

SYNTHESIS AND ABSORPTION ABILITIES OF PYRAZOLO[5,1-*c*][1,2,4]TRIAZINE-BASED DISPERSE DYES

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*A series of 13 novel pyrazolo[5,1-*c*][1,2,4]triazine-based disperse dyes was synthesized by heating ethyl pyrazolylhydrazonocynoacetate in glacial acetic acid. Solvent and acid-base influences on the wavelength of maximum absorption have been studied.*

Keywords: ethyl cyanoacetate, pyrazole, diazo coupling reaction, intramolecular cyclization, solvatochromism.

Polyfunctionally substituted heteroaromatics are biologically interesting molecules, and their synthesis has recently received considerable attention [1-3]. 5-Aminopyrazoles are versatile reagents and have been extensively utilized as synthetic starting components for preparation of several polysubstituted fused pyrazoles [4-6]. Also, fused pyrazoles are important compounds; among them there are many derivatives with a wide range of interesting properties, such as antihyperglycemic [7], analgesic [8], anti-inflammatory [9], antipyretic [9], antibacterial [10], hypoglycemic, and sedative-hypnotic activity [11, 12]. Recently, some pyrazoles were reported to have non-nucleoside HIV-1 reverse transcriptase inhibitory activity [13]. Some azopyrazole derivatives also find application in dyes [14-18], biological [19] and pharmacological [20] studies, and complexes [21, 22].

The cyclization reactions of hydrazones occupy a very important place among methods of synthesis of heterocyclic compounds, in particular, various non-fused five- and six-membered heterocycles. Among readily undergoing cyclization reactions, we point to the cyclization of pyrazolylazoketonitriles that occurs with formation of 7-aminopyrazolo[5,1-*c*][1,2,4]triazines, as it found by Partridge and Stevens [23]. This cyclization was applied to a whole series of diversely substituted pyrazolylhydrazones [24-32]. All the above-mentioned cyclization reactions are concerned with pyrazolylhydrazones unsubstituted at the nitrogen atoms where the presence of an NH group in the pyrazole ring allows them to readily undergo ring closure to the pyrazolo[5,1-*c*][1,2,4]triazine system.

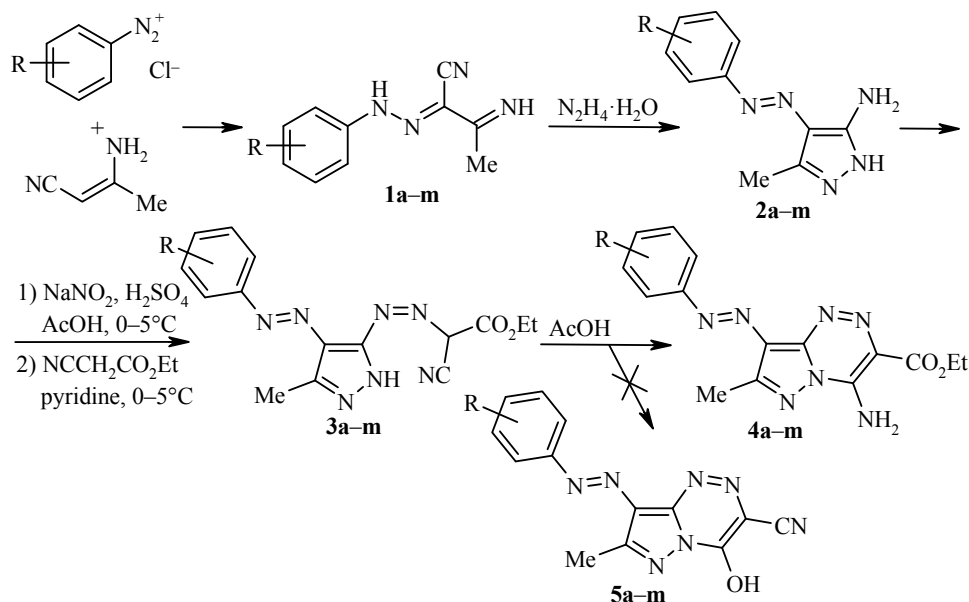
In conjunction with our interest in this class of compounds, we have reported the synthesis of some pyrazolo[5,1-*c*][1,2,4]triazines [33, 34]. In continuation of this work, we report here the synthesis of new disperse dyes series based on 7-amino-6-ethoxycarbonylpyrazolo[5,1-*c*][1,2,4]triazine. The effect of pH and solvent upon the absorption ability of dyes substituted with electron-withdrawing and electron-donating groups at their *o*-, *m*-, *p*-position was also examined in detail.

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2-Arylhrazinylidene-3-iminobutyronitriles **1a-m** and 5-amino-4-arylo-3-methyl-1*H*-pyrazoles **2a-m** were prepared according to the literature procedures [35]. Pyrazoles **2a-m** were then diazotized and coupled with ethyl cyanoacetate to yield a series of ethyl pyrazolyldiazenylcyanoacetates **3a-m**. These compounds were then heated in glacial acetic acid to provide 13 novel pyrazolo[5,1-*c*][1,2,4]triazine-based disperse dyes **4a-m**, which were characterized by elemental analysis and spectroscopic methods (Tables 1 and 2).



a R = H, **b** R = 4-NO₂, **c** R = 4-OMe, **d** R = 4-Cl, **e** R = 4-Me, **f** R = 3-NO₂, **g** R = 3-OMe, **h** R = 3-Cl, **i** R = 3-Me, **j** R = 2-NO₂, **k** R = 2-OMe, **l** R = 2-Cl, **m** R = 2-Me

TABLE 1. Physicochemical Characteristics of Compounds **4a-m**

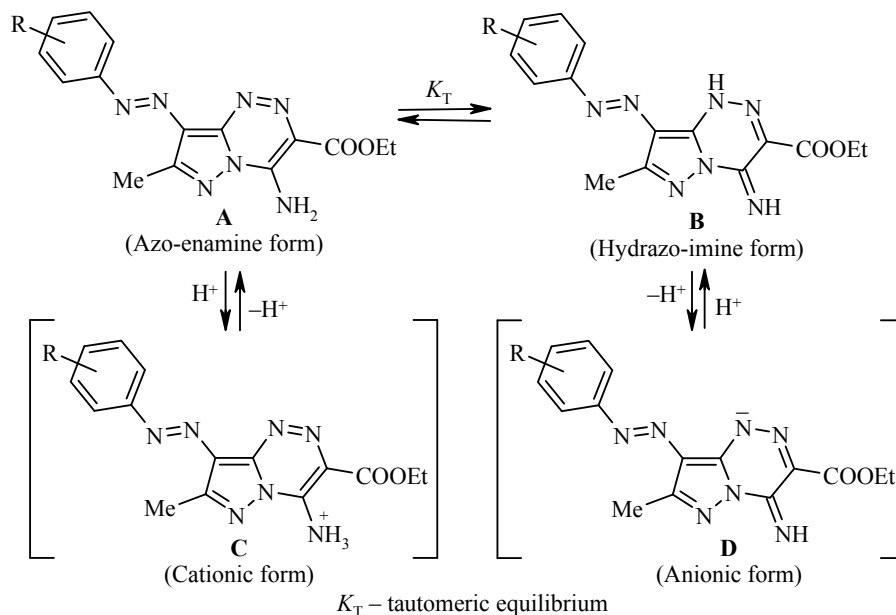
Com- pound	Empirical formula	Color	Found, %			Mp, °C	Yield, %
			Calculated, %				
			C	H	N		
4a	C ₁₅ H ₁₅ N ₇ O ₂	Pale-brown	55.51	4.69	29.82	261-262	67
			55.38	4.65	30.14		
4b	C ₁₅ H ₁₄ N ₈ O ₄	Orange	48.86	3.80	30.02	245-246	83
			48.65	3.81	30.26		
4c	C ₁₆ H ₁₇ N ₇ O ₃	Yellow	53.91	4.75	27.33	214-215	70
			54.08	4.82	27.59		
4d	C ₁₅ H ₁₄ ClN ₇ O ₂	Orange	50.24	3.86	27.08	253-254	69
			50.08	3.92	27.25		
4e	C ₁₆ H ₁₇ N ₇ O ₂	Yellow	56.88	5.13	28.67	227-228	64
			56.63	5.05	28.89		
4f	C ₁₅ H ₁₄ N ₈ O ₄	Orange	48.47	3.72	29.96	294-295	80
			48.65	3.81	30.26		
4g	C ₁₆ H ₁₇ N ₇ O ₃	Brown	54.28	4.95	27.48	214-215	74
			54.08	4.82	27.59		
4h	C ₁₅ H ₁₄ ClN ₇ O ₂	Orange	50.19	3.88	26.95	253-254	76
			50.08	3.92	27.25		
4i	C ₁₆ H ₁₇ N ₇ O ₂	Yellow	56.76	4.98	28.73	237-238	65
			56.63	5.05	28.89		
4j	C ₁₅ H ₁₄ N ₈ O ₄	Orange	48.53	3.87	30.11	268-269	86
			48.65	3.81	30.26		
4k	C ₁₆ H ₁₇ N ₇ O ₃	Yellow	54.21	4.96	27.38	237-238	74
			54.08	4.82	27.59		
4l	C ₁₅ H ₁₄ ClN ₇ O ₂	Brown	50.25	4.01	26.93	259-260	73
			50.08	3.92	27.25		
4m	C ₁₆ H ₁₇ N ₇ O ₂	Orange	56.56	4.97	28.72	230-231	70
			56.63	5.05	28.89		

TABLE 2. Spectral Characteristics of Compounds **4a-m**

Com- pound	IR spectrum, ν , cm^{-1}					^1H NMR spectrum, δ , ppm (J , Hz)		
	NH ₂	C-H Ar	C-H Alk	C=O	C-O	H Ar	H Alk	-NH-*, =NH*
4a	3433, 3382	3056	2968	1690	1075	7.91-7.82 (2H, m); 7.66-7.57 (2H, m); 7.56-7.48 (1H, m)	4.46 (2H, q, J = 6.9, OCH_2CH_3); 1.39 (3H, t, J = 6.9, OCH_2CH_3)	9.47 (1H, br. s, -NH-); 8.24 (1H, br. s, =NH)
4b	3440, 3384	3072	2985	1672	1077	8.13 (2H, d, J = 9.3); 7.60 (2H, d, J = 9.3)	4.47 (2H, q, J = 7.0, OCH_2CH_3); 1.42 (3H, t, J = 7.0, OCH_2CH_3)	9.40 (1H, br. s, -NH-); 8.62 (1H, br. s, =NH)
4c	3428, 3379	3068	2976	1686	1076	7.83 (2H, d, J = 8.5); 7.12 (2H, d, J = 8.5)	4.44 (2H, q, J = 7.0, OCH_2CH_3); 2.73 (3H, s, 7-CH ₃); 1.40 (3H, t, J = 7.0, OCH_2CH_3)	9.39 (1H, br. s, -NH-); 8.63 (1H, br. s, =NH)
4d	3436, 3387	3062	2979	1689	1074	7.77 (2H, d, J = 8.4); 7.54 (2H, d, J = 8.4)	4.35 (2H, q, J = 7.0, OCH_2CH_3); 1.29 (3H, t, J = 7.0, OCH_2CH_3)	9.36 (1H, br. s, -NH-); 8.60 (1H, br. s, =NH)
4e	3432, 3384	3068	2982	1689	1076	7.77 (2H, d, J = 8.0); 7.39 (2H, d, J = 8.0)	4.43 (2H, q, J = 6.9, OCH_2CH_3); 2.41 (3H, s, ArCH_3); 1.39 (3H, t, J = 6.9, OCH_2CH_3)	9.43 (1H, br. s, -NH-); 8.67 (1H, br. s, =NH)
4f	3435, 3387	3064	2977	1676	1086	8.54 (1H, s); 8.39-8.28 (2H, m); 7.94-7.86 (1H, m)	4.48 (2H, q, J = 7.0, OCH_2CH_3); 1.40 (3H, t, J = 7.0, OCH_2CH_3)	9.57 (1H, br. s, -NH-); 8.78 (1H, br. s, =NH)
4g	3431, 3378	3068	2964	1690	1072	7.51-7.42 (2H, m); 7.35 (1H, s); 7.11-7.03 (1H, m)	4.42 (2H, q, J = 7.0, OCH_2CH_3); 2.73 (3H, s, 7-CH ₃); 1.39 (3H, t, J = 7.0, OCH_2CH_3)	9.44 (1H, br. s, -NH-); 8.66 (1H, br. s, =NH)
4h	3436, 3376	3072	2960	1693	1073	7.87-7.82 (2H, m); 7.67-7.60 (1H, m); 7.55 (1H, s)	4.46 (2H, q, J = 7.0, OCH_2CH_3); 1.40 (3H, t, J = 7.0, OCH_2CH_3)	9.52 (1H, br. s, -NH-); 8.73 (1H, br. s, =NH)
4i	3439, 3384	3066	2975	1691	1075	7.71-7.62 (2H, m); 7.51-7.42 (1H, m); 7.32 (1H, s)	4.45 (2H, q, J = 7.0, OCH_2CH_3); 2.45 (3H, s, ArCH_3); 1.40 (3H, t, J = 7.0, OCH_2CH_3)	9.46 (1H, br. s, -NH-); 8.67 (1H, br. s, =NH)
4j	3436, 3381	3070	2991	1683	1082	8.09-8.02 (1H, m); 7.91-7.79 (2H, m); 7.76-7.65 (1H, m)	4.46 (2H, q, J = 7.0, OCH_2CH_3); 1.40 (3H, t, J = 7.0, OCH_2CH_3)	9.52 (1H, br. s, -NH-); 8.75 (1H, br. s, =NH)
4k	3440, 3378	3072	2983	1686	1081	7.63-7.56 (1H, m); 7.52-7.44 (1H, m); 7.29-7.24 (1H, m); 7.11-7.02 (1H, m)	4.43 (2H, q, J = 6.9, OCH_2CH_3); 2.74 (3H, s, 7-CH ₃); 1.40 (3H, t, J = 6.9, OCH_2CH_3)	9.42 (1H, br. s, -NH-); 8.68 (1H, br. s, =NH)
4l	3435, 3380	3069	2984	1685	1080	7.81-7.74 (1H, m); 7.74-7.67 (1H, m); 7.56-7.48 (2H, m)	4.46 (2H, q, J = 7.0, OCH_2CH_3); 1.41 (3H, t, J = 7.0, OCH_2CH_3)	9.53 (1H, br. s, -NH-); 8.74 (1H, br. s, =NH)
4m	3430, 3384	3059	2966	1686	1075	7.76-7.60 (1H, m); 7.48-7.23 (3H, m)	4.47 (2H, q, J = 6.9, OCH_2CH_3); 2.44 (3H, s, ArCH_3); 1.41 (3H, t, J = 6.9, OCH_2CH_3)	9.45 (1H, br. s, -NH-); 8.70 (1H, br. s, =NH)

*Signals of the hydrazone-imine tautomeric form.

Azo dyes **4a-m** can exist in two possible tautomeric forms, namely the azo-enamine form **A** and the hydrazo-imine form **B**. Azo-hydrazo tautomerism is not only important in dyestuff manufacture but also to the other areas of chemistry. Azo and hydrazo tautomers not only have different colors but also differ in other properties like tinctorial strength or light fastness [36, 37]. Depending on the acid-base properties of the respective compound, as well as on the solvent and pH of the solution, two charged forms, cationic (**C**) and anionic (**D**), are possible for the obtained azo dyes. The cationic form may exist in several tautomeric forms (not given in the scheme) due to different positions of the proton.



The FT-IR spectra of dyes **4a-m** showed intense amino group bands at 3440-3428 and 3387-3376 cm^{-1} (Table 2). This suggests that these dyes in the solid state exist predominantly in the azo-enamine form and not in the hydrazo-imine form. The FT-IR spectra also showed a band at 1693-1672 cm^{-1} assigned to the C=O group and did not show a band at 2200-2300 cm^{-1} that could be characteristic of the CN group. These results suggest that these dyes exist predominantly in aminoester form **4a-m** and not in hydroxynitrile form **5a-m**. The other ν value ranges were assigned to the corresponding structural features: 3072-3056 cm^{-1} (aromatic C-H), 2991-2960 cm^{-1} (aliphatic C-H), and 1086-1072 cm^{-1} (C-O). Some investigations were carried out to establish the tautomeric structure of amino-substituted arylazo dyes in the solid state using FT-IR spectra. The spectral data generally lead to the conclusion that the tautomeric equilibrium of these dyes favors of the azo-enamine form **A** [38-40].

The ^1H NMR spectra of dyes **4a-m** showed a broad singlet of the =NH (imine) group at 8.78-8.24 ppm and a broad singlet of the -NH- (hydrazo) group at 9.57-9.36 ppm, respectively. This result suggests that dyes **4a-m** in DMSO- d_6 solution exist in the hydrazo-imine form **B**. The ^1H NMR spectra also showed a quartet at 4.48-4.35 ppm and a triplet at 1.42-1.29 ppm, assigned to the ethyl group. These results confirm formation of iminoester isomer **4a-m**.

The UV-vis absorption spectra of dyes **4a-m** were recorded over the range of λ between 300-700 nm using a variety of solvents in concentrations 10^{-6} - 10^{-8} M, and the results are summarized in Table 3. The visible absorption spectra of the dyes did not correlate with the polarity of the solvent.

Each of the dyes gave a maximum absorption peak with a shoulder at a shorter wavelength in all the solvents employed, with the exception of dyes **4b,k**. The reason for this is probably that dyes **4a,c-j,l-m** exist in two tautomeric forms **A** and **B** in all the solvents used (Fig. 1). As the spectrum of dye **4b** has a second shoulder at 544 nm in DMF, it is likely that dye **4b**, besides forms **A** and **B**, exists also in anionic form **D** in DMF (Fig. 2). Dye **4k** gave a maximum absorption peak with a shoulder at a longer wavelength in acetic acid,

suggesting that dye **4k** was present in a single tautomeric form (**A** or **B**) and in the cationic form **C** in acetic acid and in two tautomeric forms in the other solvents.

TABLE 3. Influence of Solvent on Absorption Maxima ($\lambda_{\max}$, nm) of Dyes **4a-m**

Dye	DMSO	DMF	MeCN	MeOH	AcOH	CHCl ₃
4a	405, 314 (s*)	403, 314 (s)	394, 308 (s)	397, 310 (s)	396, 305 (s)	394, 310 (s)
4b	421, 380 (s)	416, 378 (s), 544 (s)	411, 369 (s)	412, 371 (s)	409, 366 (s)	412, 375 (s)
4c	412, 320 (s)	408, 320 (s)	404, 318 (s)	407, 318 (s)	404, 316 (s)	406, 318 (s)
4d	411, 309 (s)	409, 309 (s)	401, 305 (s)	403, 305 (s)	400, 307 (s)	396, 308 (s)
4e	408, 313 (s)	404, 312 (s)	397, 305 (s)	400, 306 (s)	399, 304 (s)	395, 305 (s)
4f	415, 376	411, 374 (s)	405, 332 (s)	410, 335 (s)	401, 330 (s)	401, 332 (s)
4g	409, 316 (s)	407, 315 (s)	400, 305 (s)	401, 305 (s)	400, 305 (s)	397, 304 (s)
4h	411, 318 (s)	409, 318 (s)	400, 312 (s)	402, 313 (s)	398, 310 (s)	396, 308 (s)
4i	406, 314 (s)	403, 312 (s)	396, 308 (s)	400, 309 (s)	397, 308 (s)	395, 307 (s)
4j	419, 324 (s)	415, 320 (s)	408, 316 (s)	408, 315 (s)	403, 316 (s)	402, 317 (s)
4k	414, 319 (s)	411, 324 (s)	408, 310 (s)	410, 311 (s)	406, 532 (s)	406, 310 (s)
4l	415, 314 (s)	412, 314 (s)	403, 310 (s)	403, 309 (s)	399, 306 (s)	398, 306 (s)
4m	409, 313 (s)	406, 312 (s)	398, 306 (s)	399, 306 (s)	397, 305 (s)	396, 305 (s)

*s – Shoulder.

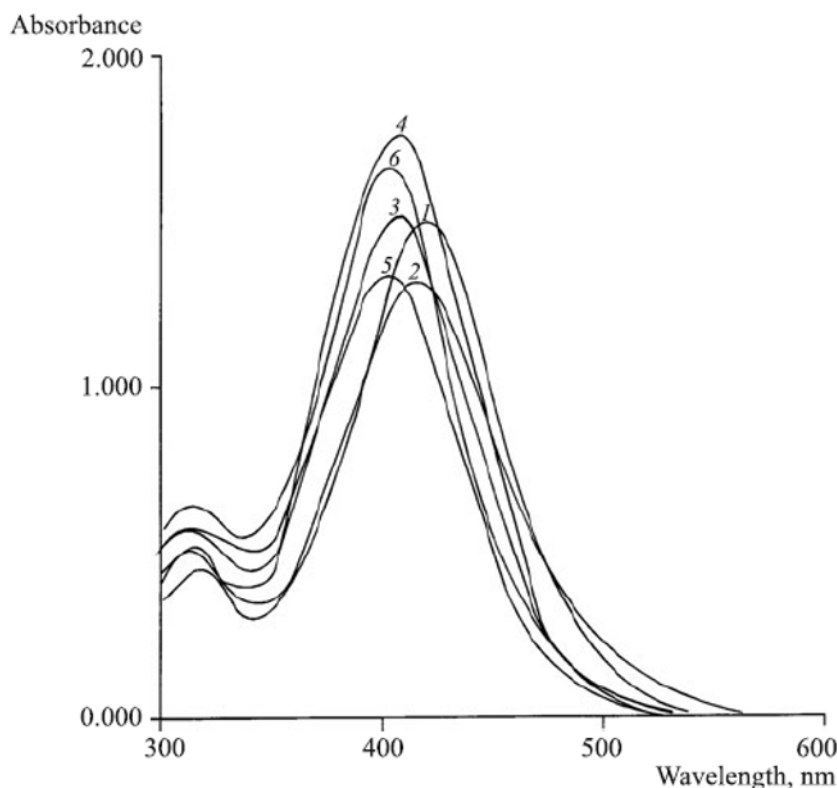


Fig. 1. Absorption spectra of dye **4j** in various solvents:
1 – DMSO, 2 – DMF, 3 – acetonitrile, 4 – methanol, 5 – acetic acid, 6 – chloroform.

It was observed that although the absorption spectra did not differ significantly in acetonitrile, methanol, acetic acid, and chloroform, with the exception of dye **4k**, $\lambda_{\max}$ of these dyes were shifted bathochromically in DMSO and DMF; for example, for compound **4a**, $\lambda_{\max}$ was at 394 nm in acetonitrile and 394 nm in chloroform,

but at 405 nm in DMSO and 403 nm in DMF (Fig. 2). Also the $\lambda_{\max}$ values for dye **4k** in DMSO and DMF were shifted bathochromically with respect to the $\lambda_{\max}$ in the other solvents.

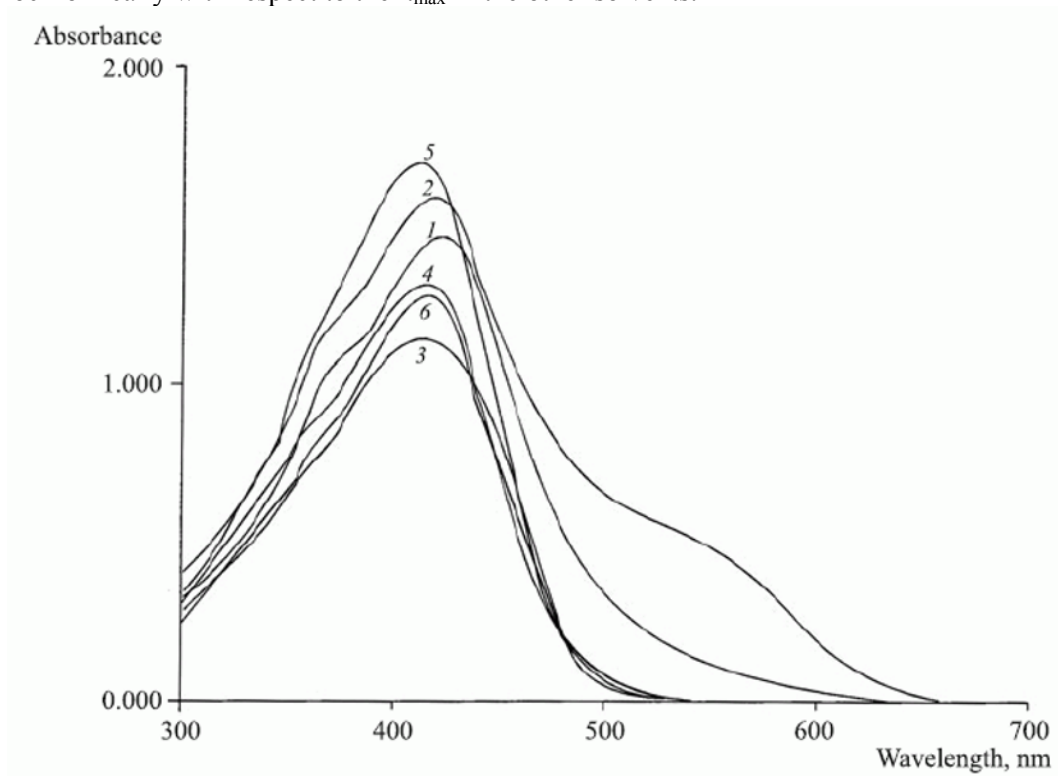


Fig. 2. Absorption spectra of dye **4b** in various solvents:
1 – DMSO, 2 – DMF, 3 – acetonitrile, 4 – methanol, 5 – acetic acid, 6 – chloroform

The effects of acid and base on the absorption of dye solutions were investigated, and the results are shown in Table 4. The absorption spectra of dyes **4a-m** in methanol were quite sensitive to the addition of base (potassium hydroxide, 0.1 M), with $\lambda_{\max}$ showing a bathochromic shift. Such an effect of base is consistent with the phenomenon of dissociation rather than azo-hydrazone tautomerism.

TABLE 4. Absorption Maxima (λ , nm) of Dyes **4a-m** in Acidic and Basic Solutions (λ , nm)

Dye	MeOH	MeOH + KOH	MeOH + HCl	CHCl ₃	CHCl ₃ + piperidine	AcOH
4a	397, 310 (s*)	441, 310 (s)	347, 392 (s)	394, 310 (s)	403, 312 (s)	396, 305 (s)
4b	412, 371 (s)	475, 338 (s)	406, 366 (s)	412, 375 (s)	413, 376 (s)	409, 366 (s)
4c	407, 318 (s)	455, 333 (s)	374, 400 (s)	406, 318 (s)	411, 318 (s)	404, 316 (s)
4d	403, 305 (s)	456, 328 (s)	358, 396 (s)	396, 308 (s)	409, 308 (s)	400, 307 (s)
4e	400, 306 (s)	450, 328 (s)	359, 394 (s)	395, 305 (s)	405, 310 (s)	399, 304 (s)
4f	410, 335 (s)	447, 327 (s)	365, 389 (s)	401, 332 (s)	422, 360 (s)	401, 330 (s)
4g	401, 305 (s)	438, 326 (s)	350, 398 (s)	397, 304 (s)	409, 312 (s)	400, 305 (s)
4h	402, 313 (s)	447, 334 (s)	346, 396 (s)	396, 308 (s)	412, 315 (s)	398, 310 (s)
4i	400, 309 (s)	433, 327 (s)	345, 396 (s)	395, 307 (s)	404, 312 (s)	397, 308 (s)
4j	408, 315 (s)	458, 329 (s)	348, 390 (s)	402, 317 (s)	422, 320 (s)	403, 316 (s)
4k	410, 311 (s)	460, 334 (s)	366, 411 (s), 525 (s)	406, 310 (s)	414, 316 (s)	406, 532 (s)
4l	403, 309 (s)	441, 327 (s)	353, 390 (s)	398, 306 (s)	412, 312 (s)	399, 306 (s)
4m	399, 306 (s)	430, 325 (s)	349, 397 (s)	396, 305 (s)	407, 310 (s)	397, 305 (s)

* s – Shoulder.

When hydrochloric acid (0.1 M) was added to the dye solutions in methanol, the $\lambda_{\max}$ showed hypsochromic shifts, with the exception of dye **4b**, and the absorption curves of the dyes were different from those in acetic acid. This suggests that in strong acidic solutions the dyes are present in a single tautomeric form (**A** or **B**) and in a cationic form **C**, except for dye **4b**. It was also observed that when hydrochloric acid (0.1 M) was added to dye **4k** solution in methanol, $\lambda_{\max}$ showed a hypsochromic shift, and a shoulder at a longer wavelength was observed which resembled the one in acetic acid. This suggests that dye **4k** was present in a single tautomeric form (**A** or **B**) and in two different cationic forms in strong acidic solutions.

Also, $\lambda_{\max}$ of the dyes showed bathochromic shifts when a small amount of piperidine was added to each of the dye solutions in chloroform (Table 4), and the absorption curves of the dyes resembled those in DMSO and DMF.

As seen in Table 3, the electron-accepting nitro and chloro groups and the electron-donating methoxy group in all positions cause bathochromic shifts in all the solvents used when compared to dye **4a**. The electron-donating methyl group in all positions causes little bathochromic shifts or does not change significantly in all the solvents used when compared to dye **4a**. It was also observed that the electron-accepting nitro and chloro groups and the electron-donating methoxy group in *o*- and *p*-positions cause larger bathochromic shifts than those in *m*-position.

Dye **4b** gave a new shoulder at 544 nm in DMF because of the electron-accepting nitro group in *p*-position, which causes formation of the anionic form **D** in DMF. Furthermore, the shoulder at 532 nm in the spectrum of dye **4k** in acetic acid is likely due to the electron-donating methoxy group in *o*-position, which favors the formation of the cationic form **C**.

Heterocyclic hydroxyazo- and aminoazo-based dyes tend to show larger solvatochromic effects than azobenzene because of the increased polarity of the dye system, especially of the excited state. Similar effects for 7-amino-3-arylazo-6-cyano-2-methylpyrazolo[5,1-*c*][1,2,4]triazines were reported in our previous work [33]. In the present paper, 4-amino-8-arylazo-7-methylpyrazolo[5,1-*c*][1,2,4]triazine-3-carboxylic acid ethyl esters **4a-m** also showed solvatochromic effects. The absorption maxima of dyes showed bathochromic shifts in DMSO and DMF compared to the other four solvents. The absorption maxima in the spectra of nitro derivatives are larger than in the case of chloro, methoxy, and methyl derivatives. It was also observed that the electron-accepting nitro and chloro groups and the electron-donating methoxy group in *o*- and *p*-positions cause larger bathochromic shifts than those in *m*-position.

In our previous work, although 7-amino-3-arylazo-6-cyano-2-methylpyrazolo[5,1-*c*][1,2,4]triazines were present in the hydrazo-imine form in acetonitrile, methanol, acetic acid, and chloroform, these dyes were present in the azo-enamine form in DMSO and DMF, except for *p*-nitro and *o*-methoxy derivatives. In this part of our study, 4-amino-8-arylazo-7-methylpyrazolo[5,1-*c*][1,2,4]triazine-3-carboxylic acid ethyl esters **4a-m** were present in two tautomeric forms in all the solvents used, except, again, for *p*-nitro (**4b**) and *o*-methoxy (**4k**) derivatives. Dye **4b** was present in two tautomeric forms and in anionic form **D** in DMF, and in only two tautomeric forms in the other solvents.

Thus, the obtained pyrazolo[5,1-*c*][1,2,4]triazine-based dyes, containing aromatic amino and ethoxycarbonyl groups, can be used as a heterocyclic diazo component for synthesis of new azo dyes and as intermediate for new heterocyclic rings. The obtained azo dyes can also be applied to polyester and/or polyamide fibers as disperse dyes and in biological-medical studies.

EXPERIMENTAL

IR spectra were recorded on a Mattson 1000 Fourier Transform infrared (FT-IR) spectrophotometer in KBr pellets. ^1H NMR spectra were recorded on a Bruker-Spectrospin Avance DTX-400 Ultra-Shield spectrometer (400 MHz) in DMSO- d_6 , using TMS as internal standard. UV-vis absorption spectra were recorded on an ATI Unicam UV-100 spectrophotometer at various concentrations (1×10^{-6} – 10^{-8} M). Change in

$\lambda_{\max}$ was also investigated when 0.1 ml of base (0.1 M KOH) and 0.1 ml of acid (0.1 M HCl) was added to the dye solutions in MeOH (1 ml; because of low solubility, concentration of dyes cannot be calculated exactly). Elemental analysis was performed on a Leco CHNS-932 analyzer. Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected.

Chemicals were obtained from Sigma-Aldrich Chemical Company and were used for syntheses without further purification. The solvents used were of spectroscopic grade.

4-Amino-8-aryloxy-7-methylpyrazolo[5,1-c][1,2,4]triazine-3-carboxylic Acid Ethyl Esters 4a-m (General Method). Nitrosylsulfuric acid was prepared by dissolving NaNO₂ (1.00 g, 14.5 mmol) in conc. H₂SO₄ (7 ml) at 70°C. 4-Aryloxy-3-methylazo-1H-pyrazol-5-amine **2a-m** (2.0 mmol) was dissolved in hot glacial AcOH (2.5 ml) and rapidly cooled in an ice/salt bath to -5°C. The solution was then added in portions over 30 min to nitrosylsulfuric acid at 0-5°C, and the mixture was stirred for a further 1 h at this temperature. Then the resulting diazonium salt solution was added in portions over 30 min to a vigorously stirred solution of ethyl cyanoacetate (0.22 g, 2.0 mmol) in pyridine (10 ml) at 0-5°C, maintaining the pH at 7-8 by simultaneous addition of solid NaOAc. The mixture was then stirred for 2 h at 0-5°C. The progress of the reaction was followed by TLC on silica gel plates using EtOAc–petroleum ether mixture, 5:2, as eluent. The resulting solid **3a-m** was filtered off, washed with cold water, and dried, then dissolved in glacial AcOH (30 ml), and refluxed for 4 h. The solvent was then evaporated *in vacuo* and the remaining product was collected by filtration, dried, and recrystallized from DMF–H₂O, 3:1.

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