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New disazo pyrazole disperse dyes: Synthesis, spectroscopic studies and tautomeric structures

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ABSTRACT

5-amino-4-arylazo-3-methyl-1-phenylpyrazoles (2a–k) were diazotised and coupled with 5-hydroxy-3-methyl-1H-pyrazole and 5-hydroxy-3-methyl-1-phenylpyrazole to generate two series disazo pyrazole disperse dyes (3a–k and 4a–k). These novel synthesized disazo pyrazole disperse dyes were characterized by elemental analysis and spectral methods. Absorption ability and tautomeric structure of synthesized disazo pyrazole disperse dyes substituted with electron-withdrawing and electron-donating groups at their *o*, *m*- *and p*-positions were also examined in detail.

1. Introduction

Simple nitrogen-containing heterocycles receive significant attention in the literature due to their exciting biological properties as well as their historical important role as pharmacophores. The synthesis, reactions and biological activities of pyrazole containing molecules, of these heterocycles, lead to an ever-expanding research area in heterocyclic chemistry and moreover; these structures appear in a large number of pharmaceutical agents and natural products. Fused pyrazoles with many different derivatives may exhibit a wide range of interesting properties such as antihyperglycemic, analgestic, anti-inflammatory, antipyretic, anti-bacterial, hypoglycaemic and sedative-hypnotic activities. Recently, some pyrazoles were reported to display nonnucleoside HIV-1 reverse transcriptase inhibitory activity [1–6]. Some azopyrazole derivatives also find applications in dyes, biological and pharmacological studies and complexes [7–12]. The condensation of β-enaminonitriles and β-ketoesters with hydrazines continues to be the most widely used method for aminopyrazole and pyrazolone formation, respectively [13–16]. The amino derivatives of pyrazoles belong to important compounds used for the preparation of other functional derivatives mainly for the synthesis of condensed heterocyclic systems [17–19].

The use of heterocyclic intermediates in the synthesis of azo disperse dyes is well established and the resultant dyes exhibit good tinctorial strength and brighter appearance than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, benzothiazole [20–23] and benzoisothiazole [24] compounds afford highly electronegative diazo components and consequently, provide a pronounced bathochromic effect compared to the corresponding benzoid compounds. Moreover, azo disperse dyes containing 5-hydroxy-3-methyl-1H-pyrazole as coupling component were reported to be in red–violet colours in the literature [25,26].

We have previously reported the synthesis of some disazo disperse dyes [27–32]. In this study, we report the synthesis of two different series of new disazo disperse dyes based on two pyrazole rings in one dye structure. The absorption ability of these dyes substituted with electron-withdrawing and electron-donating groups at their *o*, *m*- and *p*-positions was also examined in detail.

2. Experimental

2.1. General

The chemicals, used for the synthesis of the compounds, were obtained from Aldrich and Merck without further purification. The solvents used were of spectroscopic grade.

IR spectra were determined via Mattson 1000 Fourier Transform-infrared (FT-IR) spectrophotometer using 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 and chemical shifts (δ) were given in ppm. Ultraviolet–visible (UV–

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vis) absorption spectra were recorded via a Schimadzu UV-1601 double beam spectrophotometer at the wavelength of maximum absorption (λ_{max}) in a range of different solvents, i.e. DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform at various concentrations (1×10^{-6}–10^{-8}). Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. Elemental analysis was carried out using a Leco CHNS-932 analyzer.

2.2. Synthesis of 2-arylhydrazono-3-ketiminobutyronitriles (1a–k) and 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles (2a–k)

2-Arylhydrazone-3-ketiminobutyronitriles (1a–k) and 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles (2a–k) were prepared according to the literature procedures [16,33,34]. The general route for the synthesis of 2-arylhydrazono-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles is outlined in Scheme 1.

2.3. Synthesis of disperse disazo pyrazole dyes (3a–k and 4a–k)

5-Amino-4-arylazo-3-methyl-1-phenylpyrazoles (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, for 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 5-hydroxy-3-methyl-1H-pyrazole or 5-hydroxy-3-methyl-1-phenylpyrazole (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 sodium acetate solution addition. The mixture was then stirred for 2 h at 0–5 °C. The precipitated product separated upon dilution with water (50 ml) was filtered off, washed with water several times, dried and crystallized from DMF–H_2O.

2.3.1. 4-(4′-(p-nitrophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3a)

Red crystals; yield 74%; mp. 210–211 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3244 (NH), 3057 (Ar–H), 2923 (Al–H), 1663 (C═O), 1493 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.23 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 6.84–8.42 (m, 9H, ArH), 9.97 (br, 1H, OH), 11.55 (br, 1H, NH); Anal. Calcd. for $C_{20}H_{17}N_9O_3$: C: 55.68, H: 3.97, N: 29.22. Found: C: 55.12, H: 3.85, N: 29.30.

2.3.2. 4-(4′-(p-methoxyphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3b)

Yellow crystals; yield 48 %; mp. dec. > 96 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3195 (NH), 3071 (Ar–H), 2923 (Al–H), 1649 (C═O), 1497 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.27 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 3.84 (s, 3H, *p*-OCH_3), 7.09–8.01 (m, 9H, ArH), 11.70 (br, OH), 13.37 (br, NH), 13.91 (br, hydrazo NH), 14.17 (br, hydrazo NH); Anal. Calcd. for $C_{21}H_{20}N_8O_2$: C: 60.57, H: 4.84, N: 26.91. Found: C: 60.35, H: 4.89, N: 26.80.

2.3.3. 4-(4′-(p-chlorophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3c)

Yellow crystals; yield 65 %; mp. 120–121 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3188 (NH), 3064 (Ar–H), 2926 (Al–H), 1666 (C═O), 1529 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.29 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 7.47–8.13 (m, 9H, ArH), 11.74 (br, NH), 14.18 (br, hydrazo NH); Anal. Calcd. for $C_{20}H_{17}ClN_8O$: C: 57.08, H: 4.07, N: 26.63. Found: C: 56.95, H: 4.23, N: 26.55.

2.3.4. 4-(4′-(p-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3d)

Orange crystals; yield 58 %; mp. 90–91 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3188 (NH), 3047 (Ar–H), 2916 (Al–H), 1666 (C═O), 1536 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.28 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 2.38 (s, 3H, *p*-CH_3), 7.16–8.03 (m, 9H, ArH), 11.71 (br, OH), 13.30 (br, NH), 14.17 (br, hydrazo NH); Anal. Calcd. for $C_{21}H_{20}N_8O$: C: 62.99, H: 5.03, N: 27.98. Found: C: 62.90, H: 4.90, N: 27.91.

2.3.5. 4-(4′-(m-nitrophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3e)

Brown crystals; yield 68 %; mp. 131–132 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3107 (NH), 3036 (Ar–H), 2870 (Al–H), 1666 (C═O), 1525 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.21 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 7.21–8.79 (m, 9H, ArH), 9.86 (br, OH), 11.32 (br, NH), 11.81 (br, hydrazo NH), 14.13 (br, hydrazo NH); Anal. Calcd. for $C_{20}H_{17}N_9O_3$: C: 55.68, H: 3.97, N: 29.22. Found: C: 55.79, H: 3.99, N: 29.33.

2.3.6. 4-(4′-(m-chlorophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3f)

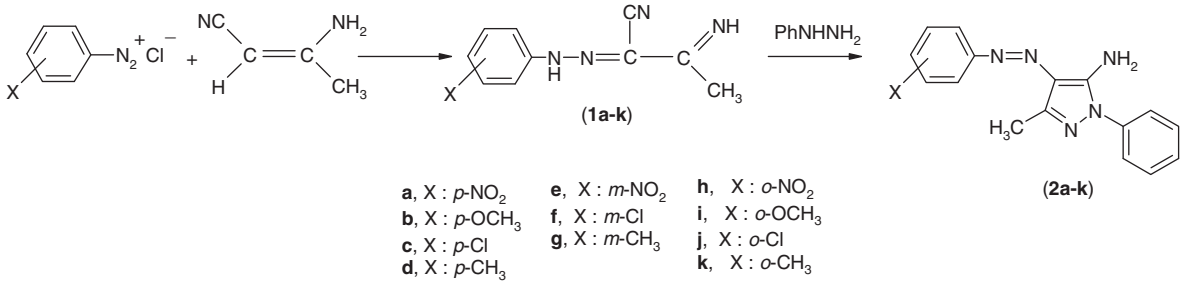
Orange crystals; yield 70 %; mp. 114–115 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3188 (NH), 3061 (Ar–H), 2926 (Al–H), 1670 (C═O), 1536 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.30 (s, 3H, CH_3), 2.71 (s, 3H, CH_3), 7.22–8.13 (m, 9H, ArH), 11.79 (br, NH), 14.17 (br, hydrazo NH); Anal. Calcd. for $C_{20}H_{17}ClN_8O$: C: 57.08, H: 4.07, N: 26.63. Found: C: 57.14, H: 3.89, N: 26.69.

2.3.7. 4-(4′-(m-methylphenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3g)

Greenish black crystals; yield 35 %; mp. 104–105 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3170 (NH), 3064 (Ar–H), 2919 (Al–H), 1659 (C═O), 1497 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.29 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 2.41 (s, 3H, *m*-CH_3), 7.04–7.95 (m, 9H, ArH), 11.74 (br, OH), 13.26 (br, NH), 14.15 (br, hydrazo NH); Anal. Calcd. for $C_{21}H_{20}N_8O$: C: 62.99, H: 5.03, N: 27.98. Found: C: 63.15, H: 5.12, N: 28.21.

2.3.8. 4-(4′-(o-nitrophenylazo)-3′-methyl-1′-phenylpyrazole-5′-ylazo)-5-hydroxy-3-methyl-1H-pyrazole (3h)

Red crystals; yield 55 %; mp. 200–201 °C (DMF–H_2O); IR (KBr): ν (cm^{-1}) = 3262 (NH), 3054 (Ar–H), 2926 (Al–H), 1670 (C═O), 1486 (N═N); ^{1}H-NMR (DMSO-d_6): δ = 2.25 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 7.29–8.22 (m, 9H, ArH), 10.12 (br, OH), 11.57 (br, NH), 13.98 (br, hydrazo NH); Anal. Calcd. for $C_{20}H_{17}N_9O_3$: C: 55.68, H: 3.97, N: 29.22. Found: C: 55.56, H: 4.03, N: 29.45.



Scheme 1. Synthesis of aminoarylazopyrazoles (2a–k).

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