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A study of Solvatochromism in diazonium coupling products of 6-flouro 4-hydroxyl-2-quinolone

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ABSTRACT

6-flouro 4-hydroxyl-2-quinolone was synthesized from cyclocondensation of corresponding dianilide and subsequently used as a potent coupling component with some diazotized aromatic amines. The prepared azo dyes were characterized by UV–vis, FT-IR, ^{1}H NMR spectroscopic techniques and elemental analysis. The solvatochromism of dyes was evaluated with respect to wavelength of maximum absorption (λ_{max}) in six solvents: acetic acid, methanol, chloroform, acetonitrile, dimethyl sulfoxide and dimethyl formamide. The color of the dyes is discussed with respect to the nature of substituents on the benzene ring. The effects of acid and base on the visible absorption spectra of the dyes were also reported. Ionization constants, pK_a, for these dyes were determined in 80 vol.% ethanol–water medium at room temperature and correlated with the substituent constant, σ_x.

1. Introduction

Heterocyclic azo dyes have attracted considerable interest and have played an important role in the development of the chemistry of dyes and dyeing process [1–6]. In this regard, azo dyes based on heterocyclic coupling components have been developed and reported in many patents and papers [7–12]. The resultant dyes have higher tinctorial strength and give brighter dyeing than those derived from benzene based coupling components [13–17]. Of these compounds, very few comparable investigations were carried out using hydroxyl quinolone derivatives. These derivatives afford very electron rich coupling components and consequently can provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds. Izzet sener et al. by using some heterocyclic amine derivatives as diazo components, investigated preparation and the tautomerism in azo dyes synthesizes from 4-hydroxy-2-quinolone [18]. According to the importance of these compounds, the present work reports the synthesis of 6-flouro-4-hydroxyl-2-quinolone and using it as coupling component in reaction with some diazotized aromatic amines as diazo components. The effects of solvents, substituents, acid and base on the visible absorption maxima of the dyes were also reported. The acid dissociation constants of the dyes were determined using electronic spectroscopic method in 80% (v/v) ethanol–water mixtures at 25 ± 2 °C. The ionic strength of the solutions was controlled to be 0.1 using a NaCl solution. The structures of coupling component and prepared dyes are depicted in Schemes 1 and 2.

2. Results and discussion

2.1. Synthesis and characterizations

6-flouro-4-hydroxyl-2-quinolone (**I**) were prepared by refluxing 2 equiv of 4-flouro aniline with dimethyl malonate and cyclocondasation of resulting dianilide in methane sulfunic acid containing 10% of phosphorus pentoxide (instead of $AlCl_3$ used by Zeigler) [19] (Scheme 1).

The IR spectra of compound (**I**) showed strong absorptions at 3500–3150 cm^{-1} for the OH and amide (NH) groups, and at 1637 cm^{-1} for the C=O group. The ^{1}H NMR spectrum (DMSO-d_6) of compound (**I**) revealed a broad peak at 11.29 ppm (1 H, b, NH), a singlet at 5.77 ppm (1H) for the C=C–H of pyridone ring, a dd at 7.27 ppm (1H, J = 8.9, 4.7 Hz), a multiplet at 7.38–7.45 ppm (2H) for the aromatic protons (Aro.-H). The proton decoupled ^{13}C NMR of this compound exhibited 9 distinct resonances at 164.16 ppm (C=O), 162 ppm (C–OH), 157 ppm (C–F), 136 ppm (C), 119 ppm (CH), 117 ppm (CH), 116 ppm (C), 108 ppm (CH) and 99.5 ppm (CH) in agreement with the quinolone structure.

The phenylazoquinolone dyes **1**–**14** were prepared by coupling 6-flouro-4-hydroxyl-2-quinolone with diazotized aniline derivatives (Scheme 2). The dyes may exist in six possible tautomeric forms, named as azo-enol-keto (T_1), azo-enol (T_2), azo-enol (T_3), hydrazone-

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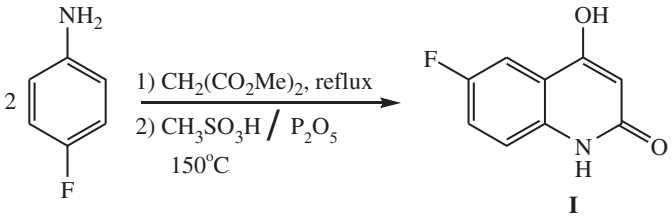


Scheme 1. Preparation of 6-flouro-4-hydroxyl-2-quinolone (**I**).

keto-enol (T_4), hydrazone-keto (T_5) and hydrazone-keto (T_6) as shown in Scheme 3.

As it can be seen in Table 1, the infrared spectra of all the dyes (in KBr) showed broad intense amide (NH–C=O) and hydroxyl (OH) bands at 3436–3288 cm^{-1}. The IR spectra also showed an intense band at 1680–1635 cm^{-1}, which was assigned to amide carbonyl group.

The ^1H NMR spectrum of all the dyes measured in DMSO-d_6 at 25 °C (Table 1) showed a multiplet from 7.18–8.50 ppm for aromatic protons, a singlet at 2.50 ppm (–CH_3, **3**), a singlet at 2.43 ppm (–CH_3, **12**), 2.49 ppm (–CH_3, **13**) and 3.82 ppm (–CH_3, **14**). The broad peaks at 16.34–14.84 ppm were assigned to tautomeric hydrazone proton (=N–NH–).The spectra of the studied compounds **1**–**14** provide additional evidence that they have the Hydrazone-keto structures T_5 and T_6 rather than the enol structures T_1–T_4. For example ^1H NMR spectrum of **10** in deuterated dimethyl sulfuxide exhibits two signals at 15.01 and 15.60 ppm with nearly equal integration ratio. Other compounds in these series show similar patterns (Table 1). These signals undoubtedly correspond to the hydrazone NH proton resonance related to hydrazone-keto forms T_5 and T_6. Further evidence for this assignment is provided by the observation that ^1H NMR spectrum of the ^{15}N-phenylhydrazone derivatives of some azo heterocycles were reported to show two doublets centered at similar regions with J = 93–100 Hz [20] indicating that the proton is attached to nitrogen atom. It was reported that the hydroxyazo OH proton resonance comes 3–5 ppm higher than NH proton resonance, hence, the OH proton resonance signal of enol forms is expected to be in region 9–12 ppm [21,22].Two attributed broad singlet peaks at 11.22–11.36 and 11.40–11.56 ppm for amide (–NH) groups are related to amide protons of two types of tautomeric forms T_5 and T_6.

2.2. Solvent effect

The absorption spectra of the prepared dyes were measured in various solvents at a concentration of approximately10^{-5} to 10^{-6} Mol. L^{-1} and were run at different concentrations. The dyes were completely soluble in DMSO. Therefore, more dilute solutions were prepared, and it was found in all cases that λ_{max} was unaffected by the dye concentration. The stock solutions of each dye were accurately prepared in DMSO and dilutions of these stocks were used for absorption measurements. The results are given in Table 2. The visible absorption spectra of the dyes did not show regular variation with the polarity of solvents.

The electronic absorption spectra of the compounds **1**–**14** in all used solvents revealed a shoulder in the region 347–411 and a band in 396–458 nm (e.g. Fig. 1 for dye **13**). It can be suggested that dyes may exist as a mixture of two tautomeric forms which are in equilibrium. These results seem to be compatible with the hydrazone rather than the azo forms depicted in Scheme 3 and are consistent with the findings on tautomerism from ^1H NMR conclusions. It was also observed that the λ_{max} values of dyes didn't change significantly in various solvents. This behavior of dyes suggests that the molecules are involved in strong intramolecular hydrogen bond.

It was also observed that the absorption curves of the dyes were not significantly sensitive to acid but is sensitive to base. The absorption spectra of the dyes in methanol didn't change significantly when 0.1 M HCl was added and the absorption curves of the dyes resembled those in acetic acid. The λ_{max} of the dyes showed hypsochromic shifts when 0.1 M KOH was added to each of the dye solutions in methanol. A typical example is shown in Fig. 2.

2.3. Substituent effects

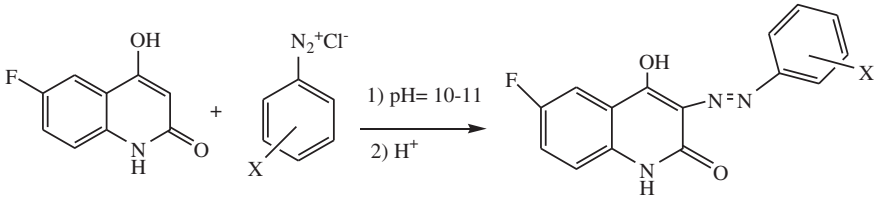
As far as absorption maxima are concerned, λ_{max} values are directly proportional to the electronic power of the substituents in the benzenoid system. As Fig. 3 depicts, a reasonable linear correlation exists between the difference in wavelength ($\Delta\lambda_{max}$) relative to that of unsubstituted dye **11** and the Hammett substituent constants (σ_m and σ_p) for relevant groups.

As it is apparent in Table 2, the introduction of electron donating methoxy group in the benzene ring resulted in bathochromic shifts in all solvents with respect to electron-accepting nitro, cyano and flouro groups (e.g. for dye **14** $\Delta\lambda = 35$ nm relative to dye **1,** $\Delta\lambda = 41$ nm relative to dye **2** in methanol). The introduction of electron-donating methyl (*m*-, *p*-) groups in the benzene rings resulted in bathochromic shifts in all solvents. The iodo (*p*-) group in the benzene ring resulted in bathochromic shifts in all solvents.

The introduction of electron-withdrawing nitro (*m*-) group in the benzene ring resulted in hypsochromic shifts in all solvents. The nitro (*p*-) group in the benzene ring resulted in bathochromic shifts in acetic acid and chloroform but did not change significantly in the other solvents. The position of all groups did not show a regular variation in all solvents. Fig. 4 compares the absorption spectra of some of the dyes with different substituents in chloroform.

2.4. Determination of pKa values of the azo dyes

The ionization constants (pK_a's) of **1** to **14** were determined in 80 vo1.% ethanol–water medium at 25 ± 2 °C and a μ of 0.1 using spectrophotometric titration method and are given in Table 3. Each compound exhibits two bands in region of 347–411 nm for anionic and 396–458 nm for the molecular species. As the pH value of the



I **1-14**

(**1**):X= *p*-NO_2	(**2**):X= *p*-CN	(**3**):X= *p*-$COCH_3$	(**4**):X= *p*-F	(**5**):X= *m*-NO_2
(**6**):X= *p*-Cl	(**7**):X= *p*-Br	(**8**):X= *m*-Cl	(**9**):X= *m*-CF_3	(**10**):X= *p*-I
(**11**):X= -H	(**12**):X= *m*-CH_3	(**13**):X= *p*-CH_3	(**14**):X= *p*-OCH_3	

Scheme 2. Synthetic routes for the preparation of azo dyes **1**–**14**.