A study on tautomeric equilibria of new hetarylazo-6-aminouracils

Zeynel Seferoğlu

Gazi University, Faculty of Science-Arts, Department of Chemistry, 06500 Teknikokullar, Ankara, Turkey
E-mail: znseferoglu@gazi.edu.tr

Abstract
A series of new heterocyclic disperse azo dyes was prepared by coupling selected diazotized heterocyclic amines with 6-aminouracil. Solvent effects on the UV-visible spectra of the dyes were evaluated. Their colors were discussed with respect to the nature of the heterocyclic ring and the substituents, and the effects of acid and base on their UV-visible absorption spectra.

Keywords: Hetarylazo uracil dyes, azo-hydrazones, solvent effects, substituent effects, absorption spectra

Introduction

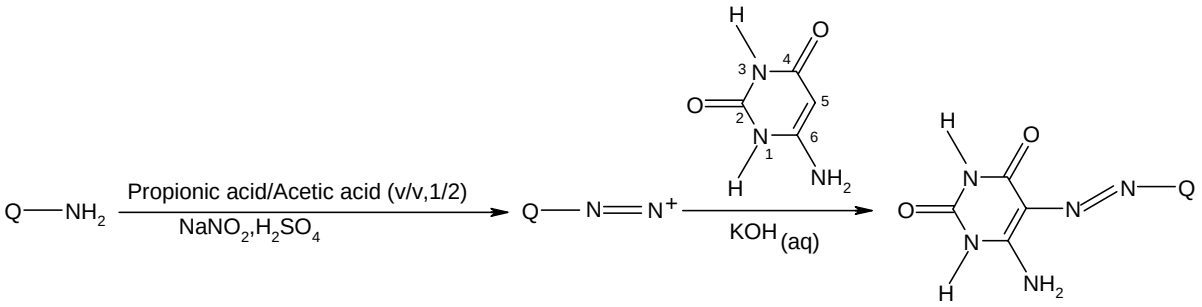
The pyrimidine nucleus has a key feature in various derivatives that are used as hypnotic drugs for the nervous system,[1] in detecting cancer, as chemotherapeutic agents, and are central to the structure of nucleic acids in living cells.[2] Some pyrimidine derivatives have biological and pharmacological activities.[3-6] Uracils are a very important class of pyrimidine derivatives, that continually attract organic chemists, medicinal chemists and photobiologists.[7,8] Some uracil derivatives exhibit significant pharmacological activity and have been used as antitumor, antibacterial, and antiviral drugs. Fluorouracil is extensively used as an anticancer agent. 5-Nitrouracil is known to inhibit thymidine phosphorylase,[9] and thio- derivatives of 5-nitrouracil show antibacterial activity.[10] Also, 5-cinnamoyl-6-aminouracil derivatives have been investigated as anticancer agents.[11] Moreover, 6-aminouracils find wide application as starting materials for the synthesis of many fused uracils of biological significance.[12] Therefore, uracils are very important for application in organic synthesis. Also, its derivatives can be used as a coupling component in dye chemistry.

Azo dyes represent the largest group of disperse dyes in the textile industry, and are used in dyeing of synthetic fibers. The dyes with heterocyclic diazo components have been intensively investigated, to produce bright and strong color shades ranging from red to greenish blue on synthetic fabrics. These results led to commercial products to replace the conventional

azobenzene disperse dyes.[13-18] Nitro-substituted aminothiophenes and aminothiazoles are primarily of importance as diazo components.[19-24] Recently, Towns has summarized the developments in azo disperse dyes derived from heterocyclic diazo components.[14] Non-textile uses of hetarylazo disperse dyes have been explored, for example in reprographic technology, functional dye applications, and non-linear optical systems.[25-27]

It is well-known that mono-azo dyes prepared from enol- and enamine- type coupling components exhibit azo-hydrazone tautomerism.[28-35] Determination of azo-hydrazone tautomerism both in solid state and solution phase is quite interesting both from theoretical and practical standpoints, since the tautomers have different technical properties and dyeing performance.[36]

In our previous studies, mono- and bis- azo dyes were synthesized and their structures and spectroscopic properties evaluated.[28-35, 37-45] Some new phenylazouracil disperse dyes were also synthesized.[34] In these studies, azo-hydrazone tautomerism was investigated for the dyes, both in the solid state and solution phase. It was observed that the dyes are in the azo form, and very stable in the solid state. In addition, their tautomeric equilibria strongly depend on the polarity of the solvent in the solution. As a continuation of this research, the synthesis of new hetarylazouracil dyes, **1-20,** was reported and their absorption spectra were evaluated in various solvents for the color-structure relationships in such dyes. The color of the dyes was discussed in relation to the nature of the heterocyclic ring and the substituents. Acid-base effects on the absorption spectra of the dyes were also studied in detail.

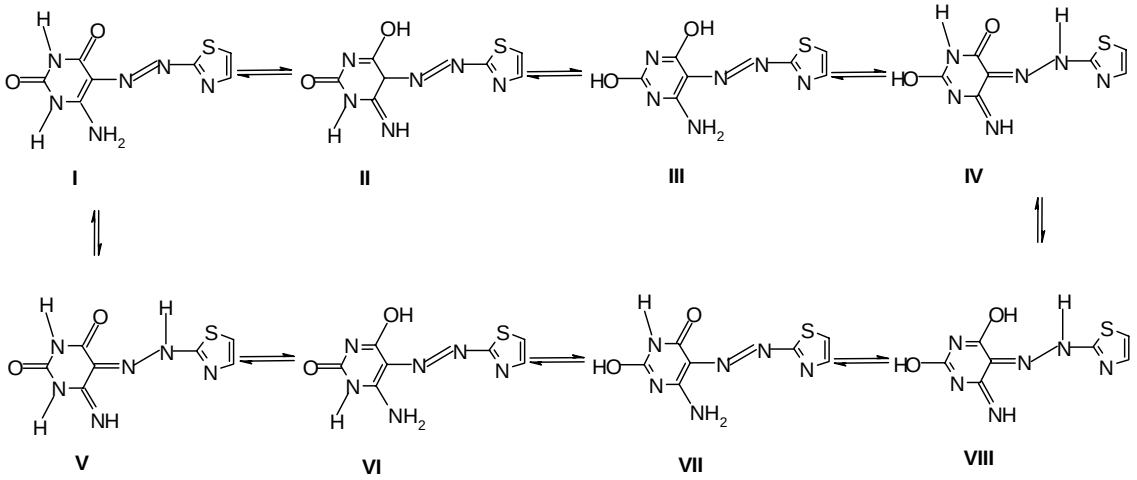


Q_1. 1, Thiazole. **2**, 5-methylthiazole. **3,** 5-nitrothiazole. **4,** 4-methylthiazole. **5,** ethylthiazol-4-yl acetate. **6**, 4-phenylthiazole. **7,** 4-(4-chloro)-phenylthiazole. **8,** 4-(4-bromo)-phenylthiazole. **Q_2. 9,** benzothiazole. **10,** 6-methoxybenzothiazole. **11,** 6-chlorobenzothiazole. **12,** 6-nitrobenzothiazole. **13,** 5,6-dimethylbenzothiazole. **Q_3. 14,** 1,3,4-thiadiazole. **15,** 5-methylthio-1,3,4-thiadiazole. **16,** 5-ethyl-1,3,4-thiadiazole. **17,** 1,2,4-triazole. **18,** 5-methylthio-1,2,4-triazole. **19,** 5-methylisoxazole. **20,** Pyridine.

Scheme 1. Synthetic pathway for the compounds **$Q_{1,2,3}$** and their structures.

Results and Discussion

Characterization of the new monoazo dyes (1-20). The hetarylazo-6-aminouracils were prepared by coupling 6-aminouracil with selected diazotized heterocyclic amines (Scheme 1). The structures of these dyes were verified by elemental analysis and spectroscopic methods (FT-IR, ^{1}H NMR and mass). Physical and spectroscopic data of the prepared dyes are given in the Experimental Section. The dyes may exist in eight tautomeric forms, as shown in Scheme 2.



Scheme 2

The IR spectra of all the dyes (in KBr) showed broad bands within the range 3480-3184 cm^{-1} due to the NH_2 band of the uracil ring, and strong carbonyl bands at 1766-1686 cm^{-1} plus a band at 3268-3108 cm^{-1}, assigned to the uracil NH groups. The other ν_{max} values of 3101-2998 cm^{-1} (aromatic H) and 2973-2782 cm^{-1} (aliphatic H) were recorded. The ^{1}H NMR spectra measured in DMSO-d_6 at 25 ^{o}C showed broad peaks at 11.81-10.54 ppm for N_3(NH), 10.76-9.98 ppm for N_1(NH), and at 8.52-6.50 ppm for amino (NH_2) protons.[34] Imine -NH and hydrazone -NH protons of a hydrazone-imine tautomer did not appear. These results show that the dyes may exist in one tautomeric form (azo-enamine, **I**) both in DMSO and solid state. The NH proton in a triazole ring (only in dye **18**) was not seen in this solvent. It is well known that the acidic proton on the heteroatom might interact (solute–solvent interactions) or exchange rapidly with the solvent molecules. Hence, the proton signal can shift downfield or not appear in the ^{1}H NMR spectra.

Solvent effect on absorption spectra of dyes in various solvents. The absorption spectra of hetaryl-azouracil dyes (**1-20**) were measured in various solvents at a concentration approximately 10^{-6}-10^{-8} *M*, run at different concentrations because of solubility problems (Table 1). All the dyes have low solubility in chloroform which is the least polar solvent I used, and the absorption spectrum was only recorded in chloroform for dye **12**.

Table 1. Influence of solvent on λ_{max} of the dyes (s = shoulder)

Dye	λ_{max} /nm				
	DMSO	DMF	Acetonitrile	Methanol	Acetic acid
1	435	439	436	421	444
2	447	444	442	437	441
3	534	531	407, 515	497	428
4	449	442	438	433	453
5	445	443	438	433	450
6	453	452	450	448	465
7	448	449	444	430	466
8	444	450	440	416	468
9	441	445	440	444	454
10	455	453	450	452	456
11	450	451	451	448	458
12	388s, 495	386, 494	358, 468	357, 453s	410
13	448	450	448	449	472
14	387, 411	402, 423	422	385, 403s	377, 402
15	434	441	431	436	426
16	417	429	413	418	424
17	382, 403	382, 405	379, 400	375, 390s	366
18	391s, 413	390, 412	391s, 410	384s, 405	389
19	368	367	361	358	363
20	397	392	387	372	379

The absorption spectra of compound **3** in various solvents and solutions are shown in Figure 1. Dye **3** showed absorption maxima at 534 nm in DMSO, 531 nm in DMF, 497 nm in methanol, 407, 515 nm in acetonitrile, and 428 nm in acetic acid. The electronic absorption spectra of dye **3** in all solvents differ significantly from those in the thiazolylazouracil dyes (**1–8**, $\mathbf{Q_1}$). Although all the thiazolylazouracil dyes showed one absorption maximum in acetonitrile, dye **3** showed two absorption maxima. It also showed larger bathochromic shifts than the other thiazolylazouracil dyes (except for acetic acid). As seen in Figure 1, dye **3** showed tautomeric equilibria in acetonitrile.

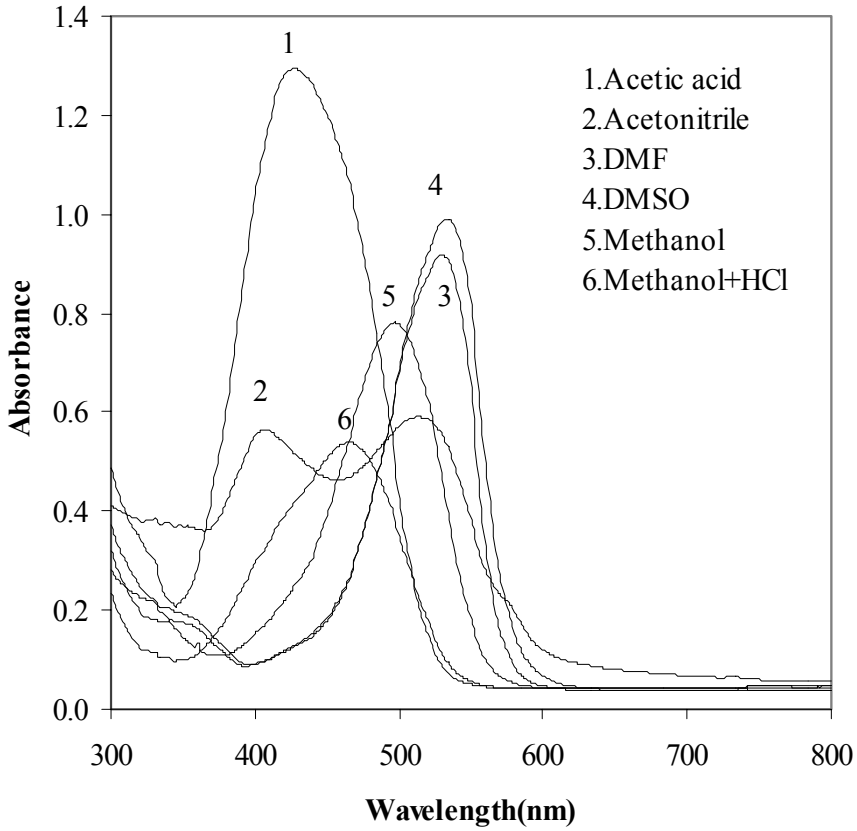


Figure 1. Absorption spectra of dye **3** in various solvents and acidic solution (the dye solutions are not at the same concentrations).

Similarly, the electronic absorption spectra of the dye **12** in all solvents differ significantly from those in the benzothiazolylazouracil dyes **(9–13, Q_2)**. The dye **12** showed one absorption maximum with a shoulder or two absorption maxima in DMSO, DMF, methanol and acetonitrile (the λ_{max} is 495 nm with a shoulder at 388 nm in DMSO, and 468, 358 nm in acetonitrile), whereas there is one absorption maximum in chloroform and acetic acid (Figure 2). The positions of the shorter wavelength shoulder or maxima are closer to the absorption maxima in chloroform, which may be indicated in azo-enamine tautomers. So, the absorption at longer wavelengths may be assigned to the hydrazone tautomer or common anion form.

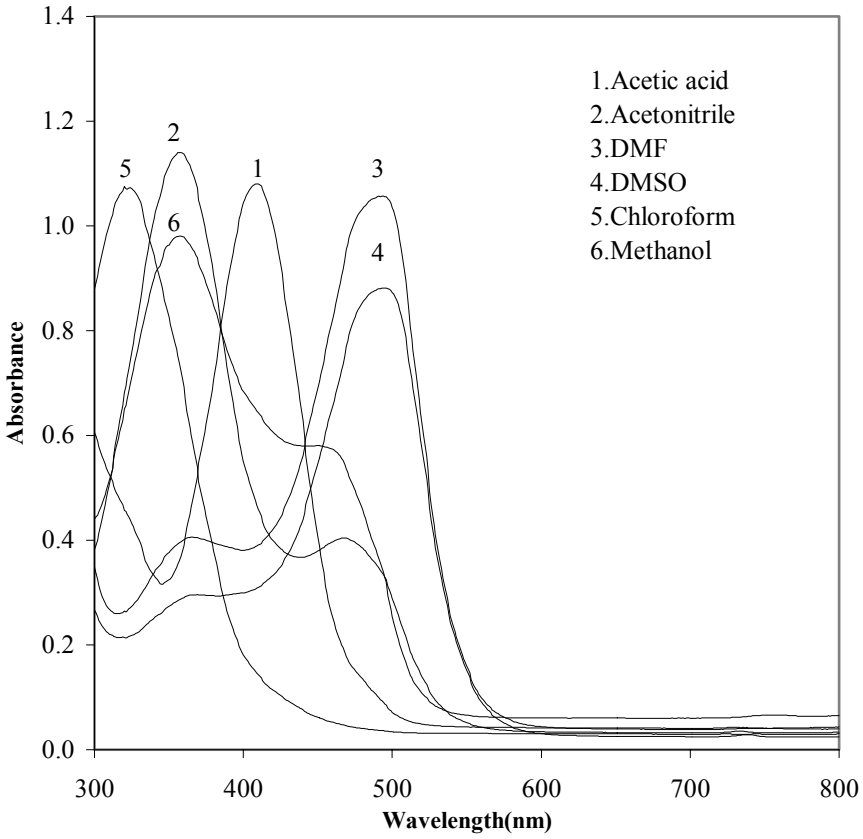


Figure 2. Absorption spectra of dye **12** in various solvents (the dye solutions are not at the same concentrations).

The absorption spectra of the other dyes (**14-20, Q$_3$**) gave a single dominant absorption band (except **14**, **17** and **18**) in all solvents. In contrast, the dyes **14**, **17** and **18** gave two absorption maxima or an absorption maximum with a shoulder, which suggests that these dyes may present in more than one tautomeric form.

The effect of acid and base on the absorption maxima of the dye solutions was evaluated, and the results are shown in Tables 2, 3 and 4. Generally, the absorption maxima of the thiazolylazouracil dyes (**1-8**) in DMSO, DMF, or methanol are not sensitive to the addition of base (piperidine or KOH). The addition of 0.1*M* KOH to solutions of dyes in methanol induced a bathochromic shift of the absorption maximum relative to its position in pure methanol (for dye **1**, $\Delta\lambda_{max}$ = 12 nm, for dye **7,** $\Delta\lambda_{max}$ = 14 nm, for dye **8,** $\Delta\lambda_{max}$ = 30 nm in methanol + KOH, relative to methanol). There was no significant change when piperidine was added to solutions of the dyes **1-8** in DMSO or DMF. This indicated that the dyes may be in their dissociated state in these solutions. These findings are in agreement with those obtained for hetarylazoquinolines and phenylazouracils[30,34] in our previous work. Presumably, the dyes exist in the anionic form in DMSO and DMF. In contrast, the absorption curves of thiazolylazouracil dyes are very sensitive to acid. The addition of 0.1*M* hydrochloric acid to solutions of dyes (except for dye **3**) in

methanol induced a bathochromic shift of the absorption maximum relative to its position in pure methanol. Dye **3** showed a hypsochromic shift upon the addition of HCl in methanol (for dye **1**, $\Delta\lambda_{max}$= 20 nm, for dye **4** $\Delta\lambda_{max}$= 17 nm in methanol+HCl relative to methanol; see Figure 1). These data indicate that a free amino group on the uracil ring might be converted into an ammonium ion in dye **3** ($-NH_2 \rightarrow -NH_3^+$). Therefore, intramolecular conjugation from the free amino group to the azo group does not appear, and the absorption band of the dye shows a hypsochromic shift.

The absorption maxima of benzothiazolylazouracil dyes (**9–13, Q_2**) in DMSO, DMF and methanol are not sensitive to the addition of base (piperidine or KOH). In contrast, the absorption curves of benzothiazolylazouracil dyes are sensitive to acid as thiazolylazouracil dyes, except for dye **9** (for dye **10,** $\Delta\lambda_{max}$= 15 nm, for dye **13** $\Delta\lambda_{max}$= 11 nm in methanol+HCl, relative to methanol). The λ_{max} values of the dyes **11** and **12** showed a hypsochromic shift upon addition of acid to the methanol.

The λ_{max} values of the dye **12** showed a large hypsochromic shift with the addition of acid to methanol, and the shoulder at longer wavelength disappeared. It is interesting that the absorption maximum obtained in acidic methanol for dye **12** are very similar to the corresponding maximum in acetic acid. Therefore, the maximum absorption of dye **12** in this acidic solution can be assigned to the cationic form. These results showed also that the dye **12** could be in the common anion-azo form in DMSO, DMF, and methanol, and the absorption maxima at longer wavelength may be the common anion form (Figure 3).

Table 2. Absorption maxima of dyes **Q_1** in acidic and basic solutions

Dye	λ_{max}/nm						
	DMSO	**DMSO + piperidine**	**DMF**	**DMF + piperidine**	**MeOH**	**MeOH + KOH**	**MeOH + HCl**
1	435	443	439	441	421	433	441
2	447	450	444	446	437	440	450
3	534	536	531	534	497	500	465
4	449	450	442	444	433	439	450
5	445	447	443	444	433	438	441
6	453	454	452	454	448	451	453
7	448	452	449	451	430	444	438
8	444	451	450	454	416	446	424

Table 3. Absorption maxima of dyes $\mathbf{Q_2}$ in acidic and basic solutions (s = shoulder)

Dye	λ_{max}/nm						
	DMSO	**DMSO + piperidine**	**DMF**	**DMF + piperidine**	**MeOH**	**MeOH + KOH**	**MeOH + HCl**
9	441	445	445	446	444	446	444
10	455	456	453	452	452	452	467
11	450	451	451	450	448	446	430
12	388s, 495	495	386, 494	493	357, 453s	452	406
13	448	450	450	450	449	450	460

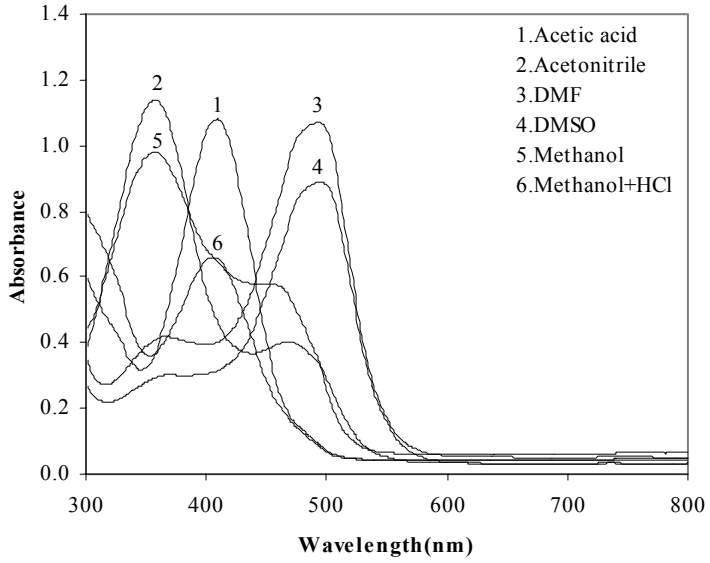


Figure 3. Absorption spectra of dye **12** in various solvents and acidic solution (the dye solutions are not at the same concentration).

The absorption maxima of the other prepared dyes (**14-20, $\mathbf{Q_3}$**) were sensitive to the addition of base and acid (piperidine, KOH, or HCl). Some of these dyes showed hypsochromic and bathochromic shifts.

Table 4. Absorption maxima of dyes **Q$_3$** in acidic and basic solution (s = shoulder)

Dye	λ_{max}/nm						
	DMSO	**DMSO + piperidine**	**DMF**	**DMF + piperidine**	**Methanol**	**Methanol + KOH**	**Methanol + HCl**
14	387, 411	400, 428	402, 423	400s, 427	385, 403s	403s, 420	383, 402s
15	434	443	441	441	436	436	426
16	417	431	429	428	418	399s, 423	386, 410
17	382, 403	382, 407	382, 405	380, 407	375, 390s	368, 386	372
18	391s, 413	391s, 419	390, 412	391s, 416	384s, 405	390s, 411	388
19	368	366	367	368	358	361	362
20	397	394	392	396	372	380	381

Substituent effect on absorption spectra of dyes in various solvents. Generally, most of the substituted dyes have higher absorption maxima than their unsubstituted analogs. In the present study, spectral data for the various substituted hetarylazouracil dyes (**1-20**) show that there is a general tendency for the visible absorption band to move bathochromically in accordance with the electron donor-acceptor groups in the diazo and coupling component. These involve a migration of electron density from the donor group toward the azo group. The prepared dyes have an NH_2 group in the coupling component as an electron- donor group. The introduction of the nitro group into the thiazole ring at the 5-position gives the greatest bathochromic shift compared with the other thiazolylazouracil dyes (**1**,**2**,**4-8**) in all solvents, with the exception of acetic acid (for dye **3** $\Delta\lambda_{max}$= 99 nm relative to dye **1** in DMSO). The presence of an electron-donating phenyl group in the 4-position of the thiazole ring gives rise to a bathochromic shift relative to the corresponding thiazole and 4-methylthiazole derivatives in all solvents (for dye **1** $\Delta\lambda_{max}$= 18 nm, for dye **2** $\Delta\lambda_{max}$= 6 nm, for dye **4** $\Delta\lambda_{max}$= 4 nm relative to dye **6** in DMSO). The weak electron-withdrawing chloro- and bromo- substituents in the *para* position of the phenyl group on the thiazole ring produced a hypsochromic shift in all solvents except for acetic acid (for dye **8** $\Delta\lambda_{max}$ = 32 nm, for dye **7** $\Delta\lambda_{max}$= 18 nm relative to dye **6** in methanol). These results are in agreement with those obtained for 4-substituted- thiazolylazopyrazolone and 4-substituted-thiazolylazo pyridine and 4-substituted- thiazolylazo indole dyes .[21,29]

The introduction of a strongly electron-accepting group such as NO_2 into the 6-position of the benzothiazole ring resulted in a large bathochromic shift in DMSO, DMF, and acetonitrile (for dye **12** $\Delta\lambda_{max}$= 54 nm relative to dye **9**, in DMSO). On the other hand, the introduction of a weak electron-accepting group such as chloro into the benzothiazole resulted in a bathochromic shift in all solvents. Also, with the introduction of the electron-donating methoxy and methyl groups into the benzothiazole ring the bathochromic shift appeared and a single tautomeric form was predominant.

The absorption maxima obtained for thiadiazolylazouracil dyes indicated that electron-donating groups (ethyl and methylmercapto) in the thiadiazole ring at the 5-position generally

give a absorb bathochromic shift when compared with the unsubstituted dye **14** in all solvents (see Table 1 for dye **15,** $\Delta\lambda_{max}$= 23 nm, for dye **16,** $\Delta\lambda_{max}$= 6 nm relative to for dye **14** in DMSO). As the electron-donating ability of the donor group increases from ethyl to mercaptomethyl derivatives of the dyes, the λ_{max} show bathochromic shifts. This shift is attributed to the stronger electron-donating ability of the methylmercapto group with respect to the ethyl group at the 5-position of the thiadiazole ring. These results indicate also that the electron-donor ethyl and methylmercapto groups stabilized the excited state of the neutral form of the dyes. Such a substituent effect provides strong evidence that the dyes exist in only one tautomeric form, namely azo-enamine form, in all solvents. Similarly, bathochromic shifts were observed upon introduction of an electron-donating methylmercapto- (SCH_3) into the triazole ring at the 5-position in all solvents (for dye **18** $\Delta\lambda_{max}$= 23 nm relative to dye **17** in acetic acid).

The thiadiazolylazo-uracil dyes **14**, **15** and **16** showed bathochromic shifts in comparison with analogous triazolylazouracil dyes **17** and **18** in all solvents (see Table 1), so the thiadiazole ring system act as a better electron donor than the triazole ring system, due to the S atom in the ring. However, the λ_{max} values of oxazolylazo- and pyridinylazouracil- dyes **19** and **20** showed hypsochromic shifts in comparison with the analogous hetarylazouracil dyes (**1**-**18**) in all solvents (Table 1). As a result, the electron-donor groups stabilize the excited state of the neutral form of the dyes whereas the strong electron-accepting groups stabilize the excited state of the common anion form of the dyes.

Hetarylazouracil disperse dyes (**1**-**20**) showed larger bathochromic shift (except for dye **19** and **20**) than phenylazouracil based dyes[34] because of increased polarity of the dye molecules in excited state.

Experimental Section

Materials and methods. The chemicals used in the synthesis of all compounds were from the Aldrich Chemical Company and used without further purification. The solvents were used of spectroscopic grade. IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr (ν are in cm^{-1}). ^1H NMR spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield in DMSO-d_6. Chemical shifts are expressed in δ units (ppm). Ultraviolet-visible (UV-Vis) absorption spectra were recorded on Analytik Jena Specord 200 spectrophotometer at the wavelength of maximum absorption (λ_{max}, in nm) in the solvents specified. A change of λ_{max} was investigated when 0.1 mL piperidine was added to 1 mL of dye solutions in DMSO and DMF, or when 0.1 mL base (potassium hydroxide, 0.1 *M*) or 0.1 ml acid (hydrochloric acid, 0.1 *M*) was added to 1 mL of the dye solutions in methanol. Mass spectra were recorded on an Agilent 5973 Network Mass Selective Detector, SIS (Direct Insertion Probe), electron impact 55 and 70 eV and AGILENT 1100 MSD and Elemental analyses were recorded on a LECO CHNS 932 by the Turkish Research Council Laboratories (Center of Science and Technology Research of Turkey).

General method for the preparation of hetarylazouracil dyes (**1-20**) Diazotization of various heterocyclic amines was effected with nitrosylsulfuric acid. A typical procedure is described below for 2-aminothiazole; all other dyes were prepared in a similar manner.

6-Amino-5-(thiazol-2-yldiazenyl)uracil (**1**)**.** 2-aminothiazole (0.2 g, 2 mmol) was dissolved in hot glacial acetic acid–propionic acid mixture (2:1, 6.0 mL) and was rapidly cooled in an ice-salt bath to -5 ^{o}C. Then, a cold solution of nitrosyl-sulfuric acid, prepared from sodium nitrite (0.15 g) and concentrated sulfuric acid (3 mL at 50 ^{o}C) was added in portions to this liquor during 30 min. Then stirred for an additional 2 h at 0 ^{o}C. Excess nitrous acid was destroyed by the addition of urea (approx. 0.1 g). And then, the diazo liquor was then added slowly to a vigorously stirred solution of 6-aminouracil (2 mmol, 0.254 g) in potassium hydroxide (2 mmol, 0.112 g) and water (10 mL). After 2 h the pH of the reaction mixture was maintained at 4-6 by addition of portions of saturated sodium carbonate solution. The mixture was then stirred for 1 h at 0-5 ^{o}C. The resulting product was filtered, washed with water, dried, and recrystallized from ethanol gave 6-amino-5-(thiazol-2-yldiazenyl)uracil as orange crystals (0.44 g, 92%, m.p. >300 ^{o}C, dec.). IR (KBr): ν_{max} 3474, 3409 (NH_2), 3127 (NH), 3012 (arom. H), 1708 (C=O), 1650 (C=N), 1554 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.12 (br, N_3H), 10.34 (br, N_1H), 8.34 (br, NH_2), 7.77 (d, 1H), 7.45 (d, 1H). Anal. Calcd for $C_7H_6N_6O_2S$ C, 35.29; H, 2.52; N, 35.29; S, 13.44. Found: C, 34.99; H, 2.58; N, 35.39.; S, 13.30%. MS (m/z, 70 eV): 239 (29.9%) $(M+1)^+$ (MW 238.23).

6-Amino-5-(5-methylthiazol-2-yldiazenyl)uracil (**2**)**.** Obtained from 2-amino-5-methylthiazole and 6-aminouracil as yellow crystals (0.43 g, 86%; m.p. >328 ^{o}C, dec.). IR (KBr): ν_{max} 3448, 3318 (NH_2), 3236, 3147 (NH), 3012 (arom. H), 2872 (aliph. H), 1734 (C=O), 1645 (C=N), 1529 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.08 (br, N_3H), 10.22 (br, N_1H), 8.12 (br, NH_2), 7.41 (s, 1H), 2.42 (s, 3H). Anal. Calcd for $C_8H_8N_6O_2S$, C, 38.10; H, 3.17; N, 33.33; S, 12.70. Found: C, 38.00; H, 3.09; N, 32.96; S, 12.61%. MS (m/z, 70 eV), 253 (100%) $(M+1)^+$, 154 (2.3%), MW 252.26.

6-Amino-5-(5-nitrothiazol-2-yldiazenyl)uracil (**3**)**.** Obtained from 2-amino-5-nitrothiazole and 6-aminouracil as red powder (0.23 g, 42%, m.p. >290 ^{o}C, dec.). IR (KBr): ν_{max} 3448, 3194 (NH_2), 3108 (NH), 3031 (arom. H), 1753, 1721 (C=O), 1657 (C=N), 1554 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 10.85 (br, N_3H), 10.31 (br, N_1H), 8.61 (s, 1H), 8.29 (br, NH_2). Anal. Calcd for $C_7H_5N_7O_4S$: C, 29.68; H, 1.77; N, 34.63; S, 11.31. Found: C, 29.51; H, 1.75; N, 34.44; S, 10.97 %. MS (m/z, 55 eV): 284 (6.5%) $(M+1)^+$ (MW 283.23).

6-Amino-5-(4-methylthiazol-2-yldiazenyl)uracil (**4**)**.** Obtained from 2-amino-4-methylthiazole and 6-aminouracil as dark yellow powder (0.42 g, 84%; m.p. 304-305 ^{o}C). IR (KBr): ν_{max} 3416 (NH_2), 3179 (NH), 3101, 3024 (arom. H), 2921 (aliph. H), 1759, 1721 (shoulder) (C=O), 1638 (C=N), 1529 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.08 (br, N_3H), 10.32 (br, N_1H), 8.29 (br, NH_2), 7.02 (s, 1H), 2.32 (s, 3H). Anal. Calcd for $C_8H_8N_6O_2S$: C, 38.10; H, 3.17; N, 33.33; S, 12.70. Found: C, 37.87; H, 3.09; N, 32.96; S, 12.61%. MS (m/z, 70 eV): 253 (41.5%) $(M+1)^+$, 154 (2.3%) (MW 252.26).

Ethyl ([2-(6-aminouracil-5-yl)diazenyl]-thiazol-4yl)acetate (5). Obtained from ethyl-2-amino-thiazol-4-ylacetate and 6-aminouracil as yellow crystals (0.57 g, 88%, m.p. dec.>300 ^{o}C) IR (KBr): ν_{max} 3448 (NH_2), 3198 (NH), 3108, 3031 (arom. H), 2973 (aliph. H), 1759, 1734 (C=O), 1638 (C=N), 1541 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.18 (br, N_3H), 10.38 (br, N_1H), 8.21 (br, NH_2), 7.21 (s, 1H), 4.11 (q, 2H, -O$\underline{CH_2}$CH$_3$), 3.78 (s, 2H, -CO$\underline{CH_2}$COOCH$_2$CH$_3$),1.24 (t, 3H, -OCH$_2\underline{CH_3}$). Anal. Calcd for $C_{11}H_{12}N_6O_4S$: C, 40.74; H, 3.70; N, 25.93; S, 9.88. Found: C, 40.63; H, 3.73; N, 26.10; S, 9.83 %. MS (m/z, 70 eV): 325 (64.6%) (MW 324.32).

6-Amino-5-(4-phenylthiazol-2-yldiazenyl)uracil (6). Obtained from 2-amino-4-phenylthiazole and 6-aminouracil as orange powder (0.48 g, 77%, m.p. 307-308 ^{o}C). IR (KBr): ν_{max} 3428 (NH_2), 3268 (NH), 3063, 3024 (arom. H), 1696 (C=O), 1627 (C=N), 1548 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.81 (br, N_3H), 10.76 (br, N_1H), 8.10-7.38 (m, 6H), 6.88 (br, NH_2). Anal. Calcd for $C_{13}H_{10}N_6O_2S$: C, 49.68; H, 3.18; N, 26.75; S, 10.19. Found: C, 49.68; H, 3.16; N, 26.16; S, 10.09%. MS (m/z, 70 eV): 315 (11.2%) (MW 314.33).

6-Amino-5-(4-(4-chlorophenyl)-2-yldiazenyl)uracil (7). Obtained from 4-(4-chloro)-phenyl-2-aminothiazole and 6-aminouracil as yellow powder (0.49 g, 71%, m.p. >328 ^{o}C, dec.). IR (KBr): ν_{max} 3328 (NH_2), 3157 (NH), 3037 (arom. H), 1759 (C=O), 1638 (C=N), 1535 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 11.18 (br, N_3H), 10.38 (br, N_1H), 8.30 (br, NH_2), 7.96 (s, 1H), 7.88 (d, 2H), 7.51 (d, 2H). Anal. Calcd for $C_{13}H_9N_6O_2SCl$: C, 44.76; H, 2.58; N, 24.10; S, 9.18. Found: C, 44.67; H, 2.49; N, 24.05; S, 9.22%. MS (m/z, 55 eV): 349.5 (16.8%): $(M+1)^+$ (MW 348.77).

6-Amino-5-(4-(4-bromophenyl)-2-yldiazenyl)uracil (8). Obtained from 4-(4-bromo)-phenyl-2-aminothiazole and 6-aminouracil as red powder (0.57 g, 73%, m.p. >332 ^{o}C, dec.). IR (KBr): ν_{max} 3442 (NH_2), 3204 (NH), 3031 (arom. H), 1766, 1727 (shoulder) (C=O), 1631 (C=N), 1535 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.28 (b, N_3H), 10.42 (b, N_1H), 8.32 (b, NH_2), 7.98 (s, 1H), 7.86 (d, 2H), 7.61(d, 2H). Anal. Calcd for $C_{13}H_{10}N_6O_2S$: C, 49.68; H, 3.18; N, 26.75; S, 10.19. Found: C, 49.68; H, 3.16; N, 26.56; S, 10.09%. MS (*m/z*, 55 eV): 394.0 (2.8%) $(M+1)^+$, 392.9 (19.8%), 394.9 (17.8%) (MW 393.22).

6-Amino-5-(benzothiazol-2-yldiazenyl)uracil (9). Obtained from 2-aminobenzothiazole and 6-amino-uracil as yellow crystals (0.29 g, 51%, m.p. 295-296 ^{o}C). IR (KBr): ν_{max} 3425, 3265 (NH_2), 3204 (NH), 3063 (arom. H), 1727 (shoulder), 1702 (C=O), 1638 (C=N), 1561 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.27 (br, N_3H), 10.57 (br, N_1H), 8.02 (br, NH_2), 7.94 (m, 1H), 7.80 (m, 1H), 7.42 (m, 1H), 7.27 (m, 1H). Anal. Calcd for $C_{11}H_8N_6O_2S$: C, 45.83; H, 2.78; N, 29.17; S, 11.11. Found: C, 45.88; H, 2.63; N, 29.03; S, 11.04 %. MS (*m/z*, 70 eV): 289 (34.2%) $(M+1)^+$ (MW 288.29).

6-Amino-5-(6-methoxy-benzothiazol-2-yldiazenyl)uracil (10). Obtained from 2-amino-6-methoxy-benzothiazole and 6-aminouracil as red powder (0.53 g, 84%, m.p. >330 ^{o}C, dec.). IR (KBr): ν_{max} 3474, 3242 (NH_2), 3144 (NH), 3044, 3005 (arom. H), 2831 (aliph. H) 1715 (C=O), 1638 (C=N), 1561 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 10.98 (br, N_3H), 10.44 (br, N_1H), 8.41 (br, NH_2), 7.79 (m, 1H), 7.53 (m, 1H), 7.05 (m, 1H), 3.84 (s, 3H, -OCH_3). Anal. Calcd for $C_{12}H_{10}N_6O_3S$: C, 45.28; H, 3.14; N, 26.40; S, 10.07. Found: C, 44.98; H, 3.16; N, 26.13; S, 9.98 %. MS (*m/z*, 70 eV): 319 (14.9%) $(M+1)^+$ (MW 318.32).

6-Amino-5-(6-chlorobenzothiazol-2-yldiazenyl)uracil (11). Obtained from 2-amino-6-chlorobenzothiazole and 6-aminouracil as red crystals (0.31 g, 49%, m.p. >300 ^{o}C, dec.). IR (KBr): ν_{max} 3448, 3268 (NH_2), 3184 (NH), 3056 (arom. H), 1708 (C=O), 1638 (C=N), 1548 (C=C) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 11.28 (br, N_3H), 10.52 (br, N_1H), 8.18 (br, NH_2), 7.73 (m, 1H), 7.40 (m, 2H). Anal. Calcd for $C_{11}H_7N_6O_2SCl$: C, 40.93; H, 2.17; N, 26.05; S, 9.92. Found: C, 40.87; H, 2.09; N, 25.96; S, 9.95%. MS (*m/z*, 55 eV): 322.95 (100%) $(M+1)^+$ (MW 322.73).

6-Amino-5-(6-nitrobenzothiazol-2-yldiazenyl)uracil (12). Obtained from 2-amino-6-nitrobenzothiazole and 6-aminouracil as orange powder (0.29 g, 44%, m.p. 275-276 ^{o}C) IR (KBr): ν_{max} 3409, 3288 (NH_2), 3109 (NH), 3012 (arom. H), 1740 (C=O), 1640 (C=N), 1515 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.18 (br, N_3H), 10.42 (br, N_1H), 8.42-7.98 (m, 3H), 7.41 (br, NH_2). Anal. Calcd for $C_{11}H_7N_7O_4S$: C, 39.64; H, 2.10; N, 29.43; S, 9.61. Found: C, 39.55; H, 2.11; N, 29.22; S, 9.55 %. MS (*m/z*, 55 eV): 334.2 (1.8%) $(M+1)^+$ (MW 333.29).

6-Amino-5-(5,6-dimethylbenzothiazol-2-yldiazenyl)uracil (13). Obtained from 2-amino-5,6-dimethylbenzothiazole and 6-aminouracil as orange powder (0.49 g, 78%, m.p. >335 ^{o}C, dec.) IR (KBr): ν_{max} 3480, 3288 (NH_2), 3140 (NH), 3024 (arom. H), 2831 (aliph. H), 1708 (C=O), 1631 (C=N), 1561 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.08 (br, N_3H), 10.51 (br, N_1H), 6.50 (br, NH_2), 6.71 (s, 1H), 6.50 (s, 1H), 2.32 (s, 3H), 2.28 (s, 3H). Anal. Calcd for $C_{13}H_{12}N_6O_2S$: C, 49.37; H, 3.80; N, 26.58; S, 10.13. Found: C, 49.12; H, 3.75; N, 26.51; S, 10.08%. MS (*m/z*, 55 eV): 317 (1.7%) $(M+1)^+$ (MW 316.34).

6-Amino-5-(1,3,4-thiadiazol-2-yldiazenyl)uracil (14). Obtained from 2-amino-1,3,4-thiadiazole and 6-aminouracil as red powder (0.42 g, 88%, m.p. >339 ^{o}C, dec.) IR (KBr): ν_{max} 3428-3262 (NH_2), 3182 (NH), 3082 (arom. H), 1731 (C=O), 1650 (C=N), 1525 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.18 (br, N_3H), 10.42 (br, N_1H), 9.28 (s, 1H), 8.48 (br, NH_2). Anal. Calcd for $C_6H_5N_7O_2S$: C, 30.13; H, 2.09; N, 41.00; S, 13.39. Found: C, 30.06; H, 2.16; N, 40.88; S, 13.41%. MS (*m/z*, 55 eV): 240 (0.8%) $(M+1)^+$ (MW 239.22).

6-Amino-5-(5-methylthio-1,3,4-thiadiazol-2-yldiazenyl)uracil (15). Obtained from 2-amino-5-methylthio-1,3,4-thiadiazole and 6-aminouracil as brown powder (0.44 g, 78%, m.p. >320 ^{o}C, dec.). IR (KBr): ν_{max} 3377 (NH_2), 3144 (NH), 3037 (arom. H), 2806 (aliph. H), 1759, 1715 (shoulder) (C=O), 1650 (C=N), 1529 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.0 (br, N_3H), 10.20 (br, N_1H), 8.48 (br, NH_2), 2.75 (s, 3H, -SCH_3). Anal. Calcd for $C_7H_7N_7O_2S_2$: C, 29.47; H, 2.46; N, 34.39; S, 22.46. Found: C, 28.98; H, 2.53; N, 34.59; S, 21.86 %. MS (*m/z*, 55 eV): 286 (6.8%) $(M+1)^+$ (MW 285.31).

6-Amino-5-(5-ethyl-1,3,4-thiadiazol-2-yldiazenyl)uracil (16). Obtained from 2-amino-5-ethyl-1,3,4-thiadiazole and 6-aminouracil as yellow powder (0.44 g, 82%, m.p. 300-301 ^{o}C). IR (KBr): ν_{max} 3377, 3284 (NH_2), 3184 (NH), 3031 (arom. H), 2966 (aliph. H), 1766, 1715 (shoulder) (C=O), 1645 (C=N), 1561 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.08 (br, N_3H), 10.32 (br, N_1H), 8.48 (br, NH_2), 3.0 (q, 2H, -$\underline{CH_2}CH_3$), 1.32 (t, 3H, -$CH_2\underline{CH_3}$). Anal. Calcd for $C_8H_9N_7O_2S$: C, 35.96; H, 3.37; N, 36.70; S, 11.99. Found: C, 35.93; H, 3.33; N, 36.64; S, 11.70 %. MS (*m/z*, 70 eV): 268 (100%) $(M+1)^+$, 154 (9.5%), 394.9 (17.8%) (MW 267.27).

6-Amino-5-(1,2,4-triazol-3-yldiazenyl)uracil (17). Obtained from 3-amino-1,2,4-triazole and 6-aminouracil as yellow powder (0.40 g, 91%, m.p. >300 ^{o}C, dec.). IR (KBr): ν_{max} 3428-3333 (NH_2), 3184 (NH), 2998 (arom. H), 1740 (C=O), 1657 (C=N), 1568 (C=C) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 13.92 (br, NH triazole), 10.79 (br, N_3H), 10.11 (br, N_1H), 8.48 (br, NH_2), 8.11 (s, 1H). Anal. Calcd for $C_6H_6N_8O_2$: C, 32.43; H, 2.70; N, 50.45. Found: C, 32.33; H, 2.61; N, 50.45 %. MS (*m/z*, 70 eV): 223 (64.9%) $(M+1)^+$ (MW 222.17).

6-Amino-5-(5-methylthio-1,2,4-triazol-3-yldiazenyl)uracil (18). Obtained from 2-amino-5-methylthio-1,2,4-triazole and 6-aminouracil as brown powder (0.44 g, 82%, m.p. >311 ^{o}C, dec.). IR (KBr): ν_{max} 3428-3314 (NH_2), 3147 (NH), 2998 (arom. H), 2928 (aliph. H), 1753 (C=O), 1645 (C=N), 1560 (C=C) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 10.54 (br, N_3H), 9.98 (br, N_1H), 8.52 (br, NH_2), 2.59 (s, 3H, $-SCH_3$). Anal. Calcd for $C_7H_8N_8O_2S$: C, 31.34; H, 2.99; N, 41.79; S, 11.94. Found: C, 31.19; H, 3.01; N, 41.74; S, 11.85%. MS (*m/z*, 70 eV): 269 (100%) $(M+1)^+$ (MW 268.26).

6-Amino-5-(5-methyl-isoxazol-3-yldiazenyl)uracil (19). Obtained from 3-amino-5-methylisoxazole and 6-amino-uracil as light yellow powder (0.44 g 93%, m.p. 307-308 ^{o}C).. IR (KBr): ν_{max} 3461-3323 (NH_2), 3227 (NH), 3056 (arom. H), 2928 (aliph. H), 1740, 1708 (shoulder) (C=O), 1638 (C=N), 1541 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 11.01 (b, N_3H), 10.42 (b, N_1H), 8.0 (b, NH_2), 6.34 (s, 1H), 2.38 (s, 3H). Anal. Calcd for $C_8H_8N_6O_3$: C, 40.68; H, 3.59; N, 35.39. Found: C, 40.62; H, 3.52; N, 35.52 %. MS (*m/z*, 70 eV): 237 (100%) $(M+1)^+$, 154 (7.5%) (MW 236.19).

6-Amino-5-(pyridin-3-yldiazenyl)uracil (20). Obtained from 3-aminopyridine and 6-aminouracil as yellow powder (0.42 g 91%, m.p.>332 ^{o}C, dec.). IR (KBr): ν_{max} 3371 (NH_2), 3265 (NH), 3012 (arom. H), 1734 (C=O), 1645 (C=N), 1561 (C=C) cm^{-1} ^{1}H NMR (DMSO-d_6): δ 10.73 (br, N_3H), 10.31 (br, N_1H), 8.88 (s, 1H), 8.47 (d, 1H), 8.31 (br, NH_2), 7.92 (d, 1H), 7.41 (m, 1H). Anal. Calcd for $C_9H_8N_6O_2$: C, 46.55; H, 3.45; N, 36.21. Found: C, 46.40; H, 3.48; N, 35.96 %. MS (*m/z*, 70 eV): 233 (56.1%) $(M+1)^+$ (MW 232.20).

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