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Synthesis and properties of some novel pyrazolone-based heterocyclic azo disperse dyes containing a fluorosulfonyl group

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ABSTRACT

A series of heteroarylazo disperse dyes derived from pyrazolones and fluorosulfonyl anilines were synthesized, and their thermal and spectral properties were investigated with respect to the effect of substituents on absorption spectra, halochromism, and solvatochromism. Heteroarylazo disperse dyes, which contain a nitro group instead of a fluorosulfonyl group *para* to the azo group in the diazo component, were also synthesized for comparative purpose. The fluorosulfonylarylazopyrazolone dyes had absorption maxima at shorter wavelength and showed lower extinction coefficients than the nitroarylazopyrazolone dyes. The synthesized dyes also exhibited positive halochromism and solvatochromism, so the absorption bands of the dyes moved toward longer wavelengths as the acidity or polarity of the solvent increased. 4-Fluorosulfonyl-substituted dyes generally showed lower thermal stability than their 4-nitro-substituted analogs, because the lower electron-withdrawing power in the diazo components tended to decrease the polarizability and dipole interactions.

1. Introduction

Environmental issues have been gaining importance in all aspects of industrial production [1], and various legislative requirements have emerged with increasing regularity to reduce the impact of dyeing processes on the environment. In response, the industry has been forced to become increasingly innovative in order to develop new products and practices that are more environmentally friendly than existing ones [2]. Therefore, innovation and developments in color chemistry and dyeing will allow the colorist to meet ever-increasing environmental restrictions, produce novel effects, and reduce processing costs.

The demand for environmentally friendly dyes with high wet fastness on polyester is increasing, and the so-called alkali-clearable disperse dyes suggest a promising new direction [3–5]. These alkali-clearable disperse dyes obviate the need for sodium hydrosulfite and significantly reduce the cost of effluent treatment. Previous studies in our group have investigated the use of novel alkali-clearable azo disperse dyes containing a fluorosulfonyl group. Azo disperse dyes of this type were hydrolyzed under alkaline conditions by an S_N2 mechanism (Scheme 1), and pseudo-first-order kinetics were determined by analysis of the dye hydrolysis using HPLC [6–8].

Dyeing with such fluorosulfonyl-containing disperse dyes showed a reasonable level of build-up, excellent wash fastness, and the option of alkali-clearance to achieve high wash fastness, replacing reductive clearing and particularly the use of sodium hydrosulfite, which places a very high biological oxygen demand on conventional disperse dyeing effluent and generates toxic aromatic amines [9–11].

The 4-(*N*,*N*-diethylamino)-4′-fluorosulfonylazobenzene dyes that have been synthesized in previous studies cover a whole gamut of colors (red to greenish blue, λ_{max} = 469–620 nm in ethanol) except the yellow shade area [9]. Recently, we have suggested arylazopyridone disperse dyes for yellow colors because they have good spectral and dyeing properties [12]. The use of heterocyclic coupling components 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 [13–24]. Pyridones and pyrazolones as coupling components have been shown to be especially important colorants for yellow to orange dyes in industrial applications [25].

In this present study, the synthesis of heteroarylazopyrazolone disperse dyes containing fluorosulfonyl groups is reported. Pyrazolone derivatives (**1,** 1-alkyl-3-methyl-5-pyrazolone) were used

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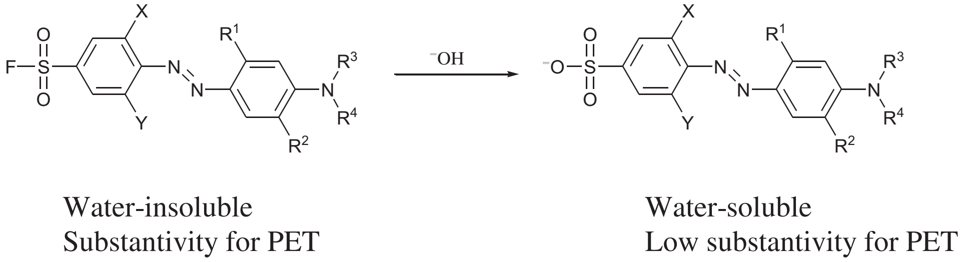


Scheme 1. Alkali hydrolysis of 4-amino-4′-fluorosulfonylazobenzene disperse dyes.

as coupling components. The thermal and spectral properties of heteroarylazopyrazolone disperse dyes containing fluorosulfonyl groups and their nitro-substituted analogs have also been investigated for comparison.

2. Experimental

2.1. General

N-Acetylsulfanilyl chloride, *p*-dioxane, ethylcyanoacetate, ethylacetoacetate, ammonium hydroxide, piperidine, methylamine, ethylamine, propionic acid, and nitrosylsulfuric acid were purchased from Aldrich and used without further purification. All other chemicals used in the synthesis and characterization were of laboratory-reagent grade.

The ^{1}H NMR spectra were measured in deuterated DMSO using an Avance 500 (Bruker, 500 MHz). Melting points were determined using a DSC 7 Perkin–Elmer Differential Scanning Calorimeter (USA, heating rate 5 °C/min, N_2 gas). The absorption spectra were measured in 1 cm quartz cells on an Agilent 8453 spectrophotometer (USA, HP). All crude products were isolated as solids and purified a combination of column chromatography and recrystallization.

2.2. Synthesis of diazo components (2)

Diazo components **2** were prepared using previously described procedures [9].

2.3. Synthesis of dyes

2.3.1. Diazotization

4-Fluorosulfonylaniline (**2a**) (0.02 mol) was diazotized in conc. hydrochloric acid (35% w/w, 6.9 mL) and water (70 mL) by adding aqueous sodium nitrite solution (2N, 10 mL) at a temperature of 0–5 °C. In the case of 2-nitro-4-fluorosulfonylaniline (**2b**), nitrosylsulfuric acid was used for the diazotization. 3.8 mL of 40wt% nitrosylsulfuric acid in sulfuric acid (0.022 mol) was added to a mixture of diazo component (0.02 mol) in acetic acid/propionic acid (4:1, 50 mL) at 0–5 °C. After 4–5 h, the completion of diazotization was checked by checking for the presence of excess nitrous acid using starch-iodide paper.

2.3.2. Coupling

The prepared diazonium salt (**3**) solution was added to the corresponding coupling component (**1**, 0.02 mol) dispersed in acetone (100 mL) for better homogeneous dispersion (rather than the conventional aqueous system) and the temperature was maintained at 0–5 °C. After 30 min, ice (130 g) was added and the solution was stirred for 2 h then allowed to reach room temperature. After 4–5 h, the pH value of the diazo liquor was adjusted to pH 5–6 by the addition of sodium acetate. The precipitated dye (**4**) was filtered, washed with water, and dried (Scheme 2). The dyes obtained were purified by combination of column chromatography using dichloromethane: hexane (1:10) as eluting solvents and recrystallization from methanol.

4a 95% yield, mp 230.5 °C. ν_{max} (KBr)/cm^{-1} 3300 (NH), 1670 (C=O), 1604 (C=C, aromatic); ^{1}H NMR (DMSO-d_6, 500 MHz, ppm). δ 2.16 (3H, s, pyrazolone-CH_3), 7.84 (2H, d, Ar-H, $J = 8.5$ Hz), 8.12 (2H, d, Ar-H, $J = 9$ Hz), 11.70 (1H, s, pyrazolone-NH), 13.16 (1H, s, NH). Anal. Calcd for $C_{10}H_9FN_4O_3S$: C 42.25, H 3.19, N 19.71, S 11.28; found: C 42.49, H 3.13, N 20.18, S 10.91.

4b 95% yield, mp 163.2 °C. ν_{max} (KBr)/cm^{-1} 1670 (C=O), 1604 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm). δ 2.30 (3H, s, pyrazolone-CH_3), 7.23 (1H, t, PhH of pyrazolone, $J = 7.4$ Hz), 7.46 (2H, t, PhH of pyrazolone, $J = 7.9$ Hz), 7.88 (2H, d, Ar-H, $J = 7.7$ Hz), 7.91 (1H, t, PhH of pyrazolone, $J = 8.9$ Hz), 8.13 (2H, d, Ar-H, $J = 8.95$ Hz), 13.22 (1H, s, NH). Anal. Calcd for $C_{16}H_{13}FN_4O_3S$: C 53.33, H 3.64, N 15.55, S 8.90; found: C 53.61, H 3.73, N 15.65, S 8.95.

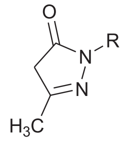
4c 94% yield, mp 205 °C. ν_{max} (KBr)/cm^{-1} 1670 (C=O). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm). δ 2.30 (s, 3H), 7.50 (2H, d, PhH of pyrazolone, $J = 9$ Hz), 7.92 (2H, d, PhH of pyrazolone, $J = 9$ Hz), 7.94 (2H, d, Ar-H, $J = 9$ Hz), 8.14 (2H, d, Ar-H, $J = 9$ Hz), 13.21 (1H, s, NH). Anal. Calcd for $C_{16}H_{12}ClFN_4O_3S$: C 48.67, H 3.06, N 14.19, S 8.12; found: C 48.89, H 3.11, N 14.16, S 8.15.

4d 90% yield, mp 208 °C. ν_{max} (KBr)/cm^{-1} 3310 (NH), 1695 (C=O), 1615 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.22 (3H, s, pyrazolone-CH_3), 8.27 (1H, d, Ar-H, $J = 9.1$ Hz), 8.57 (1H, d, Ar-H, $J = 9$ Hz), 8.94 (1H, s, Ar-H), 11.95 (1H, s, pyrazolone-NH), 14.50 (1H, s, NH). Anal. Calcd for $C_{10}H_8FN_5O_5S$: C 36.48, H 2.45, N 21.27, S 9.74; found: C 37.05, H 2.48, N 20.78, S 9.63.

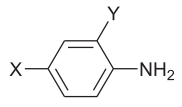
4e 93% yield, mp 180 °C. ν_{max} (KBr)/cm^{-1} 1670 (C=O), 1615 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.30 (3H, s, pyrazolone-CH_3), 7.27 (1H, t, PhH of pyrazolone, $J = 7.5$ Hz), 7.50 (2H, t, PhH of pyrazolone, $J = 7.5$ Hz), 7.89 (2H, d, PhH of pyrazolone, $J = 7.5$ Hz), 8.33 (1H, d, Ar-H, $J = 9.1$ Hz), 8.61 (1H, d, Ar-H, $J = 9.1$ Hz), 8.96 (1H, s, Ar-H), 14.55 (1H, s, NH). Anal. Calcd for $C_{16}H_{12}FN_5O_5S$: C 47.41, H 2.98, N 17.28, S 7.91; found: C 47.61, H 3.06, N 16.78, S 7.51.

4f 95% yield, mp 214 °C. ν_{max} (KBr)/cm^{-1} 1670 (C=O), 1615 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.36 (3H, s, pyrazolone-CH_3), 7.52 (2H, d, PhH of pyrazolone, $J = 7.5$ Hz), 7.92 (2H, d, PhH of pyrazolone, $J = 9$ Hz), 8.29 (1H, d, Ar-H, $J = 9$ Hz), 8.59 (1H, d, Ar-H, $J = 9$ Hz), 8.93 (1H, s, Ar-H), 14.48(1H, s, NH). Anal. Calcd for $C_{16}H_{11}ClFN_5O_5S$: C 43.69, H 2.52, N 15.92, S 7.29; found: C 43.87, H 2.59, N 15.98, S 6.83.

In order to synthesize heteroarylazopyrazolone disperse dyes containing a nitro group (**7**), the same procedure was repeated except that substituted amines containing nitro groups (**5**) were used in place of substituted amines containing fluorosulfonyl groups as diazo components (Scheme 3).

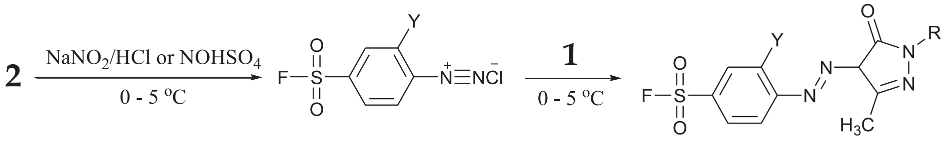


1



2

2a X = FO_2S (Y = H, NO_2)
2b X = NO_2 (Y = H, NO_2)

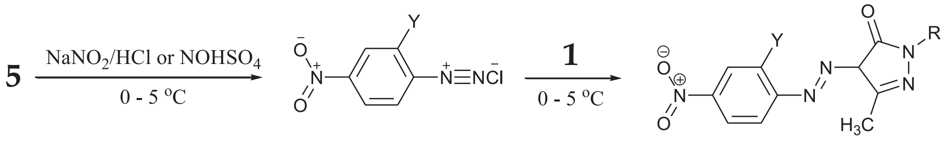


4a Y = H, R=H
4b Y = H, R =Ph
4c Y = H, R =Ph-*p*Cl
4d Y = NO_2, R =H
4e Y = NO_2, R =Ph
4f Y = NO_2, R =Ph-*p*Cl

Scheme 2. Synthesis of heteroarylazopyrazolone disperse dyes containing a fluorosulfonyl group (**4**).

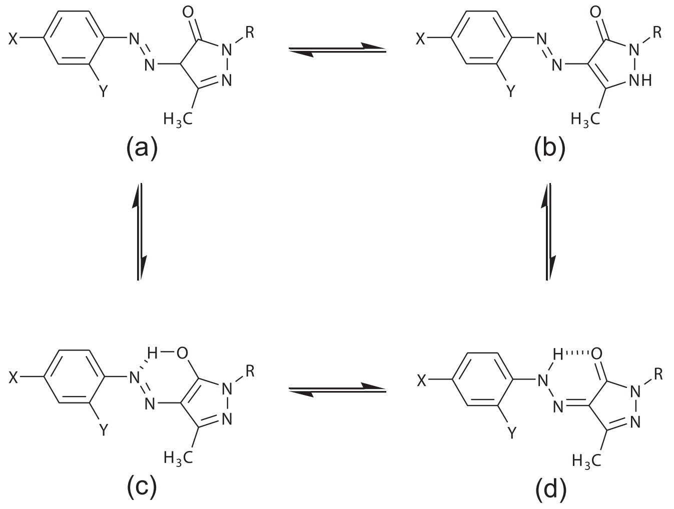
7a 95% yield, mp 269.6 °C. ν_{max} (KBr)/cm^{-1} 3310 (NH), 1676 (C=O). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.16 (3H, s, pyrazolone-CH$_3$), 7.72 (2H, d, Ar-H, J = 9.15 Hz), 8.26 (2H, d, Ar-H, J = 9.15 Hz), 11.69 (1H, s, pyrazolone-NH), 13.16 (1H, s, NH). Anal. Calcd for $C_{10}H_9N_5O_3$: C 48.58, H 3.67, N 28.33; found: C 48.56, H 3.58, N 28.37.

7b 95% yield, mp 199.8 °C. ν_{max} (KBr)/cm^{-1} 1676 (C=O), 1608 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.32 (3H, s,



7a Y = H, R=H
7b Y = H, R =Ph
7c Y = H, R =Ph-*p*Cl
7d Y = NO_2, R =H
7e Y = NO_2, R =Ph
7f Y = NO_2, R =Ph-*p*Cl

Scheme 3. Synthesis of heteroarylazopyrazolone disperse dyes containing a nitro group (**7**).



Scheme 4. The expected tautomers of the synthesized hetarylazo-5-pyrazolone dyes.

pyrazolone-CH_3), 7.22 (1H, t, PhH of pyrazolone, $J = 7.5$ Hz), 7.46 (2H, t, PhH of pyrazolone, $J = 8$ Hz), 7.8 (2H, d, Ar-H, $J = 9$ Hz), 7.89 (2H, d, PhH of pyrazolone, $J = 7.5$ Hz), 8.28 (2H, d, Ar-H, $J = 7$ Hz), 13.22 (1H, s, NH). Anal. Calcd for $C_{16}H_{13}N_5O_3$: C 59.44, H 4.05, N 21.66; found: C 59.37, H 4.02, N 21.74.

7c 95% yield, mp 243.4 °C. ν_{max} (KBr)/cm^{-1} 1676 (C=O), 1608 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.50 (3H, s, pyrazolone-CH_3), 7.53 (2H, d, Ar-H, $J = 9$ Hz), 7.85 (2H, d, PhH of pyrazolone, $J = 9$ Hz), 7.93 (2H, d, PhH of pyrazolone, $J = 9$ Hz), 8.30 (2H, d, Ar-H, $J = 9.5$ Hz), 13.20 (1H, s, NH). Anal. Calcd for $C_{16}H_{12}ClN_5O_3$: C 53.72, H 3.38, N 19.58; found: C 53.66, H 3.28, N 19.56.

7d 90% yield, mp 280 °C. ν_{max} (KBr)/cm^{-1} 3310 (NH), 1690 (C=O), 1615 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.22 (3H, s, pyrazolone-CH_3), 8.26 (1H, d, Ar-H, $J = 9.4$ Hz), 8.58 (1H, d, Ar-H, $J = 9.3$ Hz), 8.92 (1H, s, Ar-H), 11.99 (1H, s, pyrazolone-NH), 14.51 (1H, s, NH). Anal. Calcd for $C_{10}H_8N_6O_5$: C 41.10, H 2.76, N 28.76; found: C 41.00, H 2.71, N 28.75.

7e 92% yield, mp 210 °C. ν_{max} (KBr)/cm^{-1} 1676 (C=O), 1608 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.20 (3H, s, pyrazolone-CH_3), 7.26 (1H, t, PhH of pyrazolone, $J = 7.2$ Hz), 7.50 (2H, t, PhH of pyrazolone, $J = 8.1$ Hz), 7.90 (1H, d, Ar-H, $J = 7.8$ Hz), 8.14 (2H, d, PhH of pyrazolone, $J = 9$ Hz), 8.47 (1H, d, Ar-H, $J = 8.1$ Hz), 8.80 (1H, s, Ar-H), 14.55 (1H, s, NH). Anal. Calcd for $C_{16}H_{12}N_6O_5$: C 52.18, H 3.28, N 22.82; found: C 52.14, H 3.25, N 22.80.

7f 94% yield, mp 250 °C. ν_{max} (KBr)/cm^{-1} 1676 (C=O), 1608 (C=C, aromatic). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 2.35 (3H, s, pyrazolone-CH_3), 7.51 (2H, d, PhH of pyrazolone, $J = 9$ Hz), 7.9 (2H, d, PhH of pyrazolone, $J = 8.7$ Hz), 8.12 (1H, d, Ar-H, $J = 9.3$ Hz), 8.41 (1H, d, Ar-H, $J = 9.3$ Hz), 8.79 (1H, s, Ar-H), 14.48(1H, s, NH). Anal. Calcd for $C_{16}H_{11}ClN_6O_5$: C 47.71, H 2.75, N 20.87; found: C 47.81, H 2.74, N 20.76.

3. Results and discussion

3.1. Characterization

The hetarylazopyrazolone dyes **4** and **7** were prepared by coupling pyrazolone derivatives (**1**) with diazotized fluorosulfonylanilines, and their structures have been confirmed by ^{1}H NMR and FT-IR spectral data.

The dyes may exist in four possible tautomeric forms, namely two azo-keto forms (a) and (b), the azo-enol form (c), and the hydrazone-keto form (d), as shown in Scheme 4. The deprotonation of the four tautomers leads to a common anion [26]. Numerous investigations have been carried out to establish the tautomeric structures of arylazo-5-pyrazolones, both in the solid state and in solution, and a variety of spectroscopic techniques have been used. The spectral data generally lead to the conclusion that the tautomeric equilibrium of the phenylazopyrazolone dyes is in favor of the hydrazone form (d) in the solid state and in polar solvents (Scheme 4) [21,27–33]. In this study, the hydrogen-bonded NH group at the β-nitrogen appeared at 13.16–14.55 ppm in the ^{1}H NMR spectra of the dyes, which confirms that the dyes prepared exist in the hydrazone form.

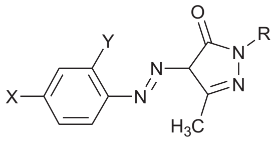
3.2. Thermal properties

Although several dyes, such as dyes **4d**, **4e**, **4f**, **7d, 7e**, and **7f**, decomposed before they reached their melting points, all of the synthesized dyes exhibited higher melting points than 4-aminoazobenzene dyes (Table 1) [9]. These properties can be attributed to intramolecular hydrogen bonds; the hydrogen atom in the hydrazone group and the carbonyl oxygen in the pyrazolone ring take part in intramolecular hydrogen bonding, which holds the molecule in a more or less planar configuration, and van der Waals forces help to achieve compact packing of the molecules.

While the relative values of the melting points cannot be easily explained in detail due to their complex dependence on a number of factors, a few general trends can be accounted for. It is well known that the thermal properties in a given series of dyes is related roughly to their molecular weights; dyes having higher molecular weight showed higher melting points because more van der Waals attractions are possible for the larger molecules, due to the higher surface area over which these forces can operate. It is also presumed that the more polar dyes, which contain more powerful electron-withdrawing groups, tend to have better thermal stability because of the increased polarizability and dipole interactions; the 4-nitro-substituted dyes (**7**) generally exhibited higher thermal stability than the 4-fluorosulfonyl-substituted dyes (**4**), and the 2-nitro-4-fluoro(or nitro)-substituted dyes (**4d**, **4e**, **4f**, **7d, 7e**, and **7f**) showed higher thermal stability than the 4-fluorosulfonyl(or nitro)-substituted dyes (**4a**, **4b**, **4c**, **7a, 7b**, and **7c**).

Compounds **4a**, **4d**, **7a,** and **7d** tend to have even higher melting points than the others because of the formation of intermolecular

Table 1
Yields and melting points of the dyes **4** and **7**.



Dye	X	Y	R	M.W.	Appearance
4a	SO_2F	H	H	284.27	Yellow
4b	SO_2F	H	Ph	360.36	Orange-yellow
4c	SO_2F	H	Ph-*p*Cl	394.81	Orange-yellow
4d	SO_2F	NO_2	H	329.26	Yellow
4e	SO_2F	NO_2	Ph	405.36	Orange-yellow
4f	SO_2F	NO_2	Ph-*p*Cl	439.81	Orange-yellow
7a	NO_2	H	H	247.21	Yellow
7b	NO_2	H	Ph	323.31	Orange-yellow
7c	NO_2	H	Ph-*p*Cl	357.75	Orange-yellow
7d	NO_2	NO_2	H	292.21	Yellow
7e	NO_2	NO_2	Ph	368.30	Orange-yellow
7f	NO_2	NO_2	Ph-*p*Cl	402.75	Orange-yellow

hydrogen bonds (Fig. 1) [34]. They are stereochemically able to have not only intramolecular hydrogen bonds but also intermolecular hydrogen bonding between adjacent molecules, whereas the other dyes (**4b**, **4c**, **4e**, **4f**, **7b**, **7c**, **7e,** and **7f**) have only intramolecular hydrogen bonding.

3.3. *Spectral properties*

3.3.1. *Absorption spectra*

Details of the visible absorption spectra of pyrazolone-based heteroarylazo disperse dyes containing fluorosulfonyl groups and their nitro analogs are summarized in Table 2. The synthesized dyes developed a color ranging from yellow to orange-yellow (354–410 nm in ethanol).

Absorption maxima (λ_{max}) values tend to be related to the strength of the electronic withdrawing or donating power in the benzenoid system [35]. Since the electronic transitions in these compounds involves a general migration of electron density from the donor group toward the azo group, the greatest effect in terms of longer wavelength is achieved by placing the substituents in the positions *ortho* or *para* to the azo group for effective conjugation [36,37].

The 4-fluorosulfonyl-substituted derivatives absorb maximally at shorter wavelengths, by 12–63 nm in ethanol, than the 4-nitro-substituted analogs, although the Hammett constant for *p*-fluorosulfonyl substitution (0.91) is greater compared to *p*-nitro substitution (0.78). However, this result is consistent with that of previous research [7,12].

The introduction of an electron-accepting substituent into the diazo component ring produced a bathochromic shift; the λ_{max} values of 2-nitro-4-fluorosulfonyl substituted azo dyes showed larger bathochromic shifts than those of 4-fluorosulfonyl substituted azo dyes by 4–11 nm in ethanol. However, the introduction of a 2-nitro group into diazo components containing 3-methyl-1H-pyrazol-5(4H)-one (**4a** vs. **4d** and **7a** vs. **7d**) does not show any remarkable inductive effects, probably because of a steric effect between nitro groups and β-nitrogen atom in azo group, as shown in conformation (a) (Fig. 2); such crowding can be relieved by rotation into conformation (b), so that a single substituent will not normally exert much of steric effect. However, when the hydrazone form is predominant over the azo form, both conformations are hindered and non-planarity is the likely outcome [38].

It is well known that, as a rule of thumb, the molar extinction coefficient (ε_{max}) increases as λ_{max} increases. For the series of synthesized dyes, ε_{max} values tend to increase with increasing electron-withdrawing capacity in the acceptor ring; the 4-nitro-substituted dyes had a higher λ_{max}, while the 4-fluorosulfonyl-substituted analogs showed higher ε_{max} values. However, the introduction of a nitro group at the 2- position of 4-nitro- or 4-fluorosulfonyl-substituted arylazo dyes caused a decrease in the extinction coefficient, probably because the steric hindrance effect is dominant over the inductive effect.

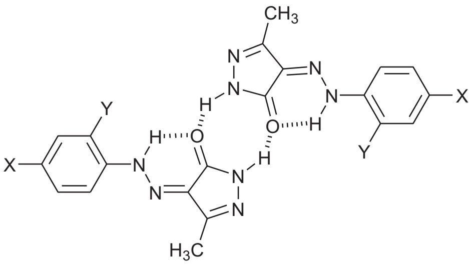


Fig. 1. Inter- and intra-molecular hydrogen bonding of heteroarylazo dye molecules containing 3-methyl-1H-pyrazol-5(4H)-one (**4a**, **4d**, **7a,** and **7d**).

Table 2
Spectral data of dyes **4** and **7** in EtOH.

Dye	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})	$\Delta\lambda_{1/2}$(nm)
4a	354	18,000	126
4b	382	26,000	86
4c	386	26,000	88
4d	346	11,000	139
4e	393	11,000	>130
4f	393	13,000	>130
7a	410	23,000	114
7b	399	31,000	77
7c	401	29,000	79
7d	409	20,000	114
7e	405	10,000	143
7f	405	11,000	132

Half-band widths ($\Delta\lambda_{1/2}$) of the absorption bands in ethanol were also determined (Table 2). In addition to the effect on λ_{max}, substituents also caused a change in the half-band width values. The value of $\Delta\lambda_{1/2}$ is a convenient criterion for the evaluation of the hue brightness of dyes; dyes with low $\Delta\lambda_{1/2}$ show bright hues while those with high values of $\Delta\lambda_{1/2}$ show dull hues. The higher $\Delta\lambda_{1/2}$ values are shown by the 2,4-dinitro derivatives (**7d**, **7e,** and **7f**) or 2-nitro-4-fluorosulfonyl derivatives (**4d**, **4e,** and **4f**), which is caused as a result of the broadening the range of energy levels of the orbitals involved in the transitions associated with light absorption.

3.3.2. *Halochromic effects*

Protonation of a substituted pyrazolone derivative gives azonium tautomers (Scheme 5), which provide a red-shifted absorption band and more intense colors than the parent dyes. Compared to the neutral dye, the ground and excited states in the azonium species are much closer together in energy, so a bathochromic shift of the first absorption band is observed on protonation, which is termed positive halochromism [39,40].

The direction of charge migration that accompanies electronic excitation in the azonium form is opposite that found in the neutral dye, and this difference suggests that substituents in the diazo component or coupling component should have opposite effects in neutral and in protonated dyes. Indeed, it can be seen that the bathochromic shift decreases steadily with the general electron-withdrawing capacity of the substituents in the diazo component ring and with the general electron-donating capacity of the substituents in the coupling component ring, and it in fact becomes negligible when two powerful electron acceptor groups (2,4-dinitro or 2-fluorosulfonyl-4-nitro) are present in the diazo component ring (Table 3). Most synthesized dyes containing two electron-withdrawing groups in the diazo component ring and/or electron-donating groups in the coupling component ring showed less positive halochromism due to the strong electronic effect, while dyes containing just one electron-accepting group in the diazo component and less powerful electron-donating groups in the coupling component ring (**4a** and **7a**) showed more positive

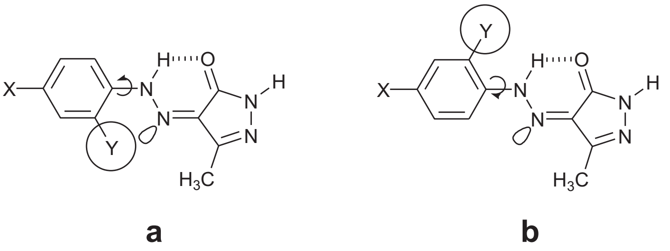
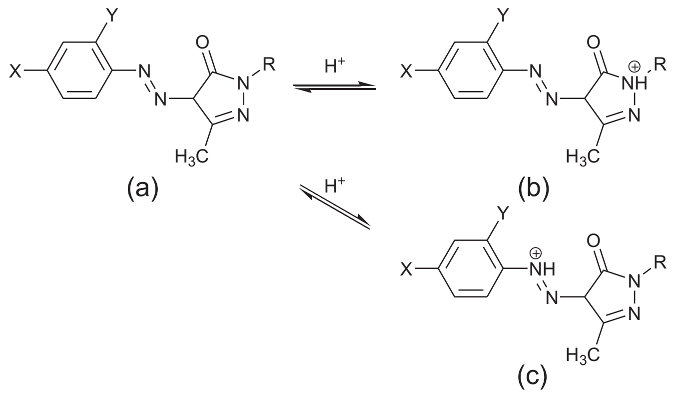


Fig. 2. Alternative conformations for an *ortho*-substituted pyrazolone azobenzene dyes.



Scheme 5. Protonation equilibrium of pyrazolone azo benzene dyes; (a) neutral dye (b) ammonium tautomer (c) azonium tautomer.

Table 4
Solvatochromic effects of the dyes **4** and **7**.

Dye	λ_{max} (nm) (Cyclohexane)	$\Delta\lambda^a$ (nm)	λ_{max} (nm) (Toluene)	$\Delta\lambda^b$ (nm)	λ_{max} (nm) (Ethanol)	$\Delta\lambda^c$ (nm)	λ_{max} (nm) (DMF)
4a	357	+27	384	−30	354	+132	486
4b	381	+7	388	−6	382	+101	483
4c	384	+6	390	−4	386	+91	476
4d	359	−9	350	−4	346	+153	499
4e	384	+12	396	−3	393	+102	495
4f	385	+15	400	−7	393	+103	496
7a	405	+7	412	−2	410	+143	553
7b	396	+7	403	−4	399	+139	538
7c	398	+6	404	−2	402	+131	533
7d	398	+18	416	−7	409	+142	551
7e	393	+21	414	−9	405	+136	541
7f	398	+18	416	−10	406	+133	539

$\Delta\lambda^a = \lambda_{max}$ (Toluene)−λ_{max} (CycloHexane); $\Delta\lambda^b = \lambda_{max}$ (Ethanol)−λ_{max} (Toluene); $\Delta\lambda^c = \lambda_{max}$ (DMF)−λ_{max} (Ethanol).

halochromism. In the case of dyes **4a** and **7a**, the easier protonation of 3-methyl-1H-pyrazol-5(4H)-one derivatives produced more positive halochromism than the other dyes.

3.3.3. Solvatochromic effects

Generally, in many dye molecules, the ground state is less polar than the excited state, so a polar solvent tends to stabilize the excited state more than the ground state. This leads to a bathochromic shift in the absorption maximum, which is termed positive solvatochromism. The interaction of a solvent with a dye molecule is greater in polar solvents, for example DMF, and it is most pronounced with a solute molecule that contains a permanent dipole. It seems highly likely that the dyes have ionized in this solvent, becoming anionic and it is not unusual for dyes in a hydrazone form to behave in this way in a basic aprotic solvent such as DMF. As the difference between the polarity of the ground and excited states is increased by the successive introduction of stronger electron-withdrawing groups into the diazo component ring of heteroarylazo disperse dyes, more marked positive solvatochromism is observed [36].

The spectral characterization of the dyes was evaluated with respect to visible absorption properties in various solvents, and the solvatochromic effects of dyes **4** and **7** are shown in Table 4. It is clear that most synthesized dyes exhibit positive solvatochromism in accordance with most donor–acceptor chromogens, so the absorption bands of the dyes move toward longer wavelengths as the polarity of the solvent increases. For example, the introduction of stronger electron acceptors into the diazo component ring led to greater differences between the λ_{max} values for their cyclohexane and DMF solutions. As the electron-withdrawing groups are introduced, the gap between the polarity of the ground and excited state grows; the amount of stabilization of the excited state relative to the ground state with increasing solvent polarity is raised, and thus the solvatochromism becomes more marked.

Table 3
Halochromic effects of the dyes **4** and **7**.

Dye	λ_{max} (nm) (EtOH)	λ_{max} (nm) (HCl/EtOH)	$\Delta\lambda$ (nm)
4a	354	403	+49
4b	382	384	+2
4c	385	386	+1
4d	346	347	+1
4e	393	395	+2
4f	393	399	+6
7a	408	418	+10
7b	398	403	+5
7c	402	404	+2
7d	409	415	+6
7e	411	413	+2
7f	412	413	+1

However, in a few cases, negative solvatochromism between ethanol and cyclohexane was observed within the general positive trend; for example, dyes **4a** and **4d**, which contain 3-methyl-1H-pyrazol-5(4H)-one in the coupling component ring and a 4-fluorosulfonyl group in the diazo component ring. Most of their ethanol solutions were slightly hypsochromically shifted compared to those in toluene, although they showed overall positive shifts between cyclohexane and ethanol (Table 4). Solvent polarity factors are, therefore, more limited in heteroarylazo disperse dyes containing a 3-methyl-1H-pyrazol-5(4H)-one; intramolecular hydrogen bonding between the hydroxyl group at the pyrazolone and azo nitrogen atoms and/or fluoro atoms in these dyes appears to be the dominant influence. Also, the relatively hypsochromic shifts in ethanol, compared with the less polar toluene, strongly indicate the existence of intermolecular hydrogen bonding between the dye molecules and the ethanol. Thus, the resultant stabilization of the ground state by these two kinds of hydrogen-bonding contribution could account for the hypsochromic shifts because the energy difference (ΔE) for the transition is increased.

4. Conclusions

In this study, a series of arylazopyrazolone disperse dyes containing fluorosulfonyl groups in their structures were prepared from the coupling reaction between pyrazolone couplers and 4-fluorosulfonylanilines, and their thermal and spectral properties were investigated and compared.

The fluorosulfonyl-substituted derivatives developed yellow to orange-yellow colors that are hypsochromically shifted compared with nitro-substituted analogs. The trends in the half-band width and the molar extinction coefficient values of the synthesized dyes can be explained by the mesomeric effect and by inductive effects of the substituents.

Most of the dyes show relatively high melting points for their class that could be due to intramolecular hydrogen bonds, because they hold the dye molecules in a plane configuration and van der Waals forces help to achieve compact packing of the molecules. The dyes that have not only intramolecular hydrogen bonding but also intermolecular hydrogen bonding between adjacent molecules showed higher melting points than those having only intramolecular hydrogen bonding. The more polar dyes that contain more powerful electron-withdrawing groups tend to have higher melting properties because of the increased polarizability and dipole interactions; the 4-nitro-substituted dyes generally exhibited higher melting points than the 4-fluorosulfonyl-substituted dyes and the 2-nitro-4-fluorosulfonyl(or nitro)-substituted dyes showed higher melting points than the 4-fluorosulfonyl(or nitro)-substituted dyes.

The substituents of the synthesized dyes affect the halochromism and solvatochromism to an extent that depends upon their electron-accepting power. The synthesized dyes generally exhibited positive halochromism and positive solvatochromism, so the absorption bands of the dyes moved toward longer wavelengths as the acidity or polarity of the solvent increased. However, in a few cases, negative solvatochromism was observed within the general positive trend, such as in the dyes containing a hydroxyl substituent at the pyrazolone unit; this feature has been attributed to intramolecular hydrogen bonding.

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