A STUDY ON TAUTOMERIC EQUILIBRIA OF SOME NEW 3-CRHLORO-4-FLUOROAMLINEMONOAZO DISPERSE DYE DERIVATIVES

Otutu, J.O.
Department of Chemistry, Faculty of Science, Delta State University, P.M.B. 1,
Abraka, Delta State, Nigeria
e-mail address: otutu47@gmail.com

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 eluciated 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 pharmacopnone 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, antidiabetic, 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-hydrazonetautomerism (Colour Index International, 1992; Karci, 2005). Determination ofazo-hydrazonetautomerism 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 carbocyclicdiazo component is reported. In addition, their absorption spectra were evaluated in various solvents for their colour-structure relationships in such dyes.

EXPERIMENTAL

Chemical Analyses

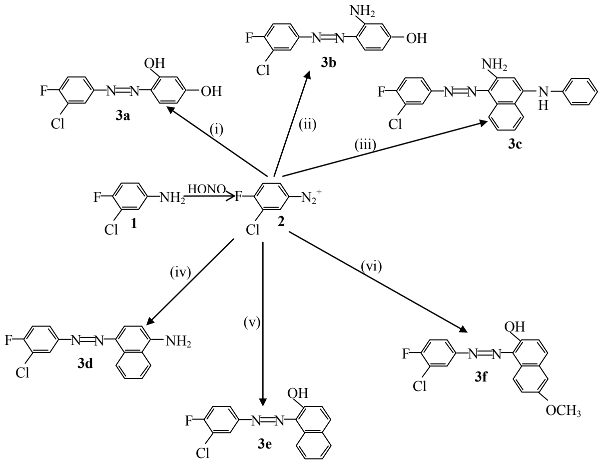
Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded with a MATTSON 1000 FT-IR spectrophotometer on KBrpellets. Proton nuclear magnetic resonance and ^{13}C-NMR were recorded on the mercury 200BB, 199.97 MHz spectrophotometer with deuterated chloroform as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are expressed as ö units (ppm). Ultraviolet (UV-Vis) absorption spectra were recorded on an ATI UnicamGenesys10SV1.200 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 $0-5^0C$, over a solution of 1,3-dihydroxybenzene(2.27g, 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.



(i)	$C_6H_6O_2$	(iv)	$C_{10}H_9N$
(ii)	C_6H_7NO	(v)	$C_{10}H_8O$
(iii)	$C_{16}H_{13}N$	(vi)	$C_{11}H_{10}O_2$

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

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

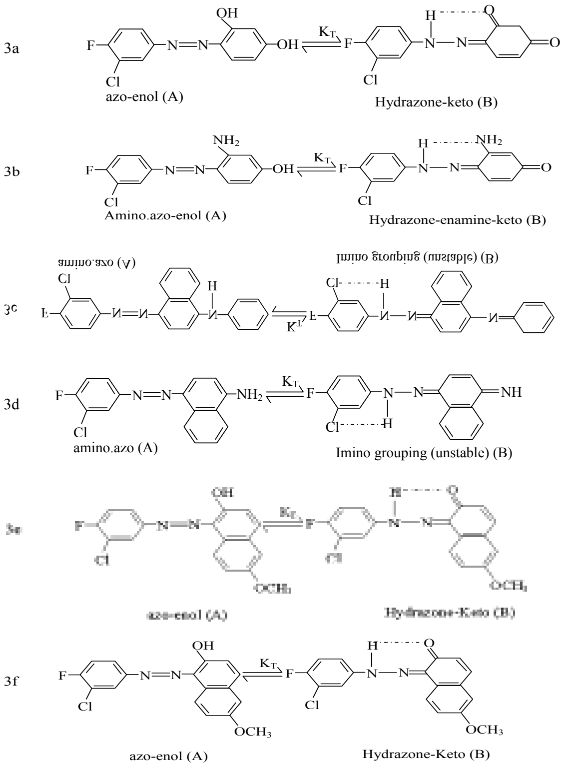
Compound **1**(3.0 g, 20.6 mmoles was dispersed in 50 ml of water. 25 ml of concentrated HC1 was added to the mixture and the amine was diazotized by adding sodium nitrite solution (4.0 g, 58 mmoles) in 10 ml of water at 0 °C with stirring over 15 minutes. Excess nitrous acid was removed by adding (3.0 g, 150 mmoles) of urea. The resultant diazonium salt solution was slowly added to a solution of N-phenylnaphthylamine (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.

RESULTS AND DISCUSSION

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

The 3-Chloro-4-fluoroaniline derived dyes were prepared by diazotising theintermediate and coupling with selected coupling components (David *et al.,* 1994; Ortega-Luoni*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 2: The tautomeric forms of dyes 3a - f

Table 1: Spectral data of synthesized dyes with assignments

Dye	Frequency (cm^{-1})	Characteristics	^{1}HNMR, δ (ppm)	^{13}C-NMR, δ /ppm	Solvent
3a	3470 3019 1634 1051 759	Ar-OH ArC-$H_{stretch}$ Ar-ring C-F C-Cl	6.50 (1H, dd, ArH) 7.00 (1H,m, ArH) 7.40 (1H, m, ArH) 7.60(1H, m, ArH) 7.80 (1H, m, ArH) 8.20 (1H, d, ArH) 13.23 (211, S, bonded OH)	76.55 77.23 77.86 117.64 119.78 120.70 121.84 123,24 125.78 126.14 127.50 129.80	$CDCl_3$
3b	3430 2975 1557 1089 750	Ar-OH, NH Ar C-$H_{stretch}$ Ar-ring C-F C-Cl	1.25 (2H, S, NH_2) 7.20 (1H, m, Ar-H) 7.54 (1H,m, ArH) 7.68(1H,m,Ar-H) 7.76(1H,m,ArH) 7.80(1H, m, ArH) 8.21 (1H, d, ArH) 3.25 (1H, S, bonded OH)	76.85 77.30 77.92 117.55 118.69 119.56 120.70 121.68 123.63 125.58 126.20	$CDCl_3$
3c	3508 1975 1596 1088 750	Ar C-$H_{stretch}$, naphthalene ring Ar-ring ArC-F Ar C-cl	6.60 - 7.41 (6H, m, naphthalene H) 7.60-86 (5H, m, ArH) 8.21 (1H,m, ArH) 8.45 (1H,m, ArH) 8.87(1H, m, ArH) 17.00 (1H, S, NH)	76.68 77.91 116.03 119.56 120.42 121.41 122.96 124.43 125.44 126.51 127.58 128.15 128.46 129.42 129.86 131.63 131.68 132.97 134.49 135.17 136.35	$CDCl_3$
3d	3450 2932 1670 1497 1096 755	Ar-OH Ar C- $H_{stretch}$, naphthalene ring Ar-ring ArC-F Ar C-Cl	12.25 (IH, s, Bonded OH) 9.00-8.20 (5H, m, Ar-H) 7.85-6.65(6H, m, naphthalene) 4.00(3H, s, O-CH_3)	76.62 77.26 77.89 116.26 119.68 120.54 121.47 122.62 125.55 126.56 127.67 128.45 129.68 131.73 132.88 134.69	$CDCl_3$
3e	3451 3018 1635 1534 1060 758	Ar-OH Ar C-$H_{stretch}$ naphthalene ring Ar-ring ArC-F Ar C-Cl	6.45 —7.81 (611, m, naphthalene H) 8.40 (1H, d, ArH) 8.00 (1H, d, ArH) 15.45(1H, S, bonded OH) 17.60(1H, S, NH)	76.72 77.35 77.85 117.38 117.83 119.54 120.76 121.94 123.29 123.60 132.95 146.50 148.16 148.19	$CDCl_3$
3f	3429 2998 1645 1594 1505 1051 664	Ar-OH ArC-$H_{stretch}$ Ar.OCH_3 naphthalene ring Ar-ring Ar C-F Ar C-Cl	3.95 (3H, 3, OCH_3) 6.45 - 7.82 (5H, m, naphthalene H) 8.20 (1H, m, ArH) 8.41 (1H, dd, ArH) 8.65 (1H, dd, ArH) 15.41 (1H, S, bonded OH) 17.20 (1H, S, NH)	58.29 76.63 77.90 106.25 108.40 109.37 113.51 114.93 116.17 117.73 118.39 119.83 120.55 123.84 126.58 130.81 134.49 147.87	$CDC1_3$

The IR spectra of dyes **3**a, **3**b and **3**f (in KBr) showed broad bands within the range 3430 – 3508 cm^{-1} due to the –OH stretching vibrations, and NH_2 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 ^{1}H-NMR spectra measured in deuterated chloroform ($CDCl_3$) at 25 ^{0}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 hydrazone-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 $CDCl_3$ and solid state. The tautomericketo forms of the dyes are also indicated by 'H-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

Dye	DMF	Acetic acid	Chloroform	Ethanol
3a	392, 412s	370	415	392
3b	385	370	391	379
3c	382s, 410	340	349	355
3d	382	490	415	418
3e	3567, 440s	499	490	490
3f	490	382, 420s	385, 425s	361

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

Dye	Empirical Formula	Yield (%)	MP (^{0}C)	R_f
3a	$C_{12}H_8N_2O_2CIF$	68	145	0.68
3b	$C_{12}H_9N_3OCIF$	94	260	0.70
3c	$C_{22}H_{15}N_3CIF$	84	140	0.59
3d	$C_{16}H_{11}N_3CIF$	88	252	0.63
3e	$C_{16}H_{10}N_2CIF$	64	130	0.78
3f	$C_{17}H_{12}N_2O_2CIF$	56	120	0.82

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 **3**b and **3**d showed one absorption maximum in all the solvents whereas dyes **3**a, **3**c, **3**e and **3**f showed one absorption maximum with a shoulder or two absorption maxima in DMF, acetic acid and chloroform for dye **3**f (the λ_{max} is 412 nm with a shoulder at 392 nm) in DMF, 382 nm with a shoulder at 410 nm, for dye **3**c, 382 nm and 385 nm with shoulder at 420 nm and 425 nm respectively in acetic acid and chloroform in dye **3**f. 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 **3**a in DMF, **3**c in DMF, **3**e in DMF and **3**f in DMF, acetic acid and chloroform. The dyes which gave two absorption maxima or an absorption maximum with a shoulder, suggests that these days 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 **3**d and **3**e showed maximum peaks at longer wavelength in acetic acid, chloroform and ethanol when compared with the absorption spectra of dyes **3**a, **3**b, **3**c and **3**f. It was also observed that dyes **3**a and **3**c in DMF, acetic acid and chloroform may exist as a mixture of tautomeric forms.

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

ACKNOWLEDGEMENT

Thanks are due to Prof. Olugbade of the Obafemi Awolowo University for the proton NMR and ^{13}CNMR measurements.

REFERENCES

Alexis, E.F., Liljana, G., Antonio, J.M., Callum, W.E. and Duncan, S. (2004). Synthesis of reactive benzotriazoleAzo Dyes for surface enhanced resonance RamanScattering. *The Analyst* **129**: 975 - 978.

ArjunaGowda, K.V., Kokila, M.K, Puttaraja, M.V. Kukiarni and Shivaprakash, N.C. (2000). Crystal and molecular structure of N-(P-nitrobenzylidene)-3-chloro-4-fluoroaniline. *Pranama Journal of Physics* **55(3):** 441 -446.

Barrot, H.K., Maui Ka, G., Suutariya, B.B., Shukla, J. and Nargund, L.V.G. (2010). Synthesis of Nitrogen mustards of fluorobenzothiazoles of pharmacological interest. *Research Journal of Pharmaceutical, Biological and Chemical Sciences* **1 (1):**124 - 129.

Boogaard, P.J., Gerard, B.B. and Sittert, J.V. (1994). Biological monitoring of Exposure to 3-chloro-4-fluoroanilme by determination of a urinary metabolite and a Haemoglobin adduct. *Supplement* **102(6):** 23 -25.

Colour Index International (1992) (3rded.). The Society of Dyers and Colourists. American Association of textile Chemists and Colourists. Bradford/England.

David, R.W. and Geoffery, II. (1994). *The Chemistry and Application of Dyes*. New York and London, Plenum Press, pp. 115 - 231.

Hallas, G. and Rnfrew, A.H.M. (1996). Representation of tautomericcolourants in the colour index.*Jour. Soc. Dyes and Colourists*, **112(7/8):** 177-216.

Karci, F. (2005). Synthesis of disazo dyes derived from heterocyclic compounds. *ColorTechnol*, **12(5):** 237 - 290.

Koh, J., Kim, S. and Jae, P.K. (2004). Synthesis and spectral properties of azohydroxypyridone disperse dyes containing a fluorosuiphonyl group. *Color Technol*ogy

120(5): 205 - 266.

Nargund, L.V.G. and Srinivasmurthy, M. (1994). Synthesis of Fluorinated thiazolidiones and azetidinoes for pharmacological screening. Bangalore University Press, pp.86 - 95.

Ortega-Luom, P., Vera, L., Astudillo, C., Guzman, M. and Ortega-Lopez, P. (2007). Synthesis of metallic Azoderivatives of 2-Amino-5-mercapto-1,3,4-thiadiazole. *Journal of Chilean Chemical. Society* **52(1):** 835- 837.

Otutu, J.O., Osabohien, E. and Efurhievwe, E.M. (2011). Synthesis and spectral properties of HetarylMonoazo dyes derived from 2-amino-5-nitrothiazole. *Oriental Journal of Chem*istry **27(4):** 1369 - 1396.

Paula, Y.B. (1995). *Organic Chemistry*. New York. Prentice-Hall Inc., pp. 658 - 659.

Samieh, F., Ahmad, M.T., Hoosbang, H. and Hojatollah, K. (2008). A synthesis of some new 4-arylidene-5(4H)-oxaloneazo dyes and an evaluation of their solvatochromic behaviour. *Arkivoc* **(15):** 115-123.

Zeynel, S. (2009). A study on tautomericequilibria of new netarylazo-6-aminouracils.*Arkivoc* **28(7):** 42—57.

Zollinger, H. (2003). *Colour Chemistry Synthesis, Properties and Application of Organic Dyes and Pigments*. Third revised edition. Wiley-VCH