COMMENTS

Comment on "Ground-State Triple Proton Transfer in 7-Hydroxyquinoline. 4. Observation in Room-Temperature Methanol and Aqueous Solutions"

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Received: January 9, 1998

Through our course of studies on the conjugated dual hydrogen-bond (CDHB) mediating proton-transfer reaction in 2-hydroxypyridine[1] and 3-hydroxyisoquinoline,[2] we have concluded that ground-state equilibria among various self-associated forms as well as excited-state proton-transfer dynamics can be fine-tuned by the CDHB effect. Recently, we have extended our investigation to other types of dual hydrogen-bonded systems in which 7-hydroxyquinoline (7HQ) is a prototype. Our results indicate the existence of various 7HQ associated species, including 7HQ enol dimer in nonpolar solvents.[3] However, Bohra et al.[4] have recently reported the existence of various 7HQ self-associated forms in room-temperature methanol solution. It is surprising to us that a similar strong aggregation effect can be observed in both nonpolar and polar (and protic) solvents. Especially 7HQ is nearly miscible with methanol at room temperature. To resolve these controversies we have therefore reinvestigated the self-association of 7HQ in room-temperature methanol solution. Figure 1a shows the excitation spectrum of 7HQ[5] obtained under the same experimental conditions as that shown in ref 4, Figure 3A. Both figures are essentially identical with excitation maximum peaks at 298 and 350 nm which were ascribed to the 7HQ enol dimer and higher-order aggregates, respectively.[4] Figure 1b shows the excitation spectrum of 7HQ in an identical solution with respect to Figure 1a, except that the excitation spectrum was obtained by using a 0.1 mm path-length cuvette.[6] Obviously, the spectral feature in Figure 1b is drastically different from that of Figure 1a, in which peaks at 298 and 350 nm disappeared; instead, a broad band maximum at 330 nm was observed. In addition, the absorption spectrum of the same solution (see Figure 1c) shows the same spectral feature as Figure 1b. We have also performed a series of excitation spectrum measurements by varying the 7HQ concentration, in which the sample cuvette of different path length was used so that the absorbance of 7HQ at 330 nm can be as low as <0.5. In contrast to the previously observed concentration-dependent excitation spectra (see Figure 3A−D in ref 4), the results show a concentration independence in the region of interest (280−360 nm), and the spectral feature is similar with its corresponding absorption spectrum.

It should be noted that most conventional fluorimeters such as SPEX 1681 Fluorolog and Hitachi (SF4500) spectrometers used in ref 4 and this study, respectively, have an effective emission-collecting portion at the center of the cuvette. When the excitation is at a right angle with respect to the collected emission, the distortion of the excitation spectrum will take place if the sample concentration is too high so that the absorbance (A) is typically >0.5. In ref 4, Figure 3A (and also Figure 1a in this study), the dip between 300 and 350 nm has a minimum at 330 nm which is coincident with the inverse of the absorption maximum (see Figure 1c), indicating that under such high concentration (9.0×10^{-3} M, $A_{330} \sim 4.7$ measured by a 1 mm path length cell) significant spectral distortion has taken place. We thus conclude that the assignment of 298 and 350 nm bands to 7HQ enol dimer and higher-order aggregates is apparently based on an experimental artifact. Therefore, although the formation of various 7HQ/methanol complexes has been widely accepted, our results, at this stage, show no spectral evidence of 7HQ enol dimer and higher-order aggregate formation in the room-temperature methanol solution.

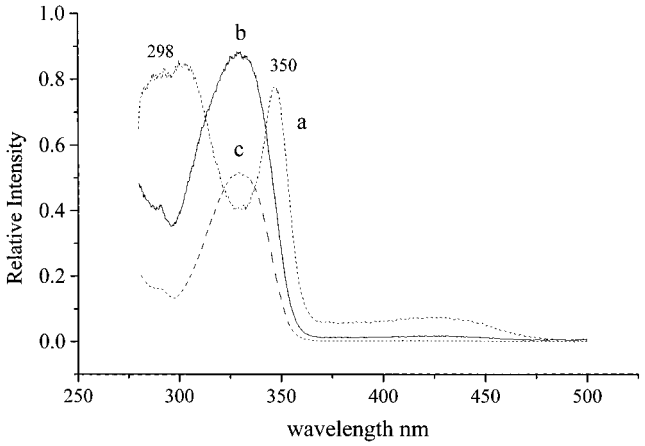

Figure 1. Fluorescence excitation spectrum of 7HQ (9.0×10^{-3} M) in methanol solution by monitoring the emission at 520 nm with (a) 1 mm (•••), (b) 0.1 mm (—) path length cuvette. (c) Absorption spectrum (---) of 7HQ (9.0×10^{-3} M) in methanol solution. When spectrum b is multiplied by a factor of 10, the spectral feature in the region of 380−460 nm is the same as that of (a).

Acknowledgment. This work was supported by the National Science Council, Taiwan, R.O.C.

References and Notes

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(5) 7HQ was purified by column chromatography (eluent 1:3 hexane: ethyl acetate) followed by twice recrystallization from spectragrade CH_3CN. Methanol was purified and dried by distillation over calcium hydride under a nitrogen atmosphere. Storing methanol over molecular sieves[4] is not recommended since this process introduces certain degrees of acid contamination. As a result, a trace of cationic 7HQ may form, which can be observed by the increasing intensity of the excitation spectrum in the region of 360−380 nm.

(6) The cell was made by assembling two edge-polished quartz plates with 0.1 mm space.

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S1089-5647(98)00741-X CCC: $15.00
Published on Web 04/07/1998