

Synthesis, characterization and spectroscopic properties of some new azo dyes derived from 6-aminopyrimidine-2, 4(1H, 3H) – dione

MOHAMMAD REZA YAZDANBAKSH* and E. MORADI-E-RUFCHAH

Department of Chemistry, Faculty of Sciences, Guilan University, Rasht (Iran).

(Received: December 12, 2008; Accepted: January 24, 2009)

ABSTRACT

A series of new azo amino uracil dyes were synthesized by diazotization of nine aromatic amines using sodium nitrite and hydrochloric acid and subsequent coupling to 6-aminopyrimidine-2, 4(1H, 3H) – dione. The effects of solvents, substituents, acid and base on the visible absorption maxima of the dyes were also discussed.

Key words: azo Uracil dyes, spectroscopic properties, tautomerism, solvent effect.

INTRODUCTION

Azo compounds have received much attention and have been widely used in many practical applications such as coloring fiber^{1,2}, photo-electronic applications³, printing systems⁴, optical storage technology^{5,6} and in analytical chemistry⁷⁻⁹. Among them, heterocyclic azo dyes attract considerable interest and play an important role in the development of the chemistry of azo compounds. In this class of azo dyes, pyridone and pyrimidine derivatives are relatively recent heterocyclic intermediates for the preparation of aryl-azo dyes^{10,11}. The azo pyridone or azo pyrimidine dyes give bright hues and are suitable for the dyeing of polyester fabrics¹². The physico-chemical properties of these aryl azo dyes are closely related to their tautomeric structures¹³. A lot of investigations on the substituted azo pyridone and pyrimidine dyes have been carried out and reviewed. For instance, Song and coworkers synthesized a series of pyridone dyes derived from 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone and evaluated their spectroscopic

properties¹⁴. However, very few investigations have been published with respect to 6-aminopyrimidine-2, 4(1H, 3H) – dione 4(6)-amino uracil] and its derivatives. In this paper, we report the synthesis of some arylazouracil dyes¹⁻⁹ (scheme 1) resulting from 4(6)-amino uracil as a coupling component and an evaluation of their visible absorption spectra with respect to the influences of substituents and solvents. The effects of acid and base on the visible absorption maxima of the dyes were also reported.

EXPERIMENTAL

General

The chemicals used in the synthesis of all dyes were purchased from Merck Chemical Company and used without further purification and all the used organic solvents were in high purity (spectroscopic grade). IR spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer in KBr. ¹H NMR spectra were determined with a Bruker FT-NMR instrument at 500 MHz in DMSO-d₆ with TMS as internal standard. Absorption spectra were recorded on a CARY 100 spectrophotometer in

various solvents. Melting points were determined on an Electrothermal 9100 melting point apparatus and uncorrected.

Synthesis of dyes

General procedure for diazotization

Aromatic amine (0.01mol) was dissolved in 5 ml of 2.0 mol.l⁻¹ hydrochloric acid (0.01mol). The solution was cooled to 0-5°C in an ice-bath and an aqueous solution of sodium nitrite (0.69g, 0.01mol) in water (4 ml) was then added drop wise for 20 min. stirring was continued for 45 min at the same temperature to give a clear solution. The resulting diazonium solution was used immediately in the coupling reaction.

Preparation of the dyes 1-9

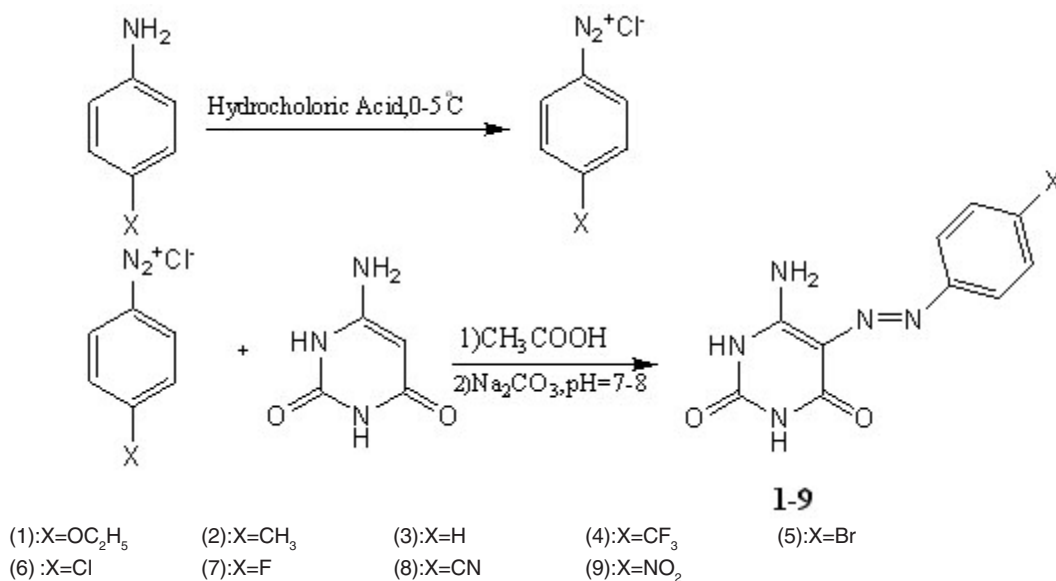
6-aminopyrimidine-2, 4(1H, 3H)-dione (1.271g, 0.01mol) was dissolved in hot glacial acetic acid (25 ml) and for the purpose of helping of its solubility acetonitrile (10 ml) and ethanol (15 ml) was added to this solution and rapidly cooled to 0°C in an ice-water bath. Then the diazonium salt prepared as above was dropped into the coupling component. The pH of the reaction mixture was maintained at 7-8 by simultaneous addition of a sodium carbonate solution. The mixture was then stirred for 2 h at 0-5°C. The progress of the reaction

was followed by TLC using DMF- EtOAc mixture (5:1 by volume) as the developing solvent and silica gel TLC plates as the stationary phase. The resulting solid was filtered, washed with cold water and ethanol and dried in the air. Recrystallization was performed in DMF-H₂O mixture. The selected physical properties and characteristic data of the synthesized dyes were measured and listed in Table 1.

RESULT AND DISCUSSION

The arylazouracil dyes 1-9 were prepared by coupling 6-aminopyrimidine-2, 4(1H, 3H) – dione with diazotized aromatic amines in hydrochloric acid (Scheme 1). The dyes may exist in eight possible tautomeric forms, namely azo-amine-diketo I, hydrazo- imine-diketo II, hydrazo- imine-diketo III, azo-imine-keto-enol IV, azo-imine-Dienol V, azo-amine-dienol VI, hydrazo-amine-keto-enol VII, hydrazo-amine-diketo VIII, as shown in scheme 2.

The arylazouracil dyes were characterized using ¹H NMR, IR and UV-visible spectroscopy (Table 1). The infrared spectra of all compounds (in KBr) showed two intense carbonyl bands at 1633-1618 cm⁻¹ and 1764-1726 cm⁻¹ related to two carbonyl groups of uracil ring. The FT-IR also



Scheme 1: Structures of the prepared dyes

Table 1: Characteristics data of dyes 1-9

Dye	FT-IR (cm ⁻¹ , KBr)	¹ H NMR (δ, ppm)	m.p (°C)	yield (%)
1.	3448(N-H),3124(N-H), 1743(C=O),1649(C=O), 1502(N=N)	1.34 (t,3H), 4.07(q,2H), 6.99 (d, J=7 Hz,2H), 7.60(d, J=7Hz,2H), 7.39(br, C=C-NH-C=O), 10.58(br, O=C-NH-C=O), 10.41(br,NH)10.81(NH), 14.12 (br, OH)	325-327	65
2.	3147(N-H), 3024(Ar _{C-H}), 1737(C=O), 1626(C=O), 1531(N=N)	2.34(s,3H),7.25(d,J=5Hz,2H), 7.55(d,J=5Hz,2H), 7.49(br, C=C-NH-C=O), 10.62(br, O=C-NH-C=O), 10.53(br,NH)10.86(NH), 14.15 (br,OH)	350	60
3.	3238(N-H), 3155(N-H), 3028(Ar _{C-H}), 1741(C=O), 1624(C=O), 1533(N=N)	7.30(t, 1H),7.45(t, 2H), 7.64(d,J=7.5Hz,2H),7.77 (br,C=C-NH-C=O), 10.67(br,O=C-NH-C=O), 10.58(br,NH)10.90(NH), 14.11 (br,OH)	320-322	60
4.	3221(N-H),3147(N-H), 3033(Ar _{C-H}),1741(C=O), 1633(C=O),1533(N=N)	7.8-7.83(overlapped,4H), 7.95(br,C=C-NH-C=O), 10.68(br,O=C-NH-C=O), 10.46(br,NH)10.99(NH)	345	72
5.	3238(N-H), 3128(N-H), 3028(Ar _{C-H}), 1732(C=O),1630(C=O),	7.62(overlapped,4H), 7.96(br,C=C-NH-C=O), 10.54(br,O=C-NH-C=O), 10.87(br,NH ₂)	345-347	70
6.	1519(N=N) 3155(N-H),3026 (Ar _{C-H})1760(C=O), 1618(C=O), 1533(N=N)	7.49-7.67(overlapped,4H), 7.67(br,C=C-NH-C=O), 10.52(br,O=C-NH-C=O), 10.74(br,NH)10.92(br,NH)	340	70
7.	3238(N-H), 3155(N-H), 3028(Ar _{C-H}), 1734(C=O),1626(C=O),	7.28(t,2H), 7.69(t,2H), 7.67(br,C=C-NH-C=O), (br,O=C-NH- 1533(N=N)10.65	343-345	60
8.	3500(N-H),3100(N-H), 2224(CN), 1726(C=O),1624(C=O), 1520(N=N)	C=O),10.65(br,NH)10.90(br,NH) 7.80(2H), 7.90(2H), 7.80(br,C=C-NH-C=O),	348-350	50
9.	3500(N-H), 3100(N-H), 1506(N=O),1324(N=O) 7.84(br,C=C-NH-C=O),	10.71(br,O=C-NH-C=O),11.03(br,NH ₂) 8.30(d,J=8Hz,2H), 7.81(d,J=8Hz, 2H), 1743(C=O),1649(C=O),1525(N=N) 10.79(br,O=C-NH-C=O),11.00(br,NH ₂)	346-348	45

showed broad bands at 3448-3124 cm^{-1} which was assigned to OH, NH and NH_2 groups. It can be suggested that these compounds may exist as the enol forms (IV, V, VI, VII) in solid state. The spectra also showed a weak band or a shoulder at 3033-3024 cm^{-1} which was assigned to aromatic C-H. The other ν_{max} values of 2970 cm^{-1} (aliphatic C-H, dye 1), 2819 cm^{-1} (aliphatic C-H, dye 2), 1136 and 1034 cm^{-1} (C-F, dye 4), 1074 cm^{-1} (C_{Ar} -Br, dye 5), 1091 cm^{-1} (C_{Ar} -Cl, Dye 6), 1203 cm^{-1} (C_{Ar} -F, Dye 7), 2224 cm^{-1} (CN, dye 8), 1506 and 1342 cm^{-1} (NO_2 , dye 9) were recorded.

The ^1H NMR spectra measured in DMSO-d_6 at 25 $^\circ\text{C}$ showed a triplet at 1.34 ppm and a quartet at 4.08 ppm ($\text{CH}_3\text{CH}_2\text{O}$ -, dye 1), a singlet at 2.34 ppm ($-\text{CH}_3$, dye 2), a multiplet from 6.98-8.33

ppm for aromatic protons (Ar-H), a broad signal from 7.39 to 7.98 ppm for one of the NH protons of uracil ring ($\text{C}=\text{C}-\text{NH}-\text{C}=\text{O}$), a broad signal from 10.58-10.79 ppm for the other uracil $\text{NH}(\text{O}=\text{C}-\text{NH}-\text{C}=\text{O})$ proton.

The dyes 1-3 and 5-7 show OH signal within the range of 13.95-14.15 ppm. These results suggest that the dyes may exist in the enol forms IV, V, VI and VII in DMSO-d_6 . The ^1H NMR analysis of dyes 1, 2, 3, 6, and 7 evidenced the non-equivalence of amino hydrogens suggesting a hydrogen bond with the azo group as described in references for similar structures I and a typical example can be seen in Figure 1 for dye 7 at 10.45 and 10.90 ppm^{15,16}.

Table 2: Influence of solvents on λ_{max} (nm) of dyes 1-9

Dye no	DMSO	DMF	Acetonitrile	Ethanol	Acetic acid	Chloroform
1	437	433	410	371 s, 413	446	450
2	397, 422 s	378	378	376	392	380
3	405	400	375	374 s, 391	406	409
4	375, 410 s	375, 400 s	409	415	416	413
5	382, 403 s	381, 413 s	394	374, 400 s	412	410
6	382, 406 s	381, 406 s	382	371, 402 s	411	415
7	369 s, 395	366, 405 s	366, 391 s	362, 388 s	406	368, 400 s
8	394	390	385	383	399	391
9	415	430, 476 s	401	398	403	402

Table 3: Absorption maxima of dyes 1-9 in acidic and basic solutions

Dye No	X	ethanol	Ethanol+NaOH	Ethanol + HCl
1	OEt	413	375	443
2	CH_3	376	378, 413 s	390
3	H	391	372	403
4	CF_3	415	375, 410 s	417
5	Br	374, 400 s	378, 405 s	411
6	Cl	371, 402 s	374	409
7	F	362, 388 s	378, 405 s	406
8	CN	383	401	394
9	NO_2	398	442	395

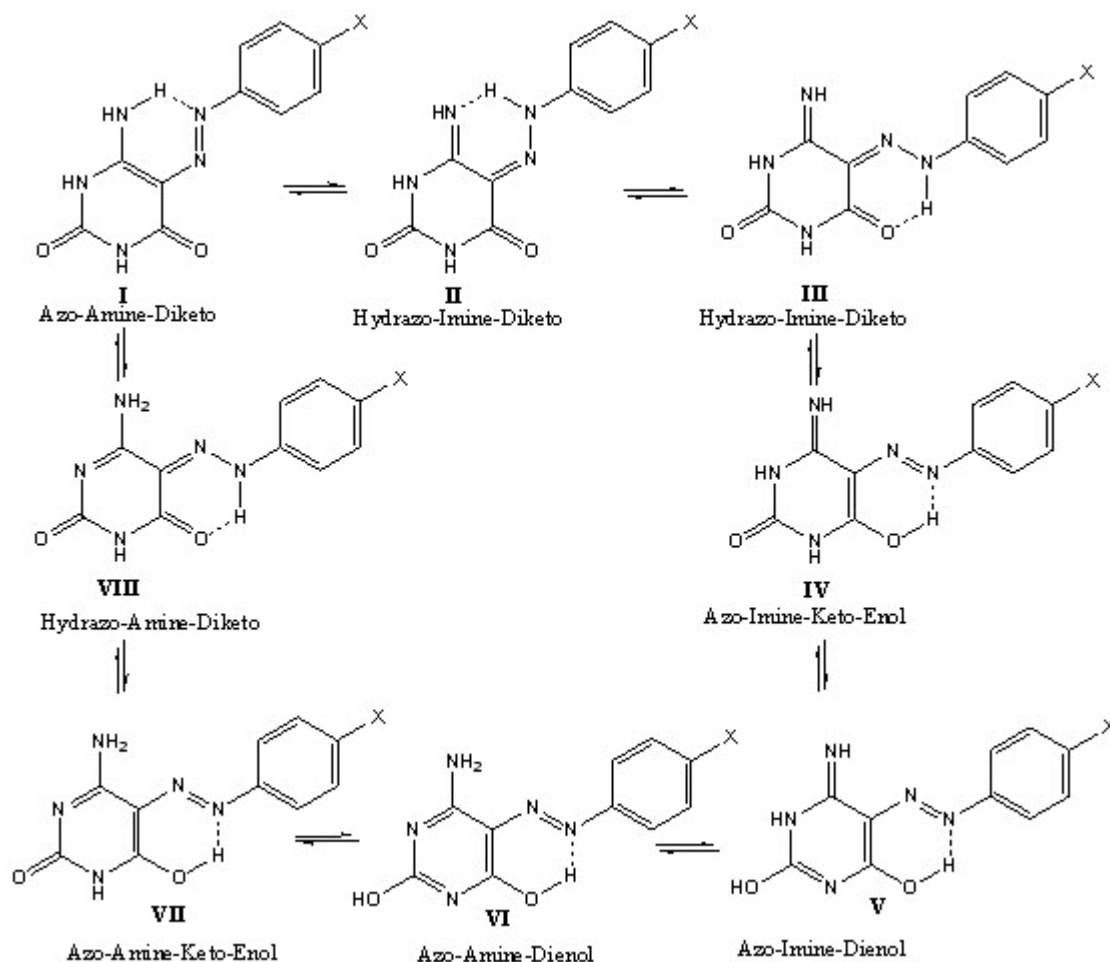
^s shoulder

Solvent effect on the absorption spectra of the dyes

UV-vis absorption spectra were recorded using a CARY 100 spectrophotometer in the wavelength range 300-600 nm. Absorption spectra of arylazouracil dyes 1-9 were measured in various solvents at a concentration approximately 10^{-5} - 10^{-6} M. The results were summarized in Table 2. The visible absorption spectra of the dyes did not show regular variation with the polarity of solvents.

The dyes showed one or two absorbances in various solvents except for dye 8. Dye 8 showed single absorbance in all used solvents. It can be suggested that dyes 8 is predominantly in the single tautomeric form in all used solvents. Dye 1 and 3 showed two absorbances in ethanol. The dye 4 showed two absorbances in DMSO and DMF. The

dyes 5 and 6 showed two absorbances in DMSO, DMF and ethanol. The dye 7 showed two absorbances in all solvents except acetic acid. Dye 9 showed two absorbances in DMF. Consequently the mentioned dyes may exist as a mixture of tautomeric forms in these solvents. Figure 2 shows the absorption spectra of dye in various solvents. It was observed that the absorption spectra of all dyes except 3 in ethanol have the lowest absorption band in the UV-vis region. For example, 5-(4-nitro phenyl azo)-6-aminopyrimidine-2, 4(1H, 3H) – dione in DMSO (dye 9, $\lambda_{\max} = 476$ nm) is shifted 78 nm upon λ_{\max} in ethanol. The λ_{\max} of dyes 1, 3 and 6 in all solvents hypsochromically shifted with respect to absorption spectra in chloroform(e.g. for dye 1 λ_{\max} is 450 nm in CHCl_3 , 437 nm in DMSO, 433 nm in DMF). But the λ_{\max} of dye 4 and dyes 5-9 showed bathochromic shift in acetic acid with respect to



Scheme 2: Possible tautomeric forms for the prepared azo dyes

absorption spectra in chloroform (e.g. for dye 5 λ_{\max} is 404 nm in CHCl_3 , 412 nm in CH_3COOH).

It was also observed that the absorption curves of the dyes were sensitive to acid and base (Table 3). The absorption spectra of the dyes in ethanol also showed bathochromic shifts when 0.1 M HCl was added except for dye 9 and absorption curves of the dyes resembled those in acetic acid.

It can be suggested that in acidic media and AcOH the dyes exists the same tautomeric form(s).

The λ_{\max} of the dyes showed slightly bathochromic shifts when 0.1 M NaOH was added to each of the dye solutions in ethanol and the absorption curves are resembled those in high basicity solvents such as DMSO and DMF. A typical example is shown in Figure 3.

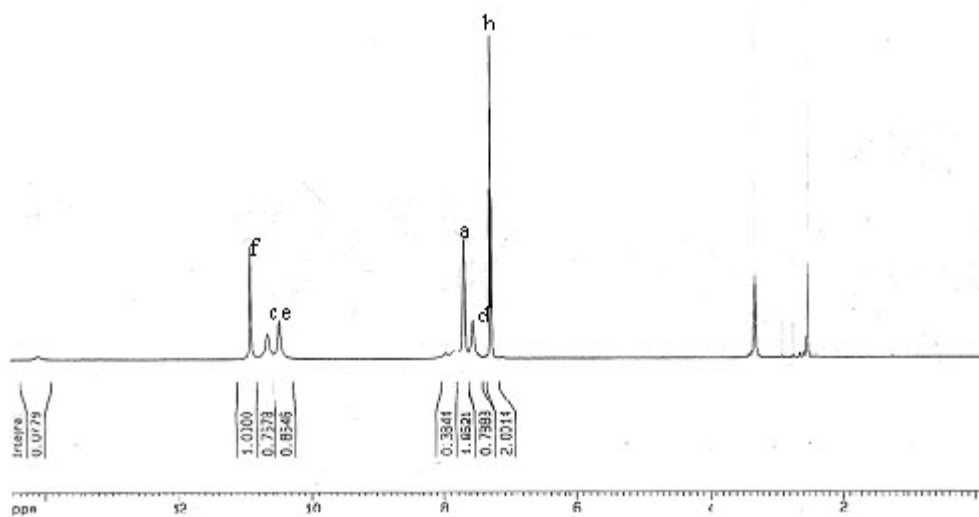


Fig. 1: ^1H NMR spectrum of dye 7 in DMSO-d_6

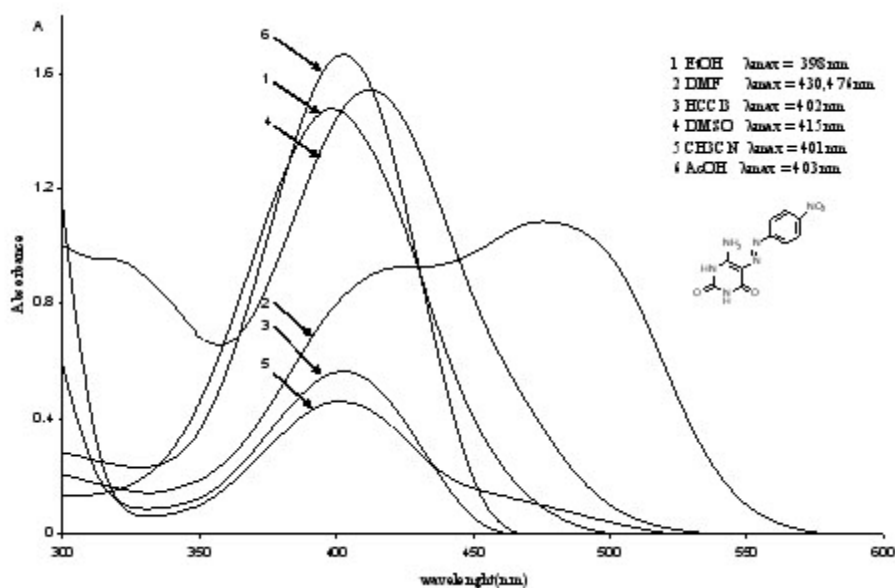


Fig. 2: Absorption spectra of dye 9 in various solvents

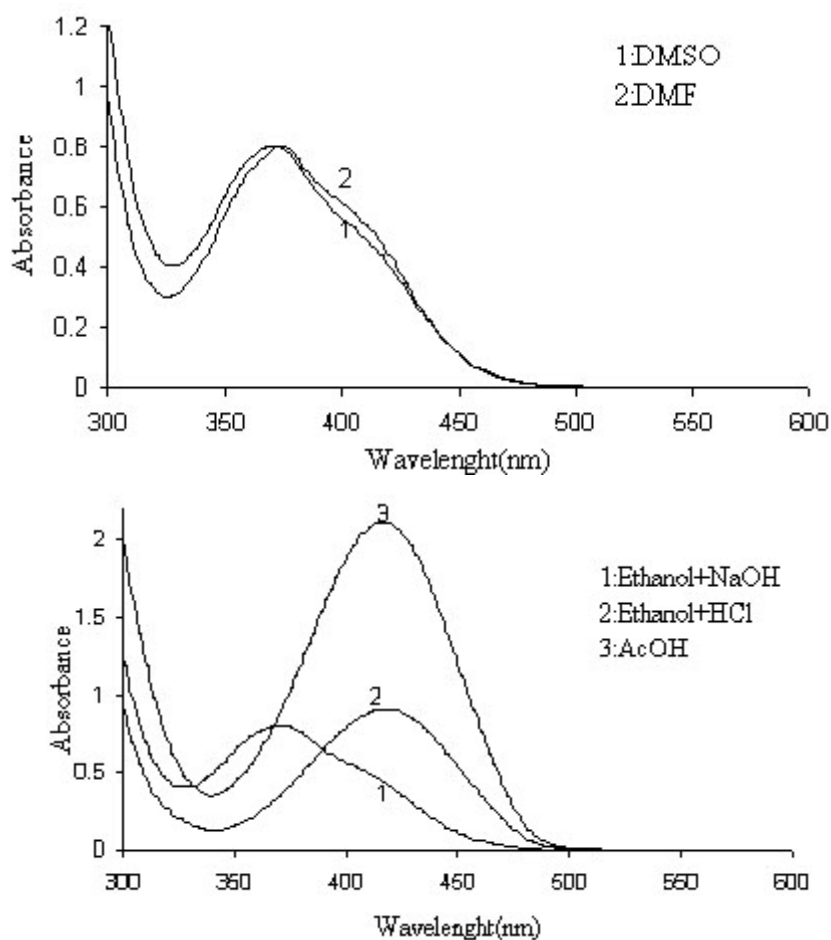


Fig. 3: Absorption spectra of dye 4 in acidic and basic solutions

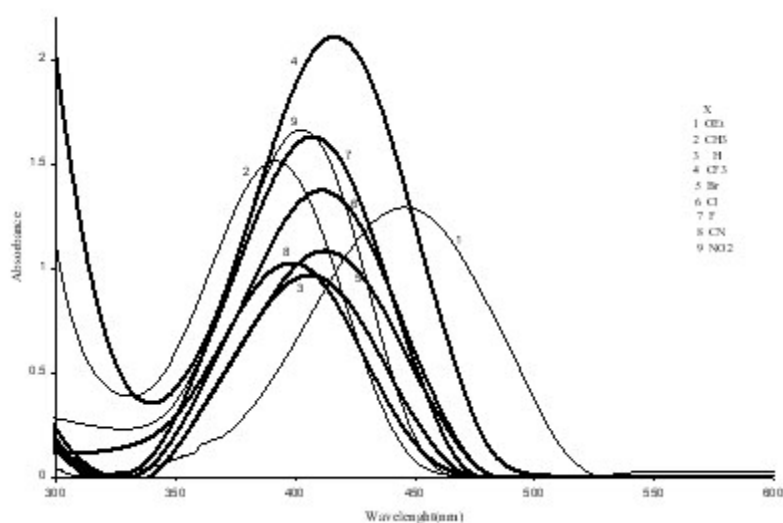


Fig. 4: Absorption spectra of dyes 1-9 in acetic acid

Substituents effects

Fig. (4) shows the absorption spectra of dyes 1-9 in acetic acid. As it is apparent in this Fig. and Table 2, on going from electron releasing group OEt to high electron withdrawing group NO₂ the maximum absorbance is shifted to lower wavelengths. The introduction of electron-donating ethoxy (-OEt) group in the benzene ring resulted in bathochromic shifts in all solvents (for dye 1 $\Delta\lambda=40$ nm relative to dye 3 for spectra in Acetic acid). It was also observed that the introduction of halogen groups (-Br,-Cl) in the benzene ring (for dye 6 $\Delta\lambda=6$ nm, $\Delta\lambda_{\text{shoulder}}=77$ nm relative to dye 3 for spectra in chloroform) resulted in bathochromic shifts in all solvents. This can be attributed to the electron-withdrawing nature of the Uracil moiety in the prepared azo dyes. The cyano group in the benzene ring resulted hypsochromic shifts in all solvents. The

trifluoromethyl (-CF₃) group in the benzene ring resulted in bathochromic shifts in all solvents except in DMF. The introduction of electron-accepting fluoro (-F) group in the benzene ring resulted in the bathochromic shifts in DMSO and acetonitrile but did not change significantly in the other solvents.

CONCLUSION

In this study, a series of new heterocyclic disperse azo dyes were prepared by coupling 4(6) - amino uracil with nine aromatic amines. The synthesized 6-aminopyrimidine-2, 4(1H, 3H) - dione azo dyes 1-9 showed solvatochromism effects because in the increased polarity of the dye system. On the other hand in azo Uracil dyes, their tautomeric equilibrium needs to be considered.

REFERENCES

- Koh, J., Greaves, A.J. *Dyes and Pigments*, **50**(1): 13 (2001).
- Sekar, N. *Colourage*, **46**: 63 (1999).
- Katz, H.E., Singer, K.D., Sohn, J.E., Dirk, C.W., King, L.A., Gordon, H.M. *J Am Chem Soc*, **109**(21): 6561 (1987).
- Abe, T., Mano, S., Yamada, Y., Yomotake, A. *J Imag Sci Technol*, **43**: 339 (1999).
- Wang, S., Shen, S., Xu, H. *Dyes and Pigments*, **44**(3): 195 (2000).
- Daidone, G., Bajardi, M.L., Plescia, S., Raffa, D., Schillaci, D., Maggio, B., Benetollo, F., Bombieri, G. *Eur J Med Chem*, **31**: 461 (1996).
- Gup, R., Gizioglu, E., Kirkan, B. *Dyes and Pigments*, **73**(1): 40 (2007).
- Amin, A.S., Mohammad, T.Y., Mousa, A.A. *Spectrochemica Acta part A*, **59**: 2577 (2003).
- Amin, A.S., Mohammad, T.Y. *Talanta*, **54**: 611 (2001).
- Lubai, C., Xing, C., Kunyu, G., Jiazhen, H., Griffiths, J. *Dyes and Pigments*, **7**(5): 373 (1986).
- Ertan, N., Eydurun, F. *Dyes and Pigments*, **27**(4), 313 (1995).
- Norris, R., Swaney, M.W., Riechers, E.H. *J. Chem. Soc.*, **65**: 2241 (1943).
- Griffiths, J. *Colour and Constitution of Organic Molecules*, Academic Press, London, 180-195 (1976).
- Song, H., Chen, K., Tian, H. *Dyes and Pigments*, **53**(3): 257 (2002).
- Kaminski, R., Lauk, U., Skrabal, P., Zollinger, H. *Helv Chim Acta*, **66**: 2002 (1983).
- Viscardi, G., Quagliotto, P., Barolo, C., Diulgheroff, N., Caputo, G., Barni, E. *Dyes and Pigments*, **54**(2): 131 (2002).