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Synthesis of 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one and its disperse azo dyes. Part 2: Hetarylazo derivatives

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Abstract

4-Amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one (**I**) was synthesized by reaction of 2-aminobenzimidazole with ethyl cyanoacetate and coupled with diazotized hetaryl amines to give the corresponding hetarylazo dyes (**1–9**). The structures of new hetarylazo dyes were confirmed by UV–vis, FT-IR and ^{1}H NMR spectroscopic techniques and elemental analysis. The solvatochromism of dyes was evaluated with respect to absorption maxima in various solvents. The color of the dyes is discussed with respect to the nature of the heterocyclic ring and the substituent therein. The effects of temperature, concentration as well as acid and base on the visible absorption maxima of the dyes are also reported.

Keywords: Azopyrimidone dyes; Heterocyclic disperse dyes; Diazo-coupling reaction; Thiazolylazo dyes; Absorption properties; Solvent effect

1. Introduction

For small organic molecules, simple nitrogen-containing heterocycles receive a large amount of attention in the literature, as a consequence of their exciting biological properties and their pharmacophores of considerable historical importance. Of these heterocycles, the synthesis, reactions and biological activities of pyrimidine containing molecules stands as an ever-expanding area of research in heterocycle chemistry and this structural motif appears in a large number of pharmaceutical agents and natural products [1–7]. However, a few comparable investigations have been carried out using imidazopyrimidines [8–9]. Some azopyrimidine derivatives also find application in dyes and complexes [10–15].

In recent years, efforts have been made to replace certain anthraquinone dyes with technically equivalent azo dyes, for both environmental and economic reasons [16]. In this regard, azo dyes based on heterocyclic amines have been developed, and the resultant dyes have higher tinctorial strength and give brighter dyeings than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afford very electronegative diazo components and, consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [17–19]. Moreover, it is well known that the ring systems of this type are useful for providing blue and green azo dyes.

In contrast to the large number of investigations on the reactivity of carboaromatic diazonium ions in general and the mechanism of their azo coupling reactions, very few comparable investigations have been made with heteroaromatic diazonium ions. Sawaguchi et al. [20] have measured the rate of azo coupling of various heteroaromatic diazonium ions with 2-naphthol-3,6-disulfonic acid. There exist an extensive patent literature on azo dyes synthesized with heteroaromatic diazonium ions since Dickey and Towne realized in the early 1950s, that industrially interesting disperse dyes can be obtained on this basis.

In this part of study, we report here the synthesis of some novel hetarylazopyrimidone dyes **1–9** resulting from the use

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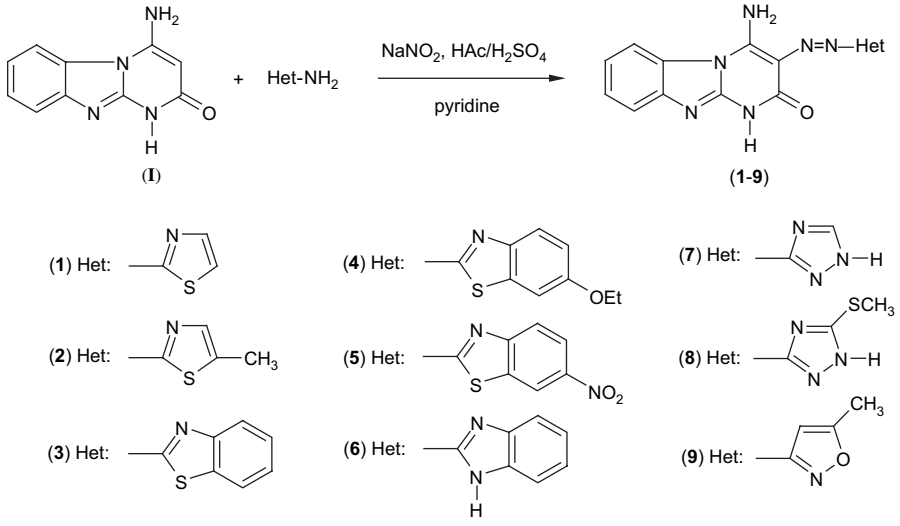


Scheme 1.

of 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one (**I**) as a coupling component and evaluation of their visible absorption spectra with respect to the influences of the solvent. The color of the dyes is discussed with respect to the nature of the heterocyclic ring and the substituents therein. The effects of acid and base on the visible absorption maxima of the dyes are also reported. The compound structures are shown in Scheme 1.

2. Result and discussion

2.1. Synthesis and characterizations

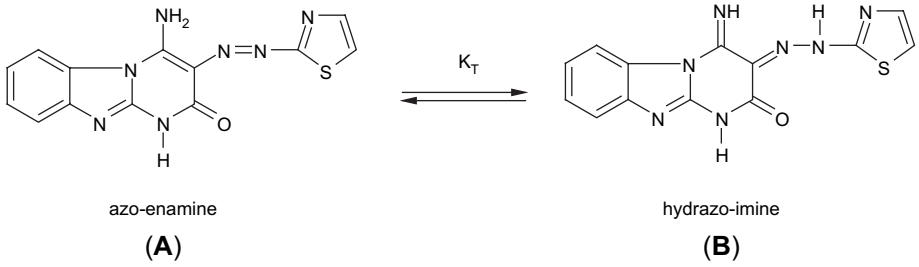
The method of synthesis of 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one and its corresponding analysis data were described in the previous part of this paper [21].

The hetarylazopyrimidone dyes (**1**–**9**) were prepared by coupling 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one with diazotized heterocyclic amines (Scheme 1). The dyes may exist in two possible tautomeric forms, namely the azo-enamine form A and the hydrazo-imine form B as shown in Scheme 2. The infrared spectra of all the dyes (in KBr) showed intense amino (NH_2) bands at 3444–3427 cm^{-1} and at 3390–3368 cm^{-1}. It can be suggested that these dyes do not exist in hydrazo-imine form in solid state. The IR spectra also showed a band at 3175–3140 cm^{-1}, which was assigned to imino group (NH). The other ν_{max} values of 3102–3052 cm^{-1} (aromatic C–H), 1698–1678 cm^{-1} (C=O) were recorded.

The ^{1}H NMR spectra measured in DMSO-d_6 at 25 °C showed a triplet at 1.36 ppm ($-CH_3$), a singlet at 2.37 ppm ($-CH_3$), a singlet at 2.47 ppm ($-CH_3$), a singlet at 2.85 ppm ($-SCH_3$), a quartet at 3.95 ppm ($-OCH_2-$), a singlet at 6.40 ppm (Aro.-H, isoxazole ring), a singlet at 7.63 ppm (Aro.-H, methylthiazole ring), two doublet at 7.42 and 7.51 ppm (Aro.-H, thiazole ring), a singlet at 8.40 ppm (Aro.-H, triazole ring), a multiplet at 7.25–9.00 ppm for aromatic protons (Aro.-H), a broad peak at 8.61–9.78 ppm for tautomeric imine (NH) and tautomeric hydrazo (NH) protons, a broad peak at 10.28–10.37 ppm (NH, pyrimidine ring), a broad peak at 10.66 ppm (NH, triazole ring), a broad peak at 10.83 ppm (NH, methylmercapto triazole ring), a broad peak at 11.93 ppm (NH, benzimidazole ring), a broad peak at 12.42–12.50 ppm for tautomeric amino (NH_2) protons. These results show that the dyes may exist as a mixture of tautomeric forms in DMSO.

2.2. Solvent effects

UV–vis absorption spectra were recorded using an ATI-Unicam UV-100 spectrophotometer in the wavelength range



Scheme 2.

Table 1
Influence of solvent on λ_{max} (nm) of dyes **1**–**9**

Dye no	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
1	391, 433 s	395, 408 s	395, 409 s	402, 420 s	404, 418 s	418, 395 s
2	440, 397 s	445, 410 s	429, 400 s	435, 410 s	437, 410 s	465
3	398, 425 s	442, 410 s	403, 420 s	409, 430 s	416, 438 s	468
4	402, 460 s	451, 415 s	433	448	451	470
5	440, 480 s	444, 474 s	355	364, 444 s	356	354
6	466, 440 s	464, 440 s	434	410, 435 s	400, 440 s	428
7	371, 410 s	378, 415 s	375	365, 394 s	365	370
8	385, 410 s	385, 412 s	386	396	388	417
9	363, 412 s	357, 410 s	355	355	360	361

s: Shoulder.

350–700 nm. Absorption spectra of hetarylazopyrimidone dyes **1**–**9** were recorded in various solvents at a concentration of 10^{-6}–10^{-8} M and these are all run at different concentrations. The results are summarized in Table 1. The pH value of all the solutions used was in the range between acidic and basic. The visible absorption spectra of the dyes did not show regular variation with the polarity of solvents.

The dyes showed single or two absorbances in all used solvents. It can be suggested that the dyes may exist as a mixture of tautomeric forms in various solvents. It was observed that the absorption spectra of the dyes in all solvents hypsochromically shifted with respect to the absorption spectra in chloroform except for dye **5**, dye **6** and dye **9** (e.g. for dye **2** λ_{max} is 465 nm in $CHCl_3$, 440 nm in DMSO, 445 nm in DMF) (Fig. 1). But the λ_{max} of dye **5** and dye **6** showed bathochromic shift in DMSO and DMF with respect to the λ_{max} in chloroform (e.g. for dye **6** λ_{max} is 428 nm in $CHCl_3$, 466 nm in DMSO, 464 nm in DMF) (Fig. 2). The absorption spectra of dye **9** in various solvents did not significantly change.

It was also observed that the absorption curves of the dyes were sensitive to base and acid (Table 2). The λ_{max} of the dyes showed bathochromic shifts when 0.1 M KOH was added to each of the dye solutions in methanol. The absorption spectra of dye **2**, dye **4**, dye **6** and dye **9** in methanol also showed bathochromic shifts when 0.1 M HCl was added. The absorption spectra of dye **1** and dye **5** in methanol showed hypsochromic shifts when 0.1 M HCl was added. Typical examples Figs. 3 and 4. The absorption spectra of dye **3**, dye **7** and dye **8** in methanol did not significantly change when 0.1 M HCl was added.

The effects of dye concentration and temperature on absorption maxima were examined (Table 3). The λ_{max} values of dyes **1**–**9** did not significantly change with dye concentration in all used solvents except for dye **1** and dye **3**. The λ_{max} values of dye **1** and dye **3** in methanol showed a red shift with decreasing concentration. When solutions of the dyes in DMSO and DMF were examined over the temperature range 25–70 °C, the λ_{max} values of dyes **1**–**9** did not change significantly.

2.3. Substituent effects

As is apparent in Table 1, the introduction of electron-donating methyl group into the thiazole ring results in bathochro mic shifts in all solvents (for dye **2** $\Delta\lambda_{max} = 50$ nm relative to dye **1** for spectra in chloroform). It was also observed that the introduction of electron-donating ethoxy group into the benzothiazole ring (for dye **4** $\Delta\lambda_{max} = 35$ nm relative to dye **3** for spectra in acetic acid) resulted in bathochromic shifts in all

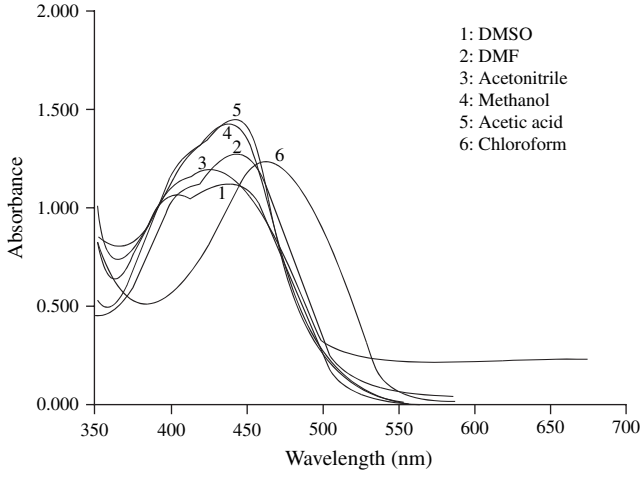


Fig. 1. Absorption spectra of dye **2** in various solvents.

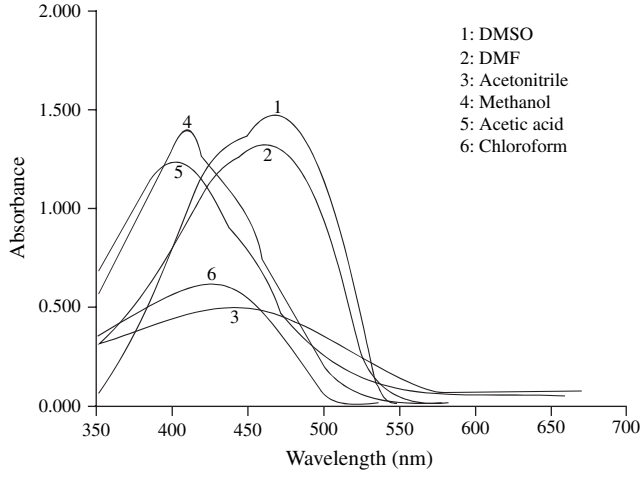


Fig. 2. Absorption spectra of dye **6** in various solvents.

Table 2
Absorption maxima of dyes **1**–**9** in acidic and basic solutions

Dye no	λ_{max} (nm)		
	Methanol	Methanol + KOH	Methanol + HCl
1	427, 400 s	459, 429 s	418
2	437, 415 s	464, 424 s	454
3	427	461, 420 s	426
4	449	465	465
5	364, 444 s	455	355
6	410, 435 s	460, 435 s	428, 461 s
7	365, 394 s	382, 412 s	365
8	404	427, 389 s	404
9	358	373	362

s: Shoulder.

the solvents. The electron-withdrawing nitro group into the benzothiazole ring results in bathochromic shifts in DMSO and DMF (for dye **5** $\Delta\lambda_{max} = 42$ nm relative to dye **3** for the spectra in DMSO) while they result in hypsochromic shifts in acetonitrile, methanol, acetic acid and chloroform. The electron-donating methylmercapto group into the triazole ring results in bathochromic shifts in all solvents (for dye **8** $\Delta\lambda_{max} = 47$ nm relative to dye **7** for spectra in chloroform).

3. Experimental

3.1. General

The chemicals used in the synthesis of all dyes were obtained from Merck Chemical Company and Aldrich Chemical Company and were used without further purification. The solvents used were of spectroscopic grade.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr. ^{1}H NMR spectra were recorded on a Bruker-Spectrospin Avance DTX 400 Ultra-Shield in DMSO-d_6 with TMS as internal reference. Absorption spectra were recorded on an ATI-Unicam UV-100 spectrophotometer in various solvents. All melting points were uncorrected.

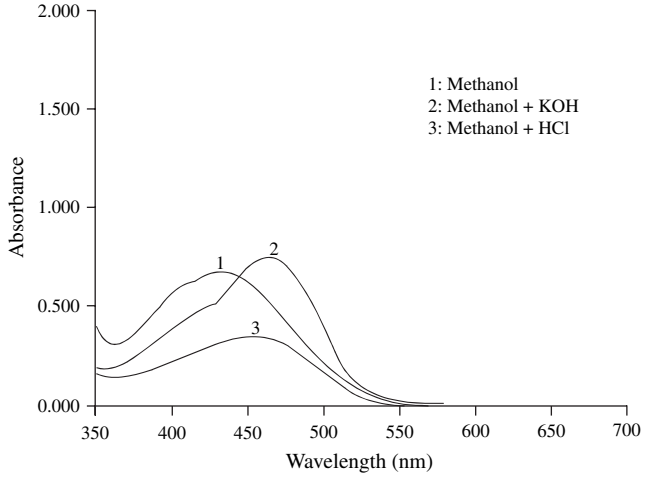


Fig. 3. Absorption spectra of dye **2** in acidic and basic solutions.

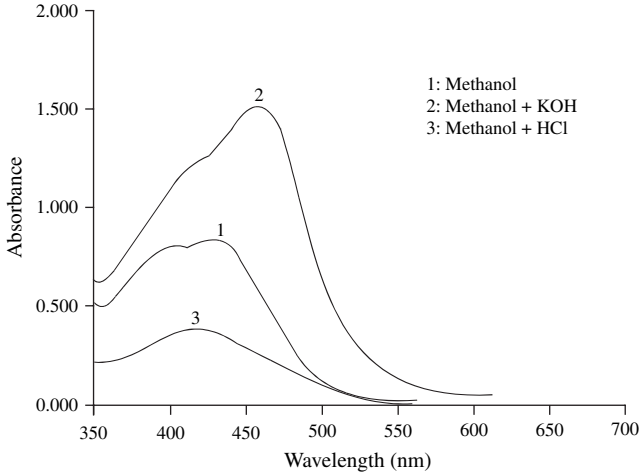


Fig. 4. Absorption spectra of dye **1** in acidic and basic solutions.

3.2. Preparation of hetarylazopyrimidone dyes

Diazotisation of the various heterocyclic amines was effected with nitrosyl sulphuric acid. A typical procedure that is described below is used for 2-aminothiazole; all other dyes were prepared in a similar manner. The yields of the dyes are in the range of 63–87%.

3.2.1. 3-(2′-Thiazolylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (*1*)

2-Aminothiazole (2.0×10^{-3} mol) was dissolved in hot glacial acetic acid (2.5 ml) and was rapidly cooled in an ice–salt bath to −5 °C. The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulphuric acid (prepared from sodium nitrite (1 g) and concentrated sulphuric acid (7 ml at 70 °C)). The mixture was stirred for an additional 1 h at 0 °C. After diazotisation was complete the azo liquor was slowly added to a vigorously stirred solution of 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one (2.0×10^{-3} mol) in pyridine. The pH of the reaction mixture was maintained at 7–8 by simultaneous addition of solid sodium carbonate in portions. The mixture was then stirred for 1 h at 0–5 °C. The progress of the reaction was followed by TLC using a DMF–water mixture (5/2 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 dried. Recrystallization from DMF–water mixture gave dark red crystals (0.52 g, 84%, m.p: dec. > 245 °C). IR (KBr): ν 3435, 3378 (NH_2), 3140 (NH), 3102 (Aro.-H), 1684 (C=O) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 12.45 (b, tautomeric NH_2), 10.30 (1H, b, NH), 8.88 (b, tautomeric NH), 8.04 (1H, m), 7.74 (1H, d), 7.51 (1H, m), 7.42 (1H, d), 7.35 (1H, m), 7.25 (1H, m).

Table 3
Influence of temperature and sample concentration on absorption maxima of dyes **1–9**

Dye no	λ_{max} (nm)													
	DMSO conc. (25 °C)	DMSO dil. (25 °C)	DMSO (70 °C)	DMF conc. (25 °C)	DMF dil. (25 °C)	DMF (70 °C)	A. nitrile conc. (25 °C)	A. nitrile dil. (25 °C)	Meth. conc. (25 °C)	Meth. dil. (25 °C)	A. acid conc. (25 °C)	A. acid dil. (25 °C)	Chl. conc. (25 °C)	Chl. dil. (25 °C)
1	391, 433 s	391, 434 s	391, 433 s	395, 408 s	395, 407 s	395, 408 s	395, 409 s	395, 410 s	402, 420 s	427, 400 s	404, 418 s	405, 419 s	418, 395 s	418, 396 s
2	440, 397 s	439, 398 s	438, 398 s	445, 410 s	443, 414 s	444, 413 s	429, 400 s	428, 400 s	435, 410 s	437, 415 s	437, 410 s	438, 410 s	465	464
3	398, 425 s	398, 424 s	397, 425 s	442, 410 s	442, 412 s	441, 412 s	403, 420 s	407, 422 s	409, 430 s	427	416, 438 s	423, 440 s	468	465
4	402, 460 s	402, 458 s	401, 458 s	451, 415 s	449, 414 s	448, 414 s	433	435	448	449	451	452	470	474
5	440, 480 s	434, 475 s	437, 478 s	444, 474 s	444, 473 s	445, 474 s	355	359	364, 444 s	364, 444 s	356	355	354	353
6	466, 440 s	467, 438 s	465, 430 s	464, 440 s	463, 438 s	460, 437 s	434	438	410, 435 s	410, 435 s	400, 440 s	405, 438 s	428	425
7	371, 410 s	376, 415 s	379, 412 s	378, 415 s	377, 416 s	378, 417 s	375	376	365, 394 s	365, 394 s	365	368	370	372
8	385, 410 s	386, 415 s	386, 415 s	385, 412 s	384, 415 s	384, 411 s	386	385	396	404	388	389	417	417
9	363, 412 s	363, 413 s	362, 410 s	357, 410 s	356, 412 s	354, 411 s	355	357	355	358	360	360	361	362

s: Shoulder, A. acid: acetic acid, Chl.: chloroform, Meth.: methanol, A. nitrile: acetonitrile, conc.: concentrated, dil.: diluted.

Anal. calcd. for $C_{13}H_9N_7OS$: C, 50.16; H, 2.91; N, 31.49; O, 5.14; S, 10.30. Found: C, 50.33; H, 2.98; N, 31.22; O, 5.27; S, 10.16%.

*3.2.2. 3-(5′-Methyl-2′-thiazolylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**2**)*

This dye was obtained from 2-amino-5-methylthiazole and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one as brown crystals (0.57 g, 87%), m.p: dec. > 267 °C; IR (KBr): ν 3435, 3368 (NH_2), 3152 (NH), 3052 (Aro.-H), 2897 (Aliph.-H), 1694 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.47 (b, tautomeric NH_2), 10.30 (1H, b, NH), 9.10 (b, tautomeric NH), 8.01 (1H, m), 7.63 (1H, s), 7.46 (1H, m), 7.40 (1H, m), 7.33 (1H, m), 2.37 (3H, s).

Anal. Calcd. for $C_{14}H_{11}N_7OS$: C, 51.68; H, 3.41; N, 30.14; O, 4.92; S, 9.85. Found: C, 51.84; H, 3.49; N, 29.91; O, 5.03; S, 9.71%.

*3.2.3. 3-(2′-Benzothiazolylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**3**)*

This dye was obtained from 2-aminobenzothiazole and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one as red crystals (0.53 g, 74%), m.p: 264–265 °C; IR (KBr): ν 3432, 3385 (NH_2), 3162 (NH), 3086 (Aro.-H), 1686 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.50 (b, tautomeric NH_2), 10.32 (1H, b, NH), 9.63 (b, tautomeric NH), 7.96 (2H, m), 7.71 (1H, m), 7.52 (1H, m), 7.47 (1H, m), 7.40 (1H, m), 7.31 (2H, m).

Anal. Calcd. for $C_{17}H_{11}N_7OS$: C, 56.50; H, 3.07; N, 27.13; O, 4.43; S, 8.87. Found: C, 56.73; H, 3.19; N, 27.04; O, 4.51; S, 8.71%.

*3.2.4. 3-(6′-Ethoxy-2′-benzothiazolylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**4**)*

This dye was obtained from *m*-chloroaniline and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one as dark red crystals (0.66 g, 82%), m.p: 263–264 °C; IR (KBr): ν 3427, 3382 (NH_2), 3151 (NH), 3067 (Aro.-H), 2895 (Aliph.-H), 1678 (C=O), 1104 (C–O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.42 (b, tautomeric NH_2), 10.37 (1H, b, NH), 9.60 (b, tautomeric NH), 8.00 (1H, m), 7.51–7.46 (3H, m), 7.37–7.30 (2H, m), 7.20 (1H, m), 3.95 (2H, q), 1.36 (3H, t).

Anal. Calcd. for $C_{19}H_{15}N_7O_2S$: C, 56.29; H, 3.73; N, 24.18; O, 7.89; S, 7.91. Found: C, 56.44; H, 3.87; N, 23.97; O, 7.96; S, 7.86%.

*3.2.5. 3-(6′-Nitro-2′-benzothiazolylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**5**)*

This dye was obtained from *p*-chloroaniline and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one as dark red crystals (0.55 g, 68%), m.p.: dec. > 254 °C; IR (KBr): ν 3439, 3383 (NH_2), 3145 (NH), 3097 (Aro.-H), 1698 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.50 (b, tautomeric NH_2), 10.30 (1H, b, NH), 9.63 (b, tautomeric NH), 9.00 (1H, m), 8.45 (1H, m), 8.00 (1H, m), 7.78 (1H, m), 7.46 (1H, m), 7.35 (1H, m), 7.28 (1H, m).

Anal. Calcd. for $C_{17}H_{10}N_8O_3S$: C, 50.25; H, 2.48; N, 27.57; O, 11.81; S, 7.89. Found: C, 50.46; H, 2.53; N, 27.42; O, 11.93; S, 7.68%.

*3.2.6. 3-(2′-Benzimidazolylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**6**)*

This dye was obtained from *o*-methoxyaniline and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one as brown crystals (0.55 g, 80%), m.p: 279–280 °C; IR (KBr): ν 3444,

3388 (NH_2), 3175 (NH), 3072 (Aro.-H), 1691 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.45 (b, tautomeric NH_2), 11.93 (1H, b, NH), 10.32 (1H, b, NH), 9.78 (b, tautomeric NH), 8.01 (1H, m), 7.50–7.45 (3H, m), 7.43–7.39 (3H, m), 7.30 (1H, m).

Anal. Calcd. for $C_{17}H_{12}N_8O$: C, 59.30; H, 3.51; N, 32.54; O, 4.65. Found: C, 59.43; H, 3.58; N, 32.41; O, 4.58%.

*3.2.7. 3-(1′,2′,4′-Triazol-3′-ylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**7**)*

This dye was obtained from 3-amino-1,2,4-triazole and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one as greenish yellow crystals (0.40 g, 67%), m.p: 224–225 °C; IR (KBr): ν 3435, 3375 (NH_2), 3161 (NH), 3077 (Aro.-H), 1692 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.50 (b, tautomeric NH_2), 10.66 (1H, b, NH), 10.28 (1H, b, NH), 9.50 (b, tautomeric NH), 8.40 (1H, s), 8.00 (1H, m), 7.50 (1H, m), 7.37 (1H, m), 7.29 (1H, m).

Anal. Calcd. for $C_{12}H_9N_9O$: C, 48.81; H, 3.07; N, 42.69; O, 5.42. Found: C, 49.02; H, 3.01; N, 42.57; O, 5.54%.

*3.2.8. 3-(5′-Methylmercapto-1′,2′,4′-triazol-3′-ylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**8**)*

This dye was obtained from 3-amino-5-methylmercapto-1,2,4-triazole and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]-pyrimidin-2-one as brown crystals (0.43 g, 63%), m.p: 310–311 °C; IR (KBr): ν 3442, 3389 (NH_2), 3168 (NH), 3094 (Aro.-H), 2881 (Aliph-H), 1687 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.50 (b, tautomeric NH_2), 10.83 (1H, b, NH), 10.30 (1H, b, NH), 9.55 (b, tautomeric NH), 8.03 (1H, m), 7.48 (1H, m), 7.39 (1H, m), 7.30 (1H, m), 2.85 (3H, s).

Anal. Calcd. for $C_{13}H_{11}N_9OS$: C, 45.74; H, 3.25; N, 36.93; O, 4.69; S, 9.39. Found: C, 45.89; H, 3.34; N, 36.78; O, 4.85; S, 9.21%.

*3.2.9. 3-(5′-Methyl-3′-isoxazolylazo)-4-amino-1H-benzo-[4,5]imidazo-[1,2-a]pyrimidin-2-one (**9**)*

This dye was obtained from 3-amino-5-methylisoxazole and 4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one as yellow crystals (0.44 g, 71%), m.p: 312–313 °C; IR (KBr): ν 3427, 3390 (NH_2), 3172 (NH), 3073 (Aro.-H), 2907 (Aliph-H), 1694 (C═O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 12.45 (b, tautomeric NH_2), 10.30 (1H, b, NH), 8.61 (b, tautomeric NH), 8.00 (1H, m), 7.46 (1H, m), 7.37 (1H, m), 7.30 (1H, m), 6.40 (1H, s), 2.47 (3H, s).

Anal. Calcd. for $C_{14}H_{11}N_7O_2$: C, 54.37; H, 3.58; N, 31.70; O, 10.35. Found: C, 54.43; H, 3.52; N, 31.58; O, 10.49%.

4. Conclusions

The synthesized 3-hetarylazo-4-amino-1*H*-benzo-[4,5]imidazo-[1,2-*a*]pyrimidin-2-one dyes (**1**–**9**) showed solvatochromic effects because of the increased polarity of the dye system. On the other hand, in hetarylazopyrimidone dyes their tautomeric equilibrium needs to be considered.

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