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Synthesis, characterization and theoretical study of new hetarylazopyrazolone dyes and investigation of their absorption spectra

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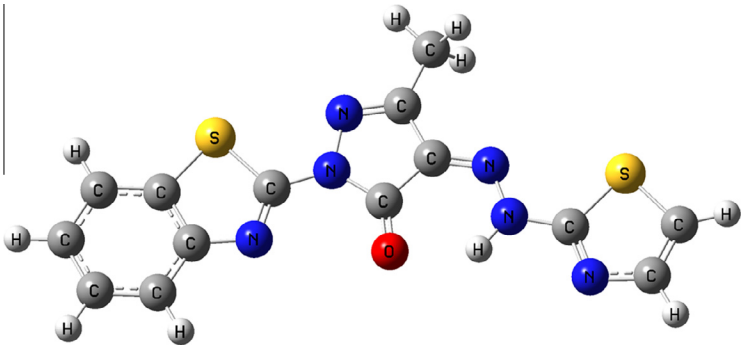
HIGHLIGHTS

- Six new hetarylazopyrazolone dyes were synthesized and characterized.
- The solvatochromic properties of the dyes were investigated.
- The structure, tautomerism and absorption spectra of dyes were investigated theoretically by DFT.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of hetarylazopyrazolone dyes were synthesized by coupling 1-(2-benzothiazolyl)-3-methylpyrazol-5-one with six heterocylic amines prepared in nitrosyl sulphuric acid. The dyes were characterized by spectral methods and elemental analysis. The solvatochromic properties of the dyes were investigated in various solvents. Additionally, acid–base, concentration, temperature and substituent effects on the visible absorbtion spectra were also examined.

The ground-state geometry of the synthesized compounds were studied by using density functional theory (DFT) calculations at the B3LYP/6-31+G(d) level of theory. The absorption spectra of the dyes are obtained by using time-dependent density functional theory (TD-DFT) method associated with the integral equation formalism polarizable continuum model (IEFPCM). Tautomerism of 1-(2-benzothiazolyl)-3-methyl-4-(2-thiazolylazo)pyrazol-5-one has been examined by means of B3LYP/6-31+G(d) method. Calculated absorption maxima are evaluated via comparison with experimental values.

1. Introduction

Heterocyclic diazo and coupling components have been used extensively in the preparation of disperse dyes. In the literature, there are many examples related with the synthesis of hetarylazo dyes and usage of them as a dyestuff for synthetic fabrics [1–22]. These dyes are characterized also by having generally excellent brightness and high extinction coefficients, relative to azo dyes derived from substituent anilines. It has also been reported that hetarylazopyrazolone derivatives which posses different chromophoric groups tend to show bathochromic shifts when compared to phenylazopyrazolones [2–5]. We have recently reported the synthesis of some novel hetarylazopyrazolone dyes [4,5], which exhibit a strong solvent dependence in their absorption spectra.

It was demonstrated that some dyes such as pyrazolone derivatives showed the property of absorption in near IR region and can be used in protection of optical record systems and optical filters [20–22]. Besides their well known dying properties, these type of hetarylazo dyes have taken a great interest by their usage in non-textile applications, especially in high technology [20–24].

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They are being used in opto-electronic systems such as laser optical recording systems, laser printing systems and thermal writing systems. Theoretical studies of azo dyes complements the experimental results and allows to establish relationship between structure and chemical properties [25–31].

The present paper reports the synthesis and characterization of some bis-hetarylmonoazo dyes using 1-(2-benzothiazolyl)-3-methylpyrazol-5-one as coupling component and evaluate their electronic spectra in various solvents for the colour–structure relationships in such dyes. The dyes were characterized with FT-IR, ^{1}H NMR, LC–MS spectroscopic techniques and elemental analysis. In continuation of our work, the structure, tautomerism and maximum absorption values of dyes were investigated theoretically by performing the density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The effects of solvent polarity on maximum absorption wavelenght was calculated using different basis set via the IEFPCM method and the results compared to experimental data. The chemical structures of these dyes are presented in formulas II-a–f (Scheme 1).

2. Experimental

2.1. General

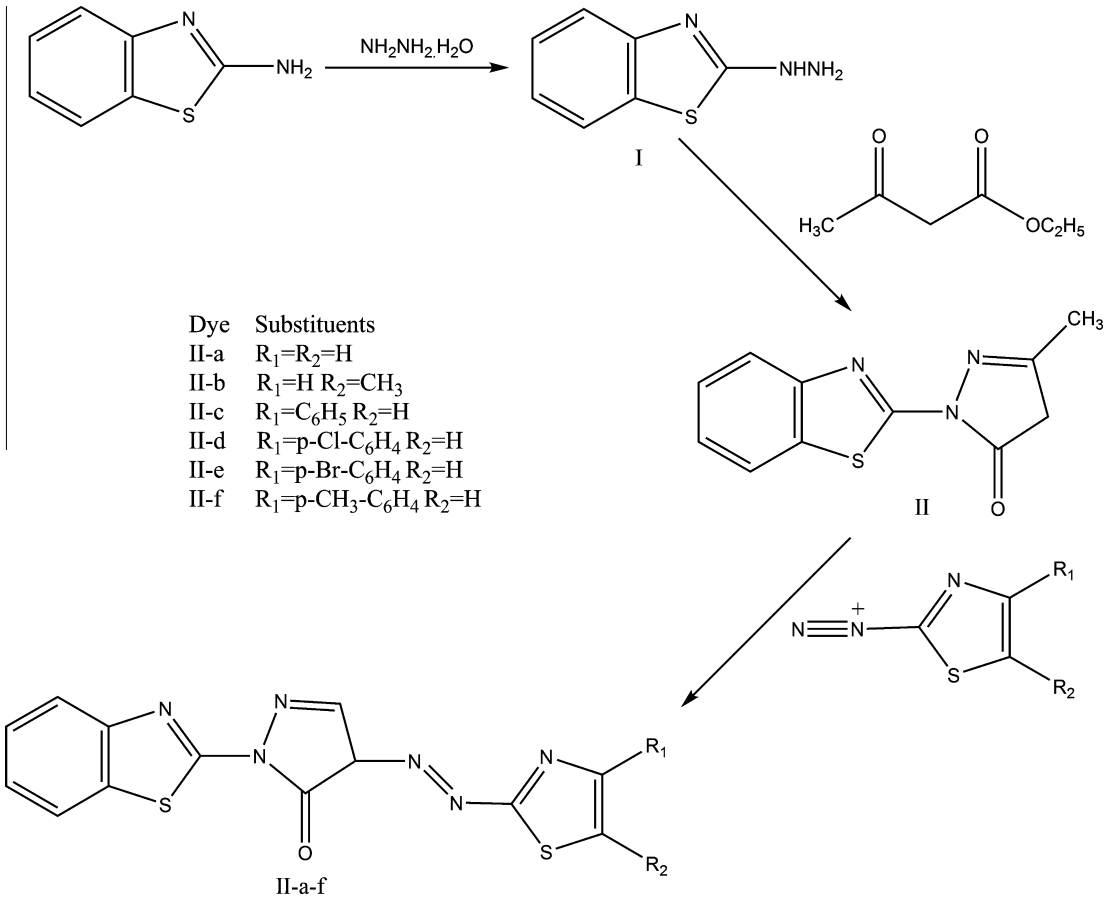
The chemicals used in the synthesis of all compounds were obtained from Merck Chemical Company or Aldrich Chemical Company and used without further purification. Infrared spectra were taken in KBr on a Mattson 1000 spectrophotometer. H^1 NMR spectra were obtained on a Bruker DPX-400 MHz spectrometer using DMSO-d_6 as solvent and TMS as internal standard. Absorption spectra were recorded on a Analiticaljena Specord 200 spectrophotometer, using DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform. Mass spectra were measured with a Micromass UK Platform II LC–MS spectrometer. Melting points were obtained with a Gallenkamp capillary melting apparatus and are given uncorrected.

2.2. Synthesis

Hetarylazopyrazolone dyes were prepared by the coupling reaction of 1-(2-benzothiazolyl)-3-methylpyrazol-5-one with diazotised heterocyclic amines in nitrosyl sulphuric acid. The routes used for the synthesis of coupling component (II) and bis-hetarylazopyrazolone dyes (II-a–f) are shown in Scheme 1. The physical properties of the dyes are shown in Table 1. The compound (I), 2-hydrazinobenzothiazole was obtained by treating 2-aminobenzothiazole with hydrazin monohydrate [32]. The coupling component 1-(2-benzothiazolyl)-3-methylpyrazol-5-one (II) was prepared from the acid catalysed reaction of 2-hydrazino benzothioazole with ethylaceto acetate in absolute ethanol [33].

2.2.1. Synthesis of 2-hydrazinobenzothiazole (I)

Into a three necked round bottomed flask 2-aminobenzothiazole (0.15 mol, 22.5 g), ethylene glycol (100 ml), hydrazine monohydrate (0.30 mol, 14.6 ml) and hydrazinium sulphate (0.15 mol, 19.5 g) were added and the mixture was refluxed at 140 °C for 2 h under nitrogen atmosphere. The product was poured into a beaker and let to cool to room temperature. Water (40 mL) was added to the crystallized product, the mixture was stirred and filtered by vacuum. The crystals were recrystallized from ethanol,



Scheme 1. The synthetic route of dyes.