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Synthesis, structure and solvatochromic properties of 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones

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Abstract: A series of some new pyridone arylazo dyes was synthesized from the corresponding diazonium salts and 3-cyano-4,6-diphenyl-2-pyridone using the classical reaction for the synthesis of the azo compounds. The structures of these dyes were confirmed by UV–Vis, FT-IR and ^{1}H-NMR spectroscopic techniques. The solvatochromism of the dyes was evaluated with respect to visible absorption properties in various solvents. The effects of solvent dipolarity/polarizability and solvent/solute hydrogen bonding interactions were analyzed by means of the linear solvation energy relationship concept proposed by Kamlet and Taft. The 2-pyridone/2-hydroxypiridine tautomeric equilibration was found to depend on the substituents as well as on the solvents.

Keywords: arylazo pyridone dyes; absorption spectra; solvent effect; substituent effect; tautomeric equilibration.

INTRODUCTION

Azo dyes are the most widely used compounds in various fields, such as dyeing of textile fibres, colouring of different materials, in biological–medical studies and advanced applications in organic synthesis.[1–6] The success of azo colorants is due to the simplicity of their synthesis by diazotization and azo coupling, to the almost innumerable possibilities presented by variation on the diazo compounds and coupling components, to the generally high molar extinction coefficient and to the medium to high light and wet fastness properties.[7] Pyridone derivatives are relatively recent heterocyclic intermediates for the preparation of arylazo dyes. The azo pyridone dyes give bright hues and are suitable for the dyeing of polyester fabrics.[8] The physico-chemical properties of arylazo pyri-

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done dyes are closely related to their tautomerism. Determination of azo-hydrazone tautomerism both in the solid state and solution phase 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 have been performed and reviewed.[9–11] It was concluded that the equilibrium between the two tautomers is influenced by the structure of the compounds and the solvent used. In previous publications, the absorption spectra of 3-cyano-6-hydroxy-4-methyl-5-(4-substituted phenylazo)-2-pyridones in different solvents were studied and the results showed that these dyes exist in the hydrazone form in the solid state and in the solvent DMSO-d_6, while equilibrium existed between the hydrazone and the azo form in different solvents.[12] The obtained dyes exhibit their colour hue in the range from orange to red-orange.

Recently, the synthesis of seventeen 3-cyano-4,6-dimethyl-5-(3- and 4-substituted phenylazo)-2-pyridones was reported.[13] The 2-pyridone/2-hydroxy-pyridine tautomeric equilibration was found to depend on the substituents as well as on the solvents. The obtained results showed that the replacement of a hydroxy group in position six in the pyridone ring of 3-cyano-6-hydroxy-4-methyl-5-(3- and 4-substituted phenylazo)-2-pyridones by a methyl group influenced a change of the azo group sensitivity to solvent effects in comparison with 3-cyano-4,6-dimethyl-5-(4-substituted phenylazo)-2-pyridones. The obtained dyes exhibited a light orange to brown-orange colour hue.

In this work, the synthesis of nine new 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones, their UV–Vis absorption spectra (200–800 nm) in fifteen solvents of different polarity and the relationship between colour and constitution of these dyes are reported. The effects of solvent and substituent on the 2-pyridone/2-hydroxypyridine tautomeric equilibrium are also reported.

RESULTS AND DISCUSSION

All of the investigated arylazo pyridone dyes were synthesized from the corresponding diazonium salts and 3-cyano-4,6-diphenyl-2-pyridone using the classical reaction for the synthesis of azo compounds.[14] The chemical structure and the purity of the obtained compounds (which, to the best of our knowledge, have not been registered in the literature) were confirmed by melting points, and ^{1}H-NMR, FT-IR and UV spectral data. The characterization data are given below.

3-Cyano-5-[(4-methoxyphenyl)azo]-4,6-diphenyl-2-pyridone (**1**). Yield: 54 %. Colour: red brown crystals; m.p.: 264–268 °C. IR (KBr, cm^{-1}): 3436 (N–H), 2212 (C–N), 1692 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 3.35 (3H, *s*, OCH$_3$), 6.88–6.99 (2H, *d*, ArH), 7.30–7.45 (2H, *m*, ArH), 7.55–7.66 (6H, *m*, ArH), 7.70–7.90 (4H, *m*, ArH), 11.67 (1H, *s*, pyridone–NH).

3-Cyano-5-[(4-methylphenyl)azo]-4,6-diphenyl-2-pyridone (**2**). Yield: 29 %. Colour: dark yellow crystals; m.p.: 243–246 °C. IR (KBr, cm^{-1}): 3376 (N–H), 2212 (C–N), 1681 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.28 (3H, *s*, CH_3), 7.08–7.22 (4H, *d*, ArH), 7.40–7.68 (6H, *m*, ArH), 7.75–8.08 (4H, *m*, ArH), 11.95 (1H, *s*, pyridone–NH).

3-Cyano-4,6-diphenyl-5-phenylazo-2-pyridone (**3**). Yield: 58 %. Colour: orange crystals; m.p.: 241–242 °C. IR (KBr, cm^{-1}): 3371 (N–H), 2212 (C–N), 1666 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.05–7.20 (3H, *m*, ArH), 7.25–7.39 (4H, *m*, ArH), 7.40–7.49 (6H, *m*, ArH), 7.50–7.70 (2H, *m*, ArH), 11.83 (1H, *s*, pyridone–NH).

3-cyano-5-[(3-methoxyphenyl)azo]-4,6-diphenyl-2-pyridone (**4**). Yield: 64 %. Colour: orange crystals; m.p.: 301–303 °C. IR (KBr, cm^{-1}): 3387 (N–H), 2212 (C–N), 1706 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 3.79 (3H, *s*, OCH_3), 6.67–6.79 (3H, *m*, ArH), 7.20–7.33 (3H, *m*, ArH), 7.45–7.70 (6H, *m*, ArH), 7.90–8.03 (2H, *d*, ArH), 11.83 (1H, *s*, pyridone–NH), 14.04 (1H, *s*, pyridine–OH).

5-[(4-Chlorophenyl)azo]-3-cyano-4,6-diphenyl-2-pyridone (**5**). Yield: 36 %. Colour: brown orange crystals; m.p.: 253–255 °C. IR (KBr, cm^{-1}): 3355 (N–H), 2222 (C–N), 1681 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.20–7.39 (2H, *d*, ArH), 7.40–7.55 (4H, *m*, ArH), 7.60–7.75 (6H, *m*, ArH), 7.90–8.00 (2H, *m*, ArH), 12.27 (1H, *s*, pyridone–NH), 13.75 (1H, *s*, pyridine–OH).

5-[(4-Bromophenyl)azo)-3-cyano-4,6-diphenyl-2-pyridone (**6**). Yield: 69 %. Colour: red brown crystals; m.p.: 292–293 °C. IR (KBr, cm^{-1}): 3351 (N–H), 2220 (C–N), 1681 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.45–7.55 (2H, *d*, ArH), 7.58–7.90 (12H, *m*, ArH), 11.76 (1H, *s*, pyridone–NH), 12.75 (1H, *s*, pyridine–OH).

3-Cyano-5-[(4-iodophenyl)azo]-4,6-diphenyl-2-pyridone (**7**). Yield: 62 %. Colour: dark brown crystals; m.p.: 276–281 °C. IR (KBr, cm^{-1}): 3454 (O–H), 3356 (N–H), 2222 (C–N), 1691 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.05–7.22 (2H, *d*, ArH), 7.25–7.46 (2H, *d*, ArH), 7.52–7.70 (6H, *m*, ArH), 7.74–7.98 (4H, *m*, ArH), 11.75 (1H, *s*, pyridone–NH), 12.57 (1H, *s*, pyridine–OH).

3-Cyano-5-[(3-nitrophenyl)azo]-4,6-diphenyl-2-pyridone (**8**). Yield: 65 %. Colour: dark orange crystals; m.p.: 282–285 °C. IR (KBr, cm^{-1}): 3484 (O–H), 3361 (N–H), 2222 (C–N), 1688 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.40–7.70 (8H, *m*, ArH), 7.76–8.30 (4H, *m*, ArH), 8.32–8.40 (2H, *d*, ArH), 11.80 (1H, *s*, pyridone–NH), 12.15 (1H, *s*, pyridine–OH).

3-Cyano-5-[(4-nitrophenyl)azo]-4,6-diphenyl-2-pyridone (**9**). Yield: 60 %. Colour: dark brown crystals; m.p.: 278–279 °C. IR (KBr, cm^{-1}): 3472 (O–H), 3350 (N–H), 2232 (C–N), 1686 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.60–7.74 (4H, *m*, ArH), 7.76–7.94 (6H, *m*, ArH), 7.96–8.12 (2H, *m*, ArH), 8.15–8.40 (2H, *m*, ArH), 12.08 (1H, *s*, pyridine–OH).

The arylazo pyridone dyes prepared in this work may exist in two tautomeric forms (Fig. 1). The infrared spectra showed an intense carbonyl band in the region 1666–1692 cm^{-1} and an intense N–H band in the region 3376–3495 cm^{-1}, which suggest that these compounds predominantly exist in the 2-pyridone tautomeric form (Fig. 1, **A**) in the solid state. The ^{1}H-NMR spectra of the dyes in DMSO-d_6 exhibit a signal for the –NH proton at the pyridone ring in the range δ 11.67–12.15 ppm. However, for azo dyes with electron-accepting substituents in the phenyl group, the ^{1}H-NMR spectra showed a signal in the range δ 12.08––14.04 ppm, corresponding to the OH proton of enol form (Fig. 1, **B**).

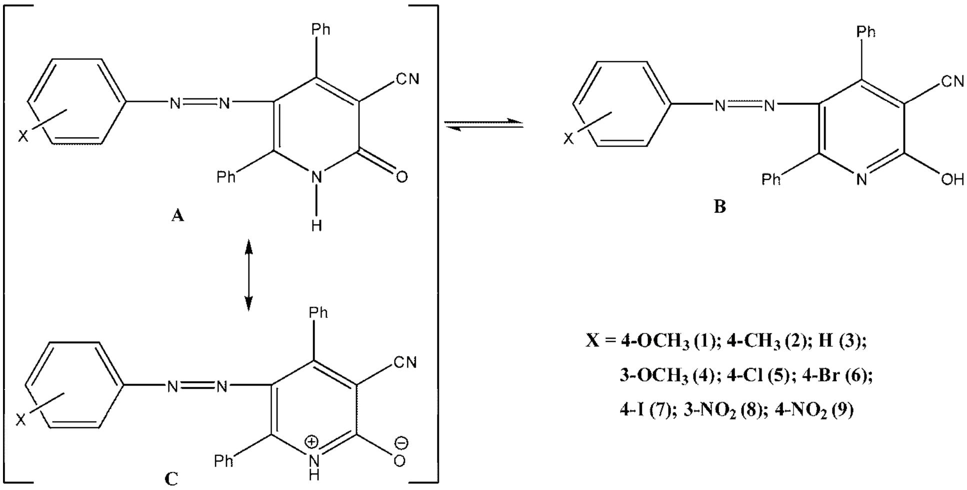

Fig. 1. Structure of dyes **1**–**9** and the equilibrium between 2-pyridone form (**A**) and 2-hydroxypyridine form (**B**) of 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones and the canonical structure (**C**).

Solvent effects on absorption spectra of the dyes

Since the tautomeric equilibria strongly depend on the nature of the media, the behaviour of arylazo pyridone dyes in various protic and aprotic solvents was studied. For this purpose, the absorption spectra of the pyridone dyes (**1**–**9**) were measured in fifteen various solvents at a concentration 10^{-4} mol dm^{-3}, and the ultraviolet absorption maxima of the electronic transitions involving the free non-bonding electrons of the azo group are given in Table I. It was found that the absorption maxima of these dyes are strongly solvent dependent and vary with solvent polarity. The dyes generally showed bathochromic shifts as the polarity of the solvents was increased. The characteristic absorption spectra of investigated azo dyes in ethanol and *N*,*N*-dimethylacetamide are shown in Figs. 2 and 3, respectively.

The equilibrium between the two tautomers is influenced by the structure of the investigated compound and the solvent used. In protic and non-dipolar aprotic solvents (alcohols, dioxane, tetrahydrofuran and acetonitrile) azo pyridone dyes with electron-donating and moderate electron-accepting substituents showed one absorption band arising from the 2-pyridone tautomeric form. Azo pyridone dyes with strong electron-accepting substituents exhibited two absorption bands in these solvents (Fig. 2). In *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide and dimethyl sulphoxide solvents, all the investigated azo pyridone dyes existed as two tautomers, due to the high basicities and high relative permitivities of these solvents (Table I and Fig. 3). The molecular extinction coefficients (ε_{max}) are higher in comparison to the 3-cyano-4,6-dimethyl-5-(4-substituted phenylazo)-2-pyridones reported previously,[13] and vary from 6000 to 38000 dm^3 mol^{-1} cm^{-1} (not listed in Table I). The ratios of the molecular extinction coefficients of the 2-pyridone form **A** and the 2-hydroxypyridine form **B** are listed in Table I for solvents and substituents where tautomeric equilibrium was found.

TABLE I. UV–Vis spectral data (λ_{max} / nm and $\varepsilon_1/\varepsilon_2$) of dyes **1**–**9** in different solvents

No.	Solvent or Substituent	4-OCH$_3$	4-CH$_3$	H	3-OCH$_3$	4-Cl	4-Br	4-I	3-NO$_2$	4-NO$_2$
1	Methanol	370	361	375	358	356	355	360,	340,	372,
								443	473	551
		–	–	–	–	–	–	2.24	1.15	1.71
2	Ethanol	373	364	374	360	359	356	359,	353,	371,
								456	484	562
		–	–	–	–	–	–	1.94	0.69	1.60
3	Propan-1-ol	375	361	374	359	355	354	361,	342,	373,
								452	484	565
		–	–	–	–	–	–	1.68	0.79	1.56
4	Propan-2-ol	375	360	371	360	356	356	360,	355,	371,
								448	487	572
		–	–	–	–	–	–	2.02	0.63	1.58
5	Butan-1-ol	375	364	373	360	356	346	362,	353,	374,
								456	485	566
		–	–	–	–	–	–	1.43	0.74	1.64
6	2-Methyl-2-propanol	372	360	375	360	356	357	357,	342,	370,
								439	403	585
		–	–	–	–	–	–	1.93	0.87	3.32
7	Butan-2-ol	373	360	353	361	358	357	360,	340,	370,
								448	485	578
		–	–	–	–	–	–	1.79	0.84	1.80
8	Dioxane	368	358	350	353	355	360	360,	330,	370,
								429	403	420
		–	–	–	–	–	–	1.08	1.06	2.05
9	Ethyl acetate	364	357	348	350	348	351	355,	332,	364,
								431	414	571
		–	–	–	–	–	–	1.25	2.46	2.90
10	Tetrahydrofuran	365	356	352	353	355	354	350,	330,	375,
								439	412	602
		–	–	–	–	–	–	0.99	1.18	1.47

TABLE I. Continued

No.	Solvent or Substituent	4-OCH_3	4-CH_3	H	3-OCH_3	4-Cl	4-Br	4-I	3-NO_2	4-NO_2
11	Acetonitrile	368	356	369	352	351	352	341,	341,	368,
								467	483	575
		–	–	–	–	–	–	1.20	0.73	0.79
12	Acetone	365,	357,	350,	353,	352,	354,	355,	340,	375,
		505	493	439	476	488	479	461	490	588
		21.50	20.02	2.42	9.40	4.55	6.49	1.11	0.71	0.79
13	Dimethyl sulphoxide	376,	368,	380,	364,	360,	361,	364,	348,	386,
		495	495	493	493	495	494	495	495	592
		14.58	16.00	10.12	4.11	3.18	2.45	0.98	0.53	0.78
14	*N*,*N*-Dimethylformamide	377,510	370,	383,	362,	403,	406,	372,	405,	521,
			493	493	488	493	493	497	495	588
		8.69	14.2	8.99	4.47	2.67	1.98	0.42	0.94	1.35
15	*N*,*N*-Dimethylacetamide	373,	360,	370,	350,	357,	355,	364,	390,	526,
		505	500	502	485	493	492	500	497	595
		10.62	14.40	10.46	5.51	2.65	3.03	0.38	0.51	0.93

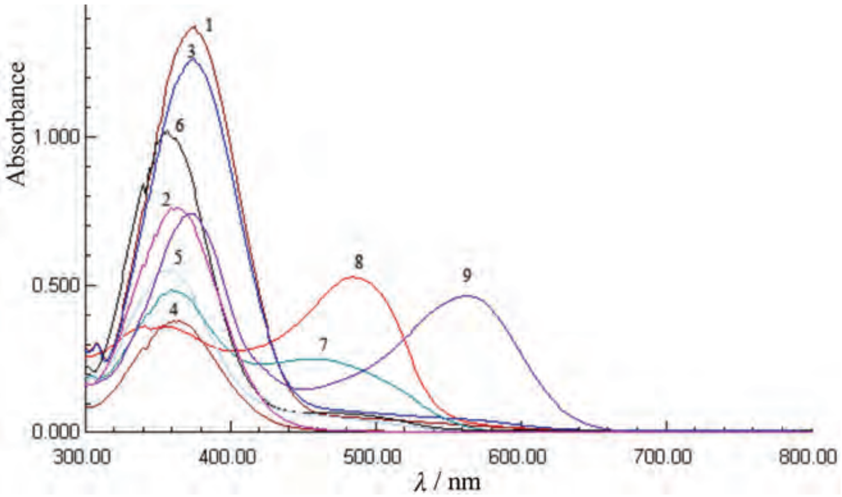

Fig. 2. Absorption spectra of the arylazo pyridone dyes (**1**–**9**) in ethanol.

By considering the equilibrium between the 2-pyridone and 2-hydroxypyridine tautomeric forms[15] in solvents of different polarity, it was found that increasing solvent polarity shifted the equilibrium towards the pyridone form.[16] This form is more dipolar than the hydroxy form due to the contribution of the charge-separated mesomeric form (Fig. 1, **C**). The present results are in agreement with this explanation. Furthermore, the hydrogen-bonding ability of the solvent plays an important role since hydrogen-bond donors tend to stabilize the oxo form (Fig. 1, **A**), whereas hydrogen-bond acceptors stabilize the hydroxy form (Fig. 1, **B**).

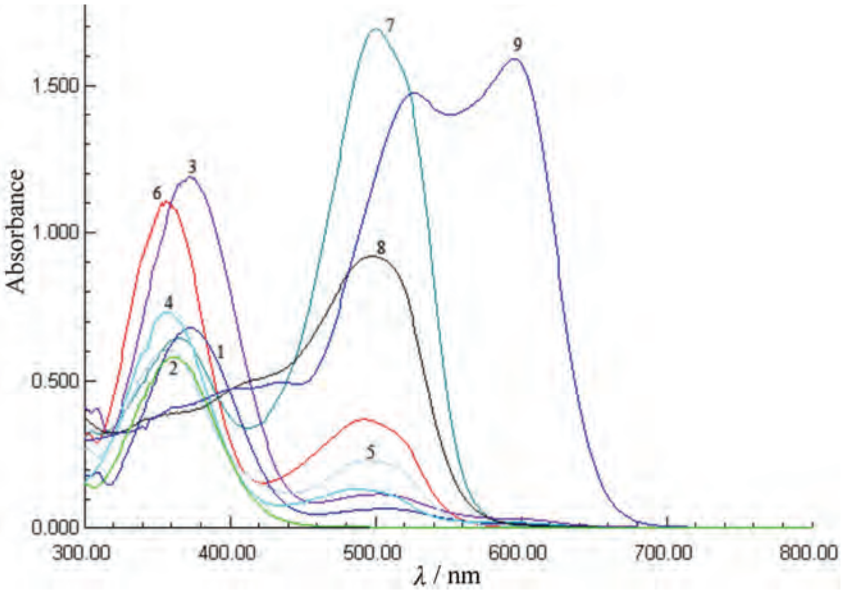

Fig. 3. Absorption spectra of the arylazo pyridone dyes (**1**–**9**) in *N*,*N*-dimethylacetamide.

The effects of solvent dipolarity/polarizability and hydrogen-bonding on the absorption spectra of 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones, and many other compounds,[17,18] can be interpreted by means of the linear solvation energy relationship (LSER) concept using a Kamlet-Taft Equation of the type:[19]

$$\nu = \nu_0 + s\pi^* + b\beta + a\alpha \qquad (1)$$

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_0 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[20] are given in Table II. The correlations of the spectroscopic data for 2-pyridone tautomeric form were realised by means of multiple linear regression analysis. It was found that absorption frequencies ν_1 for the azo dyes (Table I) in ten selected solvents (Table III) showed satisfactory correlation with the π^*, β and α parameters. The results of the multiple regressions are presented in Tables III and IV, and coefficients ν_0, s, b and a (Table III) have confidence intervals at a level of significance of 95 %. The degree of success of Eq. (1) is shown in Fig. 4 by means of a plot of ν_{max} calculated *vs.* ν_{max} observed in different solvents (the value of ν_{max} for 4-NO_2 substituted azo dye in ethyl acetate was excluded from correlation).

TABLE II. Solvent parameters[17]

No.	Solvent	π^*	α	β
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	2-Methyl-2-propanol	0.41	1.01	0.68
7	Butan-2-ol	0.40	0.80	0.69
8	Dioxane	0.55	0.37	0
9	Ethyl acetate	0.55	0.45	0
10	Tetrahydrofuran	0.58	0.55	0
11	Acetonitrile	0.75	0.31	0.19
12	Acetone	0.88	0.76	0
13	Dimethyl sulphoxide	0.71	0.48	0.08
14	*N*,*N*-Dimethylformamide	1.00	0.76	0
15	*N*,*N*-Dimethylacetamide	0.88	0.69	0

TABLE III. Regression fits to the solvatochromic parameters (Eq. (1))

Substituent	$v_0\times10^{-3}$ cm^{-1}	$s\times10^{-3}$ cm^{-1}	$b\times10^{-3}$ cm^{-1}	a$\times10^{-3}$ cm^{-1}	R[a]	S[b]	F[c]	Solvents used in the correlations[d]
4-OCH$_3$	28.67 (±0.11)	–1.49 (±0.14)	–0.75 (±0.11)	–0.68 (±0.08)	0.990	0.05	102	**2–6**, **9–11**, **13**, **15**
4-CH$_3$	29.71 (±0.32)	–1.64 (±0.33)	–1.10 (±0.25)	–0.44 (±0.17)	0.934	0.13	17	**1–7**, **10–13**
H	31.41 (±0.23)	–3.86 (±0.34)	–1.48 (±0.33)	–1.71 (±0.17)	0.993	0.13	142	**1–5**, **8–10**, **13**, **15**
3-OCH$_3$	30.00 (±0.09)	–1.54 (±0.11)	–1.31 (±0.07)	–0.43 (±0.05)	0.995	0.04	204	**1–6**, **9**, **11–13**
4-Cl	29.84 (±0.10)	–1.36 (±0.11)	–0.87 (±0.07)	–0.40 (±0.06)	0.991	0.04	111	**1**, **3–6**, **9**, **11–13**, **15**
4-Br	35.92 (±1.00)	–8.65 (±1.14)	–5.03 (±0.75)	0.99 (±0.43)	0.970	0.36	28	**1–6**, **9**, **10**, **14**, **15**
4-I	30.85 (±0.60)	–1.22 (±0.67)	–2.89 (±0.53)	–0.29 (±0.34)	0.933	0.25	14	**1–3**, **5**, **7**, **10–13**, **15**
3-NO$_2$	37.62 (±0.93)	–8.68 (±1.19)	–6.56 (±0.89)	0.89 (±0.59)	0.979	0.46	46	**1**, **2**, **4**, **5**, **7–9**, **11**, **14**, **15**
4-NO$_2$	41.88 (±0.90)	–19.49 (±1.00)	–7.68 (±0.86)	1.63 (±0.45)	0.996	0.37	235	**1–6**, **9**, **10**, **14**, **15**

[a] Correlation coefficient; [b] standard error of the estimate; [c] Fischer's test; [d] solvent numbers are given in Table I

The negative signs of the *s*, *b* and *a* coefficients for all the azo dyes (except the coefficient *a* for 4-Br, 3-NO$_2$ and 4-NO$_2$ substituted azo dyes, Table III) indicate a bathochromic shift with increasing solvent dipolarity/polarizability and solvent hydrogen-bond acceptor basicity and hydrogen-bond donor acidity. This suggests stabilization of the electronic excited state relative to the ground state.

The positive sign of the *a* coefficient for the azo dyes with electron-accepting substituents, 4-Br, 3-NO_2 and 4-NO_2, indicates a hypsochromic shift with increasing solvent hydrogen-bond donor acidity. These results show that the solvent effect on UV–Vis absorption spectra of pyridone azo dyes is very complex and strongly dependant on the nature of the groups present on the pyridone nucleus.

TABLE IV. Percentage contribution of the solvatochromic parameters

Substituent	P_{π^*} / %	P_β / %	P_α / %
4-OCH_3	51	26	23
4-CH_3	51	35	14
H	55	21	24
3-OCH_3	47	40	13
4-Cl	52	33	15
4-Br	59	34	7
4-I	28	66	6
3-NO_2	54	41	5
4-NO_2	67	27	6

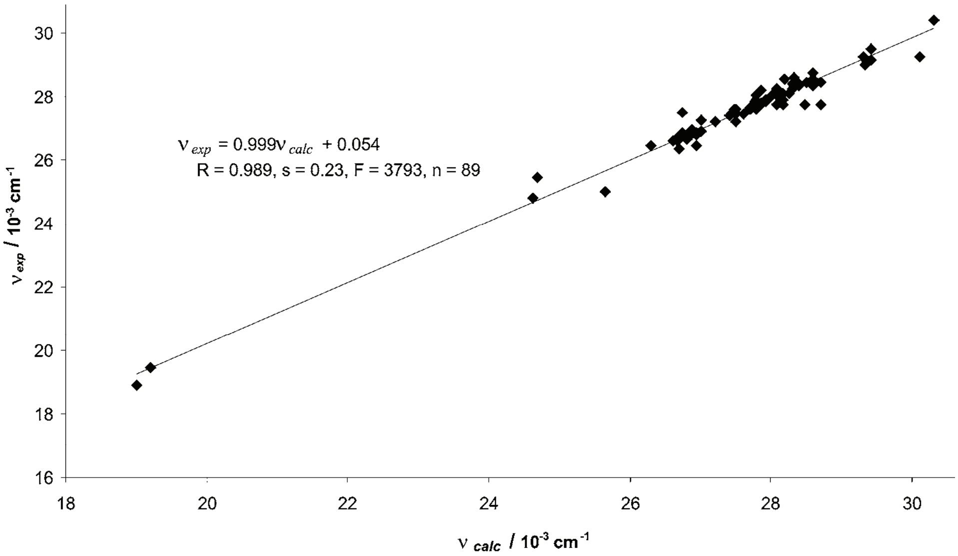

Fig. 4. The plot of ν_{max} observed against ν_{max} calculated from Eq. (1) for the 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones.

Substituent effect on the absorption spectra of the dyes in various solvents

The data from Table I confirm that the positions of the ultraviolet absorption frequencies depend on the nature of the substituents in the phenyl ring of the azo dyes. The percentage contributions of the solvatochromic parameters (Table IV) for the azo dyes with electron-donating and moderate electron-accepting substituents (4-OCH_3, 4-CH_3, H, 3-OCH_3 and 4-Cl) in the phenyl group show that most of the solvatochromism is due to solvent dipolarity/polarizability and solvent basicity rather than on the solvent acidity. These results are in accordance with the canonical structure of the 2-pyridone form of these dyes (Fig. 1, **C**). The effect of strong electron-accepting substituents (3-NO_2 and 4-NO_2) and 4-Br and 4-I is slightly different and the percentage contributions of the solvatochromic parameters show decreased proton-donating solvent effects. These results can be explained by the positive charge on the azo group in the 2-hydroxypyridine tautomer with electron-accepting substituents in the phenyl group (Fig. 5, **E**), and with a decreasing hydrogen-bond donating solvent effect when the more dipolar tautomeric form NH^+–CO^- transforms into the N=C–OH tautomeric form.

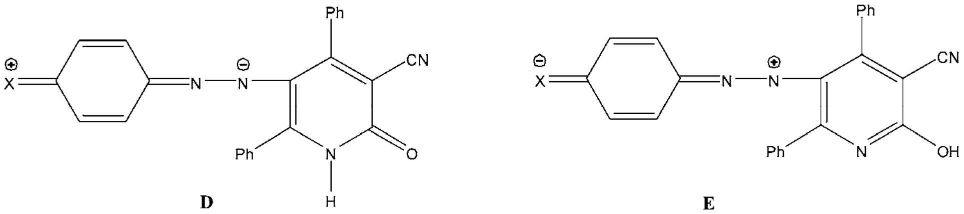

Fig. 5. Resonance effect of electron-donating (structure **D**) and electron-accepting (structure **E**) substituents of the arylazo component of the azo dyes.

In order to explain these results, the absorption frequencies were correlated by the Hammett Equation, Eq. (2), using $\sigma_{m/p}$ or $\sigma^+_{m/p}$ substituent constants:[21]

$$v = v_0 + \rho\sigma_{m/p} \qquad (2)$$

where ρ is the proportionality constant reflecting the sensitivity of the absorption frequencies to the substituent effects. The substituent constants, $\sigma_{m/p}$ and $\sigma^+_{m/p}$, measure the electronic effect of the substituents (in a given position, meta or para).

The plot v_{max} *vs*. the $\sigma_{m/p}$ substituent constants gave a correlation which showed deviations from the Hammett Equation in all dipolar aprotic solvents (*N*,*N*-dimethylacetamide, excluding the H and 4-NO_2 substituted dyes). However, a linear Hammett correlation was obtained in protic solvents (excluding the H and 4-NO_2 substituted dyes). A better correlation of v_{max} was obtained with the $\sigma^+_{m/p}$ substituent constants[22] than with the $\sigma_{m/p}$ constants in all solvents (Figs. 6 and 7), which indicates extensive delocalization in the azo group (–N=N–). The existence of the correlation presented in Fig. 6 was interpreted as evidence of the significant role of substituent effects on the 2-pyridone/2-hydroxypyridine tautomerism. Electron-donating and moderate electron-accepting substituents stabilize 2-pyridone tautomeric form, while electron-accepting substituents stabilize the 2-hydroxypyridine tautomeric form. The azo group is an electron-acceptor, hence the azo group is stabilized by the more electron-donating substituents. These results are in accordance with the resonance structure of these dyes as shown in Fig. 5, **D**.

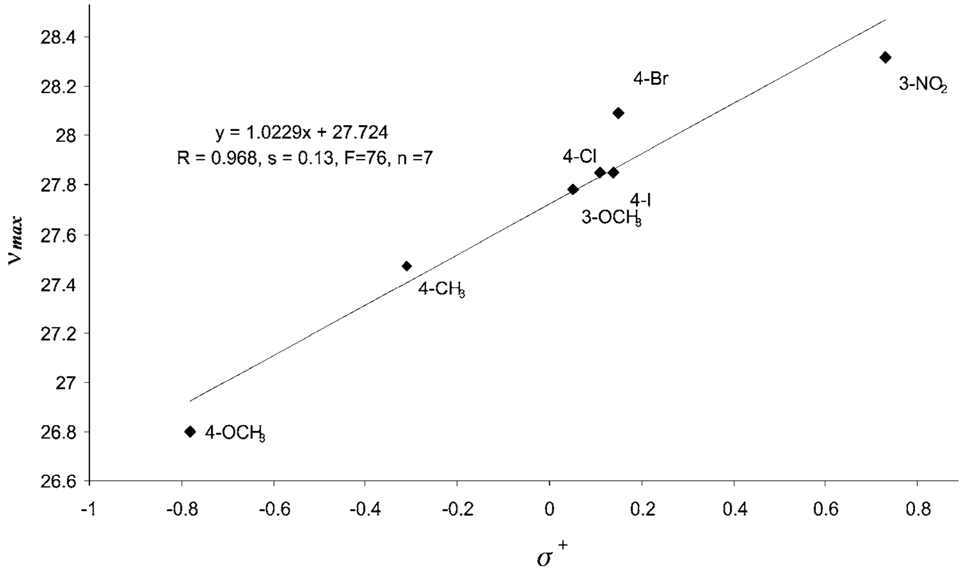

Fig. 6. Hammett correlation of ν_{max} *vs.* $\sigma^{+}_{\mathrm{m/p}}$ in ethanol.

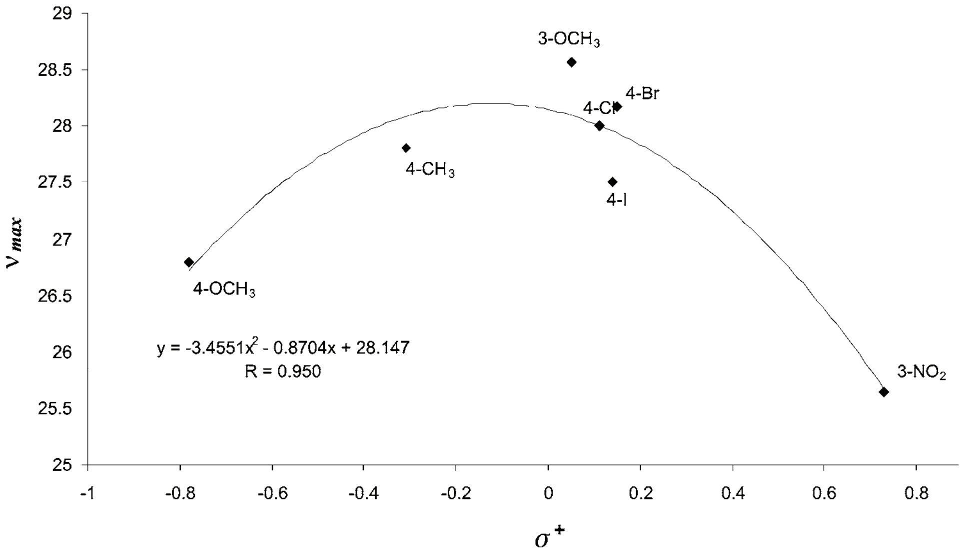

Fig. 7. Hammett correlation of ν_{max} *vs.* $\sigma^{+}_{\mathrm{m/p}}$ in *N*,*N*-dimethylacetamide.

These results are contrary to the results published in a previous work for 3-cyano-4,6-dimethyl-5-(4-substituted phenylazo)-2-pyridones.[13] The obtained results show that replacement of methyl groups in the pyridone ring of 3-cyano-4,6-dimethyl-5-(3- and4-substituted phenylazo)-2-pyridones by phenyl groups influences the change of the sensitivity of the azo group to solvent and substituent effects compared to 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2--pyridones. Additionally, two phenyl electron rich groups at the 4- and 6-position of the pyridine ring significantly changes the electronic structures of the highest populated molecular orbitals, and influences a different spatial arrangement of the investigated arylazo pyridone dyes in comparison to 3-cyano-4,6-dimethyl-5-(3- and 4-substituted phenylazo)-2-pyridones. Thus, the absorption maxima of 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones showed bathochromic effects in comparison with analogous dyes containing two methyl groups in the pyridone ring. The pyridone azo dyes system, investigated in this work, absorbed at a higher absorption maxima due to the mobility of the electronic densities across the resonating systems (structures **D** and **E**, Fig. 5). The dye system comprising the phenyl moiety absorbed bathochromically compared to the other analogues due to the longer conjugation, which stabilized charge separation in the corresponding stabilized hybrids (Fig. 5). The obtained dyes exhibit their colour hue in the range from dark-yellow to brown.

EXPERIMENTAL

General

The chemicals used in the synthesis of all the dyes were obtained from the Fluka Chemicals Company and were used without further purification. The chemical structure and the purity of the azo pyridone dyes were confirmed by melting points, and by UV–Vis, FT-IR and ^{1}H-NMR spectroscopic techniques. All melting points are uncorrected.

The IR spectra were recorded on a Bomem FTIR spectrophotometer, MB-series, in the form of KBr pellets.

The ^{1}H-NMR spectral measurements were performed on a Varian Gemini 2000 (200 MHz) instrument. The spectra were recorded at room temperature in deuterated dimethyl sulphoxide (DMSO-d_6). The chemical shifts in the ^{1}H-NMR spectra are expressed in ppm values referenced to TMS (δ_H = 0 ppm).

The UV–Vis absorption spectra were recorded in the range 200–800 nm on a Shimadzu 1700 spectrophotometer in spectroquality solvents (Fluka) using a concentration of 10^{-4} mol dm^{-3}.

*Preparation of 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones (**1–9**)*

All the investigated azo pyridone dyes were synthesized from the corresponding diazonium salts and 3-cyano-4,6-diphenyl-2-pyridone using the classical reaction for the synthesis of azo compounds.[14]

3-Cyano-4,6-diphenyl-2-pyridone was prepared from dibenzoyl methane and cyanoacetamide using a modified literature procedure.[23] Equimolar amounts of dibenzoyl methane and cyanoacetamide (10 mmol) were heated under reflux in a 50 % water/ethanol mixture (20 cm^3) in the presence of a few drops of piperidine as catalyst for 4 h. The product was purified by crystallization from ethanol (yield: 35 %, m.p.: 310–311 °C; lit.[21] m.p.: 312–313 °C).

The yields of the dyes were in the range 29–69 %. The obtained compounds were purified by crystallization from acetone and then analyzed.

CONCLUSIONS

A series of new pyridone arylazo dyes was synthesized from the corresponding diazonium salts and 3-cyano-4,6-dipenyl-2-pyridone. The solvatochromic behaviours and substituent effects in various solvents were evaluated. The results indicated that these dyes were strongly dependent on solvents and generally showed bathochromic shifts as the polarity of solvents was increased. These dyes exist dominantly in the 2-pyridone tautomeric form in the solid state. The results show that electron-donating and moderate electron-accepting substituents stabilized the 2-pyridone tautomeric form in protic and non-dipolar aprotic solvents, while in dipolar aprotic solvents the existence of two tautomers was observed. Strong electron-accepting substituents stabilized the 2-hydroxypyridine tautomer and existence of two tautomers was determined in all investigated solvents.

The satisfactory correlation of the ultraviolet absorption frequencies of the investigated arylazo pyridone dyes with the general solvatochromic equation indicates that the correct model was selected. It was demonstrated that a solvatochromic equation with three solvatochromic parameters π^*, β and α can be used to evaluate the effects of both types of hydrogen bonding and of the solvent dipolarity/polarizability effect. The obtained results showed that the replacement of the methyl groups in the pyridone ring of 3-cyano-4,6-dimethyl-5-(3- and 4-substituted phenylazo)-2-pyridones by phenyl groups in 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones influenced a change in the sensitivity of the azo group to solvent and substituent effects. The absorption maxima of the 3-cyano-4,6-diphenyl-5-(3- and 4-substituted phenylazo)-2-pyridones showed bathochromic effects in comparison with analogous dyes containing two methyl groups in pyridone ring, and exhibited their colour hue in the range from dark yellow to brown.

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ИЗВОД

СИНТЕЗА, СТРУКТУРА И СОЛВАТОХРОМНА СВОЈСТВА 3-ЦИЈАНО-4,6-ДИФЕНИЛ-5-(3- И 4-СУПСТИТУИСАНИХ ФЕНИЛАЗО)-2-ПИРИДОНА

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Серија нових пиридонских арилазо боја је синтетисана реакцијом одговарајућих диазонијум соли и 3-цијано-4,6-дифенил-2-пиридона применом класичне синтезе азо једињења. Структура синтетисаних боја је потврђена на основу података добијених из UV, FT-IR и ^{1}H-NMR спектара. Солватохромна својства боја су процењена у односу на њихову апсорпцију у видљивом делу спектра у различитим растварачима. Ефекти растварача, диполарност/поларизабилност и водонични интеракције растварач/растворак, су анализиране применом линеарне корелације солватохромних ефеката предложене од стране Kamlet-а и Taft-а. Таутомерна равнотежа 2-пиридон/2-хидроксипиридин зависи како од ефеката супституента тако и од утицаја растварача.

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