A STUDY ON TAUROMERIC EQUILIBRIA OF SOME NEW 3-CRHLORO-4-FLUROAMLINE MONOAZO DISPERSE DYE DERIVATIVES

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ABSTRACT
A series of new monoazo disperse dyes derived from 3-chloro-4-fluoroaniline have been synthesized. The six novel monoazo disperse dyes were synthesized by diazotisation of 3-chloro-4-fluoroaniline and coupling with 1-naphthylamine, 6-methoxy-2-naphthol, N-phenylnaphthylamine, 3-aminophenol, 1,3-dihydroxybenzene and 2-naphthol. The dye structures were elucidated by chemical analyses and spectral methods. The solvatochromic behaviour of these monoazo dyes in various solvents was evaluated.

Keywords: 3-chloro-4-fluoroaniline, disperse dyes, diazotisation, solvent effects, Absorption spectra.

INTRODUCTION
3-chloro-4-fluoroaniline is a versatile reagent, that has been used as a synthetic intermediate for a large number of organofluorine compounds (Arjuna et al., 2000). The derivatives of this intermediate are important compounds that possess biological activities. For instance, 3-chloro-4-fluoroaniline moiety has been found to be pharmacopone in a variety of biologically active organofluorine compounds (Nargund and Srinivasmurthy, 1994).

Benzothiazoles obtained from this intermediate are interesting group of compounds and the biological activities of this class of compounds that are reported in literature are anticancer, antitumor, amyloid-imaging agents, antimicrobial, anticonvulsant, anti-diabetic, anti-tubercular, muscarinic receptor antagonist, antibacterial activity (Barot et al., 2010). Thus, many patents and papers describe the uses of the derivatives of 3-chloro-4-fluoroaniline (Eadsforth et al., 1988; Boogaard et al., 1994), no comparable investigation has been made with the preparation of azodisperse dyes.

It is well-known that monoazo dyes prepared from enol-and enamine-type coupling compounds exhibit azo-hyrazonetautomerism (Colour Index International, 1992; Karci, 2005). Determination ofazo-hyrazonetautomerism both in solid state and solution phase is quite interesting both from theoretical and practical standpoints, since the tautomers have different technical properties and dyeing performance (Zollinger, 2003; Koh et al., 2004).

In this study, the synthesis of six novelazo disperse dyes derived from various coupling components and 3-chloro-4-fluoroaniline as the carbocyclic diazo component is reported. In addition, their absorption spectra were evaluated in various solvents for their colour-structure relationships in such dyes.

EXPERIMENTAL
Chemical Analyses
Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded with a MATTSON 1000 FT-IR spectrophotometer on KBr pellets. Proton nuclear magnetic resonance and $^{13}$C-NMR were recorded on the mercury 200BB, 199.97 MHz spectrophotometer with deuterated chloroform as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are expressed as $\delta$ units (ppm). Ultraviolet (UV-Vis) absorption spectra were recorded on an ATI UnicamGene- sys10SV1.200 series spectrophotometer. Dye privity was assessed by using Thin Layer
Chromatography (TLC).

Synthesis of Dyes

3-Chloro-4-fluorophenylazo-2, 4’-dihydroxybenzene, 3a

To a mixture of compound 1 (3.0 g, 20.6 mmoles), water (50 ml) was added, 25 ml of concentrated HCl, which was subsequently diazotized by treatment with sodium nitrite solution (4.0 g, 58 mmoles) in 10 ml of water at 0 °C with stirring for 20 minutes. The excess nitrous acid was destroyed by adding urea (3.0 g, 150 mmoles). The resulting solution of diazonium salt, 2 was slowly added with vigorous stirring at 0-5 °C, over a solution of 1,3-dihydroxybenzene (2.27 g, 20.6 mmoles) dissolved in sodium hydroxide (1 M, 30 ml) and stirring was continued for 2 hours. Finally, the brown coloured precipitate was collected by filtration, washed with distilled water and dried in air. The crude product was recrystallized out of ethanol to give 94 % yield of compound 3a. Compounds 3b and 3e were prepared similarly using this procedure.

Results and Discussion

Characterization of the new monoazo disperse dyes (3a – f).

The 3-Chloro-4-fluoroaniline derived dyes were prepared by diazotising the intermediate and coupling with selected coupling components (David et al., 1994; Ortega-Luoniet et al., 2007; Paula, 1995; Alexis et al., 2004) (Figure 1). The structures of these dyes were verified by spectroscopic methods (FT-IR, \(^{1}\)H-NMR, \(^{13}\)C-NMR and UV-VIS). The physical and spectroscopic data of the prepared dyes are given in Table 1, 2 and 3. The dyes may exist in the following tautomeric forms, as shown in scheme 2.

Scheme 1: Synthesis scheme for the preparation of dyes 3a - f

3-Chloro-4-fluorophenylazo-N-phenylphthalamide, 3c

Compound 1 (3.0 g, 20.6 mmoles) was dispersed in 50 ml of water. 25 ml of concentrated HC1 was added to the mixture and the amine was diazotized by adding sodium nitrite solution (4.0 g, 58 mmoles) in 10 ml of water at 0 °C with stirring over 15 minutes. Excess nitrous acid was removed by adding (3.0 g, 150 mmoles) of urea. The resultant diazonium salt solution was slowly added to a solution of N-phenylphthalamide (4.54 g, 20.7 mmoles) in 15 ml of acetic acid with vigorous stirring over 3 1/2 hours. The precipitate obtained was isolated by filtration, washed with water, and dried in air. Compound 3c was recrystallized out of aqueous dimethylformamide to give 84 % yield.

Compounds 3d and 3f were obtained following a procedure similar to that used for the formation of compound 3c.

Scheme 2: The tautomeric forms of dyes 3a - f
Table 1: Spectral data of synthesized dyes with assignments

<table>
<thead>
<tr>
<th>Dye</th>
<th>Frequency (cm⁻¹)</th>
<th>Characteristics</th>
<th>¹HNMR, δ (ppm)</th>
<th>¹³C-NMR, δ (ppm)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>3450</td>
<td>Ar-OOH</td>
<td>6.08 (1H, dd, ArH)</td>
<td>17.23</td>
<td>DMF</td>
</tr>
<tr>
<td>3b</td>
<td>3840</td>
<td>Ar-CH₃</td>
<td>2.01 (3H, s, CH₃)</td>
<td>23.91</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>3c</td>
<td>3850</td>
<td>Ar-OOH</td>
<td>6.08 (1H, dd, ArH)</td>
<td>17.23</td>
<td>DMF</td>
</tr>
<tr>
<td>3d</td>
<td>3860</td>
<td>Ar-CH₃</td>
<td>2.01 (3H, s, CH₃)</td>
<td>23.91</td>
<td>CDCl₃</td>
</tr>
</tbody>
</table>

The IR spectra of dyes 3a, 3b and 3f (in KBr) showed broad bands within the range 3430 – 3508 cm⁻¹ due to the –OH stretching vibrations, and NH₂ bands which are observed to overlap with the –OH bands. The weak bands at 2932 – 3019 cm⁻¹ region is typical of the aromatic C-H stretching vibrations. The bands at 1051 – 1096 cm⁻¹ and 664 – 759 cm⁻¹ are recorded for the presence of C-F and C-Cl stretching vibrations respectively.

The ¹H-NMR spectra measured in deuterated chloroform (CDCl₃) at 25 °C showed peaks at 13.23 – 15.45 ppm for bonded-OH, 17.20 – 17.80 ppm for imine and hydrazone –NH protons of a hydrazine-imine tautomer. These results shows that the dyes may exist in more than onetautomeric form with the hydrazone tautomer normally predominating compared with the azo tautomer (Gallas and Renfrew, 1996; Otutu et al., 2011) both in CDCl₃ and solid state. The tautomericketo forms of the dyes are also indicated by ¹H-NMR spectroscopy. The enolic OH signals of the enol forms of the compounds are observed while the amide NH signals of the keto forms appear around 17.20 – 1780 ppm. These data are in agreement with those previously reported for similar compounds (Kirkan and Gup, 2008).

Table 2: Influence of solvent on λ_max (nm) of the dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>DMF</th>
<th>Acetic acid</th>
<th>Chloroform</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>392</td>
<td>370</td>
<td>415</td>
<td>392</td>
</tr>
<tr>
<td>3b</td>
<td>385</td>
<td>370</td>
<td>391</td>
<td>379</td>
</tr>
<tr>
<td>3c</td>
<td>382a</td>
<td>340</td>
<td>349</td>
<td>355</td>
</tr>
<tr>
<td>3d</td>
<td>382</td>
<td>400</td>
<td>415</td>
<td>418</td>
</tr>
<tr>
<td>3f</td>
<td>3567</td>
<td>440s</td>
<td>499</td>
<td>490</td>
</tr>
</tbody>
</table>

S = Shoulder

Aminoazocolourants show no evidence of tautomeric behaviour, consequently monoazo dyes 3c and 3d gave unstable imino forms.

Table 3: Percentage yields and melting points of dyes 3a – f

<table>
<thead>
<tr>
<th>Dye</th>
<th>Empirical Formula</th>
<th>Yield (%)</th>
<th>MP (°C)</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C₇H₈N₂O₂ClF</td>
<td>68</td>
<td>145</td>
<td>0.68</td>
</tr>
<tr>
<td>3b</td>
<td>C₇H₈N₂OCIF</td>
<td>94</td>
<td>260</td>
<td>0.70</td>
</tr>
<tr>
<td>3c</td>
<td>C₇H₈N₂CIF</td>
<td>84</td>
<td>140</td>
<td>0.59</td>
</tr>
<tr>
<td>3d</td>
<td>C₇H₈N₂CIF</td>
<td>88</td>
<td>252</td>
<td>0.63</td>
</tr>
<tr>
<td>3e</td>
<td>C₇H₈N₂OCIF</td>
<td>64</td>
<td>130</td>
<td>0.78</td>
</tr>
<tr>
<td>3f</td>
<td>C₇H₈N₂O₂CIF</td>
<td>56</td>
<td>120</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Solvent effect on absorption spectra of dyes in various solvents

The electronic absorption spectra of the dyes in all solvents differ significantly from each other. Dye 3b and 3d showed one absorption maximum in all the solvents whereas dyes 3a, 3c, 3e and 3f showed one absorption maximum with a shoulder or two absorption maxima in DMF, acetic acid and chloroform for dye 3f (the $\lambda_{\text{max}}$ is 412 nm with a shoulder at 392 nm) in DMF, 382 nm with a shoulder at 410 nm, for dye 3c, 382 nm and 385 nm with shoulder at 420 nm and 425 nm respectively in acetic acid and chloroform in dye 3f. The position of the wavelength shoulder or maximum are closer to the absorption maxima. The absorption spectra of the other dyes gave a single dominant absorption band except 3a in DMF, 3c in DMF, 3e in DMF and 3f in DMF, acetic acid and chloroform. The dyes which gave two absorption maxima or an absorption maximum with a shoulder, suggests that these dyes may be present in more than one tautomeric form. The maximum absorption of these dyes shifted in the order: chloroform > acetic acid > ethanol > DMF. This is quite contrary to the order of polarity.

CONCLUSION

A series of six novel monoazo dyes were synthesized from 1,3-dihydroxybenzene, 3-aminophenol, n-phenylnaphthylamine, 1-naphthylamine, 2-naphthol, 6-methoxy-2-naphtholas coupling components and 3-chloro-4-fluoroaniline as the carbocyclic diazo component. The solvent influence on the wavelength of maximum absorption was studied. It was observed that the absorption spectra of dyes 3d and 3e showed maximum peaks at longer wavelength in acetic acid, chloroform and ethanol when compared with the absorption spectra of dyes 3a, 3b, 3c and 3f. It was also observed that dyes 3a and 3c in DMF, acetic acid and chloroform may exist as a mixture of tautomeric forms.

The dyes 3a–f can be applied to polyester and or polyamide fibres as disperse dyes. These compounds can also be used in biological-medical studies.

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REFERENCES


