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Synthesis, spectral features and biological activity of some novel hetarylazo dyes derived from 8-chloro-4-hydroxyl-2-quinolone

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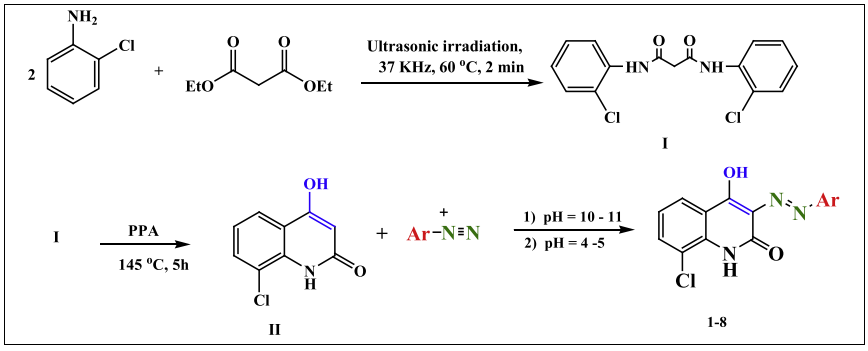
HIGHLIGHTS

- Preparation of some new azo dyes derived from 8-chloro-4-hydroxyl-2-quinolone.
- Characterization and evaluation of solvatochromic properties.
- Effects of concentration.
- Anti microbial activity of dyes were measured.

GRAPHICAL ABSTRACT

Synthetic routes for the preparation of hetarylazo dyes.



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ABSTRACT

In this study, 8-chloro-4-hydroxyl-2-quinolone was synthesized from cyclocondensation of corresponding dianilide and subsequently used as a potent coupling component with some diazotized heterocyclic amines. These compounds were characterized by UV–vis, FT-IR, ^{1}H NMR spectroscopic techniques and elemental analysis. Absorption spectra of these dyes were measured in six polar solvents and discussed with respect to the nature of solvents and substituted groups. The effects of acid, base, temperature and concentration on the visible absorption spectra of the dyes were reported. In addition, the antimicrobial activity of the dyes was explored in detail.

Introduction

Quinolones are one of the important classes of heterocyclic compounds, due to their unique biological and pharmacological activities, such as anti-thyroid, anticancer, anti-tubercular and antihypertensive, cardiotonic, diuretic and anti-inflammatory properties [1–7]. Furthermore, 4-hydroxyquinolone (4HQ) derivatives, for example L-701,324, L-703,717 and methoxy-MDL-104, 653 are one of the most potent and orally active antagonists for the glycine-binding site [8,9]. Some derivatives of quinolone are prepared by using 4-hydroxy quinolones as the starting material: for example, the reaction of 4-hydroxy-2(1*H*)-quinolones with α-acetyl-γ-butyrolactone in the presence of ammonium acetate gave pyrano[3,2-c]-quioline-2,5-diones [10]. As another example, treating 4-hydroxyquinolin-2(1*H*)-one with isatin and malononitrile in ethanol in an undivided cell in presence of sodium bromide,

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as an electrolyte, affords the spiro[indole-3,4′-pyrano [3,2-c]quinolines] that are useful for human cancer therapy and other biomedical applications [11]. Moreover, spiro[piperidine-4,4′-pyrano[3,2-c]quinolines] are prepared by the condensation of 4-hydroxyquinolone derivatives with α, β-unsaturated nitrile compounds [12].

Azo compounds are the most widely used class of dyes because of their versatile applications in various fields such as the dyeing, LCD color filters, chromophoric substrates for redox enzymes, design of optical data storage and advanced organic synthesis [13–21]. Among the azo dyes, heterocyclic azo compounds have brilliant color and chromophoric strength, excellent light, washing and sublimation fastness, as well as wide application as high level-dying agent in the dyestuff industry [22–24]. Furthermore, some heterocyclic azo compounds find application in biological and pharmacological studies [25,26]. For example, pyrazole and quinolone dyes have rich pharmaceutical applications due to antibacterial activity [27,28]. To the best of our knowledge, however, antimicrobial activity compounds containing hetarylazoquinolone dyes have not been studied so far. According to the importance of these compounds, and in continuation of our previous investigations, the synthesis of 8-chloro-4-hydroxy-2-quinolone and its application as coupling agent in reaction with some heterocyclic amines as diazo components are reported. The effects of solvents, substituent, acid and base on the visible absorption spectra of the dyes were investigated. In addition, the newly synthesised dyes were evaluated for their antimicrobial activity against *Escherichia coli*, *Bacillus subtilis*, *Micrococcus leuteus* and *Pseudomonas aeruginosa*. These dyes were active on both Gram-positive (*B. subtilis*, *M. leuteus*) and Gram-negative (*E. coli*, *Ps. aeruginosa*) bacteria. The structures of coupling component and prepared dyes are shown in Schemes 1 and 2.

Experimental

General

All starting materials were obtained from Merck Chemical Company and Aldrich Chemical Company and were used without further purification. IR spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained by FT-NMR 400 and 100 MHz Brucker apparatus in DMSO-d_6, using TMS as internal standard. The absorption spectra of the compounds were run on a Cary UV–vis double-beam spectrophotometer (Model 100). The elemental analysis was determined on a Leco CHNS-900 analyzer. Melting points were recorded with an electro-thermal apparatus and uncorrected.

Preparation of N, N′-di-(2-chlorophenyl)malonamide

2-Chloro aniline (2.55 g, 20 mmol), diethyl malonate (1.14 mL, 10 mmol) was properly mixed in a 25 mL beaker and well mixed. The obtained mixture was sonicated at frequencies of 37 kHz at 60 °C for 2 min. The crude product was recrystallized in a minimum amount of ethanol to give compound **I** as a white powder, Yield: 93%, Mp: 192–193 °C. FT-IR (KBr): ν (cm^{-1}) = 3100 (NH), 1685 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6); δ 10.39 (NH), 7.80 (2H, d, J = 8.0 Hz), 7.50 (2H, d, J = 7.6 Hz), 7.20 (2H, dd, J = 8.0, 7.6 Hz), 7.02 (2H, dd, J = 7.6, 7.2 Hz), 3.58 (2H, s, –CH$_2$-).

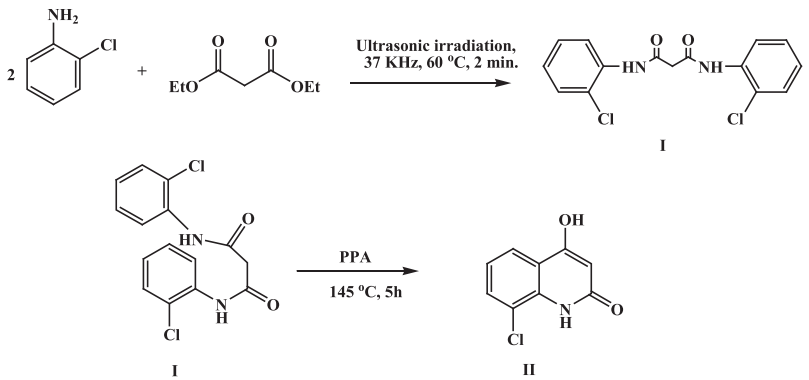
Synthesis of 8-chloro- 4-hydroxyquinoline -2-(1H)-one

The *N, N′*-di-(2-chlorophenyl)malonamide (0.65 g, 2.0 mmol) and polyphosphoric acid (3.55 g) were stirred in an oil bath for 5 h at 145 °C. Then the mixture was cooled, diluted with water and the resultant gum solidified by standing over night. The crude product was dissolved in 20 mL of sodium hydroxide solution 0.1 mol L^{-1} and the residual was filtered off. The filtrate was acidified with concentrated hydrochloric acid and the resulting precipitate was recrystallized in a minimum amount of ethanol to afford 8-chloro-4-hydroxyquinoline-2-(1*H*)-one (**II**) as creamy crystals, Yield 87%, Mp: 302–303 °C (reported 305 °C [29]). FT-IR (KBr): ν (cm^{-1}) = 3470 (OH), 3100 (NH), 1635 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6); δ 11.86 (OH), 10.41 (NH), 7.81 (1H, d, J = 8.0 Hz), 7.67 (1H, d, J = 7.6 Hz), 7.18 (1H, dd, J = 8.0, 7.6 Hz), 5.83 (1H, s). ^{13}C NMR (100 MHz, DMSO-d_6):163.94 (C=O), 162.30 (C—OH), 138.22 (C), 135.32 (C—Cl), 129.12 (CH), 126.20 (C—H), 125.17 (CH), 119.10 (C), 99.19 (CH). Anal. Calcd. for $C_9H_6ClNO_2$: C, 55.26; H, 3.09; N, 7.16;. Found: C, 5.21; H, 3.06; N, 7.12.

The general procedure for the synthesis and purification of disperse azo dyes

For the preparation of dyes **1–8**, the diazonium coupling reaction was employed. The route for synthesis of the dyes is presented in Scheme 2. A typical procedure used for preparation of dyes is described below.

Nitrosyl sulfuric acid solution was prepared from concentrated sulfuric acid (1.5 mL) and sodium nitrite (0.14 g, 2 mmol) at 70 °C and then cooled to 5 °C. This solution was added dropwise, with stirring, to 3 mL of (acetic acid + propionic acid) mixture (5:1v/v) containing 2.0 mmol of heterocyclic amines in an ice bath. The mixture was then stirred for 1.5 h at about 0–5 °C. After completion of diazotization procedure, the diazonium salt solution was added dropwise to the solution of 8-chloro 4-hydroxyquinoline -2-(1*H*)-one (0.39 g, 2.0 mmol) in sodium hydroxide (0.32 g,



Scheme 1. Preparation of 8-chloro-4-hydroxyl-2-quinolone (**II**).