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Article

Synthesis, Characterization, Absorption and Fastness Properties of Novel Monoazo Dyes Derived from 1-Phenyl-3-amino-4-(2-thiazolilazo)pyrazol-5-one

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Monosubstitute thiazolyl amines were diazotized in acetic acid, coupled to 1-phenyl-3-aminopyrazol-5-one (**1a**-**1c**) and acetylated to obtain the **2a**-**2c** dyes. The dyes were characterized by elemental analysis and spectroscopic (Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), ultraviolet (UV)) methods. The effects on the visible absorption spectra of the substituents present, solvents, pH, concentration and temperature were investigated in detail. Tautomerism of the dyes were investigated by spectroscopic methods. Fastness properties of dyes were studied using the standard method for the assessment of color fastness of textile.

Keywords: hetarylazopyrazolone, substituent effect, tautomerism, fastness

Introduction

Azo dyes are most widely used to dye polyester due to versatility. Among these azo dyes, heterocyclic moieties, e.g., pyrazolone, indole, pyrimidine, imidazole, pyridone, quinolone, coumarin, etc., provide higher tinctorial strength and brighter texture as compared to dyes based on phenylic components.[1-5]

Hetarylazo dyes based on heterocyclic diazo and coupling components have been attracted the attention of scientists in recent years.[6-12] Among these, the hetarylazopyrazolone dyes have high fluorescence, high quantum yield, superior photostability in the visible region, excellent fastness properties,[13-16] tautomeric structures[6,7,10,17] in addition to their bathochromic effects in the absorption spectra.[6,7,10,17] The absorption and emission properties of the pyrazolones can be tuned according to the properties of the solvent, especially where electron-withdrawing and electron-donating substituents are attached at the 1, 3 and 4-positions of pyrazolone ring. These pyrazolones have shown numerous properties such as non-linear optical chromophores, optical brighteners, as well as being used in solar cells,[18,19] laser printing systems, laser optical recording systems.[12,20] Some of the pyrazolones were found as biologically active and acted as medicine.[21,22]

2-Aminothiazoles are widely used in the dye industry as a coupling and diazo components in addition to their important pharmacological and biological activities.[23,24] Hetarylazo disperse dyes obtained from the coupling of heterocyclic diazo components have shown better rubbing, light and washing fastnesses properties than carbocyclic components.[25-27]

Herein we report the synthesis and derivatization of 3-amino-1-phenyl-4-(2-thiazolilazo)pyrazol-5-one (dyes **1a**-**1c**) and 3-acetamido-1-phenyl-4-(2-thiazolilazo) pyrazol-5-one (dyes **2a**-**2c**) (Scheme 1). Synthesized dyes were characterized by elemental analysis, Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) spectroscopies. The influence of substituent, solvents, pH, concentration, and temperature on their visible absorption spectra were also investigated. Tautomerism of the synthesized dyes were investigated using spectroscopic methods. Fastness properties of dyes were obtained by standard method that has been used for the color fastness of textiles. This study also contributes to the physical, spectral and tautomeric properties of hetarylazopyrazolones. In addition, the effect of oxochrome $-NH_2$ (dyes **1a**-**1c**) and chromophor $-NH-CO-CH_3$ (dyes **2a**-**2c**) substituents at the 3-position of pyrazolone ring, electron withdrawing $-NO_2$ and electron donating $-CH_3$ substituents on the thiazol ring were also investigated on the color fastness (washing, rubbing, light fastness and increase/diversify the color range) of the novel hetarylazopyrazolone dyes (Scheme 1).

Experimental

General

Reagents/reactants were either bought from Sigma-Aldrich Chemical Company (St. Louis, USA) or Merck

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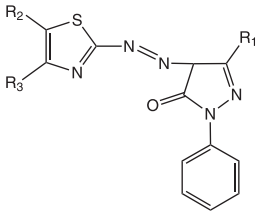
Dye	Substituents		
1a	R_1=NH_2	R_2=H	R_3=H
1b	R_1=NH_2	R_2=H	R_3=CH_3
1c	R_1=NH_2	R_2=NO_2	R_3=H
2a	R_1=NH-CO-CH_3	R_2=H	R_3=H
2b	R_1=NH-CO-CH_3	R_2=H	R_3=CH_3
2c	R_1=NH-CO-CH_3	R_2=NO_2	R_3=H



Scheme 1. The molecule formulas of the dyes.

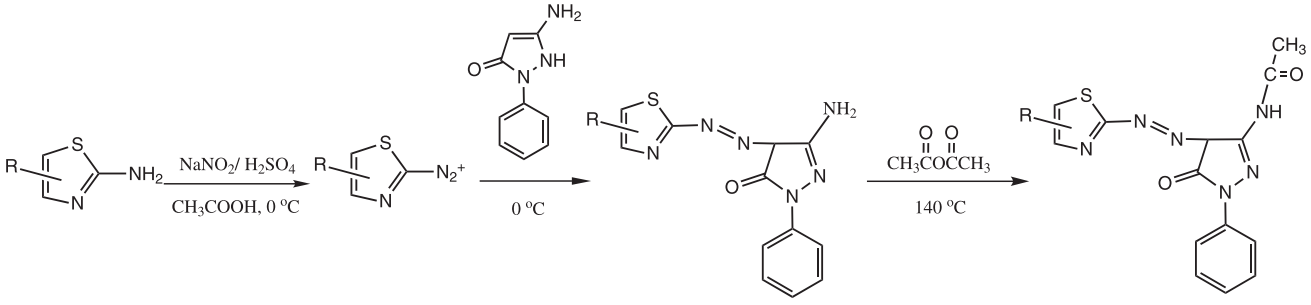
Chemical Company (Darmstadt, Germany) and used without further purification. The solvents used were of high-performance liquid chromatography (HPLC) grade. FTIR spectra were determined on a KBr disc using a MATTSON 1000 spectrophotometer Fourier Transform-Infrared (FT-IR). ^{1}H NMR spectra were recorded on a Bruker-Spectrospin Avance DTX 400 Ultra-Shield in deuterated dimethyl sulfoxide (DMSO-d_6) using trimethylsilane (TMS) as an internal standard; chemical shifts (δ) are given in ppm. Ultraviolet (UV) absorption spectra were recorded in various solvents, i.e., dimethylsulfoxide (DMSO, Merck, Darmstadt, Germany), dimethylformamide (DMF, Merck, Darmstadt, Germany), acetonitrile (Sigma-Aldrich, St. Louis, USA), methanol (Merck, Darmstadt, Germany), acetic acid (Sigma-Aldrich, St. Louis, USA) and chloroform (Merck, Darmstadt, Germany) using a ATI (UK) UNICAM UV2-100 Ultraviolet-Visible (UV-Vis) spectrophotometer. Change in λ_{max} (nm) was investigated when 0.1 mL piperidine (Merck, Darmstadt, Germany) and 0.1 mL (0.1 mol L^{-1}) trifluoroacetic acid (TFAA, Sigma-Aldrich, St. Louis, USA) were added to 1 mL dye solutions in chloroform (Merck, Darmstadt, Germany). Similarly, 0.1 mL potassiumhydroxide (KOH, Sigma-Aldrich, St. Louis, USA, 0.1 mol L^{-1}) or 0.1 mL hydrochloric acid (HCl, Sigma-Aldrich, St. Louis, USA, 0.1 mol L^{-1}) was added to 1 mL dye solutions in methanol (Merck, Darmstadt, Germany). In addition, the λ_{max} of dyes were investigated at variable temperatures and concentrations in DMF (Merck, Darmstadt, Germany). Melting points were measured with a Gallenkamp capillary melting apparatus. The light, washing and the rubbing fastness tests were performed using xenon arc lamp method (ATLAS, West Yorkshire, UK), washing method (ATLAS, West Yorkshire, UK) and crock meter method (ATLAS, West Yorkshire, UK, staining of cotton rubbing fabric), respectively.

Synthesis

Hetarylazopyrazolone dyes (**1a**-**1c**) were prepared by the coupling 3-amino-1-phenyl-2-pyrazolin-5-one with diazotized 2-thiazolyl amines in acetic acid. The dyes **2a**-**2c** (Scheme 1) were synthesized by acetylation of (**1a**-**1c**) dyes (Scheme 2). Table 1 shows physical properties of the dyes.

Synthesis of 1-phenyl-3-amino-4-(2-thiazolilazo)pyrazol-5-one (**1a**)

2-Aminothiazole (Merck, Darmstadt, Germany, 4 mmol,



Scheme 2. The synthetic route of the dyes.

Table 1. Physical properties and characterization data of the synthesized dyes

Dye	Molecular formula	Appearance	Crystallization solvent	Melting point / °C	Yield / %	C / %		H / %		N / %		S / %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1a	$C_{12}H_{10}ON_6S$	brown	acetic acid/water	218-220	87	50.35	50.06	3.49	3.56	29.37	29.14	11.18	11.34
1b	$C_{13}H_{12}ON_6S$	brown	acetic acid/water	240-242	82	52.03	51.67	4.00	4.01	28.00	27.72	10.66	10.41
1c	$C_{12}H_9O_3N_7S$	dark brown	chloroform/hexane	262-263	61	43.50	43.12	2.71	2.96	29.60	30.05	9.66	9.33
2a	$C_{14}H_{12}O_2N_6S$	dark brown	toluene	244-245	75	51.22	50.97	3.65	3.53	25.60	24.85	9.75	8.93
2b	$C_{15}H_{14}O_2N_6S$	dark brown	chloroform/hexane	250-252	77	52.63	52.11	4.09	3.92	24.56	23.89	9.35	8.78
2c	$C_{14}H_{11}O_4N_7S$	dark brown	toluene	273-275	75	45.04	45.48	2.94	2.61	26.27	25.87	8.57	8.12

404 mg) was dissolved in icy acetic acid (5 mL) and cooled to 0 °C in ice-salt bath. Nitrosyl sulfuric acid prepared with dissolving sodium nitrite (Merck, Darmstadt, Germany, 4 mmol, 304 mg) in sulfuric acid (Sigma-Aldrich, St. Louis, USA, 5.5 mL) was dropwise added into the heterocyclic amine during 30 min at 0 °C. The mixture was stirred while cold for additional 2 h. 1-Phenyl-3-aminopyrazol-5-one (Merck, Darmstadt, Germany, 4 mmol, 697 mg) and KOH (500 mg) were dissolved in water (10 mL) and cooled to 0 °C. The prepared diazonium solution was added into the reaction mixture in 30 min and stirred for additional 2 h at 0 °C. The product was precipitated out by adding dilute KOH, filtered, washed with water and air dried. Recrystallization was performed in acetic acid:water mixture (v/v) to obtain the pure brown compound with 87% yield (3.48 mmol, 995 mg), mp 218-220 °C.

The dyes **1b** and **1c** were synthesized similarly to synthesis of dye **1a**. Dye **1b** was obtained with 82% yield (3.28 mmol, 984 mg), mp 240-242 °C. Dye **1c** was synthesized with 61% yield (2.44 mmol, 808 mg), mp 262-263 °C.

Synthesis of 1-phenyl-3-acetamido-4-(2-thiazolilazo) pyrazol-5-one (**2a**)

1-Phenyl-3-amino-4-(2-thiazolilazo)pyrazol-5-one (**1a**) (2 mmol, 572 mg) and acetic anhydride (Sigma-Aldrich, St. Louis, USA, 2 mmol, 8 mL) mixture was refluxed for 5 h.[28] The mixture was added into water (200 mL) to precipitate the product at room temperature and boiled for 10 min. The product was filtered, washed with water and air dried. Recrystallization was performed in toluene (Merck, Darmstadt, Germany) to give the pure dark brown compound with 75% yield (1.5 mmol, 492 mg), mp 244-245 °C.

The dyes **2b** and **2c** were synthesized similarly to synthesis of dye **1a**. Dye **2b** was obtained with 77% yield (1.5 mmol, 527 mg), mp 250-252 °C. Dye **2c** was synthesized with 75% yield (1.5 mmol, 560 mg), mp 273-275 °C.

Dyeing method

Polyester fabric was dyed according to the carrier dyeing method in the laboratory. The carrier swells the polyester fibers, increasing interstitial space to accept more dye molecules into the polymer system.

Dyeing of polyester fabric (4 × 10 cm, 2.5 g) was performed at a liquor ratio of 100:1 and 2% owf (on weight fabric). Carrier (diphenyl, Sigma-Aldrich, St. Louis, USA, 0.5 g), dispersing agent (Sera Sperse M-15, DyeStar, Singapore, 0.25 g), ammonium sulfate ($(NH_4)_2SO_4$, Merck, Darmstadt, Germany, 0.25 g) and acetic acid (pH 5) were added into the bath (250 mL) at 40 °C. After 15 min, dye (0.05 g) was added into the bath. Once the fabric was introduced into the bath, the temperature was slowly raised up to 90 °C. After 60 min, the dye bath was cooled down to 40 °C (Figure 1).

The dyed fabric was taken out of the bath and thoroughly washed with cold then hot distilled water. Reduction cleaning was done with 1% soup solution at boiling temperature for 15 min to improve the wash fastness. The fabric was again rinsed with distilled water and dried in the air.

Assessment of fastness

The light, washing and rubbing fastness tests were carried out according to the ISO 105-B04,[29] ISO 105-C06[30] and ISO 105-X12[31] (staining of cotton rubbing fabric). The light fastness tests were determined using the international blue scale (1-8), the rubbing and washing fastness tests were determined using the international grey scale (1-5), where the maximum was ranked the best while least was the inferior.[32,33]

Results and Discussion

Structure

FTIR (KBr, ν, in cm^{-1}) spectra of all dyes showed a carbonyl band at 1664-1677 cm^{-1}, NH_2 and –NH of hydrazo form band at 3397-3467 cm^{-1}. These values suggest that all dyes are in keto-hydrazo form (T_2) in solid state.[2,3,6,8,12,17,34]

The ^{1}H NMR (δ in ppm) spectra of all the synthesized dyes were measured in DMSO-d_6. The dyes showed broad singlet peaks at 5.75-6.60 ppm (–NH_2: **1a**-**1c**) and

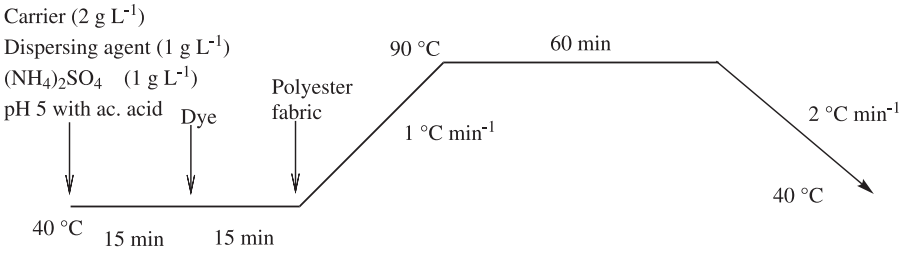


Figure 1. Disperse dyeing procedure used for polyester.

7.80-9.20 ppm (acetamido NH: **2a**-**2c**), two doublets at 7.70-8.40 ppm (thiazole ring: **1a** and **2a**), singlet at 8.00-8.50 ppm (monosubstitute thiazole ring: **1b**, **1c**, **2b** and **2c**), singlet, double and multiplets at 6.75-8.00 ppm (phenyl ring), a singlet at 2.75-2.80 ppm (thiazole $-CH_3$: **1b** and **2b**), a singlet at 3.10-3.80 ppm (acetamido CH_3: **2a**-**2c**) and a singlet at 12.30-14.40 ppm (hydrazo –NH protons: all dyes, except **2a** and **2b**). The ^{1}H NMR spectra of dyes **2a** and **2b** showed neither –NH proton of hydrazo nor the –OH proton of enol tautomer. These results suggest that dyes **1a**-**1c** and **2c** may be in keto-hydrazo form (T_2) while **2a** and **2b** may be in an anionic form (A_1) in DMSO.[8,17,34]

FTIR and ^{1}H NMR spectral data of the dyes are shown in Table 2.

Tautomerism

Tautomerism is important not only for chemical properties, but also for different properties as colors and fastness properties. For this reason, the possible tautomeric forms of examined dyes were evaluated in detail. The possible tautomeric forms of the dyes (T_1-T_6) are shown in Scheme 3.

The synthesized new dyes may exist in five possible tautomeric forms, i.e., keto-azo (T_1 and T_5), keto-hydrazo (T_2 and T_4) and enol-azo (T_3). According to the calculation results in the literature,[17,35-40] the most stable tautomeric form is keto-hydrazo form (T_2) for hetarylazopyrazolone dyes. This conclusion may occur from the intramolecular O–H bond.

Solvent effects

The absorption spectra of the synthesized dyes were measured in a range of 10^{-6}-10^{-8} mol L^{-1} in various solvents. The dielectric constants of the solvents were found in the following order: chloroform ($CHCl_3$) > acetic acid > methanol > acetonitrile > DMF > DMSO. Experimental λ_{max} values of dyes are listed in Table 3.

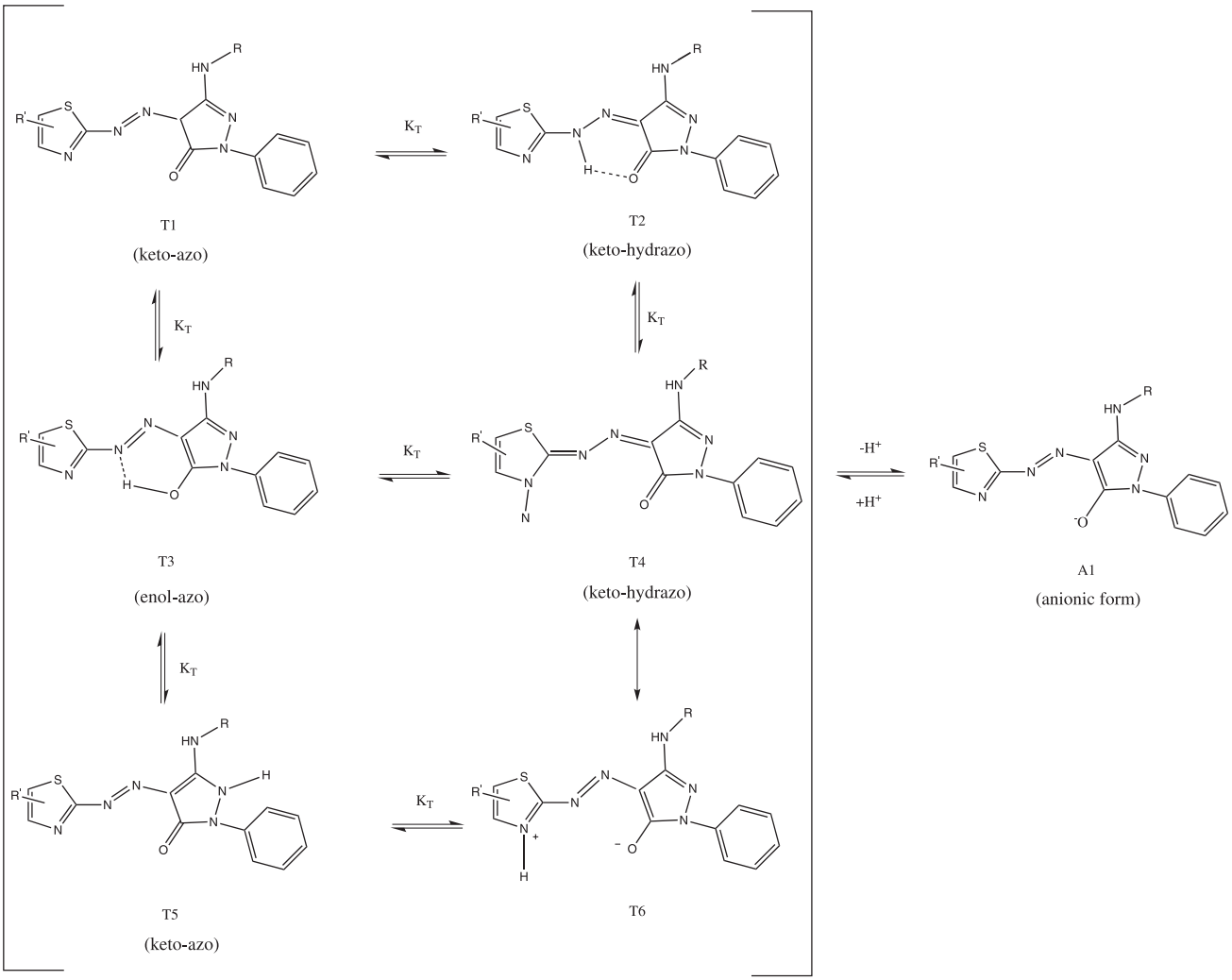
The absorption spectra of **1a**, **1b**, **2a** and **2b** showed only one λ_{max} in all solvents. Additionally, **1a** and **1b** showed a shoulder at shorter wavelength in methanol, DMF and methanol, DMF, DMSO while **2a** and **2b** showed it at shorter wavelength in chloroform only. These shoulders indicate the interchange of tautomeric or anionic forms in these solvents. These results as well as ^{1}H NMR data suggests that **1a** and **1b** may be in keto-hydrazo (T_2) and anionic form (A_1) in methanol, DMSO and DMF while **2a** and **2b** may be in the keto-hydrazo (T_4) and keto-azo form (T_1 or T_5) in chloroform while in the remaining solvents, these dyes may exist in only one tautomeric or ionic form.

Dyes **1c** and **2c** showed two maxima in chloroform, methanol, acetonitrile, DMF and DMSO which may have arisen either from the mixture of tautomeric forms or a mixture of a tautomeric and anionic form.[7,35] ^{1}H NMR data of these dyes suggest that **1c** and **2c** may be in the keto-hydrazo (T_2) and anionic form (A_1) or may be in the keto-hydrazo (T_4) and one of keto-azo forms (T_1 or T_5) in all solvents, except acetic acid. All the synthesized dyes have one maximum that may belong to the cationic form in acetic acid (one of C_1-C_6, Scheme 4).

Table 2. Spectral data for the dyes

Dye	^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm	FTIR (KBr) ν / cm^{-1}
1a	6.65 (s, 2H, NH_2), 7.00 (s, 1H, ph), 7.25 (m, 2H, ph), 7.50 (m, 2H, ph), 7.75 (d, 1H, *J* 8.0 Hz, th), 8.05 (d, 1H, *J* 8.0 Hz, th), 12.30 (s, 1H, hyd NH)	3397 (hyd NH), 3307, 3234 (NH_2), 3184, 3082 (Ar CH), 1664 (k C=O), 1592, 1503 (C=N, C=C)
1b	2.75 (s, 3H, th CH_3), 6.50 (s, 2H, NH_2), 6.75 (s, 1H, ph), 7.00 (m, 1H, ph), 7.25 (m, 1H, ph), 7.50 (m, 2H, ph), 8.10 (s, 1H, th), 13.90 (s, 1H, hyd NH)	3423 (hyd NH), 3319, 3249 (NH_2), 3185 (Ar C–H), 2922, 2830 (Al C–H), 1669 (k C=O), 1599, 1545, 1499 (C=N, C=C)
1c	5.75 (s, 2H, NH_2), 7.00 (m, 1H, ph), 7.25 (m, 2H, ph), 7.75 (s, 1H, th), 8.45 (s, 1H, ph), 8.55 (s, 1H, ph), 13.75 (s, 1H, hyd NH)	3467 (hyd NH), 3352, 3275 (NH_2), 3133, 3070 (Ar CH), 1676 (k C=O), 1592, 1548, 1471 (C=N, C=C)
2a	3.10 (s, 3H, ac CH_3), 7.30 (m, 1H, ph), 7.50 (m, 2H, ph), 8.05 (m, 2H, ph), 8.20 (d, 1H, *J* 8.0 Hz, th), 8.40 (d, 1H, *J* 8.0 Hz, th), 9.25 (s, 1H, ac NH)	3442 (ac NH), 3184, 3082 (Ar C–H), 2844 (Al C–H), 1720 (ac C=O), 1664 (k C=O), 1621 (ac NH), 1592, 1503 (C=N, C=C)
2b	2.80 (s, 3H, th CH_3), 3.90 (s, 3H, ac CH_3), 7.20 (m, 2H, ph), 7.50 (m, 2H, ph), 7.80 (s, 1H, ac NH), 7.90 (s, 1H, th), 8.05 (d, 1H, *J* 8.0 Hz, ph)	3457 (ac NH), 3082, 2928 (Ar C–H), 2838 (Al C–H), 1669 (ac C=O), 1638 (k C=O), 1604 (ac NH), 1599, 1545, 1499 (C=N, C=C)
2c	3.10 (s, 3H, ac CH_3), 6.80-7.80 (s, m, 5H, ph), 8.10 (s, 1H, th), 8.60 (s, 1H, ac NH), 14.40 (s, 1H, hyd NH)	3473 (ac NH), 3070 (Ar C–H), 2922 (Al C–H), 1720 (ac C=O), 1677 (k C=O), 1626 (ac NH), 1580, 1503, 1470 (C=N, C=C)

NMR: nuclear magnetic resonance; DMSO-d_6: dimethyl sulfoxide; FTIR: Fourier transform infrared spectroscopy; s: singlet; ph: phenyl; m: multiplet; d: doublet; th: thiazole; hyd: hydrazo; Ar: aromatic; k: keto; Al: aliphatic; ac: acetamido.



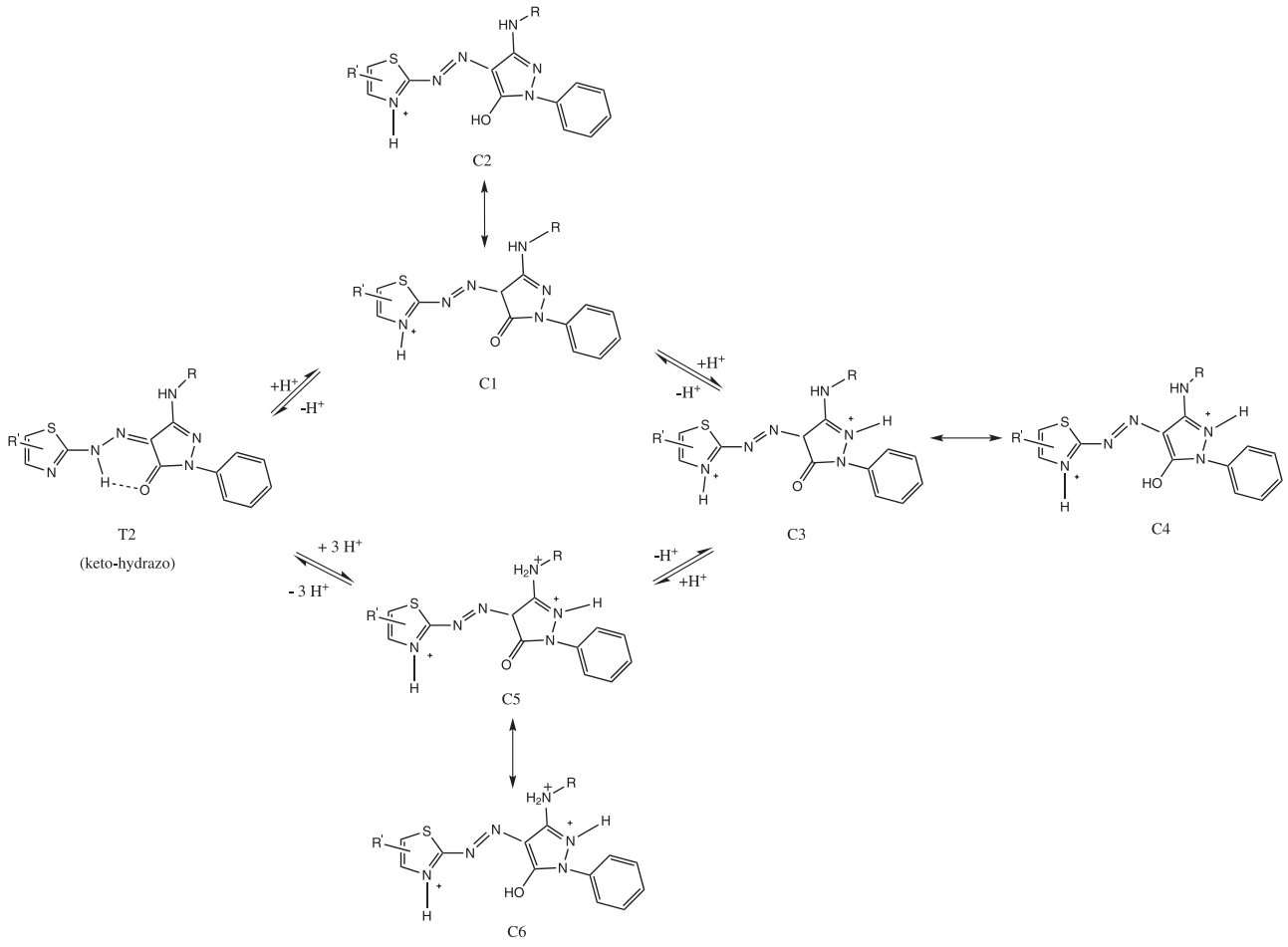
Scheme 3. Tautomeric structures and anionic forms of the dyes (R: –H, –CO–CH_3).

Table 3. λ_{max} values of the dyes

	λ_{max} / nm					
	1a	**1b**	**1c**	**2a**	**2b**	**2c**
Chloroform	394	444	366, 520	313,[a] 480	315,[a] 480	324, 480
Acetic acid	388	401	402	480	480	480
Methanol	380,[a] 424	390,[a] 439	357, 517	440	443	315, 463
Acetonitrile	393	410	366, 534	470	480	324, 480
DMF	390,[a] 437	390,[a] 443	366, 541	462	480	324, 470
DMSO	434	390,[a] 444	366, 540	467	480	324, 470

[a]Shoulder. DMF: dimethylformamide, DMSO: dimethyl sulfoxide.

The absorption maximum of dye **1a** reflected bathochromic shift in methanol, DMSO and DMF as compared to the acetic acid, chloroform and acetonitrile. As an example, **1a** shows a λ_{max} at 388, 394 and 393 nm in acetic acid, chloroform and acetonitrile, respectively, those has shifted to 424, 434 and 437 nm in methanol, DMSO and DMF, respectively (Figure 2).[17] These results indicate that **1a** may be either tautomerizing or ionizing in basic solvents such as methanol, DMSO and DMF. Dye **1b** shifted bathochromically in chloroform (λ_{max}: 444 nm) besides methanol (λ_{max}: 439 nm), DMSO (λ_{max}: 444 nm) and DMF (λ_{max}: 443 nm).[8] The absorbance of



Scheme 4. Possible cationic forms of the dyes (R: –H, –CO–CH_3).

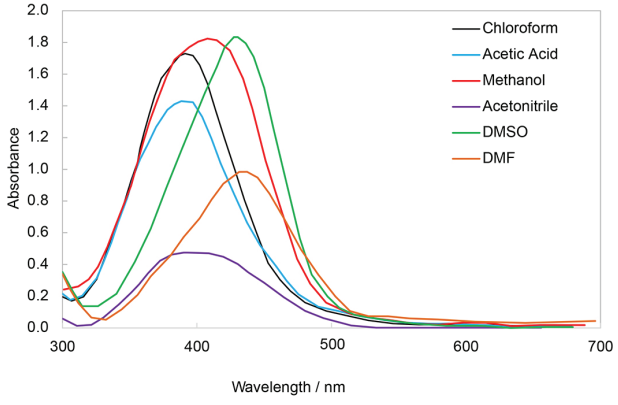


Figure 2. Absorption spectra of dye **1a** in various solvents.

dye **1c** showed two maxima in all solvents (λ_{max1}: 357, 366 nm, λ_{max2}: 517-541 nm), except acetic acid. Dye **2a** provided bathochromic shift in chloroform, acetic acid, and acetonitrile (480, 480, 470 nm), and hypsochromic shift in methanol, DMF and DMSO (440, 462, 467 nm) unlike **1a**. The λ_{max2} of **2c** were similar to that of **2a** in all solvents and λ_{max1} of **2c** were observed at 315 or 324 nm in all solvents, except acetic acid. Dye **2b** showed an absorbance at 480 nm in chloroform, acetic acid, acetonitrile, DMF and DMSO, whereas the λ_{max} value was changed to 443 nm in methanol. These findings indicate a 43 nm difference in the absorbance from DMF towards chloroform (dye **1a**).

These results reflect that the absorption behaviors of the synthesized dyes are not related to the polarity of solvents but instead to the proton-donor and acceptor properties of solvents,[41] which reinforces the ionization rather than tautomerism. To confirm this thesis, the effect of acid and base was also investigated on the absorbance. Absorbances of the synthesized dye solutions in methanol (HCl and KOH) and chloroform (trifloroacetic acid (TFAA) and piperidine) are provided in Table 4.

The absorbance peaks of **1a**-**1c** were more sensitive to acid in both chloroform and methanol. As an example, λ_{max} of **1a** shifted +55 and +23 nm in chloroform + TFAA and methanol + HCl, respectively, while it shifted +49 and +10 nm in chloroform + piperidine and methanol + KOH, respectively (Figure 3). Absorbances of **1b** and **1c** changed insignificantly when basic solution was added to their solutions in both chloroform and methanol as compared to **1a**. Dye **1b** displayed slight bathochromic shifts in the λ_{max}, i.e., +4 and

Table 4. λ_{max} values of dyes in acidic and basic solutions

Dye	λ_{max} / nm					
	$CHCl_3$	$CHCl_3$ + TFAA	$CHCl_3$ + piperidine	Methanol	Methanol + HCl	Methanol + KOH
1a	394	380,[a] 449	380,[a] 443	380,[a] 424	380,[a] 447	380,[a] 434
1b	444	390,[a] 456	390,[a] 448	390,[a] 439	390,[a] 458	390,[a] 440
1c	366, 520	401, 472[a]	366, 524	357, 517	411, 470[a]	370, 518
2a	313,[a] 480	395,[a] 457	420,[a] 457	440	400,[a] 448	400,[a] 446
2b	315,[a] 480	395,[a] 462	420,[a] 462	443	400,[a] 456	400,[a] 452
2c	324, 480	395,[a] 460	420,[a] 460	315, 463	400,[a] 478	400,[a] 473

[a]Shoulder. $CHCl_3$: chloroform; TFAA: trifloracetic acid.

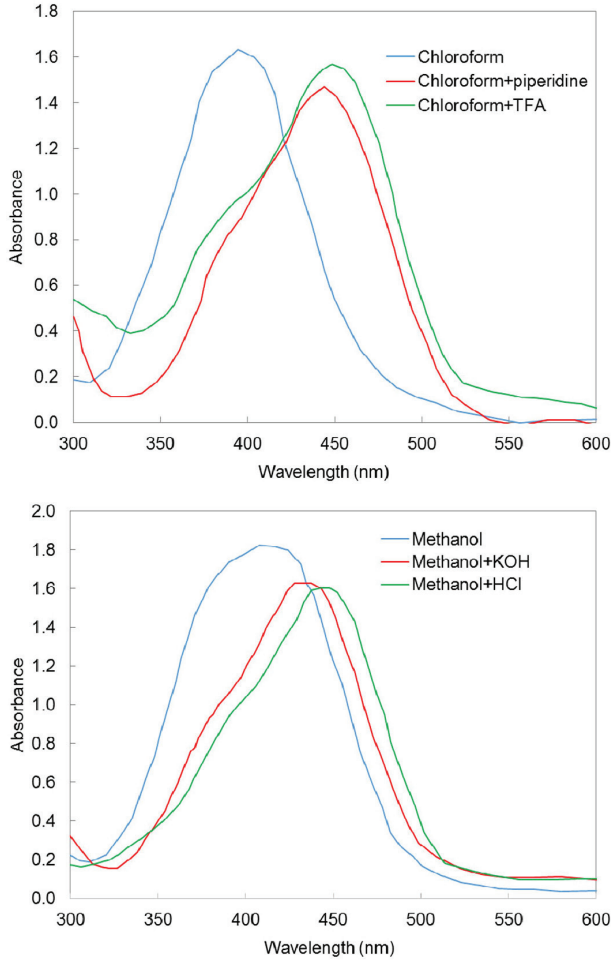


Figure 3. Absorption spectra of dye **1a** in acid and base.

+1 nm in chloroform + piperidine and methanol + KOH, respectively. Additionally, **1a** and **1b** also showed a shoulder at shorter wavelength (at 380 and 390 nm) in all acidic-basic solutions. On the other hand, **1c** shifted +35 and +54 nm in chloroform + TFAA and methanol + HCl while it showed a shoulder at 472 and 470 nm, respectively. However, λ_{max} of the same dye did not change significantly upon addition of piperidine to its chloroform solution or addition of KOH to its methanol solution. These results are similar to the literaure for hetarylazopyrazolones,[6,7,17] hetarylazocalixarenes,[11] hetarylazopyridones,[3,42] hetarylazocoumarines,[9] hetarylazoquinolines[5] and hetarylazoindoles.[10] These results suggest that **1a**-**1c** may be in a mixture of one tautomeric and cationic form in acidic solutions, while they may be in a mixture of one tautomeric and anionic form (A_1) in basic solutions.[8,10]

Dyes **2a**-**2c** showed similar hypsochromic shift (−23 nm for **2a**, −18 nm for **2b**, −20 nm for **2c**) with shoulders at 395 and 420 nm in chloroform + TFAA and chloroform + piperidine, respectively. These values sugget that **2a**-**2c** may be in a mixture of two tautomeric form in both chlorofom solutions. By contrast, the λ_{max} of **2a**-**2c** reflected slight bathochromic shift after the addition of HCl or KOH to their methanol solutions (+8, +6 nm for **2a**, +13, +9 nm for **2b**, +15, +10 nm for **2c** in acidic and basic solutions). Dyes **2a**-**2c** showed a shoulder at 400 nm in both acidic and basic methanol. Thus, these dyes may be in a mixture of tautomeric and cationic form in methanol + HCl, while they may be in a mixture of tautomeric and anionic form (A_1) in methanol + KOH.[8,10]

Absorbances of all the examined dyes in acidic and basic solutions are listed in Table 4, while Table 5 contains the effects of dye concentration and temperature on the absorbance. Results showed that absorbances changed insignificantly with concentration and temperature.

Substituent effects

Absorbance maxima of **1b** (−CH_3 on thiazole ring at 4-position) shifted bathochromically in acetic acid, methanol, acetonitrile, DMF and DMSO (6-17 nm) relative to **1a**.[6,7,8,10,17] This slight change resulted from weak electron donating effect of −CH_3. Highest effect of −CH_3 was observed in least polar solvent, i.e., chloroform (+50 nm).[17] On the other hand, **1c** (−NO_2 group on thiazole ring at 5-position) reflected both hypsochromic and bathochromical shifts in all solvents except acetic acid. The strong electron-accepting substituent (−NO_2

Table 5. λ_{max} values of the dyes in acidic and basic solution

Dye	λ_{max} / nm													
	DMSO (25 °C)		DMF (25 °C)		DMF (80 °C)	Acetonitrile (25 °C)		Methanol (25 °C)		Acetic acid (25 °C)		Chloroform (25 °C)	
	Concd.	Dilute	Concd.	Dilute		Concd.	Dilute	Concd.	Dilute	Concd.	Dilute	Concd.	Dilute
1a	434	434	390,[a] 438	390,[a] 437	380,[a] 438	393	393	380,[a] 424	380,[a] 424	389	388	396	394
1b	390,[a] 444	390,[a] 444	390,[a] 443	390,[a] 443	390,[a] 444	416	410	390,[a] 437	390,[a] 439	400	401	444	444
1c	366, 540	366, 540	366, 541	366, 541	366, 537	366, 533	366, 534	357, 517	357, 517	402	402	366, 520	366, 520
2a	467	467	462	462	462	470	470	440	440	480	480	313,[a] 486	313,[a] 480
2b	480	480	480	480	480	480	480	439	443	480	480	315,[a] 487	310,[a] 480
2c	324, 470	324, 470	324, 470	324, 470	324, 470	324, 480	324, 480	315, 461	315, 463	480	480	320, 480	324, 480

[a]Shoulder. DMSO: dimethyl sulfoxide; DMF: dimethylformamide; Concd.: concentrated.

on thiazole ring of diazo component) showed the highest bathochromical shift in acetonitrile (+141 nm); probably due to resonance stability of the aromatic system.[43]

The λ_{max} of **2b** and **2c** did not change in chloroform and acetic acid as compared to **2a**. The λ_{max} of **2b** and **2c** changed as follows: +3, +20 nm in methanol, +10, +10 nm in acetonitrile, +18, +8 nm in DMF, and +13, +3 nm in DMSO, respectively. Additionally, dye **2c** showed a second peak at 315 or 324 nm in all solvents, except acetic acid. These data indicate that **2a**-**2c**, which were obtained by the acetylation of **1a**-**1c**, are less sensitive to effect of substituent on diazo component from **1a**-**1c**. This conclusion may be related to the weak electron-donating ability of acetylamido group (–NH–CO–CH_3; chromophore group) than amino group (–NH_2; auxochrome group). Acetylation of amino group on coupling component was more effective on the absorbance of **1a**-**1c** from –CH_3 substituent on diazo component. The largest change in the λ_{max} was reflected by **2a**-**2c** in acetic acid as compared to **1a**-**1c**. The λ_{max} values of **1a**-**1c** in acetic acid are: 388, 401, and 402 nm, whereas **2a**-**2c** absorbed at 480 nm in the same solvent. In other solvents, the absorbances of **2a** and **2b** shifted bathocromically in respect to their corresponding dyes **1a** and **1b**. The shoulders at 380, 390 (in methanol, DMF) (**1a**) and 390 nm (in methanol, DMF, DMSO) (**1b**) disappeared while new shoulders appeared at 313 (**2a**) and 315 nm (**2b**) in chloroform. On the other hand, λ_{max} values of **2c** showed larger hypsochromical shifts in all solvents as compared to their corresponding dye **1c**.

Fastness properties of dyes

The colors of dyes on polyester fabric are shown in Figure 4.

Light fastness

The synthesized dyes showed high light fastness performance on polyester fabric (Table 6). The light fastness levels of dyes **2a** and **2c** (5, 3/4) were smaller than their corresponding dyes **1a** and **1c** (6, 3/4-4), however, **1b** and **2b** were similar (5). Thus, the highest light fastness level was found as 6 for dye **1a**, while the least was 3/4 for dye **2c**.

Rubbing fastness

Dyed polyester fabrics (Figure 4) displayed notable dry and wet rub fastness results (Table 6). The highest dry and wet rub fastness value was 5 for **1a** and **1b**, while the least dry and wet rub fastness was 3 for dye **2c**. The dry rub fastness values of **1c**, **2a** and **2b** (4, 5, 4/5) were slightly higher than the wet rub fastness values of same dyes (3/4, 4, 4). In addition, the rub fastness values of **2a**-**2c** (3-acetamidopyrazolone derivatives) in both wet and dry tests were slightly lower than their corresponding dyes **1a**-**1c** (3-aminopyrazolone derivatives) except the dry rub fastness of **2a**. The wet and dry rub fastness of the dyes **1a**-**1c** were 5-5, 5-5, (3/4)-4, dyes **2a**-**2c** showed

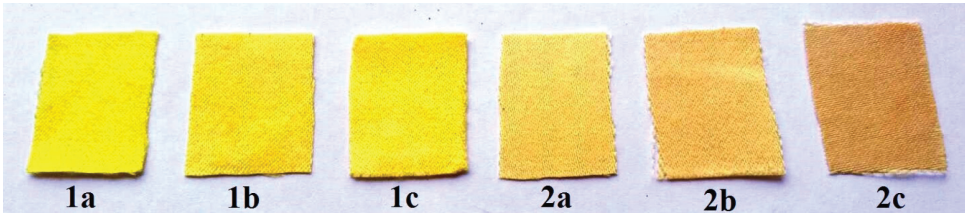


Figure 4. Colors of dyes on polyester fabric.

Table 6. Light and rubbing fastness values of the synthesized dyes

Dye	Color of dye on polyester fabric	Light fastness (ISO 105-B04)[29]	Rubbing fastness (cotton staining) (ISO 105-X12)[31]	
			Wet	Dry
1a	yellow	6	5	5
1b	yellow	5	5	5
1c	yellow	3/4-4	3/4	4
2a	yellow/orange	5	4	5
2b	yellow/orange	5	4	4/5
2c	orange/brown	3/4	3	3

Table 7. Washing fastness values of the synthesized dyes

Dye	Shade change	Multifiber staining (ISO 105:C06)[30]					
		Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
1a	5	5	5	4/5	5	5	4/5
1b	5	5	5	5	5	5	5
1c	4	4	3/4	4	4	3/4	4
2a	4/5	4/5	5	4	4/5	5	4
2b	4/5	4	5	4/5	4	4/5	4
2c	3/4	3	3/4	3	3	3/4	3

4-5, 4-(4/5), 3-3, respectively. On the other hand, dry rub fastness of **1a** and **2a** was found as 5.[32,33]

Washing fastness

The washing fastness shade change values of dyed fibers are commercially acceptable. Especially dyes **1a**, **1b**, **2a**, **2b** exhibited excellent shade change levels (4/5-5) and excellent staining levels (4-5) (Table 7). The best staining levels were found as (4/5)-5 for dyes **1a** and **1b**, whereas the least were provided by (3/4)-4 for **1c** and 3-3/4 for dye **2c**. The washing fastness values of the dyed polyester fabrics are given in Table 7.

Fastness tests results of polyester fabrics dyed with **1a**-**1c** (3-aminopyrazolone derivatives) were generally higher than those of **2a**-**2c** (3-acetamidopyrazolone derivatives). This may have occured due to the stronger binding of amino group ($-NH_2$) with polyester fibers as compared to the binding of acetamido group ($-NH-CO-CH_3$).

Conclusions

Two series of amino- and acetamido-based monoazo dyes were synthesized from 1-phenyl-3-aminopyrazol-5-on and forwarded to their characterization, UV absorption, tautomeric forms and fastness properties. Variation in the absorbance of the synthesized dyes in acidic and basic media showed that they were more sensitive towards acids. The dyes generally demonstrated bathocromic shifts in polar solvents. Nitro-substituted dye (**1c**) showed the highest bathochromic shift in DMSO and DMF. λ_{max} values of the dyes **2a**-**2c** either did not change or changed slightly while the dyes **1a**-**1c** were more sensitive to effect of substituent. In adition, keto-hydrazone (T_2) tautomer of all dyes predominantly existed in both solid state and in solution. The colors of the dyes **2a**-**2c** ($-NH-CO-CH_3$; chromophor) on polyester fabric were darker than colors of dyes **1a**-**1c** ($-NH_2$; oxochrome). This may have occured due to the absorbances of **2a**-**2c** were more bathocromic in respect to their corresponding dyes **1a**-**1c**. Fastness values of the synthesized dyes on polyester fabric demonstrated that the binding of amino group ($-NH_2$) with polyester fibers is stronger than binding of acetilamido group ($-NH-CO-CH_3$). Fastness tests as a whole were satisfactory in comparision with the literature. We suggest to use these compounds in the dye/color industry and to explore their physicochemical and biological properties.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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