

Synthesis, structure and solvatochromic properties of novel dyes derived from 4-(4-nitrophenyl)-3-cyano-2-pyridone



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ARTICLE INFO

Article history:

Received 26 December 2013

Received in revised form 18 February 2014

Accepted 17 March 2014

Available online 27 March 2014

Keywords:

Arylazo pyridone dye

Azo–hydrazone tautomerism

Solvent effect

Substituent effect

Multiparameter solvent scale

ABSTRACT

A series of ten new 5-arylazo-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone dyes was synthesized using a classical reaction for the synthesis of azo compounds. The structure of the dyes was confirmed by melting point, elemental analysis, UV–vis, FT-IR, ^1H NMR and ^{13}C NMR spectroscopic techniques. The absorption spectra were recorded in twenty solvents of different properties in the range of 300–700 nm. In order to describe the spectral changes and the solute–solvent interactions, multiparameter Kamlet–Taft and Catalan solvent scales were used. The Catalan solvent scales are found to be the most suitable for describing the solvatochromic behavior of the synthesized dyes. The effect of the substituents on the azo–hydrazone tautomeric equilibrium was analyzed using the simple Hammett equation. For the synthesized dyes, the Hammett polar susceptibility constant (ρ) was correlated through multiple regression using appropriate solvent parameters.

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1. Introduction

Heterocyclic azo dyes have attracted considerable interest and have played an important role in the development of the chemistry of dyes and dyeing process [1–6]. In this regard, azo dyes based on heterocyclic coupling components have been developed and reported in many patents and papers [7–12]. Over 50% of all colorants are azo dyes [13]. Besides their traditional role in textile dyeing, cosmetics, leather and food industries [14], azo dyes have been recently used in biological and medical studies [15], optical recording [16], dye-sensitized solar cells [17] and high technology products and innovations [18]. Due to their properties, including optical storage capacity, optical switching, holography and non-linear optical properties, polymers with azo units represent promising candidates for photoactive materials [19].

Pyridone derivatives are heterocyclic intermediates relatively recently employed for the preparation of arylazo dyes. The azo pyridone dyes give bright hues and are suitable for dyeing of polyester fabrics [20]. The physico-chemical properties of arylazo pyridones are closely related to their tautomerism. Determination of azo–hydrazone tautomers both in the solid state and solution is quite interesting both from theoretical and practical standpoints, since the tautomers have different technical properties and dyeing performances. The spectral data generally lead to the conclusion that the tautomeric equilibrium of azo pyridone dyes is in favor of the hydrazone tautomeric form in solid state and, depending on the dye structure and the solvent used, the equilibrium is predominantly in the favor of the hydrazone form in

different solvents [20–22]. From previous investigations of substituted arylazo pyridones [23,24], it has been concluded that the equilibrium between the two tautomers is influenced by the structure of the compounds and the solvent used. The introduction of electron-attracting or electron-donating substituents into the *para* or *ortho* positions of the diazo components of an azo pyridone dye, resulted in additive or subtractive color shifts and fading rates, depending on the nature and the orientation of the substituents [25].

In this work, ten new 5-arylazo-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone dyes (Scheme 1) were synthesized in order to characterize azo–hydrazone tautomerism, as well as to study the solvent and substituent effects on the electronic absorption spectra. The absorption spectra have been recorded in the range from 300 to 700 nm in twenty solvents of different properties. The Kamlet–Taft and the Catalan solvent parameters were used for describing the solute–solvent interactions and solvatochromic shifts of the UV–vis absorption band of the investigated arylazo pyridone dyes. For quantitative assessment of the substituent effects on the absorption frequencies, the simple Hammett equation was used.

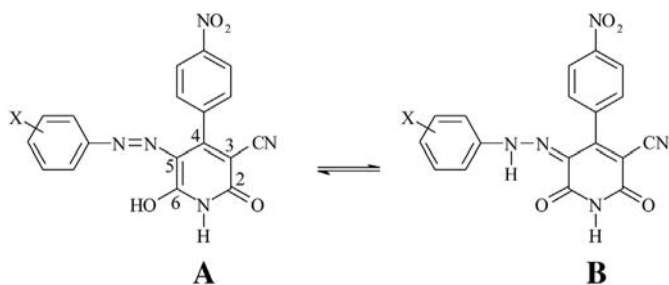
2. Experimental

2.1. General

All starting materials were obtained from Aldrich and Fluka, and were used without further purification.

The IR spectra were determined using a Bomem Fourier Transform-Infrared (FT-IR) spectrophotometer, MB-Series 100 in the form of the KBr pallets. The ^1H and ^{13}C NMR spectral measurements were

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Scheme 1. The equilibrium between azo form (A) and hydrazone form (B) of 5-arylamino-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone dyes (X = H (1), 4-CH₃ (2), 4-OH (3), 4-F (4), 3-Cl (5), 4-Br (6), 4-I (7), 4-COCH₃ (8), 4-CN (9), NO₂ (10)).

performed on a Varian Gemini 2000 (200 MHz). The spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-*d*₆). The chemical shifts are expressed in ppm values referenced to TMS. The ultraviolet–visible (UV–vis) absorption spectra were recorded on a Shimadzu 1700 spectrophotometer in the region 300–700 nm. The absorption spectra were taken in spectroscopic quality solvents (Fluka) at concentration of $5 \cdot 10^{-5}$ mol dm⁻³ and showed no dependence on the concentration. All melting points were uncorrected and are in degree Celsius. Elemental analysis was performed using a VARIO EL III elemental analyzer.

2.2. Synthesis of 5-arylamino-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone dyes (1–10)

All the investigated arylazo pyridone dyes were synthesized from the corresponding diazonium salts and 6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone using a classical reaction for the synthesis of azo compounds [26]. 6-Hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone was prepared from ethyl 4-nitrophenyl benzoylacetate and cyanoacetamide in absolute ethanol in the presence of potassium hydroxide using a modified literature procedure [27,28]. The obtained compounds were purified by crystallization from acetone and then analyzed.

The structure of the dyes was confirmed by UV–vis, FT-IR, ¹H NMR, ¹³C NMR spectroscopic technique and elemental analysis. Characterization data are given below.

2.2.1. 5-Phenylazo-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (1)

Brown crystalline solid; m.p.: 260–263 °C; yield 50%; anal. calcd. for C₁₈H₁₁N₅O₄: C, 59.84; H, 3.07; N, 19.38; found: C, 59.62; H, 2.98; N, 19.18; IR (KBr, ν/cm^{-1}): 3439 (NH of hydrazone form), 3185 (NH on heterocyclic), 2223 (CN), 1692, 1668 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 6.71 (1H, m, Ar); 7.00–7.60 (4H, m, Ar); 7.85 (2H, d, J = 9 Hz, ArNO₂); 8.45 (2H, d, J = 9 Hz, ArNO₂); 12.34 (1H, s, NH on heterocyclic); 14.69 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, δ/ppm): 161.64 (C2), 113.60 (C3), 161.02 (C4), 121.84 (C5), 159.16 (C6).

2.2.2. 5-(4-Methylphenylazo)-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (2)

Light red crystalline solid; m.p.: 222–225 °C; yield 43%; anal. calcd. for C₁₉H₁₃N₅O₄: C, 60.80; H, 3.49; N, 18.66; found: C, 60.42; H, 3.27; N, 18.44; IR (KBr, ν/cm^{-1}): 3458 (NH of hydrazone form), 3157 (NH on heterocyclic), 2226 (CN), 1674, 1658 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 2.26 (3H, s, CH₃); 7.85 (2H, d, J = 9 Hz, ArCH₃); 8.18 (2H, d, J = 9 Hz, ArCH₃); 8.35 (2H, d, J = 8.4 Hz, ArNO₂); 8.42 (2H, d, J = 9 Hz, ArNO₂); 12.31 (1H, s, NH on heterocyclic); 14.69 (1H, s, NH on hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, δ/ppm): 161.80 (C2), 115.15 (C3), 160.95 (C4), 123.35 (C5), 159.07 (C6).

2.2.3. 5-(4-Hydroxyphenylazo)-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (3)

Dark red crystalline solid; m.p.: 285–287 °C, yield 37%; anal. calcd. for C₁₈H₁₁N₅O₅: C, 57.30; H, 2.94; N, 18.56; found: C, 55.25; H, 2.78; N, 18.33; IR (KBr, ν/cm^{-1}): 3426 (NH of hydrazone form), 3203 (HN on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 6.78 (2H, d, J = 9 Hz, ArOH); 7.17 (2H, d, J = 9 Hz, ArOH); 8.18 (2H, d, J = 9 Hz, ArNO₂); 8.43 (2H, d, J = 9 Hz, ArNO₂); 9.96 (1H, s, ArOH); 12.23 (1H, s, NH on hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, δ/ppm): 161.97 (C2), 116.68 (C3), 161.04 (C4), 123.98 (C5), 158.92 (C6).

2.2.4. 5-(4-Fluorophenylazo)-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (4)

Dark brown crystalline solid; m.p.: 232–235 °C, yield 40%, anal. calcd. for C₁₈H₁₀FN₅O₄: C, 57.00; H, 2.66; N, 18.46; found: C, 48.36; H, 2.48; N, 18.23; IR (KBr, ν/cm^{-1}): 3439 (NH of hydrazone form), 3196 (NH on heterocyclic), 2225 (CN), 1697, 1656 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 7.22 (2H, d, J = 9 Hz, ArF); 7.77 (2H, d, J = 9 Hz, ArF); 8.17 (2H, d, J = 9 Hz, ArNO₂); 8.40 (2H, d, J = 9 Hz, ArNO₂); 12.20 (1H, s, NH on heterocyclic); 14.46 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, δ/ppm): 162.67 (C2), 115.00 (C3), 161.67 (C4), 123.31 (C5), 160.58 (C6).

2.2.5. 5-(3-Chlorophenylazo)-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (5)

Light brown crystalline solid; m.p.: 220–223 °C, yield 44%; anal. calcd. for C₁₈H₁₀ClN₅O₄: C, 54.63; H, 2.55; N, 17.70; found: C, 54.38; H, 2.32; N, 17.56; IR (KBr, ν/cm^{-1}): 3459 (NH of hydrazone form), 3170 (NH on heterocyclic), 2223 (CN), 1684, 1652 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 7.14–7.54 (4H, m, ArCl); 8.16 (2H, d, J = 8.4 Hz, ArNO₂); 8.43 (2H, d, J = 9 Hz, ArNO₂); 12.13 (1H, s, NH on heterocyclic); 14.58 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, δ/ppm): 162.98 (C2), 116.28 (C3), 161.04 (C4), 124.06 (C5), 159.09 (C6).

2.2.6. 5-(4-Bromophenylazo)-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (6)

Red crystalline solid; m.p.: 242–245 °C; yield 42%, anal. calcd. for C₁₈H₁₀BrN₅O₄: C, 49.11; H, 2.29; N, 15.91; found: C, 48.88; H, 2.11; N, 15.78; IR (KBr, ν/cm^{-1}): 3433 (NH of hydrazone form), 3157 (NH on heterocyclic), 2206 (CN), 1683, 1662 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 7.20 (2H, d, J = 8.8 Hz, ArBr); 7.54 (2H, d, J = 8.4 Hz, ArBr); 8.16 (2H, d, J = 9 Hz, ArNO₂); 8.42 (2H, d, J = 9 Hz, ArNO₂); 12.35 (1H, s, NH on heterocyclic); 14.54 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, δ/ppm): 162.91 (C2), 114.99 (C3), 161.60 (C4), 123.45 (C5), 160.89 (C6).

2.2.7. 5-(4-Iodophenylazo)-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (7)

Dark violet crystalline solid; m.p.: 218–221 °C, yield 35%, anal. calcd. for C₁₈H₁₀IN₅O₄: C, 44.37; H, 2.07; N, 14.37; found: C, 44.18; H, 1.98; N, 14.28; IR (KBr, ν/cm^{-1}): 3439 (NH of hydrazone form), 3145 (NH on heterocyclic), 2225 (CN), 1673, 1658 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 7.05 (2H, d, J = 7.8 Hz, ArI); 7.69 (2H, d, J = 7.8 Hz, ArI); 7.80 (2H, d, J = 8.8 Hz, ArNO₂); 8.42 (2H, d, J = 8 Hz, ArNO₂); 12.34 (1H, s, NH on heterocyclic); 14.52 (1H, s, NH of hydrazone form); ¹³C NMR (50 MHz, DMSO-*d*₆, δ/ppm): 162.69 (C2), 114.98 (C3), 161.60 (C4), 123.44 (C5), 160.88 (C6).

2.2.8. 5-(4-Acetylphenylazo)-6-hydroxy-4-(4-nitrophenyl)-3-cyano-2-pyridone (8)

Brown crystalline solid; m.p.: 235–238 °C, yield 25%, anal. calcd. for C₂₀H₁₃N₅O₅: C, 59.56; H, 3.25; N, 17.36; found: C, 59.14; H, 3.06; N, 17.34; IR (KBr, ν/cm^{-1}): 3452 (NH of hydrazone form), 3209 (NH on heterocyclic), 2224 (CN), 1680, 1658 (C=O on heterocyclic); ¹H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 2.52 (3H, s, COCH₃); 7.30 (2H, d, J =

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