

Excited state intramolecular proton transfer in amino 2-(2'-hydroxyphenyl)benzazole derivatives: Effects of the solvent and the amino group position

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Abstract

The excited-state intramolecular proton transfer (ESIPT) mechanism in six amino 2-(2'-hydroxyphenyl)benzazole derivatives were investigated in different solvents by means of UV–vis absorption and steady-state fluorescence. The amino benzazoles are fluorescent in the blue–orange region under UV radiation. Changes in the absorption, emission and excitation spectra were analyzed and correlated to the position of the amino group and the solvent polarity. The equilibrium between the conformers in solution in the ground state, confirmed by the solvatochromic effect, reflects the dual fluorescence emission presented by these dyes.

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Keywords: Conformational equilibrium; Dual fluorescence; ESIPT; Fluorescent dyes

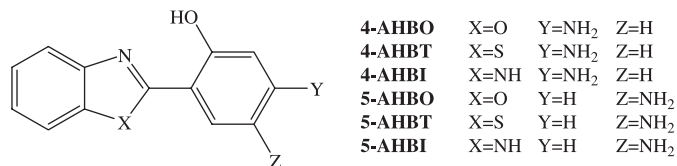
1. Introduction

Compounds emitting fluorescence through the excited-state intramolecular proton transfer (ESIPT) mechanism [1–6] have become a very attractive field of research by virtue of the widespread applications that can be envisaged for these dyes, such as UV-light polymer stabilizers [7,8], sensors [9] and laser dyes [10]. Particular interest has recently been shown in a new class of ESIPT amino benzazole derivatives, where applications such as fluorescent probes to label proteins and DNA [11] and new polymeric materials [12,13] were also reported.

Although the solvent effect on the ESIPT mechanism has been investigated experimentally [14–16] and theoretically [17–21] in several structures, a discussion concerning some amino 2-(2'-hydroxyphenyl)benzazole

derivatives (Scheme 1) is nowadays particularly interesting since the amino group being strong electron donor in the excited state, the fluorescence spectrum of amino derivatives are more sensitive to the solvent polarity than the absorption spectrum [22]. These dyes have been used as probe to discuss hydrophobic–hydrophilic environments [23], for instance, in systems that use polymers for drug delivery [22,24].

Usually in non-polar and aprotic solvents the normal or enol-*cis* (E_1) form is the most stable conformer of these dyes in the ground state. This conformer on excitation undergoes ESIPT to form the keto tautomer (K_1) (Scheme 2), which gives rise to an emission with large stokes shift. Additional conformers are described and do

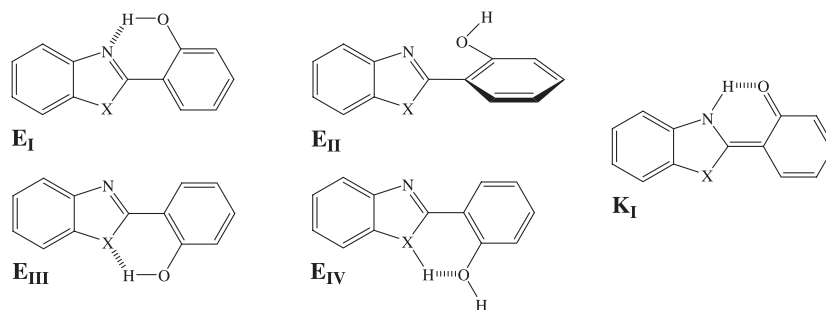


Scheme 1.

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Scheme 2.

not undergo ESIPT and are responsible for the short wavelength normal emission [16]. In protic or polar solvents, an enol-*cis* open conformer (E_{II}) can exist [25]. In non-polar solvent enol-*trans* (E_{III}) (when $X = O$ or S) and enol-*trans* open (E_{IV}) (when $X = NH$) conformers could also be stabilized [26,27]. In this way, this conformational equilibrium in solution has been observed experimentally through the dual fluorescence emission with an emission at longer wavelengths ascribed to the excited keto tautomer, and a blue-shifted one due to conformational forms which presents a normal relaxation with Stokes shift lower than 5834 cm^{-1} [21].

2. Materials and methods

The amino derivatives were prepared and purified as already described in Ref. [12]. Spectroscopic grade solvents (Merck) were used in fluorescence emission and UV-vis absorption spectroscopy measurements. UV-vis absorption spectra were recorded in a Varian Cary 50 spectrometer. Fluorescence emission and excitation spectra were measured in a Hitachi spectrofluorometer model F-4500. Spectrum correction was performed to enable measuring of a true spectrum by eliminating instrumental response such as wavelength characteristics of the monochromator or detector using rhodamine B as an internal standard (quantum counter). All experiments were performed at room temperature in a concentration range of 10^{-6} M .

3. Results and discussion

3.1. UV-vis absorption characterization

Figs. 1–3 show the normalized UV-vis absorption spectra of these dyes in dichloromethane, acetonitrile and ethanol. The relevant UV-vis data are summarized in Table 1.

An absorption band maxima ($\lambda_{\text{max}}^{\text{abs}}$) located around 331–334 and 356–372 nm, with molar extinction coefficient values (ϵ_{max}) in agreement with π - π^* transitions, could be observed in 4-AHBO and 5-AHBO, respectively. The solvatochromic effect is higher in the 5-AHBO (16 nm) if compared to 4-AHBO (3 nm). The absorption

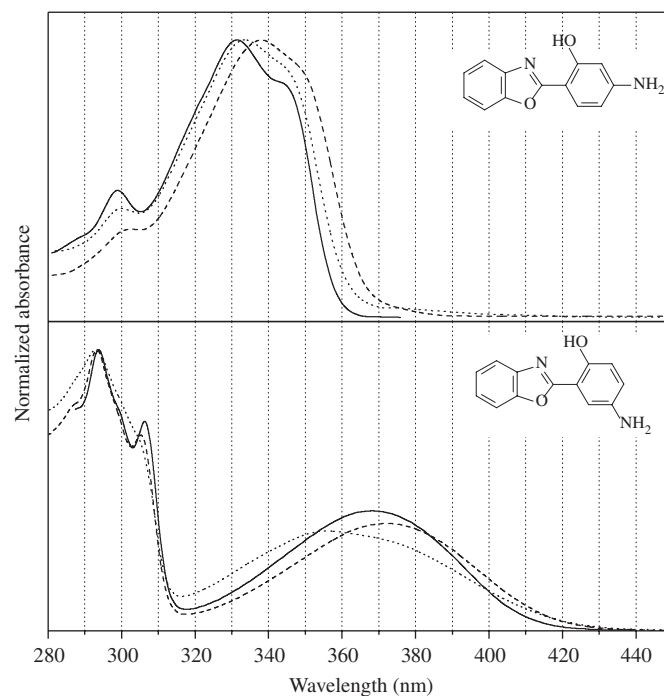


Fig. 1. Normalized absorption spectra of the amino benzoxazoles 4-AHBO and 5-AHBO in dichloromethane (solid line), acetonitrile (dash line) and ethanol (dot line).

maxima of the 4-AHBT (351–357 nm) and the 5-AHBT (368–389 nm) present a higher dependence on the solvent polarity (6 and 21 nm in 4-AHBT and 5-AHBT, respectively), which can be explained by the better electron delocalization allowed by the sulfur atom in relation to the oxygen. The same photophysical behavior was observed in the benzimidazole derivatives, with an absorption maxima at around 329–341 and 344–362 nm in 4-AHBI and 5-HBI, respectively. The 5-AHBI presents the higher dependence on the solvent polarity (18 nm) in relation to the 4-AHBI (12 nm). The UV-vis spectrum of 4-AHBI in ethanol exhibits a new peak shifted to the red which is probably attributed to protonated AHBI in the imidazolic nitrogen, as already observed in similar heterocycles [28b]. The absence of this peak in the 5-AHBI clearly indicates the electronic effect of the amino group position on the dye.

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