



Procesing '20

Zbornik radova

**Beograd
10. septembar 2020**

ZBORNIK RADOVA Proceedings

pisanih za 33. Međunarodni kongres
o procesnoj industriji



2020

ZBORNİK RADOVA
pisanih za 33. Međunarodni kongres
o procesnoj industriji
Hotel „Zepter“, Beograd
10. septembar 2020.

Izdavač
Savez mašinskih i elektrotehničkih
inženjera i tehničara Srbije (SMEITS)
Društvo za procesnu tehniku
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Tiraž
150 primeraka

CD umnožava
Paragon, Beograd

ISBN
978-86-85535-05-5

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

621(082)(0.034.2)
66.01(082)(0.034.2)

МЕЂУНАРОДНИ конгрес о процесној индустрији ПРОЦЕСИНГ (33 ; 2020 ; Београд)

Zbornik radova [pisanih za 33. Međunarodni kongres o procesnoj industriji], PROCESING '20, Beograd, 10. septembar 2020. [Elektronski izvor] / [organizatori Društvo za procesnu tehniku pri SMEITS-u [i] Katedra za procesnu tehniku Mašinskog fakulteta u Beogradu] ; [urednici Miroslav Stanojević, Aleksandar Jovović]. - Beograd : Savez mašinskih i elektrotehničkih inženjera i tehničara Srbije (SMEITS), Društvo za procesnu tehniku, 2020 (Beograd : Paragon). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemske zahteve: Nisu navedeni. - Radovi na srp. i engl. jeziku. - Nasl. sa naslovne strane dokumenta. - Tiraž 150. - Bibliografija uz svaki rad. - Abstracts.

ISBN 978-86-85535-05-5

a) Mašinstvo -- Зборници б) Процесна индустрија -- Зборници

COBISS.SR-ID 25087497

Organizatori



Društvo za procesnu tehniku
pri SMEITS-u



Katedra za procesnu tehniku
Mašinskog fakulteta u Beogradu

Održavanje 33. Procesinga finansijski je pomoglo
Ministarstvo prosvete, nauke i tehnološkog
razvoja Republike Srbije



Programski pokrovitelji

- TEHNOLOŠKO-METALURŠKI FAKULTET UNIVERZITETA U BEOGRADU
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Tipo kotlogradnja, Beograd
Wilo, Beograd
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EVALUACIJA UTICAJA RASTVARAČA I EFEKATA SUPSTITUENATA NA POLOŽAJ APSORPCIONIH MAKSIMUMA NOVIH SINTETSKIH BOJA SA PIRIDONOM KAO CENTRALNIM PRSTENOM

EVALUATION OF SOLVENT AND SUBSTITUENT EFFECTS ON ABSORPTION SPECTRA OF NEW SYNTHETIC COLORANTS WITH PYRIDONE CORE

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Azo boje predstavljaju strukturno najraznovrsniju klasu organskih jedinjenja koja sadrže jednu ili više azo grupa ($-N=N-$) koje premošćavaju dva organska motiva od kojih je bar jedan aromatičan. Od svih sintetskih postupaka za dobijanje azo boja, najviše se primenjuje klasična metoda zasnovana na kuplovanju diazonijum soli sa različitim aromatičnim jedinjenjima kao što su fenoli, naftoli, arilamini ili pirazoloni. Da su azo boje od neprocenjivog značaja u različitim granama industrije gde se primenjuju za nijansiranje tekstila, kože, plastike i kozmetičkih proizvoda, govori i činjenica da su zastupljene sa preko 60%. Cilj rada je da se ispita mogućnost primene četiri nove arilazo piridonske boje dobijene klasičnom metodom diazokuplovanja u bojenju sintetskih vlakana. Da bi se stekao uvid u način uspostavljanja intermolekulskih interakcija između proučavanih arilazo piridonskih boja i njihovog okruženja, snimljeni su odgovarajući apsorpcioni spektri u 15 rastvarača različite polarnosti, a zatim je diskutovan uticaj polarnosti rastvarača i efekata supstituenata na položaj, intenzitet i oblik apsorpcionog maksimuma. Uzimajući u obzir širok spektar primene arilazo piridonskih boja kao i činjenicu da će njihov značaj konstantno rasti, rezultati ostvareni u ovom radu predstavljaju interesantnu osnovu za buduća istraživanja.

Ključne reči: azo boje; piridon; parametri rastvarača; efekti supstituenata.

Azo dyes represent a structurally diverse class of organic dyes with one or more azo groups ($-N=N-$) as a bridge between organic residues of which at least one is an aromatic moiety. Many methods are developed for synthesis of azo compounds. The majority of these methods is based on the coupling of diazonium salts with various aromatic organic compounds such as phenols, naphthols, arylamines or pyrazolones. The importance of azo dyes is reflected in the fact that they account for 60 % of the total number of the dye structures known to be manufactured and used in the coloration of textile, leather, plastics and cosmetics. The present study aims to investigate whether four novel arylazo pyridine dyes obtained according to the most common method of diazocoupling may be used as synthetic colorants which are capable of forming noncovalent bonds with the textile substrates. To gain an insight into interaction which the investigated azo dyes establish with their environment, their absorption spectra were recorded in fifteen solvents of different polarity and the solvent/substituent effects on the UV-Vis absorption band positions, intensity and shape, were discussed. Considering the broad applications of arylazo pyridone dyes, as well as the fact that their relative importance may increase in the future, results obtained in this study serve as a basis for further investigations.

Key words: azo dyes; pyridone; solvent parameters; substituent effects.

1 Introduction

Dyes are an important class of organic molecules which are an integral part of our lives and are employed in various fields of industry i.e. textile, paint and plastic industry, dyes sensitized solar cells, optics, metal extraction and sensors. Based on the chromophore existing in these chemicals,

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they can be systematically classified as acridine dyes, azo dyes, arylmethane dyes, anthraquinone dyes, nitro dyes, xanthene dyes, and quinine-amine dyes [1]. In the recent years, azo-functionalized dyes bearing aromatic heterocyclic compounds, have attracted increasing attention due to their wide range of colors, luminosity, the simplicity of manufacture and good dyeing performance. Approximately 60% of all synthetic colorants which have been broadly applied in textile, printing, paper manufacturing and different fields of science are azo compounds [2]. Azo dyes represent a structurally diverse type of organic dyes defined by the presence in molecule of one or more azo group (-N=N-) as a bridge between organic residues of which at least one is usually an aromatic nucleus [3]. The literature review confirmed that substituted pyridine derivatives as heterocyclic coupling components have been relatively recently employed for the preparation of arylazo colorants. The advantage of arylazo pyridine compounds is reflected in the simplicity of synthesis by classical reaction of diazocoupling, the generally high molar extinction coefficient and the medium to high light and wet fastness properties [4]. In addition, a phenomenon of azo-hydrazone tautomerism which is present in these compounds containing a labile proton that can be intramolecularly exchanged, is very significant because tautomers possess diverse optical, physical and toxicological properties and different colors. In this work, a four novel arylazo pyridone dyes (Figure 1), were prepared from the corresponding mono-substituted aniline and 3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridone applying a classical method for the synthesis of the azo compounds. The chemical structure and the purity of the obtained compounds were confirmed by melting points, FT-IR, and UV-Vis spectroscopic techniques. To gain an insight into the interactions which the investigated azo dyes establish with their environment, their absorption spectra were recorded in range 300–600 nm in fifteen solvents of different polarity and the solvent/substituent effects on the UV-Vis absorption band position, intensity and shape were discussed using the correlations between the absorption maxima and various solvent parameters.

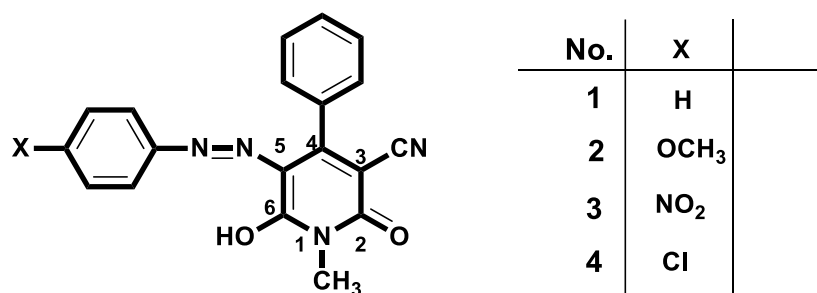


Figure 1. The chemical structure of the investigated arylazo pyridone dyes.

2 Experimental

General

Chemical used in the synthesis of dyes (1–4) were obtained from Sigma Aldrich chemical company and were used without further purification. Solvents used were of spectroscopic grade. Novel arylazo pyridone dyes (1–4) were obtained according multistep synthesis pathway illustrated on Scheme 1. The IR spectra were recorded using a Bomem MB-Series Fourier Transformer-Infrared (FT-IR) spectrophotometer in the form of KBr pellets. The ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu 1700 spectrophotometer in the region 300–600 nm. The spectra were run in spectroquality solvents (Fluka) using a concentration of 1×10^{-5} mol dm⁻³. All melting points were determined on Electrothermal apparatus and are expressed in degree Celsius.

2.1 Synthesis of 3-cyano-4-phenyl-6-hydroxy-2-pyridone (a)

Into a solution of cyanoacetamide (4.2 g; 0.022 mol) and ethylacetate (9.6 g; 0.114 mol) in absolute ethanol (10 ml) a solution of potassium hydroxide (2.8 g; 0.05 mol) in absolute ethanol (10 ml) was adding dropwise. The resulting mixture was stirred and refluxed until the reaction was completed (about 20 hours). During the reaction, the ivory product precipitated. The crude product was filtered, dissolved in 200–300 ml of hot water, acidified with concentrated HCl and recrystallized from acetone to give ivory crystals (91%), m.p. 259 °C [5].

2.2 Synthesis of sodium salt of 3-cyano-4-phenyl-6-hydroxy-2-pyridone (b)

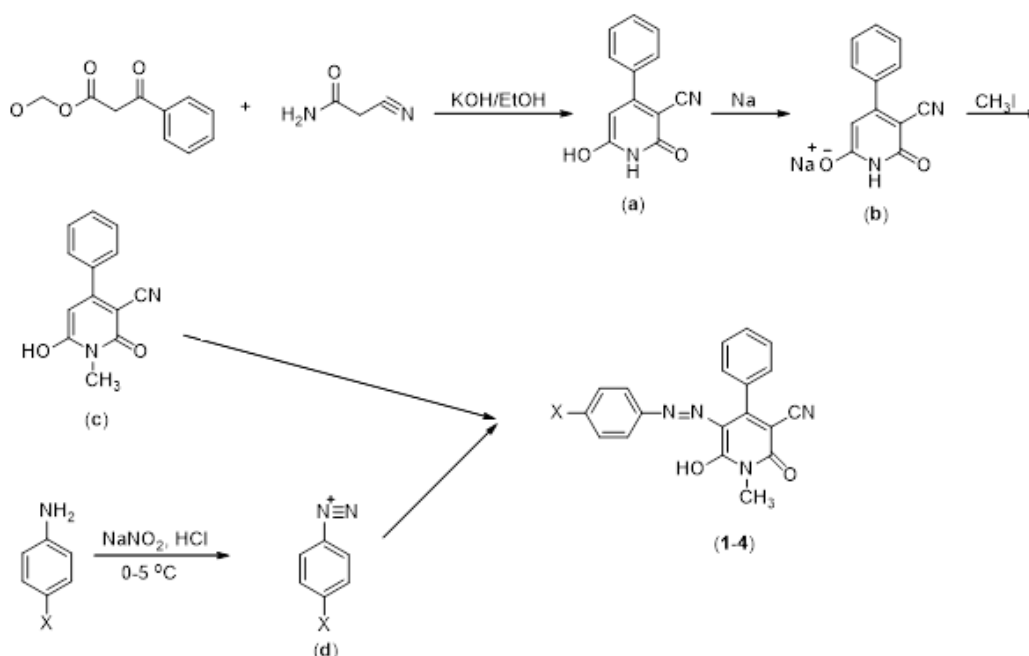
Solution of sodium (0.2 g; 0.009 mol) in absolute ethanol (6 ml) was added dropwise into the solution of 3-cyano-4-phenyl-6-hydroxy-2-pyridone (2 g; 0.009 mol) in ethanol (3.8 ml). The resulting mixture was stirred overnight and the excess of alcohol was removed by vacuum. The crude product was purified with ether.

2.3 Synthesis of 3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridone (c)

Sodium salt of 3-cyano-4-phenyl-6-hydroxy-2-pyridone (1.7 g; 0.007 mol) was dissolved in DMF (2 ml) and the methyl iodide (3.73 ml) was adding dropwise with continuous stirring.

2.4 Synthesis of 5-arylaazo-3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridone dyes (1-4)

Primary substituted amine (1.33 mol) was dissolved in aqueous hydrochloric acid (0.34 ml) and the solution of sodium nitrite (0.92 g; 0.001 mol) in water (0.53 ml) was added to it. The mixture was stirred for 40–45 minutes at 0–5 °C. The clear diazonium salt solution was slowly poured into a solution of 3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridone (1.33 mol) in aqueous potassium hydroxide (0.0074 g KOH and 0.53 ml of water) and the liquor was stirred for 1h at 0–5 °C. The resulting dye was filtered of, wash with water, dried and recrystallized from acetone. Yield, melting point and appearance of the crystals are summarized in Table 1.



Scheme 1. Multistep synthesis of arylazo pyridine dyes (1-4).

3 Results and discussion

3.1 Spectral characteristics and tautomerism

The investigated arylazo pyridine dyes may exist in two main tautomeric forms (Figure 2) which is in agreement with Wang's inference that some 5-(4-substituted)-6-hydroxy-4-methyl-3-cyano-2-pyridones occurred as two tautomers in DMF and that tautomerism was altered mainly by the nature of the substituents and the polarity of the solvents [6].

The infrared spectra of all the synthesized compounds (Table 1) regardless of the type of substituent in the azo moiety showed two intense carbonyl bands at the interval 1604–1671 cm⁻¹ which were assigned to the diketohydrazone form. The FT-IR spectra also exhibited a band at 3441–3482 cm⁻¹ which was attributed to the (-N=N-) hydrazo tautomeric form [4]. If the arylazo pyridine dyes were predominantly in the azo form, there would be no absorption band for the hydrazo group and there would be a broad absorption band for the OH-group from the pyridine ring (about 3500 cm⁻¹) and one band for the carbonyl group.

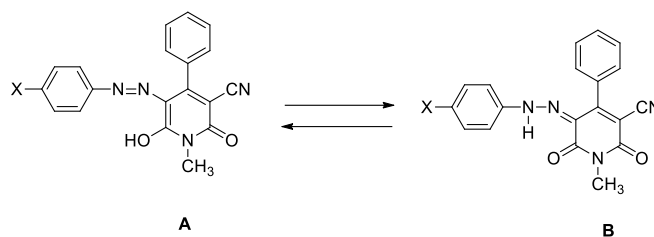


Figure 2. The equilibrium between the azo form (A) and hydrazone form (B) of the arylazo pyridine dyes (1–4).

Table 1. Physicochemical characteristics of dyes (1–4)

No.	Molecular weight (g/mol)	Melting point (°C)	Yield (%)	Color of crystals	ν_{N-H} (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	ν_{CN} (cm^{-1})
1	330	238–240	62	dark yellow	3482	1637, 1604	2215
2	360	233–240	80	dark brown	3445	1636, 1604	2215
3	375	276–280	85	brown	3447	1671, 1647	2226
4	364.5	245–250	90	light brown	3441	1648, 1604	2216

3.2 Substituent/solvent effect

Since the tautomeric equilibria strongly depends on the properties of the media, the behavior of investigated arylazo pyridone dyes (1–4) in fifteen protic and aprotic solvents was examined. For this purpose, the absorption spectra at a concentration 1×10^{-5} mol dm⁻³ were recorded over the λ range between 300 and 600 nm in the selected solvent set [4]. The characteristic absorption spectra of the 5(4-chlorophenyl)-3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridone (dye 4) in alcoholic and other solvents are presented on Figure 3. As can be seen from Figure 3, the UV-Vis absorption spectra possess a shoulder at 360 nm attributed to the azo tautomeric form and a strong band at 430 nm assigned to hydrazone tautomeric form. To explain the influence of substituents on the electronic absorption spectra, the dye without substituents (dye 1) was taken as reference. The data from Table 2 confirm that the position of the absorption maxima depends on the nature of the substituents on the benzene ring. The introduction of electron-donating substituents in the *p*-position of the benzene ring produced a red shift of the absorption maxima the compared to the unsubstituted azo dye in all solvents used. Electron-withdrawing substituents cause bathochromic/hypsochromic shifts when there is a change from polar to non-polar solvents, respectively.

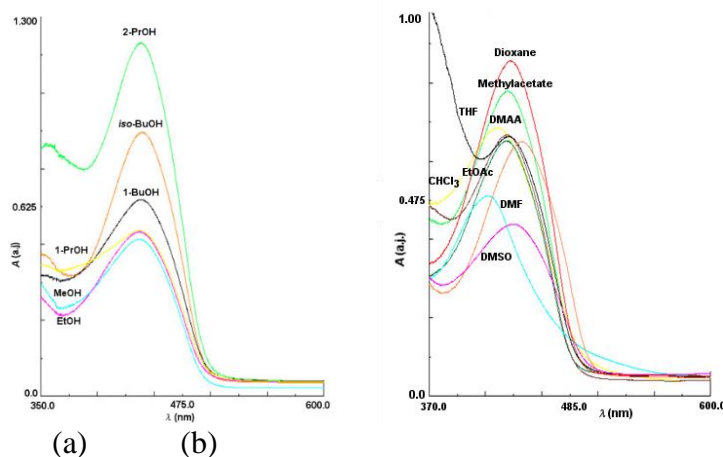


Figure 3. Wavelength-dependence of absorbance for 5-(4-chlorophenyl)-3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridone in alcohol solvents (a) and in other solvents (b).

Table 2. Absorption maxima of the hydarazone tautomer (**B**) of arylazo pyridine dyes in selected solvent set

Solvent/ λ (nm)	1	2	3	4
1. Methanol	439.0	463.4	428.2	436.6
2. Ethanol	437.4	457.2	427.6	437.6
3. 1-Propanol	434.8	461.4	432.2	437.6
4. 2-Propanol	437.6	464.4	430.4	438.4
5. 1-Buthanol	443.6	464.4	430.4	438.4
6. 2-Methyl-2-Propanol	435.2	464.2	425.8	440.0
7. Tetrahydrofuran	433.4	465.0	429.4	434.8
8. Dioxane	433.8	457.2	430.6	435.8
9. Chloroform	456.8	467.8	436.6	445.6
10. Ether	429.6	452.4	427.2	434.6
11. Methyl-acetate	432.8	458.2	431.4	434.0
12. Ethyl-acetate	431.6	458.4	431.4	433.6
13. N,N-Dimethylforma- mide	435.4	459.0	456.0	418.0
14. Dimethylsulfoxyde	442.2	464.4	437.6	439.2
15. Dimethylacetamide	437.0	462.4	433.0	425.0

To better explain these observations, the absorption frequencies for the lowest energy band of arylazo pyridine dyes were correlated by Hammett equation (1) using σ_p substituent constant:

$$\nu = \nu_0 + \rho\sigma_p \quad (1)$$

where ρ is the proportionality constant reflecting the sensitivity of absorption frequencies to the substituent effects. The plot ν_{\max} versus σ_p gives correlation which show deviations from the Hammett equation. Much better correlation coefficients were obtained when substituents on the benzene moiety with dominantly electron-donating properties were taken into consideration. The existence of this correlations has been interpreted as evidence of the significant role of substituent effects on azo-hydrazone tautomerism, since the azo group (-N=N-) is an electron-acceptor group and the imino group (-NH-) is an electron-donor, so that azo group is stabilized by the more electron-donating substituents, while an electron-withdrawing group stabilizes the hydrazine form [6].

It was observed that, although slightly positive solvatochromism is evident, the absorption spectra of examined arylazo pyridone dyes (**1–4**) did not change significantly in all solvents. An additional evidence for the effects of solvent polarity and hydrogen bonding on the 5-(4-substituted phenyl)-3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridones was obtained from the correlation of the absorption frequencies ($\nu = 1/\lambda$ in cm^{-1}) for the hydrazine tautomeric form with the Kamlet-Taft solvatochromic equation (2) of the following form:

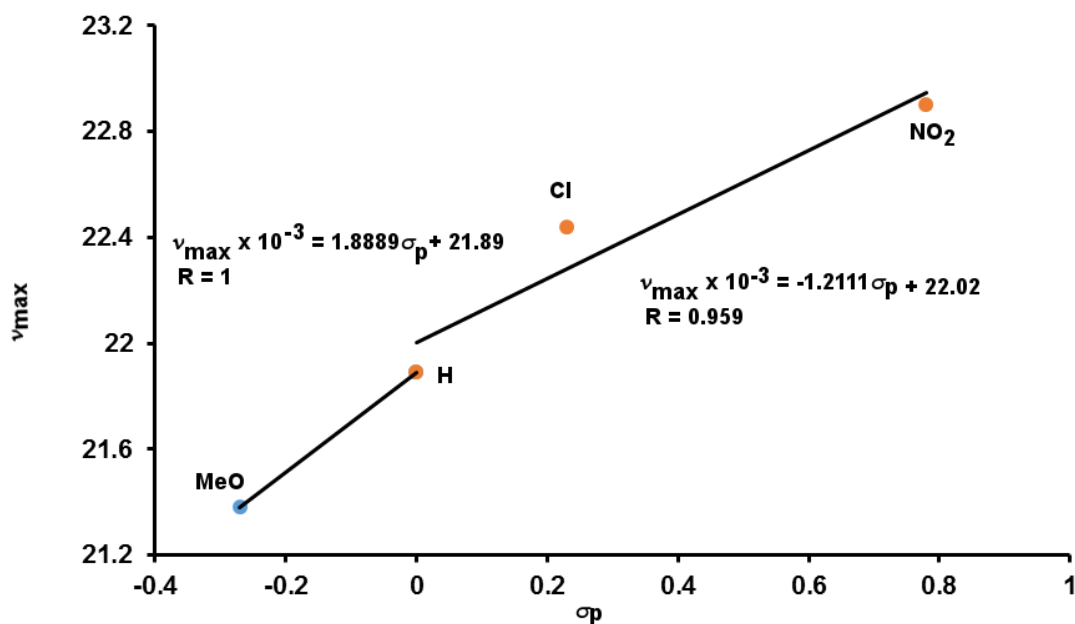


Figure 4. Relationship between ν_{max} and σ_p for arylazo pyridine dyes (1–4) in chloroform.

Table 3. Solvent parameters

Solvent	π	β	α
1. Methanol	0.60	0.66	0.98
2. Ethanol	0.54	0.75	0.86
3. 1-Propanol	0.52	0.90	0.84
4. 2-Propanol	0.46	0.84	0.76
5. 1-Buthanol	0.47	0.84	0.84
6. 2-Methyl-2-Propanol	0.41	0.11	0.68
7. Tetrahydrofuran	0.55	0.55	0.00
8. Dioxane	0.49	0.37	0.00
9. Chloroform	0.53	0.10	0.200
10. Ether	0.24	0.47	0.00
11. Methyl-acetate	0.60	0.42	0.00
12. Ethyl-acetate	0.45	0.45	0.00
13. N,N-Dimethylformamide	0.88	0.69	0.00
14. Dimethylsulfoxyde	1.00	0.76	0.00
15. Dimethylacetamide	0.88	0.76	0.00

$$v = v_0 + s\pi^* + b\beta + a\alpha \quad (2)$$

where π^* is an index of the solvent dipolarity/polarizability, β is measure of the solvent hydrogen-bonding acceptor basicity (HBA), α is a measure of the solvent hydrogen-bonding donor acidity (HBD) and v_0 is the regression value of the solute property in cyclohexane as the reference solvent. The regression coefficients s , b and a in equation (2) are a measure of the relative susceptibility of

the absorption frequencies to the indicated solvent parameters. The linear solvation energy relationship (LSER) concept developed by Kamlet and Taft represents one of the most ambitious and successful quantitative treatments of solvation effects which assumes attractive interactions between a solute and its environment enabling an estimation the ability of the investigated compounds to form hydrogen bonds. The corresponding solvent parameters are given in Table 3. The results of multiple linear regression analysis for hydrazine tautomer indicated that ν_{\max} in the selected solvent set showed satisfactory correlation with the π , β and α parameters. The results of the multiple regressions are presented in Tables 4 and 5 and the coefficients ν_0 , s , b , a fitted at the 95 % confidence level. The negative sign of coefficient a for dyes **1**, **2** and **4** and s coefficient for strong electron-attracting and electron-withdrawing substituents indicate a red shift with both increasing solvent hydrogen bond donor acidity and solvent polarity suggesting stabilization of the electronic excited state relative to the ground state. The positive sign of b coefficient for compounds **1**, **2** and **4** and s coefficient for halogen substituent illustrate a hypsochromic shifts with both increasing solvent hydrogen bond acceptor basicity and solvent polarity implying stabilization of the ground state relative to the electronic excited state. Obtained data demonstrated that the solvent effects on the position of UV-Vis absorption spectra of examined arylazo pyridone dyes is very complex and strongly dependable of the electronic influence of p -substituent on the phenyl moiety. Also electronic behavior of the nitrogen atoms of hydrazine group is diverse between derivatives with electron-donating and electron-withdrawing substituents. This phenomenon is a consequence of the difference in the conjugational or migrating ability of the electron lone pairs on the nitrogen atoms of the pyridone dyes because the strong electron-donating substituents in the phenyl moiety produce extensive delocalization in the arylazo group while the influence of the strong electron-withdrawing substituents is opposite due to positive charge on the nitrogen atom in the hydrazine tautomer [4,6].

The percentage contributions of the solvatochromic parameters (Table 5) for the investigated arylazo pyridone dyes bearing strong electron-donating or electron-withdrawing substituents on the arylazo group demonstrated that the most of the solvatochromism is consequence of the solvent dipolarity/polarizability rather than the solvent basicity/acidity. The obtained data might be explained by the effect of the positive charge on the nitrogen atom in the hydrazine tautomer and stabilization of this form mostly due to non-specific solute-solvent interactions than by hydrogen bond donating/accepting properties [4].

Table 4. Regression fits to solvatochromic parameters (2).

No.	ν_0 (10^3cm^{-1})	s (10^3cm^{-1})	b (10^3cm^{-1})	a (10^3cm^{-1})	R^a	s^b	F^c	Solvent used ^d
1	23.51 (± 0.079)	-0.86 (± 0.142)	0.040 (± 0.122)	-0.25 (± 0.062)	0.940	0.075	20	1,2,3,4,6,7,8,10, 11,12,14,15
2	22.05 (± 0.116)	-0.79 (± 0.201)	0.43 (± 0.157)	-0.53 (± 0.116)	0.865	0.117	8	3,4,5,6,8,9,10, 11,12,13,14,15
3	24.18 (± 0.257)	-2.23 (± 0.475)	-0.08 (± 0.293)	0.396 (± 0.181)	0.893	0.221	11	1,2,3,4,5,6,7,8,9,10, 12,13
4	21.87 (± 0.229)	1.39 (± 0.405)	0.850 (± 0.290)	-0.509 (± 0.171)	0.934	0.159	18	1,2,3,4,5,7,8,9, 11,12,13,15

^aCorrelation coefficient; ^bStandard error of the estimate; ^cFisher's test; ^dSolvent number as given in Table 2

Table 5. Percentage contribution of solvatochromic parameters

No.	$P\pi^*$ (%)	$P\beta$ (%)	$P\alpha$ (%)
1	74.7	3.5	21.7
2	45.1	24.6	30.3
3	80.3	2.9	14.3
4	50.6	30.9	18.5

4 Conclusion

In this work, four novel 5-(4-substitutedphenyl)-3-cyano-4-phenyl-6-hydroxy-1-methyl-2-pyridone dyes were synthesized and completely structurally characterized by melting points, FT-IR and uV-Vis spectroscopic techniques. The results indicated that the solvent effect on absorption band position is very complex and strongly dependent on the electronic influence of the substituent on the arylazo moiety. The introduction of electron-donating substituents into the *p*-position of the phenyl ring arises in strong red shift in all solvents used while presence of electron-withdrawing substituent produces slight bathochromic/hypsochromic effects. The satisfactory correlation of the ultraviolet absorption frequencies on the hydrazone tautomeric form of the azo dyes with Hammett and Kamlet-Taft equations indicated that adequate models were selected giving correct interpretation of the linear solvation energy relationships of the intricate arylazo pyridone system.

5 References

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