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# Synthesis and absorption spectra of some novel heterocyclic disazo dyes derived from pyridone and pyrazolone derivatives

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**Abstract**

Heterocyclic amines were diazotized and coupled with 3-aminocrotononitrile to give the 2-hetarylhydrazone-3-ketiminobutyronitrile (**1a–1e**) which can react with hydrazine hydrate and phenylhydrazine to afford the corresponding 5-amino-3-methyl-4-hetarylazo-1H-pyrazoles and 5-amino-3-methyl-4-hetarylazo-1-phenylpyrazoles (**2a–2j**), respectively. Then, some novel disazo dyes **3a–3j** and **4a–4j** were synthesized by diazotisation of 5-amino-3-methyl-4-hetarylazo-1H-pyrazoles and 5-amino-3-methyl-4-hetarylazo-1-phenylpyrazoles using nitrosyl sulphuric acid, coupling with 3-cyano-6-hydroxy-4-methyl-2-pyridone and 3-methyl-1H-pyrazole-5-one. The dyes were characterized by elemental analysis and spectral methods and the solvatochromic behaviour of the dyes in various solvents was evaluated. Substituent, acid and base effects on the visible absorption maxima of the dyes were also reported.


*Keywords:* Heterocyclic; Disazo dyes; Pyrazole; Pyrazolone; Pyridone; Thiazole; Benzothiazole; Solvent effect

## 1. Introduction

It is well known that nitriles are widely used as intermediates for a large number of heterocyclic compounds. Aminopyrazole compounds can be readily obtained by the reaction of nitrile derivatives with hydrazine hydrate [1–4]. Pyrazole derivatives are important intermediates that possess biological and pharmacological activities [5–8]. Some azopyrazole derivatives also find application in dyes and complexes [9–14]. 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 dyeing than those derived from aniline-based components. For instance, Hallas and coworkers [15,16] reported the synthesis of azo dyes derived from 2-aminothiophene derivatives and various heterocyclic coupling components, and their application on polyester fibres gave excellent results. On the other hand, the use of amino-substituted thiazole and benzothiazole compounds, due to their high electronegativity as diazo components, provide a pronounced bathochromic shift when compared to the corresponding benzoid compounds [17–20].

Although, many researchers have described the synthesis and dyeing properties of monoazo dyes [21–23], very few comparable investigations have been made with disazo dyes [24–26]. In this study, the synthesis of some novel disazo dyes derived from 3-cyano-6-hydroxy-4-methyl-2-pyridone and 3-methyl-1H-pyrazole-5-one as heterocyclic coupling components and 5-amino-3-methyl-4-hetarylazo-1H-pyrazoles, 5-amino-3-methyl-4-hetarylazo-1-phenylpyrazoles as heterocyclic diazo components is described. The visible absorption spectra in various solvents of these dyes are discussed.

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## 2. Experimental

### 2.1. General

The chemical used for the synthesis of the compounds was obtained from either Aldrich or Sigma and was used without further purification. The solvents were of spectroscopic grade.

Infrared 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 ($\delta$) given in ppm. Ultraviolet–visible (UV–vis) absorption spectra were recorded on an ATI-Unicam UV-100 spectrophotometer at wavelength of maximum absorption ($\lambda_{max}$) in a range of solvents, i.e. DMSO, dimethylformamide (DMF), acetonitrile, methanol, acetic acid and chloroform. Melting points were uncorrected. Characterizations data are shown in Tables 1–7.

### 2.2. Synthesis of 2-hetarylhydrazone-3-ketiminobutyronitriles (*1a–1e*)

Heterocyclic amine (2-aminothiazole, 2-amino-5-methylthiazole, 2-aminobenzo thiazole, 2-amino-6-ethoxybenzothiazole, 3-amino-5-methylisoxazole) (0.01 mol) was dissolved in hot glacial acetic acid (10 ml) and then was rapidly cooled in an ice–salt bath to −5 °C. The liquor was then added in portions, over 30 min, to a cooled mixture of nitrosyl sulphuric acid prepared from sodium nitrite (0.69 g, 0.01 mol) and concentrated sulphuric acid (7 ml) at 0 °C. The mixture was stirred for an additional 1 h at 0 °C. The diazonium salt solution was then added dropwise to a well-cooled (0–5 °C) and stirred solution of 3-aminocrotononitrile (0.82 g, 0.01 mol) in sodium acetate (2 g, dissolved in 10 ml of 50% (v/v) aqueous ethanol). The pH of the coupling mixture, in each case, was maintained at 5–6 through the coupling process by adding solid sodium acetate at 0–5 °C. Stirring was continued for 4 h at 0–5 °C and the precipitated products, which separated upon dilution with cold water (50 ml), were filtered, washed with water (3 × 50 ml), dried in air, and recrystallized to give 2-hetarylhydrazone-3-ketiminobutyronitrile (**1a–1e**) (Scheme 1) [26].

### 2.3. Synthesis of 5-amino-3-methyl-4-hetarylazo-1H-pyrazoles and 5-amino-3-methyl-4-hetarylazo-1-phenylpyrazoles (*2a–2j*)

Hydrazine hydrate (0.5 g, 0.01 mol) or phenylhydrazine (1.08 g, 0.01 mol) was added to solutions of **1a–1e** (0.01 mol) in 30 ml ethanol. The reaction mixture was heated under reflux for 3–4 h and then cooled to room temperature;

Table 1
Spectral data for compounds **1a–1e** and **2a–2j**

| Compound no. | FT-IR (cm$^{-1}$, in KBr) | | | | | $^1$H NMR[a] ($\delta$, ppm) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\nu_{NH_2}$ | $\nu_{N-H}$ | $\nu_{Arom.-H}$ | $\nu_{Al-H}$ | $\nu_{CN}$ | Arom.-H | Alip.-H | X–H | Solvent |
| **1a** | – | 3236 | 3067 | 2958 | 2223 | 7.98 (1H, d), 7.76 (1H, d) | 2.48 (3H, s) | 8.82 (1H, b, NH), 8.40 (1H, b, NH) | $CDCl_3$ |
| **1b** | – | 3239 | 3078 | 2973 | 2218 | 7.80 (1H, s) | 2.47 (3H, s), 2.52 (3H, s) | 8.80 (1H, b, NH), 8.41 (1H, b, NH) | $CDCl_3$ |
| **1c** | – | 3234 | 3072 | 2971 | 2226 | 8.00–7.54 (4H, m) | 2.48 (3H, s) | 8.81 (1H, b, NH), 8.40 (1H, b, NH) | $CDCl_3$ |
| **1d** | – | 3236 | 3080 | 2966 | 2225 | 7.90–7.00 (3H, m) | 1.36 (3H, t), 2.50 (3H, s), 4.30 (2H, q) | 8.81 (1H, b, NH), 8.40 (1H, b, NH) | $CDCl_3$ |
| **1e** | – | 3237 | 3075 | 2978 | 2229 | 6.52 (1H, s) | 2.47 (3H, s), 2.50 (3H, s) | 8.80 (1H, b, NH), 8.37 (1H, b, NH) | $CDCl_3$ |
| **2a** | 3418, 3375 | 3258 | 3093 | 2953 | – | 8.00 (1H, d), 7.79 (1H, d) | 2.48 (3H, s) | 13.98 (1H, b, NH), 6.61 (2H, b, $NH_2$) | $CDCl_3$ |
| **2b** | 3422, 3374 | 3251 | 3098 | 2958 | – | 7.81 (1H, s) | 2.48 (3H, s), 2.52 (3H, s) | 14.06 (1H, b, NH), 6.69 (2H, b, $NH_2$) | $CDCl_3$ |
| **2c** | 3432, 3369 | 3263 | 3087 | 2962 | – | 8.06–7.55 (4H, m) | 2.46 (3H, s) | 14.00 (1H, b, NH), 6.67 (2H, b, $NH_2$) | $CDCl_3$ |
| **2d** | 3427, 3358 | 3258 | 3094 | 2973 | – | 8.02–7.10 (3H, m) | 1.37 (3H, t), 2.49 (3H, s), 4.34 (2H, q) | 13.91 (1H, b, NH), 6.58 (2H, b, $NH_2$) | $CDCl_3$ |
| **2e** | 3423, 3366 | 3255 | 3096 | 2959 | – | 6.50 (1H, s) | 2.47 (3H, s), 2.52 (3H, s) | 13.88 (1H, b, NH), 6.64 (2H, b, $NH_2$) | $CDCl_3$ |
| **2f** | 3417, 3361 | – | 3097 | 2955 | – | 8.02 (1H, d), 7.75 (1H, d), 7.75–7.58 (5H, m) | 2.48 (3H, s) | 6.64 (2H, b, $NH_2$) | $CDCl_3$ |
| **2g** | 3425, 3360 | – | 3088 | 2967 | – | 7.80 (1H, s), 7.70–7.50 (5H, m) | 2.47 (3H, s), 2.50 (3H, s) | 6.65 (2H, b, $NH_2$) | $CDCl_3$ |
| **2h** | 3431, 3357 | – | 3079 | 2964 | – | 8.00–7.30 (9H, m) | 2.48 (3H, s) | 6.62 (2H, b, $NH_2$) | $CDCl_3$ |
| **2i** | 3429, 3348 | – | 3086 | 2958 | – | 7.84–7.08 (8H, m) | 1.38 (3H, t), 2.50 (3H, s), 4.32 (2H, q) | 6.60 (2H, b, $NH_2$) | $CDCl_3$ |
| **2j** | 3426, 3357 | – | 3099 | 2960 | – | 6.54 (1H, s) 7.66–7.55 (5H, m) | 2.46 (3H, s), 2.55 (3H, s) | 6.59 (2H, b, $NH_2$) | $CDCl_3$ |

[a] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

Table 2
Elemental analysis of compounds **1a–1e** and **2a–2j**

| Compound no. | Molecular formula (m. wt) | m.p.[a] (°C) (colour) | Yield (%) | Elemental analysis: calc. (found) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | S |
| **1a** | $C_7H_7N_5S$ (193.2) | dec. >156 (orange) | 86 | 43.51 (43.68) | 3.65 (3.57) | 36.24 (35.91) | 16.59 (16.37) |
| **1b** | $C_8H_9N_5S$ (207.3) | dec. >175 (red) | 91 | 46.36 (46.59) | 4.38 (4.42) | 33.79 (33.65) | 15.47 (15.28) |
| **1c** | $C_{11}H_9N_5S$ (243.3) | dec. >200 (orange) | 79 | 54.30 (54.19) | 3.73 (3.68) | 28.79 (28.67) | 13.18 (12.83) |
| **1d** | $C_{13}H_{13}N_5OS$ (287.3) | dec. >196 (red) | 83 | 54.34 (54.47) | 4.56 (4.65) | 24.37 (24.09) | 11.16 (10.81) |
| **1e** | $C_8H_9N_5O$ (191.2) | dec. >145 (yellow) | 68 | 50.26 (50.44) | 4.74 (4.66) | 36.63 (36.47) | – |
| **2a** | $C_7H_8N_6S$ (208.2) | 247–248 (orange) | 85 | 40.37 (40.12) | 3.87 (3.79) | 40.36 (40.16) | 15.40 (15.10) |
| **2b** | $C_8H_{10}N_6S$ (222.3) | 269–270 (orange) | 89 | 43.23 (43.48) | 4.53 (4.49) | 37.81 (37.79) | 14.43 (14.29) |
| **2c** | $C_{11}H_{10}N_6S$ (258.3) | 302–303 (red) | 78 | 51.15 (51.39) | 3.90 (3.84) | 32.54 (32.45) | 12.41 (12.27) |
| **2d** | $C_{13}H_{13}N_5OS$ (287.3) | 265–266 (brown) | 73 | 51.64 (51.48) | 4.67 (4.73) | 27.80 (27.66) | 10.61 (10.39) |
| **2e** | $C_8H_{10}N_6O$ (206.2) | 243–244 (yellow) | 78 | 46.60 (46.83) | 4.89 (4.83) | 40.76 (40.59) | – |
| **2f** | $C_{13}H_{12}N_6S$ (284.3) | 201–201 (orange) | 61 | 54.91 (55.06) | 4.25 (4.13) | 29.56 (29.36) | 11.28 (11.04) |
| **2g** | $C_{14}H_{14}N_6S$ (298.4) | 208–209 (red) | 65 | 56.36 (56.17) | 4.73 (4.65) | 28.17 (27.88) | 10.75 (10.61) |
| **2h** | $C_{17}H_{14}N_6S$ (334.4) | 231–232 (orange) | 69 | 61.06 (61.24) | 4.22 (4.32) | 25.13 (24.90) | 9.59 (9.37) |
| **2i** | $C_{19}H_{18}N_6OS$ (378.5) | 174–175 (red) | 60 | 60.30 (60.54) | 4.79 (4.88) | 22.21 (21.87) | 8.47 (8.15) |
| **2j** | $C_{14}H_{14}N_6O$ (282.3) | 171–172 (yellow) | 57 | 59.56 (59.39) | 5.00 (4.92) | 29.77 (29. 58) | – |

[a] Recrystallization from ethanol/$H_2O$.

Table 3
Spectral data for dyes **3a–3j**

| Dye no. | FT-IR ($cm^{-1}$) in KBr | | | | | | $^1$H NMR[a] ($\delta$, ppm) in DMSO-$d_6$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\nu_{N-H}$ | $\nu_{C-H\ (arom.)}$ | $\nu_{C-H\ (alip.)}$ | $\nu_{C\equiv N}$ | $\nu_{C=O}$ | $\nu_{C-O}$ | Arom.-H | Alip.-H | X–H |
| **3a** | 3257 | 3074 | 2960 | 2244 | 1686, 1656 | – | 8.00 (1H, d), 7.79 (1H, d) | 2.46 and 2.74 (3H, s, pyrazole-$CH_3$), 2.59 and 2.89 (3H, s, pyridone-$CH_3$) | 12.18 and 12.33 (b, OH), 13.60 and 14.00 (b, NH), 14.96 and 15.10 (b, NH) |
| **3b** | 3255 | 3075 | 2982 | 2235 | 1697, 1654 | – | 7.91 and 7.70 (1H, s) | 2.44 and 2.74 (3H, s, pyrazole-$CH_3$), 2.48 and 2.82 (3H, s, thiazole-$CH_3$), 2.56 and 2.88 (3H, s, pyridone-$CH_3$) | 12.15 and 12.26 (b, OH), 13.50 and 13.90 (b, NH), 14.99 and 15.06 (b, NH) |
| **3c** | 3244 | 3094 | 2987 | 2222 | 1703, 1665 | – | 8.07–7.55 (4H, m) | 2.47 and 2.72 (3H, s, pyrazole-$CH_3$), 2.62 and 2.88 (3H, s, pyridone-$CH_3$) | 12.21 and 12.30 (b, OH), 13.75 and 14.08 (b, NH), 14.99 and 15.05 (b, NH) |
| **3d** | 3249 | 3050 | 2968 | 2218 | 1698, 1663 | 1056 | 7.95–7.10 (3H, m) | 1.37 (3H, t, ethoxy-$CH_3$), 2.46 and 2.73 (3H, s, pyrazole-$CH_3$), 2.60 and 2.89 (3H, s, pyridone-$CH_3$), 4.13 (2H, q, ethoxy-$CH_2$) | 12.15 and 12.31 (b, OH), 13.67 and 14.00 (b, NH), 14.94 and 15.03 (b, NH) |
| **3e** | 3255 | 3081 | 2973 | 2223 | 1707, 1663 | – | 6.52 (1H, s) | 2.46 and 2.74 (3H, s, pyrazole-$CH_3$), 2.48 and 2.79 (3H, s, isoxazole-$CH_3$), 2.61 and 2.90 (3H, s, pyridone-$CH_3$) | 12.09 and 12.28 (b, OH), 13.54 and 13.95 (b, NH), 14.94 and 15.02 (b, NH) |
| **3f** | 3264 | 3085 | 2971 | 2238 | 1681, 1630 | – | 8.05 (1H, d) 7.85 (1H, d) 7.70–7.56 (5H, m) | 2.47 (3H, s, pyrazole-$CH_3$), 2.60 (3H, s, pyridone-$CH_3$) | 12.15 (b, OH), 13.64 (b, NH) |
| **3g** | 3259 | 3083 | 2976 | 2241 | 1693, 1639 | – | 7.77 (1H, s), 7.69–7.56 (5H, m) | 2.45 (3H, s, pyrazole-$CH_3$), 2.50 (3H, s, thiazole-$CH_3$), 2.58 (3H, s, pyridone-$CH_3$) | 12.16 (b, OH), 13.62 (b, NH) |
| **3h** | 3256 | 3052 | 2971 | 2236 | 1684, 1630 | – | 7.97–7.35 (9H, m) | 2.46 (3H, s, pyrazole-$CH_3$), 2.60 (3H, s, pyridone-$CH_3$) | 12.18 (b, OH), 13.58 (b, NH) |
| **3i** | 3259 | 3074 | 2981 | 2232 | 1668, 1631 | 1059 | 7.85–7.03 (8H, m) | 1.34 (3H, t, ethoxy-$CH_3$), 2.38 (3H, s, pyrazole-$CH_3$), 2.72 (3H, s, pyridone-$H_3$), 4.11(2H, q, ethoxy-$CH_2$) | 12.15 (b, OH), 13.54 (b, NH) |
| **3j** | 3258 | 3077 | 2987 | 2232 | 1696, 1658 | – | 6.50 (1H, s), 7.70–7.58 (5H, m) | 2.47 (3H, s, pyrazole-$CH_3$), 2.52 (3H, s, isoxazole-$CH_3$), 2.58 (3H, s, pyridone-$CH_3$) | 12.21 (b, OH), 13.60 (b, NH) |

[a] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

Table 4
Spectral data for dyes **4a–4j**

| Dye no. | FT-IR ($cm^{-1}$) in KBr | | | | | $^1$H NMR[a] ($\delta$, ppm) | | |
|---|---|---|---|---|---|---|---|---|
| | $\nu_{N-H}$ | $\nu_{C-H\ (arom.)}$ | $\nu_{C-H\ (alip.)}$ | $\nu_{C=O}$ | $\nu_{C-O}$ | Arom.-H | Alip.-H | X–H |
| **4a** | 3281 | 3072 | 2967 | 1676 | – | 7.96 (1H, d), 7.45 (1H, d) | 2.15 and 2.74 (3H, s, pyrazolone-$CH_3$), 2.57 and 2.90 (3H, s, pyrazole-$CH_3$) | 11.58 and 11.74 (b, NH), 13.43 (b, NH), 13.70 and 13.90 (b, NH or OH) |
| **4b** | 3272 | 3065 | 2984 | 1678 | – | 7.67 (1H, s) | 2.14 and 2.74 (3H, s, pyrazolone-$CH_3$), 2.48 (3H, s, thiazole-$CH_3$), 2.55 and 2.90 (3H, s, pyrazole-$CH_3$) | 11.56 and 11.72 (b, NH), 13.38 (b, NH), 13.68 and 13.80 (b, NH or OH) |
| **4c** | 3259 | 3077 | 2966 | 1681 | – | 8.07–7.50 (4H, m) | 2.17 and 2.74 (3H, s, pyrazolone-$CH_3$), 2.60 and 2.90 (3H, s, pyrazole-$CH_3$) | 11.66 and 11.82 (b, NH), 13.62 (b, NH), 13. 72 and 13.90 (b, NH or OH) |
| **4d** | 3260 | 3066 | 2980 | 1634 | 1068 | 7.94–7.12 (3H, m) | 1.37 (3H, t, ethoxy-$CH_3$), 2.16 and 2.72 (3H, s, pyrazolone-$CH_3$), 2.58 and 2.90 (3H, s, pyrazole-$CH_3$), 4.12 (2H, q, ethoxy-$CH_2$) | 11.62 and 11.80 (b, NH), 13.48 (b, NH), 13. 70 and 13.86 (b, NH or OH) |
| **4e** | 3269 | 3069 | 2979 | 1678 | – | 6.50 (1H, s) | 2.13 and 2.73 (3H, s, pyrazolone-$CH_3$), 2.47 (3H, s, isoxazole-$CH_3$), 2.56 and 2.89 (3H, s, pyrazole-$CH_3$) | 11.60 and 11.75 (b, NH), 13.38 (b, NH), 13. 70 and 13.82 (b, NH or OH) |
| **4f** | 3260 | 3088 | 2979 | 1632 | – | 8.08 (1H, d), 7.86 (1H, d), 7.78–7.45 (5H, m) | 2.16 (3H, s, pyrazolone-$CH_3$), 2.58 (3H, s, pyrazole-$CH_3$) | 13.40 (b, NH), 13.70 (b, OH) |
| **4g** | 3275 | 3059 | 2975 | 1625 | – | 7.79 (1H, s), 7.70–7.49 (5H, m) | 2.14 (3H, s, pyrazolone-$CH_3$), 2.47 (3H, s, thiazole-$CH_3$), 2.60 (3H, s, pyrazole-$CH_3$) | 13.43 (b, NH), 13.66 (b, OH) |
| **4h** | 3256 | 3052 | 2988 | 1630 | – | 7.98–7.40 (9H, m) | 2.20 (3H, s, pyrazolone-$CH_3$), 2.54 (3H, s, pyrazole-$CH_3$) | 13.50 (b, NH), 13.75 (b, OH) |
| **4i** | 3268 | 3082 | 2981 | 1631 | 1060 | 7.96–7.44 (8H, m) | 1.36 (3H, t, ethoxy-$CH_3$), 2.16 (3H, s, pyrazolone-$CH_3$), 2.54 (3H, s, pyrazole-$CH_3$), 4.16 (2H, q, ethoxy-$CH_2$) | 13.52 (b, NH), 13.72 (b, OH) |
| **4j** | 3255 | 3073 | 2963 | 1636 | – | 7.70–7.55 (5H, m), 6.51 (1H, s) | 2.14 (3H, s, pyrazolone-$CH_3$), 2.48 (3H, s, isoxazole-$CH_3$), 2.58 (3H, s, pyrazole-$CH_3$) | 13.40 (b, NH), 13.74 (b, OH) |

[a] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

Table 5
Elemental analysis of dyes **3a–3j** and **4a–4j**

| Dye no. | Molecular formula (m. wt) | m.p.[a] (°C) (colour) | Yield (%) | Elemental analysis: calc. (found) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | S |
| **3a** | $C_{14}H_{11}N_9O_2S$ (369.4) | dec. >190 (red) | 73 | 45.52 (45.69) | 3.00 (2.91) | 34.13 (33.88) | 8.68 (8.45) |
| **3b** | $C_{15}H_{13}N_9O_2S$ (383.4) | dec. >230 (orange) | 69 | 46.99 (47.13) | 3.42 (3.51) | 32.88 (32.64) | 8.36 (8.19) |
| **3c** | $C_{18}H_{13}N_9O_2S$ (419.4) | dec. >267 (red) | 48 | 51.55 (51.83) | 3.12 (3.24) | 30.06 (29.87) | 7.65 (7.51) |
| **3d** | $C_{20}H_{17}N_9O_3S$ (463.5) | dec. >168 (black) | 64 | 51.83 (51.97) | 3.70 (3.84) | 27.20 (27.00) | 6.92 (6.76) |
| **3e** | $C_{15}H_{13}N_9O_3$ (367.3) | dec. >267 (red) | 53 | 49.05 (49.17) | 3.57 (3.49) | 34.32 (34.26) | – |
| **3f** | $C_{20}H_{15}N_9O_2S$ (445.5) | 109–110 (brown) | 76 | 53.93 (54.04) | 3.39 (3.47) | 28.30 (28.16) | 7.20 (7.03) |
| **3g** | $C_{21}H_{17}N_9O_2S$ (459.5) | 152–153 (yellow) | 71 | 54.89 (54.97) | 3.73 (3.58) | 27.44 (27.30) | 6.98 (6.77) |
| **3h** | $C_{24}H_{17}N_9O_2S$ (495.5) | 232–233 (orange) | 55 | 58.17 (57.95) | 3.46 (3.53) | 25.44 (25.21) | 6.47 (6.38) |
| **3i** | $C_{26}H_{21}N_9O_3S$ (539.6) | 183–184 (orange) | 65 | 57.88 (57.80) | 3.92 (3.89) | 23.36 (23.06) | 5.94 (5.75) |
| **3j** | $C_{21}H_{17}N_9O_3$ (443.4) | 163–164 (yellow) | 59 | 56.88 (56.95) | 3.86 (3.93) | 28.43 (28.32) | – |
| **4a** | $C_{11}H_{11}N_9OS$ (317.3) | 288–289 (orange) | 62 | 41.63 (41.52) | 3.49 (3.58) | 39.73 (39.66) | 10.10 (9.95) |
| **4b** | $C_{12}H_{13}N_9OS$ (331.4) | 287–288 (red) | 71 | 43.50 (43.64) | 3.95 (3.84) | 38.04 (37.83) | 9.68 (9.55) |
| **4c** | $C_{15}H_{13}N_9OS$ (367.4) | 318–319 (red) | 57 | 49.04 (49.12) | 3.57 (3.61) | 34.31 (34.24) | 8.73 (8.60) |
| **4d** | $C_{17}H_{17}N_9O_2S$ (411.4) | 239–240 (brown) | 82 | 49.63 (49.50) | 4.16 (4.22) | 30.64 (30.55) | 7.79 (7.67) |
| **4e** | $C_{12}H_{13}N_9O_2$ (315.3) | 307–308 (orange) | 67 | 45.71 (45.86) | 4.16 (4.23) | 39.98 (39.81) | – |
| **4f** | $C_{17}H_{15}N_9OS$ (393.4) | 168–169 (yellow) | 69 | 51.90 (51.84) | 3.84 (3.93) | 32.04 (31.87) | 8.15 (8.06) |
| **4g** | $C_{18}H_{17}N_9OS$ (407.5) | 147–148 (yellow) | 75 | 53.06 (53.18) | 4.21 (4.15) | 30.94 (30.81) | 7.87 (7.73) |
| **4h** | $C_{21}H_{17}N_9OS$ (443.5) | 231–232 (orange) | 63 | 56.87 (56.96) | 3.86 (3.78) | 28.42 (28.37) | 7.23 (7.16) |
| **4i** | $C_{23}H_{21}N_9O_2S$ (487.5) | 189–190 (red) | 86 | 56.66 (56.74) | 4.34 (4.27) | 25.86 (25.73) | 6.58 (6.45) |
| **4j** | $C_{18}H_{17}N_9O_2$ (391.4) | 160–161 (yellow) | 74 | 55.24 (55.39) | 4.38 (4.18) | 32.21 (31.93) | – |

[a] Recrystallization from DMF/ethanol.

Table 6
Influence of solvent on $\lambda_{max}$ (nm) of dyes **3a–3j** and **4a–4j**

| Dye no. | DMSO | DMF | Acetonitrile | Methanol | Acetic acid | Chloroform |
|---|---|---|---|---|---|---|
| **3a** | 480, 374 s | 476, 372 s | 468, 367 s | 471, 367 s | 470, 367 s | 474, 372 s |
| **3b** | 484, 380 s | 480, 378 s | 472, 373 s | 475, 373 s | 477, 373 s | 478, 378 s |
| **3c** | 489, 374 s | 486, 373 s | 474, 367 s | 479, 365 s | 480, 365 s | 483, 373 s |
| **3d** | 501, 393 s | 497, 390 s | 488, 388 s | 492, 386 s | 492, 391 s | 494, 397 s |
| **3e** | 458, 331 s | 460, 332 s | 447, 322 s | 448, 325 s | 447, 320 s | 453, 322 s |
| **3f** | 381 | 379 | 372 | 372 | 374 | 376 |
| **3g** | 396 | 393 | 388 | 388 | 390 | 391 |
| **3h** | 455 | 451 | 440 | 442 | 442 | 444 |
| **3i** | 465 | 461 | 454 | 454 | 456 | 458 |
| **3j** | 440 | 438 | 427 | 429 | 432 | 434 |
| **4a** | 357, 464 s | 355, 461 s, 580 s | 350, 456 s | 351, 458 s | 349, 454 s | 352, 461 s |
| **4b** | 362, 469 s | 362, 466 s, 592 s | 357, 461 s | 355, 461 s | 357, 459 s | 360, 465 s |
| **4c** | 358, 476 s | 357, 470 s, 610 s | 350, 467 s | 350, 468 s | 351, 464 s | 354, 468 s |
| **4d** | 362, 480 s | 360, 476 s, 615 s | 352, 472 s | 354, 474 s | 354, 468 s | 357, 478 s |
| **4e** | 324, 440 s | 322, 437 s, 550 s | 316, 432 s | 316, 431 s | 315, 427 s | 320, 437 s |
| **4f** | 432 | 429, 538 s | 420 | 424 | 422 | 427 |
| **4g** | 436 | 433, 542 s | 424 | 425 | 424 | 430 |
| **4h** | 454 | 451, 550 s | 444 | 447 | 446 | 449 |
| **4i** | 466 | 461, 556 s | 458 | 453 | 456 | 460 |
| **4j** | 398 | 400, 510 s | 394 | 395 | 394 | 396 |

Abbreviation: s, shoulder.

the precipitated products separated upon dilution with water (50 ml) were filtered off, washed with water (3 × 50 ml), dried in air and recrystallized to give 5-amino-3-methyl-4-hetarylazo-1H-pyrazoles and 5-amino-3-methyl-4-hetarylazo-1-phenylpyrazoles (**2a–2j**) (Scheme 1) [26].

### 2.4. Synthesis of disazo pyridone (*3a–3j*) and pyrazolone dyes (*4a–4j*)

Diazotisation of **2a–2j** was affected with nitrosyl sulphuric acid. A typical procedure is that described below used for 5-amino-3-methyl-4-thiazolylazo-1H-pyrazole (**2a**) and 3-cyano-6-hydroxy-4-methyl-2-pyridone; all other dyes were prepared in a similar manner.

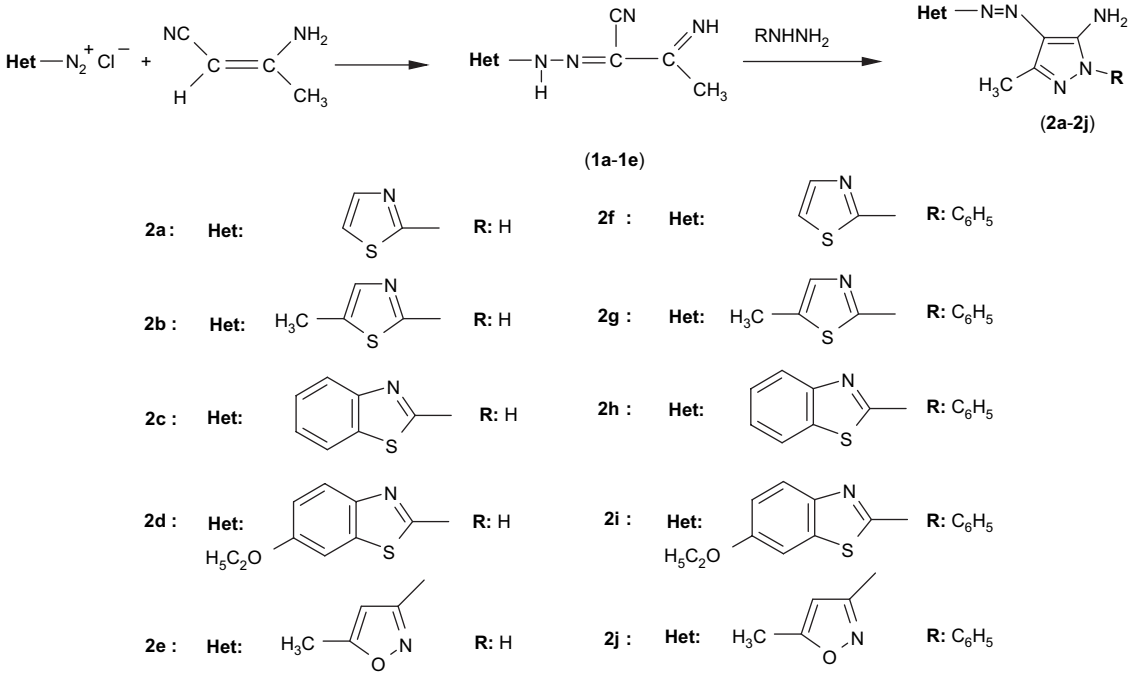
#### 2.4.1. 5-(3′-methyl-4′-(thiazole-2″-ylazo)-1′H-pyrazole-5′-ylazo)-3-cyano-6-hydroxy-4-methyl-2-pyridone (*3a*)

Nitrosyl sulphuric was prepared by dissolving sodium nitrite (0.14 g) in concentrated sulphuric acid (4 ml) at 0 °C. 5-Amino-3-methyl-4-(thiazole-2′-ylazo)-1H-pyrazole (**2a**) ($2.0 \times 10^{-3}$ mol) was dissolved in hot glacial acetic acid (2.5 ml) and rapidly cooled in an ice–salt bath to −5 °C. The solution was then

Table 7
Absorption maxima of dyes **3a–3j** and **4a–4j** in acidic and basic solutions

| Dye no. | $\lambda_{max}$ (nm) | | | | | |
|---|---|---|---|---|---|---|
| | Methanol | Methanol + KOH | Methanol + HCl | Chloroform | Chloroform + piperidine | Acetic acid |
| **3a** | 471, 367 s | 535, 375 s | 491, 370 s | 474, 372 s | 547, 365 s | 470, 367 s |
| **3b** | 475, 373 s | 540, 378 s | 499, 374 s | 478, 378 s | 540, 373 s | 477, 373 s |
| **3c** | 479, 365 s | 540, 377 s | 482, 368 s | 483, 373 s | 523, 373 s | 480, 365 s |
| **3d** | 492, 386 s | 548, 386 s | 497, 388 s | 494, 397 s | 531, 386 s | 492, 391 s |
| **3e** | 448, 325 s | 507, 326 s | 448, 326 s | 453, 322 s | 485, 320 s | 447, 320 s |
| **3f** | 372 | 374 | 385 | 376 | 373 | 374 |
| **3g** | 388 | 387 | 397 | 391 | 390 | 390 |
| **3h** | 442 | 481 | 473 | 444 | 444 | 442 |
| **3i** | 454 | 486 | 495 | 458 | 459 | 456 |
| **3j** | 429 | 430 | 431 | 434 | 432 | 432 |
| **4a** | 351, 458 s | 370, 515 s | 358, 490 s | 352, 461 s | 369, 574 s | 349, 454 s |
| **4b** | 355, 461 s | 372, 514 s | 362, 499 s | 360, 465 s | 372, 574 s | 357, 459 s |
| **4c** | 350, 468 s | 373, 533 s | 354, 470 s | 354, 468 s | 371, 600 s | 351, 464 s |
| **4d** | 354, 474 s | 376, 542 s | 356, 478 s | 357, 478 s | 378, 610 s | 354, 468 s |
| **4e** | 316, 431 s | 350, 482 s | 315, 430 s | 320, 437 s | 335, 534 s | 315, 427 s |
| **4f** | 424 | 442, 520 s | 432, 484 s | 427 | 444, 546 s | 422 |
| **4g** | 425 | 448, 522 s | 428, 480 s | 430 | 452, 552 s | 424 |
| **4h** | 447 | 468, 542 s | 448 | 449 | 470, 562 s | 446 |
| **4i** | 453 | 474, 548 s | 453 | 460 | 478, 566 s | 456 |
| **4j** | 395 | 422, 492 s | 398 | 396 | 425, 548 s | 394 |

Abbreviation: s, shoulder.



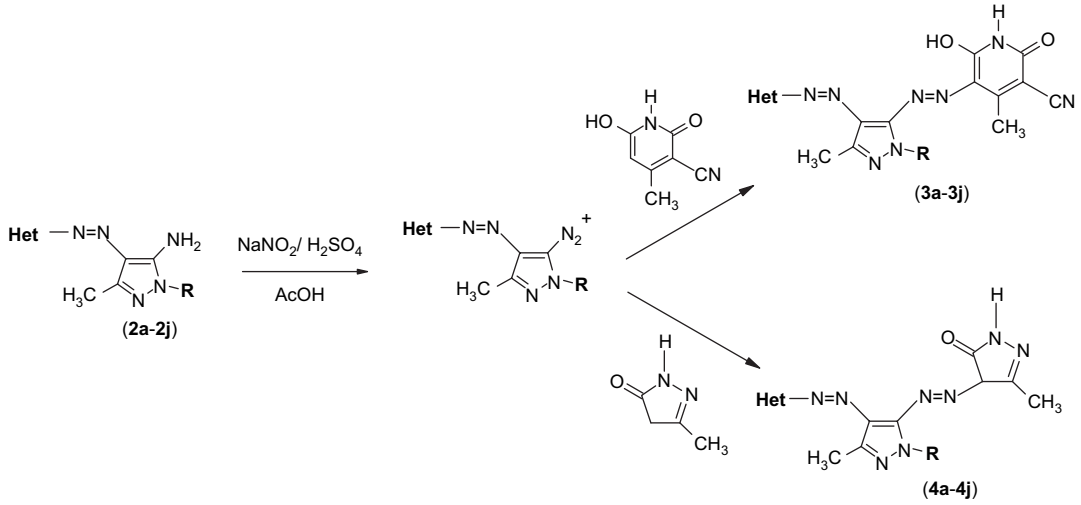

Scheme 1.

added in portions over 30 min to nitrosyl sulphuric acid at 0–5 °C and the mixture was stirred for a further 1 h at this temperature. 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 ($2.0 \times 10^{-3}$ mol) in potassium hydroxide ($2.0 \times 10^{-3}$ mol) and water (2 ml) at 0–5 °C. The pH of the coupling mixture, in each case, was maintained at 5–6 through the coupling process by adding solid sodium acetate. The mixture was then stirred for 1 h at 0–5 °C. The progress of the reaction was followed by thin layer chromatography (TLC) using a DMF–water mixture (5:2 by volume) as developing solvent and silica gel TLC plates as the stationary phase. The resulting solid was filtered, washed with cold water ($3 \times 30$ ml) and dried in air. Recrystallization from DMF–$H_2O$ mixture gave red crystals (**3a**).

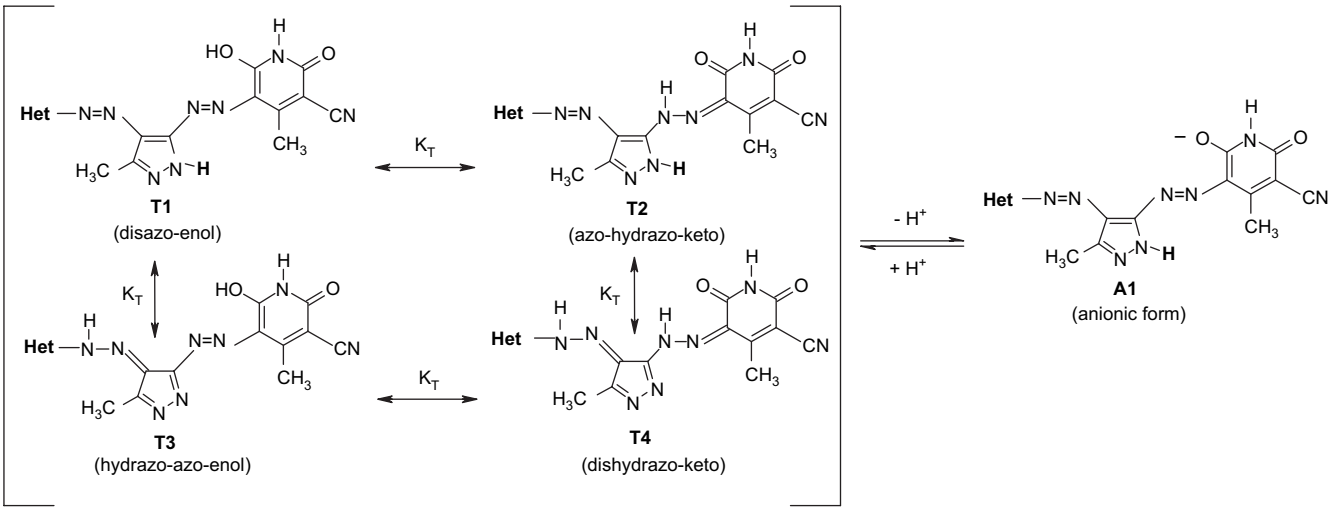
## 3. Results and discussion

### *3.1. Azo-hydrazo tautomerism*

Keto-enol tautomerism is not only of utmost importance to the dyestuff manufacturer, but also in other areas of chemistry. Keto-enol tautomers display not only different colours, but also have different tinctorial strengths (and hence economics) and different properties, e.g. light fastness. The heterocyclic disazo pyridone dyes (**3a–3j**) and disazo pyrazolone dyes




Scheme 2.



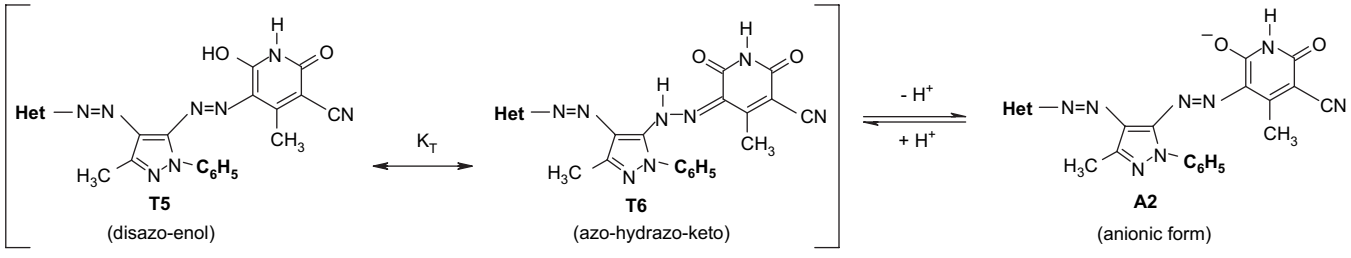

Scheme 3.

(**4a–4j**) were prepared by coupling 3-cyano-6-hydroxy-4-methyl-2-pyridone and 3-methyl-1H-pyrazole-5-one with diazotized 5-amino-3-methyl-4-hetarylazo-1H-pyrazoles and 5-amino-3-methyl-4-hetarylazo-1-phenylpyrazoles (Scheme 2). Dyes **3a–3e** can exist in four possible tautomeric forms, namely, the disazo-enol form **T1**, the azo-hydrazo-keto form **T2**, the hydrazo-azo-enol form **T3** and the dishydrazo-keto form **T4** as shown in Scheme 3. Also, dyes **3f–3j** can exist in two possible tautomeric forms, namely, the disazo-enol form **T5** and the azo-hydrazo-keto form **T6** as shown in Scheme 4. The deprotonation of tautomeric forms of **3a–3e** and **3f–3j** lead to common anions **A1** and **A2**.

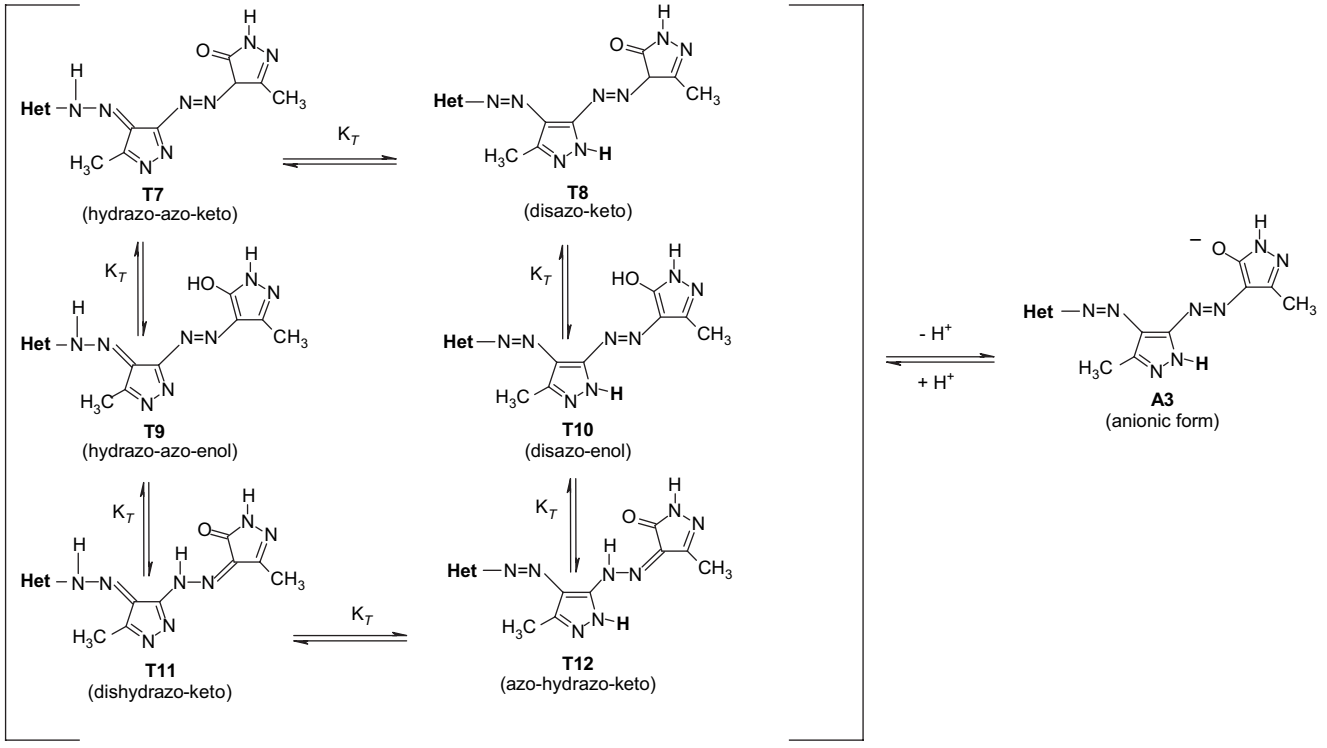
Dyes **4a–4e** can exist in six possible tautomeric forms, namely, the hydrazo-azo-keto form **T7**, the disazo-keto form **T8**, the hydrazo-azo-enol form **T9**, the disazo-enol form **T10**, the dishydrazo-keto form **T11** and the azo-hydrazo-keto form **T12** as shown in Scheme 5. Also, dyes **4f–4j** can exist in three possible tautomeric forms, namely, the disazo-keto form **T13**, the azo-hydrazo-keto form **T14** and the disazo-enol form **T15** as shown in Scheme 6. The deprotonation of tautomeric forms of **4a–4e** and **4f–4j** lead to common anions **A3** and **A4**.

The infrared spectra of dyes **3a–3j** and **4a–4j** (in KBr) showed intense two carbonyl bands at 1707–1630 $cm^{-1}$ and a carbonyl band at 1681–1625 $cm^{-1}$, respectively. It can be suggested that these dyes do not exist as the disazo-enol forms (**T1** and **T10**) and the hydrazo-azo-enol forms (**T3** and **T9**) in the solid state. Numerous investigations were carried out to establish the tautomeric structure of azo pyridine and azo pyrazolone in the solid state using a variety of spectroscopic techniques. The spectral data generally lead to the conclusion that the tautomeric equilibrium of the azo pyridone and azo pyrazolone dyes is in favor of the hydrazone form in the solid state [26–32]. The FT-IR spectra of dyes **3a–3j** and **4a–4j** also showed a band at 3281–3244 $cm^{-1}$, which was assigned to the imino group (NH). The other $\nu_{max}$ values of 3094–3050 $cm^{-1}$ (aromatic C–H), 2988–2960 $cm^{-1}$ (aliphatic C–H), 2244–2218 $cm^{-1}$ (C≡N of dyes **3a–3j**) were recorded.

The $^1$H NMR spectra of dyes **3a–3e** measured in DMSO-$d_6$ at 25 °C showed two singlets at 2.44–2.46 and 2.72–2.74 ppm ($CH_3$ of pyrazole ring), two singlets at 2.56–2.62 and 2.88–2.90 ppm ($CH_3$ of pyridone ring), two broad peaks at 12.09–12.21 and 12.26–12.33 ppm for –OH protons, two broad peaks at 13.50–13.75 and 13.90–14.08 ppm for –NH protons (pyridone ring), two broad peaks at 14.94–14.99 and 15.02–15.10 ppm for –NH protons (pyrazole ring or hydrazo form) (Table 1). These results suggest that dyes **3a–3e** may be a mixture of several tautomeric forms in DMSO. The $^1$H NMR spectra of dyes **3f–3j** showed a singlet at 2.38–2.47 ppm ($CH_3$ of pyrazole ring), a singlet at 2.58–2.72 ppm ($CH_3$ of pyridone ring), a broad peak at 12.15–12.21 ppm for –OH or –NH protons (disazo-enol or azo-hydrazo-keto forms of pyridone ring), a broad peak at 13.54–13.62 ppm for –NH protons (pyridone ring) (Table 1). These results suggest that dyes **3f–3j** are in favor of the predominantly single tautomeric form (**T5** or **T6**) in DMSO.




Scheme 4.

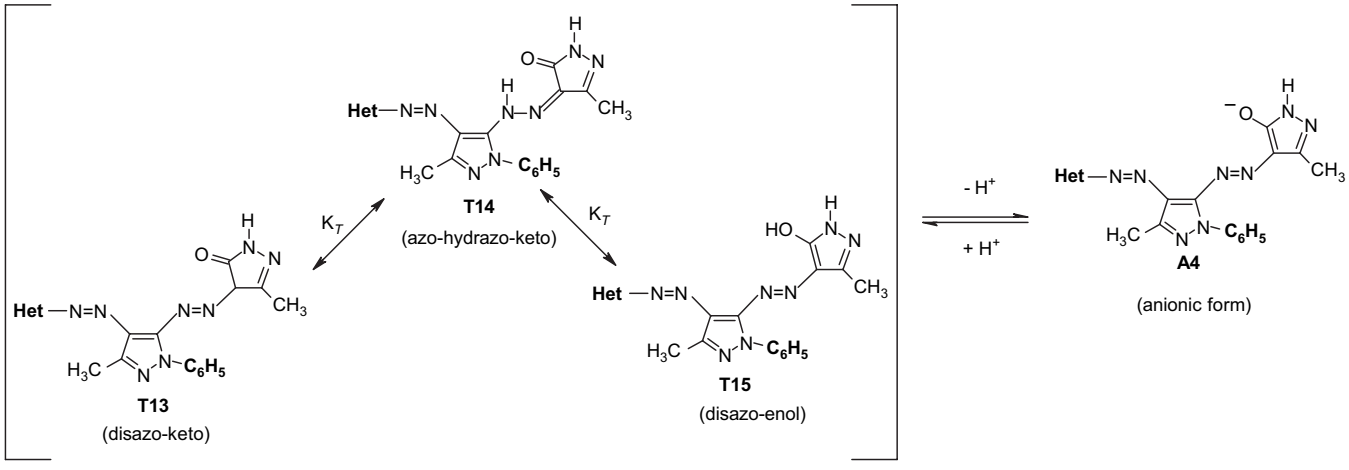



Scheme 5.

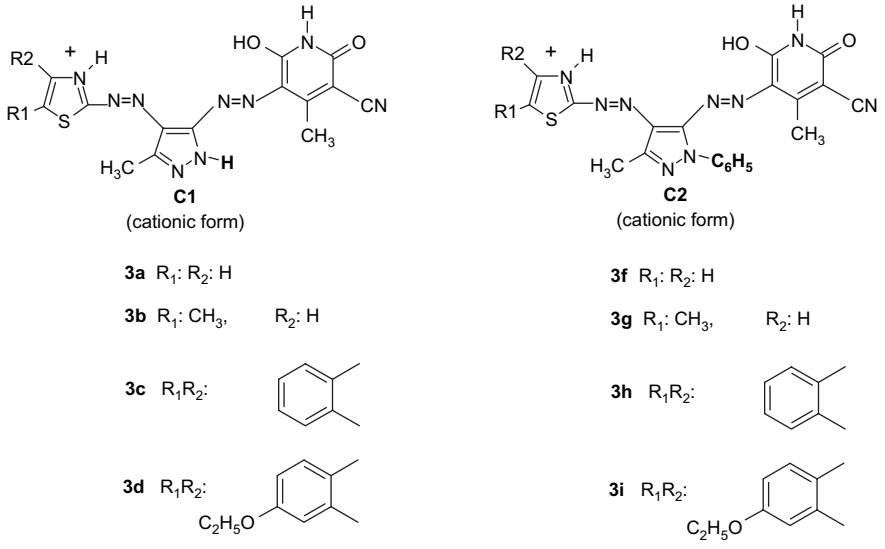
The $^1$H NMR spectra of dyes **4a**–**4e** measured in DMSO-$d_6$ at 25 °C showed two singlets at 2.13–2.17 and 2.72–2.74 ppm ($CH_3$ of pyrazolone ring), two singlets at 2.55–2.60 and 2.89–2.90 ppm ($CH_3$ of pyrazole ring), two broad peaks at 11.56–11.66 and 11.72–11.82 ppm for –NH protons (azo and hydrazo forms of pyrazole ring), a broad peak at 13.38–13.62 ppm for –NH protons (1-H of pyrazolone ring), and two broad peaks at 13.68–13.72 and 13.80–13.90 ppm for –NH and –OH protons (hydrazo and enol forms of pyrazolone ring) (Table 2). These results suggest that dyes **4a**–**4e** may be a mixture of several tautomeric forms in DMSO. The $^1$H NMR spectra of dyes **4f**–**4j** showed a singlet at 2.14–2.20 ppm ($CH_3$ of pyrazolone ring), a singlet at 2.54–2.60 ppm ($CH_3$ of pyrazole ring), a broad peak at 13.40–13.52 ppm for –OH or –NH protons (enol or hydrazo forms of pyrazolone ring), a broad peak at 13.66–13.75 ppm for –NH protons (1-H of pyrazolone ring) (Table 2). These results suggest that dyes **4f**–**4j** are in favor of the predominantly single tautomeric form (**T14** or **T15**) in DMSO.

### 3.2. Solvent effects

UV–vis absorption spectra were recorded using an ATI-Unicam UV-100 spectrophotometer in the wavelength range 300–700 nm. Absorption spectra of dyes **3a**–**3j** and **4a**–**4j** were recorded in various solvents at a concentration of




Scheme 6.




Scheme 7.

$\sim 10^{-6}$–$10^{-8}$ M and these are all run at different concentrations. The results were summarized in Table 4. The pH value of all solutions used was in the range between acidic and basic. The visible absorption spectra of the dyes did not show regular variation with the polarity of solvents.

Dyes **3a**–**3e** showed two absorbances and dyes **3f**–**3j** showed a single absorbance in all used solvents. It can be suggested that dyes **3a**–**3e** may be a mixture of tautomeric forms in various solvents. But dyes **3f**–**3j** is predominantly in the single tautomeric form in all used solvents. Dyes **4a**–**4e** showed two absorbances and dyes **4f**–**4j** showed a single absorbance in DMSO, acetonitrile, methanol, acetic acid and chloroform. Dyes **4a**–**4e** showed three absorbances and dyes **4f**–**4j** showed two absorbances in DMF. It can be suggested that dyes **4a**–**4e** may be a mixture of tautomeric forms while dyes **4f**–**4j** are predominantly in the single tautomeric form in DMSO, acetonitrile, methanol, acetic acid and chloroform. But dyes **4a**–**4j** may be a mixture of tautomeric form(s) and an anionic form in DMF. The results regarding solvatochromism are consistent with the findings on tautomerism from $^1$H NMR work. The results obtained from $^1$H NMR spectra showed that dyes **3a**–**3e** and **4a**–**4e** may be a mixture of several tautomeric forms and dyes **3f**–**3j** and **4f**–**4j** are in favor of the predominantly single tautomeric form in DMSO. Similar results were also obtained from UV–vis spectra. It was observed that dyes **3a**–**3e** and **4a**–**4e** may be a mixture of several tautomeric forms and dyes **3f**–**3j** and **4f**–**4j** are in favor of the predominantly single tautomeric form in solutions when UV–vis spectra of dyes were investigated.

It was also observed that the absorption spectra of dyes **3a**–**3j** and **4a**–**4j** in DMSO and DMF little bathochromically shifted with respect to the absorption spectra in chloroform (e.g. for dye **3a**, $\lambda_{max}$ is 474 nm in $CHCl_3$, 480 nm in DMSO, 476 nm in DMF (Fig. 1); for dye **4b**, $\lambda_{max}$ is 360 nm in $CHCl_3$, 362 nm in DMSO, 362 nm in DMF (Fig. 2)). It was also observed that the absorption spectra of dyes **3a**–**3j** and **4a**–**4j** in acetonitrile, methanol and acetic acid hypsochromically shifted with respect to the absorption spectra in chloroform. Furthermore, the absorption spectra of dyes **4a**–**4j** showed a shoulder at 510–615 nm in DMF (Fig. 2).

The absorption curves of dyes **3a**–**3e** were very sensitive to base. The $\lambda_{max}$ of dyes **3a**–**3e** showed large bathochromic shifts when a small amount of piperidine was added to each of the dye solutions in chloroform (Table 5). A typical

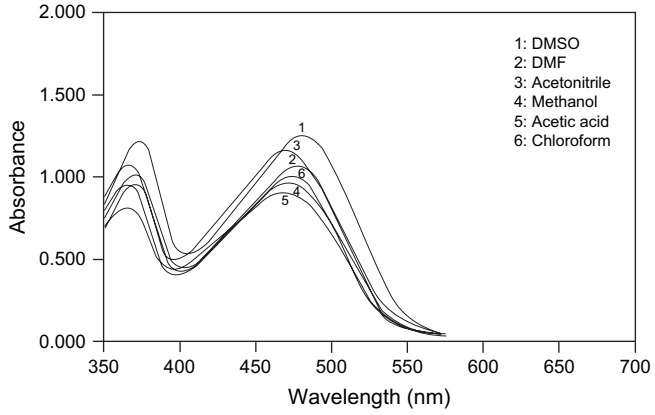



Fig. 1. Absorption spectra of dye **3a** in various solvents.

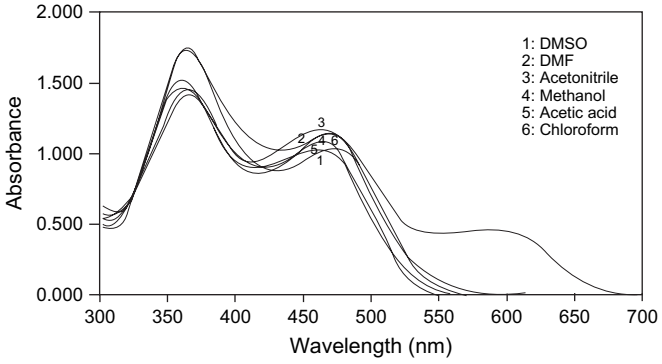



Fig. 2. Absorption spectra of dye **4b** in various solvents.

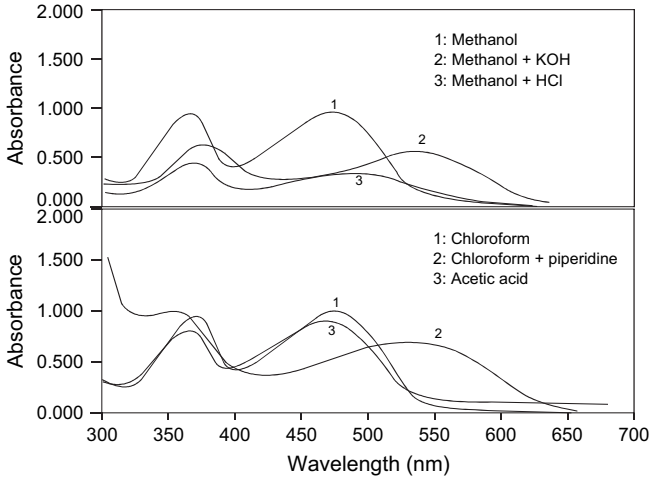



Fig. 3. Absorption spectra of dye **3a** in acidic and basic solutions.

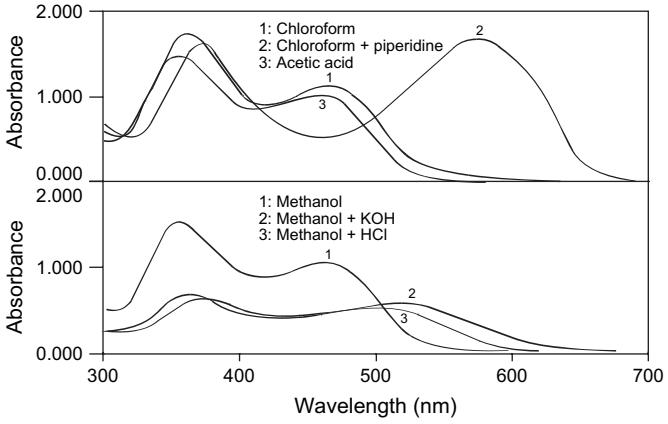


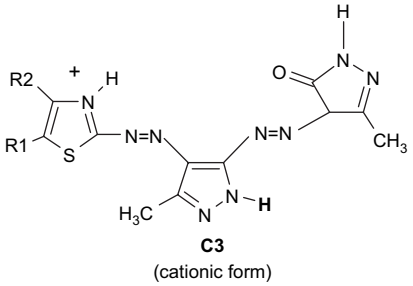

Fig. 4. Absorption spectra of dye **4b** in acidic and basic solutions.

example is shown in Fig. 3. The $\lambda_{max}$ of dyes **3f**–**3j** did not significantly change when a small amount of piperidine was added to each of the dye solutions in chloroform. The $\lambda_{max}$ of dyes **3a**–**3e**, **3h** and **3i** in methanol also showed bathochromic shift when 0.1 M KOH was added. The absorption spectra of dyes **3a**–**3d** and **3f**–**3i** in methanol showed large bathochromic shifts when 0.1 M HCl was added. The absorption spectra of dyes **3e** and **3j** in methanol did not significantly change when 0.1 M HCl was added. These results indicate that dyes **3a**–**3e**, **3h** and **3i** may be a mixture of tautomeric forms and an anionic form (**A1** or **A2**) in strong basic solutions. Also, dyes **3a**–**3d** and **3f**–**3i** may be a mixture of tautomeric forms and a cationic form (**C1** or **C2**) in strong acidic solutions (Scheme 7).

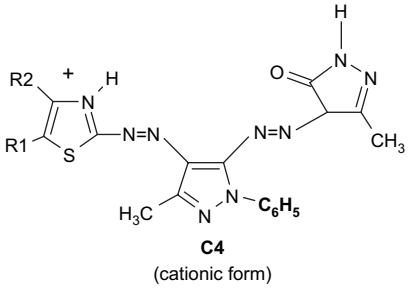
The absorption curves of dyes **4a**–**4j** were also very sensitive to base. The $\lambda_{max}$ of dyes **4a**–**4j** showed large bathochromic shifts when a small amount of piperidine was added to each of the dye solutions in chloroform (Table 5) and absorption curves of the dyes resembled those in DMF. A typical example is shown in Fig. 4. The $\lambda_{max}$ of dyes **4a**–**4j** in methanol also showed bathochromic shift when 0.1 M KOH was added and absorption curves of the dyes resembled those in DMF. The absorption spectra of dyes **4a**, **4b**, **4f** and **4g** in methanol showed large bathochromic shifts when 0.1 M HCl was added. The absorption spectra of dyes **4c**–**4e** and **4h**–**4j** in methanol did not significantly change when 0.1 M HCl was added. These results indicate that dyes **4a**–**4j** may be a mixture of tautomeric forms and an anionic form (**A3** or **A4**) in DMF and basic solutions. Also, dyes **4a**, **4b**, **4f** and **4g** may be a mixture of tautomeric forms and a cationic form (**C3** or **C4**) in strong acidic solutions (Scheme 8).

### 3.3. Substituent effects

As is apparent in Table 4, the introduction of electron-donating methyl group into the thiazole ring and the introduction of electron-donating ethoxy group into the benzothiazole ring result in bathochromic shifts in all solvents (for dye **3g**, $\Delta\lambda = 15$ nm relative to dye **3f** for spectra in DMSO and for dye **3i**, $\Delta\lambda = 10$ nm relative to dye **3h** for spectra in DMSO; for dye **4b**, $\Delta\lambda = 8$ nm relative to dye **4a** for spectra in chloroform and for dye **4i**, $\Delta\lambda = 12$ nm relative to dye **4h** for spectra in DMSO). The observed bathochromism upon introduction of electron donor methyl and ethoxy groups is in agreement with the theory. The densities of electrons that are added to delocalization are increased due to electron donor methyl and ethoxy groups that is why bathochromic shift has occurred. It was also




**C3**
(cationic form)




**C4**
(cationic form)

**4a** $R_1$: $R_2$: H

**4b** $R_1$: $CH_3$, $R_2$: H

**4f** $R_1$: $R_2$: H

**4g** $R_1$: $CH_3$, $R_2$: H

Scheme 8.

observed that the introduction of phenyl group into the pyrazole ring (for dyes **3a**–**3j**) results in hypsochromic shifts in all used solvents (for dye **3f**, $\Delta\lambda = -99$ nm relative to dye **3a**; for dye **3g**, $\Delta\lambda = -88$ nm relative to dye **3b** for spectra in DMSO). The introduction of phenyl group into the pyrazole ring (for dyes **4a**–**4j**) results in bathochromic shifts in all used solvents (for dye **4f**, $\Delta\lambda = +95$ nm relative to dye **4a**; for dye **4g**, $\Delta\lambda = +74$ nm relative to dye **4b** for spectra in DMSO). But, when the absorption spectra of 1H-pyrazole dyes **4a**–**4e** are compared with the absorption spectra of 1-phenyl-pyrazole dyes **4f**–**4j**, a shoulder was observed at longer wavelength.

We have recently reported the synthesis of some novel disazo pyridone and pyrazolone dyes [26], containing two heterocyclic rings and one carbocyclic ring in one molecular. In this study, we reported the synthesis of some novel disazo pyridone and pyrazolone dyes, containing three heterocyclic rings in one molecular. In our previous work, disazo pyridone and pyrazolone dyes showed a single absorbance in all used solvents. But, in this study, 1H-pyridone and 1H-pyrazolone showed two absorbances in all used solvents, attributed to heterocyclic thiazole, benzothiazole and isoxazole rings. In our previous work, 1H-pyridone and 1H-pyrazolone dyes showed dissociation in basic solutions. Similarly, in this work, 1H-pyridone and 1H-pyrazolone dyes showed dissociation in basic solutions, attributed to acidity of 1H of pyrazole ring.

## 4. Conclusions

In this work, disazo pyridone and pyrazolone dyes have been synthesized. Characterization and absorption ability of 20 novel disazo based dyes (**3a**–**3j** and **4a**–**4j**) were studied. The absorption spectra results of dyes **3a**–**3e** and **4a**–**4e** may be a mixture of several tautomeric forms in all used solvents. Dyes **3f**–**3j** and **4f**–**4j** are in favor of the predominantly single tautomeric form in all used solvents. Furthermore, dyes **3a**–**3e** and **4a**–**4e** may be a mixture of tautomeric forms and an anionic form in basic solutions. Also, dyes **3a**–**3d**, **3f**–**3i**, **4a**, **4b**, **4f** and **4g** may be a mixture of tautomeric forms and a cationic form in strong acidic solutions. The introduction of electron-donating methyl group into the thiazole ring and the introduction of electron-donating ethoxy group into the benzothiazole ring result in bathochromic shifts in all solvents.

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