COMMENTS

Comment on “On the Evidence Obtained by Exciting 7-Azaindole at 320 nm in 10^{-2} M Solutions”

Pi-Tai Chou,* Yi-Ming Cheng, Wei-Shan Yu, and Shih-Chieh Pu

Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Received: October 22, 2002; In Final Form: March 26, 2003

Femtosecond techniques have been applied actively in studying the dynamics of excited state double proton transfer (ESDPT) in the 7-azaindole (7AI) dimer.[1,2] However, the interpretation of ESDPT dynamics has raised many controversies in terms of a one-step[1,3] versus two-step[2,4] mechanism. Very recently, on the basis of concentration-dependent absorption and fluorescence excitation spectra, Catalán[5] reported that in addition to the planar dimeric form (dimer D) there exists another aggregate species (β-species), possibly possessing a dimeric structure with a different strain, when the concentration of 7AI is as high as 10^{-2} M in 3-methylpentane.[6] Upon excitation, both forms undergo ESDPT, giving rise to the 480 tautomer emission. Accordingly, the author concluded that the interpretation of femtosecond results, in particular the two-step mechanism, cannot be deemed conclusive.

Although the interpretation is sound, the excitation spectra illustrated in Figures 6−8, which are one of the core issues in ref 5, deserve more careful examination. In ref 5, the excitation spectra of 0.02 M 7AI (Figure 6) apparently differ from those of 2×10^{-3} (Figure 7) and 1×10^{-4} M (Figure 8) in 3-methylpentane. The results render further support for the existence of various 7AI aggregate species. Conventionally, the excitation spectra at high concentrations are acquired by either 45° or front-face excitation to avoid the interferences from reabsorption and noneffectively collected emissions. However, even using these two types of configurations, caution must still be taken in consideration of the nonlinearity between the number of molecules being excited and the absorbance when the prepared concentration is high. In this study, using a front-face excitation configuration (SPEX 1681 Fluorolog), Figure 1a shows the excitation spectra of 7AI (0.02 M) tautomer emission acquired with a cell path length of 1.0 mm.[7] The spectra resemble those shown in ref 5, Figure 6 (see Figure 1b in this study). Upon using a 0.01 mm cell length, Figure 1c reveals a significantly different excitation spectrum from Figure 1a and b. More importantly, the spectral feature in Figure 1c is similar to the absorption spectrum of 0.02 M 7AI taken with a 0.01 mm cell (see Figure 1d). The slight spectral difference is mainly due to the uncorrected wavelength-dependent response of the fluorometer. Because all spectra were obtained under the same concentration of 0.02 M, we concluded that spectral distortions must occur in Figure 1a,b.

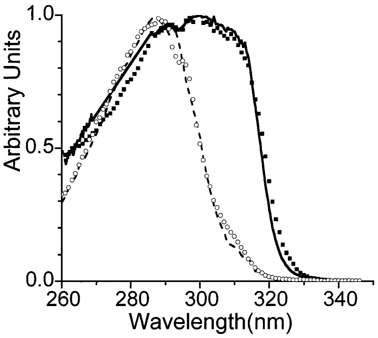

Figure 1. (a, ■) Excitation spectra of 7AI (0.02 M) acquired with a cell path length of 1.0 mm in 3-methylpentane. The emission was monitored at 480 nm. (b, −) Excitation spectra taken from Figure 6 of ref 5. (c, ○) Same condition as in (a) except for using a 0.01 mm cell length. (d, - - -) Absorption spectrum of 0.02 M 7AI taken with a 0.01 mm cell.

The results can be rationalized by the relationship between the intensity of excitation light being absorbed, I', and the absorbance, A, expressed as

$$\frac{I'}{I_0} = 1 - \mathrm{e}^{-2.303A} = 1 - \sum_{n=0} \frac{1}{n!}(-2.303A)^n$$

where I_0 denotes the initial excitation intensity. Only when A is rather small, e.g., <0.2, can the $n = 2$ term be neglected so that I' is proportional to A. For the 0.02 M 7AI in 3-methylpentane, the absorbance was measured to be ∼13 at the peak maximum of ∼290 nm with a 1.0 mm cell. Thus, the nonlinearity for I' versus A should occur in the region <310 nm, whereas a good linearity still holds at >320 nm, resulting in a significant distortion of the excitation spectra shown in Figure 1a,b.

One should note that in the solution phase, the choice of the spectral onset depends on the overall spectral feature and hence cannot be determined from a significantly distorted excitation spectrum. For example, we calculate the intensity at the defined 335-nm spectral onset in Figure 6, ref 5, to be ∼1/100 of the excitation maximum. Taking the same ratio, the excitation spectrum shown in Figure 1c gives an onset wavelength shifted significantly to ∼322 nm, which is similar to previously reported values of 315−320 nm.[1b,2c]

We thus conclude that the existence of various 7AI aggregates in hydrocarbon solvents, at least, could not be inferred from the excitation spectra shown in ref 5, Figures 6−8. Without performing the temperature-dependent absorption[5] and femtosecond dynamic experiments,[1,2] we cannot nor do we intend to make any conclusions regarding whether various 7AI aggregates exist in 0.02 M solution at 298 K, and consequently the differentiation between the one-step and two-step ESDPT mechanism. However, the significance of ref 5 is mainly in the existence of various 7AI aggregate species at high concentrations, which is of prime importance in the interpretation of the

10.1021/jp022272p CCC: $25.00

femtosecond ESDPT dynamics at room temperature. We thus feel this comment is appropriate and timely.

References and Notes

(1) (a) Takeuchi, S.; Tahara, T. *Chem. Phys. Lett.* **1997**, *277*, 340. (b) Takeuchi, S.; Tahara, T. *J. Phys. Chem. A* **1998**, *102*, 7740. (c) Takeuchi, S.; Tahara, T. *Chem. Phys. Lett.* **2001**, *347*, 108.

(2) (a) Douhal, A.; Kim, S. K.; Zewail, A. H. *Nature* **1995**, *378*, 260. (b) Chachisvilis, M.; Fiebig, T.; Douhal, A.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 669. (c) Fiebig, T.; Chachisvilis, M.; Manger, M.; Zewail, A. H.; Douhal, A.; Garcia-Ochoa, I.; de La Hoz Ayuso, A. *J. Phys. Chem. A* **1999**, *103*, 7419.

(3) (a) Catalán, J.; Pérez, P.; Del Valle, J. C.; de Paz, J. L. G.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5799. (b) Catalán, J. *J. Am. Chem. Soc.* **2002**, *124*, 5940.

(4) Folmer, D. E.; Wisniewski, E. S.; Hurley, S. M.; Castleman, A. W., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12980.

(5) Catalán, J. *J. Phys. Chem. A* **2002**, *106*, 6738.

(6) In solution phase, a thin path length (e.g., ≤1 mm) cell is generally applied in the femtosecond approaches to achieve a desired temporal resolution. This, in combination with the necessity of preparing a dominant dimeric form, led to the use of high 7AI concentrations of $\sim 10^{-2}$ M in most of the femtosecond studies.

(7) The cell was made by assembling two edge-polished quartz plates with various Teflon spacers.