



Synthesis, structure and study of azo-hydrazone tautomeric equilibrium of 1,3-dimethyl-5-(arylo)-6-amino-uracil derivatives



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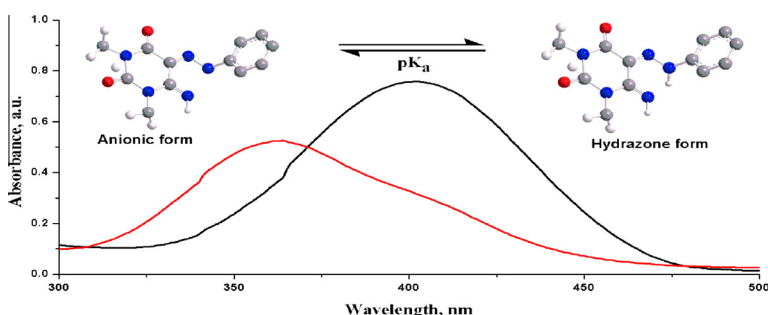
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HIGHLIGHTS

- Crystal structure of 1,3-dimethyl-5-phenylazo-6-aminouracil.
- Evidenced azo- and hydrazone forms of azo-derivatives of 6-aminouracil.
- Studied solvent effects on the absorption maxima of the azo-dyes.
- Studied photo-physical property of the azo-dyes.
- Evaluated acid-dissociation constant (pK_a) values of the dyes.

GRAPHICAL ABSTRACT



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ABSTRACT

Azo dyes, 1,3-dimethyl-5-(arylo)-6-aminouracil (aryl = $-C_6H_5$ (**1**), $-p-CH_3C_6H_4$ (**2**), $-p-ClC_6H_4$ (**3**), $-p-NO_2C_6H_4$ (**4**)) were prepared and characterized by UV-vis, FT-IR, 1H NMR, ^{13}C NMR spectroscopic techniques and single crystal X-ray crystallographic analysis. In the light of spectroscopic analysis it evidences that of the tautomeric forms, the azo-enamine-keto (**A**) form is the predominant form in the solid state whereas in different solvents it is the hydrazone-imine-keto (**B**) form. The study also reveals that the hydrazone-imine-keto (**B**) form exists in an equilibrium mixture with its anionic form in various organic solvents. The solvatochromic and photophysical properties of the dyes in various solvents with different hydrogen bonding parameter were investigated. The dyes exhibit positive solvatochromic property on moving from polar protic to polar aprotic solvents. They are fluorescent active molecules and exhibit high intense fluorescent peak in some solvents like DMSO and DMF. It has been demonstrated that the anionic form of the hydrazone-imine form is responsible for the high intense fluorescent peak. In addition, the acid-base equilibrium in between neutral and anionic form of hydrazone-imine form in buffer solution of varying pH was investigated and evaluated the pK_a values of the dyes by making the use of UV-vis spectroscopic methods. The determined acid dissociation constant (pK_a) values increase according to the sequence of $2 > 1 > 3 > 4$.

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Introduction

Azo compounds, bearing the functional group $R-N=N-R'$, in which R and R' can be either aryl or alkyl, exhibit vivid colors, especially reds, oranges, and yellows resulted from π -electron

delocalization through aromatic moieties. Therefore, they have been used as dyes, known as azo dyes, in textile, food, printing and cosmetic industries [1,2]. The rich chemistry of the azo compounds is associated with several important biological reactions such as protein synthesis, carcinogenesis, azo reduction monoamine oxidase inhibition mutagenic, immune chemical affinity labeling, nitrogen fixation, important medical and industrial uses [3,4]. Recently, in the last two decades, there has been a rapid

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growing interest for their potential applications in miscellaneous areas such as photochromic materials, non-linear optical (NLO) devices, liquid-crystalline displays (LCDs), dye-sensitized solar cells (DSSCs), sensors and indicators as well as biological-medicinal studies [5–10].

Among the azo dyes, heterocyclic azo dyes attract considerable interest and play an important role in the development of the chemistry of azo compounds. Furthermore, some heterocyclic azo compounds have also found use as ligands to generate a special category of metal azo complexes which are exploited enormously in the manufacture of colorimetric sensors-which lend themselves to cations and anions [11–13]. Of the heterocycleazo dyes, pyridone and pyrimidine derivatives are relatively recent heterocyclic intermediates for the preparation of aryl-azo dyes [14,15].

Moreover, the applications of azo-dyes are strongly dependent on the photophysical properties of azo-hydrazone tautomerism which has been used to some extent for dye location characterization in surfactant micelles and textile fibers [16,17], photographic systems [18], dyeing protein [19,20], bleaching [21,22], and probe molecules to characterize catalysts [23,24]. Both the tautomers exhibit different optical and physical properties. The hydrazone form that absorbs light at longer wavelengths was therefore found to be rendered higher photoconductivity to dual-layer photoreceptors [18] and it is therefore often commercially preferred. The phenomenon of azo-hydrazone tautomerism correlates the mobility of a labile proton across a molecule through a conjugated system where the proton remains in association with intra-molecular hydrogen bonding between donor-acceptor atoms. Such phenomenon arises when azo dyes contains OH or NHR group conjugated with the azo group.

Study of azo-hydrazone tautomerism mechanism is therefore extremely important and highly demanding for controlling the molecular properties of these systems depending on the polarity and pH of the medium. The study of this property on some dyes has been accomplished and reported [22,25–28] elsewhere. The above observations have drawn our attention and motivated to investigate such interesting property of azo-hydrazone tautomerism on azo-dyes with a backbone of 6-aminouracil derivative. Uracil derivatives, which have pyrimidine-like structure (uracil = pyrimidine-2,4-dione), have an elegance role in heterocyclic chemistry [29]. They have aroused much interest owing to their potential applications in medicine and photobiology [30]. Pyrimidine dyes in some cases prepared from 6-aminouracils have found industrial applications in hypnotic drugs [31], in living cells, in detecting cancer [32] and having pharmacological and biological activities [33]. The detail synthesis of azo derivatives of uracil has been paid attention recently and aryl/hetarylazo derivatives of uracil or 1,3-dimethyl-6-aminouracil have been reported [34–37] by several authors. However, so far no report on the isolation of single crystal X-ray structure analysis of azo-derivatives of 1,3-dimethyl-

6-aminouracil has been reported. The crystal structure of Cu(II), and Rh(III) complex of 1,3-dimethyl-5-(phenylazo)-6-aminouracil had been reported [38,37]. A formation of super-complex of the cationic form of 1,3-dimethyl-5-(phenylazo)-6-aminouracil with AuX_2^- ($X = Cl$ or Br) and its crystal structure had also been reported [39,40]. In this contribution, we report (i) a modified route of synthesis of four azo-derivatives of 1,3-dimethyl-6-aminouracil (Scheme 1); (ii) first time the X-ray crystal structure of 1,3-dimethyl-5-(phenylazo)-6-aminouracil of its azo-tautomeric form which is found stable in the solid state, (iii) the study of solvatochromic property in various organic solvents with different hydrogen bonding parameters and azo-hydrazone tautomeric equilibrium in aqueous solution of varying pH to evaluate the pK_a values, and (iv) the potential photophysical property of the derivatives of 1,3-dimethyl-5-(arylamino)-6-aminouracil.

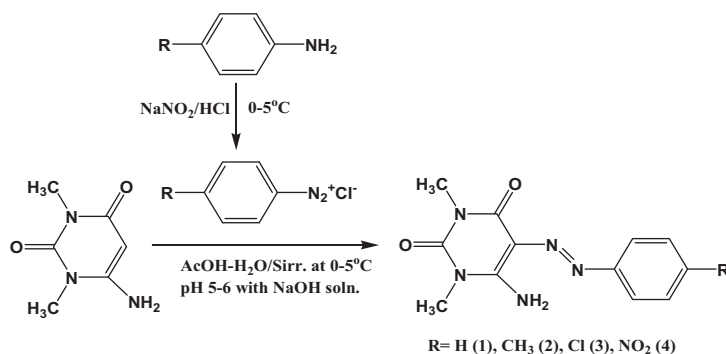
Experimental

Material and instruments

All chemicals were of reagent grade, purchased from Merck, Aldrich, and Himedia and were used without further purification. All solvents were of A. R. grade and used for synthesis and spectroscopic studies. 1,3-Dimethyl-6-aminouracil was prepared following the reported method [41]. For the studies of equilibrium constant double distilled water was used.

Standard Buffer solutions with pH 1.5, 2.0, 3.48, 3.8, 4.39, 4.76, 5.13, 6.04, 9.0, 9.6, 10.0, 10.4, 10.8, and 12.0 were prepared by following the traditional procedure from double distilled water with HCl, NaOH, $Na_2B_4O_7$, $NaHCO_3$, Na_2CO_3 , and KCl. The constant ionic strength of 0.1 M was maintained with KCl solution. In most cases, the pH needed to be adjusted using a pH meter and the drop-wise addition of either 1 M HCl or 1 M NaOH to 1 L of solution. The accurate pH for each buffer solution was measured with a Systonics digital pH meter 335.

Melting points were determined on a Labtech Digital melting point apparatus with a heating rate of 2 °C/min and not corrected. IR spectra were recorded on a Perkin Elmer; model RX-1 FT-IR spectrophotometer in the region 4000–400 cm^{-1} making KBr pellets of all dyes. 1H NMR and ^{13}C NMR spectra were recorded on a Bruker (AC) 300 MHz and a Bruker DRX-500 MHz FT-NMR spectrometer in $CDCl_3$ as the solvent and TMS the internal standard. The electronic spectra were determined on a Shimadzu UV-vis-1800 spectrophotometer. Quartz cuvettes were used for measurements in solution. Fluorescence spectra of all dyes were recorded in different solvents on a Perkin Elmer spectrofluorometer, model LS55. Excitation and emission slits were set to 10 and 5 nm, respectively. Elemental analyses were made by a Perkin Elmer 2400 series-II analyzer and the results agreed well with the calculated values.



Scheme 1. A general reaction scheme of synthesis of dyes (1–4).

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