INTRODUCTION

Phenothiazine and phenoxazine and their derivatives were mainly traditionally applied as dyes and pigments in industry, but with time, found wider applications as antioxidant in lubricants and fuel, polymerization stabilizers, pesticides/insecticides, biological stains or labelings, acid-base indicators and as drugs [1,2]. Lauth’s violet (1) and Meldola (2) were foremost known phenothiazine and phenoxazine commercial dyes [3,4]. Meldola dyes are good colourant for papers and textiles.

The intense colouration of phenothiazines and phenoxazine derivatives necessitated the functionalization of the parent structures with a few of synthesizing new dyes and pigments. Okafor and Okoro had reported the synthesis of new nonlinear polycyclic azaphenoxazine dyestuffs [5,6]. We have also recently described a rapid access to new angular phenothiazine and phenoxazine dyes via palladium catalyzed cross-couplings [1]. As a result of our interest in synthesis of new dyes, a convenient syntheses of new derivatives of phenoxazine and benzoxazinophenothiazine employing classical organic synthetic procedures is now reported.

EXPERIMENTAL

Melting points was determined with a Fischer-Johns apparatus and were uncorrected. $^1$H NMR data were recorded with Brucker DPX 400 MHz spectrophotometer relative to TMS as internal standard. The chemical shifts and coupling constant $^3$J were reported in ppm ($\delta$) and Hz respectively. UV-visible spectra were recorded on Cecil 7500 Aquarius 7000 Series Spectrometer at Chemistry Advance Laboratory (CAL), Sheda Science and Technology Complex (Shestco) Abuja, using matched 1cm quartz cells and methanol as solvent. Elemental analyses were obtained on Heraeus CHN-O rapid analyzer.

10-Amino-6-chlorobenzo[a]phenoxazin-5-one (5):

To a mixture of 2,4-diaminophenol (4 g, 32 mmol) and anhydrous sodium trioxocarbonate(IV) (3.3 g, 31 mmol) in 250 mL two-necked flask equipped with magnetic stirrer, thermometer and reflux condenser, was added a solution of benzene (100 mL) and methanol as solvent. Elemental analyses were obtained on Heraeus CHN-O rapid analyzer.

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acetamide 

211-213 °C. UV-visible (MeOH) λ\(_{\text{max}}\): 450 (3.49); 621 (2.99). IR (KBr, \(v_{\text{max}}\), cm\(^{-1}\)):\(1631\) (C=O). 1H NMR (MeOH-d\(_4\)): 8.71-7.22 (16H, m, Ar-H). Anal. calcd. (found) for C\(_{22}\)H\(_{14}\)N\(_2\)O\(_2\): C, 78.09 (78.44); H, 4.17 (4.32); N, 8.28 (8.32).

The crude precipitate was filtered, washed with cold water and the crude product extracted from water (10 mL × 3). The combined extracts were dried with MgSO\(_4\) and concentrated in vacuum. The slurry poured into 100 mL of distilled water and stirred. It was left overnight, filtered and crude product washed with water and recrystallized from toluene to afford the titled compound. Yield: 8.5 g, 85 %; m.p.: > 300 °C. UV-visible (MeOH) λ\(_{\text{max}}\): 250 (3.44); 481 (3.99). IR (KBr, \(v_{\text{max}}\), cm\(^{-1}\)):\(1615\) (C=O). 1H NMR (CDCl\(_3\)): 8.91 (1H, s, -CONH); 8.61-7.02 (12H, m, Ar-H); 1.62 (3H, s, -CH\(_3\)). Anal. calcd. (found) for C\(_{28}\)H\(_{22}\)N\(_2\)O\(_2\): C, 77.73 (77.84); H, 3.85 (3.92); N, 8.50 (8.42).

N-(5-Oxo-6-phenyl-5H-benzo[a]phenoxazin-10-yl)acetamide (7): In a dried 250 mL two-neck round bottom flask containing 10-aminoo-6-phenylbenzo[a]phenoxazin-5-one (19 g, 0.056 mol), acetic anhydride (5 mL, 0.052 mol) was added 5 mL of glacial acetic acid and Zn dust (0.08 g) and the entire mixture refluxed for 10 h. The solvent was distilled off at the end of the reaction and slurry poured into cold water (300 mL) and warmed to dissolve inorganic material. It was left overnight, filtered and crude product washed with water and recrystallized from toluene to afford the titled compound as dark purple powder. Yield: 8.5 g, 85 %; m.p.: > 300 °C. UV-visible (MeOH) λ\(_{\text{max}}\): 250 (3.44); 481 (3.99). IR (KBr, \(v_{\text{max}}\), cm\(^{-1}\)):\(1615\) (C=O). 1H NMR (CDCl\(_3\)): 8.91 (1H, s, -CONH); 8.61-7.02 (12H, m, Ar-H). Anal. calcd. (found) for C\(_{28}\)H\(_{22}\)N\(_2\)O\(_2\): C, 77.73 (77.84); H, 3.85 (3.92); N, 8.50 (8.42).

N-(Benzo[a][1,4]benzoxazo[3,2-c]phenothiazine (9): 2-Aminothiophenol (2 g, 17 mmol) and anhydrous sodium carbonate (1.8 g, 17 mmol) were added into 250 mL round bottom flask containing a solution of benzene (60 mL) and DMF (40 mL) and equipped with a magnetic stirrer, thermometer and reflux condenser. The mixture was warmed for 45 min until complete dissolution was achieved. Then 10-aminoo-6-chlorobenzo[a]phenoxazin-5-one (5 g, 17 mmol) was added and the entire mixture refluxed for 10 h. The solvent was distilled off at the end of the reaction and slurry poured into cold water (300 mL) and warmed to dissolve inorganic material. It was left overnight, filtered and crude product washed with water and recrystallized from toluene to afford the titled compound as dark purple powder. Yield: 8.5 g, 85 %; m.p.: > 300 °C. UV-visible (MeOH) λ\(_{\text{max}}\): 250 (3.44); 481 (3.99). IR (KBr, \(v_{\text{max}}\), cm\(^{-1}\)):\(1615\) (C=O). 1H NMR (CDCl\(_3\)): 8.91 (1H, s, -CONH); 8.61-7.02 (12H, m, Ar-H). Anal. calcd. (found) for C\(_{28}\)H\(_{22}\)N\(_2\)O\(_2\): C, 77.73 (77.84); H, 3.85 (3.92); N, 8.50 (8.42).

RESULTS AND DISCUSSION

Anhydrous base catalyzed coupling of 2,4-diaminophenol with 2,3-dichloro-[1,4]naphthoquinone gave 6-chlorobenzo[a]phenoxazin-5-one (5 g, 17 mmol) and anhydrous sodium carbonate (1.8 g, 17 mmol) were added into 250 mL round bottom flask containing a solution of benzene (60 mL) and DMF (40 mL) and equipped with a magnetic stirrer, thermometer and reflux condenser. The mixture was warmed for 45 min until complete dissolution was achieved. Then 10-aminoo-6-chlorobenzo[a]phenoxazin-5-one (5 g, 17 mmol) was added and the entire mixture refluxed for 10 h. The solvent was distilled off at the end of the reaction and slurry poured into cold water (300 mL) and warmed to dissolve inorganic material. It was left overnight, filtered and crude product washed with water and recrystallized from toluene to afford the titled compound as dark purple powder. Yield: 8.5 g, 85 %; m.p.: > 300 °C. UV-visible (MeOH) λ\(_{\text{max}}\): 250 (3.44); 481 (3.99). IR (KBr, \(v_{\text{max}}\), cm\(^{-1}\)):\(1615\) (C=O). 1H NMR (CDCl\(_3\)): 8.91 (1H, s, -CONH); 8.61-7.02 (12H, m, Ar-H). Anal. calcd. (found) for C\(_{28}\)H\(_{22}\)N\(_2\)O\(_2\): C, 77.73 (77.84); H, 3.85 (3.92); N, 8.50 (8.42).
In another development, compound 5 was reacted with 2-aminothiophenol to obtain 12-aminobenzo[\(a\)]\([1,4]\)benzoxazino[3,2-c]phenothiazine (9) in high yield as dark purple high melting powder.

Acetylation and diazotization of compound 9 supply \(N\)-(benzo[\(a\)]benzo[5,6][1,4]oxazino[3,2-c]phenothiazin-12-yl)acetamide (10) and \(N\)-(benzo[\(a\)]benzo[5,6][1,4]oxazino[3,2-c]phenothiazin-12-yl)azo-\(\beta\)-naphthol (11). Compounds 10 and 11 are new polycyclic triangular shape benzoxazino-phenothiazine dyes (Scheme-II). Their structures were established by combined spectroscopic and analytical data.

The synthesized compounds impart pink and light pink on cotton fabrics. Among the compounds studied, only compound 11 exhibited a low colour property. Compounds 7, 8, 9 and 10 showed very high fastness to both mild and strong soap. Their light fastness is only fair and may be improved by increasing the amount of mordants used.

### Conclusion

Highly coloured and new angular phenoxazine and triangular benzoxazinophenothiazine dyestuffs were obtained via acetylation and diazotization of 10-amino-6-phenylbenzo[a]phenoxazin-5-one and 12-aminobenzo[a][1,4]benzoxazino[3,2-c]phenothiazine respectively.

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