

Synthesis, properties and colour assessment of some new 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones

DUŠAN MIJIN^{1*#}, GORDANA UŠĆUMLIĆ^{1#}, NADA PERIŠIĆ-JANJIĆ^{2#}, IVAN TRKULJA¹,
MAJA RADETIĆ^{3#} and PETAR JOVANČIĆ³

¹Department of Organic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, POB 3503, 11120 Belgrade, ²Department of Chemistry, Faculty of Science, University of Novi Sad, 21000 Novi Sad and ³Textile Engineering Department, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, POB 3503, 11120 Belgrade, Serbia and Montenegro (e-mail: kavur@tmf.bg.ac.yu)

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Abstract: A series of 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones were synthesized, starting from acetylacetone and arenediazonium salt, followed by condensation with cyanoacetamide using a modified literature procedure. The experimental investigation included modification of the synthetic procedure in terms of solvent, temperature, isolation techniques as well as purification and identification of the products. The azo dyes were characterized by melting point, IR, UV/Vis, ¹H NMR and MS data. HPLC analyses were also performed. The 2-hydroxypyridine/2-pyridone tautomeric equilibration was found to depend on the polarity of the applied solvents. A colour assessment of the solid dyes and dyed polyester fabrics was also performed and the correlation between the colour and the structure of the dyes is discussed.

Keywords: aryl azo dyes, 2-pyridones, UV-Vis absorption spectrum, substituent effect, HPLC analysis, colour assessment.

INTRODUCTION

The arylazo pyridone dyes are a very important class of colorants. 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 of the diazo compounds and the coupling components, to their generally high molar extinction coefficient, and to their medium to high light and wet fastness properties.¹ A series of azo dyes was derived from pyridone as the coupling component and various diazonium salts.^{2–11} Arylazo dyes containing the pyridone ring were also prepared from β -diketones and arylhydrazones followed by condensation with

* Corresponding author.

Serbian Chemical Society active member.

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cyanoacetamide.¹² The absorption of these monoazo dyes was limited to the spectral region between green-yellow and orange. A few of the pyridone azo dyes had a deep colour such as red or violet. The physico-chemical properties of arylazo pyridone dyes are closely related to their tautomerism. Several investigations on substituted arylazo pyridones were carried out and reviewed.^{2,3,13} It was concluded that the equilibrium between the two tautomers is influenced by the structure of the compounds and the solvents used.

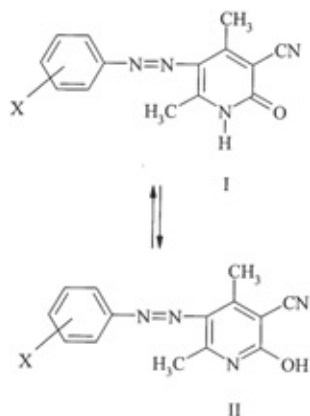


Fig. 1. The equilibrium between the 2-pyridone form (I) and 2-hydroxypyridine form (II) of the 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones (X as given in Table I).

In this work, ten 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones (Fig. 1, structure I) were synthesized by a modified literature procedure, starting from acetylacetone and an arenediazonium salt and then condensation with cyanoacetamide, in very good yield and excellent purity. It was shown that 2-hydroxypyridine/2-pyridone tautomerism in these dyes occurred. A colour assessment of the solid dyes and dyed polyester fabrics was also carried out.

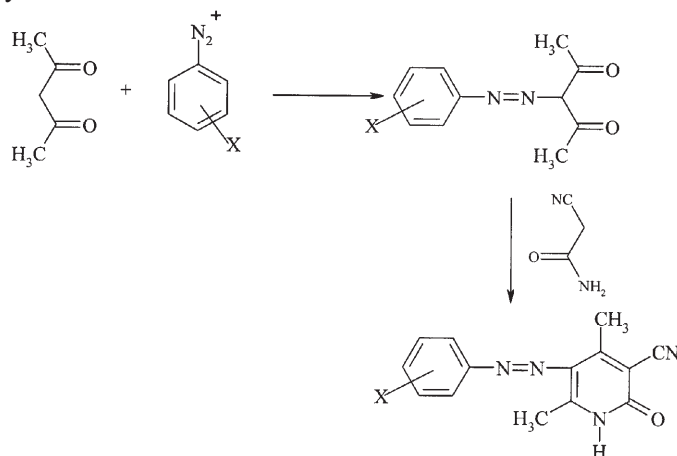
RESULTS AND DISCUSSION

Synthesis

All of the investigated azo pyridone dyes were synthesized by the diazotisation–coupling reaction, as shown in Scheme 1. In this procedure acetylacetone was coupled with diazotised substituted aniline to give an intermediate (3-(substituted phenylazo)-2,4-pentanedione), which was then cyclized with cyanoacetamide to yield a pyridone azo dye. Eight of the synthesized pyridone azo dyes are new compounds and only 5-phenylazo-4,6-dimethyl-3-cyano-2-pyridone and 5-(4-chlorophenylazo)-4,6-dimethyl-3-cyano-2-pyridone were previously synthesized by the same method.¹² The chemical structure and the purity of the obtained compounds were confirmed by their melting points, IR, UV/Vis, ¹H NMR and MS data. HPLC analyses were also performed. The characteristics of the synthesized pyridone azo dyes are given in Tables I – III.

The arylazo pyridone dyes prepared in this study may exist in two tautomeric forms (Fig. 1). The infrared spectra of all the synthesized dyes (Table II) showed

the absence of a carbonyl band but an intense hydroxyl band in the region 3425–3553 cm^{-1} , suggesting that these compounds exist predominantly in the 2-hydroxypyridine tautomeric form in the solid state.



Scheme 1. Synthesis of the 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones according to ref. 12.

TABLE I. Synthesis and properties of the 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones

Dye No.	Substituent X	Yield ^a %	Mp °C	HPLC purity ^b %	M ⁺ m/z
1	H	81	285	100	253
2	3-C ₂ H ₅	72	>280	100	281
3	3-OCH ₃	75	300	100	283
4	4-Cl	75	>300	100	278
5	3-Cl	70	>300	100	287
6	4-COCH ₃	75	>280	100	295
7	3-CN	80	>280	97.0	278
8	4-CN	80	>280	100	278
9	3-NO ₂	70	>280	100	298
10	4-NO ₂	70	>280	89.3	298

^a Isolated yield. ^b Eluent: acetonitrile/water

TABLE II. IR and ¹H NMR spectral data of the 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones

Dye No.	ν_{CN} cm^{-1}	ν_{OH} cm^{-1}	¹ H NMR (DMSO- <i>d</i> ₆) δ/ppm
1	2214	3522	2.46 (<i>s</i> , 3H, CH ₃), 2.55 (<i>s</i> , 3H, CH ₃), 7.29–7.63 (<i>m</i> , 5H, C ₆ H ₅)
2	2213	3553	1.20 (<i>t</i> , 3H, CH ₃ CH ₂), 2.26 (<i>s</i> , 3H, CH ₃), 2.32 (<i>s</i> , 3H, CH ₃), 2.66 (<i>q</i> , 2H, CH ₃ CH ₂), 7.14–7.50 (<i>m</i> , 4H, C ₆ H ₄)
3	2214	3534	2.46 (<i>s</i> , 3H, CH ₃), 2.54 (<i>s</i> , 3H, CH ₃), 3.80 (<i>s</i> , 3H, OCH ₃), 7.69–7.88 (<i>m</i> , 4H, C ₆ H ₄)

TABLE II. Continued

Dye No.	ν_{CN} cm^{-1}	ν_{OH} cm^{-1}	$^1\text{H NMR (DMSO-}d_6)$ δ/ppm
4	2202	3431	2.46 (<i>s</i> , 3H, CH ₃), 2.53 (<i>s</i> , 3H, CH ₃), 7.46–7.64 (<i>m</i> , 4H, C ₆ H ₄)
5	2215	3533	2.49 (<i>s</i> , 3H, CH ₃), 2.55 (<i>s</i> , 3H, CH ₃), 7.32–7.60 (<i>m</i> , 4H, C ₆ H ₄)
6	2208	3500	2.50 (<i>s</i> , 6H, CH ₃ + COCH ₃), 2.60 (<i>s</i> , 3H, CH ₃), 7.78–7.83 (<i>m</i> , 4H, C ₆ H ₄)
7	2213	3425	2.49 (<i>s</i> , 3H, CH ₃), 2.54 (<i>s</i> , 3H, CH ₃), 7.60–7.94 (<i>m</i> , 4H, C ₆ H ₄)
8	2215	3530	2.46 (<i>s</i> , 3H, CH ₃), 2.54 (<i>s</i> , 3H, CH ₃), 7.69–7.88 (<i>m</i> , 4H, C ₆ H ₄)
9	2214	3534	2.46 (<i>s</i> , 3H, CH ₃), 2.57 (<i>s</i> , 3H, CH ₃), 7.70–8.30 (<i>m</i> , 4H, C ₆ H ₄)
10	2209	3425	2.49 (<i>s</i> , 3H, CH ₃), 2.60 (<i>s</i> , 3H, CH ₃), 7.78–8.30 (<i>m</i> , 4H, C ₆ H ₄)

The $^1\text{H NMR}$ spectra of studied dyes exhibit two signals for methyl groups in the range $\delta = 2.20 - 2.60$ ppm also corresponding to the enol form.¹⁴

UV-Vis absorption spectra

The ultraviolet absorption maxima (λ_{max}) of the electronic transitions involving the free non-bonding electrons of the azo group of the 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones and the molecular extinction coefficients (ϵ_{max}) in six solvents are given in Table III. The spectra were run in spectroquality solvents (Fluka) using concentrations of 5×10^{-5} M.

TABLE III. Absorption spectral data of the arylazo pyridone dyes in various solvents

Dye No.	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}} 10^{-4}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)							
	Methanol	Ethanol	Chloroform	Dioxane	DMF	DMSO		
1	348 (1.25)	357 (1.27)	350 (0.95)	353 (0.89)	360 (0.76)	402 (0.87)	367 (0.70)	398 (0.78)
2	348 (1.44)	350 (1.36)	350 (0.96)	355 (1.06)	365 (1.30)	400 (0.76)	370 (0.75)	400 (0.68)
3	351 (1.18)	352 (1.08)	353 (0.84)	358 (0.78)	363 (0.81)	390 (0.90)	368 (0.56)	402 (0.70)
4	355 (1.44)	356 (1.18)	371 (1.04)	374 (0.96)	363 (0.93)	425 (0.75)	370 (0.86)	412 (0.72)
5	354 (1.38)	357 (1.20)	355 (1.12)	385 (0.92)	362 (0.97)	400 (0.70)	364 (0.82)	415 (0.70)
6	353 (1.50)	355 (1.32)	352 (1.10)	354 (0.68)	360 (1.30)	440 (0.50)	368 (1.20)	430 (0.40)
7	352 (1.32)	353 (1.12)	351 (1.08)	352 (0.76)	351 (1.06)	409 (0.50)	357 (1.16)	419 (0.70)
8	356 (1.16)	360 (1.10)	363 (1.00)	367 (0.92)	380 (0.96)	431 (0.56)	362 (1.40)	436 (0.60)
9	360 (1.44)	362 (1.40)	363 (0.90)	364 (0.87)	358 (1.34)	410 (0.72)	361 (0.90)	414 (0.96)
10	362 (1.54)	366 (1.24)	371 (0.96)	378 (1.00)	375 (1.30)	457 (0.40)	368 (0.64)	472 (0.60)

The data in Table III confirm that the positions of the ultraviolet absorption maxima depend on the nature of the substituents of the diazo component. Introduction of a substituent into the diazo component predominantly leads to a bathochromic shift of the long-wavelength absorption maximum as compared to that of the unsubstituted dye. The stronger was the electron-withdrawing effect of substituents, the more bathochromic was the shift of the absorption maximum of the dye.

From the data given in Table III it can be seen that the trend of the shift of the UV absorption maxima of investigated compounds was identical in all the employed solvents. The visible absorption spectra of the dyes were found to exhibit a strong dependence on the solvent. It was observed (Table III, Fig. 2) that although in methanol, ethanol, chloroform and dioxane the absorption spectra of the dyes did not change significantly, the λ_{max} of the dyes shifted considerably in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) and showed the existence of two tautomers. A consideration of the equilibrium between the 2-pyridone and 2-hydroxypyridine tautomeric forms^{15,16} in solvents of varying polarity indicated the equilibrium shifts towards the pyridine form with increasing solvent polarity.¹⁷ This form is more dipolar than the hydroxy form due to a contribution of the charge-separated mesomeric form $-\text{HN}=\overset{+}{\text{C}}-\text{O}^-$. 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 (I), whereas hydrogen-bond acceptors stabilize the hydroxy form (II).

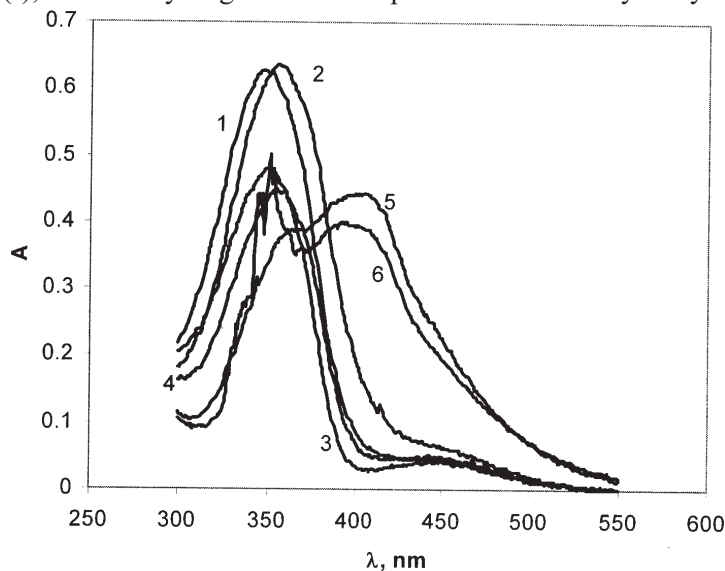


Fig. 2. UV/Vis absorption spectra of dye **1** in different solvents: 1-methanol, 2-ethanol, 3-chloroform, 4-dioxane, 5-DMF, 6-DMSO.

The results obtained in this study show that the oxo form of the 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones exists in methanol,

ethanol, dioxane and chloroform, while the hydroxy form predominates in *N,N*-dimethylformamide and dimethyl sulfoxide due to high basicities and high relative permittivities of these solvents.

Colour assessments

Colour of the synthesized dyes in the solid form. The CIELAB coordinates of the synthesized pyridone dyes in the solid form are given in Table IV. Although all the investigated dyes show a yellow hue, a comparison of the L^* , a^* , b^* values indicates that the synthesized dyes differ in colour. The lightness (L^*) of the solid dyes ranges from 40.68 to 66.66. Dyes with a stronger electron acceptor group, such as nitro and acetyl group in the para position are less red (lower values of a^*) and less yellow (lower values of b^*) compared to the other dyes from this series. Weaker electron acceptors in para position impart redder and yellower colour to the dyes. Substituents in the meta position have only a slight influence on the colour of the solid dyes (Fig. 3).

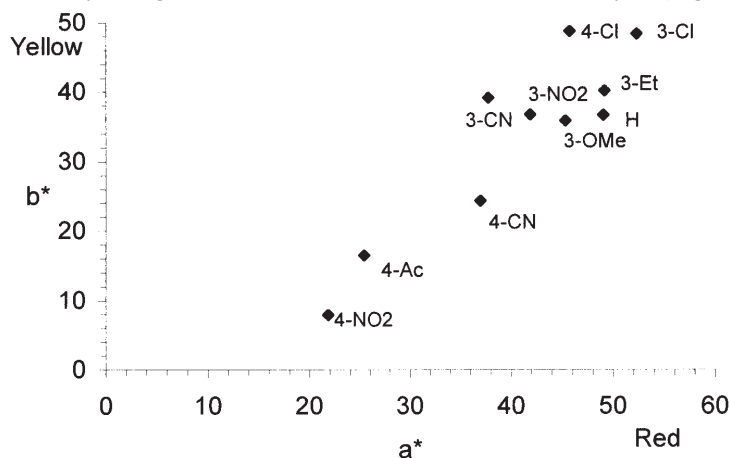


Fig. 3. CIELAB coordinates (a^* , b^*) of the synthesized dyes in the solid form.

TABLE IV. CIELAB coordinates of the synthesized dyes in the solid form

Dye No.	L^*	a^*	b^*	C^*	h
1	52.15	49.07	36.71	61.28	36.80
2	52.36	49.17	40.17	63.49	39.25
3	50.16	45.33	35.83	57.78	38.32
4	66.66	45.74	48.73	66.83	46.81
5	57.28	52.29	48.36	71.23	42.76
6	45.45	25.40	16.47	30.27	32.96
7	58.43	37.74	39.10	52.31	48.38
8	45.35	36.96	24.31	44.24	33.34
9	51.71	41.89	36.76	55.74	41.27
10	40.68	21.82	7.90	23.21	19.91

Colour of dyed polyester fabric. The CIELAB coordinates of the synthesized pyridone dyes on polyester fabric are shown in Table V. The hue values (h^*) range from 80.00 to 88.38, indicating the yellow colour of all the investigated dyes. The variation of substituents insignificantly affects the lightness of the dyes on polyester fabric. However, dyes with a $-Cl$ group in the meta or para position, which show darker and lighter colour, respectively, are exceptions. The chroma values (C^*) of dyes with substituents in the para position are considerably lower compared to the other dyes. In addition, consideration of the a^* and b^* parameters revealed that groups in para position imply a less yellow colour. The parameter a^* increased in the following order: 4-CN > 4-NO₂ > 4-Ac > 4-Cl, indicating a redder colour of the dyed polyester fabrics. It can be observed in Fig. 4 that the points corresponding to dyes with substituents in the meta position are quite scattered, showing a significant increase of the b^* parameter compared to dyes with substituents in para position on polyester fabrics. However, most of the dyes with substituents in meta position are similarly coloured, *i.e.*, the a^* and b^* parameters are in the narrow range from 4.14–4.91 and 42.94–52.46, respectively. The exceptions are dyes with 3-Cl and 3-Et groups which are more yellow and particularly more red in comparison with all the other investigated dyes.

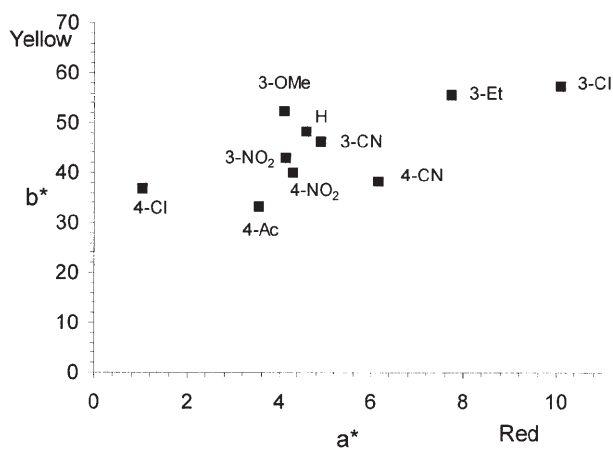


Fig. 4. CIELAB coordinates (a^* , b^*) of the synthesized dyes on polyester fabric.

TABLE V. CIELAB coordinates of the synthesized dyes on polyester fabric

Dye No.	L^*	a^*	b^*	C^*	h
1	83.66	4.59	48.38	48.60	84.57
2	82.37	7.74	55.73	56.26	82.09
3	82.74	4.10	52.46	52.62	85.53
4	86.44	1.04	36.82	36.83	88.38
5	81.07	10.10	57.28	58.16	80.00
6	84.77	3.55	33.19	33.38	83.90

TABLE V. Continued

Dye No.	L^*	a^*	b^*	C^*	h
7	83.51	4.91	46.27	46.53	83.94
8	83.67	6.16	38.11	38.61	80.81
9	84.23	4.14	42.94	43.13	84.49
10	83.80	4.28	40.06	40.29	83.90

CONCLUSION

Eight new 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones were synthesized by a modified procedure, starting from acetylacetone and an arenediazonium salt which was then followed by condensation with cyanoacetamide, in very good yields and excellent purities.

These dyes exist in the 2-hydroxypyridine tautomeric form in the solid state and in the solvent DMSO- d_6 . The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence which did not show a regular variation with the dielectric constant of the solvent. The results show that the 2-pyridone form of 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones exists in methanol, ethanol, dioxane and chloroform, while in solvents of high basicities and high relative permittivity (DMF and DMSO) the dyes predominantly exist in the hydroxy form. These dyes could be potentially suitable for the dyeing of polyester fabric, giving yellow hues.

EXPERIMENTAL

Equipments

The IR spectra were recorded on a Bomem FTIR spectrophotometer, MB series in the form of KBr pellets. The ^1H NMR spectra were recorded as solutions in DMSO- d_6 using a Varian Gemini-200 instrument, with tetramethylsilane as the internal standard. The mass spectra were recorded on a Micromass Platform II spectrometer. The UV-Vis absorption spectra were taken in the region between 200–600 nm using a Secoman Anthelie 2 Advanced spectrophotometer in 1.00 cm cells at 25 ± 0.1 °C. The HPLC analyses were performed on a Hewlett-Packard 1100 MSD. Dyeing was performed using a Mathis Polycolor P laboratory dyeing machine (Werner Mathis AG, Switzerland). The colour parameters were measured using a Spectraflash SF 300 (Datacolour International, USA).

Materials

All used material were obtained from Fluka and were used without further purification.

Synthesis of 5-(3- and 4-substituted phenylazo)-4,6-dimethyl-3-cyano-2-pyridones

The procedure was taken from ref. 12 and modified: To a solution of acetylacetone (0.01 mol) in 30 ml of ethanol, sodium acetate (3.0 g) was added. The mixture was cooled to 0 °C for 10 min and a cooled solution of arenediazonium chloride (prepared from 0.01 mol of amine and the appropriate quantities of HCl and NaNO_2)¹⁸ was added under stirring. The stirring was continued for one hour after which the solid was collected, washed with 2×10 ml of water and 2×10 ml of ethanol, and dried in the air.

The obtained product (0.01 mol) was dissolved in 30 ml of ethanol and added to a mixture of 0.01 mol of sodium ethoxide and 0.01 mol of cyanoacetamide. A few drops of piperidine were then

added. The mixture was mixed and refluxed at 80 °C for 3 h. The resulting solid product was collected by filtration and washed with 2 × 10 ml of water and 2 × 10 ml ethanol. The obtained crystals were then crystallized from *N,N*-dimethylformamide.

Colour assessment

Solid dyes. The colour parameters of the solid dyes (D65 illumination, 10° observer) were determined using a Spectraflash SF 300 (Datacolour International, USA). The solid dyes were prepared in the form of tablets using a standard IR press.

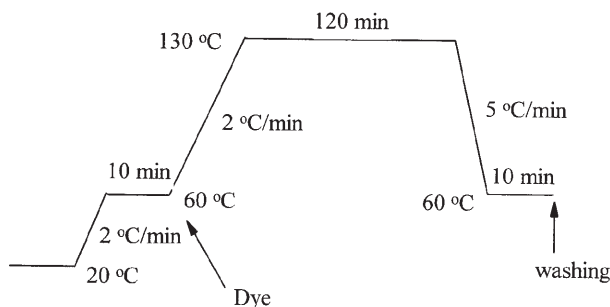


Fig. 5. The employed dyeing profile of polyester fabric.

Dyeing and colour assessment of dyed fabrics. Polyester fabrics were dyed with a 1 % o.w.f. disperse dye in the presence of 0.5 g/L of the levelling agent Egasol SP (Bezema, Switzerland) and 1 g/L of the dispersing agent CHT Dispergator SMS (Bezema, Switzerland). Dyeing was performed in 150 ml stainless steel dye pots using a Mathis Polycolor P (Werner Mathis AG, Switzerland) laboratory dyeing machine, at a liquor-to-material ratio of 20 : 1. The dyeing procedure is shown in Fig. 5. Previously wetted samples were placed in the bath containing the levelling and dispersing agents. The temperature was raised at 2 °C/min to 60 °C, where it was held for 10 min. The dye was then added and the pH of the bath was adjusted to 4 – 5 with acetic acid (10 %). The temperature was then raised at 2 °C/min to 130 °C. After 2 h of dyeing at 130 °C, the solution was rapidly cooled at 5 °C/min to 60 °C. The fabrics were rinsed in cold tap water and washed for 15 min at 80 °C in a bath containing 2 g/L NaDBS and 1 g/L Na₂CO₃ at a liquor-to-material ratio of 50 : 1. Subsequently, the samples were thoroughly rinsed in tap water and dried at room temperature. The colour parameters were measured (D₆₅ illuminant, 10° observer) using a Spectraflash SF 300 (Datacolor International, USA).

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ИЗВОД

СИНТЕЗА, СВОЈСТВА И ОБОЈЕНОСТ НЕКИХ НОВИХ 5-(3- И 4-СУПСТИТУИСАНИХ ФЕНИЛАЗО)-4,6-ДИМЕТИЛ-3-ЦИЈАНО-2-ПИРИДОНА ДУШАН МИЈИН¹, ГОРДАНА УШЋУМЛИЋ¹, НАДА ПЕРИШИЋ-ЈАЊИЋ², ИВАН ТРКУЉА¹, МАЈА РАДЕТИЋ³ И ПЕТАР ЈОВАНЧИЋ³

¹Каџедрa за орґанску хемију, Технолошко-мeјталуршки факултeтeй, Београд, ²Каџедрa за хемију, Природно-математички факултeтeй, Нови Сад и ³Каџедрa за тeкстeилно инжeњерсџиво, Технолошко-мeјталуршки факултeтeй, Београд

У оквиру рада синтетисани су 5-(3- и 4-супституисани фенилазо)-4,6-диметил-3-цијано-2-пиридини, кондензацијом производа реакције ацетилацетона и одговарајуће диазонијумове соли са цијаноацетамидом. Добијене азо боје су окарактерисане темпе-

ратурама топљења, IR, UV/Vis, ¹H NMR и MS подацима. Чистоћа добијених боја испитивана је HPLC методом. Утврђено је да равнотежа 2-хидроксипиридин/2-пиридон зависи од поларности растварача. Одређени су параметри обојења полиестарских тканина бојених синтетисаним азо бојама. Такође је испитивана и обојеност азо боја у чврстом облику.

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