



ORIGINAL ARTICLE

Synthesis, structure and solvatochromic properties of some novel 5-aryloxy-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes: Hydrazone-azo tautomeric analysis



Adel Alimmari, Bojan Božić, Dušan Mijin, Aleksandar Marinković, Nataša Valentić, Gordana Ušćumlić *

Department of Organic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 3503, 11120 Belgrade, Serbia

Received 7 September 2012; accepted 1 October 2013
Available online 11 October 2013

KEYWORDS

Aryloxy pyridone dye;
Absorption spectra;
Solvent effect;
Azo-hydrazone tautomerism;
Multiparameter solvent scale

Abstract A series of eleven new 5-aryloxy-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes was synthesized and their absorption spectra were recorded in twenty solvents in the range 300–600 nm. Different solvent parameters, such as microscopic solvent polarity, E_T^N , relative permittivity, ϵ_r , refractive index, n , the Kamlet–Taft and the Catalan parameters were used for the evaluation of the solute–solvent interactions and the solvatochromic shifts of the UV–vis absorption maxima of the hydrazone tautomeric form of the investigated aryloxy pyridone dyes. The Catalan solvent scales are found to be the most suitable for describing the solvatochromic behavior of the dyes.

© 2013 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

Azo compounds are very important in the field of dyes, pigments and advanced materials (Waring and Hallas, 1990). Over 50% of all colorants are azo dyes (Chudgar and Oakes, 2003)

* Corresponding author. Tel.: +381 113303869; fax: +381 113370387.

E-mail address: goca@tmf.bg.ac.rs (G. Ušćumlić).

Peer review under responsibility of King Saud University.



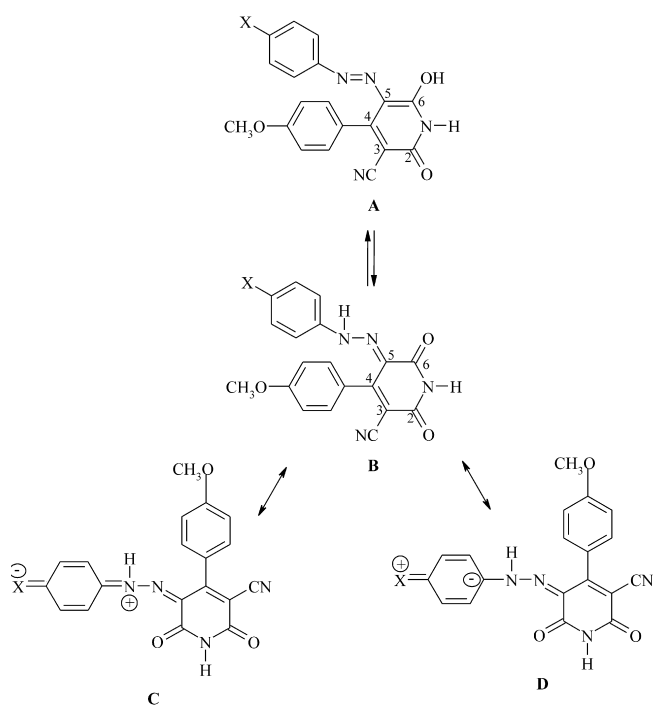
Production and hosting by Elsevier

and they are the most widely used compounds in various areas, such as dyeing of textile fibers, coloring of different materials, in biological–medical studies and advanced applications in organic synthesis (Zollinger, 1987; Bhatti and Seshadri, 2004; Tanaka et al., 1999; Hallas, 1979; Kawaguchi, 1984; Krishnankutty et al., 2009; Chen and Wang, 1991). The success of azo colorants is in the simplicity of their synthesis, in almost innumerable possibilities presented by variation on the diazo compounds and coupling components, due to the generally high molar extinction coefficient, as well as to the medium to high light and wet fastness properties (Chen and Wang, 1991). In recent years, azo dyes have attracted wide interest and found many uses in materials for optical applications

and in the analysis. Due to their properties, including optical storage capacity, optical switching, holography and non-linear optical properties, polymers with azo units represent promising candidates for photoactive materials (He et al., 2000).

Pyridone derivatives are heterocyclic intermediates relatively recently employed for the preparation of arylazo dyes. The azo pyridone dyes give bright hues and are suitable for the dyeing of polyester fabrics (Cee et al., 1988). The physico-chemical properties of arylazo pyridones are closely related to their tautomerism. The determination of azo-hydrazone tautomers both in the solid state and solution is quite interesting both from theoretical and practical standpoints, since the tautomers have different technical properties and dyeing performances. Several investigations on substituted arylazo pyridones, with respect to their visible absorption spectra in various solvents, have been carried out and reviewed (Wang and Wang, 1990; Peng et al., 1991; Ertan et al., 1995; Ušćumlić et al., 2004; Mijin et al., 2006). It has been concluded that the equilibrium between the two tautomers is influenced by the structure of the compounds and the solvent used. The introduction of electron-attracting or electron-donating substituents into the para or ortho positions of the diazo components of an azo pyridone dye, resulted in additive or subtractive color shifts and fading rates, depending on the nature and the orientation of the substituents (Wang and Wang, 1990).

In this work, eleven new 5-arylamino-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes (Scheme 1) were synthesized in order to characterize azo-hydrazone tautomer-



Scheme 1 The equilibrium between azo form (A) and hydrazone form (B) of 5-arylamino-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes (X = H (1), F (2), Cl (3), Br (4), I (5), OH (6), CH₃ (7), OCH₃ (8), COCH₃ (9), CN (10), NO₂ (11)). Resonance effect of electron-accepting (structure C) and electron-donating (structure D) substituents of the arylazo component on the hydrazone tautomer.

ism, as well as to study the solvent and substituent effects on the electronic absorption spectra. The absorption spectra were recorded in the range from 300 to 600 nm in twenty solvents of different properties. Different solvent parameters, such as microscopic solvent polarity, E_T^N , relative permittivity, ϵ_r , refractive index, n , the Kamlet–Taft and the Catalan parameters were used for describing the solute–solvent interactions and solvatochromic shifts of the UV–vis absorption band of the investigated arylazo pyridone dyes. For quantitative assessment of the substituent effects on the absorption frequencies, the simple Hammett equation was used.

2. Experimental

2.1. General

All starting materials were obtained from Aldrich and Fluka, and were used without further purification.

The IR spectra were determined using a Bomem Fourier Transform-Infrared (FT-IR) spectrophotometer, MB-Series 100 in the form of the KBr pallets. The ¹³C and ¹H NMR spectral measurements were performed on a Varian Gemini 2000 (200 MHz). The spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-*d*₆). The chemical shifts are expressed in ppm values referenced to TMS. The ultraviolet–visible (UV–vis) absorption spectra were recorded on a Shimadzu 1700 spectrophotometer in the region 200–600 nm. The absorption spectra were taken in spectro quality solvents (Fluka) at a concentration of 5×10^{-5} mol dm⁻³ and showed no dependence on the concentration. All melting points were uncorrected and are in degree Celsius. The elemental analysis was performed using a VARIO EL III elemental analyzer.

2.2. Synthesis of 5-arylamino-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes

All the investigated arylazo pyridone dyes were synthesized from the corresponding diazonium salts and 6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone using classical reaction for the synthesis of the azo compounds (Vogel, 1978). 6-Hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone was prepared from ethyl 4-methoxyphenyl benzoylacetate and cyanoacetamide in absolute ethanol in the presence of potassium hydroxide using a modified literature procedure (Roch et al., 1980). The obtained compounds were purified by crystallization from acetone and then analyzed.

The structure of the dyes was confirmed by UV–vis, FT-IR, ¹H NMR, ¹³C NMR spectroscopic technique and elemental analysis.

2.2.1. 5-Phenylazo-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (1)

Orange crystalline solid; m.p.: 235–238 °C; yield 50%; anal. calcd. for C₁₉H₁₄N₄O₃: C, 65.89; H, 4.07; N, 16.18; found: C, 65.94; H, 3.89; N, 16.08; FT-IR (KBr, ν/cm^{-1}): 3432 (NH of hydrazone form), 3137 (NH on heterocyclic), 2223 (CN), 1663, 1641 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆): 3.88 (3H, s, OCH₃); 7.12 (2H, d, $J = 8.4$ Hz, Ar-OCH₃); 7.28–7.42 (5H, m, ArH); 7.53 (2H, d, $J = 9.0$ Hz,

Ar-OCH₃); 12.18 (1H, s, NH on heterocyclic); 14.69 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 162.12 (C₂); 99.82 (C₃); 161.48 (C₄); 117.25 (C₅); 160.64 (C₆).

2.2.2. 5-(4-Fluorophenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (2)

Yellow crystalline solid; m.p.: 262–265 °C; yield 41%; anal. calcd. for C₁₉H₁₃FN₄O₃: C, 62.64; H, 3.60; N, 15.38; found: C, 62.48; H, 3.58; N, 15.34; FT-IR (KBr, ν/cm^{-1}): 3425 (NH of hydrazone form), 3206 (NH on heterocyclic), 2221 (CN), 1697, 1659 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 3.87 (3H, s, OCH₃); 7.12 (2H, d, *J* = 9.0 Hz, Ar-F); 7.20–7.33 (4H, m, Ar-F + Ar-OCH₃); 7.52 (2H, d, *J* = 9.0 Hz, Ar-OCH₃); 12.17 (1H, s, NH on heterocyclic); 14.46 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.98 (C₂); 99.84 (C₃); 161.40 (C₄); 119.30 (C₅); 160.65 (C₆).

2.2.3. 5-(4-Chlorophenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (3)

Light orange crystalline solid; m.p.: 265–268 °C; yield 44%; anal. calcd. for C₁₉H₁₃ClN₄O₃: C, 59.93; H, 3.44; N, 14.71; found: C, 60.08; H, 3.34; N, 14.63; FT-IR (KBr, ν/cm^{-1}): 3435 (NH of hydrazone form), 3213 (NH on heterocyclic), 2221 (CN), 1697, 1660 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 3.88 (3H, s, OCH₃); 7.12 (2H, d, *J* = 8.8 Hz, Ar-OCH₃); 7.35 (2H, d, *J* = 8.8 Hz, Ar-Cl); 7.45 (2H, d, *J* = 7.6 Hz, Ar-Cl); 7.52 (2H, d, *J* = 7.4 Hz, Ar-OCH₃); 12.19 (1H, s, NH on heterocyclic); 14.58 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.93 (C₂); 100.31 (C₃); 161.32 (C₄); 118.83 (C₅); 160.49 (C₆).

2.2.4. 5-(4-Bromophenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (4)

Dark yellow crystalline solid; m.p.: 270–273 °C; yield 40%; anal. calcd. for C₁₉H₁₃BrN₄O₃: C, 53.67; H, 3.08; N, 13.18; found: C, 54.06; H, 3.02; N, 13.08; FT-IR (KBr, ν/cm^{-1}): 3435 (NH of hydrazone form), 3206 (NH on heterocyclic), 2221 (CN), 1695, 1659 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 3.88 (3H, s, OCH₃); 7.12 (2H, d, *J* = 8.4 Hz, Ar-Br); 7.28 (2H, d, *J* = 8.4 Hz, Ar-OCH₃); 7.51 (2H, d, *J* = 8.4 Hz, Ar-Br); 7.58 (2H, d, *J* = 9.0 Hz, Ar-OCH₃); 12.20 (1H, s, NH on heterocyclic); 14.54 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.91 (C₂); 100.33 (C₃); 161.31 (C₄); 119.10 (C₅); 160.45 (C₆).

2.2.5. 5-(4-Iodophenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (5)

Dark orange crystalline solid; m.p.: 257–260 °C; yield 25%; anal. calcd. for C₁₉H₁₃IN₄O₃: C, 48.32; H, 2.77; N, 11.86; found: C, 48.36; H, 2.68; N, 11.78; FT-IR (KBr, ν/cm^{-1}): 3438 (NH of hydrazone form), 3202 (NH on heterocyclic), 2215 (CN), 1699, 1660 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 3.88 (3H, s, OCH₃); 7.05–7.17 (4H, m, Ar-I + Ar-OCH₃); 7.52 (2H, d, *J* = 9.0 Hz, Ar-I); 7.74 (2H, d, *J* = 8.4 Hz, Ar-OCH₃); 12.19 (1H, s, NH on

heterocyclic); 14.52 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.96 (C₂); 100.28 (C₃); 161.51 (C₄); 119.27 (C₅); 160.49 (C₆).

2.2.6. 5-(4-Hydroxyphenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (6)

Dark red crystalline solid; m.p.: 233–236 °C; yield 37%; anal. calcd. for C₁₉H₁₄N₄O₄: C, 62.98; H, 3.89; N, 15.46; found: C, 62.76; H, 3.76; N, 15.32; FT-IR (KBr, ν/cm^{-1}): 3412 (NH of hydrazone form), 3218 (NH on heterocyclic), 2214 (CN), 1691, 1643 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 3.87 (3H, s, OCH₃); 6.28 (2H, d, *J* = 8.4 Hz, Ar-OH); 7.05 (2H, d, *J* = 9.0 Hz, Ar-OH); 7.21 (2H, d, *J* = 9.0 Hz, Ar-OCH₃); 7.50 (2H, d, *J* = 9.0 Hz, Ar-OCH₃); 9.96 (1H, s, Ar-OH); 12.08 (1H, s, NH on heterocyclic); 14.69 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 162.27 (C₂); 97.85 (C₃); 161.85 (C₄); 119.30 (C₅); 160.89 (C₆).

2.2.7. 5-(4-Methylphenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (7)

Dark orange crystalline solid; m.p.: 233–236 °C; yield 42%; anal. calcd. for C₂₀H₁₆N₄O₃: C, 66.66; H, 4.48; N, 15.55; found: C, 66.52; H, 4.42; N, 15.52; FT-IR (KBr, ν/cm^{-1}): 3425 (NH of hydrazone form), 3201 (NH on heterocyclic), 2214 (CN), 1654, 1643 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 2.30 (3H, s, CH₃); 3.88 (3H, s, OCH₃); 7.54 (2H, d, *J* = 9.0 Hz, Ar-CH₃); 7.21 (4H, s, Ar-CH₃ + Ar-OCH₃); 7.75 (2H, d, *J* = 8.4 Hz, Ar-OCH₃); 12.14 (1H, s, NH on heterocyclic); 14.52 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 162.13 (C₂); 99.18 (C₃); 161.40 (C₄); 117.26 (C₅); 160.98 (C₆).

2.2.8. 5-(4-Methoxyphenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (8)

Dark brown crystalline solid; m.p.: 232–235 °C; yield 27%; anal. calcd. for C₂₀H₁₆N₄O₄: C, 63.82; H, 4.28; N, 14.89; found: C, 63.78; H, 4.32; N, 14.90; FT-IR (KBr, ν/cm^{-1}): 3347 (NH of hydrazone form), 3225 (NH on heterocyclic), 2212 (CN), 1662, 1648 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 3.76 (3H, s, N-Ar-OCH₃); 3.88 (3H, s, OCH₃); 6.59 (4H, m, N-Ar-OCH₃ + Ar-OCH₃); 7.45 (2H, d, *J* = 8.4 Hz, N-Ar-OCH₃); 7.50 (2H, d, *J* = 8.4 Hz, Ar-OCH₃); 12.10 (1H, s, NH on heterocyclic); 14.63 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.75 (C₂); 99.02 (C₃); 161.75 (C₄); 119.01 (C₅); 160.78 (C₆).

2.2.9. 5-(4-Acetylphenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (9)

Dark yellow crystalline solid; m.p.: 267–270 °C; yield 22%; anal. calcd. for C₂₁H₁₆N₄O₄: C, 64.94; H, 4.15; N, 14.43; found: C, 64.78; H, 4.08; N, 14.36; FT-IR (KBr, ν/cm^{-1}): 3438 (NH of hydrazone form), 3206 (NH on heterocyclic), 2215 (CN), 1698, 1675 (C=O on heterocyclic): ¹H NMR (200 MHz, DMSO-*d*₆): 3.76 (3H, s, N-Ar-OCH₃); 3.88 (3H, s, COCH₃); 6.95 (4H, m, N-Ar-OCH₃ + Ar-COCH₃); 7.45 (2H, d, *J* = 8.4 Hz, N-Ar-OCH₃); 7.50 (2H, d, *J* = 8.4 Hz,

Ar-COCH₃); 12.10 (1H, s, NH on heterocyclic); 14.63 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.86 (C₂); 101.22 (C₃); 161.27 (C₄); 116.81 (C₅); 160.40 (C₆).

2.2.10. 5-(4-Cyanophenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (**10**)

Yellow crystalline solid; m.p.: 279–282 °C; yield 25%; anal. calcd. for C₂₀H₁₃N₅O₃: C, 64.69; H, 3.53; N, 18.86; found: C, 64.48; H, 3.42; N, 18.50; FT-IR (KBr, ν/cm⁻¹): 3425 (NH of hydrazone form), 3221 (NH on heterocyclic), 2227 (CN), 1678, 1654 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆): 3.88 (3H, s, Ar-OCH₃); 7.05 (2H, d, *J* = 9.0 Hz, Ar-CN); 7.13 (2H, d, *J* = 9.0 Hz, Ar-OCH₃); 7.21 (2H, d, *J* = 9.0 Hz, Ar-CN); 7.84 (2H, d, *J* = 8.4 Hz, Ar-OCH₃); 12.28 (1H, s, NH on heterocyclic); 14.41 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.75 (C₂); 101.86 (C₃); 161.24 (C₄); 118.88 (C₅); 160.75 (C₆).

2.2.11. 5-(4-Nitrophenylazo)-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone (**11**)

Dark yellow crystalline solid; m.p.: 275–278 °C; yield 23%; anal. calcd. for C₁₉H₁₃N₅O₅: C, 58.31; H, 3.35; N, 17.90; found: C, 58.22; H, 3.42; N, 17.82; FT-IR (KBr, ν/cm⁻¹): 3431 (NH of hydrazone form), 3213 (NH on heterocyclic), 2214 (CN), 1689, 1675 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆): 3.89 (3H, s, Ar-OCH₃); 7.06 (2H, d, *J* = 8.8 Hz, Ar-OCH₃); 7.15 (2H, d, *J* = 9.0 Hz, Ar-NO₂); 7.52 (2H, d, *J* = 8.4 Hz, Ar-OCH₃); 8.24 (2H, d, *J* = 9.0 Hz, Ar-NO₂); 12.31 (1H, s, NH on heterocyclic); 14.34 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, carbon atoms in pyridone ring): 161.68 (C₂); 102.28 (C₃); 161.22 (C₄); 119.85 (C₅); 160.33 (C₆).

3. Results and discussion

3.1. Spectral characteristics and tautomerism

The arylazo pyridone dyes, prepared in this work can exist in two tautomeric forms (Scheme 1). The infrared spectra of all synthesized dyes showed two intense carbonyl bands at about 1642 and 1699 cm⁻¹, which were assigned to the diketohydrazone form. The spectra exhibited broad bands in the region 3137–3225 cm⁻¹ and 3421–3438 cm⁻¹ which were assigned to the N–H group from pyridone ring and hydrazone form, respectively.

The ¹H NMR spectra of the dyes exhibit a broad signal near 14.34–14.69 ppm. This signal corresponds to imine NH proton resonance of the hydrazone form (Scheme 1, Structure B). In our previous publication (Ušćumlić et al., 2004), spectroscopical investigation of ten 5-arylamino-6-hydroxy-4-methyl-3-cyano-2-pyridone dyes showed that these dyes exist in the hydrazone tautomeric form in the solid state and in the solvent DMSO-*d*₆, with N–H peaks in the range 14.35–14.87 ppm. The ¹H NMR spectra of some azo pyridone dyes in CF₃COOD/CDCl₃ have been reported (Ertan and Gurkan, 1997) and showed that these dyes exist in the hydrazone form with NH peaks in the range of 15.1–15.6 ppm. The ¹³C NMR studies of some N-alkyl

derivatives of azopyridones in solutions in CDCl₃ and DMSO-*d*₆ led to the conclusion that pyridone azo dyes exist in the hydrazone form (Lučka and Machaček, 1986; Cee et al., 1988). Our experimental results are in agreement with these results.

3.2. Solvent effects on the UV-vis absorption spectra

The electronic absorption spectra of 5-arylamino-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes (**1**–**11**) were measured at room temperature in twenty solvents in the range 300–600 nm and the characteristic spectra in representative solvents are shown in Fig. 1. The UV-vis spectra of all dyes showed a weak band at about 330–360 nm and a strong band

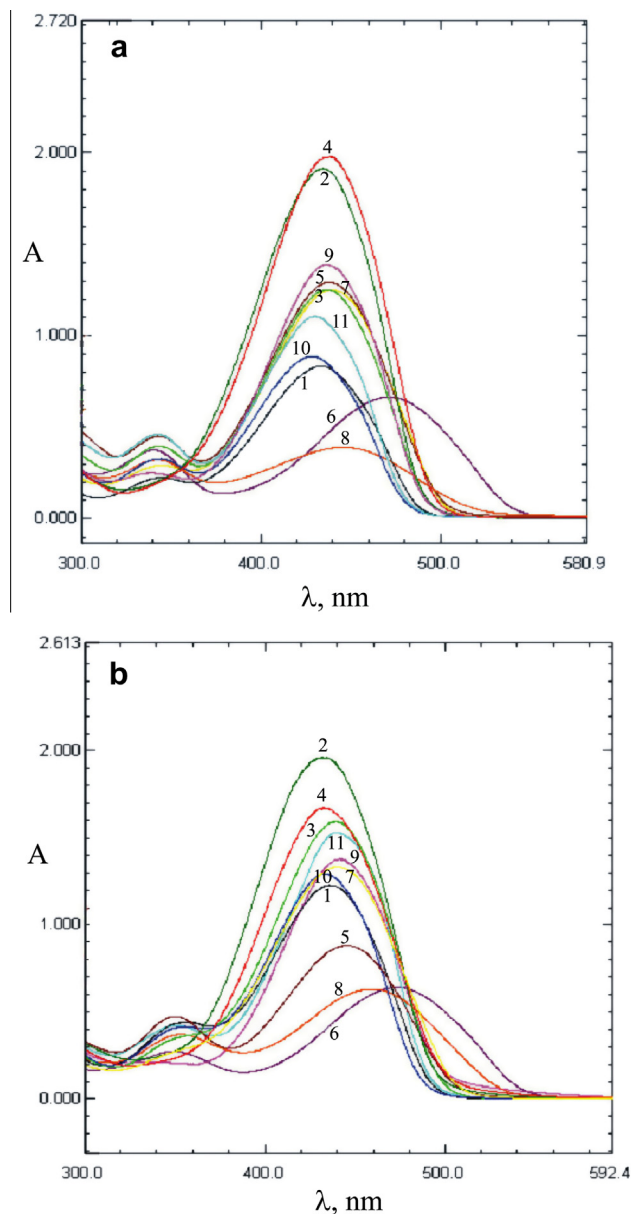


Figure 1 The UV-vis absorption spectra of 5-arylamino-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes in ethanol (a) and dimethyl sulfoxide (b).

Table 1 The absorption frequencies of the investigated compounds (1–11) in selected solvents.

Solvent/No.	$\nu_{\max} \times 10^{-3} \text{ (cm}^{-1}\text{)}$										
	1	2	3	4	5	6	7	8	9	10	11
Dioxane	23.20	23.22	23.02	22.90	22.79	21.73	22.88	22.12	23.18	23.34	23.18
Diisopropyl ether	23.32	23.26	23.10	23.06	22.90	21.70	22.80	22.00	23.24	23.59	23.54
Diethyl ether	23.28	23.27	23.13	23.12	22.92	21.70	22.94	22.22	23.19	23.54	23.51
Chloroform	22.78	22.78	22.52	22.57	22.32	21.57	22.40	21.48	22.73	23.09	22.96
Ethyl acetate	23.27	23.26	23.14	23.08	22.89	21.77	23.06	22.21	23.01	23.54	23.34
Methyl acetate	23.25	23.15	23.08	22.90	22.91	21.73	22.95	22.10	23.16	23.52	23.32
Tetrahydrofuran	23.18	23.15	23.07	23.00	22.84	21.56	22.95	22.14	23.02	23.40	23.22
Cyclohexanone	22.81	23.00	22.97	22.98	22.70	21.44	22.75	21.98	22.85	23.30	23.13
2-Butanol	22.96	22.92	22.92	22.83	22.60	21.03	22.73	22.37	23.08	23.24	22.88
1-Butanol	22.97	22.96	22.89	22.78	22.70	21.00	22.67	22.37	23.18	23.28	22.87
2-Propanol	23.06	23.10	22.90	22.87	22.90	21.12	22.98	22.94	22.86	23.32	23.42
1-Propanol	22.98	23.06	22.88	22.85	22.93	21.16	22.84	22.55	22.84	23.26	23.28
Acetone	23.21	23.12	23.10	23.14	22.84	21.65	22.86	22.16	23.23	23.47	23.35
Ethanol	23.07	23.12	22.92	22.90	22.97	21.74	23.05	22.63	22.93	23.42	23.39
Ethylene glycol	22.73	22.73	22.68	22.57	22.35	21.11	22.53	22.22	22.57	23.09	22.83
Methanol	23.09	23.00	22.89	22.84	22.85	21.28	22.79	22.50	22.95	23.38	23.25
Acetonitrile	23.18	23.13	23.00	23.00	22.73	21.68	22.77	22.18	22.95	23.37	23.18
<i>N,N</i> -Dimethylformamide	23.15	23.24	23.09	23.46	22.68	21.28	23.42	22.04	22.82	23.25	22.71
<i>N,N</i> -Dimethylacetamide	23.07	23.26	22.99	22.96	22.65	21.25	22.70	22.08	22.78	23.23	23.04
Dimethyl sulfoxide	22.95	23.04	22.77	22.84	22.43	21.14	22.65	21.83	22.65	23.04	22.78

at 420–480 nm which were assigned to azo and hydrazone tautomeric forms, respectively. The absorption maxima, which correspond to a transition in which electron density is transferred from the hydrazone –NH group to the pyridone carbonyl group (lower energy band), are presented in Table 1, and were studied in this paper.

The physical parameters of the solvents used are listed in Table 2: relative permittivity, ϵ_r , refractive index, n , the E_T^N (Reichardt, 2003) and corresponding Kamlet–Taft (Kamlet et al., 1983) and Catalan (Catalan, 2009) solvent parameters. The solvents are arranged with increasing their relative permittivity.

To explain the effects of solvents and substituents on electronic absorption spectra of azo pyridone dyes, the absorption maxima of the lower energy band of the unsubstituted dye (1) in different solvents, were taken as the reference. The data from Table 1 confirm that the positions of the UV–vis absorption frequencies depend on the nature of the used solvent and substituent on the benzene ring of the coupling component. The introduction of electron-donating substituents in the benzene ring produced bathochromic shift of absorption maxima as compared to that of the unsubstituted azo dye in all solvents (Fig. 1). Electron-attracting substituents caused bathochromic or hypsochromic

Table 2 The physical parameters of the solvents.

No.	Solvent	ϵ_r	n	E_T^N	Kamlet–Taft			Catalan			
					π^*	β	α	<i>SP</i>	<i>SdP</i>	<i>SB</i>	<i>SA</i>
1	Dioxane	2.21	1.4224	0.164	0.49	0.37	0.00	0.737	0.312	0.444	0.000
2	Diisopropyl ether	3.80	1.3680	0.105	0.27	0.49	0.00	0.625	0.324	0.657	0.000
3	Diethyl ether	4.20	1.3524	0.117	0.24	0.47	0.00	0.617	0.385	0.562	0.000
4	Chloroform	4.81	1.4459	0.259	0.53	0.10	0.20	0.783	0.614	0.071	0.047
5	Ethyl acetate	6.02	1.3724	0.228	0.45	0.45	0.00	0.656	0.603	0.542	0.000
6	Methyl acetate	6.68	1.3614	0.253	0.60	0.42	0.00	0.645	0.637	0.527	0.000
7	Tetrahydrofuran	7.58	1.4072	0.207	0.55	0.55	0.00	0.714	0.634	0.591	0.000
8	Cyclohexanone	15.00	1.4648	0.281	0.68	0.53	0.00	0.760	0.745	0.482	0.000
9	2-Butanol	16.56	1.3971	0.506	0.40	0.80	0.69	0.656	0.706	0.888	0.221
10	1-Butanol	17.51	1.3993	0.586	0.47	0.84	0.84	0.674	0.655	0.809	0.341
11	2-Propanol	19.92	1.3772	0.546	0.48	0.84	0.76	0.633	0.808	0.830	0.283
12	1-Propanol	20.45	1.3856	0.617	0.52	0.90	0.84	0.658	0.748	0.782	0.367
13	Acetone	20.56	1.3587	0.355	0.62	0.48	0.08	0.651	0.907	0.475	0.000
14	Ethanol	24.55	1.3614	0.654	0.54	0.75	0.86	0.633	0.783	0.658	0.400
15	Ethylene glycol	31.69	1.4475	0.790	0.92	0.52	0.90	0.777	0.910	0.534	0.717
16	Methanol	32.66	1.3284	0.762	0.60	0.66	0.98	0.608	0.904	0.545	0.605
17	Acetonitrile	35.94	1.3441	0.460	0.66	0.40	0.19	0.645	0.974	0.286	0.044
18	<i>N,N</i> -Dimethylformamide	36.71	1.4305	0.386	0.88	0.69	0.00	0.759	0.977	0.613	0.031
19	<i>N,N</i> -Dimethylacetamide	37.78	1.4384	0.377	0.88	0.76	0.00	0.763	0.987	0.650	0.028
20	Dimethyl sulfoxide	46.45	1.4793	0.444	1.00	0.76	0.00	0.830	1.000	0.647	0.072

shifts when there is a change from polar to non-polar solvents, respectively.

3.3. Correlation of solvatochromic shifts with the solvent parameters

3.3.1. Absorption maxima of hydrazone form as a function of dispersive interaction and the empirical solvent polarity index E_T^N

In order to explain the solvatochromic behavior of azo pyridone dyes, their spectral properties are correlated with different solvent polarity scales.

The dispersive interaction function, $f(n)$ gives an indication of the atomic and electronic polarization part of the intermolecular interaction occurring between solutes dissolved in solutions. The dispersive function is given by the relation:

$$f(n) = \frac{n^2 - 1}{n^2 + 1} \quad (1)$$

where n is the refractive index of solvent. The correlation of the absorption frequencies ν_{\max} of the hydrazone tautomers and the solvent dispersive function, $f(n)$, proves that dispersion forces can strongly influence the position of the azo pyridone dyes' visible absorption band. The linear relations are obtained for two isolated solvent classes (Table 3). The plot of ν_{\max} for all studied dyes vs. relative permittivity gives the correlation which shows deviation from linearity in all investigated solvents indicating that the relative permittivity is not the sole parameter governing the solvent shift (data not shown). These results indicated that specific effects have an important influence on solvatochromism of investigated dyes.

The empirical solvent polarity index, E_T^N is also used to study the solvent-solute interaction for all studied azo pyridone dyes. The plot of the absorption maxima of the dyes against the solvent empirical polarity scale gives the linear relation for two separated solvent classes (Fig. 2). The results

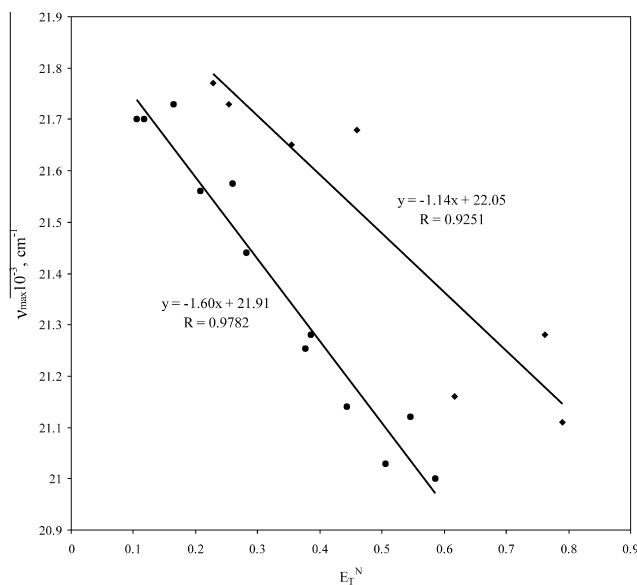


Figure 2 The correlation of ν_{\max} of the dye **6** with E_T^N (excluded ethanol).

of correlation between ν_{\max} and E_T^N values can be explained by taking into account that E_T^N parameter represents a dipolarity/polarizability and acidity but not basicity contribution of the solvent.

3.3.2. Correlation with multiparameter solvent polarity scales

The effect of solvent dipolarity/polarizability and hydrogen bonding on the absorption spectra is interpreted by means of linear solvation energy relationship (LSER) using a Kamlet-Taft solvatochromic Eq. (2) (Kamlet et al., 1981) of the following form:

Table 3 The results of the correlation between ν_{\max} and the solvent dispersive function $f(n)$.

Dyes	ν_{\max} vs. $f(n)$	Solvent excluded from the calculation ^a
1	I. $\nu_{\max} = -4.04 f(n) + 24.50$ ($R = 0.935$, $n = 9$) II. $\nu_{\max} = -5.09 f(n) + 24.61$ ($R = 0.920$, $n = 11$)	
2	I. $\nu_{\max} = -3.50 f(n) + 24.31$ ($R = 0.976$, $n = 6$) II. $\nu_{\max} = -6.50 f(n) + 25.06$ ($R = 0.969$, $n = 10$)	(1, 16, 18, 19)
3	I. $\nu_{\max} = -4.70 f(n) + 24.61$ ($R = 0.906$, $n = 6$) II. $\nu_{\max} = -8.14 f(n) + 25.49$ ($R = 0.923$, $n = 11$)	(16, 17, 18)
4	I. $\nu_{\max} = -3.41 f(n) + 24.11$ ($R = 0.955$, $n = 7$) II. $\nu_{\max} = -5.83 f(n) + 24.62$ ($R = 0.807$, $n = 10$)	(8, 16, 18)
5	I. $\nu_{\max} = -5.35 f(n) + 24.55$ ($R = 0.919$, $n = 13$) II. $\nu_{\max} = -6.60 f(n) + 24.71$ ($R = 0.932$, $n = 7$)	
6	I. $\nu_{\max} = -8.35 f(n) + 24.19$ ($R = 0.943$, $n = 12$) II. $\nu_{\max} = -5.33 f(n) + 22.77$ ($R = 0.923$, $n = 5$)	(1, 4, 8)
7	I. $\nu_{\max} = -5.56 f(n) + 24.73$ ($R = 0.954$, $n = 8$) II. $\nu_{\max} = -7.78 f(n) + 25.22$ ($R = 0.954$, $n = 9$)	(16, 17, 18)
8	I. $\nu_{\max} = -10.26 f(n) + 25.67$ ($R = 0.921$, $n = 11$) II. $\nu_{\max} = -12.23 f(n) + 25.80$ ($R = 0.955$, $n = 8$)	(11)
9	I. $\nu_{\max} = -5.09 f(n) + 24.73$ ($R = 0.916$, $n = 8$) II. $\nu_{\max} = -3.35 f(n) + 23.92$ ($R = 0.916$, $n = 9$)	(1, 15, 18)
10	I. $\nu_{\max} = -4.12 f(n) + 24.78$ ($R = 0.940$, $n = 7$) II. $\nu_{\max} = -3.52 f(n) + 24.38$ ($R = 0.921$, $n = 11$)	(13, 14)
11	I. $\nu_{\max} = -7.70 f(n) + 25.72$ ($R = 0.905$, $n = 15$) II. $\nu_{\max} = -8.19 f(n) + 25.52$ ($R = 0.999$, $n = 5$)	

^a Solvent number as given in Table 2.

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

where π^* is an index of the solvent dipolarity/polarizability, β is a measure of the solvent hydrogen-bonding acceptor (HBA) basicity, α is a measure of the solvent hydrogen-bonding donor (HBD) acidity, 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 Eq. (2) measure the relative susceptibilities of the absorption frequencies to the indicated solvent parameters. The solvent parameters are given in Table 2. The correlations of the absorption frequencies ν_{\max} for hydrazone tautomer were carried out by means of multiple linear regression analysis. The results are presented in Tables 4 and 5, and coefficients v_0 , s , b and a (Table 4) fit at the 95% confidence level.

The influence of solvent on the shift of ν_{\max} is additionally analyzed using the linear solvation energy relationship (LSER) model of Catalan (Catalan, 2009), given by Eq. (3):

$$v = v_0 + aSA + bSB + cSP + dSdP \quad (3)$$

where SA , SB , SP and SdP characterize solvent acidity, basicity, polarizability and dipolarity of a solvent, respectively and a – d are the regression coefficients describing the sensitivity of the absorption maxima to the different types of the solvent–solute interactions. The advantage of this concept in regard to the Kamlet–Taft solvatochromic model is that it gives a possibility to separate non-specific solvent effects into two terms: dipolarity and polarizability. The results of the multiple regressions are presented in Tables 6 and 7.

It was found that absorption frequencies of hydrazone form for azo dyes in selected solvents show satisfactory correlation with π^* , β and α as well as with SdP , SP , SB and SA parameters. However, the multiple regression analysis of the ν_{\max} data using the Kamlet–Taft model in which non-specific solvent effects are included in single parameter π^* , leads to a smaller correlation quality (R) and/or smaller number of solvents (n) which are included in correlations. The advantage of Catalan solvatochromic model stems from the separation of non-specific interaction on polarity and polarizability solvent effects. As it can see from Tables 5 and 7 the solvent

Table 5 Percentage contribution of solvatochromic parameters (Eq. (2)).

No.	Substituent	P_{π^*} (%)	P_{β} (%)	P_{α} (%)
1	H	34.4	22.6	43.0
2	F	43.6	23.4	33.0
3	Cl	57.3	24.4	18.3
4	Br	37.1	27.8	35.1
5	I	48.2	40.6	11.2
6	OH	25.7	51.3	23.0
7	CH ₃	49.5	23.3	27.2
8	OCH ₃	51.4	20.9	27.7
9	COCH ₃	81.8	0.0	18.2
10	CN	61.1	25.6	13.3
11	NO ₂	78.9	9.2	11.9

polarizability is the main factor that influences on the spectral shifts of all investigated compounds.

From the analysis of absorption frequencies according to Kamlet–Taft Eq. (2) it was found that the negative sign of a coefficient (excluding CH₃O substituent) and s coefficient for all arylazo dyes (Table 4) indicates a bathochromic shifts with both increasing solvent hydrogen-bond acidity and solvent dipolarity/polarizability. This suggests stabilization of the electronic excited state relative to the ground state. The positive sign of b coefficient for all investigated dyes (excluding 3, 6, 7 and 10) indicates a hypsochromic shifts with an increasing solvent hydrogen-bond acceptor basicity which suggests stabilization of the ground state relative to the electronic excited state.

The percentage contribution of solvatochromic parameters (Table 5) for all azo dyes, showed (excluding 1 and 6) that the most of the solvatochromism is due to solvent dipolarity/polarizability rather than on the hydrogen-bond acidity or basicity.

Moreover, the multiparameter regression analysis according to Catalan Eq. (3) showed negative sign of a coefficient (excluding CH₃O substituent) and c coefficient for all arylazo dyes (Table 6). This indicates a bathochromic shifts with an

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

No.	Substituent	$v_0 \cdot 10^{-3}$ (cm ⁻¹)	$s \cdot 10^{-3}$ (cm ⁻¹)	$b \cdot 10^{-3}$ (cm ⁻¹)	$a \cdot 10^{-3}$ (cm ⁻¹)	R^a	s^b	F^c	n^d
1	H	23.30 (±0.064)	−0.32 (±0.063)	0.21 (±0.100)	−0.40 (±0.046)	0.9787	0.041	61	12
2	F	23.30 (±0.063)	−0.41 (±0.065)	0.22 (±0.105)	−0.31 (±0.048)	0.9654	0.047	37	12
3	Cl	23.41 (±0.061)	−0.47 (±0.060)	−0.20 (±0.088)	−0.15 (±0.036)	0.9593	0.042	38	14
4	Br	23.05 (±0.060)	−0.36 (±0.062)	0.27 (±0.101)	−0.34 (±0.045)	0.9505	0.050	31	14
5	I	22.87 (±0.074)	−0.69 (±0.077)	0.58 (±0.124)	−0.16 (±0.053)	0.9643	0.055	31	11
6	OH	22.22 (±0.127)	−0.39 (±0.125)	−0.78 (±0.198)	−0.35 (±0.092)	0.9728	0.081	47	12
7	CH ₃	23.34 (±0.073)	−0.51 (±0.077)	−0.24 (±0.101)	−0.28 (±0.046)	0.9714	0.048	33	10
8	OCH ₃	22.39 (±0.084)	−0.69 (±0.111)	0.28 (±0.131)	0.37 (±0.050)	0.9670	0.065	48	14
9	COCH ₃	23.39 (±0.045)	−0.72 (±0.158)	^e	−0.16 (±0.040)	0.9605	0.057	65	14
10	CN	23.85 (±0.064)	−0.55 (±0.064)	−0.23 (±0.104)	−0.12 (±0.045)	0.9587	0.053	38	14
11	NO ₂	23.93 (±0.065)	−1.12 (±0.084)	0.13 (±0.046)	−0.17 (±0.065)	0.9683	0.070	60	16

^a Correlation coefficient.

^b Standard error of the estimate.

^c Fisher's test.

^d Number of solvents included in correlation.

^e Negligible value with high standard error.

Table 6 Regression fits to solvatochromic parameters (Eq. (3)).

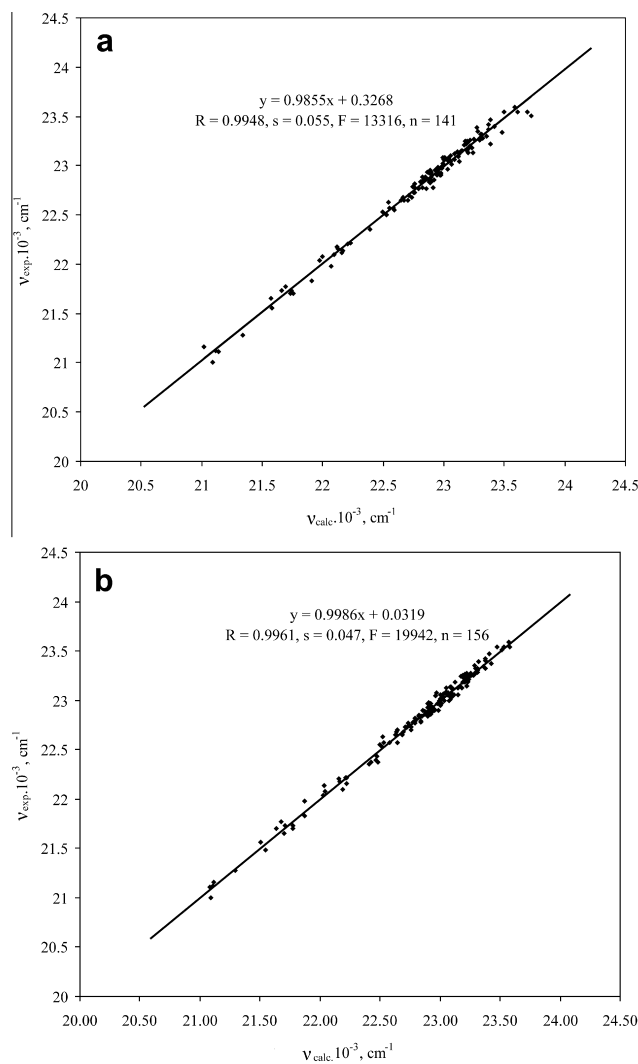
No.	Substituent	$\nu_0 \cdot 10^{-3}$ (cm ⁻¹)	$d \cdot 10^{-3}$ (cm ⁻¹)	$c \cdot 10^{-3}$ (cm ⁻¹)	$b \cdot 10^{-3}$ (cm ⁻¹)	$a \cdot 10^{-3}$ (cm ⁻¹)	R^a	s^b	F^c	n^d
1	H	24.03 (±0.132)	-0.11 (±0.038)	-0.95 (±0.169)	-0.16 (±0.070)	-0.53 (±0.041)	0.9936	0.024	136	12
2	F	23.66 (±0.175)	0.22 (±0.094)	-1.31 (±0.263)	0.51 (±0.096)	-0.57 (±0.074)	0.9542	0.059	25	15
3	Cl	23.92 (±0.105)	-0.29 (±0.074)	-0.83 (±0.158)	-0.20 (±0.063)	-0.29 (±0.047)	0.9776	0.033	48	14
4	Br	23.70 (±0.159)	0.15 (±0.069)	-1.47 (±0.215)	0.44 (±0.094)	-0.56 (±0.067)	0.9674	0.054	33	14
5	I	24.35 (±0.167)	-0.25 (±0.081)	-2.25 (±0.225)	0.40 (±0.114)	-0.25 (±0.067)	0.9664	0.055	35	15
6	OH	23.69 (±0.418)	-0.27 (±0.111)	-1.61 (±0.525)	-1.46 (±0.216)	-0.46 (±0.125)	0.9814	0.071	46	12
7	CH ₃	23.97 (±0.211)	-0.31 (±0.103)	-1.72 (±0.268)	0.64 (±0.110)	-0.25 (±0.083)	0.9580	0.067	25	14
8	OCH ₃	23.51 (±0.260)	0.29 (±0.140)	-2.81 (±0.382)	0.58 (±0.122)	0.45 (±0.111)	0.9638	0.084	36	16
9	COCH ₃	24.09 (±0.165)	-0.46 (±0.080)	-1.11 (±0.264)	/ ^e	-0.32 (±0.079)	0.9633	0.059	47	15
10	CN	24.61 (±0.159)	-0.28 (±0.082)	-1.30 (±0.252)	-0.21 (±0.104)	-0.25 (±0.070)	0.9684	0.049	34	14
11	NO ₂	25.02 (±0.147)	-0.24 (±0.065)	-2.50 (±0.197)	0.23 (±0.078)	-0.21 (±0.062)	0.9792	0.051	70	17

^a Correlation coefficient.^b Standard error of the estimate.^c Fisher's test.^d Number of solvents included in correlation.^e Negligible value with high standard error.**Table 7** Percentage contribution of solvatochromic parameters (Eq. (3)).

No.	Substituent	P_{SDP} (%)	P_{SP} (%)	P_B (%)	P_A (%)
1	H	6.3	54.3	9.1	30.3
2	F	8.4	50.2	19.5	21.9
3	Cl	18.0	51.6	12.4	18.0
4	Br	5.7	56.1	16.9	21.3
5	I	7.9	71.4	12.8	7.9
6	OH	7.1	42.4	38.4	12.1
7	CH ₃	10.6	58.9	21.9	8.6
8	OCH ₃	7.0	68.0	14.0	11.0
9	COCH ₃	24.3	58.7	0.0	17.0
10	CN	13.7	63.7	10.3	12.3
11	NO ₂	7.5	78.6	7.2	6.7

increasing solvent hydrogen-bond acidity and solvent polarizability. The positive sign of b coefficient for all investigated dyes (excluding **1**, **3**, **6** and **10**) indicates a hypsochromic shifts with increasing solvent hydrogen-bond acceptor basicity. The negative sign of d coefficient (excluding **2**, **4** and **8**) indicates a bathochromic shifts with increasing solvent dipolarity. The percentage contribution of solvatochromic parameters (Table 7) for all azo dyes showed that solvent polarizability is the most important parameter which influences the absorption frequency shifts. Solvent hydrogen-bond acidity and basicity have a moderate influence on solvatochromism, whereby the effect of solvent acidity has a more significant impact compared with the solvent basicity. Solvent dipolarity (Table 7) has a negligible impact on solvatochromism.

All the results obtained using Kamlet–Taft and Catalan model indicate that the solvent effects on azo-hydrazone equilibrium and UV–vis absorption spectra of the investigated azo pyridone dyes are very complex. This also indicated that the electronic behavior of the nitrogen atoms of hydrazone group is somewhat different between derivatives with electron-donating and electron-accepting substituents (Scheme 1, Structures C and D). In all cases, the use of the Catalan scale gives better regressions than the Kamlet–Taft model. The advantage of the Catalan model derived from the division of non-specific

**Figure 3** Experimental vs. calculated values of ν_{\max} from Eq. (2) (A) and Eq. (3) (B).

solvent characteristics on solvent polarizability and dipolarity allows better insight into the influence of these interactions on solvatochromism. The degree of success of Eqs. (2) and (3) is shown in Fig. 3 for all investigated compounds, and excellent linear relationships between the experimental values of ν_{\max} and the predicted absorption maxima calculated with Eqs. (2) and (3) are observed.

3.4. Substituents effects on the UV-vis absorption spectra

As seen in Table 1, the absorption spectra of 3–8 dyes were shifted bathochromically in all used solvents when compared to dye 1. The absorption spectra of the dyes with electron-accepting substituents were generally shifted hypsochromically in all used solvents (excluding dipolar aprotic solvents). It is well known that the absorption maxima of the hydrazone tautomeric form of an azo dye shift to higher wavelengths when substituents with electron donating characteristics are introduced into the ring of the diazo component. In contrast, electron-accepting substituents generally produce hypsochromic shift. The results presented in Table 1 are in agreement with this conclusion. The observed relationship between the substituent constants and the absorption maxima strongly suggests that the absorption maxima of the lower energy band of investigated azo dyes originate from hydrazone tautomeric form (Scheme 1, B).

The linear free energy relationship (LFER) concept was applied to the ν_{\max} of the studied arylazo pyridone dyes with the aim to get an insight into factors determining the absorption maxima shifts. The transmission of electronic substituent effects was studied using the Hammett Equation, Eq. (4) (Hammett, 1937):

$$s = \rho \cdot \sigma + h \quad (4)$$

where s is a substituent-dependent value: absorption frequencies (ν_{\max}), ρ is the proportionality constant reflecting the sensitivity of the ν_{\max} to the substituent effects, σ is the corresponding substituent constant (measures the electronic effect of the substituents), and h is the intercept (i.e., describes the unsubstituted member of the series).

The plot ν_{\max} vs. the σ_p and σ_{p+} (Brown and Okamoto, 1958) and σ_{p+} (Charton, 1981) substituent constants gave a correlation which showed deviations from the Hammett Equation in all dipolar aprotic solvents. However, a linear Hammett

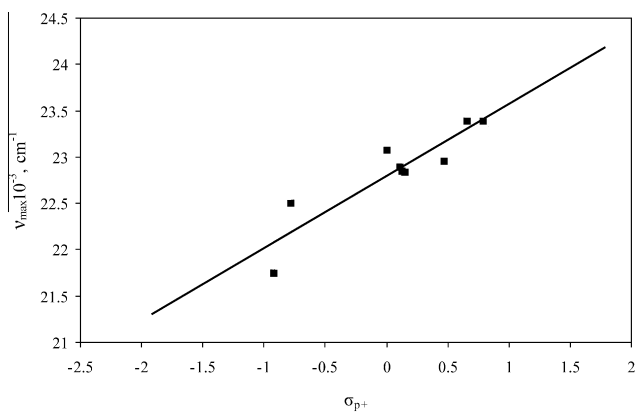


Figure 4 Relationship between ν_{\max} and σ_{p+} for arylazo pyridone dyes in ethanol (excluding 2 and 7).

correlation was obtained in protic and non-dipolar aprotic solvents (excluding 2 and 7) (Fig. 4). A better correlation of ν_{\max} was obtained with the σ_{p+} substituent constants than with the σ_p constants (except dipolar aprotic solvents), which indicates extensive delocalization in the aryl azo group. The existence of these correlations was interpreted as an evidence of significant effect of substituent on azo-hydrazone tautomerism. The azo group ($-\text{N}=\text{N}-$) is an electron-acceptor group and the imino group ($-\text{NH}-$) is an electron-donor, so that azo group is stabilized by the more electron-donating substituents, while an electron-accepting group stabilizes the hydrazone form. Satisfactory linear dependence with positive slope presented in Fig. 4 and Eq. (5) confirms the presence of a hydrazone form in the observed solvent.

$$\begin{aligned} \nu_{\max} &= 0.776\sigma_{p+} + 22.794 \quad (r = 0.910, s = 0.22, F \\ &= 33, n = 9) \end{aligned} \quad (5)$$

4. Conclusion

In this work, eleven new 5-arylazo-6-hydroxy-4-(4-methoxyphenyl)-3-cyano-2-pyridone dyes were synthesized. Characterization and the absorption ability of the dyes were studied. All the synthesized dyes exist in the hydrazone tautomeric form in the solid state and the dyes were predominantly as hydrazones in all the employed solvents. The results showed that the solvent effect on the absorption maxima of the investigated arylazo pyridone dyes is very complex and strongly depends on the nature of the substituent on the arylazo component. The introduction of electron-donating substituents into the arylazo ring results in strong bathochromic shifts in all solvents. These solvatochromic properties are evident for the hydrazone tautomeric form. The effect of electron-accepting substituents is different and produces slight bathochromic or hypsochromic shifts of the absorption maxima. The solvatochromism of the arylazo pyridone dyes was analyzed with E_T^N , ϵ_r and n solvent parameters and by multilinear regressions with Catalan and Kamlet–Taft solvents scales. Catalan solvent scales are more appropriate than the Kamlet–Taft scales for describing the solvatochromism of the azo dyes. The obtained results show that the solvent polarizability is the main factor which influences the shift of absorption maxima, whereas the solvent dipolarity, acidity and basicity are less important.

Acknowledgements

The authors acknowledge the financial support of the Ministry of Education and Science of the Republic of Serbia (Grants No. 172013).

References

- Bhatti, H.S., Seshadri, S., 2004. *Color. Technol.* 120, 151–155.
- Brown, H.C., Okamoto, Y., 1958. *J. Am. Chem. Soc.* 80, 4979–4987.
- Catalan, J., 2009. *J. Phys. Chem. B* 113, 5951–5960.
- Cee, A., Horakova, B., Lyčka, A., 1988. *Dyes Pigm.* 9, 357–369.
- Charton, M., 1981. *Prog. Phys. Org. Chem.* 13, 119–251.
- Chen, C.C., Wang, I.J., 1991. *Dyes Pigm.* 15, 69–82.

- Chudgar, R.J., Oakes, J., 2003. Dyes, Azo, in Kirk-Othmer Encyclopedia of Chemical Technology. Available from: <<http://www.onlinelibrary.wiley.com>>.
- Ertan, N., Gurkan, P., 1997. *Dyes Pigm.* 33, 137–147.
- Ertan, N., Eyduran, F., Gurkan, P., 1995. *Dyes Pigm.* 27, 313–320.
- Hallas, G.J., 1979. *J. Soc. Dyers Col.* 95, 285–294.
- Hammett, L.P., 1937. *J. Am. Chem. Soc.* 59, 96–103.
- He, J., Bian, S., Li, L., Kumar, J., Tripathy, S., Samuelson, L., 2000. *J. Phys. Chem. B* 104, 10513–10521.
- Kamlet, M.J., Abboud, J.M., Taft, R.W., 1981. *Prog. Phys. Org. Chem.* 13, 485–630.
- Kamlet, M.J., Abboud, J.M., Abraham, M.H., Taft, R.W., 1983. *J. Org. Chem.* 48, 2877–2887.
- Kawaguchi, K., 1984. *Chem. Pharm. Bull.* 32, 3291–3298.
- Krishnankutty, K., Ummathur, M.B., Ummer, P., 2009. *J. Serb. Chem. Soc.* 74, 1273–1282.
- Lučka, A., Macháček, V., 1986. *Dyes Pigm.* 7, 171–185.
- Mijin, D., Ušćumlić, G., Perišić-Janjić, N., Valentić, N., 2006. *Chem. Phys. Lett.* 418, 223–229.
- Peng, Q., Li, M., Gao, K., Cheng, L., 1991. *Dyes Pigm.* 15, 263–274.
- Reichardt, C., 2003. *Solvents and Solvent Effects in Organic Chemistry*, third ed. Wiley-VCH, Weinheim.
- Roch, J., Müller, E., Narr, B., Nickl, J., Haarmann, W., 1980. US 4182887.
- Tanaka, K., Matsuo, K., Nakanishi, A., Jo, M., Shiota, H., Yamaguchi, M., Yoshino, S., Towns, A.D., 1999. *Dyes Pigm.* 42, 3–28.
- Ušćumlić, G., Mijin, D., Valentić, N., Vajs, V., Sušić, B., 2004. *Chem. Phys. Lett.* 397, 148–153.
- Vogel, A.I., 1978. *A Text-book of Practical Organic Chemistry*, fourth ed. Longman, London.
- Wang, P.Y., Wang, I.Y., 1990. *Textile Res. J.* 60, 519–524.
- Waring, D., Hallas, G., 1990. *The Chemistry and Application of Dyes*. Plenum, New York.
- Zollinger, H., 1987. *Color Chemistry; Synthesis, Properties and Application of Organic Dyes and Pigments*, third ed. VCH, Weinheim.