Indian Journal of Chemistry
Vol. 65, August 2026, 736-744
DOI: 10.56042/ijc.v65i8.19957

Synthesis, characterization, electronic and fastness properties of novel hetarylazopyrazolones

Fatma Erol

Vocational School of Technical Sciences, Gazi University, Ostim-06374, Ankara, Turkey
E-mail: fnuralin@gazi.edu.tr

Received 22 May 2025; accepted (revised) 8 August 2026

Herein is reported the synthesis, characterization, tautomeric forms, absorbances and color fastness of novel hetarylazopyrazolone-based dyes. Monosubstitued benzothiazolyl amines have been subjected to diazotization in CH_3COOH and bound to 1-phenyl-3-aminopyrazol-5-one (1a-c). The $–NH_2$ (amino) group has been converted to –NH-CO-CH_3 (acetamido) which provides the target dyes (2a-c). The structure of the target dyes have been elucidized using elemental analysis, FT-IR and ^{1}H NMR. The effect of substituent, solvent, *p*H, concentration and temperature have also been studied using electronic spectroscopy. The dyes show tautomerism that have been studied using spectrophotometric techniques. Standard methods have been used to analyze various fastness properties of the prepared dyes to assess the color fastness of textile. Dyes **1a**, **1b**, **2a** and **2b** show one maximum in the tested solvents and these dyes are found to possess excellent fastness.

Keywords: Hetarylazopyrazolone, Solvent effect, Substituent effect, Fastness, Tautomer

Hetarylazo dyes based on heterocyclic diazo compounds possess higher tinctorial strength and dye brightness as compared to aniline-based azo dyes[1-5]. Among these, the hetarylazopyrazolone dyes are more interesting due to their versality applications as nonlinear optical (NLO) chromophores, solar cells and solvatochromic probes[6,7]. Some pyrazolone derivatives show absorption bands in near IR. These dyes are being used in laser printing and laser optical recording systems[8,9]. On the other hand, both benzothiazoles[10,11] and pyrazolones are biologically as well as pharmacologically activite[12-14]. In addition, 2-aminobenzothiazole and it's derivatives are commonly utilized in the coloring field as coupling reagent and and diazo-components. Fastness properties such as light, rubbing and washing of the hetarylazo-dispersed-dyes prepared from the heterocyclic coupling and the heterocyclic diazo components are more beneficial than carbocyclics[15-18]. In addition hetarylazopyrazolone dyes have tautomeric structures[19-21]; they shows bathochromic shift on their absorption spectra[5,19,21].

In this study, we have synthesized 1-phenyl-3-amino-4-(2-benzothiazolilazo)pyrazol-5-one (1a-c) and 1-phenyl-3-acetamido-4-(2-benzothiazolilazo) pyrazol-5-one (2a-c) as shown in Scheme 1. The structure and chemical properties of the synthesized dyes were analyzed dyes were characterised by various techniques including elemental analysis, FT-IR and ^{1}H NMR. The effect of substituent, solvent, acid, base, temperature and concentration on their absorbences were also examined. The prepared dyes can interconvert into tautomers that was analyzed by spectroscopy. Standard procedures for color fastness of textile were used to evaluate the fastness of dyes *i.e*. rubbing, washing, increase/diversify and light fastness.

Experimental Section

General

Chemical reagents and reactants were either bought from Aldrich or Merck. HPLC-grade solvents were used througout the study. ^{1}H and ^{13}C NMR (Bruker-Spectrospin Avance DTX 400 Ultra-Shield) spectra were obtained using in DMSO-d_6 and TMS as an internal standard; chemical shifts (δ) are given in ppm. For FTIR (Mattson 1000 spectrophotometer) analysis, samples were impregnated in potassium bromide discs. Absorption spectra (UNICAM UV2-100 spectro-photometer) were obtained in dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile, methanol, acetic acid and chloroform. Separately, the λ_{max}(nm) of the prepared dyes were investigated at

various temperature and concentrations in dimethylformamide. Variation in the λ_{max} was measured by adding 0.1 mL of piperidine and 0.1 mL (0.1 mol L^{-1}) of trifloroacetic acid (TFAA) to 1 mL dye solutions in chloroform. In a similar way, 0.1 mL base (potassium hydroxide (KOH), 0.1 mol L^{-1}) or 0.1 mL hydrochloric acid ((HCl), 0.1 mol L^{-1}) into 1 mL of the methanolic dye solutions. Melting points were recorded by Gallenkamp capillary melting apparatus.

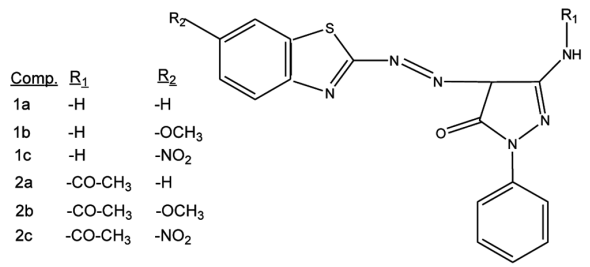
Synthesis

Compounds (1a-c) were prepared by the coupling 3-amino-1-phenyl-2-pyrazolin-5-one
(4 mmol) with diazotized benzothiazolyl amines (4 mmol) in acetic acid and the comp. (2a-c) were synthesized by acetylation of compounds **1a-c**. All Compounds were synthesized as synthesis method in our previous report[22] (Scheme 2).

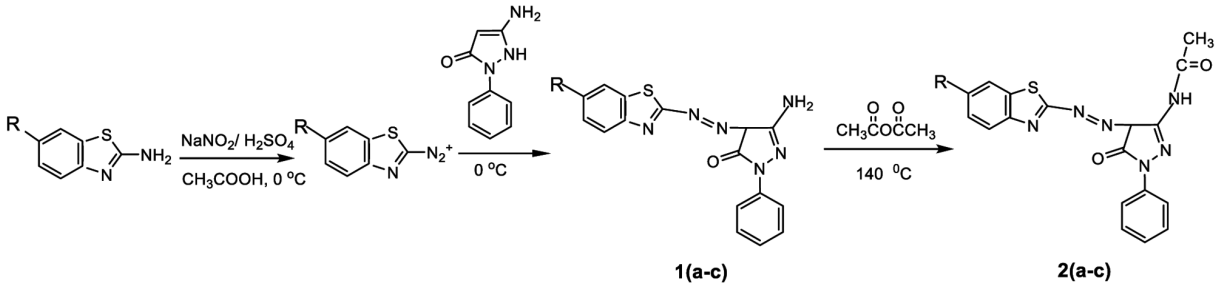
Dyeing Method and Fastness Tests

Polyester fabric (4×10 cm, 2.5 g) was dyed by carrier dyeing method in the laboratory. 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 (*p*H 5) were added into the bath (250 mL) (Fig. 1). Fastness tests were performed according to the ISO standards (Table 1). The rubbing test was performed by the Crock Meter Method (staining of cotton rubbing fabric) while light fastness test was performed by Xenon Arc Lamp Method. The washing fastness test was performed by the washing method of ATLAS, UK. The light fastness tests were evaluated using the international blue scale (1-8), the rubbing and washing fastness tests were determined using the international grey scale (1-5).

The dyeing procedure and fastness tests were performed as described in our previous report[22].



Scheme 1 — The moleculer formula of the dyes



Scheme 2 — The synthetic scheme for preparation of the dyes

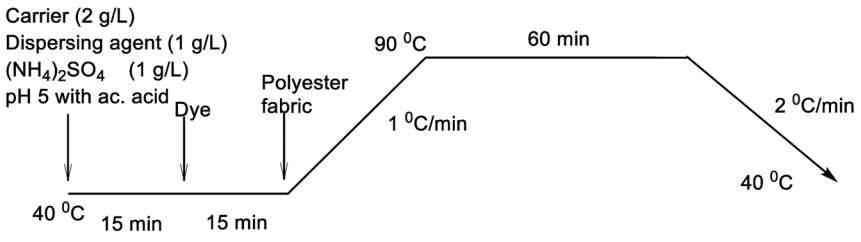


Fig. 1 — Disperse dyeing procedure used to dye for polyester

Results and Discussion

Structure

1-Phenyl-3-amino-4-(2-benzothiazolilazo)pyrazol-5-one, 1a: Brown solid (1.05g, 78% yield), Crist. chloroform-hexane. m.p.209-211°C. FT-IR (KBr): 3435(hyd NH), 3339, 3192(NH), 3063(Ar CH), 1670(k C=O), 1638, 1590, 1491 cm^{-1} (C=N, C=C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.50(s, 2H, -NH_2), 7.00-7.25(m, 5H, ph), 7.30(d, 2H, *J*= 8.0 Hz bth), 7.75(d, 2H, *J* =8.0 Hz bth), 13.75(s, 1H, hyd -NH-). Anal. Found: C, 56.95;

Table 1 — Light, rubbing and washing fastness values of the prepared dyes

Dye	The color of dye on polyester fabric	Light Fastness (ISO105-B04) (Ref. 32)	Rubbing fastness (ISO 105-X12) (Ref. 33) (cotton staining)		Shade change	Washing fastness (ISO 105-C06) (Ref. 34) Multifiber staining					
			Wet	Dry		Acetate	Cotton	Nylon 6.6	Polyester	Acrylic	Wool
1a	Yellow	6	5	5	5	4/5	5	5	5	4/5	5
1b	Yellow	6	4/5	5	5	5	4/5	5	5	5	4/5
1c	Dark Yellow	4	4	4/5	4	3/4	3/4	4	4	4	4
2a	Yellow	5	4/5	5	4/5	4/5	4/5	5	5	4/5	4
2b	Yellow	5	4/5	4/5	4/5	4/5	5	5	4/5	5	4
2c	Dark Yellow	3/4-4	3/4	3/4	3/4	3/4	3/4	4	4	3/4	3

H, 3.81; N, 25.25; S, 9.11. Calcd: C, 57.14; H, 3.57; N, 25.01; S, 9.52%.

1-Phenyl-3-amino-4-(6-methoxy-2-benzothiazolilazo) pyrazol-5-one, 1b: Brown solid (1.35g, 92% yield), Crist. acetic acid-water. m.p.247-249°C. FT-IR (KBr): 3467(hyd NH), 3290, 3281(NH), 3184(Ar CH), 2988, 2933(Al CH), 1666(k C=O), 1636, 1595, 1470 cm^{-1} (C=N, C=C); ^{1}H NMR(400 MHz, DMSO-d_6): δ 3.60 (s, 3H, OCH_3), 6.40(s, 2H, NH_2), 6.80-7.00(m, 4H, ph), 7.25(d, 1H, bth, *J* =8.0 Hz), 7.50(d, 1H, *J* =8.0 Hz bth), 7.75(s, 1H, bth), 13.20(s, 1H, hyd NH). Anal. Found: C, 55.89; H, 3.62; N, 22.91; S, 8.38. Calcd: C, 55.73; H, 3.82; N, 22.95; S, 8.74%.

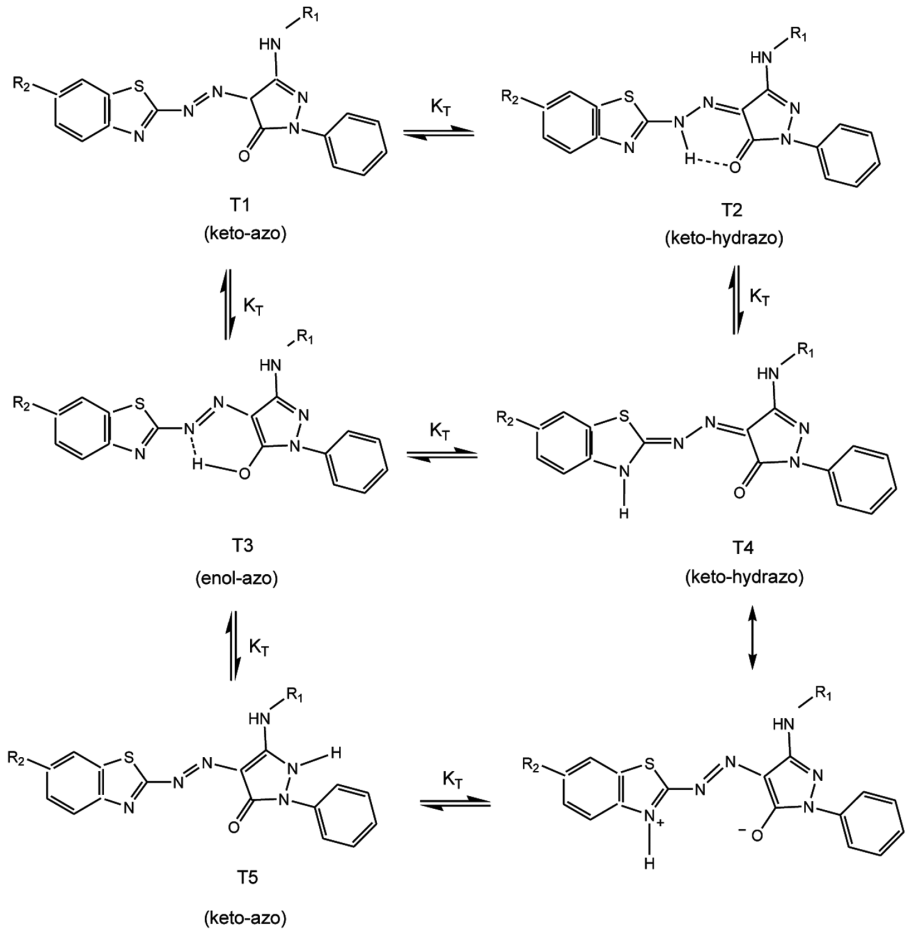
1-Phenyl-3-amino-4-(6-nitro-2-benzothiazolilazo)pyrazol-5-one, 1c: Brown solid (0.93g, 61% yield), Crist. acetic acid-water. m.p.301-302°C. FT-IR (KBr): 3423 (hyd NH), 3389, 3265(NH), 3185, 3070(Ar CH), 1677(k C=O), 1585, 1553, 1503 cm^{-1} (C=N, C=C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.80(s, 2H, NH_2), 7.25-7.45(m, 4H, ph), 7.60(d, 1H, *J* =8.0 Hz, bth), 7.90(s, 1H,bth), 8.00(d, 1H, *J* =8.0 Hz,bth), 14.00(s, 1H, hyd NH). Anal. Found: C, 50.13; H, 3.07; N, 26.05; S, 8.21. Calcd: C, 50.39; H, 2.88; N, 25.72; S, 8.39%.

1-Phenyl-3-acetamido-4-(2-benzothiazolilazo)pyrazol-5-one, 2a: Dark brown solid (1.12g, 74% yield), Crist. chloroform-hexane. m.p.230-232°C. FT-IR (KBr): 3454(hyd NH), 3082(Ar CH), 2938(Al CH), 1718(ac C=O), 1664(k C=O), 1592(ac NH), 1548, 1503 cm^{-1} (C=N, C=C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.10(s, 3H, ac CH_3), 7.30(m, 2H, ph), 7.55(m, 4H, ph), 8.05(d, 2H, *J* =8.0 Hz, bth), 8.20(d, 1H, *J*= 8.0 Hz, bth), 8.40(d, 1H, *J* =8.0 Hz bth), 9.25(s, 1H, ac-NH). Anal. Found: C, 57.56; H, 3.37; N, 22.65; S, 7.93. Calcd: C, 57.14; H, 3.70; N, 22.22; S, 8.46%.

1-Phenyl-3-acetamido-4-(6-methoxy-2-benzothiazolilazo)pyrazol-5-one, 2b: Dark brown solid (1.32g, 81% yield), Crist. toluene-hexane. m.p.262-263°C. FT-IR (KBr): 3469(hyd NH), 3070, 2998(Ar CH), 2935, 2844(Al CH), 1703(ac C=O), 1644(k C=O), 1595(ac NH), 1533, 1470 cm^{-1} (C=N, C=C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.90(s, 3H, ac CH_3), 3.90(s, 3H, OCH_3), 7.10(m, 2H, ph), 7.20(m, 2H, ph), 7.40(d, 1H, *J*= 8.0 Hz, bth), 7.75(s, 1H, bth), 7.90(s, 1H, ac-NH), 8.10(d, 1H, *J* =8.0 Hz, bth). Anal. Found: C, 56.23; H, 3.59; N, 23.02; S, 7.43. Calcd: C, 55.88; H, 3.93; N, 20.58; S, 7.84%.

1-Phenyl-3-acetamido-4-(6-nitro-2-benzothiazolilazo)pyrazol-5-one, 2c: Dark brown solid (1.05g, 62% yield), Crist. Toluene. m.p.317-319°C. FT-IR (KBr): 3478(hyd NH), 3070(Ar CH), 2838(Al CH), 1720(ac C=O), 1677(k C=O), 1614(ac NH), 1580, 1503, 1470 cm^{-1} (C=N, C=C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.10(s, 3H, ac CH_3), 7.25(m, 2H, ph), 7.30-7.50(m, 3H, ph), 8.05(s, 1H, bth), 8.20(d, 1H, *J*= 8.0 Hz, bth), 8.40(d, 1H, *J*= 8.0 Hz, bth), 9.25(s, 1H, ac-NH). (s:singlet, m:multiplet, d:doublet, ph:phenyl, bth:benzothiazole, hyd:hydrazo, Ar:aromatic, k:keto, Al:aliphatic, ac:acetamido). Anal. Found: C, 53.45; H, 3.57; N, 20.11; S, 7.23. Calcd: C, 52.81; H, 3.18; N, 20.53; S, 7.82%.

The FT-IR spectra of all compounds showed carbonyl (keto) bands around 1666-1677 cm^{-1}, while -NH bands (hydrazo) around 3423-3467 cm^{-1} (Supplementary Information) which means that all the compounds are in keto-hydrazo form (T2) in their solid state[8,19,20,22-25] (Scheme 3). ^{1}H NMR (400 MHz, DMSO-d_6:δ/ppm) spectra of the comp. (1a-c) showed a singlet at 13.20-14.00 ppm for -NH protons of hydrazo forms, while ^{1}H NMR spectra of the comp. (2a-c) didn't show this band (Supplementary Information). It means that the comp. (1a-c) are in



Scheme 3 — Possible tautomeric forms of the dyes (R_1: –H, –CO-CH_3, R_2: –H, –OCH_3, –NO_2) Solvent Effects

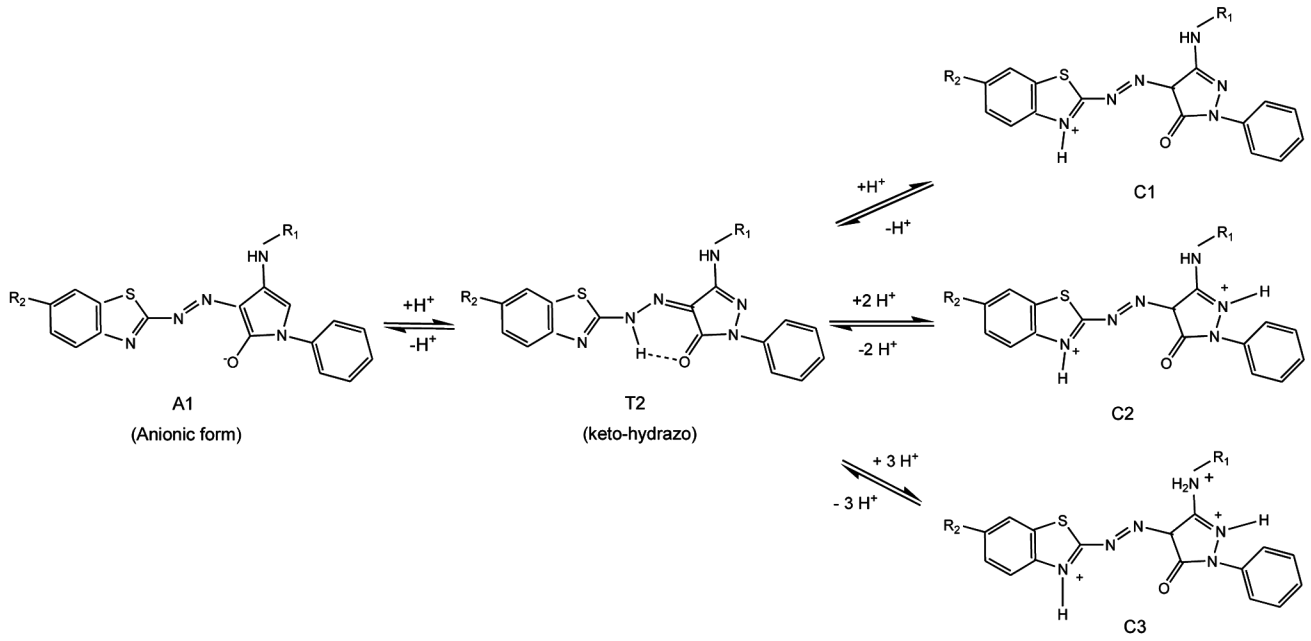
Table 2 — Experimental λ_{max} (nm) values of the dyes in UV-visible region of the spectrum

Solvents	Dyes absorbance (nm)					
	1a	1b	1c	2a	2b	2c
Chloroform	390[s]	450	345	482	330[s]	343
	453		482		482	483
Acetic acid	390	417	388	480	330[s]	340
			480		480	480
Methanol	390[s]	453	352	468	330[s]	331
	436		469		469	480
Acetonitrile	390[s]	440	354	480	330[s]	335
	432		477		480	480
DMF	390[s]	452	358	478	335[s]	343
	448		496		480	484
DMSO	390[s]	444	356	477	335[s]	346
	433		491		480	483

[s]Shoulder, DMSO:dimethyl sulfoxide, DMF:dimethylformamide

keto-hydrazo form (T2), but the comp. (2a-c) are in keto-azo form (T1) in DMSO (Ref. 4,26,27) (Scheme 3).

Absorbances of the synthesized compounds were obtained in various solvents at a concentration of 10^{-6}-10^{-8} mol L^{-1}. Various solvents were used according to their increasing dielectric constants *i.e.* chloroform, acetic acid, methanol, acetonitrile, dimethylformamide and dimethylsulfoxide. Experimental λ_{max} (nm) of the synthesized dyes are provided in Table 2.



Scheme 4 — Anionic and cationic forms of the dyes

Dyes **1a**, **1b** and **2a**, **2b** showed one maximum in the tested solvents. In addition, dye **1a** and **2b** also reflected shoulders at 390 nm (except **1a** in acetic acid) 330 and 335 nm (for **2b**) in all solvents. These shoulders stresses either the interchanging of the tautomeric or the ionic form in these tested solvents. The obtained results, together with the results obtained from the ^{1}H NMR, suggest that dyes **1a** and **2b** are in keto-hydrazo (T2) and anionic form (A1) in methanol, dimethylsulfoxide and dimethylformamide while in keto-hydrazo (T2) and keto-azo form (T1 or T5) in chloroform and acetonitrile. Dye **1a** may occur in form of a single tautomer or one cationic form while **2b** may exist in either a mixture of two tautomeric forms or may be in mixture of one tautomeric and one cationic form in acetic acid (Scheme 4). The dyes **1b** and **2a** existed in one tautomeric or ionic form in all the tested solvents.

Dyes **1c** and **2c** reflected 2 maximum absorbances in all the tested solvents. This may be due to either the presence of both tautomers or a mix of one tautomer and one ionic form[18,21]. Dye **1c** may be existing in the keto-hydrazo (T2) and ionic form (A1) or may be in the keto-hydrazo (T4) and one keto-azo (T1 or T5) while dye **2c** may be in one tautomeric form except keto-hydrazo form (T2) and ionic form or may be in mixture of two tautomeric forms except keto-hydrazo form (T2) in all solvents as suggested by the ^{1}H NMR data.

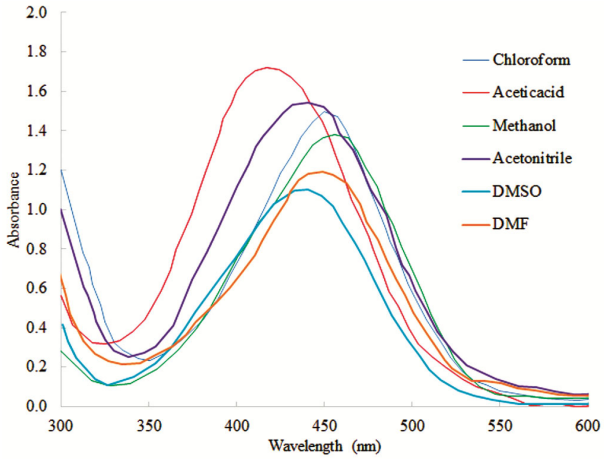


Fig. 2 — Absorbances of dye **1b** in various solvents

The absorbance of **1a** showed bathochromic shift in dimethylformamide (448nm), chloroform (453nm), methanol (436 nm), acetonitrile (432 nm) and dimethylsulfoxide (433 nm) when compared with acetic acid (390 nm). Also, dye **1b** has shorter λ_{max} value in acetic acid (417 nm) compared with the other solvents (440-452 nm) (Fig. 2). The dye **1a** has highest λ_{max} value is in chloroform while the dye **1b** has highest λ_{max} in chloroform, dimethylformamide and methanol *i.e.* 450, 452 and 453 nm, respectively[27].

Dye **1c** showed $2\lambda_{max}$ in all the tested solvents (345-358 and 469-496 nm). Dye **2a** has more bathochromic shift in acetonitrile, acetic acid, and chloroform (482, 480, 480nm). On the other hand, it

Table 3 — λ_{max} (nm) values of dyes in acidic and basic solution

Dye	Chloroform	Chloroform +TFAA[a]	Chloroform +Piperidine	Methanol	Methanol +HCI	Methanol +KOH
1a	390[s] 453	390[s] 456	390[s] 453	390[s] 436	455	390[s] 443
1b	450	486	460	453	477	457
1c	345 482	398 480[s]	345 482	352 469	400 480[s]	352 473
2a	482	443	460	468	480	477
2b	330[s] 482	330[s] 456	343[s] 477	330[s] 469	400[s] 482	430[s] 480
2c	343 483	325[s] 469	343[s] 495	331 480	400[s] 493	430[s] 490

[a]Trifloracetic acid, [s]Shoulder

showed hypsochromic shift in methanol, dimethylformamide and dimethylsulfoxide (469, 478, 477 nm) unlike dye **1a**. Dye **2b** has very similar absorption values in all solvents except methanol and it has one shoulder at 330 or 335 nm in all solvents. Same dye has least λ_{max} *i.e.* 469 nm in methanol showing more bathochromic shift (480-482 nm) in other solvents. The λ_{max} values of dye **2c** were similar to **2b** in all solvents where the second absorbance peak was observed at more shorter λ_{max} (331-346 nm). These findings indicate that the difference between the absorption in most polar dimethylsulfoxide and in the least polar chloroform was 20 nm (dye **1a**).

The obtained results of the synthesised dyes showed no relevance of the absorption behaviours to the polarity of solvent. Rathar, there was some relevance to their proton-donor and proton-acceptour properties. Such effects of these solvents demonstrated that there is ionisation rather than tautomerism[20-22].

The acid/base (HCl/KOH) effect on the absorbances of the synthesized dyes in methanol and chloroform after the addition of trifloroacetic acid or piperidine are given in Table 3.

The absorption curves of dyes (1a-c) were acid-sensitive in both chloroform and methanol as compare to the base. For example, λ_{max} of dye **1b** shifted +36 nm and +24 nm in mixtures of chloroform and TFAA and methanol and HCI.The same dye showed a shift of +10 nm in a mixture of chloroform and piperidine while showed +4 nm shift in methanol and KOH (Fig. 3). These results show a correlation with our previous results[22]. The λ_{max} of dyes **1a** and **1c** did not change in chloroform and piperidine whereas they reflected less shifts *i.e.* +7 and +10 nm in methanol and KOH. Additionally, a shoulder was observed in **1a**

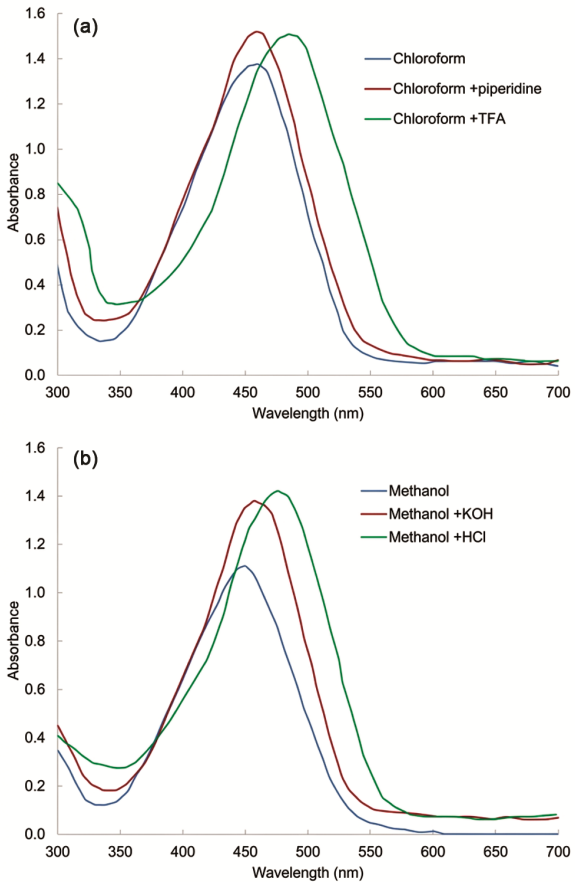


Fig. 3 — Absorbances of dye **1b** in acid and base

at shorter wavelenght (390 nm) in mixtures *i.e.* chloroform and TFAA, chloroform andpiperidine and methanol and KOH; while this should was absent in methanol and HCI solution. Contrarily, **1c** showed +48 and +53 nm shift in solutions of methanol and HCI and chloroform and TFAA, respectively. In the same dye, a shoulder was observed at 480 nm in both acidic solutions. These results are similar to the reports regarding

Table 4 — The λ_{max} (nm) of the prepared dyes at various temperatures and concentrations in various solvents

Dye	DMSO		DMF			Acetonitrile		Methanol		Acetic acit		Chloroform	
	25°C		25°C		80°C	25°C		25°C		25°C		25°C	
	concd.	dilute	concd.	dilute		concd.	dilute	concd.	dilute	concd.	dilute	concd.	dilute
1a	390[s]	390[s]	390[s]	390[s]	390[s]	390[s]	390[s]	390[s]	390[s]	390	389	390[s]	390[s]
	434	433	448	447	448	432	432	436	437			453	453
1b	444	444	452	452	453	440	440	453	453	417	417	450	450
1c	354	354	358	358	358	354	354	352	352	388	388	345	345
	491	492	496	496	494	477	477	469	469	480	480	482	482
2a	477	477	478	478	477	480	480	468	469	480	480	482	482
2b	335[s]	335[s]	335[s]	335[s]	335[s]	330[s]	330[s]	330[s]	330[s]	330[s]	330[s]	330[s]	330[s]
	480	480	480	480	480	480	480	469	469	480	480	482	482
2c	346	346	343	343	343	335	335	331	331	340	340	343	343
	483	483	484	483	483	480	480	480	480	480	480	483	484

[s]Shoulder, DMSO:dimethyl sulfoxide, DMF:dimethylformamide, Concd.:concentrated.

hetarylazopyrazolones[19-22], hetarylazopyridones[25,28], hetarylazocalixarenes[29], hetarylazocoumarines[3] hetarylazoquinolines[30] and hetarylazoindoles[5]. In the light of these results, it can be suggested that dyes **1a** and **1c** may be present as a mix of one tautomer with cationic form (one of the C_1–C_3 form) in acidic solutions (except dye **1a** in methanol and HCl), mix of both tautomers in chloroform and piperidine or one tautomer with an anion (A_1) in methanol and KOH solution. Furthermore, the dye **1b** may be in one cationic form (one of the C_1–C_3 from) in acidic solutions while in anionic form (A_1) in basic solutions[5,25].

The absorption peaks of dyes (2a-c) were more acid-sensitive in both methanol and chloroform. For example, absorption maxima of **2a** showed +12 and –39 nm shift in methanol and HCI and chloroform and TFAA, while in methanol and KOH and chloroform and piperidine, the same dye showed +9 and –22 nm shift, respectively. The λ_{max} of dyes (2a-c) reflected hypsochromic shift in both chloroform and TFAA and chloroform and piperidine solutions (except dye **2c** in chloroform and piperidine). These λ_{max} values are; -39, -22 nm for **2a**, -26, -5nm for **2b**, and -14, +12nm for **2c**. By contrast, the λ_{max} of the same dyes provided slight bathochromic shift when HCI or KOH were added to their methanolic solutions (2a: +12, +9 nm; **2b**: +13, +11 nm; **2c**: +13, +10 nm in acidic/basic methanolic solutions). Dyes **2b** and **2c** reflected shoulders in all acid and basic solutions. These results indicate that **2b** and **2c** may be a mix of one tautomer and cationic form (one of the C_1-C_3) in acidic solution. On the other hand dye **2a** may be in cationic form (one of the C_1-C_3 from) in methanol and HCI, while it may in anionic form (A_1) in methanol and KOH (Ref. 5,25).

Absorbances of all the dyes in acidic and basic media are given in Table 3. Effect of the dye concentration and temperature on the absorbance is provided in Table 4. It is observed that absorbances did not change significantly change with concentration and temperature.

Substituent Effects

Absorption spectra of dye **1b** (-OCH_3 group on benzothiazole ring at 6 position) showed slight bathochromic shift in methanol, acetonitrile, dimethylformamide and dimethylsulfoxide (17, 8, 4 and 11nm, respectively). On the contrary, **1b** reflected slight hypsochromic shift in comparatively less polar solvent *i.e.* chloroform (-3 nm); relative to the dye **1a** (Ref. 5,19-21,27). This slight change was a result of electron donating effect of -OCH_3 group. -OCH_3 group was most effective in the acetic acid (+27 nm). In addition, the shoulder of dye **1a** at 390 nm was not observed in **1b** in all the solvents. Contrarily, **1c** (-NO_2 on benzothiazole ring at position -6) showed higher hypso-bathochromic shifts in all the tested solvents (λ_{max1}: 345-388 nm, λ_{max2}: 469-496 nm). The strong electron-withdrawing substituent -NO_2 on benzothiazole ring of diazo component reflected the highest λ_{max} value in the most polar solvents dimethylformamide and dimethylsulfoxide (496 and 491nm). It showed highest bathochromic shift in the acetic acid (+90 nm) when compared with the **1a**; like dye **1b**. Such effect of this group may be due to the resonance stability[31].

The absorbance maxima of **2b** and **2c** unchanged in acetic acid and acetonitrile but slightly changed in

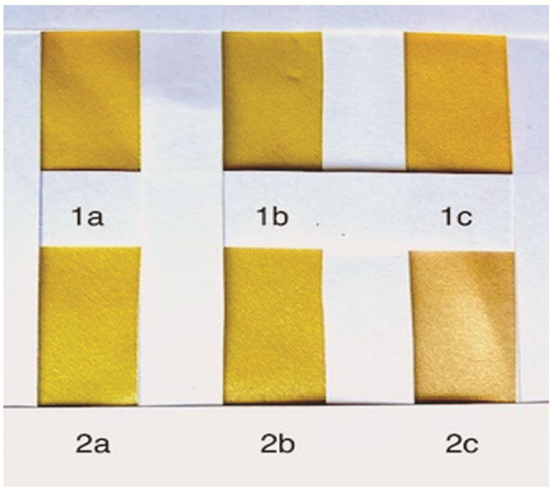


Fig. 4 — Colors of the dyes on polyester fabric

other solvents in respect to **2a**. λ_{max} changes of **2b** and **2c** are; 0, +1 nm in chloroform, +1, +12 nm in methanol, +2, +6 nm in dimethylformamide, +3, +6 nm in dimethylsulfoxide. In addition, **2b** provided a sholder at 330 or 335 nm in the tested solvents while **2c** showed second λ_{max} at 331-346 nm.

Dyes **2a-c**, and acetylated **1a-c** were less effected by the type of substituent; probably due to weak electron-donating ability of acetamido chromophore (-NH-CO-CH_3) than the auxochrome (-NH_2). Furthermore, unlike **1c**, acetylation of amino group affected the absorbance of **1a** and **1b**. The largest change of λ_{max} values occured in acetic acid of dyes **2a** and **2b** compared with dyes **1a** and **1b**. Absorbance maxima of **1a** and **1b** in acetic acid was 390 and 417 nm, whereas **2a** and **2b** showed 480 nm λ_{max} in the same solvent. Dyes **2a** and **2b** showed bathochromic shift comparative to their parent dyes *i.e*. **1a** and **1b**. The shoulder of **1a** at 390 nm appeared in dye **2b** at 330 or 335 nm in all solvents. On the other hand, λ_{max1} values of dye **2c** shifted hypsochromically in all solvents while λ_{max2} values of the same dye either unchange or changed slightly inrespect to its corresponding dye **1c**. The largest change in the λ_{max1} and λ_{max2} of dye **2c** occured in acetic acid (-48nm) and dimethylformamide (-12nm).

Fastness Properties

Fig. 4 shows the colors of the synthesized dyes on polyester fabric.

Light Fastness

As clear from Table 1, disperse dyes exhibited higher light fastness over the polyester fabric. Looking at the values, the light fastness levels of 2 (2a-c) (5, 5, 3/4-4) were lesser as compared their parent dyes **1a-c** (6, 6, 4). This means that the best light fastness level is 6 for **1a** and **1b**, while the least light fastness level is 3/4 -4 for **2c** (Ref. 15-18, 22).

Rubbing Fastness

Table 1 shows the rubbing and light fastness results of the prepared dyes. Dyed polyester fabric reflected excellent dry/wet rub fastness. Dye **1a** showed the highest wet rub fastness *i.e*. 5 while the same value for the dry rub fastness was provided by **1a**, **1b** and **2a**. Dye **2c** showed the least dry rub fastness and wet rub fastness *i.e*. 3/4. Dyes **1b**, **1c** and **2a** showed higher dry rub fastness (5, 4/5, 5) than their wet fastness (4/5, 4, 4/5) while dry and wet rub fastness of **2b** was the same (4/5). Both dry and web rub fastness of **2a-c** (3-acetamidopyrazolones) were slightly smaller when compared with their parent dyes *i.e*. **1a-c** (3-aminopyrazolones); except the dry rub fastness of **1a** and **2a** (5) and wet rub fastness of **1b** and **2b** (4/5). The wet rub fastness and dry rub fastness of **1a-c** are: 5-5, 4/5-5, 4 -4/5 while of **2a-c** are: 4/5-5, 4/5-4/5, 3/4-3/4 (Ref. 15-18, 22).

Washing Fastness

The change in the shade related to wash fastness of the dyed fibers are at the commercially acceptable level. Dyes **1a**, **1b**, **2a** and **2b** have admirable shade change levels of 4/5 -5 and staining levels of 4-5. Dyes **1a** and **1b** showed best staining (4/5, -5), whereas **1c** and **2c** showed the leasts *i.e*. 3/4 -4 and 3-4, respectively[15-18]. Table 1 shows the washing fastness of the synthesized dyes on the dyed polyester fabric.

As Table 1 shows, the fastness values of **1a-c** (3-aminopyrazolone derivatives) were higher as compared to that of **2a-c** (3-acetamidopyrazolone derivatives); probably due to the fact that amino group (-NH) binds more strongly with polyester fibers than the acetamido group (-NH-CO-CH_3).

Conclusion

UV absorbances, tautomerism and fastness properties of the acetamido-based and primery amino monoazo dyes, synthesized from 1-phenyl-3-aminopyrazol-5-one, were investigated. The absorbance behaviours of the synthesised dyes were more acid-sensitive that is related to the proton-donor and acceptour properties of the solvents used and absorption peaks of dyes. The dyes showed

bathchromic shifts in the polar solvents in general. The largest bathochromic shift was reflected by the nitro substituted **1c** in the diazo component in dimethylformamid and dimethylsulfoxide. Absorption maxima of dyes **2a-c** either unchanged or the change was very slight in these solvents. Absorbances of the dyes did not change significantly change with concentration and temperature. Dyes **1a-c** were more senstitive when the substituents were varied. According to the spectral data of the dyes, that all the compounds are in keto-hydrazo form (T2) in their solid state. The dyes **1a-c** are in keto-hydrazo form (T2), but the comp. **2a-c** are in keto-azo form (T1) in DMSO. The colors of **2a-c** (chromophore, -NH-CO-CH_3) were darker than their parent dyes *i.e*. **1a-**c (-NH_2, oxochrome); probably due to the fact that absorbance of **2a-c** were more bathochromic. Fastness tests showed satisfactory results when compared to the literature. Noteworthy, dyes **1a**, **1b**, **2a** and **2b** possessed excellent fastness. Fastness test of the polyester dyed fabrics showed that the binding of amino group (-NH_2) with the fibers of polyester is more strong than acetamido (-NH-CO-CH_3). The dyes synthesized in this study can be used in the dye industry.

Supplementary Information

Supplementary information is available in the website https://nopr.niscpr.res.in/handle/123456789/58776.

References

1 Seferoğlu Z & Ertan N, *Phos Sulf Rel Ele*, 183 (2008) 1236.
2 Bianchini R, Bonanni M, Corsi M & Infantino A S, *Tetrahedron*, 68 (2012) 8636.
3 Karcı F & Ertan N, *Color Technol,* 121 (2005) 153.
4 Towns A D, *Dyes Pigm*, 42 (1999) 3.
5 Seferoğlu Z & Ertan N, *Russ J Org Chem*, 43 (2007) 1035.
6 Matsuoka M, *Infrared Absorbing Dyes*, Vol. 1, 4th ed., (Plenum Press: New York and London, UK) 1990.
7 Matsuoka M, *J Soc Dyers Col,* 105 (1989) 167.
8 Emandi A, Serban I & Bandula R, *Dyes Pigm,* 41 (1999) 63.
9 Bach H, Anderle K, Fuhrmann T & Wendorff J H, *J Phys Chem,* 100 (1996) 4135.
10 Baumann M, Baxendale R, Ley S V & Nikbin N, *Beilstein J Org Chem,* 7 (2011) 442.
11 Baumann M & Baxendale R, *Beilstein J Org Chem*, 9 (2013) 2265.
12 Sarıkavaklı N, Koç E, Aljohani M M H & Mustafa S K, *Orient J Chem*, 36 (2020) 1194.
13 Alam M, Nami S A A, Parveen M, Lee D U & Park S, *Chin Chem Lett*, 23 (2012) 1039.
14 Küçükgüzel S G, Rollas S, Erdeniz H, Kiraz M, Ekinci A C & Vidin A, *Prog Drug Res,* 35 (2000) 761.
15 El-Borai M A, Rizk H F, El-Hefnawy G B, Ibrahim S A, Aser S S & El-Sayed H F, *Fibers Poly,* 17 (2016) 729.
16 Abdel M A M E, Fathy A & Amer G A M, *Dyes Pigm,* 92 (2012) 902.
17 Ho Y W, *Dyes Pigm,* 64 (2005) 223.
18 Bakan E, Karcı F & Avinc O, *Fibers Polym,* 19 (2018) 670.
19 Aktan E, Ertan N & Uyar T, *J Mol Struc,* 1060 (2014) 215.
20 Ertan N, *Dyes Pigm,* 44 (2000) 41.
21 Karcı F & Ertan N, *Dyes Pigm,* 55 (2002) 99.
22 Erol F*, J Braz Chem Soc*, 31 (2020) 1815.
23 Song H, Chen K & Tian H, *Dyes Pigm,* 53 (2002) 257.
24 Ertan N & Eyduran F, *Dyes Pigm*, 27 (1995) 313.
25 Karcı F & Karcı F, *Dyes Pigm,* 76 (2008) 147.
26 Aktan E, Seferoglu Z, Hokelek T & Sahin E, *Color Tech,* 128 (2012) 371.
27 Aktan E, Babur B, Seferoğlu Z, Hokelek T & Sahin E, *J Mol Struc,* 1002 (2011) 113.
28 Peng Q, Li M, Gao K & Cheng L, *Dyes Pigm,* 18 (1992) 271.
29 Sener I, Karcı F, Kılıc E & Deligoz H, *Dyes Pigm,* 62 (2004) 141.
30 Saylam A, Seferoğlu, Z & Ertan N, *Dyes Pigm,* 76 *(*2008) 470.
31 Babür B & Ertan N, *Spectrochim Acta Part A,* 131 (2014) 319.
32 ISO 105-B04: Textiles-Tests for Colour Fastness-Part B04:Colour Fastness to Artificial Weathering: Xenon Arc Fading Lamp Test, *International Organization foStandardization,* Geneve (1994).
33 ISO 105-X12: Textiles-Tests for Colour Fastness-Part X12:Colour Fastness to Rubbing, *International Organization for Standardization*, Geneve (2016).
34 ISO 105-C06: Textiles-Tests for Colour Fastness-Part C06:Colour Fastness to Domestic And Commercial Laundering, *International Organization for Standardization* Geneve (2010).