

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 ¹H 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.

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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.

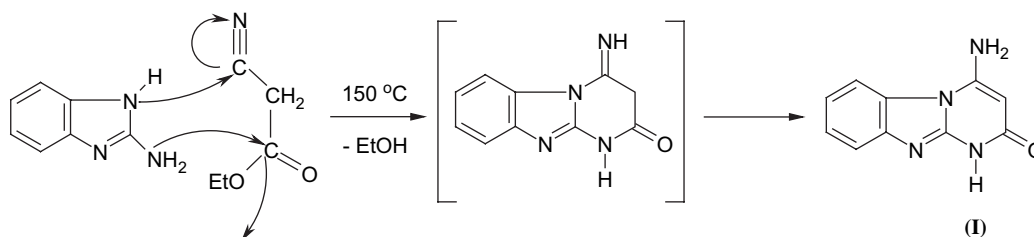
2. Results and discussion

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 (NH₂), at 3124 cm⁻¹ for the imino group (NH) and at 1686 cm⁻¹ for the C=O group. The ¹H NMR spectrum (DMSO-*d*₆) of compound **I** revealed a broad peak at δ: 10.04 ppm (1H, b) (NH), a broad peak at δ: 7.28 ppm (2H, b) (NH₂) and a singlet at δ: 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-1H-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 $3434\text{--}3420\text{ cm}^{-1}$ and at $3395\text{--}3371\text{ cm}^{-1}$. 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 $3180\text{--}3129\text{ cm}^{-1}$, which was assigned to imino group (NH). The other ν_{max} values of $3106\text{--}3053\text{ cm}^{-1}$ (aromatic C–H) and $1698\text{--}1659\text{ cm}^{-1}$ (C=O) were recorded.

The ^1H NMR spectra measured in $\text{DMSO-}d_6$ at $25\text{ }^\circ\text{C}$ showed a singlet at $2.52\text{--}2.26\text{ ppm}$ ($-\text{CH}_3$), a singlet at $3.75\text{--}3.65\text{ ppm}$ ($-\text{OCH}_3$), a multiplet at $9.48\text{--}6.82\text{ ppm}$ for aromatic protons (Aro.-H), a broad peak at $10.18\text{--}10.11\text{ ppm}$ (NH), a broad peak at $11.94\text{--}10.76\text{ ppm}$ for tautomeric amino (NH_2) protons and a broad peak at $10.18\text{--}8.81\text{ ppm}$ 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

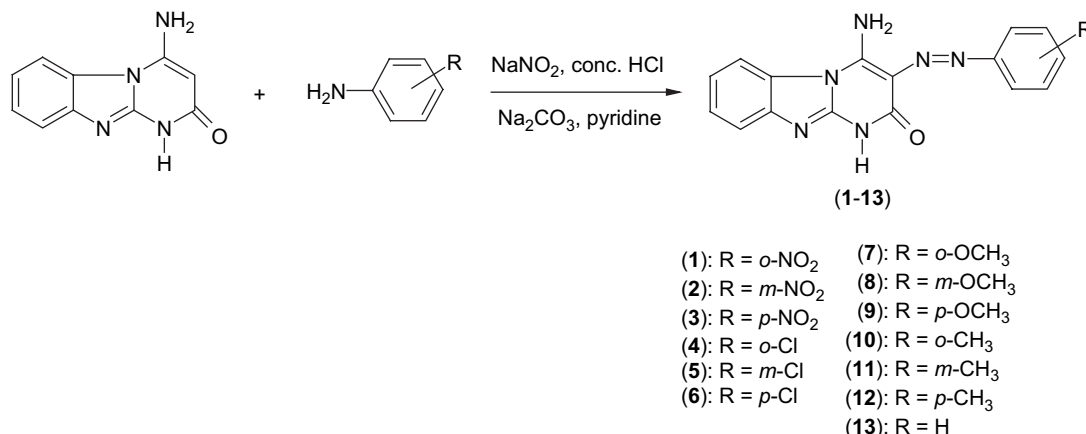
UV–vis absorption spectra were recorded using an ATI-Unicam UV-100 Spectrophotometer in the

wavelength range $300\text{--}700\text{ nm}$. Absorption spectra of phenylazopyrimidone dyes **1–13** were recorded in various solvents at a concentration of $10^{-6}\text{--}10^{-8}\text{ M}$ 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** λ_{max} is 400 nm in CHCl_3 , 388 nm in DMSO, 384 nm in DMF) (Fig. 1). But the λ_{max} of dye **3** showed bathochromic shift in DMSO and DMF with respect to the λ_{max} in chloroform (e.g. for dye **3** λ_{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 λ_{max} of the dyes showed hypsochromic shifts when 0.1 M KOH



Scheme 2.

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