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Synthesis and solvatochromism of some hydroxy substituted phenyl azo pyridone dyes

ABSTRACT

Aryl azo dyes are widely used due to their excellent physicochemical properties (primarily high value of the molar extinction coefficient and great resistance to light and wet processing) and the fact that can be obtained in a simple method of diazotization and coupling. In this paper, three new dyes of 5-(hydroxy substituted phenylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone were synthesized by a diazo coupling reaction. The obtained dyes were characterized by melting point, IR, NMR, and UV-Vis spectroscopy. Given the fact that the structure of the molecule and interactions obtained with the surrounding medium can affect its activity, the possibility of azo hydrazo tautomerism has been studied, as the influence of the position of the substituent present (orto-, meta- and para position). In addition, the effect of the solvent used was determined by applying a solvatochromic model using the LSER method (linear solvation energy relationship). Obtaining information about the inter- and intramolecular relationships that newly synthesized compounds can achieve may be of great importance for all further investigations and their potential application as biologically active compounds.
Keywords: *Aryl azo dyes, carbonitrile, synthesis, azo-hydrazone tautomerism, solvatochromism, intermolecular interaction*

1. INTRODUCTION

Azo dyes are compounds containing at least one diazenyl group (R–N=N–R') in their structure and account for more than 60% of the known commercial dyes. During synthesis, when the coupling component is a pyridone derivative, and the diazo component is a carbocyclic or heterocyclic compound, aryl azo pyridone dyes are obtained [1,2]. These dyes are widely used due to their high molar extinction coefficient and great resistance to light and wet processing [3,4]. Mostly they are applied in the textile industry for dying synthetic fabrics, but also as components of LCD screens and ink-jet graphic colors [4-6]. Recent medical and biological research in the field of azo derivatives has opened up the possibility of their use as antimicrobial, antioxidant, and antitumor agents [8-10]. Considering previous studies, it is clear that newly synthesized compounds based on

azo dyes would be interesting candidates for the investigation of potential biological activity. Every biological study is preceded by a detailed physicochemical characterization. In this work, three dyes of 5-(hydroxy substituted phenylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone were synthe-sized by reaction of diazo coupling, starting from aminophenols (2-, 3- and 4-substituted) and 6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile as coupling components. Information about inter- and intramolecular interactions that occur between dissolved dyes and the surrounding medium was obtained by UV-Vis spectro-photometry which is a simple, and economical technique. The activity of a molecule can depend on the type and strength of these interactions, and their quantification is important for the further potential application of the investigated compound. Using UV-Vis spectrophotometry azo-hydrazone tautomerism of synthesized dyes was also examined. Absorption spectra of three newly synthesized aryl azo pyridone dyes have been recorded in eighteen solvents of different properties in the range from 300 to 600 nm. The solvent's effect on the shifts of absorption maxima was interpreted with two solvatochromic models, first

proposed by Kamlet and Taft (eq. 1) and second by Catalan (eq. 2), using the LSER method (Linear Solvation Energy Relationship).

$$v_{max} = v_0 + s\pi^* + a\alpha + b\beta \qquad (1)$$

$$v_{max} = v_0 + aSA + bSB + cSP + dSdP \qquad (2)$$

v_{max} represents the frequency in the used solvent, v_0 is frequency in a standard solvent, α, and SA represent acidity, β, and SB basicity, π^* dipolarity/polarizability of the solvent, while SP is polarizability, and SdP dipolarity of the solvent. s, a, b, c, and d are regression coefficients of the eqs. 1 and 2 [11-15].

2. EXPERIMENTAL PART

2.1. Synthesis of 5-(hydroxy substituted phenylzo)-3-cyano-6-hydroxy-4-methyl-2-pyridone

The process of the synthesis of three new azo dyes is shown in Scheme 1. In the first step, ethyl acetoacetate (1) and cyanoacetamide (2) react to give 3-cyano-6-hydroxy-4-methyl-2-pyridone (3) [16]. The selected aniline (4) is diazotized at a low temperature to give the diazonium salt (5). The dissolved and cooled pyridone (3) reacts with the synthesized diazonium salt, resulting in pyridone azo dyes (6) [17]. In this work, three anilines were used: 2-aminophenol, 3-aminophenol and 4-aminophenol, to obtain the dyes 6-hydroxy-5-(2-hydroxy phenylazo)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (compound/color 1), 6-hydroxy-5-(3-hydroxy phenylazo)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (compound/color 2) and 6-hydroxy-5-(4-hydroxy phenylazo)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (compound/color 3). Synthetic dyes are characterized by melting point (*Stuart SMP30 melting point apparatus*), IR (*Thermo ScientificNicolet iS10 spectrometer*) and UV-vis spectroscopy (*Shimadzu UV–vis 1800*), NMR (*Bruker Ascend 400 apparatus in dimethyl sulfoxide*, DMSO–d$_6$). Preparation of 3-cyano-6-hydroxy-4-methyl-2-pyridone was prepared according to a modified, earlier published procedure. A homogenous mixture of 2.6 g (0.02 mol) ethyl acetoacetate (1-Scheme 1), 1.68 g (0.02 mol) cyanoacetamide (2-Scheme 1), 1.12 g (0.02 mol) of freshly powdered potassium hydroxide was irradiated for 4 min in a microwave oven at 200 W. The mixture was then treated with 30 ml H$_2$O at low heating (100 W) until complete dissolution. After cooling, the solution was filtered. Concentrated hydrochloric acid was added (pH = 1) and formed white product was filtered, washed with water (2 × 5 mL) and vacuum dried (at 60 °C for 4 h). Crystallization from acetone yielded pyridone (3-Scheme 1) in the form of white crystals.
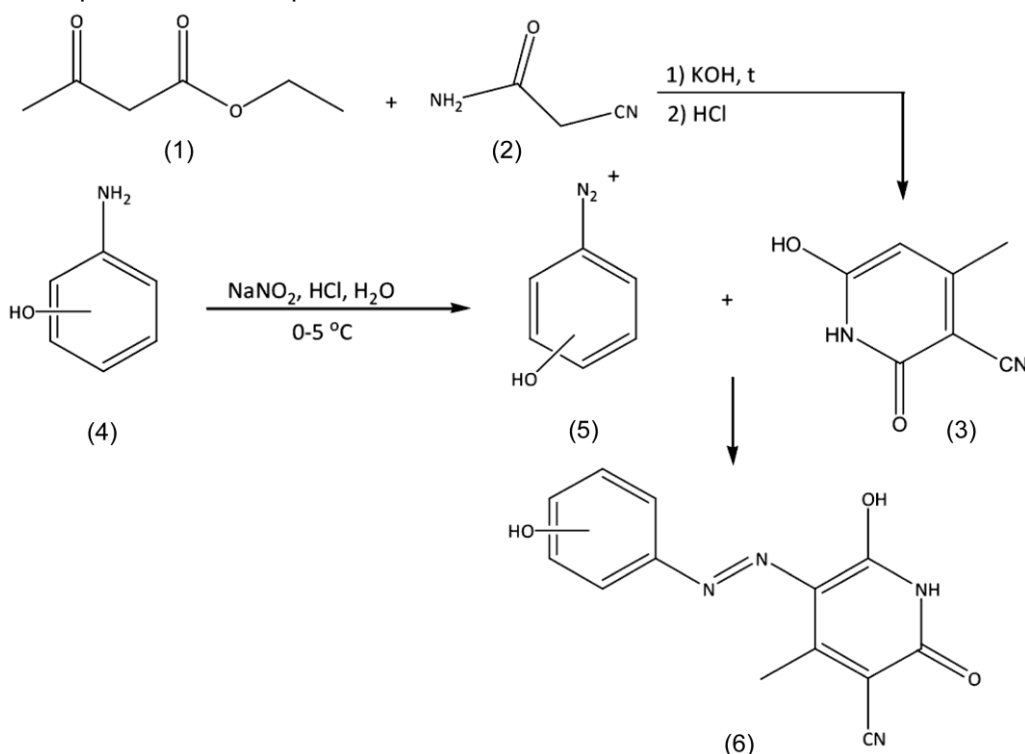
Scheme 1. Synthesis process of 5-(substituted phenylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone (color 1: 2-OH; color 2: 3-OH and color 3: 4-OH)

Šema 1. Postupak sinteze 5-(hidoksi supstituisanih fenilazo)-3-cijano-6-hidroksi-4-metil-2-piridona (boja 1: 2-OH; boja 2: 3-OH i boja 3: 4-OH)

2.2. UV characterization of 5-(hydroxy substituted phenylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone

Three synthesized azo dyes were also characterized using UV-Vis spectrometry. Absorption spectra were recorded in the range of 300 to 600 nm in eighteen solvents of different properties and at different pH values. For investigation of solvatochromic properties of azo dyes nine protic and nine aprotic solvents of spectroscopic quality were used (*Sigma Aldrich*): methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, *i*-butanol, *i*-propanol, *t*-butanol, acetic-acid, acetonitrile (ACN), *N,N*-dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), chloroform, ethyl-acetate (EtAc), tetrahydrofurane (THF), 1,4-dioxane and diethyl-ether. Working solutions of each investigated compound were prepared in a concentration of 4×10^{-5} mol/dm^3. The azo-hydrazone tautomerism was investigated in some of the solvents used at different pH values (pH = 1, in a pure solvent, and at pH = 13). pH of the solutions was adjusted using cc HCl and solid NaOH (dissolved using ultrasound).

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of 5-(hydroxy substituted phenylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone

Characterization of the synthesized dyes (color, melting points, yields, IR, and NMR characterization) is given in Table 1. The results of the IR analysis of all three colors indicate their similarity. This is understandable because all three colors have the same molecular formula and molar mass. The only difference is the position of the OH group in the diazo component, which affects small changes in the position of the bands in the IR spectrum.

Table 1. Characterization of the synthesized dyes (color, melting points, yields, IR and NMR characterization)

Tabela 1. Karakterizacija sintetisanih boja (boja, tačka topljenja, čistoća, IR i NMR karakterizacija)

		Starting pyridone (3)	Color 1	Color 2	Color 3
color		white	orange	dark-brown	red-purple
Melting points, 0C		315–316	278–280	287–289	283–285
Yield, %		60	52	59	58
IR characterization	O-H, cm-1	-	-	3355	3461
	N-H, cm-1	-	3138, 3242	3162	3176, 3276
	CN, cm-1	2223	2234	2219	2226
	C=O, cm-1	1590	1651, 1645	1654	1661, 1647
NMR characterization (400 MHz, DMSOd6)		2.33 (s, 3H, CH3), 5.591 (s, 1H, 5H)	2.49 (3H, s, CH$_3$), 6.95 (2H, q, J=8.0 Hz), 7.13 (1H, t, J=8.0 Hz), 7.65 (1H, d, J=8.0 Hz), 10.79 (1H, s, OH), 11.96 (1H, s, NH Py), 14.91 (1H, s, NH hydrazone)	2.48 (3H, s, CH$_3$), 6.68 (1H, d, J=8.0 Hz), 7.02 (2H, d, J=8.0 Hz), 7.24 (1H, t, J=8.0 Hz), 9.86 (1H, s, OH), 11.99 (1H, s, NH Py), 14.50 (1H, s, NH hydrazone)	2.47 (3H, s, CH$_3$), 6.86 (2H, d, J=8.0 Hz), 7.51 (2H, d, J=8.0 Hz), 9.94 (1H, s, OH), 11.90 (1H, s, NH Py), 14.85 (1H, s, NH hydrazone)

It was found that crystals of the dye 3 obtained during synthesis have the hydrazone form. In the case of color 1, it was concluded that the hydrazone and azo forms were in equilibrium. For dye 2, only one broadband is observed at about 1654 cm^{-1}, which indicates the possibility of the azo form.

3.2. Azo-hydrazone tautomerism of 5-(hydroxy substituted phenylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone

Azo-hydrazo tautomerism is characteristic of dyes that have an electron-donating group. Tautomers are distinguished by their physical and chemical characteristics: color, stability, and color intensity. Almost all commercial azo dyes are obtained in the hydrazone form and have absorption maxima at a higher wavelength relative to the azo form, causing the bathochromic shifting (from the standard red-orange hydrazone form to the blue azo form). In Scheme 2 the azo-hydrazone tautomerism is shown. This process is caused by a change in the pH value of the solution where the dye is dissolved [18,19]. When one maximum appears in the spectrum only one form is present, while two maxima indicate that tautomerism occurs, with each of the maxima belonging to one tautomer.

Azo form   Hydrazon form
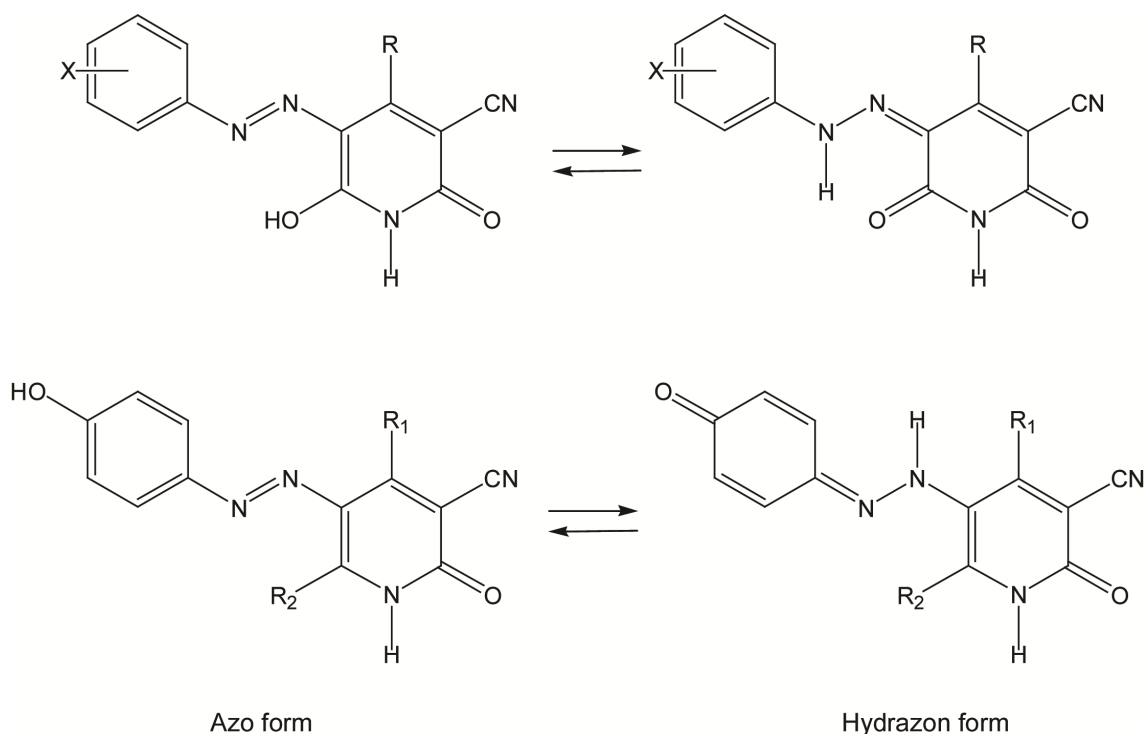
Scheme 2. Azo-hydrazone tautomerism of 5-(hydroxy substituted phenylazo)-3-cyano-6-hydroxy -4-methyl-2-pyridone

Šema 2. Azo-hidrazon tautomerija 5-(hidoksi supstituisanih fenilazo)-3-cijano-6-hidroksi-4-metil-2-piridona

Table 2. Wavenumbers at the absorption maximum of the azo, hydrazone and neutral forms of the investigated dyes

Tabela 2. Talasni brojevi na maksimumu apsorpcije za azo, hidrazon i neutralne oblike ispitivanih boja

Solvent	Color	$v_{max} \cdot 10^{-3}$, cm^{-1} pH = 1	$v_{max} \cdot 10^{-3}$, cm^{-1} pure solvent	$v_{max} \cdot 10^{-3}$, cm^{-1} pH = 13	$|\Delta v_{(pH1-pH13)}| \cdot 10^{-3}$, cm^{-1}
ACN	1	21.52	21.60	21.60	0.08
	2	22.40	22.50	22.53	0.13
	3	21.22	21.37	21.33	0.11
Chloroform	1	21.30	21.37	21.37	0.07
	2	21.91	22.31	22.24	0.33
	3	21.04	21.11	21.17	0.13
DMF	1	21.20	21.53	21.15	0.05
	2	21.00	22.43	22.80	1.80
	3	21.27	21.27	23.77	2.50
DMSO	1	21.22	21.55	21.10	0.12
	2	22.28	22.54	24.49	2.21
	3	21.43	21.29	24.52	3.09
Ethanol	1	21.35	21.83	21.46	0.11
	2	22.63	22.73	25.57	2.94
	3	21.51	21.62	24.95	3.44

The absolute values of the differences between the absorption maxima of the azo and hydrazone forms of the tested compounds (Table 2) indicate that the azo-hydrazone tautomerism is present in the extremely polar solvents DMF, DMSO, and ethanol, but not in ACN and chloroform (except for Color 2 in chloroform). Azo-hydrazone tautomerism is not registered in ACN although it is a polar solvent. The reason for this result can be explained by the reduced basicity properties of ACN compared to the other tested polar solvents. The stronger basicity properties of the solvent cause

the greater stability of the azo form (free OH group) of the tested compounds and azo-hydrazone tautomerism is presented. From the obtained results it is also concluded that the position of the substituent on the benzene ring has a significant role in the process of azo-hydrazone tautomerism. The tautomerism was not observed with the ortho-substituted benzene ring (color 1), with the meta-substituted one (color 2) it was present to a significant extent, while the highest possibility for tautomerism was observed with the para-substituted compound (color 3). These results are a consequence of steric hindrance in the case of the ortho-substituted derivative and the impossibility of electron delocalization through the molecule. In the case of meta and para-substituted compounds, delocalization is possible, resulting in the azo-hydrazone tautomerism. Para- substituted compounds have the greatest possibility of electron delocalization and the most noticeable azo-

hydrazone tautomerism. Proofs that investigated dyes obtain hydrazone form are very small changes between the absorption spectra recorded in pure solvents and spectra obtained in an acidic medium (pH=1). The formation of azo forms of the investigated dyes is more successful at higher pH and temperature. Spectra of all tested compounds show that the hydrazone form is more dominant.

3.3. Solvatochromism of 5-(hydroxy substituted phenylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone

The solvatochromic effect have only those organic molecules whose chromophores contain π-electrons and free electron pairs, i.e. where $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ electron transitions can occur [20]. The absorption maxima of tested compounds in all solvents are in the range of 438 to 478 nm. Tables 3 and 4 show the values of the absorption frequencies recorded at the absorbance maximum.

Table 3. Wavenumbers ($v \cdot 10^{-3}$, cm^{-1}) of all investigated compounds in protic solvents

Tabela 3. Talasni brojevi ($v \cdot 10^{-3}$, cm^{-1}) svih ispitivanih jedinjenja u protičnim rastvaračima

Solvents	Methanol	Ethanol	n-propanol	n-butanol	n-pentanol	i-butanol	i-propanol	t-butanol	Acetic acid
Color 1	21.95	21.83	21.80	21.75	21.71	21.68	21.67	21.52	21.82
Color 2	22.82	22.73	22.65	22.59	22.65	22.64	22.62	22.46	22.73
Color 3	21.78	21.62	21.59	21.54	21.52	21.50	21.48	21.25	21.59

Table 4. Wavenumbers ($v \cdot 10^{-3}$, cm^{-1}) of all investigated compounds in aprotic solvent

Tabela 4. Talasni brojevi ($v \cdot 10^{-3}$, cm^{-1}) svih ispitivanih jedinjenja u aprotičnim rastvaračima

Solvents	ACN	DMSO	DMF	DMA	Chloroform	EtAc	THF	Dioxane	Ether
Color 1	21.60	21.55	21.53	21.47	21.37	21.32	21.30	21.24	21.17
Color 2	22.50	22.54	22.43	22.40	22.31	22.28	22.25	22.21	22.13
Color 3	21.37	21.29	21.27	21.23	21.11	21.08	21.05	20.98	20.92

Quantitative analysis of the interactions that occur between the investigated colors and the surrounding medium was performed by the LSER method, using two solvatochromic models, Kamlet-Taft's (equation 1) and Catalan's (equation 2) [11-15]. The results of both models are shown in Tables 5 and 6.

Table 5. Results of Kamlet-Taft's solvatochromic model

Tabela 5. Rezultati Kamlet-Taft-ovog solvatohromnog modela

	$v_0 \cdot 10^{-3}$, cm^{-1}	$a \cdot 10^{-3}$, cm^{-1}	$b \cdot 10^{-3}$, cm^{-1}	$s \cdot 10^{-3}$, cm^{-1}	r^2	F
Color 1	20.918 ±0.065	0.501 ±0.038	0.218 ±0.038	0.496 ±0.098	0.945	80
Color 2	21.898 ±0.058	0.441 ±0.034	0.209 ±0.054	0.457 ±0.071	0.946	82
Color 3	20.649 ±0.079	0.550 ±0.046	0.245 ±0.074	0.506 ±0.081	0.933	65

Table 6. Results of Catalan's solvatochromic model

Tabela 6. Rezultati Catalan-ovog solvatohromnog modela

	$v_0 \cdot 10^{-3}$, cm^{-1}	$a \cdot 10^{-3}$, cm^{-1}	$b \cdot 10^{-3}$, cm^{-1}	$c \cdot 10^{-3}$, cm^{-1}	$d \cdot 10^{-3}$, cm^{-1}	r^2	F
Color 1	21.031 ±0.236	0.835 ±0.092	0.115 ±0.080	/	0.427 ±0.090	0.928	42
Color 2	21.902 ±0.206	0.756 ±0.080	0.133 ±0.070	/	0.366 ±0.079	0.930	43
Color 3	20.843 ±0.279	0.910 ±0.108	0.141 ±0.095	/	0.442 ±0.107	0.918	36

Based on the values of the obtained correlation coefficients (r^2 = 0.918-0.946), it can be concluded that both models are suitable for quantitative analysis of interactions between tested dyes and the surrounding medium. All regression coefficients (a, b, and s for Kamlet-Taft's and a, b, c, and d for Catalan's model) have positive values. This indicates that with the increase of acidity, basicity, dipolarity, and polarizability of the used solvents absorption maxima of the investigated compounds will shift towards smaller wavelengths (hypsochromic shift). The results of Kamlet-Taft's model show that the acidity of the solvent, as well as the dipolarizability/polarizability, have almost equal effects on the solvatochromic properties of the tested compounds. On the other hand, Catalan's solvatochromic model shows that acidic interactions are the most dominant, while the polarizability of the used solvent affects to a lesser extent the solvatochromic properties of the investigated dyes. Both solvatochromic models point out basicity as a property of the solvent that has the smallest effect on the spectral characteristics of the tested azo dyes. A better overview of the obtained interactions (the share of regression coefficients expressed in percentages) is given in Table 7.

Table 7. Percentages of regression coefficients for the Kamlet-Taft's and Catalan's solvatochromic models

Tabela 7. Procentni udeli regresionih koeficijenata Kamlet-Taft-ovog i Catalan-ovog solvatohromnog modela

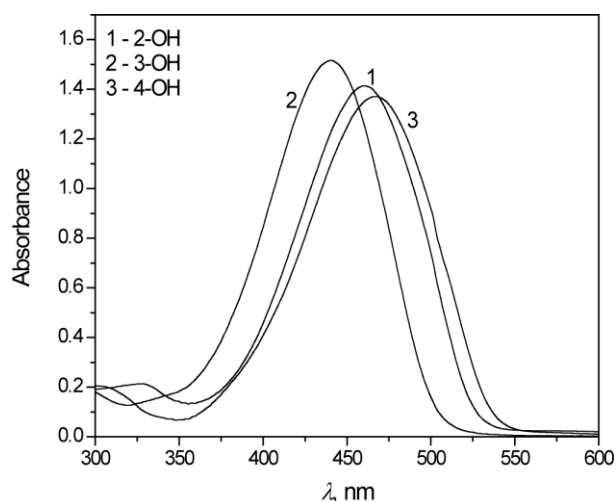|	Kamlet-Taft's solvatochromic model			Catalan's solvatochromic model			
	a, %	b, %	s, %	a, %	b, %	c, %	d, %
Color 1	41.23	17.94	40.82	58.93	10.94	0	30.35
Color 2	39.84	18.88	41.23	60.24	10.60	0	29.16
Color 3	42.27	18.83	38.89	60.95	9.44	0	29.60

Figure 1. Absorption spectra of all tested azo dyes recorded in ethanol

Slika 1. Apsorpcioni spektri svih ispitivanih azo boja snimljeni u etanolu

Results obtained by solvatochromic models are in agreement with the assumption based on the structures of the tested dyes – many basicity centers and therefore a high possibility of electron delocalization. Stronger acidity properties of the surrounding medium, as well as increasing in the polarizability/dipolarity, increase obtained interactions. On the other hand, investigated dyes have less expressed acidity properties, and therefore basicity of the surrounding medium does not have a significant influence on the solvatochromic behavior of the investigated dyes. In order to analyze the effect of the substituent on the absorption maxima shifting, in Fig. 1 the absorption spectra of all three tested compounds in ethanol are shown. As can be seen, absorption maxima of colors 1 and 3 (ortho and para-substituted) are very close and there is a batochromic shifting in relation to the spectra of color 2 (meta-substituted). The same results are obtained in Tables 3 and 4. The hydroxyl group placed in the meta position cannot cause extended

electron delocalization through the rest of the molecule as well as when the same group is in the ortho and para positions. Therefore, obtained results of the spectral analysis of the tested dyes agree with their structural characteristics.

4. CONCLUSION

In this work, three pyridone azo dyes were synthesized starting from 3-cyano-6-hydroxy-4-methyl-2-pyridones (yield: 52,0-58.8%). The structure of the obtained azo dyes was confirmed by melting point, IR, and NMR spectra. It was found that crystals of the dye 3 obtained during synthesis have the hydrazone form. In the case of color 1, it was concluded that the hydrazone and azo forms were in equilibrium. For dye 2, only one broadband is observed at about 1654 cm^{-1}, which indicates the possibility of the azo form. Based on the obtained results of UV-Vis analysis, it can be concluded that all dyes in the solvents used are in the hydrazone form (acetonitrile, ethanol, chloroform, DMSO, DMF). With the addition of hydrochloric acid to the solutions of the tested dyes, no major changes in the position of the absorption maxima are observed, which confirms the previous statement. The addition of a strong base leads to a minor (chloroform) or major changes (DMF, DMSO, and ethanol) in the appearance and position of the absorption maxima and here the hydrazone form is dominant. The greatest possibility for tautomerism was observed with color 3, slightly less with color 2, while with color 1 it almost does not occur. The reason for this type of behavior is the position of the present substituent on the benzene ring. The solvatochromic properties of the tested azo dyes were quantified using two solvatochromic models; Camlet-Taft's and Catalan's. Both models can be used successfully and give very similar results. The strongest effect on the solvatochromism of the tested compounds has the acidity of the surrounding medium. Smaller effects have the dipolarity/polarizability, while basicity is the solvent's property that has the least influence on the solvatochromism. The position of the substituent on the benzene ring has also affected spectral changes: the spectra of the ortho- and para-substituted compounds are very similar, while the one obtained for the meta-substituted azo dye is shifted hypsochromic compared to the previous two.

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IZVOD

SINTEZA I SOLVATOHROMIZAM NEKIH HIDROKSI SUPSTITUISANIH FENILAZO PIRIDONSKIH BOJA

Aril azo boje imaju široku primenu zbog svojih odličnih fizičko-hemijskih svojstava (prvenstveno visoke vrednosti molarnog ekstinkcionog koeficijenta i velike otpornosti na svetlost i vlagu) i činjenice da se mogu dobiti jednostavnom metodom diazotizacije i kuplovanja. U ovom radu susintetisane tri boje 5-(hidroksi supstituisane fenilazo)-3-cijano-6-hidroksi-4-metil-2-piridona reakcijom diazo kuplovanja. Dobijene boje su okarakterisane tačkom topljenja, IR, NMR i UV-Vis spektroskopijom. S obzirom na to da struktura molekula i ostvarene interakcije sa okolnim medijumom mogu uticati na aktivnost ispitivanih jedinjenja, proučavan je solvatohromizam i mogućnost azo-hidrazon tautomerije, kao i uticaj položaja prisutnog supstituenta (orto-, meta- i para pozicija) u strukturi ispitivanih jedinjenja. Pored toga, kvantitatifikovan je efekat korišćenih rastvarača primenom dva solvatohromna modela koristeći LSER metodu (linear solvation energy relationship). Dobijanje informacija o inter- i intra-molekulskim interakcijama koje sintetizovana jedinjenja mogu da ostvare su od velike važnosti za sva dalja istraživanja i njihovu potencijalnu primenu kao biološki aktivnih jedinjenja.

Ključne reči: Aril azo boje, karbonitil, sinteza, azo-hidrazon tautomerija, solvatohromizam, inetrmolekulske interakcije