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Solvatochromism of 5-(4-substituted arylazo) -4-phenyl-6-methyl-3-cyano-2-pyridones

ABSTRACT

Eight 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones were synthesized by reaction of benzoylacetone and arendiazonium salt, followed by condensation with cyanoacetamide. Absorption spectra of all azo pyridone dyes were recorded in twelve protic and aprotic solvents in the range of 200-600 nm. A simple Hammett equation was used to study the effect of the substituents on the absorption spectra of these azo dyes. The solute-solvent interactions were clarified on the basis of linear solvation energy relationships concept proposed by Kamlet and Taft. The results showed that the solvent effects on the absorption spectra of the investigated azo dyes were very complex and strongly dependent on the nature of the substituents on the phenylazo group.

Keywords: Arylazo pyridone dyes, solvent effects, substituent effects, absorption spectra.

1. INTRODUCTION

The azo pyridone dyes belong to disperse dyes that are used for dyeing of the synthetic fibers. Since the synthetic fibers usage increased during 20th century, development of new dyes was necessary. In seventies, arylazo pyridone dyes were introduced [1]. These monoazo dyes are characterized by bright hues and can be used for dyeing of polyester fabrics and printing [2,3]. As other azo colorants, they can be synthesized by diazotization and azo coupling and have generally high molar extinction coefficient, as well as the medium to high light and wet fastness properties [4]. Due to the presence of hydroxy group in pyridone moiety, arylazo pyridone dyes can exhibit azo-hydrazone tautomerism [5]. Since tautomers have different technical properties, it is quite interesting from theoretical and practical view to determine the form in which dyes are in the solid state as well as in the solution.

A large number of studies on substituted arylazo pyridones have been carried out and reviewed [6-22]. It has been concluded that the equilibrium between the two tautomers is influenced by the structure of the compounds and the solvent used. In our previous publications, the absorption spectra of 5-(4-substituted arylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones was studied in different solvents and the results showed that these dyes existed in the hydrazone form in the solid state and in the solvent DMSO-*d*₆ [11].

Also, the synthesis of seventeen 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones was reported [12]. The 2-pyridone/2-hydroxypyridine tautomeric equilibrium was found to depend upon the substituents as well as upon the solvents. It was established that these dyes existed in the 2-hydroxypyridine tautomeric form in the solid state and in the solvent DMSO-*d*₆. The obtained results showed that the replacement of methyl group by hydroxy group in the position six in pyridone ring of 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones, influenced the changes of azo group sensitivity to solvent effects relative to 5-(4-substituted arylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones. Different systems with variation of pyridone rings as well as phenylazo components [11-22] were synthesized and studied.

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Among synthesized arylazo pyridone dyes, different 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones were prepared [23-27] using two synthetic pathways: either by diazotization and coupling with pyridone or by diazotization and coupling with diketone followed by ring closure of pyridone ring [1]. For the

synthesis of the reported dyes in this work, the second pathway was used [14,24,27,28].

In this work, we report the synthesis of eight 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones (Figure 1), UV-vis absorption spectra (200-600 nm) in twelve solvents of different polarity, and the study of the substituent and the solvent effects on the UV-vis spectra.

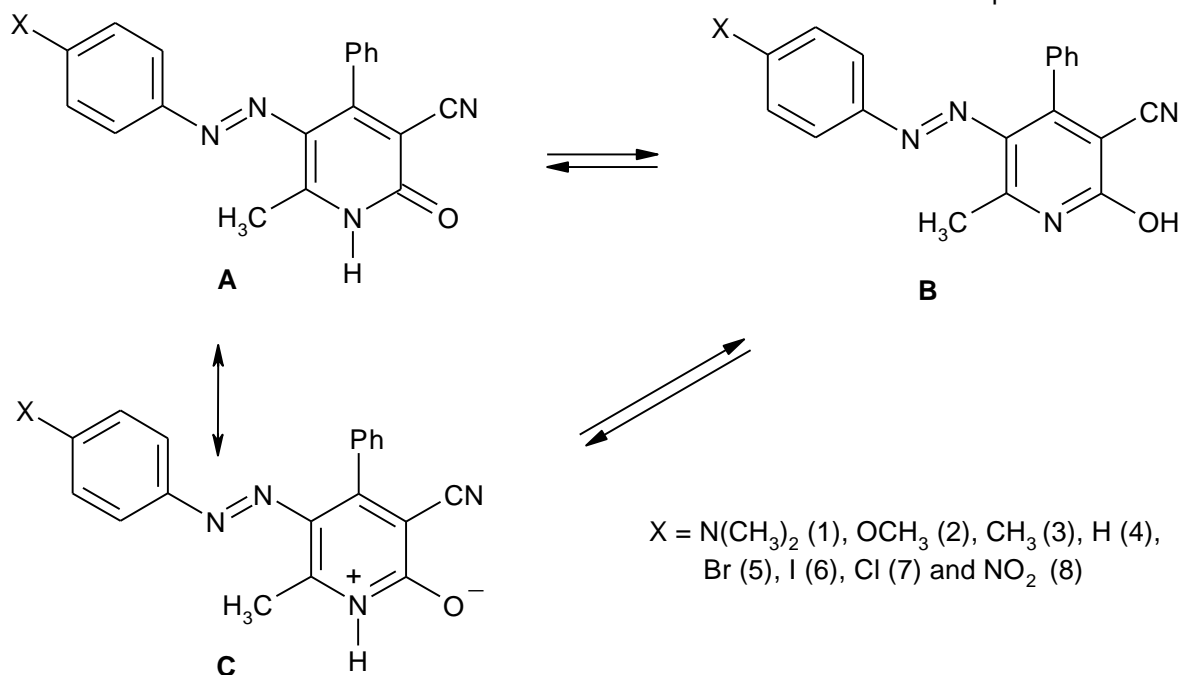


Figure 1. The equilibrium between 2-pyridone form (A) and 2-hydroxypyridine form (B) of 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones and canonical structure (C).

Slika 1. Ravnoteža između 2-piridonskog (A) i 2-hidroksipiridinskog oblika (B) 5-(4-supstituisanih arilazo)-4-fenil-6-metil-3-cijano-2-piridona i kanonske strukture (C)

2. EXPERIMENTAL PART

2.1. Materials and methods

All chemicals were obtained commercially mostly from Aldrich (USA) and Fluka and used without any further purification. The chemical structure and the purity of the azo dyes were confirmed by melting points, ¹H NMR, FTIR and UV-vis spectra. The melting points were determined in capillary tubes using Electrothermal Melting Point Apparatus. The FTIR spectra were recorded on a Bomem FTIR Spectrophotometer, MB-Series in the form of the KBr pellets. ¹H NMR spectra were recorded in DMSO-*d*₆ using Varian Gemini-200 instrument, with tetramethylsilane as an internal standard. The ultraviolet absorption spectra were recorded in the region 200-600 nm on a Shimadzu 1700 spectrophotometer in 1.00 cm cells at 25±0.1 °C. The spectra were run in spectra quality solvents (Fluka) using concentration of 5x10⁻⁵ M.

2.2. Synthesis

All of the investigated azo pyridone dyes were synthesized by the diazotization-coupling reaction, starting from benzoylacetone and arendiazonium salt, followed by condensation with cyanoacetamide using modified literature procedure [27,28].

General procedure. The procedure was taken from ref. 27 and modified: To a solution of benzoylacetone (0.01 mol) in 30 ml of ethanol, 3.0 g of sodium acetate was added. Mixture was cooled to 0 °C for 10 min and cooled solution of arendiazonium chloride (prepared from 0.01 mol of amine and the appropriate quantities of HCl and NaNO₂) was added with stirring. Stirring was continued for one hour and the solid was collected, washed with 2x10 ml of water and 2x10 ml of ethanol, and dried on the air.

The obtained product (0.01 mol) was dissolved in 30 ml of ethanol and added to a mixture of 0.01 mol of sodium hydroxide and 0.01 mol of

cianoacetamide. The reaction mixture was mixed and refluxed at 80 °C for 3 hours. The resulting solid product was collected by filtration and washed with 2x10 ml of water and 2x10 ml ethanol. Obtained crystals were then crystallized from ethanol. The main product was then isolated by silica gel column chromatography using a mixture of methanol and ethyl acetate in the ratio 4:1.

5-(4-*N,N*-dimethylaminophenylazo)-4-phenyl-6-methyl-3-cyano-2-pyridone (1).

Brown solid substance. Yield 28 %, mp. 248-250 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3446 (OH), 2219 (CN), 1638 (C=O on heterocyclic). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.06 (6H, s, N(CH₃)₂), 2.50 (3H, s, 6-CH₃), 6.20-6.30 (2H, d, 3,5-position on arylazo group), 6.80-7.00 (7H, m, 2,6-position on arylazo and phenyl group).

5-(4-methoxyphenylazo)-4-phenyl-6-methyl-3-cyano-2-pyridone (2).

Orange solid substance. Yield 30 %, mp. 269-270 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3361 (OH), 2211 (CN), 1647 (C=O on heterocyclic). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.58 (3H, s, 6-CH₃), 3.78 (3H, s, OCH₃), 6.90-7.00 (2H, d, 3,5-position on arylazo group), 7.30-7.50 (7H, m, 2,6-position on arylazo and phenyl group).

5-(4-methylphenylazo)-4-phenyl-6-methyl-3-cyano-2-pyridone (3).

Dark orange solid substance. Yield 26 %, mp. 289-290 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3389 (OH), 2214 (CN), 1626 (C=O on heterocyclic). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.31 (3H, s, CH₃ on arylazo group), 2.60 (3H, s, 6-CH₃), 7.10-7.50 (9H, m, on arylazo and phenyl group).

5-phenylazo-4-phenyl-6-methyl-3-cyano-2-pyridone (4).

Dark orange solid substance. Yield 28 %, mp. 277-279 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3345 (OH), 2211 (CN). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.63 (3H, s, 6-CH₃), 7.20-7.50 (10H, m, on arylazo and phenyl group).

5-(4-bromophenylazo)-4-phenyl-6-methyl-3-cyano-2-pyridone (5).

Orange solid substance. Yield 29 %, mp. 258-260 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3387 (OH), 2210 (CN), 1647 (C=O on heterocyclic). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.63 (3H, s, 6-CH₃), 7.10-7.62 (9H, m, on arylazo and phenyl group).

5-(4-iodophenylazo)-4-phenyl-6-methyl-3-cyano-2-pyridone (6).

Brown orange solid substance. Yield 26 %, mp. 244-245 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3380 (OH), 2206 (CN), 1653 (C=O on heterocyclic). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.63 (3H, s, 6-CH₃), 6.95-7.05 (2H, d, 3,5-position on arylazo group), 7.15-7.50 (5H, m, phenyl group), 7.70-7.80 (2H, d, 2,6-position on arylazo).

5-(4-chlorophenylazo)-4-phenyl-6-methyl-3-cyano-2-pyridone (7).

Light orange solid substance. Yield 33 %, mp. 260-262 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3439 (OH), 2214 (CN), 1636 (C=O on heterocyclic). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.64 (3H, s, 6-CH₃), 7.19-7.50 (9H, m, on arylazo and phenyl group).

5-(4-nitrophenylazo)-4-phenyl-6-methyl-3-cyano-2-pyridone (8).

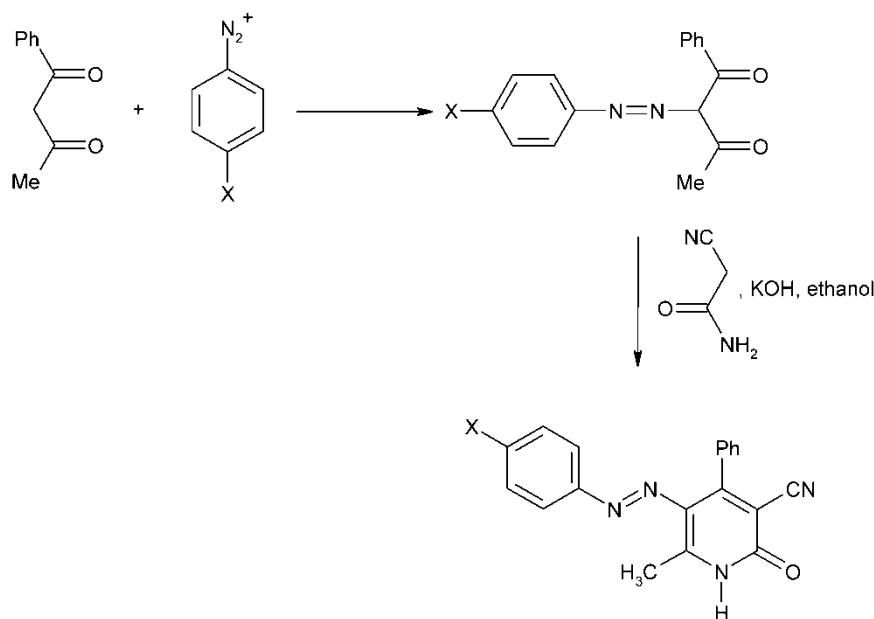
Red orange solid substance. Yield 36 %, mp. 271-273 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3412 (OH), 2210 (CN), 1647 (C=O on heterocyclic). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm : 2.70 (3H, s, 6-CH₃), 7.22-7.58 (7H, m, 3,5-position on arylazo and phenyl group), 8.19-8.24 (2H, d, 2,6-position on arylazo group).

3. RESULTS AND DISCUSSION

It is known that the reaction of cyanoacetamide with unsymmetrical methylaryl-1,3-diketones, catalyzed by a base, yield a mixture of possible positional isomers [29,30]. It was reported [31,32] that a fairly wide range of the substituents in the phenyl ring give 4-Ph and 6-Ph products in the different ratios. The 4-Ph/6-Ph ratio increased in the same order as the susceptibility of the corresponding carbonyl group to nucleophilic attack. Together with the electronic effect of the phenyl group, the degree of diketone enolization also affected the ratio of isomers. This finding was corroborated by the proposed mechanism of the reaction, based on the kinetic and stereochemical data [33].

In the present work, the arylazo pyridone dyes were prepared by the diazotization-coupling reaction, starting from benzoylacetone and arendiazonium salt, followed by condensation with cyanoacetamide as given in Scheme 1.

The presence of the two isomers, and their ratio were determined by ¹H NMR, on the basis of the chemical shifts for CH₃ groups (Table 1). The ratio of 6-CH₃/4-CH₃ data indicated the predominance of the isomer with phenyl group in the position 4, *i.e.* methyl group in the position 6. The main product was isolated by column chromatography and used in the study.



Scheme 1. Synthesis of 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones

Šema 1. Sinteza 5-(4-supstituissanih arilazo)-4-fenil-6-metil-3-cijano-2-piridona

Table 1. The ratio of the isomers after the synthesis

Tabela 1. Odnos izomera posle sinteze

X	N(CH ₃) ₂	OCH ₃	CH ₃	H	Br	I	Cl	NO ₂
6-CH ₃ :4-CH ₃	100:1	1.85:1	1.89:1	1.61:1	2.08:1	2.43:1	2.63:1	2.17:1

The arylazo pyridone dyes, prepared in this work, may exist in two tautomeric forms (Figure 1). The infrared spectra of all synthesized dyes showed presence of weak carbonyl band and the intense hydroxyl band in the region 3380-3446 cm⁻¹, which suggested that these compounds predominantly existed in the 2-hydroxypyridine tautomeric form in the solid state.

The UV-vis absorption frequencies of the electronic transitions involving the free non-bonding electrons of the azo group of the 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones in twelve protic and aprotic solvents and their molar extinction coefficients are given in Table 2.

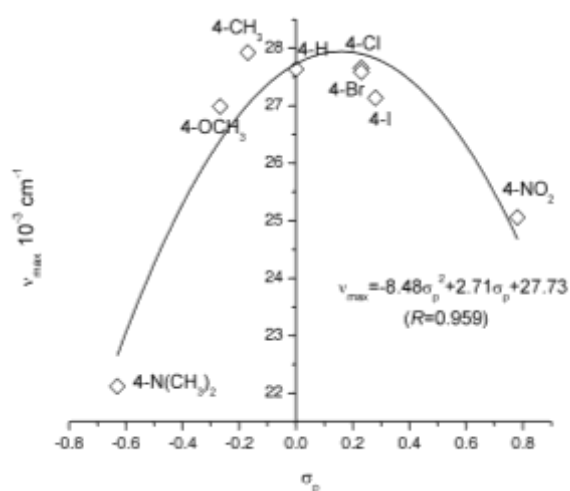
The data from Table 1 confirmed that the position of the UV-vis frequencies depended on the nature of the substituents in the position 4 of arylazo component. In order to explain these results, the absorption frequencies were correlated by Hammett equation using σ_p substituent constants [34]. The plot ν_{max} versus σ_p substituent constants gave correlation that showed deviations from the Hammett equation in all protic solvents (Figure 2). However, the linear Hammett correlation was obtained in dimethyl sulfoxide (Figure 3). The existence of these correlations was interpreted as evidence of the significant role of substituent

effects on 2-pyridone/2-hydroxypyridine tautomerism. The equilibrium between the two tautomers was influenced by the structure of the investigated compounds and applied solvents. In protic solvents, electron-donating and moderate electron-accepting substituents stabilized 2-pyridone tautomeric form, while strong electron-accepting substituents stabilized 2-hydroxypyridine form.

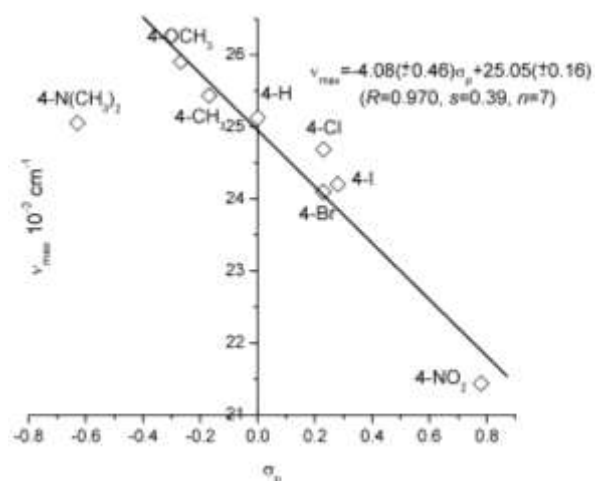
In *N,N*-dimethylformamide, *N,N*-dimethylacetamide and dimethyl sulfoxide, all of the investigated azo pyridone dyes existed in 2-hydroxypyridine tautomeric form, due to the high basicities and high relative permittivities of these solvents. By considering the equilibrium between 2-pyridone and 2-hydroxypyridine tautomeric forms [35] in solvents of different polarity, it was found that increasing solvent polarity shifted the equilibrium towards the pyridone form [36]. This form was more dipolar than the hydroxy form, due to the contribution of the charge-separated mesomeric form (Figure 1, C). Our results were in agreement with this explanation. Furthermore, the hydrogen-bonding ability of the solvent played an important role since hydrogen-bond donors tended to stabilize the oxo form (Figure 1, A) whereas hydrogen-bond acceptors stabilized the hydroxy form (Figure 1, B).

Table 2. UV-vis spectral data (ν_{max} 10^3 cm^{-1} and ϵ_{max} dm^3 mol^{-1} cm^{-1}) of 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridonesTabela 2. UV-vis spektralni podaci (ν_{max} 10^3 cm^{-1} i ϵ_{max} dm^3 mol^{-1} cm^{-1}) 5-(4-supstituisanih arilazo)-4-fenil-6-metil-3-cijano-2-piridona

No.	Solvent / Substituent		N(CH ₃) ₂	OCH ₃	CH ₃	H	Br	I	Cl	NO ₂
1.	Methanol	ν_{max}	22.12	26.99	27.93	27.64	27.58	26.45	27.66	25.06
		ϵ_{max}	7340	32230	15000	19840	16690	26590	18960	14910
2.	Ethanol	ν_{max}	22.22	27.32	27.28	27.03	26.70	26.60	26.84	25.22
		ϵ_{max}	5620	12400	13570	20300	12500	14250	17280	4320
3.	Propan-1-ol	ν_{max}	22.05	27.58	27.66	27.58	27.55	26.42	26.95	24.94
		ϵ_{max}	5910	9710	23700	18360	13870	28740	22060	13140
4.	Propan-2-ol	ν_{max}	21.98	27.32	27.21	26.67	26.63	26.25	26.67	24.69
		ϵ_{max}	2070	5570	11570	24740	15620	16980	15180	8730
5.	Butan-1-ol	ν_{max}	22.30	26.92	27.38	27.43	26.88	26.60	26.77	26.25
		ϵ_{max}	7570	19500	13680	25610	13230	18500	16150	4330
6.	<i>N,N</i> -Dymethylformamide	ν_{max}	21.67	24.87	25.00	24.81	24.06	24.04	24.12	21.03
		ϵ_{max}	15470	35240	23400	27830	26590	24150	22370	25330
7.	<i>N,N</i> -Dimethylacetamide	ν_{max}	21.74	24.97	24.84	24.48	23.72	23.75	24.13	20.49
		ϵ_{max}	20300	19870	14780	30100	39570	22700	22800	23700
8.	Dimethyl sulfoxide	ν_{max}	27.51	25.91	25.44	25.13	24.10	24.21	24.69	21.44
		ϵ_{max}	11030	11240	21070	22960	26470	24980	31010	25070
9.	Acetonitrile	ν_{max}	21.98	25.91	25.71	25.61	24.63	24.57	24.07	21.93
		ϵ_{max}	11780	14430	19330	18080	20270	22320	33110	10750
10.	Ethyl acetate	ν_{max}	22.12	27.55	28.01	28.01	27.74	26.63	27.97	26.70
		ϵ_{max}	5840	11940	16250	23280	17830	26130	27380	11370
11.	Chloroform	ν_{max}	21.91	27.51	27.55	27.78	27.78	27.62	27.77	26.70
		ϵ_{max}	10100	35240	8140	19670	6950	14510	3990	10890
12.	Dioxane	ν_{max}	22.22	26.08	26.49	26.28	25.64	25.64	26.28	23.75
		ϵ_{max}	14510	29140	34360	25240	39990	39990	12100	25810

Figure 2. Relationship between ν_{max} and σ_p substituent constants for the 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones in methanol

Slika 2. Korelacija apsorpcionih frekvencija sa σ_p konstantama supstituenata za 5-(4-supstituisane arilazo)-4-fenil-6-metil-3-cijano-2-piridone u metanolu

Figure 3. Relationship between ν_{max} and σ_p substituent constants for the 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones in dimethyl sulfoxide

Slika 3. Korelacija apsorpcionih frekvencija sa σ_p konstantama supstituenata za 5-(4-supstituisane arilazo)-4-fenil-6-metil-3-cijano-2-piridone u dimetil sulfoksidu

The effects of solvent dipolarity/polarizability and hydrogen bonding on the 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones were interpreted by the linear solvation energy relationship [37] using a Kamlet-Taft general solvatochromic equation of the form:

$$\nu = \nu_o + s\pi^* + b\beta + a\alpha \quad (1)$$

where π^* is a measure of the solvent dipolarity/polarizability, β is the scale of the solvent hydrogen bond acceptor (HBA) basicities, α is the scale of the solvent hydrogen bond donor (HBD) acidities and ν_o is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s , b and a in Eq. 1 measure the relative susceptibilities of the solvent-dependent solute property (absorption frequencies) to the indicated solvent parameters.

The solvent parameters [38] are shown in Table 3. The correlations of the spectroscopic data were carried out by means of multiple linear regression analysis. It was found that the absorption frequencies for investigated azo dyes in ten selected solvents (Table 4) showed satisfactory correlation with π^* , β and α parameters.

The results of the multiple regressions are presented in Tables 4 and 5. The negative sign of the coefficients s and b for all pyridone azo dyes (Table 4) indicated a bathochromic shifts with both

increasing solvent dipolarity/polarizability and solvent hydrogen bond acceptor capability. This suggested stabilization of the electronically excited state relative to the ground state. The positive sign of coefficient a for all azo dyes indicated a hypsochromic shifts with increasing of hydrogen-bond donor capability of the solvent.

Table 3. Solvent parameters [38]

Tabela 3. Parametri rastvarača [38]

No.	Solvent	π^*	β	α
1.	Methanol	0.60	0.62	0.93
2.	Ethanol	0.54	0.77	0.83
3.	Propan-1-ol	0.52	0.83	0.78
4.	Propan-2-ol	0.48	0.95	0.76
5.	Butan-1-ol	0.47	0.88	0.79
6.	<i>N,N</i> -Dimethylformamide	0.88	0.69	0
7.	<i>N,N</i> -Dimethylacetamide	0.88	0.76	0
8.	Dimethyl sulfoxide	1.00	0.76	0
9.	Acetonitrile	0.75	0.31	0.19
10.	Ethyl acetate	0.55	0.45	0
11.	Chloroform	0.58	0	0.44
12.	Dioxane	0.55	0.37	0

Table 4. Regression fits to solvatochromic parameters (Eq. 1)^a

Tabela 4. Rezultati korelacije apsorpcionih frekvencija sa solvatohromnim parametrima (jednačina 1)^a

Substituent X	ν_o 10 ³ cm ⁻¹	s 10 ³ cm ⁻¹	b 10 ³ cm ⁻¹	a 10 ³ cm ⁻¹	R ^b	s ^c	F ^d	n ^e
N(CH ₃) ₂	22.91 (±0.21)	-1.06 (±0.28)	-0.38 (±0.20)	0.11 (±0.13)	0.916	0.10	10	10
OCH ₃	28.36 (±0.80)	-3.13 (±1.06)	-0.99 (±0.40)	1.61 (±0.46)	0.96 7	0. 32	2 8	1 0
CH ₃	28.53 (±0.67)	-3.25 (±0.88)	-1.14 (±0.33)	1.93 (±0.38)	0.981	0.27	53	10
H	28.62 (±0.80)	-3.30 (±1.06)	-1.63 (±0.40)	2.13 (±0.46)	0.977	0.32	41	10
Cl	27.81 (±1.65)	-3.16 (±2.18)	-1.70 (±0.83)	2.70 (±0.94)	0.930	0.66	13	10
Br	28.34 (±1.30)	-3.72 (±1.71)	-1.91 (±0.65)	2.71 (±0.74)	0.960	0.52	23	10
I	28.27 (±1.04)	-3.51 (±1.37)	-2.70 (±0.52)	2.27 (±0.59)	0.967	0.41	29	10
NO ₂	29.58 (±1.84)	-8.32 (±2.44)	-2.56 (±0.92)	2.57 (±1.05)	0.960	0.74	24	10

^a The dimethyl sulfoxide and ethyl acetate were excluded from the correlation set to all substituents except dimethylamino derivative where dimethyl sulfoxide and chloroform were excluded.

^b Correlation coefficient, ^c Standard error of the estimate, ^d Fisher's test, ^e Number of solvents used.

Table 5. Percentage contributions of the nonspecific ($P\pi^*$) and specific ($P\beta$ and $P\alpha$) solvent interaction

Tabela 5. Procentualni udeli nespecifičnih ($P\pi^*$) i specifičnih ($P\beta$ i $P\alpha$) interakcija sa rastvaračem

Compound	$P\pi^*$ %	$P\beta$ %	$P\alpha$ %
$N(CH_3)_2$	68.39	24.52	7.09
OCH_3	54.62	17.28	28.10
CH_3	51.42	18.04	30.54
H	46.81	23.12	30.07
Cl	41.80	22.49	35.71
Br	44.60	22.90	32.50
I	41.39	31.84	26.77
NO_2	61.86	19.03	19.11

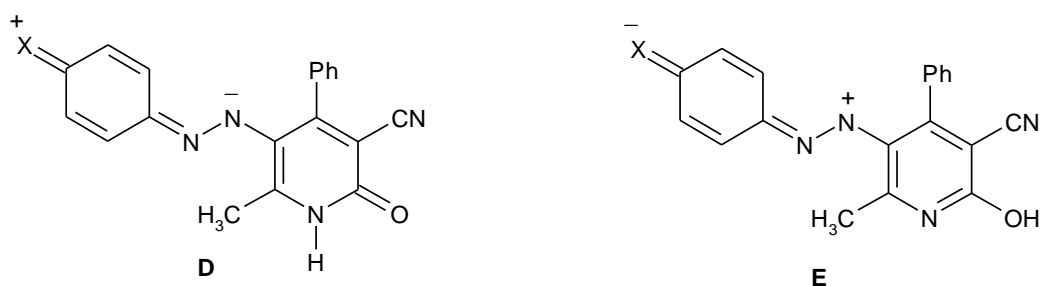


Figure 4. Resonance effect of electron-donating (structure D) and electron-accepting (structure E) substituents in the position 4 of arylazo component of the azo dyes

Slika 4. Rezonancijski efekat elektron-donorskih (struktura D) i elektron-akceptorskih (struktura E) supstituenata u položaju 4 arilazo komponente azo boja

These results were in accordance with the results published in our previous work for 5-(4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones [12]. The obtained results showed that the replacement of methyl by phenyl group in the pyridone ring of 5-(4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones, influenced the changes of azo group sensitivity to solvent effects compared to 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones. The pyridone azo dye system investigated in this work, absorbed at higher absorption maxima due to the mobility of electronic transmission across the resonating systems and thus longer conjugation which stabilized charge separation in the corresponding stabilized hybrid (structure D and E, Figure 4). These results were in accordance with the explanation of the substituent and the solvent effects on 2-pyridone/ 2-hydroxypyridine tautomeric equilibrium as presented above by Hammett and Kamlet-Taft equations.

4. CONCLUSIONS

Eight 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones were synthesized by modified literature procedure. The satisfactory

This suggested stabilization of the ground state relative to the electronically excited state. The percentage contributions of the solvatochromic parameters (Table 5) for azo dyes with a strong electron-donating substituents, such as the dimethylamino group, and a strong electron-accepting substituents, such as the nitro group, showed that a major contribution of the solvatochromism was due to solvent dipolarity/polarizability. These results were in accordance with canonical structure of D and E and their stabilization was accounted to the solvent dipolarity/polarizability (non-specific solute-solvent interactions) rather than to solvent basicity and acidity properties (Figure 4).

correlation of the ultraviolet absorption frequencies of the investigated azo dyes with Hammett equation indicated that the selected model gave a correct interpretation of the linear solvation energy relationships of the complex system of the 5-(4-substituted arylazo)-4-phenyl-6-methyl-3-cyano-2-pyridones in applied solvents. We demonstrated that a solvatochromic equation with three solvatochromic parameters π^* , β and α could be used to evaluate the effects of the both types of hydrogen bonding and of the solvent dipolarity/polarizability effect. The results showed that the solvent effects on UV-vis absorption spectra of the investigated pyridone azo dyes was very complex and strongly dependent on the nature of the substituents on the arylazo components. These dyes existed in the 2-hydroxypyridine tautomeric form in the solid state and in aprotic dipolar solvents and there was an equilibrium between 2-pyridone and 2-hydroxypyridine form in protic solvents. The results showed that the replacement of methyl group by phenyl group in pyridone ring of 5-(4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones, produced bathochromic shifts relative to 4,6-dimethyl

pyridone azo dyes due to extended delocalization through the investigated molecular structure.

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IZVOD

SOLVATOHROMIZAM 5-(4-SUPSTITUISANIH ARILAZO)-4-FENIL-6-METIL-3-CIJANO-2-PIRIDONA

Osam 5-(4-supstituisanih arilazo)-4-fenil-6-metil-3-cijano-2-piridona je sintetizovano reakcijom benzoilacetona i arendiazonijumove soli, i kondenzacijom nastalog proizvoda sa cijanoacetamidom. Apsorpcioni spektri dobijenih arilazo piridonskih boja su snimljeni u dvanaest protičnih i aprotičnih rastvarača u opsegu od 200-600 nm. Za proučavanje uticaja supstituenata na apsorpcione spektre ispitivanih azo boja korišćena je prosta Hametova jednačina. Interakcije rastvorak-rastvarač su razjašnjene na osnovu koncepta linearne korelacije energije solvatacije, koji su predložili Kamlet i Taft. Rezultati pokazuju da su efekti rastvarača na apsorpcione spektre istraženih azo boja veoma kompleksni i jako zavise od prirode supstituenata na fenilazo grupi.

Ključne reči: arilazo piridonske boje, uticaj rastvarača, uticaj supstituenata, apsorpcioni spektri.

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