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The Synthesis of New Imino-Derivative of Benzo [A] Phenoxazinone Dyes

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ABSTRACT

*The objective of the study was to synthesize imino derivatives of phenoxazines and then study their dyeing properties. 6-Chloro-10-aminobenzo[a]phenoxazine-5-one **3** was prepared by condensation of 2,4-diaminophenol **1** with 2,3-dichloro-1,4-naphthoquinone **2** in an alkaline medium. Further treatment of **3** with 4-chlororbenzaldehyde **4**, 4-fluorobenzaldehyde **5**, 4-amino-3,5-dimethylbenzaldehyde **6**, 4-methoxybenzaldehyde **7** and 4-methylbenzaldeyde **8**, respectively gave the derivatives: 6-Chloro-10-(4-chlorophenylimino)benzo[a]phenoxazin-5-one **9**, 6-Chloro-10-[(4-fluorophenylimino)benzo [a]phenoxazine-5-one **10**,10-{(4-amino-3,5-dimethylbenzylidine)amino}-6-chlorobenzo [a] phenoxazine-5-one **11**, 6-Chloro-10-{(2-methoxybenzylidine)amino}benzo[a]phenoxazine-5-one **12**, 6-Chloro-10-(4-methylphenyl-imino) benzo[a]phenoxazin-5-one **13**. These derivatives were characterised using UV-visible, FT-IR, ^{1}H-NMR spectroscopy and elemental analytical data. The results from the evaluation of the dyeing fastness properties of these compounds showed that they have moderate to good fastness properties on cotton fibres.*

Keywords: Phenoxazine, 2,4-Diaminophenol, 2,3-Dichloro-1,4-naphthoquinone, 4-Chlororbenzaldehyde, 4-Methoxybenzaldehyde, Dyeing, Colour.

INTRODUCTION

Interest in the chemistry of dyes during the last quarter of the last century led to the synthesis of large number of dyestuffs, prominent amongst them is meldola blue from phenoxazine ring (1). Meldola blue was employed as pigment for textiles, paper and paints; it also have some desirable properties as florescent probes (2). The phenoxazine ring is also a component of numerous naturally occurring compounds such as Ommochromes, fungal metabolites, Questiomycins and Actimycins which are responsible for colouration of wings, cuticle and eyes of insects [1,2]. The introduction of the synthetic fibers, nylon, polyesters and ployacrylonitrile during the 1900s produced the next significant challenge due to lack of light fastness [3]. Phenoxazine dyes were once widely used for silk dyeing but due to their lack of light fastness; they have disappeared from the market [4] Colour fastness is one of the important factors in the minds of the consumers and consequently the outstanding properties of dyed materials are based on their colour fastness [3]. In 1947 the International Organization for Standardization (ISO) instituted a colour subcommittee to grade fastness [5]. Apart from their dyeing properties, phenoxazine and its derivatives exhibit wide spectrum of pharmacological profile [6,7]. Also, in addition, compounds having azomethine group exhibits antimicrobial activities (8-10), antioxidant and anti-proliferative properties [8-11]. This study aimed at applying new phenoxazine compounds as dyes to cotton fabric materials and evaluating their fastness properties.

MATERIALS AND METHODS

Melting points of synthesized compounds were determined using Fischer Johns scientific melting point apparatus and are uncorrected. The reactions were monitor with coated TLC plates, Uv-lamp and infrared spectrophotometer. Ultraviolet and visible spectra were recorded on Jen-way 6405 UV/Vis spectrophotometer and absorption maximum is given in nanometer (nm). Infrared spectra data were obtained on FTIR and absorption were in wave number (cm-1). All reagents were obtained from commercial sources (Sigma Aldrich chemicals, Germany) and were used without further purification. The dye characterisation was evaluated.

Chloro-10-amino-benzo[a]phenoxazin-5-one (3)

(150 mL) at room temperature, in a round-bottom flask for 30 min. 2,3-dichloro-1,4-napthoquinone (9.08 g, 40 mmol) was later added and the reaction mixture was stirred at room temperature for 6 h. The solvent was distilled off in vacuum; water (50 mL) added to the reddish-brown solid, stirred to dissolve the inorganic material and then filtered by suction. The solid-crude was further washed with 5% HCl and air-dried. The crude was recrystallized from ethanol-DMF mixture to give 6-chloro-10-aminobenzo[a]phenoxazin-5-one: melting point: 194-196°C, yield (8.60 g, 89 %), UV-Visible λmax (EtOH/DMF): 313, 388, and 469. IR (ν max cm-1): 3444-3324 (N-H), 3049 (=C-H), 1791, 1698 (C=O), 1609 (C=C) 1175, 1017, 810.). δH (400 MHz CDCl3) : 5.52 (2H, s, br, NH2), 7.6 – 6.8 (7H, m, Ar-H). Anal. Calcd for C16H8ClNO2: C, 64.77; H, 3.06; N, 9.44. Found: C, 64.56; H, 2.97; N, 9.60.

General method for preparation of Schiff base derivatives

General method for preparation of Schiff base derivatives

A mixture of 4-chlorobenzaldehyde (1.0 g, 8.06 mmole) and 6-chloro-10-aminobenzo[a]phenoxazine-5-one (2.4 g, 8.04 mmole) was stirred in a solution of water (15 cm^3) and ethanol (5 cm^3) at room temperature for 1 h. The crude formed was collected by filtration, washed with water, dried and recrystallized from a mixture of ethanol (15 cm^3) and DMF (5 cm^3) to give pure compound 6-chloro-10-[(4-chlorophenylimino)benzo[a]- phenoxazin-5-one as a dark-brown solid after recrystallization from a mixture of ethanol (15 cm^3) and DMF (5 cm^3): (m.p; 233-238°C, yield 2.28 g, 70.15 %). Ultraviolent maximum absorption bands in ethanol/DMF, $\lambda_{max:}$ (nm): 308 369, 429, 493, 540. FT-Infrared: 3060 (=C-H stretch), 1750 (C=O) 1687 (CH=N) 1590 (C=C).). δ_H (400 MHz $CDCl_3$) : 5.8 (H, s, HC=), 8.2 – 7.5 (11H, m, Ar-H). Anal. Calcd for $C_{23}H_{12}Cl_2N_2O_2$: C, 65.89; H, 2.88; N, 6.68. Found: C, 65.56; H, 2.97; N, 9.66.

6-Chloro-10-(4-fluorophenylimino)benzo[a]phenoxazin-5-one (10)

6-Chloro-10-[(4-fluorophenylimino)benzo[a]-phenoxazin-5-one as black solid (m. p; 220-222°C, yield 2.12, 67 %). Ultraviolent maximum absorption bands in ethanol/DMF, $\lambda_{max:}$ (nm): 298, 357, 402, 462, 510. FT-Infrared: 3090 (=C-H stretch). 1725 (C=O), 1675 (CH=N), 1502 (C=C). δ_H (400 MHz $CDCl_3$) : 6.1 (H, s, HC=), 8.5 – 7.2 (11H, m, Ar-H). Anal. Calcd for $C_{23}H_{12}ClFN_2O_2$: C, 68.58; H, 3.00; N, 6.95. Found: C, 68.56; H, 2.97; N, 6.91.

10-{(4-amino-3,5-dimethylbenzylidine)amino}-6-chlorobenzo[a]phenoxazine-5-one (11)

Black solid after recrystallization from a mixture of ethanol; Ultraviolent maximum absorption bands in ethanol/DMF, $\lambda_{max:}$ (nm): 308, 389, 482, 535. FT-Infrared: 3050 (=C-H stretch). 1721(C=O), 1665 (CH=N), 1602, 1475 (C=C). δ_H (400 MHz $CDCl_3$) : 2.5 - 3.0 (6H, m), 6.2 (H, s, HC=), 8.8 – 6.7 (9H, m, Ar-H), 9.5 (2H, NH_2). Anal. Calcd for $C_{25}H_{18}ClN_3O_2$: C, 70.18; H, 4.24; N, 9.82. Found: C, 70.22; H, 4.27; N, 9.76.

-Chloro-10-{(2-methoxybenzylidine)amino}benzo[a]phenoxazine-5-one (12)

Dark-brown solid after recrystallization from a mixture of ethanol; Ultraviolent maximum absorption bands in ethanol/DMF, $\lambda_{max:}$ (nm): 278, 346, 389, 495, 545. FT-Infrared: 3090 (=C-H stretch). 2970 (C-H, CH_3), 1810 (C=O), 1680 (CH=N), 1570, 1510 (C=C). δ_H (400 MHz $CDCl_3$) : 3.4 - 3.5 (3H, s, -OCH_3), 6.0 (H, s, HC=), 8.2 – 7.5 (10H, m, Ar-H). Anal. calcd for $C_{23}H_{12}Cl_2N_2O_2$: C, 65.89; H, 2.88; N, 6.68. Found: C, 65.56; H, 2.97; N, 9.66.

6-Chloro-10-(4-methylphenylimino)benzo[a]phenoxazin-5-one (13)

Dark-brown solid after recrystallization from a mixture of ethanol; Ultraviolent maximum absorption bands in ethanol/DMF, $\lambda_{max:}$ (nm): 260, 328, 387, 493, 530. FT-Infrared: 3070 (=C-H stretch). 2890 (C-H, CH_3), 1721 (C=O); 1672 (CH=N), 1502, 1480 (C=C). 2.2 - 2.3 (3H, s, CH_3), 6.2 (H, s, HC=), 8.3 – 6.6 (11H, m, Ar-H). Anal Calcd for $C_{24}H_{15}ClN_2O_2$: C, 72.27; H, 3.79; N, 7.02. Found: C, 72.36; H, 3.97; N, 7.21.

Analysis of the synthesized compounds for their fastness properties

Preparation of dye solution

Dye sample (1.0 g) was weighed into a beaker and little amount of water was added to make it into paste after which it was made up to 100 cm^3 with water at 50°C. The sparingly suspension was heated for 5 min with addition of calculated amount of sodium hydrosulfite to aid proper dissolution and formation of leuco-base. Cotton material (2.0 g) to be dyed was scoured with soap and rinsed in water and was introduced into the dye bath solution and dyeing commenced for 30 min at 60°C, after which the fabric was removed and oxidized in air. The dyed fabric was heated in a mild alkaline detergent solution at boiling temperature and finally of and rinsed in water to remove any loose dye particle from the fabric. The fabric was then air dried and tested for fastness properties.

On the other hand, the fabric was mordanted by introducing the scoured fabric into 2 % solution of potassium dichromate, Alum, stannous chloride and iron sulphate in each case respectively for 30 min at 60°C after which the fabric were then dyed in the dye bath for 30 min at 60°C. The dyed fabric was air dried and tested for fastness properties.

Light fastness

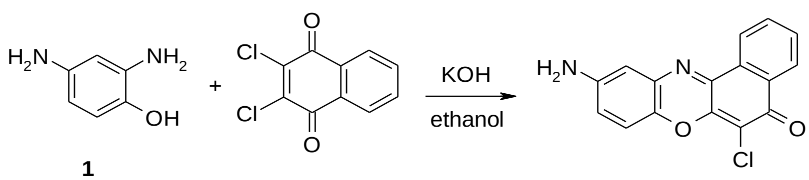
One set of the dyed fabric was exposed to sunlight for one week and the other set was kept in polythene, away from light for one week. The two sets were rated in grey scale.

Wash fastness

The dye fabrics were made into sets. One set of the fabric was washed in mild soap while the second set in a strong soap. The washed fabrics were compared with the unwashed ones in a grey scale.

RESULTS AND DISCUSSION

2,4-diaminophenol condensed and cyclised with 2,3-dichloro-1,4-naphthoquinone under reflux in an alkaline medium for 6 h and after work-up to gave 6-Chloro-10-aminobenzo[a]phenoxazine-5-one **3**. FT-IR spectra show bands at 3444-3324 (N-H) and 1761, 1698 (C=O), (Figure 1).



1 **2** **3**

Figure 1: Synthesis of 6-chloro-10-aminobenzo[a]phenoxazin-5-one (intermediate) 3

Further condensation of 6-Chloro-10-aminobenzo[a]phenoxazin-5-one with 4-chlororbenzaldehyde **4**, 4-fluorobenzaldehyde **5**, 4-amino-3,5-dimethylbenzaldehyde **6**, 2-methoxybenzaldehyde **7**, and 4-methylbenzaldeyde **8**, respectively gave the following derivatives: 6-Chloro-10-(4-chlorophenylimino)benzo[a]phenoxazin-5-one **9**, 6-Chloro-10-[(4-fluorophenylimino)]benzo[a]phenoxazine-5-one **10**, 10-[(4-amino-3,5-dimethyl- benzylidine)-amino]-6-chlorobenzo[a]phenoxazine-5-one **11**, 6-Chloro-10-[(2-methoxybenzylidine)-amino]benzo[a]phenoxazine-5-one **12** and 6-Chloro-10-(4-methylphenylimino)benzo[a]phenoxazin-5-one **13**. FT-IR spectral of all the compounds gave strong bands at 1841-1720 for (C=O) of carbonyl and 1680-1665 for (CH=N) functional groups; however absence of bands at 3440-3350 for (N-H) in all the products except for compound **11** was an evidence that the condensation reactions of the amino group of the intermediate with the carbonyl was achieved successfully (Figure 2).

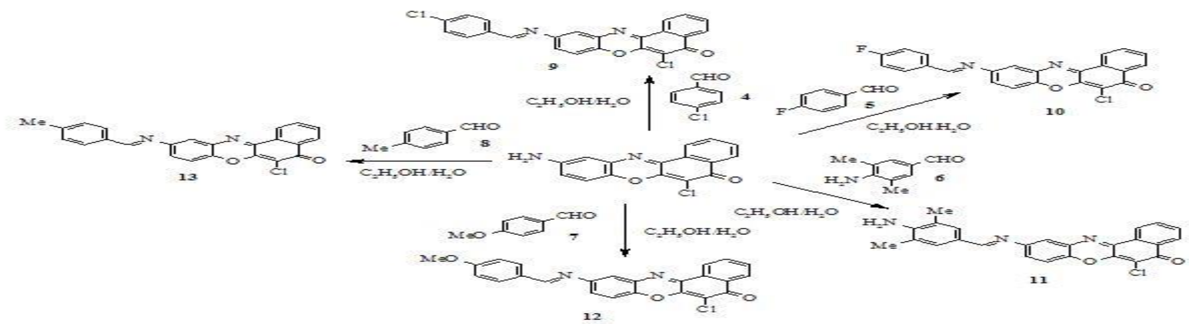


Figure 2: Synthesis of the Imino derivatives

All the compounds were tested for their fastness properties and from the observations; some of them have good fastness properties.

Results of the fastness properties of the dyes/mordants as presented in the tables

The findings resulted from light and wash fastness testing of the dyes/mordants on the dyed fabric are presented in the tables. Some of the mordants utilized with the synthesized dyes enhanced the fastness properties to light and washing with mild soaps. The observation of the fastness properties the dyes suggested that they can serve as industrial colourants in the needed industries

Table 1: Fastness of the intermediate (6-Chloro-10-aminobenzo [a] phenoxazine-5-one (3)

Wash fastness				
Sample/Mordants	**Fabric colour**	**Light fastness**	**Mild soap**	**Strong soap**
Intermediate (3)	Light-brown	02-03	02-03	02-03
Alum	Brown	02-03	03-04	02-03
$K_2Cr_2O_7$	Brown	01-02	02-03	02-03
Stannous chloride	Brown	02-03	03-04	02-03
$FeSO_4$	Dark brown	02-03	03-04	02-03
Note: Scale: 1-2---Most colour change, 2-3---Colour change, 3-4---Slight colour change, 4-5---Colour retained				

In Table 1, it was observed that the compound that was mordanted with (alum, $K_2Cr_2O_7$ and $FeSO_4$) exhibited good fastness to wash with mild soap whereas the other mordant showed fair fastness properties. None showed good fastness to both light and strong soap (Table 2).

Table 2: Fastness properties of the new compounds without mordants

Wash resistance				
Dye sample	**Fabric colour**	**Light fastness**	**Mild soap**	**Strong soap**
9	Brown	03-04	02-03	01-02
10	Yellow	03-04	03-04	01-02
11	Dark brown	02-03	03-04	02-03
12	Black	02-03	02-03	01-02
13	Brown	01-02	02-03	01-02

Observation shows that samples 9 and 10 have good light fastness, while 10 and 11 have good fastness to mild soap (Table 3).

Table 3: Fastness properties of 6-chloro-10-[(4-chlorobenzylidine)imino]benzo[a]- phenoxazin-5-one (9) with mordants

Wash resistance				
Dye sample/mordants	**Fabric colour**	**Light fastness**	**Mild soap**	**Strong soap**
Alum	Brown	03-04	02-03	01-02
Potassium dichromate	Brown	02-03	01-02	01-02
Stannous chloride	Yellowish-brown	03-04	02-03	01-02
$FeSO_4$	Brown	03-04	03-0004	03-04

Compound (9) mordanted with Alum, $SnCl_2$, $FeSO_4$ exhibited good fastness to light. $FeSO_4$ also showed fastness to light, mild and strong soap.

Table 4: Fastness properties of 6-chloro-10-[(4-fluorobenzylidine)imino]benzo[a]- phenoxazin-5-one (10) with mordants.

			Wash fastness	
Dye sample/mordants	**Fabric Colour**	**Light Fastness**	**Mild Soap**	**Strong Soap**
Alum	Yellow	3-4	2-3	2-3
$K_2Cr_2O_7$	Yellow	3-4	2-3	2-3
Stannous chloride	Light yellow	3-4	3-4	2-3
$FeSO_4$	Brownish- yellow	4-5	4-5	3-4

Result from Table 4 shows that, the dye sample mordanted with $FeSO_4$ exhibited excellent fastness property to both light and mild soap and very good to strong soap whereas others showed fair to good fastness properties.

Table 5: Fastness properties of 10-[(4-amino-3,5-dimethylbenzylidine)imino]-6-chlorobenzo[a]phenoxazin-5-one (11) with mordants.

			Wash fastness	
Dye sample/mordants	**Fabric colour**	**Light fastness**	**Mild soap**	**Strong soap**
Alum	Brown	01-02	03-04	02-03
$K_2Cr_2O_7$	Brown	01-02	02-03	01-02
Stannous chloride	Brown	02-03	02-03	03-04
$FeSO_4$	Dark-brown	04-05	04-05	03-04

Result from Table 5 shows that dye sample mordanted with $FeSO_4$ exhibited the superior fastness property to light and mild soap. Alum mordant showed good fastness to wash with mild soap. Stannous chloride also showed good fastness property to wash with strong soap.

Table 6: Fastness properties of 6-chloro-10-amino-[(4-methoxybenzylidine)imino]- benzo[a]phenoxazin-5-one (12) with mordants

Wash resistance				
Dye sample/mordants	**Fabric colour**	**Light fastness**	**Mild soap**	**Strong soap**
Alum	Black	02-03	02-03	01-02
$K_2Cr_2O_7$	Black	02-03	01-02	01-02
Stannous chloride	Black	03-04	03-04	03-04
$FeSO_4$	Black	02-03	03-04	03-04

Results from Table 6, in wash fastness, dye sample mordanted with $SnCl_2$ and $FeSO_4$ showed better fastness than Alum and $K_2Cr_2O_7$ while Alum and $K_2Cr_2O_7$ showed poor fastness to strong soap.

Table 7: Fastness properties of 6-Chloro-10-(4-methylphenylimino)benzo[a]phenoxazin-5-one (13) with mordants

Wash fastness				
Dye sample/mordants	**Fabric colour**	**Light fastness**	**Mild soap**	**Strong soap**
Alum	Dark brown	01-02	02-03	02-03
$K_2Cr_2O_7$	Light-brown	02-03	02-03	02-03
Stannous chloride	Dark-brown	01-02	03-04	03-04
$FeSO_4$	Dark-brown	01-02	03-04	02-03

From Table 7 dye sample mordanted with stannous chloride, $FeSO_4$ exhibited good fastness to wash with mild soap whereas others showed good fastness to wash with mild and strong soap.

CONCLUSION

Some imino derivatives of angular phenothiazine has been synthesized and evaluated for their dyeing fastness properties. The results from the study shows that the compounds synthesized can be used as industrial colourants as they exhibited good to very good fastness properties when mordanted.

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