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Azo-8-hydroxyquinoline dyes: The synthesis, characterizations and determination of tautomeric properties of some new phenyl- and heteroarylazo-8-hydroxyquinolines

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ABSTRACT

Two series of new heterocyclic and carbocyclic disperse azo dyes based on 8-hydroxyquinoline were prepared and characterized by FT-IR, ^{1}H NMR, mass spectroscopic techniques and elemental analysis. Their solvatochromic properties in different solvents were investigated and their absorption spectra were strongly solvent dependent. The acid and base effects on this equilibrium were also examined. In addition, the colors of dyes were discussed with respect to the nature of the carbocyclic and heterocyclic rings and substituent therein. To determine the tautomeric forms of the prepared dyes in solid state, X-ray data for 5-(5-methylthiazol-2-yldiazenyl)-8-hydroxyquinoline were recorded. The X-ray results showed that the dye exists as an azo tautomer in the solid state.

1. Introduction

It is well known that, because of their versatile application in various fields such as the dyeing of textile fibers, the coloring of different materials and biological–medicinal studies, the azo compounds are the most widely used class of dyes. They are also used in the fields of non-linear optics (NLO), optical data storage, advanced applications in organic synthesis and analytical chemistry as acid–base, redox and metallochromic indicator [1–5].

In recently, monoazo dyes have became the most important type of azo dyes. The monoazo dyes based on heterocyclic amines have been developed and the resultant dyes have higher tinctorial strength and give brighter than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, benzothiazole, isothiazole, thiadiazole, and thiophene compounds afford very electronegative diazo components and consequently, provide a pronounced bathochromic effect compared to the benzenoid compounds [6–12]. In addition, heterocyclic coupling component such as pyridone, pyrazolone, pyrimidine, thiophene, quinoline, and indole derivatives is also very important for industrial and other advanced applications [1]. Therefore, the synthesis and investigation of spectroscopic properties of many monoazo dyes containing one or two heterocyclic rings in molecule have been studied in the past decades [7–22].

The chemical properties of quinoline and its derivatives have been widely discussed because of their biological relevance, coordination capacity and their use as metal extracting agent [23]. They have attracted special interest due to their therapeutic properties. On the other hand, quinoline sulfonamides have been used in the treatment of cancer, tuberculosis and malaria [24]. Several quinoline derivatives possess chemotherapeutic activity and act as antimalaria and antiallergic agents [25]. They show broad-spectrum efficiency against multiple herpes viruses and they have a potential role for the treatment of a variety of infections [26]. 8-Hydroxyquinoline is one of the most important derivatives of quinoline because of its chelator properties for important metal ions [27]. 8-Hydroxyquinoline and its derivatives have high antibacterial activities [28,29]. Some of the 8-hydroxyquinoline derivatives and their complexes with transition metals were reported to be active against some bacteria and DNA [30,31]. In addition, azo compounds based on 8-hydroxyquinoline derivatives play a central role as chelating agents for a large number of metal ions [1,2,5,30–42]. Although 8-hydroxyquinoline azo dyes have bacteriostatic action, they have not been an indication of commercial value as textile dyes [43]. On the other hand, 8-hydroxyquinoline azo dyes derived from the sulfonamide derivatives were employed on textiles. Mordant dyeing with these acid azo dyes showed very good fastness properties on wool and nylon fibers [44]. In addition, some 8-hydroxyquinoline and azo derivatives found numerous applications in analytical chemistry as chromophoric and metallochromic indicators [45]. Although many papers were described in the synthesis and some properties of phenylazo-8-

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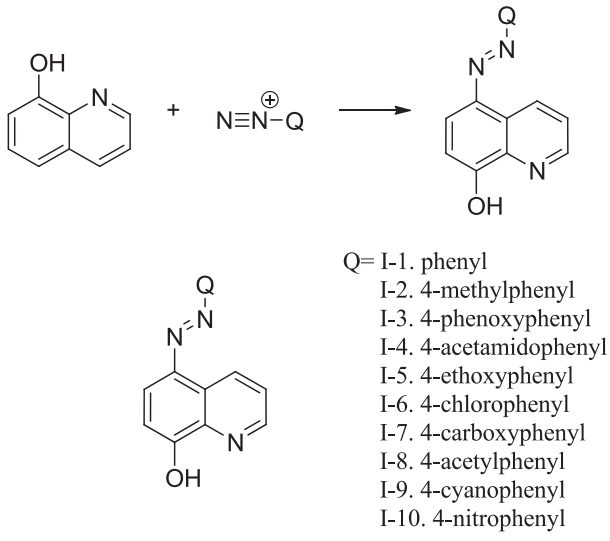

Fig. 1. Synthetic pathway and structure of phenylazo-8-hydroxyquinolines (**I 1–10**).

hydroxyquinolines [37,39,40,43,45], only few heteroarylazo-8-hydroxyquinolines were synthesized [38,46–49]. However, the solvatochromic properties of these dyes were not investigated in detail.

In our previous paper, we synthesized some new heteroarylazo 8-hydroxyquinoline dyes and evaluated their tautomeric equilibria in solution. In continuation of our work, we aimed to find new data for supporting tautomeric equilibria of these dyes. For this purpose, some novel various substituted heteroarylazo-8-hydroxyquinoline dyes were synthesized and their absorption spectra were compared with the absorption spectra of substituted phenylazo-8-hydroxyquinolines in various solvents. The color of the dyes was discussed in relation to the nature of the carbocyclic and heterocyclic rings and the substituents therein. Acid–base effects on the absorption spectra of the dyes were also studied in detail. The molecular structures of 5-(5-methylthiazol-2-yldiazenyl)-8-hydroxyquinoline obtained by X-ray diffraction analysis were also evaluated. 5-(2-carboxyphenyldiazenyl)-8-hydroxyquinoline was also used as a model compound for the determination of tautomeric equilibria of phenylazoquinoline dyes.

2. Results and discussion

The phenylazoquinoline dyes (**I 1–10**) were prepared by coupling 8-hydroxyquinoline with diazotized aniline derivatives with $NaNO_2$ in HCl/H_2O mixture (Fig. 1). The heteroarylazoquinoline dyes (**II 1–12**) were prepared by coupling 8-hydroxyquinoline with diazotized 2-aminothiazole, 2-aminobenzothiazole derivatives and 2-aminobenzimidazole in nitrosyl sulfuric acid (Fig. 2). The structures of prepared dyes have been confirmed by FT-IR, ^1H NMR, mass spectral data and elemental analysis. The all prepared

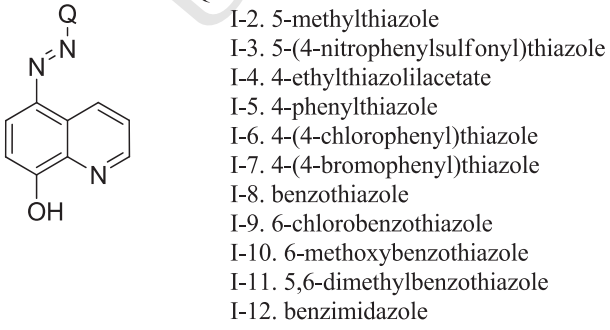

Fig. 2. Structure of heteroarylazo-8-hydroxyquinolines (**II 1–12**).

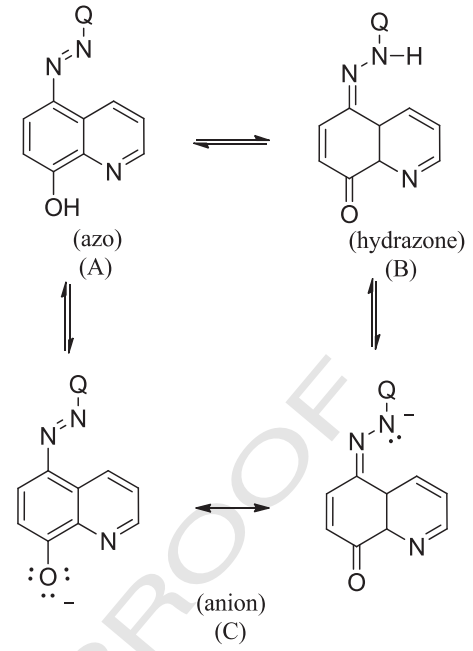

Fig. 3. Azo-hydrazone tautomeric and anionic form of phenyl- and heteroarylazo-8-hydroxyquinolines.

dyes may exist in two possible tautomeric forms, namely azo form A and hydrazone B as depicted in Fig. 3. The deprotonation of two tautomers leads to common anion C (Fig. 3).

The infrared spectra of the prepared dyes (**I 1–10** and **II 1–12**) (in KBr) showed strong and broad band within the range 3448–3147 cm^{-1} corresponding to quinoline ν_{O-H}. The broad value reveals that the –OH group was involved in intra- and intermolecular H-bonding. Some researcher suggested that 8-hydroxyquinolines and their phenylazo derivatives contain intramolecular H-bond in solid state [50,51]. The other study showed that they were stable in azo form because of intermolecular H-bond in solid state [37,52,53]. On the other hand, Basu Baul and co-workers suggested that phenylazo-8-hydroxyquinoline dyes were in azo form and may contain intra- and intermolecular H-bond in solid state [40].

In this work, to determine the tautomeric forms of the dyes in solid state, X-ray data for 5-(5-methyl-2-thiazolylazo)-8-hydroxyquinoline (**II-2**) (Figs. 4 and 5) were recorded. Suitable single crystals were obtained by slow evaporation from ethanol/H_2O in one week. The crystal structure of this dye showed only strong intramolecular H-bond between the hydroxy H and the quinoline N atoms (O–H–N = 2.212 Å). This result suggests that the synthesized dyes can be stable as azo in solid state. The other ν_{max} values at 3077–3040 (aromatic CH), at 2986–2851 (aliphatic CH) were recorded.

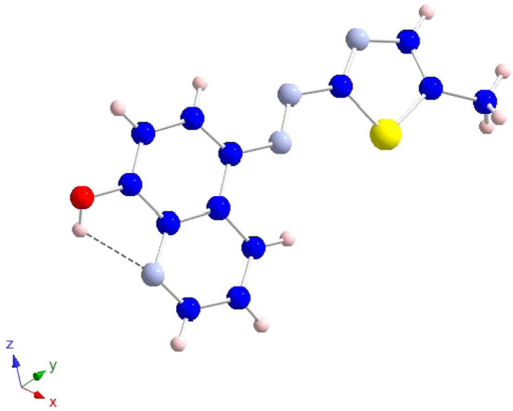

Fig. 4. Structure of a molecule of dye **II-2** in the crystal.

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