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Synthesis and spectral properties of alkali-clearable azo disperse dyes containing a fluorosulfonyl group

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Abstract

A series of alkali-clearable azo disperse dyes containing a fluorosulfonyl group in their structures were synthesised. Various 4-fluorosulfonylanilines which were used as diazo components were prepared from *N*-acetylsulfanilyl chloride and coupled with corresponding coupling components to give 4-(*N,N*-diethylamino)-4′-fluorosulfonylazo benzene dyes. Depending on the various substituents present in the diazo component, absorption maxima varied from 469 to 620 nm in ethanol. The spectral properties of the synthesized dyes were examined with respect to the effects of substituents in absorption spectra, halochromism and solvatochromism. Thus, the appropriate Hammett substituent constants could be related to the observed absorption spectra and halochromism of the dyes prepared. In particular, the differences in dipole moments calculated by using computational method gave reliable predictions of solvatochromic effects.

Keywords: Alkali-clearable azo disperse dye; Fluorosulfonyl group; Halochromism; Solvatochromism; Hammett substituent constants; Dipole moments

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1. Introduction

The demand for environmentally friendly dyes of high wet fastness on polyester is increasing. In addition, there are rising global legislative pressures to reduce the impact of dyeing processes on the environment through reductions in effluent discharge as well as in the use of energy and materials. Alkali-clearable disperse dyes offer a means of tackling both of these challenges simultaneously [1]. These so-called alkali-clearable disperse dyes obviated the need for sodium hydrosulfite and significantly reduced the cost of effluent treatment.

In previous work, we suggested novel alkali-clearable azo disperse dyes containing a sulfonyl fluoride group. Azo disperse dyes containing a fluorosulfonyl group are hydrolysed under alkaline condition by S_N2 mechanism, and pseudofirst-order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC [2] (Scheme 1). Also, the use of a fluorosulfonyl containing disperse dye showed a reasonable level of build up, excellent wash fastness and offers the option of alkali clearance to achieve high wash fastness, replacing reductive clearing

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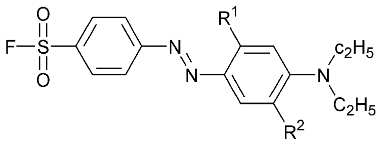

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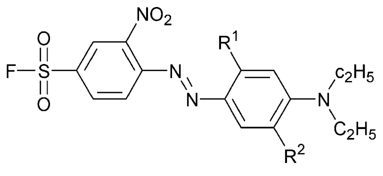

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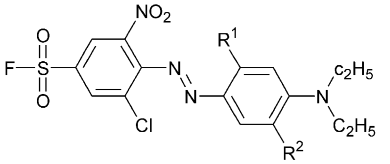

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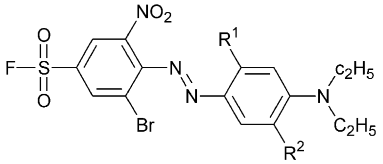

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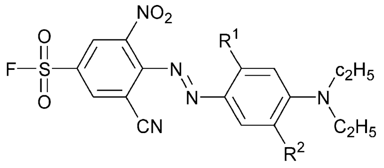

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R^1 = H, NHAc, R^2 = H, OMe

and particularly sodium hydrosulfite, which places a very high BOD on conventional disperse dyeing effluent and the generates aromatic amines.

In this study, we reported the synthesis of some diazo components and the subsequent monoazo disperse dyes containing a fluorosulfonyl group, 4-(*N,N*-diethylamino)-4′-fluorosulfonylazobenzene derivatives (**1**–**5**) as well as the spectral properties of the various dyes prepared.

2. Experimental

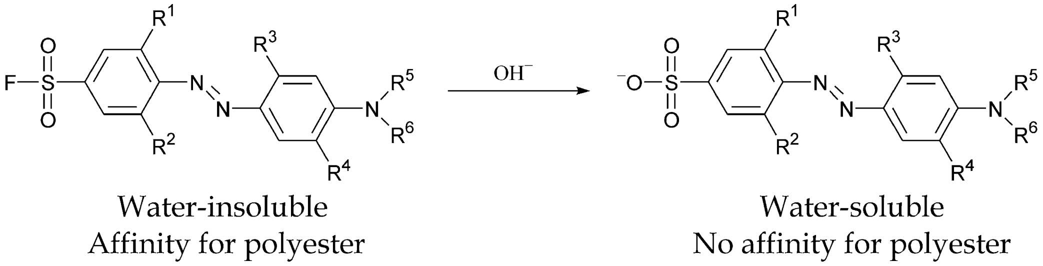
2.1. General information

The ^{1}H-NMR spectra were obtained with a Jeol JNM-FX 200 at 200 MHz for solutions in an appropriate deuterated solvent. Elemental analyses were carried out on a LECO CHNS-932 for C, H, N and S.

Melting points were determined using a DSC 7, Perkin-Elmer (USA) Differential Scanning Calorimetry (heating rate 5 °C/min, N_2 gas). The absorption spectra were measured in 1 cm quartz cells on UVIKON 860 spectrophotometer (USA, KONTRON, scan speed 250 nm/min).

All the chemicals used in the synthesis and characterisation were of laboratory-reagent grade. All crude products were isolated as solids and purified by a combination of column chromatography and recrystallization.

The dipole moments of the ground state and first excited states were computed and the differences in dipole moment between two states were calculated in order to predict the solvatochromic effects of synthesized dyes. The 'HyperChem Pro 5.1' software package was used in order to optimise the geometry of the dye structure by using molecular mechanical methods, conducting the iterative energy-minimizing routines with the steepest descent and Polak–Ribiere algorithms. The semi-empirical methods were also examined with respect to geometry optimisation, but were found to be no more satisfactory than the molecular mechanical methods. The optimised geometrical structures of dyes were used in an



Scheme 1. Alkali-hydrolysis of azo disperse dyes containing a fluorosulfonyl group.

attempt to quantify the dipole moments by using 'MOPAC' application in 'CS Chem3D Pro' software package. MOPAC is a molecular computation application that features a number of widely-used, semi-empirical methods.

2.2. Synthesis of diazo components (Scheme 2)

2.2.1. 4-Fluorosulfonylaniline (**8**)

N-Acetylsulfanilyl chloride (**6**, 60.0 g) was stirred into a solution of KF (89.5 g) in 120 ml of water and 120 ml of *p*-dioxane for 3 h under reflux, then drowned onto ice, washed with warm tap water (pH 4–5) and the precipitate (**7**, *N*-acetylsufanilyl fluoride) was collected. This precipitate was refluxed in the mixture of ethanol (50.0 ml) and conc. HCl (50.0 ml) for 1 h then drowned onto ice, and filtered, giving white powder (**8**, 4-fluorosulfonylaniline). 23.9 g (53.2%), m.p. 69 °C. ^{1}H-NMR (d_6-DMSO): δ 3.2 (2H, s, Ar–NH$_2$), 6.7 (2H, d, ArH), 7.6 (2H, d, ArH), Elemental analysis: found C, 41.01; H, 3.44; N, 7.89; S, 18.20% ($C_6H_6FNO_2S$ requires C, 41.14; H, 3.45; N, 8.00; S, 18.30%).

2.2.2. 2-Nitro-4-fluorosulfonylaniline (**10**)

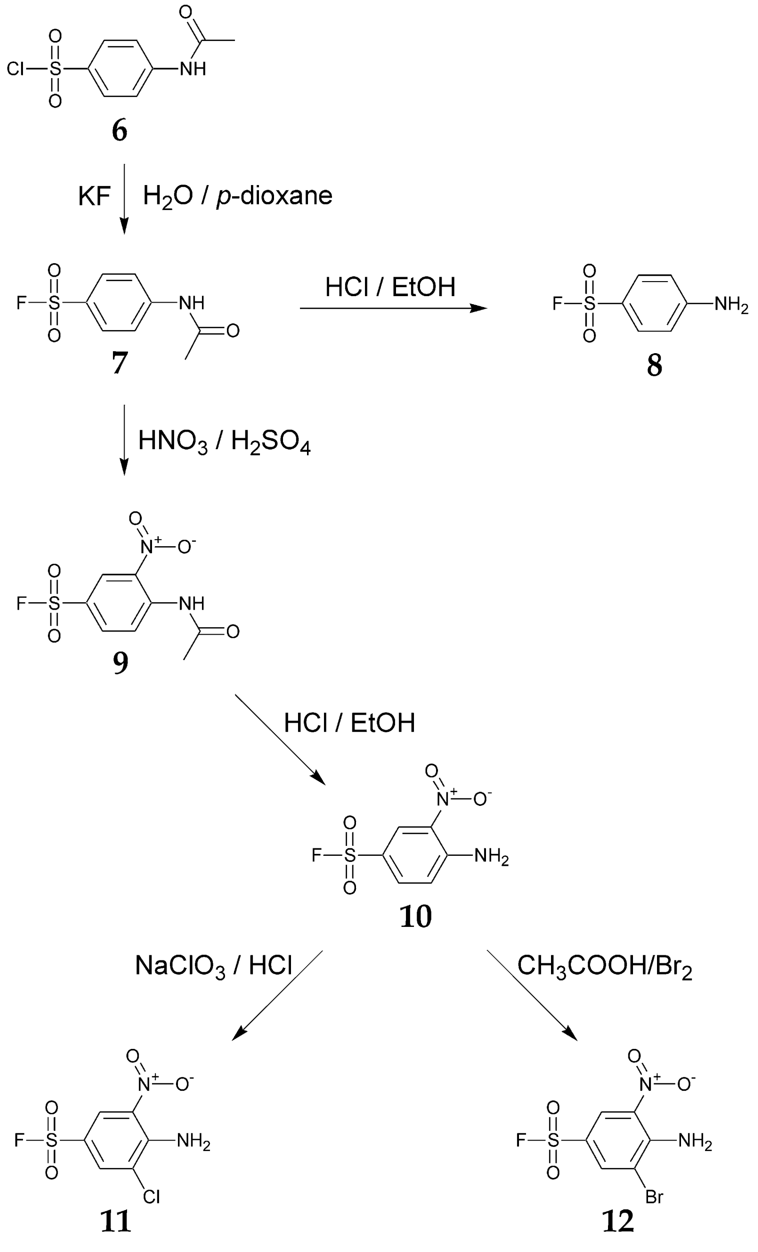
N-Acetylsufanilyl fluoride (**7**, 21.7 g) was dissolved in concentrated sulphuric acid (120 ml), cooled to 4 °C and a mixture of 70.0% nitric acid (12.7 ml) and conc. sulphuric acid (14.0 ml) added dropwise maintaining the temperature at 4–6 °C. After 1 h the reaction mixture was drowned onto ice. The precipitate (**9**, *N*-acetyl-2-nitrosulfanilyl fluoride) was isolated by filtration, washed with water, and dried at 50 °C. This solid was dispersed in the mixture of conc. HCl/EtOH (50.0 ml/50.0 ml) solution and refluxed for 1 h and drowned onto ice. The precipitate (**10**, 2-nitro-4-fluorosulfonylaniline) was isolated by filtration, washed with water, and dried at 50 °C. This product was purified by crystallization from ethanol, giving yellow needle. 9.60 g (43.6%), m.p. 151.7 °C. ^{1}H-NMR (d_6-DMSO): δ 3.3 (2H, s, Ar-NH$_2$), 7.2 (1H, d, ArH), 7.9 (1H, d, ArH), 8.6 (1H, d, ArH). Elemental analysis: found C, 33.13; H, 2.13; N, 12.13; S, 14.26% ($C_6H_5FN_2O_4S$ requires C, 32.73; H, 2.29; N, 12.72; S, 14.56%).

2.2.3. 2-Nitro-4-fluorosulfonyl-6-chloroaniline (**11**)

2-Nitro-4-flurosulfonylaniline (**10**, 10.0 g) was dispersed in conc. HCl (51.0 ml), cooled to 0–5 °C, and a sodium chlorate (5.85 g) dissolved in water (8.0 ml) added dropwise ensuring maintaining the temperature at 0–5 °C. This reaction mixture was left to stir at room temperature. After 16 h reaction mixture was drowned onto ice and precipitate (**11**, 2-nitro-4-fluorosulfonyl-6-chloroanilne) was collected, washed with water and dried at room temperature, giving pale yellow powder. 10.75 g (93.0%), m.p. 132.5 °C. ^{1}H-NMR (d_6-DMSO): δ 3.4 (2H, s, Ar–NH$_2$), 8.3 (1H, d, ArH), 8.6 (1H, d, ArH). Elemental analysis: found C, 28.91; H, 1.33; N, 10.23; S, 12.55% ($C_6H_4ClFN_2O_4S$ requires C, 28.30; H, 1.58; N, 11.00; S, 12.59%).

2.2.4. 2-Nitro-4-fluorosulfonyl-6-bromoaniline (**12**)

2-Nitro-4-flurosulfonylaniline (**10**, 10.0 g) was dispersed in glacial acetic acid (100 ml) and bromine (2.8 ml) was added. Reaction mixture was warmed to 75 °C for 2 h then drowned onto ice and the precipitate (**12**, 2-nitro-4-fluorosulfonyl-6-bromoaniline) was collected, filtered, washed with water and dried at 50 °C, giving yellow solid. 12.8



Scheme 2. Overall schemes of diazo components synthesis.

g (94.3%), m.p. 123.8 °C. ^{1}H-NMR (d_6-DMSO): δ 3.4 (2H, s, Ar–NH_2), 8.4 (1H, d, ArH), 8.6 (1H, d, ArH). Elemental analysis: found C, 23.89; H, 1.31; N, 9.10; S, 10.62% ($C_6H_4BrFN_2O_4S$ requires C, 24.10; H, 1.35; N, 9.37; S, 10.72%).

The overall schemes of diazo components synthesis are given in Scheme 2.

2.3. Synthesis of dyes

2.3.1. Diazotization

$NaNO_2$/HCl solution was used for the diazotization of 4-fluorosulfonylaniline. The 0.02 mol of 4-fluorosulfonylaniline (**8**) was diazotized in 6.9 ml of conc. HCl and 70.0 ml of water, by adding

0.020 mol of $NaNO_2$ at a temperature of 0–5 °C. After 4–5 h the completion of diazotization was checked using a solution of 4-(*N*,*N*-dimethylamino) benzaldehyde and the pH value of the diazo liquor was then adjusted to pH 5–6 by adding sodium acetate.

In the case of the substituted fluorosulfonylanilines (**10**–**12**), nitrosylsulfuric acid was used for the diazotization. Nitrosylsulphuric acid (3.8 ml) was added to a mixture of diazo component (0.020 mol) in acetic acid/propionic acid (4:1, 50.0 ml) at 0–5 °C. After 4–5 h, the completion of diazotization was checked using a solution of 4-(*N*,*N*-dimethylamino) benzaldehyde.

2.3.2. Coupling procedure

The 0.020 mol of diazonium liquor was added to a solution containing 0.020 mol of coupling component, 100 ml of methanol, and 100 g of ice. After 4–5 h, completion of coupling was checked by 10.0% H-acid solution, and the pH value of the diazo liquor was then adjusted to pH 5–6 by adding sodium acetate. The precipitated dyes (**1**–**4**) were filtered, washed with water and dried. The dyes were purified by crystallization from methanol.

2.3.3. Cyanodehalogenation

Dye **4** (4.0 mmol) was stirred at 90 °C with CuCN (4.8 mmol) and DMF (20.0 ml) for 3 h. The reaction mixture was drowned onto ice and the precipitate collected was washed with water and suction dried. The filter cake was slurried in dichloromethane, filtered and the filtrate was evaporated to give solid dye (**5**) (Scheme 3). The dyes were purified by crystallization and/or gravity column chromatography.

The yields and melting points of the synthesized 4-(*N*,*N*-diethylamino)-4′-fluorosulfonyl azobenzene dyes (**1**–**5**) are given in Table 1.

3. Results and discussion

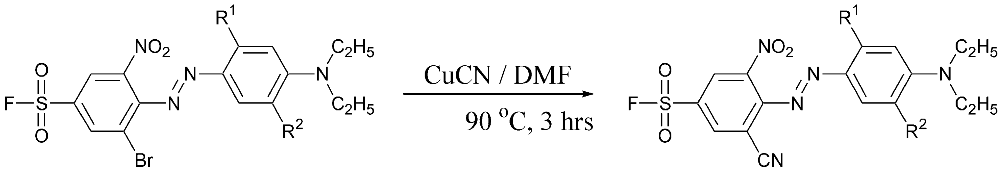
3.1. Synthesis of dye intermediates and dyes

The diazo components (**8**, **10**–**12**) for the synthesis of azo disperse dyes containing a fluorosulfonyl group were prepared (Scheme 2).

The fluorination of *N*-acetylsulfanilyl chloride (**6**) was carried out prior to all the other reactions, such as nitration, chlorination, bromination and deacetylation since the chlorosulfonyl group is very unstable under these reaction conditions. Also, 4-fluorosulfonyl aniline (**7**) was nitrated to *N*-acetyl-2-nitrosulfanilyl fluoride (**9**) and then deacetylated to 2-nitro-4-fluorosulfonylaniline (**10**) since the terminal amino group could be attacked by nitrionium ion (NO_2^+) during nitration reaction if the nitration is followed by deacetylation. Prolonged treatment with the nitrating mixture resulted in a lowering of the yield and purity of the product by forming by-products; it is advisable, therefore, to remove the product immediately after the nitration is complete.

The deacetylation of *N*-acetylsufanilyl fluoride (**7**) and *N*-acetyl-2-nitrosulfanilyl fluoride (**9**) was carried out under weak acidic condition since the fluorosulfonyl group is susceptible to alkali hydrolysis even around the neutral pH at high temperature.

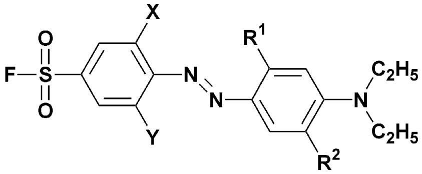
The majority of dyes synthesized were found to contain only very small amounts of impurities and purification was carried out through recrystallization. However, several dyes such as the dyes **5a**, **5b** and **5c** were found to contain somewhat large amounts non-reacted starting material of similar R_f values to the dye that could not be removed by recrystallization, necessitating the use of column chromatography. All column chromatography was carried out at atmospheric pressure; a slower



4 **5**

Scheme 3. Cyanodehalogenation reaction.

Table 1
Yields and melting points of the dyes **1**–**5**



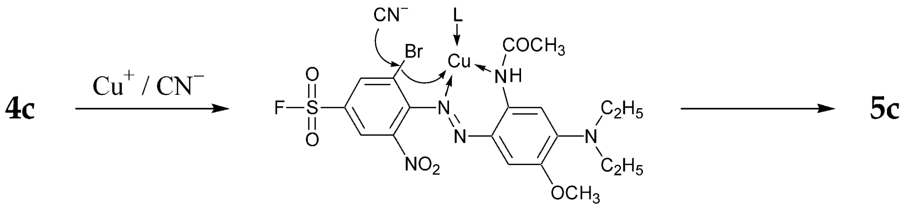
Dye	X	Y	R^1	R^2	Yield (%)	m.p. (°C)	Appearance
1a	H	H	H	H	97.6	150.1	Scarlet solid
1b	H	H	CH_3	H	86.8	117.0	Shiny purple crystal
1c	H	H	$NHCOCH_3$	OCH_3	54.3	118.5	Greenish brown solid
2a	NO_2	H	H	H	62.7	146.3	Greenish brown solid
2b	NO_2	H	CH_3	H	84.1	142.8	Shiny green solid
2c	NO_2	H	$NHCOCH_3$	OCH_3	38.7	(204.3)[a]	Dark green solid
3a	NO_2	Cl	H	H	44.6	198.5	Shiny purple solid
3b	NO_2	Cl	CH_3	H	50.4	163.0	Shiny violet solid
3c	NO_2	Cl	$NHCOCH_3$	OCH_3	32.6	174.2	Green solid
4a	NO_2	Br	H	H	58.9	(199.8) [a]	Shiny purple solid
4b	NO_2	Br	CH_3	H	63.2	146.3	Violet solid
4c	NO_2	Br	$NHCOCH_3$	OCH_3	33.9	(198.6) [a]	Green solid
5a	NO_2	CN	H	H	28.4	(203.7) [a]	Violet solid
5b	NO_2	CN	CH_3	H	31.1	213.0	Greenish blue solid
5c	NO_2	CN	$NHCOCH_3$	OCH_3	30.2	(267.0) [a]	Dark green crystal

[a] Decomposition temperatures before melting points.

elution rate proved to be the only successful means of eliminating such impurities. Dye purity was confirmed by DSC.

The reaction of aromatic halides with CuCN in DMF (Scheme 3) was originally studied by Friedman [3]. The mechanism of copper assisted nucleophilic substitution reaction has also been explored by Lindely [4]. The reaction of *ortho*-bromo azo disperse dyes with cuprous cyanide usually takes place in aprotic polar solvents such as DMF or DMSO. The dye forms a complex with Cu (I), which helps the nucleophilic substitution of Br by CN. Most copper catalysed nucleophilic substitutions take place in relatively severe conditions. However, if the reactant has an appropriate structure and can provide ligand for the formation of the cuprous complexes, the reaction can take place in a mild condition. It is well established that for halogenated azo disperse dyes, forming the cuprous complex is the crucial step for the cyanodehalogenation reaction [5]. In line with this, it was found that the cyanodehalogenation yield of dye **4c** (89.1%) was higher than that of dye **4a** (48.2%) and **4b** (49.2%). Presumably, the reason for the higher yield of cyanodehalogenation of dye **4c** is that the lone electron pair of the nitrogen in acylamino group promotes the copper cyanide displacement by giving the electrons to the copper ion (Scheme 4).

All the purified dyes exhibited well-defined melting points characteristic of pure compounds. Several dyes, such as dyes **2c**, **4a**, **4c**, **5a** and **5c**, were decomposed before they reach the melting points (Table 1). While it would be unwise to attempt to explain in detail their relative values, because of the complex dependence of the melting points on a number of factors, a few general trends can be accounted for. The dyes prepared from low melting diazo components tended to have low melting points themselves and the factors determining high melting points were preserved in the dyes from high melting arylamines. The more polar dyes, which contain electron-withdrawing groups, tended to melt at higher temperatures, for example, the nitro-substituted dyes (**2**–**5**) generally exhibited higher melting points than non-substituted



Scheme 4. Copper promoted bromine displacement mechanism of dye **4c** (L = ligand).

dyes (**1**). It was also found that the melting points in a given series of dyes is related roughly to the molecular weight; the dyes having bigger molecular weight showed higher melting points.

4-(*N,N*-Diethylamino)-4′-fluorosulfonylazobenzene dyes with 6′-cyano groups showed higher thermal stability than analogues with a 6′-chloro or a 6′-bromo group, which may be a result of increased polarity and/or the rod like shape of the cyano group being more conductive to efficient packing in the crystal structure. Of the 4-(*N,N*-diethylamino)-4′-fluorosulfonylazobenzene derivatives, dye **5c** (decomposition at 267.0 °C) shows the highest thermal stability and dye **1b** the lowest thermal stability (melting at 117.0 °C).

3.2. Spectral properties

3.2.1. Absorption spectra

The colour gamut of the synthesized dyes spans almost all of the visible spectrum, from orange having λ_{max} 469 nm, to blue having λ_{max} 620 nm in ethanol. Data concerning the spectra of the dyes in ethanol (λ_{max}, ε_{max} and $\Delta\lambda_{1/2}$) are listed in Table 2.

It is well known that λ_{max} values are directly proportional to the electronic power of the substituents in the benzenoid system [6]. Since the electronic transition in these compounds involves a general migration of electron density from the donor group towards the azo group, the greatest effect in terms of longer wavelength is achieved by placing the substituents in the positions *ortho*- or *para*- to azo group, for effective conjugation [7,8].

Predictably, as shown in Table 2, the introduction of an electron-accepting substituent into the diazo component ring of an azobenzene which contains a donor group in the coupling component ring produced a bathochromic shift; the λ_{max} values of 2′-nitro-4′-fluorosulfonyl substituted azo dyes showed more bathochromic shift than that of 4′-fluorosulfonyl substituted azo dyes by 44–54 nm. In the case of 2′,4′,6′-trisubstituted azo dyes, the extent of the shift towards the blue was in the order H < Cl ≈Br < CN for substituents *ortho* to the azo linkage, which is the same order in the Hammett σ constants. In particular, the longer wavelength raging from 25 to 41 nm shown by the 6′-cyano substituted dye compared with that of the 6′-chloro or 6′-bromo compound can be related not only to the electronic effects of the substituents but also to the smaller steric requirements of the rod-like cyano group, which emphasise the importance of having a less bulky group ortho to the azo linkage to produce maximum shifts towards the blue.

Table 2
Spectral data of dyes **1**–**5**

Dye	λ_{max} (EtOH) (nm)	ε_{max} (EtOH) (I mol^{-1} cm^{-1})	$\Delta\lambda_{1/2}$ (EtOH) (nm)
1a	469	36 000	97
1b	478	38 000	102
1c	519	33 000	107
2a	513	38 000	105
2b	524	40 000	106
2c	573	43 000	100
3a	520	32 000	124
3b	539	36 000	118
3c	595	33 000	98
4a	522	34 000	119
4b	542	38 000	116
4c	594	39 000	100
5a	540	39 000	110
5b	580	42 000	99
5c	620	–[a]	78

[a] Solubility was not enough to measure the ε_{max} value.

The absorption wavelength can also be increased by increasing the number of electron donor groups in the coupling component. Thus, the more effective the donor substituent, the more bathochromic is the shift, as shown in Table 2; of the synthesized 4-(*N,N*-diethylamino)-4′-fluorosulfonylazobenzene derivatives, the dyes **1c**–**5c** containing 2-acylamino-5-methoxy substituent showed greater bathochromic shift than rest of them. Recent evidence suggested that intramolecular hydrogen-bonding between the azo nitrogen and hydrogen in the acylamino group is responsible for these effects.

It is well known as a 'rule of thumb' that molar extinction coefficient increases as $\lambda_{\max}$ increases. For the series of synthesized dyes, $\varepsilon_{\max}$ values tend to increase with increasing electron withdrawing capacity in the acceptor ring in the absence of steric effects. Introduction of one *ortho*-substituent does not lead to much steric hindrance and the loss of planarity because, of the two conformations available to the dye (Fig. 1), conformation (a) can be adopted in which steric hindrance is minimal relative to (b) where there is a significant steric clash between the substituent and the electron lone pair orbital of the azo nitrogen atom more remote from the substituents [9]. Evidence that the former, less hindered, conformation is adopted by a dye in solution has been obtained from ^{13}C NMR data [10], and in the solid state from X-ray crystallographic studies [11].

Taking a closer look reveals that the additional incorporation of chloro- or bromo- *ortho* to the azo linkage in the 2′-substituted diazo component causes a reduction in $\varepsilon_{\max}$ value while an equivalent cyano substituent does not. When two *ortho*-substituents are present in the same ring, both conformations (a) and (b) are strained, and thus the molecule is trapped in a non-planar situation [12]. Consequently, *ortho*-substituted bulky groups, particularly spherical substituents like Br and Cl cause rotation out of the molecular plane so as to minimize the steric compression, leading to a resultant reduction in $\varepsilon_{\max}$. On the other hand, in the case of *ortho*-cyano substituted dyes, it had only small steric effects because of their rod-like shape, therefore, the intensity increase caused by the electronic effect of cyano group is not so much counterbalanced by sterically-induced hypochromism.

Half-band widths of the absorption bands in EtOH were also determined (Table 2). In addition to the effect on $\lambda_{\max}$, substituents also cause 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 highest $\Delta\lambda_{1/2}$ values are shown by the 2′-nitro-4′-fluorosulfonyl-6′-chloro or 2′-nitro-4′-fluorosulfonyl-6′-bromo derivatives (**3**, **4**), which means the disturbance of the spatial structure must result in reduction of the conjugation effect and a hypochromic effect compared to the dyes in which such interactions does not take place. 2′-Nitro-6′-cyano substituted dyes, especially dye **5c** ($\Delta\lambda_{1/2=}78$) showed the brightest hue, which could be ascribed to a small steric effect because of their rod-like shape. Also, acylamino substituent ensures the brightest shade as a result of intramolecular hydrogen-bonding [5] (Fig. 2).

3.2.2. Halochromic effects

Protonation of a 4-aminoazobenzene derivative gives the azonium tautomers which provide a red-shifted absorption band and more intense colours than the parent dyes. Comparison with the neutral dye, in the azonium species, the ground and excited states are much closer together in energy terms

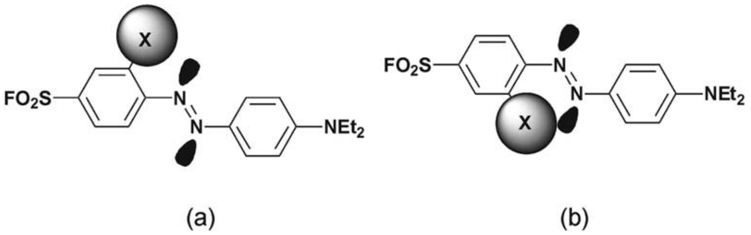


Fig. 1. *Trans*-conformations available to a singly *ortho*-substituted monoazo dye.

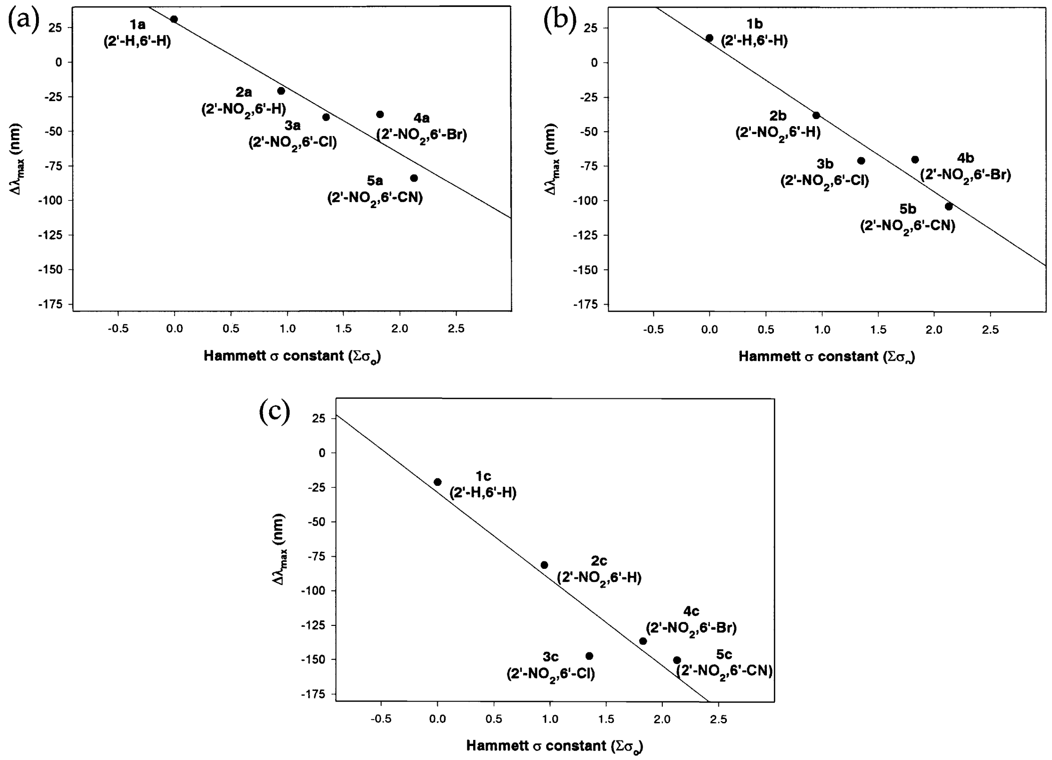


Fig. 2. Relation between Hammett σ constant and halochromic shift for the dyes **1**–**5**: $\Sigma\sigma_o\sigma_{2'} + \sigma_{6'}$, $\Delta\lambda_{max} = \lambda_{max}$ (azonium)$-\lambda_{max}$ (neutral), $\sigma_{2'}, \sigma_{6'}$ = Hammett σ constant in the 2′- and 6′-positions for the substituents; (a) **1a**–**5a**; $\Delta\lambda_{max} = -47.64\Sigma\sigma_o + 29.24$, $\sigma_{\Delta\lambda=0} = 0.668$, $r = -0.956$; (b) **1b**–**5b**; $\Delta\lambda_{max} = -54.01\Sigma\sigma_o + 14.62$, $\sigma_{\Delta\lambda=0} = 0.316$, $r = -0.977$; (c) **1c**–**5c**; $\Delta\lambda_{max} = -62.73\Sigma\sigma_o - 28.47$, $\sigma_{\Delta\lambda=0} = -0.254$, $r = -0.940$.

Table 3
Halochromic effects of the dyes **1**–**5**

Dye	λ_{max} (EtOH) (nm)	λ_{max} (HCl/EtOH) (nm)	$\Delta\lambda$ (nm)
1a	469	500	+31
1b	478	496	+18
1c	519	498	−21
2a	513	492	−21
2b	524	486	−38
2c	573	492	−81
3a	520	480	−40
3b	539	468	−71
3c	595	448	−147
4a	522	484	−38
4b	542	472	−70
4c	594	458	−136
5a	540	479	−51
5b	580	476	−104
5c	620	470	−150

so that a bathochromic shift of the first absorption band is observed on protonation, which is termed 'positive halochromism' [13,14].

The direction of charge migration accompanying electronic excitation in the azonium form is opposite to that found in the neutral dye and this difference suggests that substituents in the diazo component or coupling component should have the opposite effect in neutral and in protonated dyes. Indeed, electron donors, by stabilizing the azonium excited state relative to the ground state, produce increased bathochromic shifts (Table 3).

Applying the Hammett equation, a linear correlation can be drawn between the wavelength shift, $\Delta\lambda$ ($\lambda_{azonium}-\lambda_{neutral}$) and the appropriate Hammett σ constant in accordance with theoretical expectations [15–17]. Indeed, as Fig. 3 depicts, a reasonable linear correlation exists between the difference in the absorption maxima of azonium

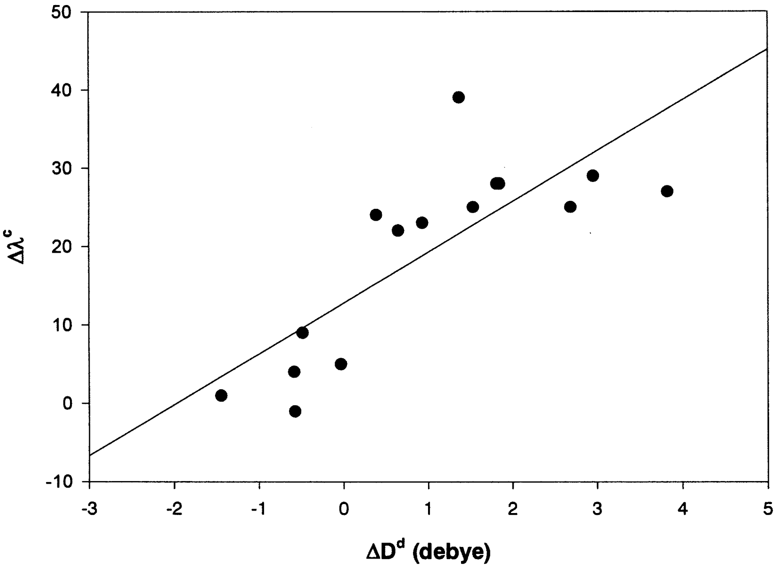


Fig. 3. Correlation between calculated ΔD and solvatochromic effects of the dyes **1**–**5** (regression analysis); $\Delta\lambda^c = 6.48\Delta D + 12.78$, $r = 0.791$, $\Delta\lambda^c = \lambda_{max}$ (EtOH)$-\lambda_{max}$ (C_6H_{12}).

form and neutral form ($\Delta\lambda_{max}$) and Hammett σ constants for relevant substituents in the benzenoid system. Also, it can be seen that the bathochromic shift decreased steadily with the general electron withdrawing capacity of the substituents in diazo components ring and the general electron donating capacity of the substituents in coupling components ring, and in fact became negative especially when more than two powerful electron acceptor groups are present in the diazo components ring. Most synthesized dyes containing two or three electron withdrawing groups and/or powerful electron donating groups in coupling component ring showed negative halochromism due to the strong electronic effect (**1c**, **2**–**5**) while dye containing just one electron accepting group in diazo components and less powerful electron donating groups in coupling component ring showed positive halochromism (**1a**, **1b**). The experimental results show that the substituents X, Y affect the halochromism to an extent which depends on their electron accepting power. Therefore, by using appropriate substituents, it is possible to design dyes that show no colour change in acid ($\Delta\lambda = 0$) and which in theory should make good textile dyes, where pH sensitivity is undesirable [16]. In the case of this series of dyes, the estimated Hammett σ constant values for no colour change under acidic condition are 0.668, 0.316 and −0.254, respectively.

3.2.3. Solvatochromic effects

Generally, in many dye molecules, the ground state is less polar than the excited state so that a polar solvent will tend to stabilize the excited state more than the ground state, leading 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 ethanol, which possess a strong permanent dipole, and is most pronounced with a solute molecule that contains a permanent dipole. As the difference between the polarity of the ground and excited states is increased by the successive introduction of stronger electron-withdrawing groups in the diazo component ring of a 4-aminoazobenzene, more marked positive solvatochromism is observed.

It is clear from Table 4 that most synthesised dyes exhibit a positive solvatochromism in accordance with most donor–acceptor chromogens so that the absorption band of dyes moves toward

Table 4
Solvatochromic effects of the dyes **1**–**5**

Dye	λ_{max} (C_6H_{12}, nm)	$\Delta\lambda^{a}$ (nm)	λ_{max} (C_7H_8, nm)	$\Delta\lambda^{b}$ (nm)	λ_{max} (EtOH, nm)	$\Delta\lambda^{c}$ (nm)	ΔD^{d} (debye)
1a	447	+13	460	+9	469	+22	0.645
1b	455	+13	468	+10	478	+23	0.933
1c	518	+11	529	−10	519	+1	−1.444
2a	489	+17	506	+7	513	+24	0.386
2b	499	+17	516	+8	524	+25	1.536
2c	574	+7	581	−8	573	−1	−0.575
3a	493	+20	513	+7	520	+27	3.826
3b	514	+17	531	+8	539	+25	2.685
3c	590	+10	600	−5	595	+5	−0.033
4a	493	+19	512	+10	522	+29	2.952
4b	514	+17	531	+11	542	+28	1.812
4c	585	+14	599	−5	594	+9	−0.486
5a	501	+47	548	−8	540	+39	1.372
5b	552	+18	570	+10	580	+28	1.845
5c	624	+4	628	−8	620	+4	−0.585

[a] $\Delta\lambda = \lambda_{max}$ (C_7H_8)$-\lambda_{max}$ (C_6H_{12})

[b] $\Delta\lambda = \lambda_{max}$ (EtOH)$-\lambda_{max}$ (C_7H_8)

[c] $\Delta\lambda = \lambda_{max}$ (EtOH)$-\lambda_{max}$ (C_6H_{12}) in nm

[d] ΔD = dipole moment (first excited state)−dipole moment (ground state) in debye calculated by HyperChem and CS Chem 3D.

longer wavelengths as the polarity of the solvent increases. For example, the introduction of stronger electron acceptors in the diazo component ring led to greater differences between λ_{max} values for their cyclohexane and ethanol solutions. As the electron-withdrawing groups are introduced, the gap between the polarity of the ground and excited states grows; the amount of stabilization of the excited state relative to the ground state on increasing solvent polarity is raised and thus the solvatochromism becomes more marked.

However, in a few cases, negative solvatochromism was observed within the general positive trend, for example, dyes **1c**–**5c** containing a 2-acylamino-5-methoxy substituents. Most of their ethanol solutions were slightly hypsochromic 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 2-acylamino substituted dyes and intramolecular hydrogen-bonding between the 2-acylamino and azo nitrogen atoms in these dyes appears to be the more 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 hypsochromic shifts since ΔE for the transition is increased.

The relation between ΔD (differences in dipole moment between ground state and first excited state) and the overall shifts ($\Delta\lambda^{c}$) for the dyes **1**–**5** were shown in Fig. 4; the expected relationship of increased difference being accompanied by greater solvatochromism does appear to be hold reasonably well. The bigger ΔD the dyes have, the greater solvatochromism shift they showed.

Also, the dyes having positive ΔD values showed positive solvatochromism (**1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b** and **5b**) while those having negative ΔD values showed negative solvatochromism (**1c**, **2c**, **3c**, **4c** and **5c**) between toluene and ethanol although there is one exception of dye **5a** (Fig. 5). In particular, the negative solvatochromism of the dyes containing a 2-acylamino-5-methoxy substituent

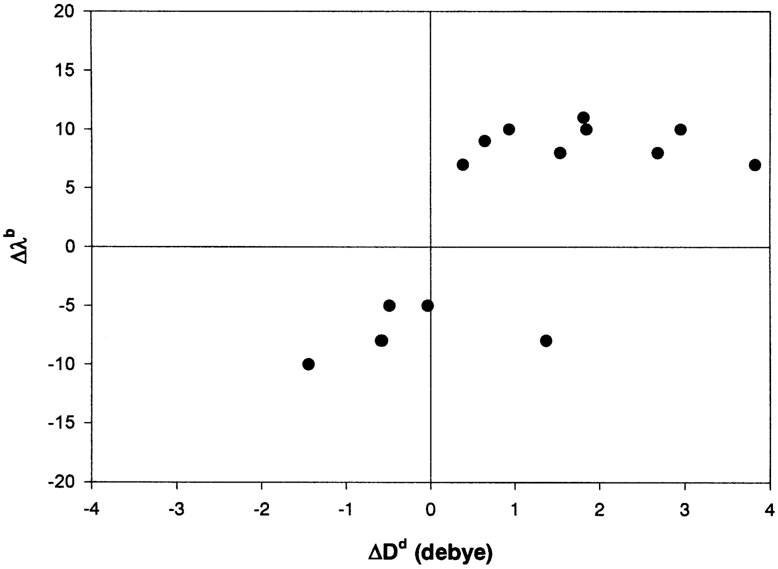


Fig. 4. Correlation between calculated ΔD and solvatochromic effects of the dyes **1**–**5**; $\Delta\lambda^b = \lambda_{max}$ (EtOH)$-\lambda_{max}$ (C_7H_8).

is supported by their negative values of ΔD between toluene and ethanol ($\Delta\lambda^b$) is supported by their negative values of ΔD. Therefore, from the dipole moments of the ground state and the excited states, it is possible not only to predict whether that dye will exhibit solvatochromism, but also, which type in some cases.

4. Conclusions

Alkali-clearable monoazo disperse dyes containing a fluorosulfonyl group in their diazo component ring have been prepared from the coupling reaction between 4-fluorosulfonylanilines and corresponding coupling components and their spectral properties were investigated. The 4-fluorosulfonylanilines were readily obtained by using the fluorination, nitration, chlorination, bromination and deacetylation reaction. From the point of view of the absorption spectra, λ_{max} values of the variously substituted dyes shift from orange to blue (469–620 nm in EtOH) in line with the appropriate Hammett substituent constant. Also, 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 inductive effect of the substituents in combination with the steric effects.

Applying the Hammett equation to the halochromism of the synthesised dyes, a reasonable linear correlation was drawn between the wavelength shift, $\Delta\lambda$ ($\lambda_{azonium}-\lambda_{neutral}$) and the appropriate Hammett σ constant in accordance with theoretical expectations. Most synthesized dyes containing two or three electron withdrawing groups and/or powerful electron donating groups in coupling component ring show negative halochromism due to the strong electronic effect.

Most dyes exhibited overall positive shifts between cyclohexane and ethanol, however, in a few cases, negative solvatochromism was observed within the general positive trend, for example, the dyes containing a 2-acylamino-5-methoxy substituents, which is due to the intramolecular hydrogen-bonding. A reasonable linear correlation was obtained between the difference in dipole moment and the extent of solvatochromic effects; difference in dipole moment between the excited state and the first excited state, which was calculated by using HyperChem and CS Chem3D softwares, provided reasonable predictions in the extent and the direction of solvatochromism for the dyes prepared. Therefore, the dipole moments appear to be a reasonable measure for the theoretical prediction of solvatochromism of the 4-(*N,N*-diethylamino)-4′-fluorosulfonylazobenzene dyes.

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