F. Karcı[1*], F. Karcı[2]

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

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

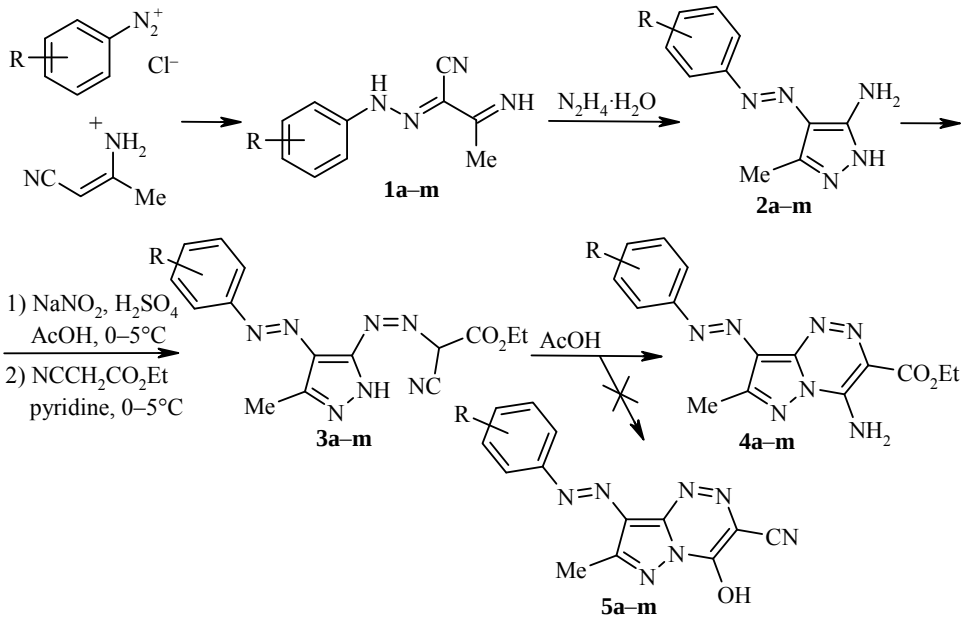
Keywords: ethyl cyanoacetate, pyrazole, diazo-coupling reaction, intramolecular cyclization, solvatochromism.

Polyfunctionally substituted heteroaromatics are biologically interesting molecules and their synthesis has recently received considerable attention [1–3]. 5-Amino pyrazoles 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 have 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 want to point to the cyclization of pyrazolylazoketonitriles that occurs with formation of 7-aminopyrazolo[5,1-*c*][1,2,4]triazines, as it has been found by Partridge and Stevens [23]. This cyclization was applied to a whole series of diversely substituted pyrazolylhydrazones [24–32]. All 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 the ring closure to 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.

2-Arylhydrazinylidene-3-iminobutyronitriles **1a**–**m** and 5-amino-4-arylazo-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 (Table 1, 2).



a R = H, **b** R = 4-NO_2, **c** R = 4-OMe, **d** R = 4-Cl, **e** R = 4-Me, **f** R = 3-NO_2, **g** R = 3-OMe, **h** R = 3-Cl, **i** R = 3-Me, **j** R = 2-NO_2, **k** R = 2-OMe, **l** R = 2-Cl, **m** R = 2-Me

Table 1

Physicochemical characteristics of compounds 4a–m

Compound	Empirical formula	Color	Found, % / Calculated, %			Mp, °C	Yield, %
			C	H	N		
4a	$C_{15}H_{15}N_7O_2$	Pale brown	55.51 / 55.38	4.69 / 4.65	29.82 / 30.14	261–262	67
4b	$C_{15}H_{14}N_8O_4$	Orange	48.86 / 48.65	3.80 / 3.81	30.02 / 30.26	245–246	83
4c	$C_{16}H_{17}N_7O_3$	Yellow	53.91 / 54.08	4.75 / 4.82	27.33 / 27.59	214–215	70
4d	$C_{15}H_{14}ClN_7O_2$	Orange	50.24 / 50.08	3.86 / 3.92	27.08 / 27.25	253–254	69
4e	$C_{16}H_{17}N_7O_2$	Yellow	56.88 / 56.63	5.13 / 5.05	28.67 / 28.89	227–228	64
4f	$C_{15}H_{14}N_8O_4$	Orange	48.47 / 48.65	3.72 / 3.81	29.96 / 30.26	294–295	80
4g	$C_{16}H_{17}N_7O_3$	Brown	54.28 / 54.08	4.95 / 4.82	27.48 / 27.59	214–215	74
4h	$C_{15}H_{14}ClN_7O_2$	Orange	50.19 / 50.08	3.88 / 3.92	26.95 / 27.25	253–254	76
4i	$C_{16}H_{17}N_7O_2$	Yellow	56.76 / 56.63	4.98 / 5.05	28.73 / 28.89	237–238	65
4j	$C_{15}H_{14}N_8O_4$	Orange	48.53 / 48.65	3.87 / 3.81	30.11 / 30.26	268–269	86
4k	$C_{16}H_{17}N_7O_3$	Yellow	54.21 / 54.08	4.96 / 4.82	27.38 / 27.59	237–238	74
4l	$C_{15}H_{14}ClN_7O_2$	Brown	50.25 / 50.08	4.01 / 3.92	26.93 / 27.25	259–260	73
4m	$C_{16}H_{17}N_7O_2$	Orange	56.56 / 56.63	4.97 / 5.05	28.72 / 28.89	230–231	70

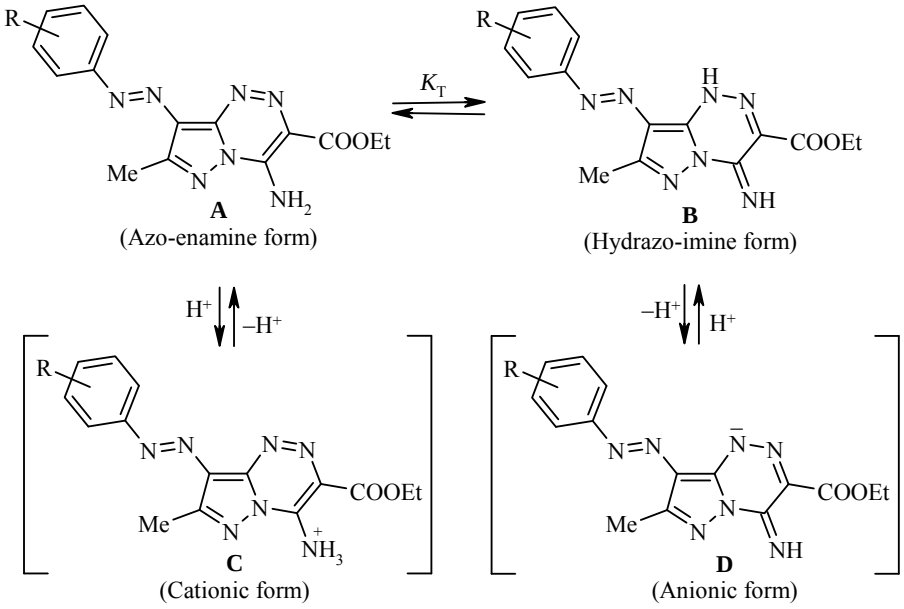
Table 2

Spectral characteristics of compounds 4a–m

Compound	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 $OC\underline{H}_2CH_3$); 2.77 (3H, s, 7-CH_3); 1.39 (3H, t, *J* = 6.9, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.79 (3H, s, 7-CH_3); 1.42 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 3.87 (3H, s, OCH_3); 2.73 (3H, s, 7-CH_3); 1.40 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.66 (3H, s, 7-CH_3); 1.29 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.75 (3H, s, 7-CH_3); 2.41 (3H, s, $ArC\underline{H}_3$); 1.39 (3H, t, *J* = 6.9, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.80 (3H, s, 7-CH_3); 1.40 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 3.87 (3H, s, OCH_3); 2.73 (3H, s, 7-CH_3); 1.39 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.77 (3H, s, 7-CH_3); 1.40 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.76 (3H, s, 7-CH_3); 2.45 (3H, s, $ArC\underline{H}_3$); 1.40 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.65 (3H, s, 7-CH_3); 1.40 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 3.98 (3H, s, OCH_3); 2.74 (3H, s, 7-CH_3); 1.40 (3H, t, *J* = 6.9, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.78 (3H, s, 7-CH_3); 1.41 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$)	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, $OC\underline{H}_2CH_3$); 2.77 (3H, s, 7-CH_3); 2.44 (3H, s, $ArC\underline{H}_3$); 1.41 (3H, t, *J* = 6.9, $OCH_2C\underline{H}_3$)	9.45 (1H, br. s, –NH–); 8.70 (1H, br. s, =NH)

* Signals of the hydrazo-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 to the dyestuff manufacturer, 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.



K_T – tautomeric equilibrium

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 predominantly exist in azo-enamine form, not in the hydrazo-imine form. The FT-IR spectra also showed a band at 1693–1672 cm^{-1} assigned to C=O group and did not show a band at 2200–2300 cm^{-1}, that could be characteristic for CN group. These results suggest that these dyes predominantly exist in aminoester form **4a**–**m**, not in hydroxynitrile form **5a**–**m**. The other ν value ranges were assigned to the respective structural features: 3072–3056 cm^{-1} (aromatic C–H), 2991–2960 cm^{-1} (aliphatic C–H), 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 are in favor of the azo-enamine form (**A**) [38–40].

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

Table 3

Influence of solvent on absorption maxima (λ_{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.

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 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 of this is probably that dyes **4a**,**c**–**j**,**l**–**m** exist in two tautomeric forms **A** and **B** in all used solvents (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 the cationic form **C** in acetic acid and in two tautomeric forms in the other solvents.

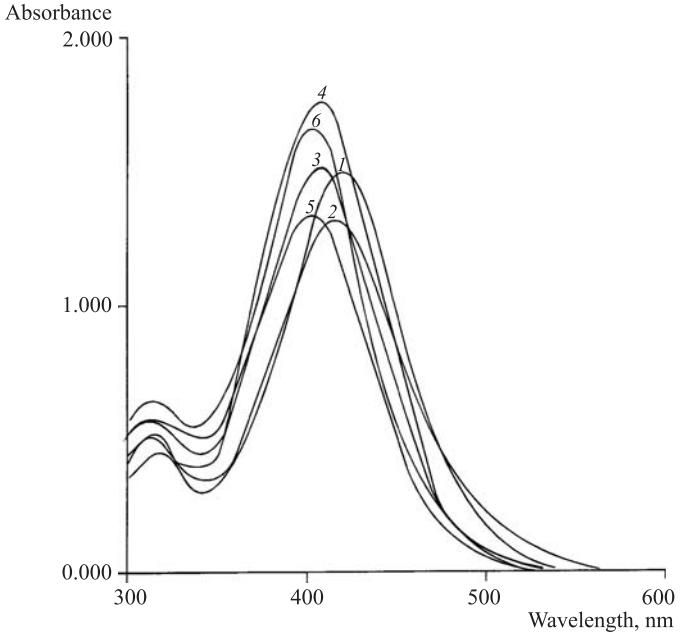


Fig. 1. Absorption spectra of dye **4j** in various solvents:
1 – DMSO, *2* – DMF, *3* – acetonitrile, *4* – methanol, *5* – acetic acid, *6* – chloroform

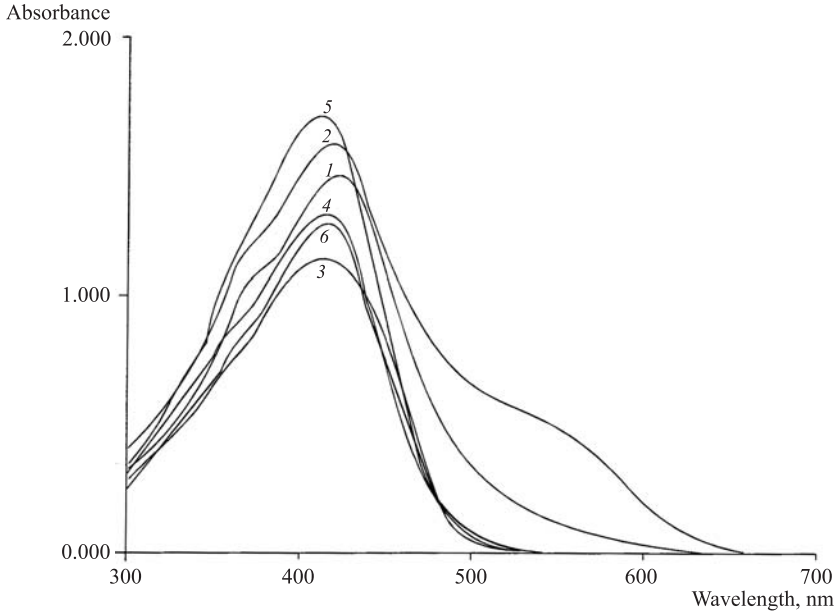


Fig. 2. Absorption spectra of dye **4b** in various solvents:
1 – DMSO, *2* – DMF, *3* – acetonitrile, *4* – methanol, *5* – acetic acid, *6* – chloroform

It was observed that although in acetonitrile, methanol, acetic acid, and chloroform the absorption spectra did not differ significantly, with the exception of dye **4k**, λ_{max} of these dyes shifted were bathochromically in DMSO and DMF; for example, for compound **4a**, λ_{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 λ_{max} values for dye **4k** in DMSO and DMF were shifted bathochromically with respect to the λ_{max} in the other solvents.

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 the dyes **4a**–**m** in methanol were quite sensitive to the addition of base (potassium hydroxide, 0.1 M), with λ_{max} showing a bathochromic shifts. Such an effect of base is consistent with the phenomenon of dissociation rather than azo-hydrazone tautomerism.

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

Also, λ_{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 absorption curves of the dyes resembled those in DMSO and DMF.

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.

As seen in Table 3, electron-accepting nitro and chloro groups and electron-donating methoxy group in all positions cause bathochromic shifts in all used solvents when compared to dye **4a**. Electron-donating methyl group in all positions causes little bathochromic shifts or does not change significantly in all used solvents when compared to dye **4a**. It was also observed that electron-accepting nitro and chloro groups and 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 favors the formation of the cationic form **C**.

Heterocyclic hydroxy-azo and amino-azo based dyes tend to show larger solvatochromic effects than azo-benzene 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**, too, showed solvatochromic effects. The absorption maxima of dyes showed bathochromic shifts in DMSO and DMF than 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 electron-accepting nitro and chloro groups and electron-donating methoxy group in *o*- and *p*-positions causes 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 hydrazo-imine form in acetonitrile, methanol, acetic acid, and chloroform, these dyes were present in azo-enamine form in DMSO and DMF, except for *p*-nitro and *o*-methoxy derivatives. In this part of 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 used solvents, except, again, for *p*-nitro (**4b**) and *o*-methoxy (**4k**) derivatives. Dye **4b** was present in two tautomeric forms and an 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 an intermediates 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 discs. ^{1}H NMR spectra were recorded on a Bruker-Spectrospin Avance DTX-400 Ultra-Shield spectrometer (400 MHz) in DMSO-d_6, using TMS as the 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 of λ_{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 dye solutions in MeOH (1 ml; because of low solubility, concentration of dyes can not be calculated exactly). Elemental analysis was performed on a Leco CHNS-932 analyzer. Melting points determined on an Electrothermal 9100 melting point apparatus and are uncorrected.

The 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-arylazo-7-methylpyrazolo[5,1-*c*][1,2,4]triazine-3-carboxylic acid ethyl esters 4a–m (General Method). Nitrosylsulfuric acid was prepared by dissolving $NaNO_2$ (1.00 g, 14.5 mmol) in conc. H_2SO_4 (7 ml) at 70°C. 4-Aryl-3-metylazo-1*H*-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 nitrosylsulphuric acid at 0–5°C, and the mixture 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, 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–H_2O, 3:1.

REFERENCES

1. F. Freeman, *Synthesis*, 925 (1981).
2. Y. Tominaga, Y. Honkawa, M. Hara, A. Hosomi, *J. Heterocycl. Chem*., **27**, 775 (1990).
3. U. Hanefeld, C. W. Rees, A. J. P. White, D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, **13**, 1545 (1996).
4. A. G. A. Elagamey, F. M. A.-A. El-Taweel, *J. Prakt. Chem*., **333**, 333 (1991).
5. F. M. A. Latif, M. A. Barsy, E. A. Elrady, M. Hassan, *J. Chem. Res., Synop.*, **12**, 696 (1999).
6. K. Senga, T. Novinson, R. H. Springer, R. P. Rao, D. E. O'Brien, R. K. Robins, H. R. Wilson, *J. Med. Chem*., **18**, 312 (1975).
7. S. P. Singh, D. Kumar, *Heterocycles*, **31**, 855 (1990).
8. L. H. Sternbach, *Prog. Drug Res*., **22**, 229 (1978).
9. N. Jaiswal, R. Jaiswal, J. Barthwal, K. Kishor, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem*., **20B**, 252 (1981).
10. S. G. Küçükgüzel, S. Rollas, H. Erdeniz, M. Kiraz, A. C. Ekinci, A. Vidin, *Eur. J. Med. Chem*., **35**, 761 (2000).
11. L. R. S. Dias, M. J. Alvim, A. C. C. Freitas, E. J. Barreiro, A. L. P. Miranda, *Pharm. Acta Helv.*, **69**, 163 (1994).

12. J. W. Lyga, R. M. Patera, M. J. Plummer, B. P. Halling, D. A. Yuhas, *Pestic. Sci*., **42**, 29 (1994).
13. M. J. Genin, C. Biles, B. J. Keiser, S. M. Poppe, S. M. Swaney, W. G. Tarpley, Y. Yagi, D. L. Romero, *J. Med. Chem.*, **43**, 1034 (2000).
14. N. Ertan, *Dyes Pigm.*, **44**, 41 (2000).
15. A. K. Khalil, M. A. Hassan, M. M. Mohamed, A. M. El-Sayed, *Dyes Pigm.*, **66**, 241 (2005).
16. A. Emandi, I. Serban, R. Bandula, *Dyes Pigm.*, **41**, 63 (1999).
17. P. C. Tsai, I. J. Wang, *Dyes Pigm.*, **64**, 259 (2005).
18. Y. W. Ho, *Dyes Pigm.*, **64**, 223 (2005).
19. F. Karcı, N. Şener, M. Yamaç, İ. Şener, A. Demirçalı, *Dyes Pigm*., **80**, 47 (2009).
20. E. E. Oruc, B. Kocyigit-Kaymakcioglu, B. Oral, H.Z. Altunbas-Toklu, L. Kabasakal, S. Rollas, *Arch. Pharm*., **339**, 267 (2006).
21. S. S. Kandil, F. I. Abdel-Hay, R. M. Issa, *J. Therm. Anal. Calorim.*, **63**, 173 (2001).
22. S. A. Abdel-Latif, *Synth. React. Inorg. Met.-Org. Chem*., **31**, 1355 (2001).
23. M. V. Partridge, M. F. G. Stevens, *J. Chem. Soc. C*, 1127 (1966).
24. E. J. Gray, M. F. G. Stevens, G. Tennant, R. J. S. Vevers, *J. Chem. Soc., Perkin Trans. 1*, **14**, 1496 (1976).
25. M. H. Elnagdi, M. R. H. El-Moghayar, D. H. Fleita, E. A. A. Hafez, S. M. Fahmy, *J. Org. Chem*., **41**, 3781 (1976).
26. M. H. Elnagdi, M. R. H. Elmoghayar, E. M. Kandeel, M. K. A. Ibrahim, *J. Heterocycl. Chem*., **14**, 227 (1977).
27. M. H. Elnagdi, E. M. Zayed, M. A. E. Khalifa, S. A. Ghozlan, *Monatsh. Chem*., **112**, 245 (1981).
28. H. A. Hammouda, A. A. El-Barbary, M. A. F. Sharaf, *J. Heterocycl. Chem*., **21**, 945 (1984).
29. K. U. Sadek, M. A. Selim, M. A. El-Maghraby, *J. Chem. Eng. Data*, **30**, 514 (1985).
30. A. A. El-Agamey, M. R. H. El-Moghayar, M. H. Elnagdi, *Pharmazie*, **40**, 176 (1985).
31. M. M. Girges, M. A. Hanna, A. A. Fadda, *Chem. Pap.*, **47**, 186 (1993).
32. A. M. Farag, K. M. Dawood, Z. E. Kandeel, *Tetrahedron*, **52**, 7893 (1996).
33. F. Karcı, İ. Şener, A. Demirçalı, N. Burukoğlu, *Color. Technol.*, **122**, 264 (2006).
34. F. Karcı, F. Karcı, *Dyes Pigm.*, **76**, 97 (2008).
35. F. Karcı, *Color. Technol.*, **121**, 275 (2005).
36. M. A. Metwally, E. Abdel-Latif, A. M. Khalil, F. A. Amer, G. Kaupp, *Dyes Pigm.*, **62**, 181 (2004).
37. H. Joshi, F. S. Kamounah, G. Van Der Zwan, C. Gooijer, L. Antonov, *J. Chem. Soc., Perkin Trans 2*, 2303 (2001).
38. F. Karcı, A. Demirçalı, İ. Şener, T. Tilki, *Dyes Pigm.*, **71**, 90 (2006).
39. F. Karcı, A. Demirçalı, *Dyes Pigm.*, **71**, 97 (2006).
40. F. Karcı, A. Demirçalı, *Dyes Pigm.*, **74**, 288 (2007).

[1] *Pamukkale University, Faculty of Science-Arts,*
D Block, Kınıklı Campus, Denizli 20017, Turkey
e-mail: fkarci@pau.edu.tr

Received 9.02.2012
In revised version 16.11.2012

[2] *Pamukkale University, Higher Vocational School of Denizli,*
30 Fakülte St., Kınıklı, Denizli 20020, Turkey
e-mail: fati@pau.edu.tr