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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 1: Phenylazo derivatives

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**Abstract**

The reaction of 2-aminobenzimidazole with ethyl cyanoacetate gave access to an efficient synthesis of 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one (**I**) in excellent yield. A series of novel phenylazopyrimidone dyes were prepared by linking *o*-, *m*-, *p*-nitroaniline, *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-anisidine, *o*-, *m*-, *p*-toluidine and aniline to 4-amino-1*H*-benzo[4,5]imidazo-[1,2-*a*]pyrimidin-2-one (**I**). The prepared compounds were characterized by UV–vis, FT-IR and $^1$H NMR spectroscopic techniques and elemental analysis. The effect of varying pH and solvent upon the absorption ability of phenylazopyrimidones substituted with electron-withdrawing and electron-donating groups at their *o*-, *m*-, *p*-position was examined.


*Keywords:* Azopyrimidone dyes; Disperse dyes; Diazo-coupling reaction; Absorption properties; Solvent effect; Substituent effect

## 1. Introduction

Some pyrimidine derivatives possess biological and pharmacological activities [1–6]. The interesting biological activities reported pyrimidines have stimulated chemist to develop the chemistry of this class of compounds. However, very few comparable investigations have been carried out using imidazopyrimidines [7,8]. Some azopyrimidine derivatives also find application in dyes and complexes [9–14]. Although a number of papers have been published concerning the synthesis of pyrimidine and azopyrimidine derivatives, those containing an azoimidazo pyrimidine system of pyrimidines have not yet been reported. In continuation of our work, we report here the synthesis of 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one (**I**) and its disperse phenylazo dyes (**1–13**). The spectral characteristics of prepared compounds are also reported. The compound structures are shown in Schemes 1 and 2.

## 2. Results and discussion

### 2.1. Synthesis and characterizations

Heating of 2-aminobenzimidazole with excess of ethyl cyanoacetate at 150 °C afforded the 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one (**I**) (Scheme 1). The IR spectra of compound **I** showed strong absorptions at 3425–3390 cm$^{-1}$ for the amino group ($NH_2$), at 3124 cm$^{-1}$ for the imino group (NH) and at 1686 cm$^{-1}$ for the C=O group. The $^1$H NMR spectrum (DMSO-$d_6$) of compound **I** revealed a broad peak at $\delta$: 10.04 ppm (1H, b) (NH), a broad peak at $\delta$: 7.28 ppm (2H, b) ($NH_2$) and a singlet at $\delta$: 7.15 ppm (1H, s) assigned for the C=C–H of pyrimidone ring.

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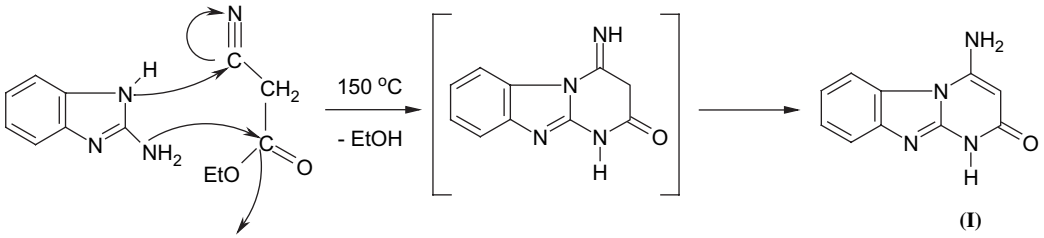



Scheme 1.

The phenylazopyrimidone dyes (**1**–**13**) were prepared by coupling 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one with diazotized aniline derivatives (Scheme 2). 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 3. The infrared spectra of all the dyes (in KBr) showed intense amino ($NH_2$) bands at 3434–3420 $cm^{-1}$ and at 3395–3371 $cm^{-1}$. It can be suggested that these dyes do not exist as the hydrazo-imine form in solid state. The IR spectra also show a band at 3180–3129 $cm^{-1}$, which was assigned to imino group (NH). The other $\nu_{max}$ values of 3106–3053 $cm^{-1}$ (aromatic C–H) and 1698–1659 $cm^{-1}$ (C=O) were recorded.

The $^1H$ NMR spectra measured in DMSO-$d_6$ at 25 °C showed a singlet at 2.52–2.26 ppm ($-CH_3$), a singlet at 3.75–3.65 ppm ($-OCH_3$), a multiplet at 9.48–6.82 ppm for aromatic protons (Aro.-H), a broad peak at 10.18–10.11 ppm (NH), a broad peak at 11.94–10.76 ppm for tautomeric amino ($NH_2$) protons and a broad peak at 10.18–8.81 ppm for tautomeric imine (NH) and tautomeric hydrazo (NH) protons. These results show that the dyes may exist as a mixture of tautomeric forms in DMSO.

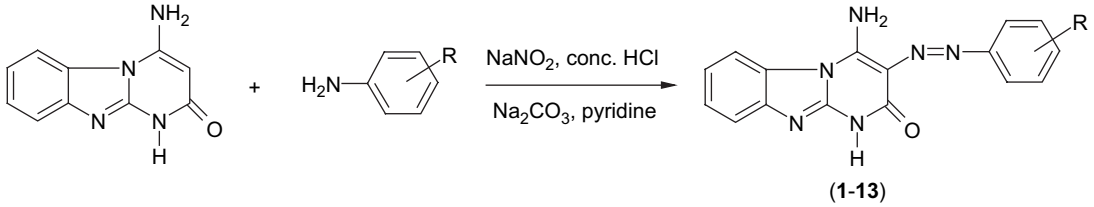
### 2.2. Solvent effects

UV–vis absorption spectra were recorded using an ATI-Unicam UV-100 Spectrophotometer in the wavelength range 300–700 nm. Absorption spectra of phenylazopyrimidone dyes **1**–**13** 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 solutions used was in the range between acidic and basic.

The dyes showed two absorbances in various solvents except dyes **2**–**6**. Dyes **2** and **6** showed single absorbance in all used solvents. Dyes **3**–**5** showed single absorbance in acetonitrile, methanol, acetic acid and chloroform. It can be suggested that dyes **2** and **6** are predominantly in the single tautomeric form in all used solvents and dyes **3**–**5** are predominantly in the single tautomeric form in acetonitrile, methanol, acetic acid and chloroform. But the other dyes may exist as a mixture of tautomeric forms in various solvents.

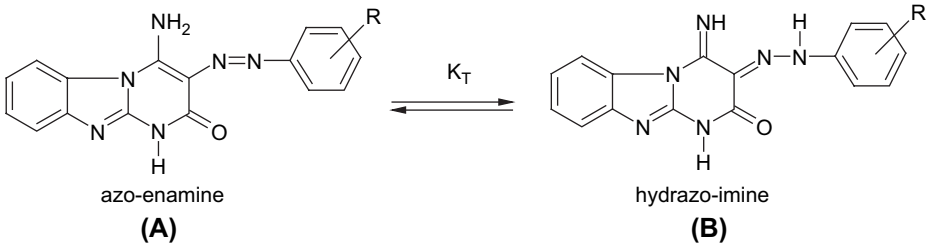
It was observed that the absorption spectra of the dyes in all solvents hypsochromically shifted with respect to the absorption spectra in chloroform except for dye **3** (e.g. for dye **6** $\lambda_{max}$ is 400 nm in $CHCl_3$, 388 nm in DMSO, 384 nm in DMF) (Fig. 1). But the $\lambda_{max}$ of dye **3** showed bathochromic shift in DMSO and DMF with respect to the $\lambda_{max}$ in chloroform (e.g. for dye **3** $\lambda_{max}$ is 397 nm in $CHCl_3$, 500 nm in DMSO, 413 nm in DMF) (Fig. 2).

It was also observed that the absorption curves of the dyes were sensitive to acid and base Table 2. The $\lambda_{max}$ of the dyes showed hypsochromic shifts when 0.1 M KOH




(**1**): R = *o*-$NO_2$
(**2**): R = *m*-$NO_2$
(**3**): R = *p*-$NO_2$
(**4**): R = *o*-Cl
(**5**): R = *m*-Cl
(**6**): R = *p*-Cl
(**7**): R = *o*-$OCH_3$
(**8**): R = *m*-$OCH_3$
(**9**): R = *p*-$OCH_3$
(**10**): R = *o*-$CH_3$
(**11**): R = *m*-$CH_3$
(**12**): R = *p*-$CH_3$
(**13**): R = H

Scheme 2.




Scheme 3.

was added to each of the dye solutions in methanol with the exception of dyes **4**, **5**, **10** and **11** and the absorption curves of the dyes resembled those in DMSO. The absorption spectra of the dyes in methanol also showed bathochromic shift when 0.1 M HCl was added and the absorption curves of the dyes resembled those in acetic acid. A typical example is shown in Fig. 3.

### 2.3. Substituent effects

As is apparent in Table 1, the introduction of electron-withdrawing nitro (*o*-) group in the benzene ring resulted in bathochromic shifts in all solvents. However, the nitro (*m*-) group in the benzene ring resulted in hypsochromic shifts in all solvents. The nitro (*p*-) group in the benzene ring resulted in bathochromic shifts in DMSO and DMF but did not change significantly in the other solvents.

The introduction of electron-withdrawing chloro (*o*-) group in the benzene ring resulted in bathochromic shifts in DMSO, DMF, acetic acid and chloroform. The chloro (*m*-) group in the benzene ring resulted in bathochromic shifts in DMSO, acetic acid and chloroform, but produced hypsochromic shifts in DMF, acetonitrile and methanol. The chloro (*p*-) group in the benzene ring resulted in hypsochromic shifts in all solvents.

The introduction of electron-donating methoxy (*o*-, *m*-, *p*-) groups in the benzene rings resulted in hypsochromic shifts in all solvents except for dye **7**. The $\lambda_{max}$ value of dye **7** in chloroform showed bathochromic shift with respect to the $\lambda_{max}$ value of dye **13** in chloroform.

The introduction of electron-donating methyl (*o*-, *m*-) groups in the benzene rings resulted in hypsochromic shifts in all solvents except for dye **11**. The $\lambda_{max}$ values of dye **11** in acetic acid and chloroform did not change significantly with respect to the $\lambda_{max}$ values of dye **13** in acetic acid and chloroform. The absorption spectra of dye **12** in all solvents did not change with respect to the absorption spectra of dye **13** in all solvents. The position of all groups did not show a regular variation in all solvents.

## 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

Table 1
Influence of solvent on $\lambda_{max}$ (nm) of dyes **1**–**13**

| Dye no | DMSO | DMF | Acetonitrile | Methanol | Acetic acid | Chloroform |
|---|---|---|---|---|---|---|
| **1** | 416, 356 s | 414, 363 s | 414, 351 s | 413, 348 s | 416, 339 s | 419, 355 s |
| **2** | 386 | 380 | 389 | 382 | 393 | 396 |
| **3** | 500, 425 s | 413, 477 s | 394 | 396 | 396 | 397 |
| **4** | 404, 423 s | 403, 420 s | 396 | 395 | 410 | 412 |
| **5** | 398, 419 s | 388, 423 s | 382 | 387 | 400 | 406 |
| **6** | 388 | 384 | 389 | 387 | 393 | 400 |
| **7** | 390, 412 s | 385, 408 s | 393, 411 s | 393, 412 s | 393, 422 s | 422, 390 s |
| **8** | 387, 412 s | 386, 415 s | 390, 407 s | 387, 407 s | 396, 414 s | 397, 418 s |
| **9** | 372, 416 s | 372, 413 s | 374, 415 s | 384, 410 s | 386, 414 s | 395, 420 s |
| **10** | 373, 413 s | 371, 410 s | 365, 412 s | 364, 415 s | 368, 414 s | 378, 417 s |
| **11** | 384, 416 s | 373, 416 s | 359, 406 s | 365, 406 s | 398, 416 s | 400, 418 s |
| **12** | 393, 419 s | 393, 416 s | 395, 410 s | 395, 409 s | 400, 424 s | 402, 420 s |
| **13** | 392, 415 s | 392, 415 s | 395, 416 s | 395, 415 s | 398, 418 s | 400, 418 s |

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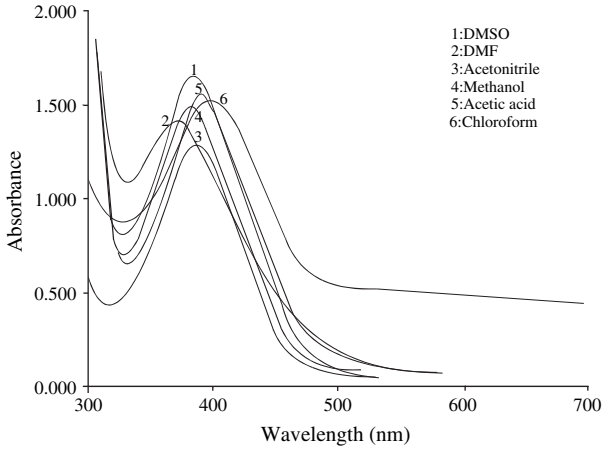


Fig. 1. Absorption spectra of dye **6** in various solvents.

reference. Absorption spectra were recorded on an ATI-Unicam UV-100 Spectrophotometer in various solvents. All melting points were uncorrected.

### 3.2. Preparation of 4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (*1*)

A mixture of 2-aminobenzimidazole (1 g, 7.5 mmol) and ethyl cyanoacetate (5.10 g, 45 mmol) was heated at 150 °C with stirring for 2 h [15]. The reaction mixture was diluted with ethanol. The solid product so formed was collected by filtration and washed with ether. Recrystallization from DMF/ethanol gives 1.21 g (81% yield), m.p: 299–300 °C; IR (KBr): $\nu$ 3425, 3390 ($NH_2$), 3214 (NH), 3079 (Aro.-H), 1686 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 10.04 (1H, b, NH), 7.28 (2H, b, $NH_2$), 7.98, 7.54–7.50 (4H, m, Aro.-H), 7.15 (1H, s, C=C–H); MS: 200 ($M^+$).

Anal. Calcd. for $C_{10}H_8N_4O$: C, 60.00; H, 4.03; N, 27.99; O, 7.99. Found: C, 59.91; H, 4.02; N, 28.01; O, 7.97%.

Table 2
Absorption maxima of dyes **1**–**13** in acidic and basic solutions

| Dye no | $\lambda_{max}$ (nm) | | | |
|---|---|---|---|---|
| | Methanol | Methanol + KOH | Methanol + HCl | Chloroform |
| **1** | 413, 348 s | 410, 350 s | 415, 340 s | 419, 355 s |
| **2** | 382 | 371 | 393 | 396 |
| **3** | 396 | 421, 474 s | 397 | 397 |
| **4** | 395 | 400, 425 s | 410 | 412 |
| **5** | 387 | 395, 420 s | 400 | 406 |
| **6** | 387 | 383 | 394 | 400 |
| **7** | 393, 412 s | 370, 410 s | 399, 420 s | 422, 390 s |
| **8** | 387, 407 s | 380, 400 s | 395, 410 s | 397, 418 s |
| **9** | 384, 410 s | 370, 405 s | 390, 410 s | 395, 420 s |
| **10** | 364, 415 s | 375, 407 s | 365, 412 s | 378, 417 s |
| **11** | 365, 406 s | 385, 415 s | 397, 415 s | 400, 418 s |
| **12** | 395, 409 s | 390, 418 s | 398, 422 s | 402, 420 s |
| **13** | 395, 415 s | 390, 412 s | 395, 418 s | 400, 418 s |

s: Shoulder.

### 3.3. Preparation of phenylazopyrimidone dyes

Diazotisation of the various carbocyclic amines was effected with HCl. A typical procedure that is described below used *o*-nitroaniline; all other dyes were prepared in a similar manner. The yields of the dyes are in the range of 67–93%.

#### 3.3.1. 3-(o-Nitrophenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (*1*)

A solution of *o*-nitrophenyldiazonium chloride, which was prepared from *o*-nitroaniline (0.21 g, 1.5 mmol), sodium nitrite (0.11 g, 1.5 mmol) and conc. HCl (4 mL) in water (10 mL) was added slowly to a cold 5 °C solution of 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one (0.3 g, 1.5 mmol) in pyridine (10 mL) to give orange suspension. The resulting solid was filtered, washed with cold water, dried and recrystallized from DMF/$H_2O$ mixture to give 3-(*o*-nitrophenylazo)-4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one (yield, 0.48 g

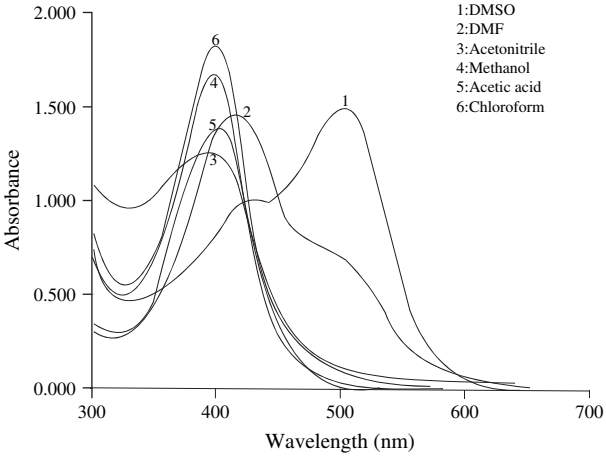


Fig. 2. Absorption spectra of dye **3** in various solvents.

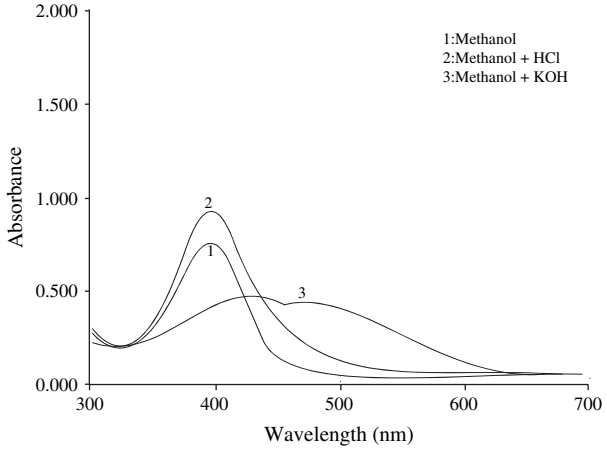


Fig. 3. Absorption spectra of dye **3** in acidic and basic solutions.

(91%), m.p: dec. > 320 °C). IR (KBr): $\nu$ 3434, 3381 ($NH_2$), 3145 (NH), 3106 (Aro.-H), 1695 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 10.76 (b, tautomeric $NH_2$), 10.15 (1H, b, NH), 9.15 (b, tautomeric NH), 9.00 (1H, m), 8.77 (1H, m), 8.65 (1H, m), 8.37 (1H, m), 8.02 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m).

Anal. Calcd. for $C_{16}H_{11}N_7O_3$: C, 55.02; H, 3.17; N, 28.07; O, 13.74. Found: C, 55.13; H, 3.19; N, 28.01; O, 13.79%.

### 3.3.2. 3-(m-Nitrophenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (2)

This dye was obtained from *m*-nitroaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as orange crystals (0.43 g, 83%), m.p: dec. > 320 °C; IR (KBr): $\nu$ 3428, 3371 ($NH_2$), 3132 (NH), 3097 (Aro.-H), 1698 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 10.76 (2H, b, $NH_2$), 10.15 (1H, b, NH), 9.48 (1H, m), 8.82 (1H, m), 8.60 (1H, m), 8.52 (1H, m), 8.01 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m).

Anal. Calcd. for $C_{16}H_{11}N_7O_3$: C, 55.02; H, 3.17; N, 28.07; O, 13.74. Found: C, 55.18; H, 3.20; N, 27.97; O, 13.82%.

### 3.3.3. 3-(p-Nitrophenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (3)

This dye was obtained from *p*-nitroaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as brown crystals (0.49 g, 93%), m.p: dec. > 320 °C; IR (KBr): $\nu$ 3422, 3383 ($NH_2$), 3137 (NH), 3089 (Aro.-H), 1686 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 10.80 (b, tautomeric $NH_2$), 10.15 (1H, b, NH), 9.23 (b, tautomeric NH), 8.75 (2H, m), 8.47 (2H, m), 8.01 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m).

Anal. Calcd. for $C_{16}H_{11}N_7O_3$: C, 55.02; H, 3.17; N, 28.07; O, 13.74. Found: C, 55.27; H, 3.11; N, 27.99; O, 13.85%.

### 3.3.4. 3-(o-Chlorophenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (4)

This dye was obtained from *o*-chloroaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as greenish yellow crystals (0.39 g, 76%), m.p: 305–306 °C; IR (KBr): $\nu$ 3429, 3385 ($NH_2$), 3151 (NH), 3079 (Aro.-H), 1677 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.94 (b, tautomeric $NH_2$), 10.16 (1H, b, NH), 9.92 (b, tautomeric NH), 8.08 (1H, m), 8.01 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m), 7.26 (1H, m), 7.07 (1H, m), 6.99 (1H, m).

Anal. Calcd. for $C_{16}H_{11}ClN_6O$: C, 56.73; H, 3.27; Cl, 10.47; N, 24.81; O, 4.72. Found: C, 56.91; H, 3.33; Cl, 10.52; N, 24.43; O, 4.67%.

### 3.3.5. 3-(m-Chlorophenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (5)

This dye was obtained from *m*-chloroaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as orange crystals (0.36 g, 71%), m.p: 294–295 °C; IR (KBr): $\nu$ 3425, 3388 ($NH_2$), 3142 (NH), 3053 (Aro.-H), 1659 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.94 (b, tautomeric $NH_2$), 10.16 (1H, b, NH), 9.90 (b, tautomeric NH), 8.01 (1H, m), 7.86 (1H, m), 7.78 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m), 7.29 (1H, m), 7.15 (1H, m).

Anal. Calcd. for $C_{16}H_{11}ClN_6O$: C, 56.73; H, 3.27; Cl, 10.47; N, 24.81; O, 4.72. Found: C, 56.87; H, 3.35; Cl, 10.58; N, 24.47; O, 4.59%.

### 3.3.6. 3-(p-Chlorophenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (6)

This dye was obtained from *p*-chloroaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as greenish yellow crystals (0.40 g, 78%), m.p: 295–296 °C; IR (KBr): $\nu$ 3434, 3390 ($NH_2$), 3164 (NH), 3071 (Aro.-H), 1690 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.94 (2H, b, $NH_2$), 10.17 (1H, b, NH), 8.01 (1H, m), 7.77 (2H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m), 7.28 (2H, m).

Anal. Calcd. for $C_{16}H_{11}ClN_6O$: C, 56.73; H, 3.27; Cl, 10.47; N, 24.81; O, 4.72. Found: C, 56.85; H, 3.38; Cl, 10.51; N, 24.53; O, 4.64%.

### 3.3.7. 3-(o-Methoxyphenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (7)

This dye was obtained from *o*-methoxyaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as red crystals (0.39 g, 77%), m.p: 302–303 °C; IR (KBr): $\nu$ 3427, 3375 ($NH_2$), 3180 (NH), 3072 (Aro.-H), 2881 (Aliph-H), 1687 (C=O), 1106 (C–O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.91 (b, tautomeric $NH_2$), 10.15 (1H, b, NH), 9.81 (b, tautomeric NH), 8.01 (1H, m), 7.74 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m), 7.29 (1H, m), 7.12 (1H, m), 7.10 (1H, m), 3.75 (3H, s).

Anal. Calcd. for $C_{17}H_{14}N_6O_2$: C, 61.07; H, 4.22; N, 25.14; O, 9.57. Found: C, 61.19; H, 4.28; N, 24.97; O, 9.64%.

### 3.3.8. 3-(m-Methoxyphenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (8)

This dye was obtained from *m*-methoxyaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as brown crystals (0.41 g, 81%), m.p: 293–3294 °C; IR (KBr): $\nu$ 3425, 3378 ($NH_2$), 3157 (NH), 3071 (Aro.-H), 2854 (Aliph-H), 1692 (C=O), 1124 (C–O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.92 (b, tautomeric $NH_2$), 10.16 (1H, b, NH), 10.25 (b, tautomeric NH), 8.01 (1H, m), 7.71 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m), 7.21 (2H, m), 6.82 (1H, m), 3.71 (3H, s).

Anal. Calcd. for $C_{17}H_{14}N_6O_2$: C, 61.07; H, 4.22; N, 25.14; O, 9.57. Found: C, 61.23; H, 4.32; N, 25.02; O, 9.69%.

### 3.3.9. 3-(p-Methoxyphenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (9)

This dye was obtained from *p*-methoxyaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as greenish yellow crystals (0.37 g, 73%), m.p: 296–297 °C; IR (KBr): $\nu$ 3430, 3387 ($NH_2$), 3143 (NH), 3074 (Aro.-H), 2872 (Aliph-H), 1693 (C=O), 1109 (C–O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.92 (b, tautomeric $NH_2$), 10.15 (1H, b, NH), 9.60 (b, tautomeric NH), 8.01 (1H, m), 7.72 (2H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (1H, m), 6.94 (2H, m), 3.65 (3H, s).

Anal. Calcd. for $C_{17}H_{14}N_6O_2$: C, 61.07; H, 4.22; N, 25.14; O, 9.57. Found: C, 61.38; H, 4.34; N, 25.09; O, 9.72%.

### 3.3.10. 3-(o-Methylphenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (10)

This dye was obtained from *o*-methylaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as greenish yellow crystals (0.33 g, 69%), m.p: 303–304 °C; IR (KBr): $\nu$ 3434, 3395 ($NH_2$), 3161 (NH), 3066 (Aro.-H), 2907 (Aliph-H), 1687 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.90 (b, tautomeric $NH_2$), 10.13 (1H, b, NH), 8.95 (b, tautomeric NH), 8.01 (1H, m), 7.75 (1H, m), 7.47 (1H, m), 7.39 (1H, m), 7.33 (2H, m), 7.01 (1H, m), 6.97 (1H, m), 2.52 (3H, s).

Anal. Calcd. for $C_{17}H_{14}N_6O$: C, 61.14; H, 4.43; N, 26.40; O, 5.03. Found: C, 61.27; H, 4.52; N, 26.13; O, 5.11%.

### 3.3.11. 3-(m-Methylphenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (11)

This dye was obtained from *m*-methylaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as greenish yellow crystals (0.32 g, 67%), m.p: 301–302 °C; IR (KBr): $\nu$ 3420, 3374 ($NH_2$), 3129 (NH), 3075 (Aro.-H), 2863 (Aliph-H), 1683 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.90 (b, tautomeric $NH_2$), 10.11 (1H, b, NH), 8.81 (b, tautomeric NH), 8.03 (1H, m), 7.74 (2H, m), 7.46 (1H, m), 7.40 (1H, m), 7.31 (1H, m), 7.12 (2H, m), 2.26 (3H, s).

Anal. Calcd. for $C_{17}H_{14}N_6O$: C, 61.14; H, 4.43; N, 26.40; O, 5.03. Found: C, 61.32; H, 4.57; N, 26.09; O, 5.24%.

### 3.3.12. 3-(p-Methylphenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (12)

This dye was obtained from *p*-methylaniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as orange crystals (0.33 g, 69%), m.p: dec. > 300 °C; IR (KBr): $\nu$ 3428, 3382 ($NH_2$), 3139 (NH), 3089 (Aro.-H), 2855 (Aliph-H), 1691 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.90 (b, tautomeric $NH_2$), 10.17 (1H, b, NH), 9.60 (b, tautomeric NH), 8.02 (1H, m), 7.80 (2H, m), 7.46 (1H, m), 7.40 (1H, m), 7.31 (1H, m), 7.17 (2H, m), 2.37 (3H, s).

Anal. Calcd. for $C_{17}H_{14}N_6O$: C, 61.14; H, 4.43; N, 26.40; O, 5.03. Found: C, 61.27; H, 4.59; N, 26.21; O, 5.35%.

### 3.3.13. 3-(Phenylazo)-4-amino-1H-benzo[4,5]imidazo[1,2-a]pyrimidin-2-one (13)

This dye was obtained from aniline and 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]pyrimidin-2-one as orange crystals (0.38 g, 84%), m.p: dec. > 300 °C; IR (KBr): $\nu$ 430, 3373 ($NH_2$), 3146 (NH), 3064 (Aro.-H), 1688 (C=O) $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$ 11.90 (b, tautomeric $NH_2$), 10.12 (1H, b, NH), 9.60 (b, tautomeric NH), 8.03 (1H, m), 7.91 (2H, m), 7.48 (1H, m), 7.42 (1H, m), 7.33 (3H, m), 6.97 (1H, m).

Anal. Calcd. for $C_{16}H_{12}N_6O$: C, 63.15; H, 3.97; N, 27.62; O, 5.26. Found: C, 63.39; H, 4.03; N, 27.21; O, 5.42%.

## 4. Conclusions

In this work, 4-amino-1*H*-benzo[4,5]imidazo[1,2-*a*]-pyrimidin-2-one and its disperse azo dyes have been synthesized. Characterization and absorption ability of 13 novel phenylazopyrimidone based dyes (**1**–**13**) were studied. The absorption spectra results of these dyes (**1**–**13**) revealed that these compounds do exist in forming azo-enamine and hydrazo-imine form species.

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