$	10.648(2)	10.265(1)	13.293(7)
$c/\text{\AA}$	12.161(2)	14.268(1)	14.225(7)
$\alpha/^\circ$	68.052(2)	86.996(1)	110.394(7)
$\beta/^\circ$	80.481(2)	79.720(1)	100.655(7)
$\gamma/^\circ$	87.950(2)	77.078(1)	103.706(8)
$V/\text{\AA}^3$	1149.4(3)	1085.23(14)	1277.6(7)
Z/D_{calcd} (g/cm^3)	2/1.265	2/1.438	2/1.284
$F(000)$	448	488	516
μ/mm^{-1}	0.286	0.317	0.270
$h_{\text{min}}/h_{\text{max}}$	–12/12	–9/10	–9/6
$k_{\text{min}}/k_{\text{max}}$	–13/13	–12/13	–15/15
$l_{\text{min}}/l_{\text{max}}$	–15/13	–18/15	–16/16
Data/parameters	7895/272	7424/288	9345/330
Final R indices	$R_1 = 0.0481$ $wR_2 = 0.1334$	$R_1 = 0.0576$ $wR_2 = 0.1757$	$R_1 = 0.0760$ $wR_2 = 0.2280$
S	0.989	1.023	0.952
Max/min $\Delta\rho/e \text{\AA}^{-3}$	0.326/–0.449	1.306/–1.160	0.459/–0.399

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

1H), 4.08 (m, 2H), 3.70 (t, $J = 5$ Hz, 2H), 2.53 (s, 3H). Main FT–IR absorptions (KBr pellets, cm^{-1}): 3446 (vs), 2229 (m), 1655 (vs), 1500 (s), 1365 (m), 790 (m), 705 (m). Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{ClN}_5\text{O}_4\text{S}$: C, 45.98; H, 2.57; N, 17.88%. Found: C, 46.18; H, 2.69; N, 18.02%. Negative ESI–MS in acetonitrile: $m/z = 390.50$ (100%), $[\text{M}-\text{H}]^-$. Dye

Table 2
Selected bond distances (\AA) and angles ($^\circ$) for dyes **4**, **7**- CH_3OH and **8**.

Bond distances		Bond angles	
4			
N2–C5	1.376(3)	N3–N2–C5	109.8(2)
N2–N3	1.293(2)	N2–N3–C7	121.7(2)
N3–C7	1.352(3)	N3–C7–C11	114.4(2)
C7–C11	1.430(3)	N3–C7–C8	124.8(2)
C7–C8	1.450(3)		
O2–C8	1.221(3)		
N4–C8	1.404(3)		
N4–C9	1.386(3)		
N4–C14	1.474(3)		
7-CH₃OH			
N2–C4	1.380(3)	N3–N2–C4	117.1(2)
N2–N3	1.318(3)	N2–N3–C9	120.2(2)
N3–C9	1.318(3)	N3–C9–C13	115.7(2)
C9–C13	1.445(3)	N3–C9–C10	123.0(2)
C9–C10	1.469(3)	O2–C5–O1	115.1(2)
N4–C10	1.375(3)		
N4–C11	1.401(3)		
N4–C14	1.475(4)		
O1–C5	1.387(4)		
O1–C6	1.430(5)		
O2–C5	1.387(4)		
O2–C7	1.429(5)		
C10–O3	1.232(3)		
8			
N2–C4	1.377(5)	N3–N2–C4	117.7(4)
N2–N3	1.319(5)	C9–N2–N3	119.2(4)
N3–C9	1.320(5)	N3–C9–C10	115.1(4)
C9–C13	1.439(6)	N3–C9–C13	123.8(4)
C9–C10	1.432(6)	O2–C5–O1	121.6(5)
O1–C5	1.360(6)		
O1–C6	1.431(8)		
O2–C5	1.343(6)		
O2–C7	1.442(6)		
C13–O3	1.236(5)		

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