

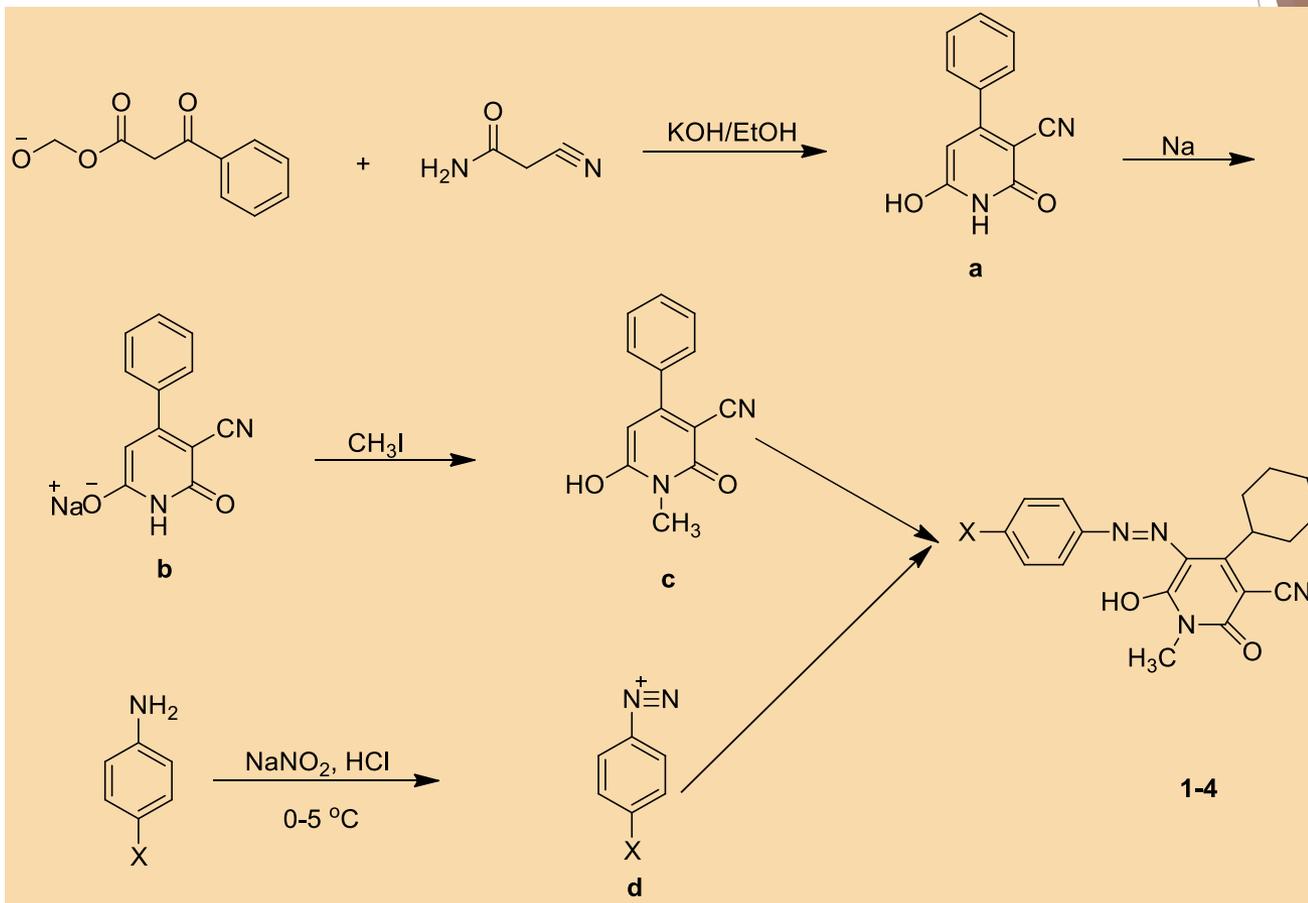
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*EVALUATION OF SOLVENT AND SUBSTITUENT EFFECTS
ON ABSORPTION SPECTRA OF NEW SYNTHETIC
COLORANTS WITH PYRIDONE CORE*

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- *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.*
- *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.*

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



Scheme 1. Synthesis of compounds 1-4.

Spectral characteristics and tautomerism:

➤ The investigated arylazo pyridine dyes may exist in two main tautomeric forms (Figure 1) 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.

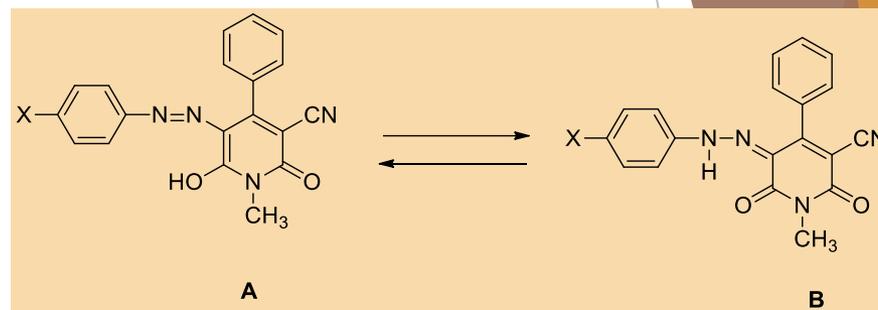


Figure 1: The equilibrium between the azo form (A) and hydrazine form (B) of the arylazo pyridine dyes (1–4).

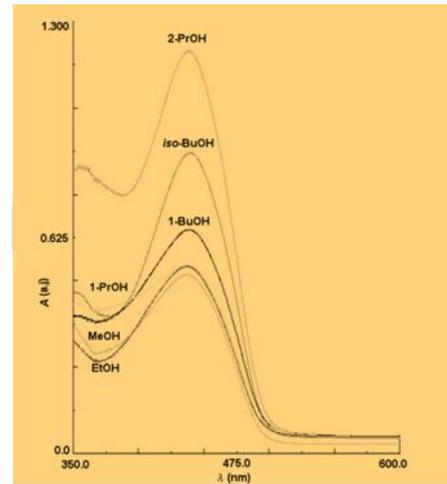
- The infrared spectra of all the synthesized compounds (Table 1) regardless of the type of substituent in the azo moiety showed two intense carbonyl bands at the interval 1604–1671 cm^{-1} which were assigned to the diketohydrazone form.
- The FT-IR spectra also exhibited a band at 3441–3482 cm^{-1} which was attributed to the (-N=N-) hydrazo tautomeric form.

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

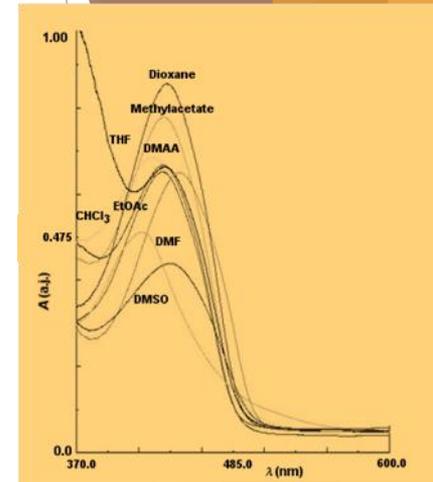
No.	Molecular weight (g/mol)	Melting point ($^{\circ}\text{C}$)	Yield (%)	Color of crystals	$\nu_{\text{N-H}}$ (cm^{-1})	$\nu_{\text{C=O}}$ (cm^{-1})	ν_{CN} (cm^{-1})
1	330	238–240	62	dark yellow	3482	1637, 1604	2215
2	360	233–240	80	dark brown	3445	1636, 1604	2215
3	375	276–280	85	brown	3447	1671, 1647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

Substituent/solvent effect:

- 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 2.
- As can be seen from Figure 2, 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.



(a)



(b)

Figure 2. 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).

- 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 (Figure 3):

$$\nu = \nu_0 + \rho\sigma_p$$

- 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.

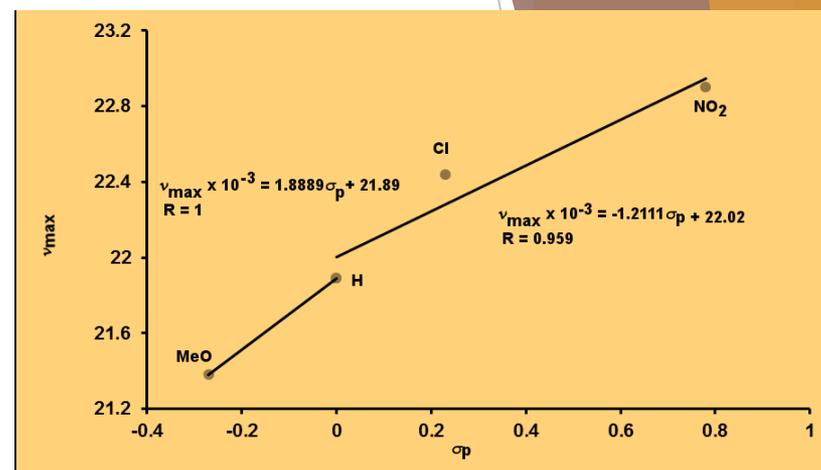


Figure 3: Relationship between ν_{\max} and σ_p for arylazo pyridine dyes (1–4) in chloroform.

➤ 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:

$$\nu = \nu_0 + s\pi^* + b\beta + a\alpha$$

➤ 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.

Table 2: Regression fits to solvatochromic parameters.

No.	ν_0 (10^3 cm^{-1})	s (10^3 cm^{-1})	b (10^3 cm^{-1})	a (10^3 cm^{-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

➤ The results of the multiple regressions are presented in Tables 2 and 3 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.

➤ The percentage contributions of the solvatochromic parameters (Table 3) 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.

Table 3: 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

➤ 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.

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.*