

## Hetarylazopyridone Dyes and Their Spectroscopic Properties

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**Abstract:** The synthesis of some new pyridone dyes by coupling 3-cyano-4-methyl-6-hydroxy-2(1H)-pyridone with diazotized primer heteroaromatic amines is reported. The effects of acid-base, temperature, concentration and solvent on visible absorption spectra of these dyes were discussed.

**Keywords:** Pyridone; Hetarylamine; Absorption spectra, Hydrazone, Tautomerism

## Hetarilazopiridon Boyarmaddeleri ve Spektroskopik Özellikleri

**Özet:** Diazolanmış pirimer heteroaromatik aminlerin 3-siyano-4-metil-6-hidroksi-2(1H)-piridon ile kenetlenmesinden bazı yeni piridon boyarmaddeleri sentezleri belirtildi. Bu boyarmaddelerin görünür bölge absorpsiyon spektrumları üzerine asit-baz, sıcaklık, derişim ve çözücü etkileri araştırıldı.

**Anahtar Kelimeler:** Pyridone; Hetarylamine; Absorption spectra, Hydrazone, Tautomerism

### Introduction

Azo compounds are very important in the fields of dyes, pigments and advanced materials [1]. Some hetarylazopyridone dyes were reported in our previously studies [2, 3]. Wang and co-workers are explained that bis(hetaryl)azo dyes are relatively rare, and also useful as advanced materials [4]. For example, Song and co-workers have purposed that pyridone dyes have potential application for DVD-R optical record disc [5].

In this study, some new hetarylazo pyridones dyes (Figure 1) were prepared by coupling 3-cyano-4-methyl-6-hydroxy-2(1H)-pyridone with diazotized 2-amino-5-nitro-1,3-thiazole, 2-amino-1,3-thiadiazole, 2-amino-1,3,4-triazole, 5-amino-1H-tetrazole and 3-amino-5-Methyl-isoxazole in nitrosyl sulphuric acid. The various effects on visible absorption spectra of these dyes were examined.

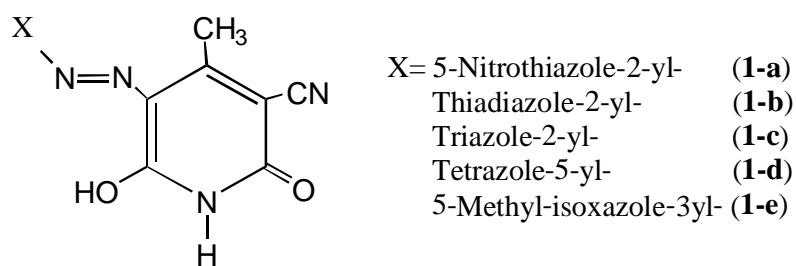


Figure 1

## Experimental

3-cyano-6-hydroxy-4-methyl-2(1H)pyridone was prepared from ethyl acetoacetate and cyanoacetamide using the method described in the literature [6]. Hetaryl amines were of chemical grade and used without further purification. The solvents used were of spectroscopic grade.

IR spectra were determined in KBr with on a Mattson 1000 FT-IR spectrometer. <sup>1</sup>H-NMR spectra were recorded on a Bruker Avance DPX 400 spectrometer in DMSO-*d*<sub>6</sub>. Absorption spectra were recorded on a Shimadzu UV-1601 spectrophotometer in various solvent. Elemental microanalysis for C, H, N and S were performed on a LECO CHNS 932 elemental analyzer. Melting points were observed on Electrothermal 9100, and were uncorrected.

**General Procedure:** 3-cyano-6-hydroxy-5-[(1,3-thiadiazole-2-yl)azo]-4-methyl-2(1H)-pyridone is given as illustrative; all other dyes were prepared in a similar manner. Characterization data are shown in Tables 1 and 2.

**Preparation of 3-cyano-5-[(1,3-thiadiazole-2-yl)azo]-6-hydroxy-4-methyl-2(1H)-pyridone (1a):** 2-aminothiadiazole (0,007 mole) was dissolved in hot glacial acetic acid (30 mL) and was rapidly cooled in an ice-salt bath to -5°C. The liquor was then gradually stirred into a cold solution of nitrosyl sulphuric acid (prepared from 0.0077 mole sodium nitrite and 7 mL concentrated sulphuric acid at 70°C). After diazotization was complete, the diazo liquor was slowly added to a vigorously stirred solution of

compound **1** in KOH (0,007 mole) and water (30 mL), and the mixture was then stirred for a further 30 min. The solution was partly neutralized with KOH and the precipitated coloured solid filtered, washed with cold water and dried, and crystallized from DMSO-Ethanol mixture.

Table 1. Elemental Analysis Data for The Dyes (**1a-e**).

Comp. no	Molecular Formula	C (%)		H (%)		N (%)		S (%)		m.p. (°C)	Yield (%)
		Calcd.	Found	Calcd.	Fond	Calcd.	Found	Calcd.	Found		
<b>1a</b>	C <sub>10</sub> H <sub>6</sub> N <sub>6</sub> O <sub>4</sub> S	39,22	38,57	1,97	1,39	27,44	26,74	10,47	10,84	>290*	32
<b>1b</b>	C <sub>9</sub> H <sub>6</sub> N <sub>6</sub> O <sub>2</sub> S	41,22	42,16	2,31	1,64	32,05	31,83	12,23	12,52	>270*	30
<b>1c</b>	C <sub>9</sub> H <sub>7</sub> N <sub>7</sub> O <sub>2</sub>	44,09	43,34	2,88	3,33	39,99	38,91	-	-	>295*	28
<b>1d</b>	C <sub>8</sub> H <sub>6</sub> N <sub>8</sub> O <sub>2</sub>	39,03	39,62	2,46	2,73	45,52	45,49	-	-	>220*	24
<b>1e</b>	C <sub>11</sub> H <sub>9</sub> N <sub>5</sub> O <sub>3</sub>	50,97	50,68	3,50	2,89	27,02	26,63	-	-	>300*	75

\*: decomposed.

Table 2. Spectral Data for the Dyes (**1a-e**).

Comp.no	IR (cm <sup>-1</sup> )			<sup>1</sup> H-NMR (ppm)		
	n <sub>C=N</sub>	n <sub>C=O</sub>	n <sub>N-H</sub>	d <sub>Ar-H</sub>	d-CH <sub>3</sub>	d <sub>N-H</sub>
<b>1a</b>	2244	1708 1676	3224 3220	8,634 (1H, s)	2,440 (3H, s)	11,908 (1H,br)
<b>1b</b>	2210	1670 1635	3125	9,270 (1H, s)	2,391 (3H, s)	12,265 (1H,br)
<b>1c</b>	2228	1698 1671	3240	8,552 (1H, s)	2,417 (3H, s)	14,555-14,195 (1H,d) 12,105 (1H,br)
<b>1d</b>	2223	1682 1652	3462	-	2,461 (3H, s)	12,263 (1H,br)
<b>1e</b>	2226	1686 1671	3278	6,624 (1H, s)	2,412 (3H, s) 2,361 (3H, s)	14,227 (1H,br) 12,158 (1H,br)

s=singlet; d=doublet; br=broad

## Result and discussion

The hetarylazopyridone dyes may be exist in two tautomeric forms, namely the azohydroxypyridone form **A** and the diketohydrazone form **B** (Figure 2). Since the <sup>1</sup>H-NMR spectra of the dyes (**1a-e**) aren't observed a signal belong to C5-H proton around 6,5-5,5 ppm, the dyes (**1a-e**) aren't exist the azodiketopyridone form (the third tautomeric form). This result is in agreement with the results of our previously works [2, 5]. Deprotonation of the two tautomers lead to a common anion **C**, as shown in Figure 2.

In the  $^1\text{H-NMR}$  spectra of dye **1d** in DMSO, it was not observe a signal (belong to 1H-tetrazole proton). In literature [7], while in the  $^1\text{H-NMR}$  spectrum of Methyl 3-(1H-tetrazol-5-yl)bicyclo[1.1.1]pentane-1-carboxilate, it is present a signal at 9,5 ppm for NH proton in  $\text{CDCl}_3$ , in the  $^1\text{H-NMR}$  spectrum of (S)-2-[3-(1H)-Tetrazol-5-yl][1.1.1]pent-1-yl]glycine, it isn't present a signal for NH proton in  $\text{D}_2\text{O}$ . These results have explained that the 1H-tetrazole proton (N-H) is active in proton acceptor solvents such as DMSO. The signal of triazole proton (dye **1c**, Table 3) is split into doublet due to shielding by nearby CH proton. This doublet signal wasn't observed when the solution of the dyes **1c** in  $\text{DMSO-}d_6$  was treatment with  $\text{D}_2\text{O}$ . All spectral data of these dyes (**1a-e**) are shown in Table 3.

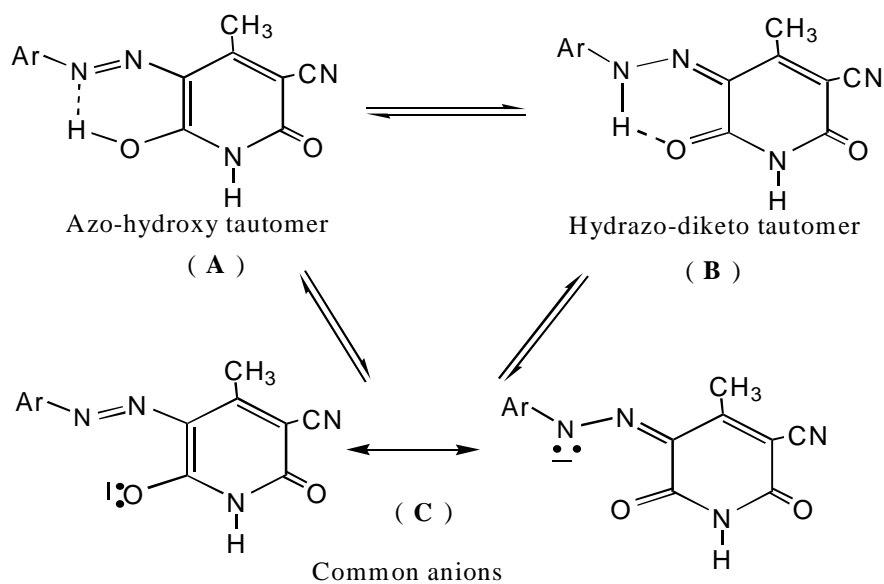


Figure 2

Table 3. Absorption maxima of dyes 1a-e in some solvents, acidic and basic solutions.

Comp. no	Acetic acid	$\text{CHCl}_3$	$\text{CHCl}_3$ + Piperidine	Acetone	$\text{CH}_3\text{OH}$	$\text{CH}_3\text{OH}$ + HCl	$\text{CH}_3\text{OH}$ + NaOH	DMF	DMF + Piperidine	DMSO	DMSO + Piperidine
<b>1a</b>	431	436 524 <sup>+</sup>	540 480	437 555,5 <sup>+</sup>	532	430	535,5	572,5	573 510 <sup>s</sup>	574	574 510 <sup>s</sup>
<b>1b</b>	395	406 465 <sup>+</sup>	465,5 451 <sup>s</sup> 435 <sup>s</sup>	398,5 466 <sup>+</sup>	426,5	393	429,5 455 <sup>+</sup>	435 460 <sup>+</sup>	435 460 <sup>+</sup>	429,5 468 <sup>+</sup>	435 468 <sup>+</sup>
<b>1c</b>	399	399,5*	450 420 <sup>s</sup>	398,5	404,5 450 <sup>s</sup>	404,5 448 <sup>s</sup>	390,5 421 <sup>s</sup>	410,5 440 <sup>s</sup>	410,5 440 <sup>s</sup>	407	413,5 445 <sup>+</sup>
<b>1d</b>	377	387	408 428 <sup>s</sup>	379	390	375,5	390 428 <sup>s</sup>	426,5	426,5 440 <sup>s</sup>	394	394
<b>1e</b>	388	391,5	393,5 420 <sup>s</sup>	385,5	386	385,5	390	399,5 440 <sup>s</sup>	399,5 440 <sup>s</sup>	390,5	400 440 <sup>s</sup>

<sup>+</sup>: second band; <sup>s</sup>: shoulder; \*: lower soluble

The FT-IR spectra (in KBr) of the dyes (**1a-e**) showed CN group at  $\sim 2230\text{ cm}^{-1}$  bands and two intense carbonyl bands at  $\sim 1700\text{-}1600\text{ cm}^{-1}$ ; intensities of the two bands are very similar, and the latter band is related to intramolecularly hydrogenbonded carbonyl. It was therefore assigned to the diketohydrazone form **B**.

Visible absorption spectra of the dyes (**1a-e**) were recorded in various solvents at a concentration of approximately  $10^{-6}\text{ M}$ . Visible absorption maxima of the dyes in various solvents are given in Table 3, and example absorption spectra for dye **1a** are shown in Figure 3. The visible absorption spectra of the dyes (**1a-e**) were found to exhibit a strong dependence which did not show a regular variation with the dielectric constants of the solvents.

In Raman spectroscopic studies of arylazonaphthols, it was concluded that the hydrazone form is converted to the azo anion form in basic media [8, 9]. Peng et. al. have reported the same results for N-alkyl derivatives of arylazopyridones from  $^{13}\text{C}$  chemical shift displacements at different pH in DMSO-water mixtures [10].

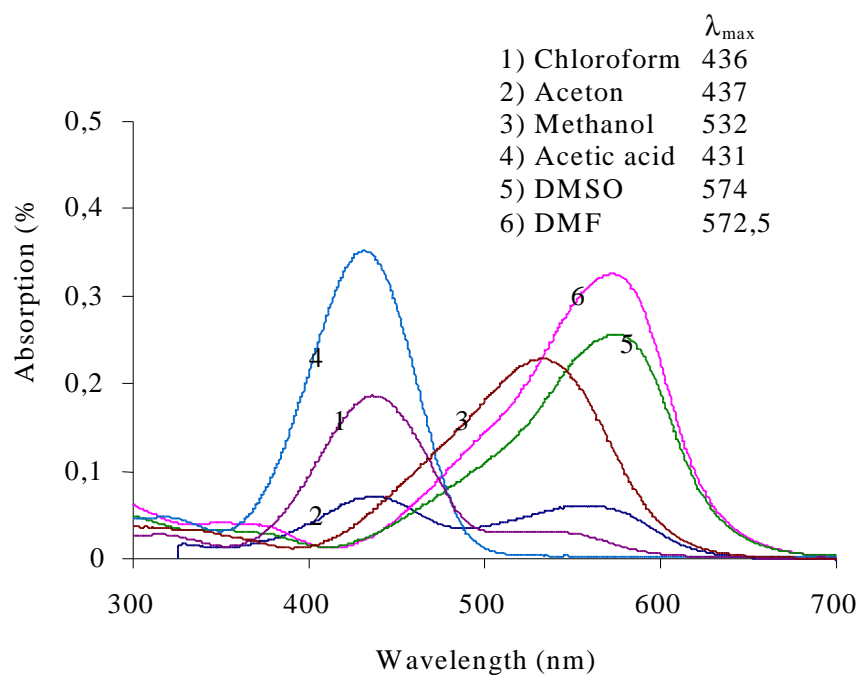


Figure 3. Absorption spectra of compound **1a** in various solvents.

We also know that there is an equilibrium between hyrazone form and common-anion form hetarylazopyridones from our previously works [2, 10, 11]. This equilibrium is depended on the acidity of solvents such as glacial acetic acid and chloroform; the

dyes give a blue shift of  $\lambda_{\max}$  and are basically in the neutral form. In proton accepting solvents such as DMF and DMSO, the dyes give a red shift of  $\lambda_{\max}$  and exist mainly in the common anion form. Such an effect of solvent is consistent with the phenomenon of dissociation rather than azo-hyrazone tautomerism.

It was observed that although in glacial acetic acid, chloroform and acetone (except **1b**) the absorption spectra of the dyes did not change significantly,  $\lambda_{\max}$  of the dyes shifted considerably in methanol, DMF and DMSO (Table 3).  $\Delta\lambda_{\max}$  of the dyes (**1a-e**) is 8-135, 5 nm and the largest shifts belong to compound **1a**. It was observed that the absorption curves of the dyes were very sensitive to acids and bases.  $\lambda_{\max}$  of the dyes showed large bathochromic shifts when a small amount of piperidine was added in  $\text{CHCl}_3$  (Figure 4), and  $\lambda_{\max}$  values of the dyes approached their values in DMF, DMSO and methanol, and the absorption curves of the dyes differentiated. Similarly, when they (**1a-e**) were added to each of the dye solutions in DMF and DMSO,  $\lambda_{\max}$  values and absorption spectra curves of the dyes didn't change in DMF, changed in DMSO (Table 3), respectively.

$\lambda_{\max}$  of the compounds in methanol showed large hypsochromic shifts when 0, 1 M HCl solution was added, being nearly the same as those observed in acetic acid. In contrast, addition of a small amount of 0, 1 M NaOH to the ethanolic solutions of the dyes didn't cause significantly a change in the spectra (Table 3, Figure 5).

This indicates that the dyes (**1a-e**) exist in a dissociated state in methanol, DMSO and DMF. These results are in agreement with those of the obtained similar works by Ertan and Peng [2, 10]. Therefore, the structures of dyes prepared were assigned to any of tautomeric forms in acidic medium and to the common anion form in basic medium. The results have showed that this equilibrium exists in solutions of hetarylazopyridones and they could be ionised even in proton accepting solvents.

The strongly electron withdrawing nitro group has a significant influence on the dissociation. Ertan has reported the same results for hetarylazopyridones and hetarylazopyrazoles dyes [2, 11].

The effect of sample concentration on the equilibrium was also examined. The  $\lambda_{\max}$  value of the dyes **1a-e** didn't change with compound concentration in all used solvents.

Solutions of the dyes **1a-e** in all used solvents were examined in the temperature range 25-75 °C and  $\lambda_{\max}$  values of the dyes **1a-e** did not change significantly. These

results have supported the dissociation equilibrium of hetaryzopyridones in proton accepting solvents, which do not involve change of energy.

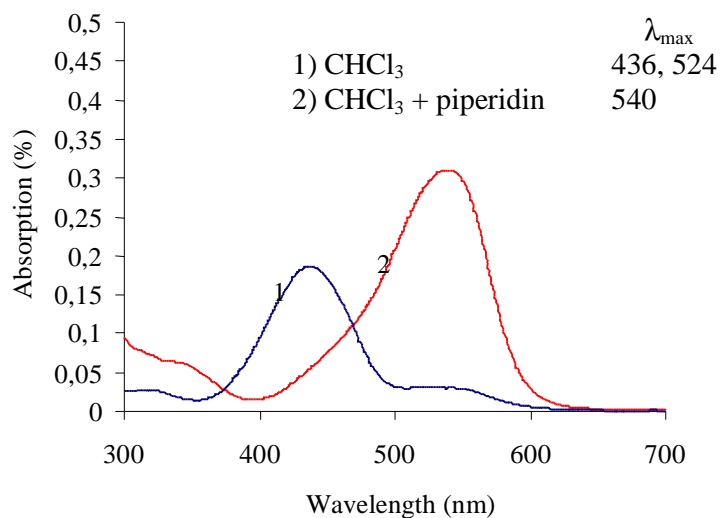


Figure 4. Absorption spectra of compound **1b** in CHCl<sub>3</sub> and + piperidine.

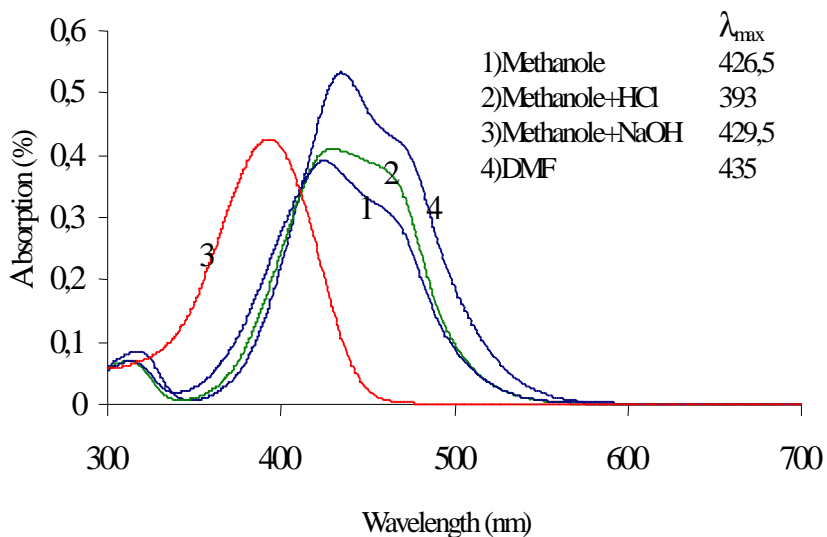


Figure 5. Absorption spectra of compound **1b** in methanol, + acid, + base and DMF.

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