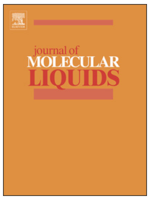
Journal of Molecular Liquids xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



Synthesis, solvatochromic properties and antimicrobial activities of some novel pyridone-based disperse disazo dyes

Fati Karcı [a],*, Fikret Karcı [b], Aykut Demirçalı [b], Mustafa Yamaç [c]

[a] Department of Chemistry and Chemical Processing Technologies, Pamukkale University, Denizli, Turkey
[b] Department of Chemistry, Faculty of Science-Arts, Pamukkale University, Denizli, Turkey
[c] Department of Biology, Faculty of Science-Arts, Eskişehir Osmangazi University, Eskişehir, Turkey

ARTICLE INFO

Article history:
Received 6 May 2013
Accepted 12 August 2013
Available online xxxx

Keywords:
Disazo dyes
Solvatochromism
Antimicrobial activity
Pyridone dyes
Tautomeric structure

ABSTRACT

In this study, 5-amino-4-arylazo-3-methyl-1H-pyrazoles (**2a**–**l**) were diazotized and coupled with 3-cyano-6-hydroxy-4-methyl-2-pyridone to give pyridone-based disperse disazo dyes (**3a**–**l**). The newly synthesized twelve pyridone-based disperse disazo dyes were characterized by elemental analysis and spectral methods. The solvatochromic properties and antimicrobial activities of these disazo disperse dyes were also examined in detail.

1. Introduction

It is well known that nitriles are widely used as intermediates for many heterocyclic compounds. The aminopyrazole compounds have been easily obtained by the reaction of nitrile derivatives with hydrazine hydrate [1–6]. Pyrazole and pyridone derivatives are important intermediates that possess biological and pharmacological activities [7–10]. Some azopyrazole derivatives also find application in dyes and complexes [11–13]. The use of heterocyclic coupling component and diazo components in the synthesis of azo disperse dyes is well established, and the resultant dyes exhibit good tinctorial strength and brighter shade properties than those derived from aniline-based components. For instance, Hallas et al. [14,15] reported the synthesis of azo dyes derived from 2-aminothiophene derivatives and various heterocyclic coupling components, and their application on polyester fibers which leads to excellent results. On the other hand, the use of amino-substituted thiazole and benzothiazole, being very electronegative diazo components, produce a pronounced bathochromic shift when compared to the corresponding benzoid compounds [16–19].

Although, many patents and papers describe the synthesis, tautomeric structures and dyeing properties of monoazo dyes [20–26], very few comparable investigations have been made with disazo dyes [27–31]. In this study, the synthesis and antimicrobial activities of some novel pyridone-based disperse disazo dyes which were derived from 5-amino-4-arylazo-3-methyl-1H-pyrazoles as heterocyclic diazo components were reported. Moreover, solvatochromic properties and tautomeric forms of these dyes were also examined in detail.

2. Experimental

2.1. General

The chemicals which were used for the synthesis of the compounds were obtained from Aldrich and Merck Chemical Company without further purification. The solvents used were in spectroscopic grade. IR spectra were determined using a Mattson 1000 Fourier Transform-infrared (FT-IR) spectrophotometer on a KBr disc. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield in deuterated dimethylsulphoxide (DMSO-d_6) using tetramethylsilane (TMS) as the internal reference; chemical shifts were (δ) given in ppm. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Shimadzu UV-1601 double beam spectrophotometer at the wavelength of maximum absorption (λ_{max}) in a range of solvents, i.e. DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform at the various concentrations (1×10^{-6}–10^{-8}). Change of λ_{max} was also investigated when 0.1 ml base (potassium hydroxide, 0.1 M) and 0.1 ml acid (hydrochloric acid, 0.1 M) were added to dye solutions in methanol (1 ml). Melting points were determined on an Electrothermal 9100 melting point apparatus and they are uncorrected. Elemental analyses were done on a Leco CHNS-932 analyzer.

---

* Corresponding author. Tel.: +90 258 2135681; fax: +90 258 2118065.
E-mail address: fati@pau.edu.tr (F. Karcı).

0167-7322/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2013.08.005

*2.2. Synthesis of 2-arylhydrazono-3-ketiminobutyronitriles (**1a–l**) and 5-amino-4-arylazo-3-methyl-1H-pyrazoles (**2a–l**)*

2-Arylhydrazone-3-ketiminobutyronitriles (**1a**–**l**) and 5-amino-4-arylazo-3-methyl-1H-pyrazoles (**2a**–**l**) were prepared according to the literature procedures [27]. The general route for the synthesis of 2-arylhydrazono-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1H-pyrazoles is outlined in Scheme 1.

*2.3. Synthesis of pyridone-based disperse disazo dyes (**3a**–**l**)*

5-Amino-4-arylazo-3-methyl-1H-pyrazoles (0.01 mol) were dissolved in a mixture of glacial acetic acid and concentrated hydrochloric acid (20 ml, ratio 1:1) and the solution was then cooled to 0–5 °C. Sodium nitrite (0.69 g, 0.01 mol) in water (10 ml) was then added to this solution dropwise with vigorous stirring, about 1 h, while cooling at 0–5 °C. Then the resulting diazonium solution was added in portions over 30 min to a vigorously stirred solution of 3-cyano-6-hydroxy-4-methyl-2-pyridone (1.50 g, 0.01 mol) in KOH (0.56 g, 0.01 mol) and water (10 ml) between 0 and 5 °C, maintaining the pH at 7–8 by simultaneous addition of sodium acetate solutions. The mixture was then stirred for 2 h between 0 and 5 °C. The precipitated product was separated upon dilution with water (50 ml) and then filtered off, washed with water several times, dried and crystallized from DMF–H_2O, respectively. The general route for the synthesis of disazo dyes **3a**–**l** is outlined in Scheme 1.

*2.3.1. 5-[3′-Methyl–4′-(p-nitrophenylazo)-1′H-pyrazole-5′-ylazo]-3-cyano-6-hydroxy-4-methyl-2-pyridone (**3a**)*

Orange crystals; yield 84%; mp. 333–334 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3234–3133 (3 NH), 3069 (Ar-H), 2998 (Al-H), 2225 (CN), 1681, 1668 (2 C═O); ^1H NMR (DMSO-d_6): δ = 2.74 (s, 3H, 3-CH_3 pyrazole), 2.90 (s, 3H, 4-CH_3 pyridone), 7.60 (d, 2H, J = 9.2, ArH), 8.13 (d, 2H, J = 9.3, ArH), 12.10 (br, 1H, pyridone NH), 13.25 (br, 1H, pyrazole NH), 15.14 (br, 1H, OH or tautomeric hydrazo NH); Anal. Calcd. for $C_{17}H_{13}N_9O_4$: C: 50.13, H: 3.22, N: 30.95. Found: C: 50.28, H: 3.25, N: 30.74.

*2.3.2. 5-[3′-Methyl–4′-(p-methoxyphenylazo)-1′H-pyrazole-5′-ylazo]-3-cyano-6-hydroxy-4-methyl-2-pyridone (**3b**)*

Brown crystals; yield 72%; mp. 274–275 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3238–3130 (3 NH), 3050 (Ar-H), 2997 (Al-H), 2223 (CN), 1680, 1666 (2 C═O); ^1H NMR (DMSO-d_6): δ = 2.74 (s, 3H, 3-CH_3 pyrazole), 2.90 (s, 3H, 4-CH_3 pyridone), 3.86 (s, 3H, *p*-OCH_3), 7.12 (d, 2H, J = 8.5, ArH), 7.83 (d, 2H, J = 8.3, ArH), 12.05 (br, 1H, pyridone NH), 13.23 (br, 1H, pyrazole NH), 15.10 (br, 1H, OH or tautomeric hydrazo NH); Anal. Calcd. for $C_{18}H_{16}N_8O_3$: C: 55.10, H: 4.11, N: 28.56. Found: C: 55.23, H: 4.07, N: 28.84.

*2.3.3. 5-[3′-Methyl–4′-(p-chlorophenylazo)-1′H-pyrazole-5′-ylazo]-3-cyano-6-hydroxy-4-methyl-2-pyridone (**3c**)*

Red crystals; yield 79%; mp. 320–321 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3262–3188 (3 NH), 3058 (Ar-H), 2981 (Al-H), 2225 (CN), 1695, 1676 (2 C═O); ^1H NMR (DMSO-d_6): δ = 2.75 (s, 3H, 3-CH_3 pyrazole), 2.92 (s, 3H, 4-CH_3 pyridone), 7.54 (d, 2H, J = 8.4, ArH), 7.77 (d, 2H, J = 8.4, ArH), 12.15 (br, 1H, pyridone NH), 13.42 (br, 1H, pyrazole NH), 15.13 (br, 1H, OH or tautomeric hydrazo NH); Anal. Calcd. for $C_{17}H_{13}ClN_8O_2$: C: 51.46, H: 3.30, N: 28.24. Found: C: 51.26, H: 3.37, N: 28.39.

*2.3.4. 5-[3′-Methyl–4′-(p-methlyphenylazo)-1′H-pyrazole-5′-ylazo]-3-cyano-6-hydroxy-4-methyl-2-pyridone (**3d**)*

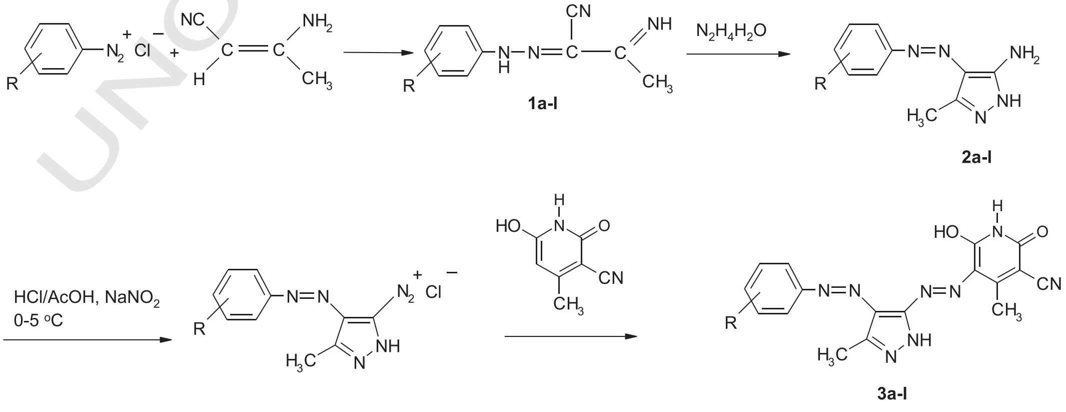
Orange crystals; yield 63%; mp. 228–229 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3246–3121 (3 NH), 3063 (Ar-H), 2993 (Al-H), 2222 (CN), 1689, 1670 (2 C═O); ^1H NMR (DMSO-d_6): δ = 2.41 (s, 3H, *p*-CH_3), 2.74 (s, 3H, 3-CH_3 pyrazole), 2.89 (s, 3H, 4-CH_3 pyridone), 7.39 (d, 2H, J = 7.9, ArH), 7.77 (d, 2H, J = 8.0, ArH), 12.12 (br, 1H, pyridone NH), 13.43 (br, 1H, pyrazole NH), 15.12 (br, 1H, OH or tautomeric hydrazo NH); Anal. Calcd. for $C_{18}H_{16}N_8O_2$: C: 57.44, H: 4.28, N: 29.77. Found: C: 57.62, H: 4.35, N: 29.56.

*2.3.5. 5-[3′-Methyl–4′-(m-nitrophenylazo)-1′H-pyrazole-5′-ylazo]-3-cyano-6-hydroxy-4-methyl-2-pyridone (**3e**)*

Orange crystals; yield 81%; mp. 324–325 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3226–3136 (3 NH), 3083 (Ar-H), 2954 (Al-H), 2227 (CN), 1677, 1660 (2 C═O); ^1H NMR (DMSO-d_6): δ = 2.74 (s, 3H, 3-CH_3 pyrazole), 2.89 (s, 3H, 4-CH_3 pyridone), 7.86–8.64 (m, 4H, ArH), 12.20 (br, 1H, pyridone NH), 13.55 (br, 1H, pyrazole NH), 15.18 (br, 1H, OH or tautomeric hydrazo NH); Anal. Calcd. for $C_{17}H_{13}N_9O_4$: C: 50.13, H: 3.22, N: 30.95. Found: C: 50.31, H: 3.28, N: 31.12.

2.3.6. 5-[3′-Methyl–4′-(m-methoxyphenylazo)-1′H-pyrazole-5′-ylazo]-3-cyano-6-hydroxy-4-methyl-2-pyridone (3f)

Red crystals; yield 69%; mp. 307–308 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3225–3145 (3 NH), 3021 (Ar-H), 2961 (Al-H), 2231 (CN), 1677, 1661 (2 C═O); ^1H NMR (DMSO-d_6): δ = 2.74 (s, 3H, 3-CH_3 pyrazole), 2.90 (s, 3H, 4-CH_3 pyridone), 3.86 (s, 3H, *m*-OCH_3), 7.00–7.98 (m, 4H, ArH), 12.10 (br, 1H, pyridone NH), 13.34 (br, 1H, pyrazole NH), 15.20 (br, 1H, OH or tautomeric hydrazo NH); Anal. Calcd. for



a R = *p*-NO_2, **b** R = *p*-OCH_3, **c** R = *p*-Cl, **d** R = *p*-CH_3, e R = *m*-NO_2, f R = *m*-OCH_3, g R = *m*-Cl, h R = *m*-CH_3, i R = *o*-NO_2, j R = *o*-OCH_3, k R = *o*-Cl, l R = *o*-CH_3

Q2 **Scheme 1.**

Please cite this article as: F. Karcı, et al., J. Mol. Liq. (2013), http://dx.doi.org/10.1016/j.molliq.2013.08.005