

New Angular Phenoxazine and Triangular Benzoxazinophenothiazine Dyestuffs

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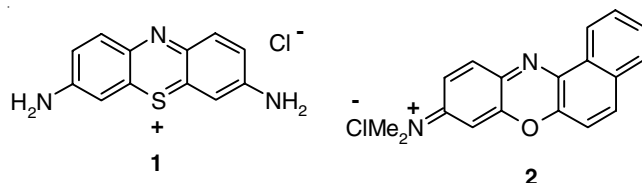
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In this study, the synthesis of new angular phenoxazine and triangular benzoxazinophenothiazine dyestuffs is described. This was achieved by the synthesis of 10-amino-6-chlorobenzo[a]phenoxazin-5-one intermediate. The intermediate was converted into 10-amino-6-phenylbenzo[a]phenoxazin-5-one by Suzuki-Miyaura cross-coupling with phenyl boronic acid. Acetylation as well as diazotization of the intermediate supplied *N*-(oxo-6-phenyl-5*H*-benzo[a]phenoxazin-10-yl) acetamide and *N*-(oxo-6-phenyl-5*H*-benzo[a]phenoxazin-10-yl)-azo- β -naphthol in high yields as new dyes respectively. In another development, the intermediate 10-amino-6-chlorobenzo[a]phenoxazin-5-one was reacted with another mole of 2,3-dichloro-1,4-naphthoquinone to afford 12-aminobenzo[a][1,4]benzoxazino[3,2-*c*]phenothiazine which was acetylated to obtain *N*-(benzo[a]benzo[5,6][1,4]oxazino[3,2-*c*]phenothiazin-12-yl)acetamide. The reaction of 2-naphthol with diazotized 12-aminobenzo[a][1,4]benzoxazino[3,2-*c*]phenothiazine gave *N*-(benzo[a]benzo[5,6][1,4]oxazino[3,2-*c*]phenothiazin-12-yl)-azo- β -naphthol as new dye. Structural assignments were confirmed by spectral and elemental analytical data.

Keywords: Phenoxazine, Phenothiazine, Benzophenoxazine, Dyestuffs.

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. ¹H NMR data were recorded with Bruker DPX 400 MHz spectrophotometer relative to TMS as internal standard. The chemical shifts and coupling constant *J* were reported in ppm (δ) 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 DMF (10 mL). The mixture was boiled for 0.5 h followed by addition of 2,3-dichloro-1,4-naphthoquinone (7.26 g, 32 mmol) and the entire mixture refluxed with continuous stirring for 5 h. At the end of the reaction the solvent was distilled off

in vacuum. The slurry poured into 100 mL of distilled water and the crude product filtered out. The crude was recrystallized from aqueous ethanol to obtain the titled compound. Yield: 8.5 g, 85 %; m.p.: 181-183 °C. UV-visible (MeOH) λ_{max} : 450 (3.49); 621 (2.99). IR (KBr, ν_{max} , cm^{-1}): 1631 (C=O). ^1H NMR (CDCl_3): 5.2 (2H, br, -NH₂); 8.31-7.24 (14H, m, Ar-H). Anal. calcd. (found) for C₁₆H₉N₂O₂Cl: C, 66.77 (66.64); H, 3.06 (3.22); N, 9.44 (9.32).

10-Amino-6-phenylbenzo[a]phenoxazin-5-one (6): To a clean dry three-necked 10 mL round bottom flask containing 3 mL of dioxane was added 10-amino-6-chlorobenzo[a]phenoxazin-5-one (297 mg, 1 mmol), phenylboronic acid (146 mg, 1.2 mmol) and K₂CO₃ (276 mg, 2 mmol) and the entire mixture warmed to 40 °C under inert atmosphere. This was followed by addition of Pd(OAc)₂ (9 mg, 4 mol %) and Xphos (33 mg, 7 mol %) and the entire mixture heated at 80 °C for 8 h. The reaction was cooled to room temperature and evaporated the solvent. This was followed by addition of 5 mL of water and the crude product extracted from water (10 mL × 3). The combined extracts were dried with MgSO₄ and concentrated in vacuum to obtain the crude product which was purified by column chromatography (5 % EtOAc)/95 % hexane to get the pure compound. Yield: 210 mg, 62 %; m.p.: 203-205 °C. UV-visible (MeOH) λ_{max} : 461 (3.49); 725 (3.77). IR (KBr, ν_{max} , cm^{-1}): 1645 (C=O). ^1H NMR (CDCl_3): 4.81 (2H, br, -NH₂); 8.71-7.22 (16H, m, Ar-H). Anal. calcd. (found) for C₂₂H₁₄N₂O₂: C, 78.09 (78.44); H, 4.17 (4.32); N, 8.28 (8.32).

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-amino-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 flask equipped with refluxed condenser. The mixture was gently boiled for 1 h and the hot liquid poured in a thin stream into 250 mL beaker containing 100 mL of water and stirred. The crude precipitate was filtered, washed with cold water and dried. The dried crude product was recrystallized from methanol-acetone mixture yielded the titled compound as reddish microcrystalline powder. Yield: 15 mg, 71 %; m.p.: 211-213 °C. UV-visible (MeOH) λ_{max} : 324 (3.41); 411 (3.49); 665 (3.77). IR (KBr, ν_{max} , cm^{-1}): 1645, 1710 (C=O). ^1H NMR (CDCl_3): 8.91 (1H, s, -CONH); 8.61-7.02 (12H, m, Ar-H); 1.62 (3H, s, -CH₃). Anal. calcd. (found) for C₂₄H₁₆N₂O₃: C, 75.78 (75.84); H, 4.24 (4.42); N, 7.36 (7.52).

10-(2-Hydroxy-naphthalen-1-yl-azo)-6-phenylbenzo[a]phenoxazin-5-one (8): 10-Amino-6-phenylbenzo[a]phenoxazin-5-one (8 g, 24 mmol) was dissolved in a mixture of concentrated hydrochloric acid (16 mL) and water (16 mL) followed by addition of a solution of 4 g of sodium nitrite in 20 mL of water. The diazotization was carried on at temperature ≤ 5 °C. Thereafter a solution of 2-naphthol (4.0 g, 28 mmol) in 45 mL of 10 % sodium hydroxide solution was prepared at a temperature ≤ 5 °C. The stirred solution of 2-naphthol was added to cold diazonium salt solution gradually while stirring. The resultant golden yellow mixture was allowed to stand on iced bath for 0.5 h with occasional stirring after which it was filtered through suction and recrystallized from aqueous ethanol. Yield: 10 g, 78 %; m.p.: 187-189 °C. UV-visible (MeOH) λ_{max} : 350 (3.41);

511 (3.42); 735 (4.07). IR (KBr, ν_{max} , cm^{-1}): 3451 (-OH) 1635 (C=O), 1440 (-N=N-). ^1H NMR (CDCl_3): 8.71-6.82 (18H, m, Ar-H); 5.41 (1H, br, s, -OH). Anal. calcd. (found) for C₃₂H₁₉N₃O₃: C, 77.73 (77.84); H, 3.85 (3.92); N, 8.50 (8.42).

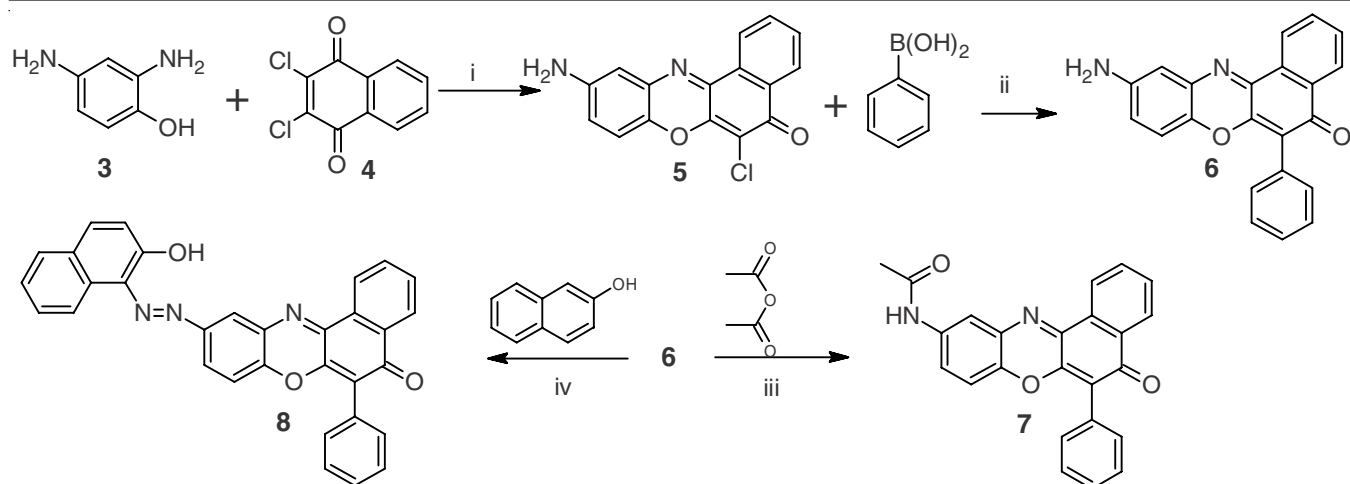
12-Aminobenzo[a][1,4]benzoxazino[3,2-c]phenothiazine (9): 2-Aminothiophenol (2 g, 17 mmol) and anhydrous sodium carbonate (1.8 g, 17 mmol) were added into 250 mL round bottom flask containing a solution of benzene (60 mL) and DMF (40 mL) and equipped with a magnetic stirrer, thermometer and reflux condenser. The mixture was warmed for 45 min until complete dissolution was achieved. Then 10-amino-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_{max} : 250 (3.44); 481 (3.99). IR (KBr, ν_{max} , cm^{-1}): 3050 (Ar-H); 860, 852. ^1H NMR (CDCl_3): 9.11 (2H, br, -NH₂); 8.31-7.24 (11H, m, Ar-H). Anal. calcd. (found) for C₂₂H₁₃N₃OS: C, 71.92 (71.84); H, 3.54 (3.32); N, 11.44 (11.32).

N-(Benzo[a]benzo[5,6][1,4]oxazino[3,2-c]phenothiazin-12-yl)acetamide (10): The titled compound was similarly prepared as compound 7 except 12-aminobenzo[a][1,4]-benzoxazino[3,2-c]phenothiazine (21 g, 0.057 mol) was used in place of 10-amino-6-phenylbenzo[a]phenoxazin-5-one (19 g, 0.056 mol). Yield: 17 g, 74 %; m.p.: > 300 °C. UV-visible (MeOH) λ_{max} : 284 (3.21); 519 (3.44); 715 (4.07). IR (KBr, ν_{max} , cm^{-1}): 1720 (C=O). ^1H NMR (CDCl_3): 8.91 (1H, s, -CONH); 8.61-7.02 (11H, m, Ar-H); 1.50 (3H, s, -CH₃). Anal. calcd. (found) for C₂₄H₁₅N₃O₂S: C, 70.40 (70.45); H, 3.69 (3.42); N, 10.26 (7.52).

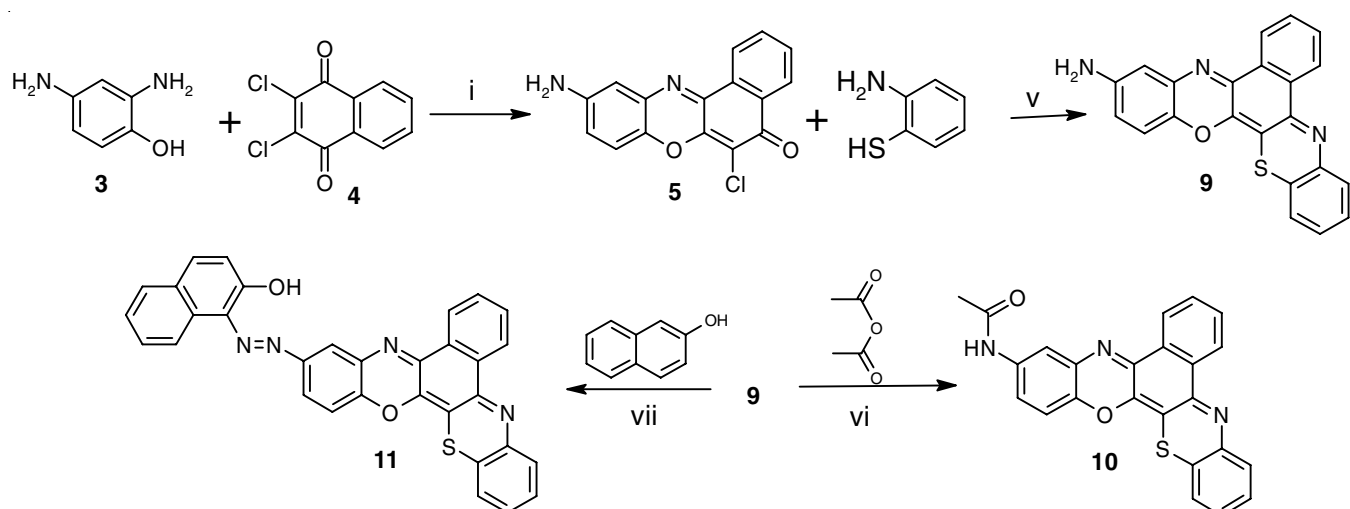
N-(Benzo[a]benzo[5,6][1,4]oxazino[3,2-c]phenothiazin-12-yl)azo- β -naphthol (11): The titled compound was prepared in a similar procedure to compound 8, except 12-aminobenzo[a][1,4]benzoxazino[3,2-c]phenothiazine (8 g, 22 mmol) was used in place of 10-amino-6-phenylbenzo[a]phenoxazin-5-one (8 g, 24 mmol). Yield: 8.5 g, 77 %; m.p.: 280 (dec.). UV-visible (MeOH) λ_{max} : 350 (3.41); 471 (3.42); 785 (4.07). IR (KBr, ν_{max} , cm^{-1}): 3355 (-OH); 1510 (-N=N-). ^1H NMR (CDCl_3): 8.81-6.82 (14H, m, Ar-H); 6.10 (1H, br, s, -OH). Anal. calcd. (found) for C₃₂H₁₈N₄O₂S: C, 73.55 (73.64); H, 3.47 (3.52); N, 10.72 (10.52).

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**) as orange solid after recrystallization from ethanol. The arylation of compound **5** via Suzuki-Miyaura reaction supplied 10-amino-6-phenylbenzo[a]phenoxazin-5-one (**6**) as yellow solid. Acetylation and diazotization of compound **6** afforded *N*-(5-oxo-6-phenyl-5H-benzo[a]phenoxazin-10-yl)-acetamide (**7**) and 10-(2-hydroxy-naphthalen-1-yl-azo)-6-phenylbenzo[a]phenoxazin-5-one (**8**), respectively (**Scheme-I**). The structures of the prepared compounds were established by combined spectroscopic and analytical data.



Scheme-I: (Reaction conditions and reagents) i = $\text{Na}_2\text{CO}_3/\text{C}_6\text{H}_6\text{-DMF}$; ii = $\text{Pd}(\text{OAc})_2/\text{XPhos}$, K_2CO_3 , 1,4-dioxane; iii = glacial CH_3COOH , Zn dust; iv = NaNO_2/HCl , $T \leq 5^\circ\text{C}$



Scheme-II: (Reaction conditions and reagents) i/v = $\text{Na}_2\text{CO}_3/\text{C}_6\text{H}_6\text{-DMF}$; vi = glacial CH_3COOH , Zn dust; vii = NaNO_2/HCl , $T \leq 5^\circ\text{C}$

In another development, compound **5** was reacted with 2-aminothiophenol to obtain 12-amino-6-phenyl-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- β -naphthol (**11**). Compounds **10** and **11** are new polycyclic triangular shape benzoxazinophenothiazine 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-amino-6-phenylbenzo[*a*][1,4]benzoxazino[3,2-*c*]phenothiazine respectively.

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