Dyes and Pigments 53 (2002) 257–262
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Short communication

Synthesis of novel dyes derived from 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone

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Received 18 December 2001; received in revised form 9 January 2002; accepted 15 February 2002

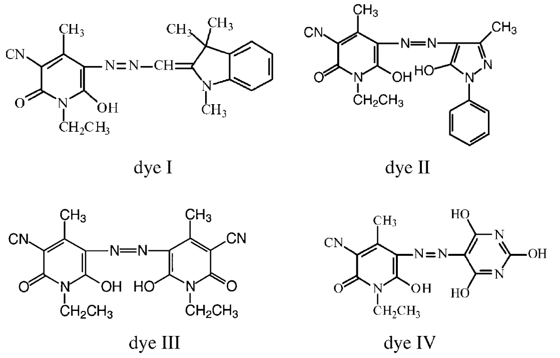
Abstract

The properties and the diazotisation process of 1-ethyl-5-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone were described. The conditions of the coupling reaction were also discussed and a series of new azo dyes using 1-ethyl-5-cyano-6-hydroxy-4-methyl-3-amino-2-pyridone as diazo components were synthesized. The absorption properties of these new azo dyes were investigated in various solvents and the mixture solvent of chloroform/DMSO with different volume ratios. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Pyridone; Azo dye; Diazotisation; Diazo component

1. Introduction

There have been a series of azo dyes using pyridone as coupling components [1–5]. Because that some ramification of pyridone have not good electron-rich rings, the absorption of these monoazo dyes using pyridone as coupling components was limited to be a region between green-yellow and orange spectral region. There are few pyridone azo dyes that have deep color such as red or violet. And so far little attention was paid to the pyridone azo dyes using pyridone as diazo components, too. In this present work, we studied the properties of 1-ethyl-5-cyano-6-hydroxy-4-methyl-3-amino-2-pyridone and prepared some new azo dyes by coupling 1,3,3-trimethyl-2-metheneindoline, 1-phenyl-3-methyl-5-pyrazolone, 1-ethyl-3-cyano-6-hydroxy-4-methyl-2-pyridone and barbituric acid with the diazo salt of 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone. The chemical structures of the new azo dyes were shown in Scheme 1.



Scheme 1. Chemical structures of the new azo dyes.

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PII: S0143-7208(02)00021-9

Because there are some electron-withdrawing groups on the pyridone ring, which becomes a good diazo component, the color of these dyes is deep. Their solutions have absorption in red spectral region. We expect they would have promising use for textile. Moreover, $\lambda_{\max}$ of some dyes such as dye **I** and dye **III** is between 560 and 600 nm, and they have good solubility in some organic solvents. Therefore, they have potential application for DVD-R optical record disc.

2. Experimental

IR spectra of the dyes were carried out on a Nicolet 5SXC or Nicolet Magna-IR550 instrument using KBr tabulating. ^{1}H-NMR spectra were measured on Bruker AVANCE 500 at 500 MHz in deuterium solvents, with TMS as an internal reference. EI mass spectra (70 eV) were recorded on a HP5989A or Micromass GCT, LCT spectrometer. Visible absorption spectra were recorded on a Shimadzu UV-260 Spectrophotometer. 1 N HCl and 1 N NaOH were used to adjust the pH values of the solutions, which were measured on a pH value meter (S-3C) with range of pH = 0–14 and accuracy of 0.01.

1-Ethyl-3-cyano-6-hydroxy-4-methyl-2-pyridone was prepared from ethyl acetoacetate, cyano-acetotate and ethylamine using the method described in the literature [6]. 1-Ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone was prepared according to our previous publication [7].

2.1. Diazotisation of 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone

1-Ethyl-5-cyano-6-hydroxy-4-methyl-3-amino-2-pyridone (0.01 mol) was dissolved in sodium hydrate solution (40 ml water, 0.01 mol sodium hydrate). Glacial acetic acid (3 ml) was added into it and the mixture was cooled in ice-salt bath to 0–5 °C. Within 15 min sodium nitrite solution (40 ml water, 0.7 g sodium nitrite) was dropped into the mixture and it was further stirred for 1 h. The solution became a blue suspension. At that time the diazotisation has been completed.

2.2. Preparation of the dye I

The diazo salt (0.01 mol) solution of the 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone was filtered and the solid was dissolved in ethanol (40 ml). 1, 3, 3-trimethyl-2-metheneindoline (0.01 mol) was rapidly added to the diazo salt ethanol solution. The mixture was stirred for 5 h and filtered. The solid was washed and recrystallized with ethanol. Blue crystal was obtained.

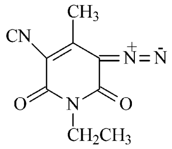
2.3. General preparation procedure of the dyes I, III and IV

The coupling components (0.01 mol) was dissolved in sodium hydrate solution (40 ml water, 0.01 mol sodium hydrate) and cooled to 0–5 °C in a ice salt bath. The pH value was regulated to 7–8. The diazo salt of 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone was stirred into the coupling component solution. During the procedure, the pH value was maintained within 7–8. The mixture was stirred for 4 h, then the pH value was regulated to 3–4. The mixture was further stirred for 1 h and then filtered. The solid was washed with water and then recrystallized with ethanol.

3. Results and discussion

3.1. Characteristics of the diazo salt

1-Ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone belongs to *o*-amino phenols. It is easy to be oxidized while being diazotized. So the acid used to diazotize 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone can not be hydrochloric acid or sulfuric acid, but glacial acetic acid. We filtered the diazo salt solution and obtained a blue-green solid. m.p.: 57–60 °C. IR spectra show two vibrations of the carbonyl group at the position 1685and 1640 cm^{-1}, the vibration of the nitrile group at 2229 cm^{-1} and a strong vibration of cumulative double bond within 2125–2167 cm^{-1}. From these data we can conclude that the structure of the diazo salt should be:



The procedure formed is proposed in Scheme 2 [8].

3.2. Coupling reaction and structures of the azo dyes

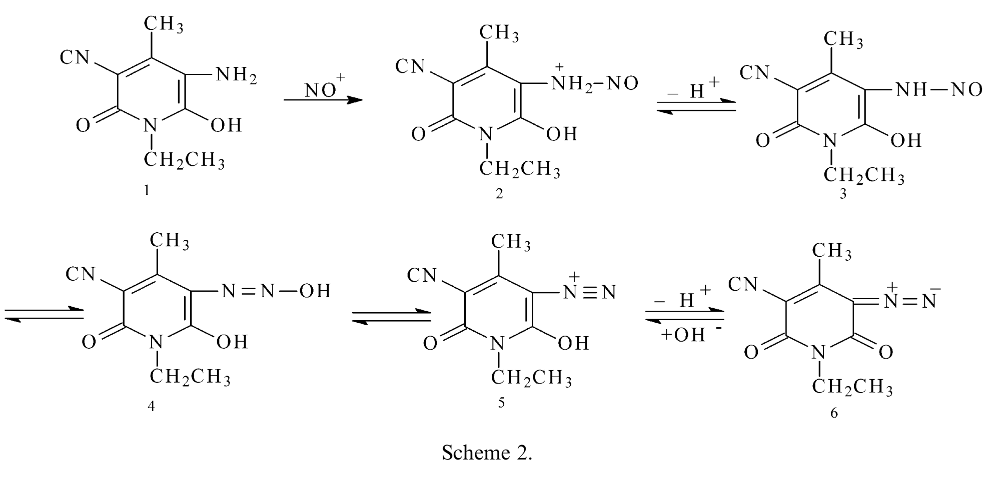
The diazo salt of 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone does not react with aromatic amines in the acidity solutions ($pH < 7.0$). The products are mixtures when they react with phenols in the strong alkaline solutions ($pH > 8.0$). But it can react with the compound containing reactive methene when the pH value is within 7–8. The structure 6 shown in Scheme 2 will exist stable in the acidic solution, but it has not got coupling capacity under this condition. When the pH value of the solution is within 7–8, the structure 6 can change to the structure 5 in Scheme 2, which can react with the components, especially the reactive methene compound. But the diazo salt changes from blue suspension to clear red solution under the strong alkaline condition, which lose the coupling capacity. The reason is not very clear. It is possible that the diazo salt condenses with itself.

We use 1, 3, 3-trimethyl-2-methene indoline, 1-phenyl-3-methyl-5-pyraazolone, 1-ethyl-3-cyano-6-hydroxy-4-methyl-2-pyridone and barbituric acid as coupling components and obtain the azo dyes **I**, **II**, **III** and **IV** shown in Scheme 1, respectively. The IR, ^{1}H-NMR and MS spectra data of them were listed in Table 1.

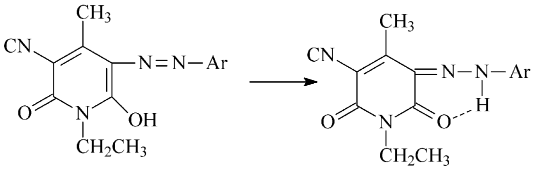
It is clear from the IR spectra results that the diazotion component of the dyes show two characteristic vibration: the carbonyl group within the region $\nu_{C=O}$ 1625–1675 cm^{-1} and the nitrile group 2208–2230 cm^{-1}. On the basis of the two carbonyl vibrations we can conclude that there is a shift of equilibrium to pyridine-2,6-dione configuration and the dyes exist in the hydrazone form in the solid state. The typical equilibrium is shown in Scheme 3.

The ^{1}H-NMR spectrum shows a characteristic singlet for the CH_3 group at the 4-position, a characteristic triplet for the CH_3 group and a characteristic quadrate for the CH_2 group at the 1-position. And the spectrum also clearly shows that these dyes exist in the azo form in the absolute solvent because there is no the characteristic wide singlet NMR signal for the –NH-hydrogen bond. Moreover, there is some distortion of the peak of some groups on the pyridone ring in some dyes such as dye **III** and dye **IV**. We think that this would be caused by the proton-transfer equilibrium [9,10] shown in Scheme 4.

Because there is a lot of hydroxyl in these dyes and they are easy to lose the water during the ionization, there is no molecular ion peak in MS spectra of some dyes. But there is fragment information of some molecules losing water.



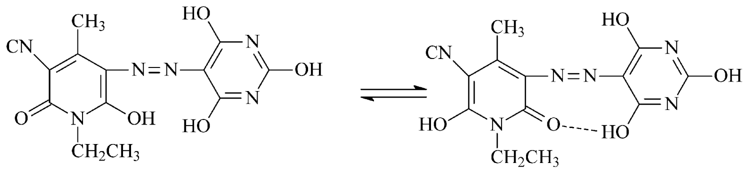
Scheme 2.



Scheme 3.

3.3. Absorption spectral data

Visible absorption spectral data of these azo dyes in various solvents are given in Table 2, and the spectra of dye **II** in various solvents is shown in Fig. 1. The visible spectra of the dyes were found to exhibit a strong solvent dependence,



Scheme 4.

Table 1
Structure data for the dyes

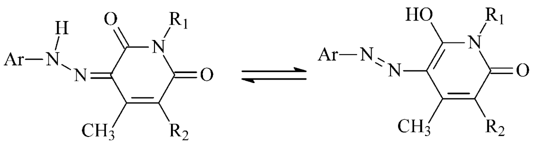
Dye	Yield (%)	Melting point (°C)	IR (cm^{-1})		MS *m*/*z* (rel. int.)	^{1}H-NMR (ppm)
			$\nu_{C=O}$	$\nu_{C\equiv N}$		
I	93	193–195	1625 1660	2230	377 (9.83) 177 (9.36) 173 (43.26) 158 (100.00) 143 (21.90)	1.24 (*t*, 3H, ethyl –CH_3) 1.77 (*s*, 6H, –C $(CH_3)_2$) 2.5 (*s*, 3H, pyridone–CH_3) 3.23 (*s*, 3H, –N–CH_3) 4.07 (*q*, 2H, –CH_2–) 6.45 (*s*, 1H, =CH–) 6.75 (*d*, 1H, *J*=7.87 Hz, Ar-H) 6.98 (*t*, 1H, *J*=7.43 Hz, 7.45 Hz, Ar-H) 7.21 (*d*, 1H, *J*=7.30 Hz, Ar-H) 7.24 (*t*, 1H, *J*=7.65 Hz, 4.93 Hz, Ar-H)
II	90	175–177	1628 1670	2218	205 (5.22) 201 (19.97) 177 (40.94) 174 (61.57) 77 (100.00)	1.10 (*t*, 3H, ethyl–CH_3) 2.31 (*s*, 3H, pyrazole–CH_3) 2.46 (*s*, 3H, pyridone–CH_3) 3.89 (*q*, 2H, –CH_2–) 7.21 (*t*, 1h, *J*=7.07 Hz, 7.39 Hz, Ar-H) 7.45 (*t*, 2H, *J*=7.80 Hz, 8.01 Hz, Ar-H) 7.87 (*d*, 2H, *J*=7.43 Hz, Ar-H)
III	94	>300	1625 1665	2208	204 (30.07) 177 (100.00) 150 (49.16) 134 (61.98) 107 (92.60)	1.05 (*t*, 3H, ethyl–CH_3) 1.99 (*s*, 3H, pyridone–CH_3) 3.76 (*m*, 2H,–CH_2–)
IV	81	>300	1640 1675	2218	332 (9.42) 177 (15.43) 150 (13.40) 134 (13.67) 128 (100.00)	1.06 (*m*,3H, ethyl–CH_3) 2.22 (*s*,3H,pyridone–CH_3) 3.78 (*q*,2H,–CH_2–)

which did not show a regular variation with the dielectric constants of the solvent. It was observed that although in ethanol, acetone and chloroform the absorption spectra of the dyes **I** and **II** did not change significantly, $\lambda_{\max}$ of the dyes shifted considerably in DMF and DMSO (e.g. $\lambda_{\max}$ of dye I is 580 nm in acetone and 468 nm in DMF, 592 nm in DMSO) (Table 3). But when it comes to the dyes **III** and **IV**, the results are different. The absorption spectra of the dyes **III** and **IV** did not change significantly in acetone, DMF and DMSO, but $\lambda_{\max}$ of them showed hypsochromic shifts in ethanol.

Table 2
Absorption spectra data for the dyes ($\lambda_{\max}$/nm, $\varepsilon_{\max}/10^4$ M^{-1} cm^{-1})

Dye		Solvent				
		Ethanol	Acetone	Chloroform	DMF	DMSO
I	$\lambda_{\max}$	585	580	584	468	592
	$\epsilon_{\max}$	2.55	3.87	3.13	3.53	2.58
II	$\lambda_{\max}$	488	486	482	535, 492	535
	$\epsilon_{\max}$	2.55	3.75	2.29	1.49, 1.53	0.82
III	$\lambda_{\max}$	569	585	Insoluble	587	586
	$\epsilon_{\max}$	1.72	2.66	Insoluble	2.35	1.91
IV	$\lambda_{\max}$	504	511	Insoluble	513	512
	$\epsilon_{\max}$	1.87	1.48	Insoluble	1.94	0.64

According to the reports of Qinji Peng et al. [11,12] and Ertan et al. [13] we know that there is equilibrium between hydrazone form and azo form for pyridone azo dyes. The equilibrium can be represented as Scheme 5. Our experiments are in agreement with this result. The absorption spectra of dye **II** at different volume ratios of the mixture solvents of chloroform/DMSO are shown in Fig. 2. From it we can see that there is an isobestic point in it, and with the increase of the volume content of DMSO, the absorption of the



Scheme 5. The equilibrium between hydrazone form and azo form.

Table 3
Absorption spectral data for dye **II** at different pH values

pH	2.5	4.5	5.6	7.8	8.0	8.8	9.6
$\lambda_{\max}$/nm	477	477	473	488	445	445	445

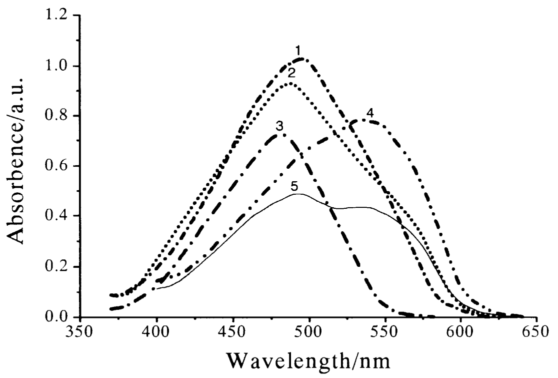


Fig. 1. Absorption spectra of dye **II** in different solvents: 1. acetone; 2. ethanol; 3. chorolform; 4. DMSO; 5. DMF.

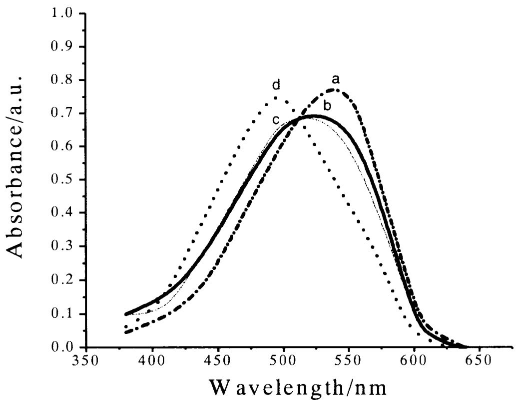


Fig. 2. Absorption of dye **II** in different volume ratios (a, 1/4; b, 3/2; c, 7/3; d, 4/1) of chloroform/DMSO.

azo form increase, while that of the hydrazone form decreases.

But from the absorption spectral data of dye **II** we can see that there are both the decrease in $\lambda_{\max}$ for hydrazone form and azo anion when a small amount of hydrochloric acid or sodium hydrate was added into the absolute ethanol. The reason may be followed: previous experiments in the literature [11–13] used pyridone as coupling component, but we here use it as diazo components. When a small amount of sodium hydrate was added into the dye solution, the hydroxyl on the pyridone ring becomes the hydroxyl anion, which is a strong electron-donor group. So $\lambda_{\max}$ of the azo anion showed hypsochromic shifts compared with azo dyes.

4. Conclusion

1-Ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone is unstable, and its diazotion can't be carried out in general method. Its diazotization should be carried out by using glacial acetic acid. The diazo salt of 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-amino-2-pyridone exists stable in the form of intramolecular salt. It does not react with the coupling components under the acidic condition, and however, it is unstable under the strong alkaline condition. But the diazo salt of 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-amino-2-pyridone can react with the coupling component with reactive methene when the pH value is between 7 and 8. Some new deep color pyridone azo dyes, in which 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-amino-2-pyridone is a diazo component, are synthesized. These dyes exist in the hydrazone form in the solid state and there is equilibrium between hydrazone form and azo form in the solvents for these pyridone azo dyes.

Acknowledgements

This work was supported by NSFC/China (29836150) and Shanghai Scientific and Technology Committee and Shanghai Education Committee.

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