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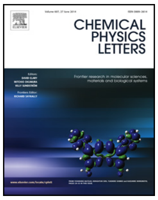

# Solvent and structural effects on the spectral shifts of 5-(substituted phenylazo)-3-cyano-6-hydroxy-1-(2-hydroxyethyl)-4-methyl-2-pyridones

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ABSTRACT

Spectral properties, solvatochromism and azo-hydrazone tautomerism of ten 5-(substituted phenylazo)-3-cyano-6-hydroxy-1-(2-hydroxyethyl)-4-methyl-2-pyridones in twenty-two solvents are investigated. For quantitative evaluation of the solvent effects on the UV–vis absorption maxima, the principles of the linear solvation energy relationships are used, i.e. models proposed by Kamlet–Taft and Catalán. Linear free energy relationships are applied to the UV–vis absorption spectra and correlation of absorption frequencies with Hammett substituent constants are performed. Furthermore, the influence of the electronic nature of the substituents on $^1$H and $^{13}$C NMR shifts is investigated by simple and extended Hammett equations, as well as by Swain–Lupton equation.

## 1. Introduction

Due to the advantages of the easy production, low cost and excellent optical properties, azo dyes have emerged as an important group of organic compounds in the various fields of the industry. They find application in the textile dyeing, cosmetics, food industries and optical recordings [1,2], as well as in the scientific research. In the last few years, azo dyes are recognized to be efficient dye-sensitized solar cells [3]. Azo compounds have also been subjects of medical and biological studies [4,5]. Hydrazones, as one of the tautomeric form of the azo dyes, are well known pharmacologically active synthetic compounds. Some hydrazones have been introduced as potential antitubercular drugs [6] and some are claimed to possess anti-inflammatory activity [7].

Disperse pyridone dyes represent a class of heterocyclic azo dyes widely used in the textile industry due to their good technical features [1]. The structure of arylazo pyridone dyes, along with their spectral properties and tautomerism have been reported previously [8–11]. Arylazo pyridone dyes exhibit azo-hydrazone tautomerism when hydroxy group is conjugated with the azo bridge. According to the literature, azo dyes having different 3-cyano-6-hydroxy-4-methyl-2-pyridones as a coupling component exist in hydrazone form in the solid state [12]. In the solutions, depending on the dye structure and the used solvent, the equilibrium is predominantly shifted in the favor of the hydrazone form.

In this work, spectral properties and solvatochromism of ten previously synthesized and thoroughly characterized aryl azo pyridone dyes are reported [13] (Figure 1). Their UV–vis absorption spectra were recorded in twenty-two solvents of different polarity and their emission spectra were recorded in methanol. For quantitative elucidation of specific and nonspecific interactions between solvent and dye molecules, linear solvation energy relationships (LSERs) concepts have been used. Linear free energy relationships (LFERs) have been applied to their UV–vis frequencies, $^1$H and $^{13}$C NMR chemical shifts.

## 2. Experimental

### 2.1. Materials and measurement

Solvents were purchased from Aldrich, Fluka and Merck and were used without any further purification. The IR spectra were acquired using a Bomem MB-Series 100 Fourier Transformation-infrared (FT-IR) spectrophotometer in the form of KBr pellets. The $^1$H and $^{13}$C NMR spectra were taken on a Varian Gemini 2000 (50 Hz and 200 Hz, respectively) in deuterated dimethyl

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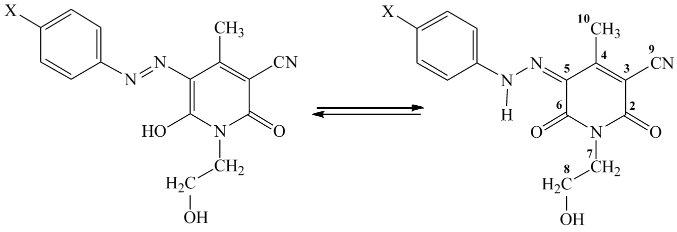

X= OH (**1**), OMe (**2**), Me (**3**), H (**4**), Cl (**5**), Br (**6**), $COCH_3$ (**7**), COOH (**8**), CN (**9**), $NO_2$ (**10**)

**Figure 1.** Azo-hydrazone tautomerism of the investigated dyes.

sulfoxide (DMSO-$d_6$) with tetramethylsilane (TMS) as an internal standard. The ultraviolet–visible (UV–vis) absorption spectra were recorded on a Schimadzu 1700 spectrophotometer in the region 200–700 nm. Fluorescence spectra were measured using a Fluorolog-3 spectrofluorimeter (Jobin Yvon Horiba, France) equipped with a 450 W Xe lamp and a photomultiplier tube. The slits on the excitation and emission beams were fixed at 5 nm and 5 nm, respectively. The spectra were corrected for dark counts. Each reported value was average of three scans, with integration time 0.1 s. Emission spectra were measured upon excitation at the wavelength of the absorption maximum in methanol. All spectral measurements were carried out at room temperature (25 °C).

## 3. Results and discussion

### 3.1. Spectral characteristics and tautomerism

According to the FT-IR data previously reported [13], the investigated dyes exist in the hydrazone form in the solid state. This is concluded from the two intense bands in the regions 1618–1641 $cm^{-1}$ belonging to the C2 carbonyl group, and 1661–1684 $cm^{-1}$ originating from C6 carbonyl group present in the hydrazone form. Additional evidence supporting this conclusion is broad band in the region 3410–3509 $cm^{-1}$ ascribed to N—H proton. $^{13}C$ NMR shifts from two carbonyl groups (160.1–161.0 ppm) in the pyridone ring and $^{1}H$ NMR shifts in the region 14.28–14.84 ppm corresponding to the N—H hydrazone proton strongly suggest the presence of the hydrazone form in DMSO-$d_6$. UV–vis spectra of the investigated dyes (**1**–**10**) in ethanol are given in Figure 2A. Intense bands appearing in the region 427.0–466.5 nm are ascribed to the intramolecular charge transfer (ICT) of the hydrazone tautomeric form. Electron accepting substituents in the phenyl ring cause hypsochromic shift of UV–vis maxima with respect to the unsubstituted dye (**4**), while electron donating groups induce opposite (bathochromic) effect. Equilibrium among two tautomeric forms is shifted completely toward the hydrazone form in the all selected solvents except in highly dipolar solvents (*N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA) and formamide) in which both azo and hydrazone forms are present (Figure 2B). The UV–vis absorption frequencies of the investigated compounds (**1**–**10**) in twenty-two solvents are presented in Table 1. From Table 1 it can be concluded that UV–vis spectra of the hydrazone tautomeric form are more strongly dependent on the change of the substituents than on the change of the nature of the solvents.

Fluorescence technique is additionally performed in order to determinate the electronic effects of different substituents on ICT process of the investigated dyes. These aryl azo pyridone dyes exhibit significant fluorescence properties (Figure S1, Supplementary material). From the obtained emission spectra in methanol, it can be concluded that dyes with electron donating groups (**1** (547 nm); **2** (538 nm); **3** (511 nm)) show bathochromic effect with respect to the unsubstituted dye (**4** (502 nm)), while strong accepting groups (**7** (493 nm); **8** (497 nm); **9** (490 nm); **10** (487 nm)) cause moderate hypsochromic shift of the emission maxima. Substituents with positive mesomeric and negative inductive effect (**5** (510 nm); **6** (510 nm)) induce negligible bathochromic shift. The results from fluorescence analysis are in accordance with UV–vis absorption spectra.

### 3.2. LSER analysis

In order to describe manifold interactions between pyridone dye and solvent molecules, UV–vis frequencies of the hydrazone form are correlated with different polarity scales. One of the methods used for quantitative characterization of these interactions is the Kamlet–Taft equation [14]:

$$\nu_{\max} = \nu_0 + a\alpha + b\beta + s\pi* \qquad (1)$$

Each parameter describes a certain type of specific or non-specific interactions. The Kamlet–Taft $\pi^*$ parameter denotes dipolarity/polarizability of the solvent, $\alpha$ and $\beta$ describe solvent hydrogen bond donor capacity (HBD) and hydrogen bond acceptor capacity (HBA), respectively (Table S1, Supplementary material). Solvent-independent correlation coefficients $a$, $b$ and $s$ reflect individual contribution of the corresponding solvent effect on the UV–vis shifts. The correlations of the absorption frequencies $\nu_{\max}$ for the hydrazone tautomer have been realized by means

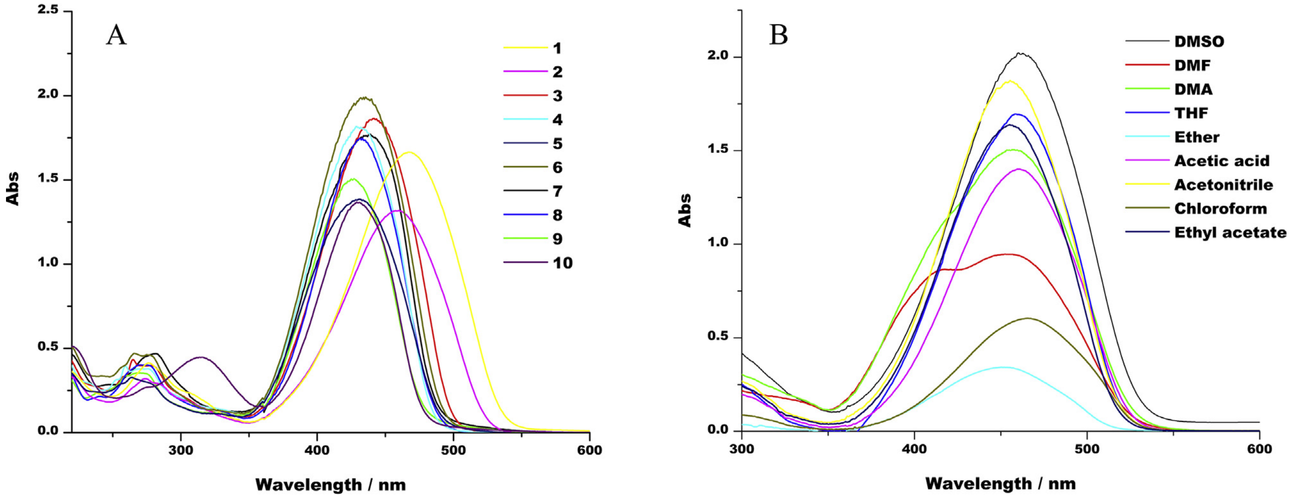

**Figure 2.** UV–vis spectra (A) of the investigated dyes in ethanol; (B) of the dye **2** in the selected solvents.