

Solvent polarity and intramolecular hydrogen bonding effects on the photophysical properties of 1-amino-9,10-anthraquinone dye

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Abstract

Photophysical properties of 1-amino-9,10-anthraquinone (1AAQ) dye have been investigated in different solvents using steady-state and time-resolved fluorescence measurements. The behavior of the dye is different in nonpolar solvents than in other solvents of moderate to higher polarities. In nonpolar solvents, the absorption and fluorescence maxima ($\bar{\nu}_{\text{abs}}$ and $\bar{\nu}_{\text{fl}}$, respectively) are largely blue-shifted and fluorescence quantum yields (Φ_f) and fluorescence lifetimes (τ_f) are unusually higher in comparison to those in other solvents. Further, in nonpolar solvents, the fluorescence decay kinetics is strongly temperature-dependent, while decay kinetics is temperature-independent in all other solvents of moderate to higher polarities. The differences in the behavior of 1AAQ dye in nonpolar and other solvents are suggestive of a structural change in the dye in the two sets of solvents. It is inferred that this structural change arises through the 1-NH₂ group of the dye. Deuterium isotope effect on the fluorescence decays of the dye in nonpolar and polar solvents also supports the above structural changes. To obtain further supportive evidences for the above structural changes, ab initio quantum chemical studies have been carried out on the ground and excited state structures of the dye under different environmental conditions. Correlating different experimental and theoretical results we infer that in nonpolar solvents 1AAQ dye adopts a nonplanar conformation where as in all other solvents the dye adopts a planar conformation with strong intramolecular charge transfer (ICT) character. Present results also indicate a strong role of intramolecular hydrogen bonding on the deexcitation mechanism of the excited state of the dye both in its nonplanar and planar ICT structures.

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1. Introduction

Amino- and hydroxy-substituted quinones are important class of molecules of having immense importance in dye industry, biology, and pharmaceutical chemistry [1–9]. Many of these molecules are reasonably fluorescent and their fluorescence characteristics have often been used to investigate the excited state properties of these molecules [10–14]. The effects of intra- and intermolecular hydrogen bonding on the photophysical properties of amino- and hydroxy-quinones have been investigated quite extensively [10–14]. Excited state proton transfer reaction has been shown to play a significant role in the deexcitation

mechanism for some of these excited molecules [10–14]. Due to the presence of the quinonoid moiety, these molecules act as good electron acceptors and extensive studies have been carried out to investigate the reduced radical characteristics of these molecules using both pulse radiolysis and laser flash photolysis techniques [15–22]. Due to good electron accepting properties, a variety of quinones and substituted quinones have also been used in exploring the dynamics and mechanism of electron transfer processes under both intramolecular and intermolecular conditions [23–27].

Though photochemistry of different quinone derivatives have been the subject of intense research for many years [1–5,9–14], the effect of solvent polarity on their photophysical properties are not that systematically studied. In the literature, photophysical properties of amino- and hydroxy-substituted quinones are mostly discussed in relation to the effect of intramolecu-

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lar hydrogen bonding on the deexcitation mechanism of the S_1 state [9–14], and also on the S_1 to T_1 intersystem crossing (ISC) process [9–14,19–22]. It is reported that the S_1 state of amino- and hydroxy-substituted quinones are mostly of intramolecular charge transfer (ICT) character [9–14,19–22]. In our recent studies with aminocoumarin dyes, e.g. coumarin-120 (C120; 7-NH₂-4-CH₃-1,2-benzopyrone) and coumarin-151 (C151; 7-NH₂-4-CF₃-1,2-benzopyrone), the molecules that are also known to have ICT character both in the ground and excited electronic states, it has been observed that depending on solvent polarity these dyes can adopt either a nonplanar or a planar intramolecular charge transfer (ICT) conformation and accordingly display drastically different photophysical properties in nonpolar and polar solvents [28,29]. Further, in their nonplanar conformation, the S_1 state of these dyes shows an additional nonradiative deexcitation channel, which is absent in their planar ICT structure. Assuming the possibility of similar conformational changes for the amino-substituted quinones, we have recently investigated photophysical properties of 2-amino-9,10-anthraquinone (2AAQ) dye in solvents of varying polarities [30]. Interestingly it has been observed that 2AAQ displays substantially different photophysical properties in lower polarity solvents than in other solvents of medium to higher polarities. From the experimental results supported by Quantum chemical calculations, it has been understood that in nonpolar solvents 2AAQ dye exists in a nonplanar structure, with its 2-NH₂ plane away from that of the 9,10-anthraquinone moiety whereas in other solvents the dye exists in a polar ICT structure, where the amino lone pair of the 2-NH₂ group is in strong resonance with the anthraquinone π -cloud. These structural changes for 2AAQ dye in nonpolar and other solvents are exactly similar to those reported earlier by us for the coumarin dyes, C120 and C151. In the present work, photophysical properties of 1-amino-9-10-anthraquinone (1AAQ) dye have been investigated in different solvents and solvent mixtures of varying polarities to understand if structural changes similar to those in 2AAQ, C120 and C151 are also possible for 1AAQ dye. Unlike 2AAQ, C120 and C151 dyes, there is a possibility of strong intramolecular hydrogen bonding in 1AAQ, involving one of the hydrogen atoms of the 1-NH₂ group and the adjacent quinonoid oxygen. It is thus also interesting to know if such hydrogen bonding does have any effect on the possible structural changes of the dye in nonpolar and other solvents. Chemical structures of 1AAQ, 2AAQ, C120 and C151 dyes are shown in Chart 1 for an easy comparison.

2. Materials and methods

1AAQ was obtained from TCI (Tokyo, Japan) and purified by repeated crystallization from cyclohexane–ethyl acetate solvent mixture. All the solvents used were of spectroscopic grade, obtained either from Spectrochem (Mumbai, India), S.D. Fine Chemical (Mumbai, India), SISCO Research Laboratories (Mumbai, India), E. Merck (Mumbai, India) or Fluka (Buchs, Switzerland).

Absorption spectra were recorded using a JASCO (Tokyo, Japan) spectrophotometer model V530. Fluorescence spectra were recorded with corrections for the wavelength-dependent instrument responses using a Hitachi (Tokyo, Japan) spectrofluorimeter model F-4010. The Φ_f values were measured by a comparative method [31,32], using Φ_f of 1AAQ in benzene as the reference ($\Phi_f^R = 0.058$; [13]). For all fluorescence measurements, the optical density (O.D.) of the solutions was kept quite low (~ 0.2) at the excitation wavelength.

Fluorescence lifetimes of 1AAQ in different solvents were measured using time-correlated-single-photon-counting (TCSPC) spectrometers, either from Edinburgh Instrument, Edinburgh, U.K. (model 199) or from IBH, Glasgow, U.K. (model IBH Data Station Hub). The TCSPC setup from Edinburgh Instrument uses a hydrogen flash lamp (25 kHz) for sample excitation and the instrument response function for this setup is ~ 1.2 ns at FWHM. The details of this spectrometer are described elsewhere [33]. In the TCSPC setup from IBH, a 455 nm nano-LED was used for sample excitation and the instrument response function for this setup is ~ 1.2 ns at FWHM. Observed fluorescence decays were analyzed following a re-convolution procedure [34], using a proper instrument response function, obtained by replacing the sample cell with a light scatterer (suspended TiO₂ particles in water). For all the cases, the decays were seen to fit well with a single-exponential function, as judged from the reduced χ^2 values and the distribution of the weighted residuals among the data channels [34]. For all the accepted fits, the χ^2 values were within 1.00–1.20, and the distribution of the weighted residuals were quite random among the data channels used [34].

To study deuterium isotope effect on the fluorescence decay characteristics of 1AAQ dye, following procedure was adopted to exchange the amino hydrogens of the dye with deuterium atoms [10,13]. About 1 ml of D₂O was added to about 5 ml solution of 1AAQ in hexane. The mixture was thoroughly shaken for about 5 min. The mixture was then allowed for

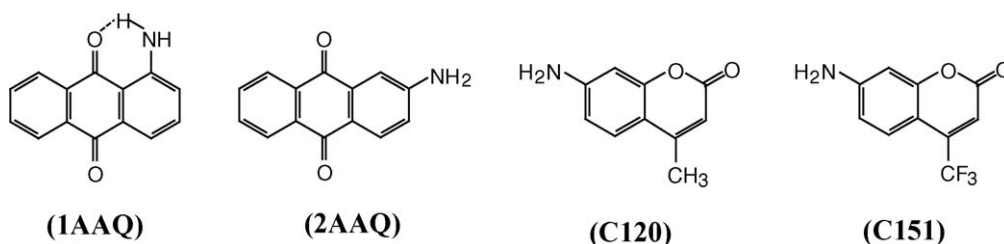


Chart 1.

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