6738 *J. Phys. Chem. A* **2002,** *106,* 6738−6742

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

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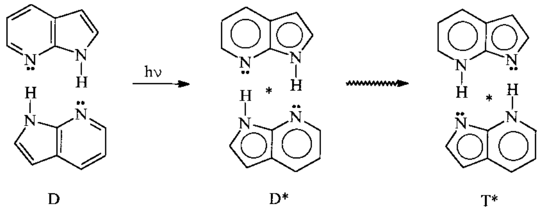
Received: June 13, 2001; In Final Form: April 11, 2002

Careful analysis of the UV absorption spectra for 2×10^{-2} M solutions of 7-azaindole (7AI) in 3-methylpentane and *n*-hexane revealed that the onset of the first absorption band lies at ca. 335 nm, i.e., it is bathochromically shifted by 15 nm with respect to the onset of the band for the doubly-H-bonded dimer (D), so an additional aggregate species must exist in solution. Interestingly, this new species, like the doubly-H-bonded dimer, also emits in the region around 480 nm. The corresponding fluorescence excitation spectra confirm that the onset of the excitation lies between 335 and 340 nm. The presence of two different molecular structures in the red edge of the first absorption band, which undergo a proton transfer reaction on photoexcitation, seriously questions the model of Zewail et al. that because of two kinetic rates measured and ascribed to proton-transfer processes, the biprotonic transfer on photoexcitation in a 2×10^{-2} M solution of 7AI excited at 320 nm is a nonconcerted mechanism.

Introduction

The discovery of a double proton transfer[1] in an electronically excited model base pair, namely, 7-azaindole (7AI) dimer (Scheme 1), has promoted extensive experimental and theoretical research into the 7AI doubly-H-bonded dimer (D) since 1969. These studies[2] have revealed unexpected complexity in the photophysics of both singlet and triplet excited states in this dimer D.

SCHEME 1



The finding of Zewail et al.[3] in 1995 that subjecting the dimer to femtosecond laser-pulsed photoexcitation followed by femtosecond laser-pulsed ionization with time-of-flight mass spectrometry to detect the resulting ions of mass 236 (e.g., D^+) provided a biexponential signal ($\tau_1 = 650$ fs, $\tau_2 = 3.3$ ps) raised strong controversy. These authors ascribed their finding to the double proton transfer in dimer D of 7AI taking place via a zwitterionic intermediate (I) generated by a single-proton transfer that subsequently underwent another single-proton transfer to complete the double-proton process and yield the tautomeric structure T* (see Scheme 2).

SCHEME 2

$$D^* \xrightarrow{\tau_1 = 650\ \text{fs}} I^* \xrightarrow{\tau_2 = 3.3\ \text{ps}} T^*$$

In 1997, Takeuchi and Tahara[4] examined the dimer excited-state dynamics in the double proton-transfer reaction of 7AI by femtosecond fluorescence up-conversion in *n*-hexane, with excitation at 270 nm, and used Scheme 3, which involves no zwitterionic intermediate, to account for the decays found ($\tau_1 = 1.1$ ps and $\tau_2 = 3.2$ ns).

SCHEME 3

$$D^* \xrightarrow{\tau_1 = 1.1\ \text{ps}} T^* \xrightarrow{\tau_2 = 3.2\ \text{ns}} T$$

A few months later, in 1998, Zewail et al.[5] studied this condensed-phase reaction and concluded that "as in the gas-phase work[3], we believe that the non-concerted pathway is significant but that, on the global PES, both trajectories of the symmetric and asymmetric vibrational motions must be considered." That same year, Takeuchi and Tahara[6] reported the results of painstaking experimental work that involved exciting a 7AI solution in *n*-hexane at 270, 280, and 290 nm, using a temporal resolution of 280 fs; they confirmed Scheme 3, which was proposed in their previous work, and hence ruled out a nonconcerted character for the process.

In 1999, Zewail et al.[7] studied the dynamics of this process using real-time femtosecond transient absorption and fluorescence up-conversion techniques to excite a 2×10^{-2} M 7AI solution in 3-methylpentane at 320 nm. They thought it crucial to excite dimer D near the onset of its S_1 excited electronic state as they believed that exciting it above the proton-transfer barrier would result in the process taking place in a concerted manner as found by Takeuchi and Tahara. The two kinetics assigned to the proton transfer have led to the work in question[7] being cited[8] as the definitive demonstration that the process is nonconcerted. Kasha, Catalán, et al.[9−12] and Takeuchi and Tahara[13] have reported theoretical and experimental arguments on *the concerted nature of the double proton transfer* and provided explanations consistent with the experimental results of Zewail et al.[5,7]

The need for 7AI to occur largely in dimer form (D) in hydrocarbon solutions at room temperature has led some authors to study 7AI solutions in the 10^{-2} M concentration region. Such high concentrations for photophysical work result in the $S_0 \rightarrow S_1$ transition exhibiting such high peak absorbances (ca. 130

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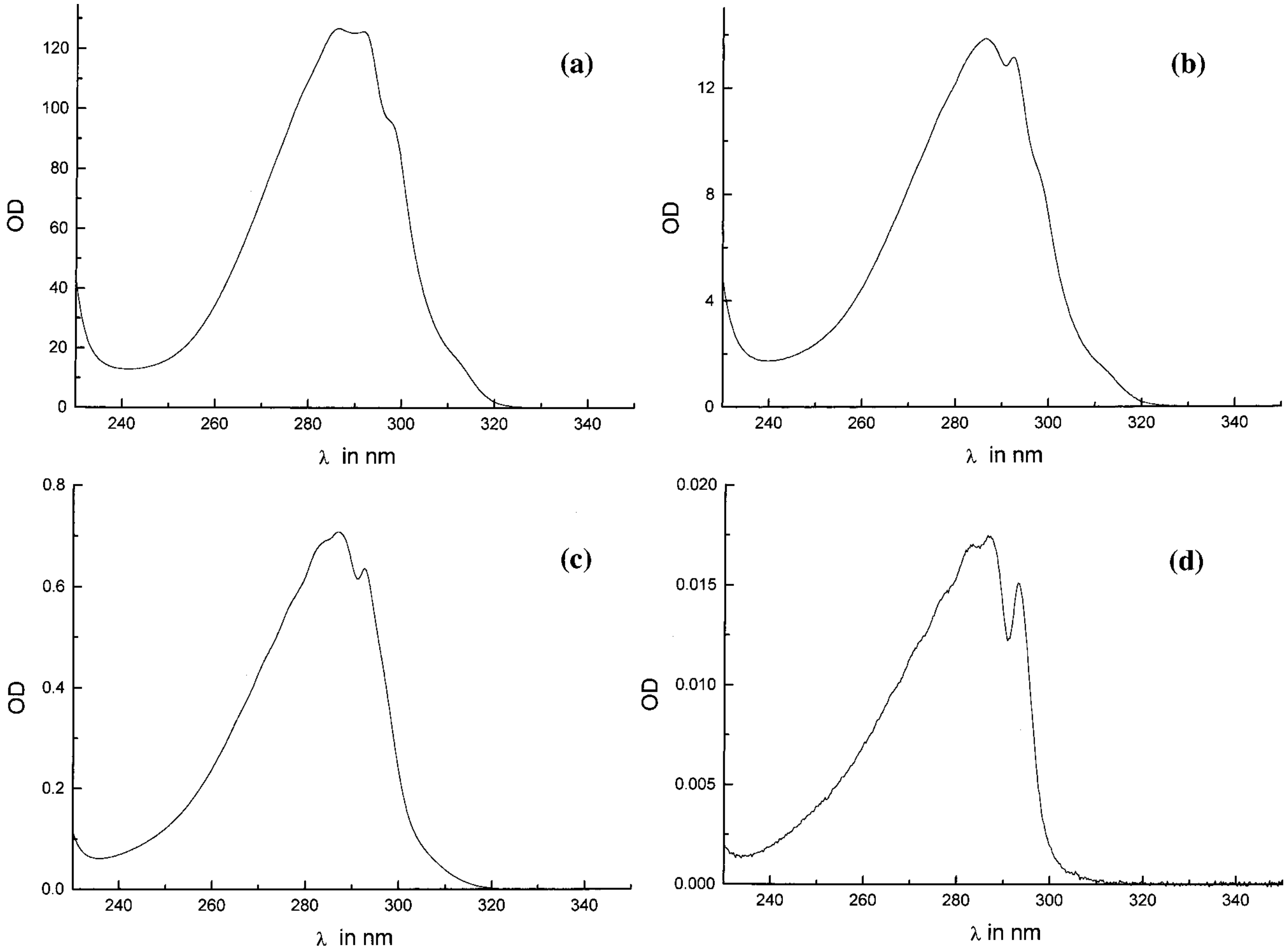

Figure 1. UV absorption spectra of 7AI in 3-methylpentane at (a) 0.02 M, (b) 0.002 M, (c) 0.0001 M, and (d) 2 × 10^{-6} M.

OD with cells of 1 cm light path) that they readily generate optical artifacts hindering photophysical analysis of the problem. Also, the risk exists for the compound to occur in more than one aggregate form.

In this work, we carefully examined the steady-state photophysics of a 2 × 10^{-2} M solution of 7AI in the hydrocarbon solvents used by Zewail et al.[7] (3-methylpentane) and Takeuchi and Tahara[6] (*n*-hexane). Special emphasis was placed on the potential dependence of the conclusions drawn by the former research group[7] on the fact that the sample was excited at 320 nm.

Experimental Section

Absorption spectra were recorded on a Cary 05 spectrophotometer, using cells of appropriate optical paths to obtain quality spectra. The instrument was calibrated prior to use to confirm that it met the stringent quality specifications set by the manufacturer Varian for this equipment.

Emission and excitation spectra were recorded on an Aminco-Bowman AB2 spectrofluorimeter, which was also rechecked prior to use. The slit widths used were as follows: 2 and 4 nm in the respective excitation and emission monochromators for emission spectra, and 2 and 8 nm in respective monochromators for fluorescence excitation spectra.

3-Methylpentane (3MP) was over 99% pure and supplied by Aldrich, while *n*-hexane (n-Hx) was Uvasol-grade (Merck) and contained less than 0.005% moisture. All 7AI solutions were prepared from freshly opened bottles of the two solvents. 7AI was over 99% pure and purchased from Sigma.

Results and Discussion

On the 0_0^0 Components of the $S_0 \rightarrow S_1$ Electronic Transitions in 7AI Monomer and Dimer. The 0_0^0 component of the $S_0 \rightarrow S_1$ electronic transition in 7AI monomer appears around 289 nm. In the gas phase, Hassan and Hollas[14] located it at 34 630.73 cm^{-1} (288.76 nm); Fuke et al.,[15] using the MPI supersonic jet technique, identified it at 34 639 cm^{-1} (288.69 nm); Kim and Bernstein,[16] using jet-cooled one-color TOFMS located it at 34 634 cm^{-1} (288.73 nm); Illich,[17] using an argon matrix, found it to occur at 289.00 ± 0.03 nm; Taylor[18] located it at 292.5 nm; and, using 2-methylbutane as solvent, Catalán and Kasha[2] found it to occur at 293.0 nm, with its onset at 305 nm.

Fuke and Kaya[19] located the 0_0^0 component of the $S_0 \rightarrow S_1$ electronic transition in dimer D of 7AI at a very low temperature in the gas phase at 32 252 cm^{-1} (310 nm); Taylor[18] found it to occur at 315.5 nm in 3-methylpentane at 77 K; and Catalán and Kasha located it at 315 nm (with the onset at 320 nm) in 2-methylbutane.

On the basis of the foregoing, Ingham and El-Bayouni[20] stated that the monomer absorption at 315 nm in CCl_4 or 3-methylpentane is negligible; also, Takeuchi and Tahara[6] asserted that the absorption of 7AI monomer at 315 nm in *n*-hexane is zero over the concentration range from 7.5 × 10^{-5} to 5 × 10^{-3} M. This is consistent with the finding of Catalán and Kasha[2] that the onset for the monomer lies at about 305 nm.

In their latest work on 7AI, Zewail et al.[7] excited a 2 × 10^{-2} M solution of 7AI in 3-methylpentane at 320 nm and found two different fluorescence emissions, namely, one centered at

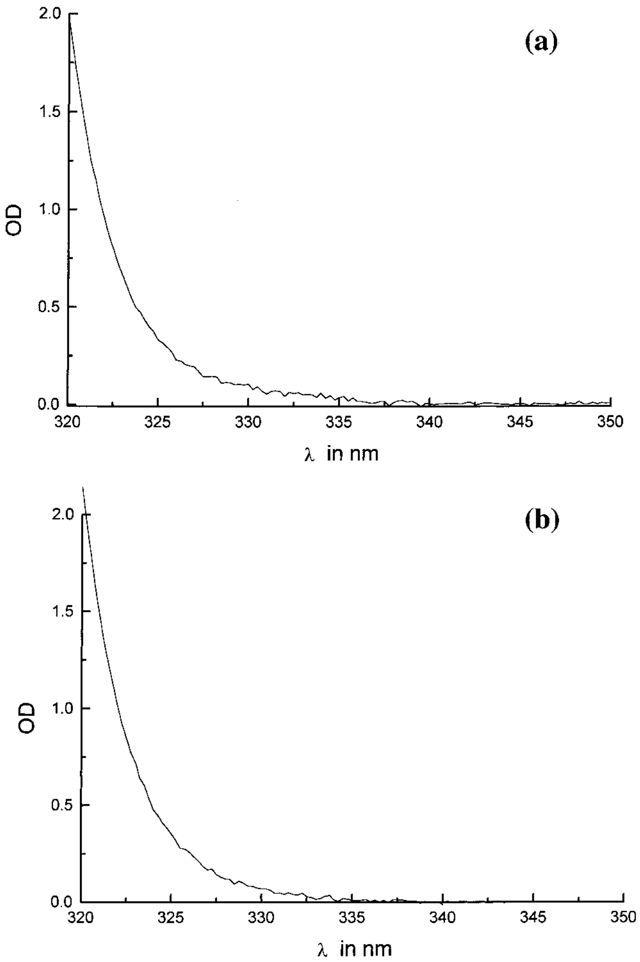

Figure 2. Absorption spectra between 350 and 220 nm of 0.02 M 7AI in (a) 3-methylpentane and (b) *n*-hexane solutions, obtained with a cell of 1 cm in optical path.

350 nm that they assigned to the monomer and another centered at 480 nm that they ascribed to the dimer tautomer (T). On the basis of the foregoing, if a 2 × 10^{-2} M solution of 7AI is excited[7] at 320 nm, its monomer could never have been excited because this form exhibits no absorption at such a wavelength, unless the uncertainty in energy of excitation, not stated, was so high that centring the excitation at 320 nm resulted in actual excitation below 305 nm (i.e., a corresponding uncertainty greater than ±15 nm in this UV region). If the monomer was not the species excited at 320 nm, then a 7AI aggregate species other than dimer D must have been excited. This 7AI aggregate species (α) emmiting at 350 nm does not give proton phototransfer.

On the Absorption Spectrum for a 2 × 10^{-2} M Solution of 7AI. Figure 1 shows the UV absorption spectra between 350 and 230 nm for solutions containing 2 × 10^{-2}, 2 × 10^{-3}, 1 × 10^{-4}, and 2 × 10^{-6} M 7AI in 3MP; the spectra obtained in *n*-Hx are not shown because they were virtually identical. The first two spectra (a,b) were obtained by using cells of 0.1 mm light path, and the third and fourth ones (c,d) were obtained with cells of 1 cm; in any case, all four are shown as if they had been obtained with the latter cell. The spectrum for a 2 × 10^{-6} M solution can clearly be assigned to 7AI monomer;[2,17] on the other hand, the envelopes of the other three spectra, obtained at higher concentrations, reveal a differential proportion of the monomer and dimer forms (D) in these solutions.

Note that the onset of the UV absorption spectrum for a 2 × 10^{-2} M solution of 7AI in both 3MP and *n*-Hx lies at ca. 335 nm (see Figure 2). This suggests that the solution contains not only the monomer (with its onset at 305 nm) and the normal dimer (D, with its onset at 320 nm), but also at least one additional aggregate that absorbs at 335 nm. Figure 3 shows the spectrum obtained as the difference between the UV spectra in the 340−320 nm region for two solutions in both 3MP and

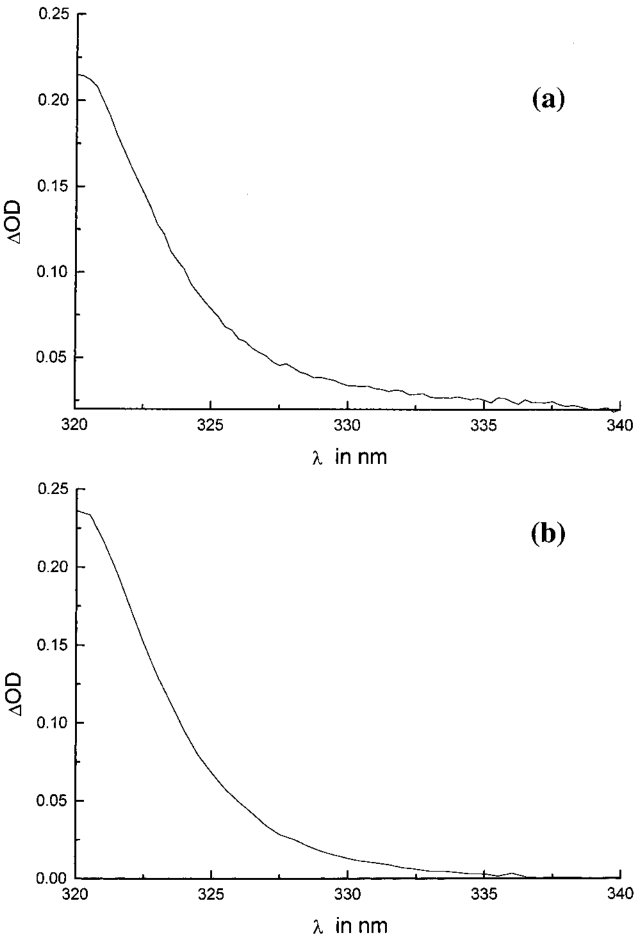

Figure 3. Absorption spectra difference of 0.02 and 0.002 M 7AI in (a) 3-methylpentane and (b) *n*-hexane solutions.

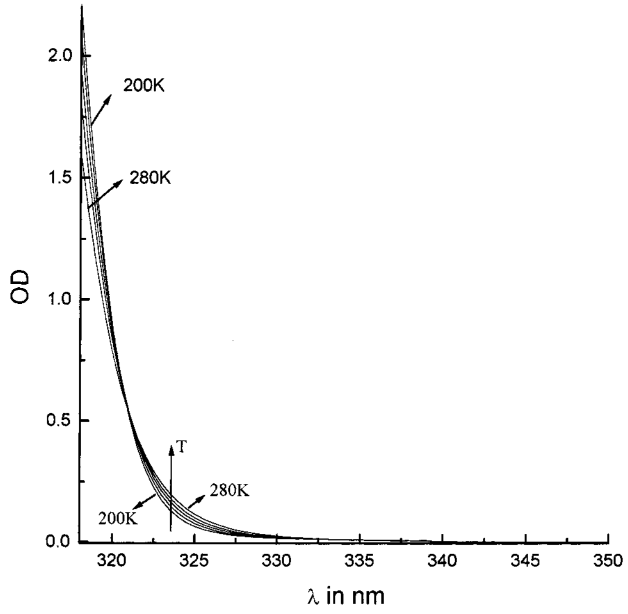

Figure 4. Absorption spectra of 0.02 M concentration of 7AI in *n*-hexane obtained at 280, 260, 240, 220, and 200 K.

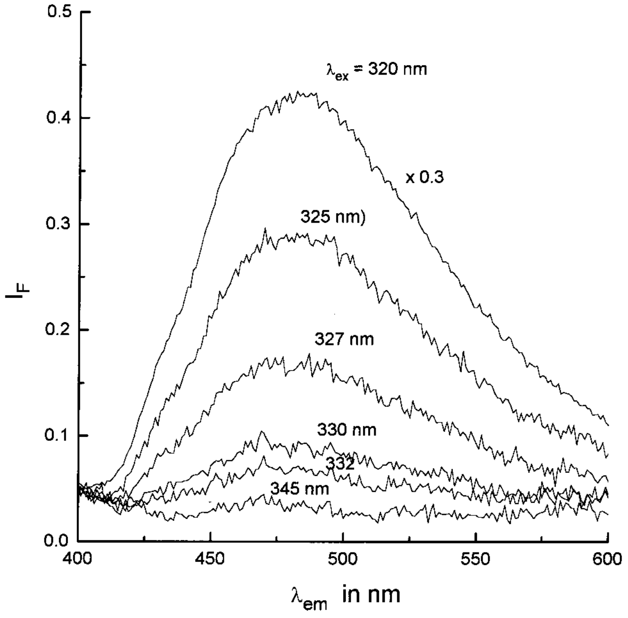

Figure 5. Fluorescence emission spectra of 0.02 M concentration of 7AI in 3-methylpentane upon excitation at the several wavelengths indicated in this figure and at room temperature.

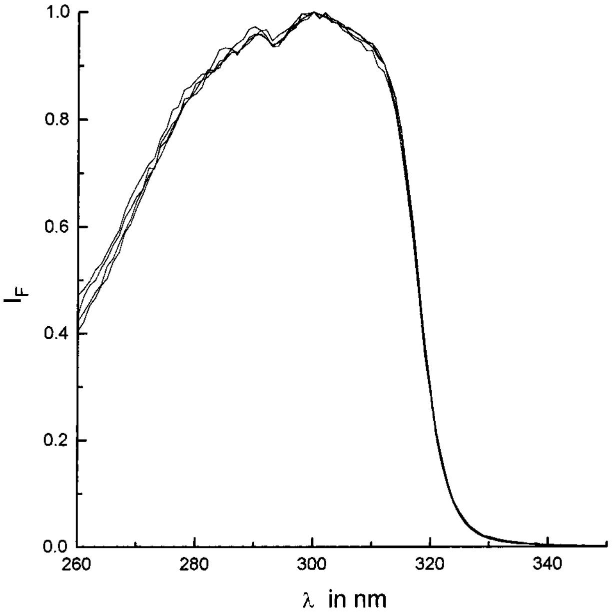

Figure 6. Fluorescence excitation spectra monitoring at 440, 480, 520, and 540 nm for a 0.02 M 3-methylpentane solution of 7AI at room temperature. These spectra are drawn normalized at their peak maximum.

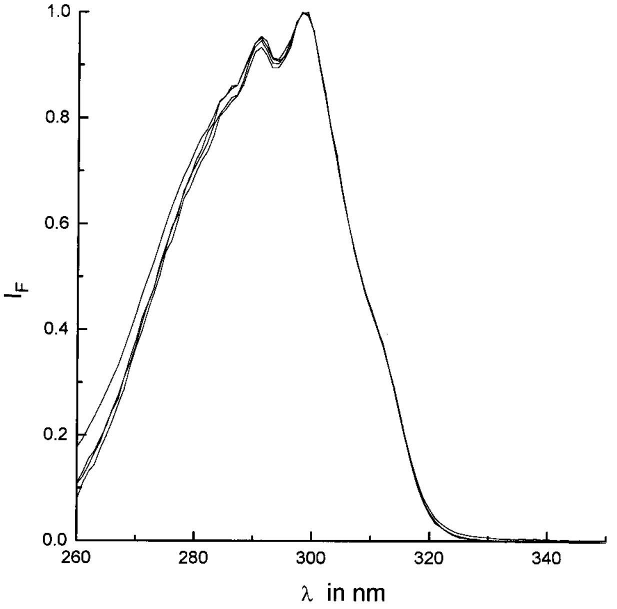

Figure 7. Fluorescence excitation spectra monitoring at 440, 480, 520, and 540 nm for a 0.002 M 3-methylpentane solution of 7AI at room temperature. These spectra are drawn normalized at their peak maximum.

n-Hx (one containing 2×10^{-2} and the other 2×10^{-3} M 7AI), using a cell of 1 cm light path, which was multiplied by a factor of 10. Based on the onset for the monomer and dimer, and also on the fact that the concentration difference is offset, the spectra of Figure 3 cannot be assigned to an improper balance between the monomer and dimer D or to impurities potentially contained in the sample; rather, the difference spectrum should be ascribed to the presence of a new aggregate form of 7AI (β) in the 2×10^{-2} M solution and also, possibly, in the 2×10^{-3} M solution.

Further proof that the new absorption, with an onset around 330 nm, is a new 7AI aggregate form resulting from the high concentration of the sample is provided by the spectra of Figure 4. As can be seen, as the temperature is gradually lowered, this molecular form β reverts to the most stable form in hydrocarbon solvents (i.e., the planar dimer, D).[11] Furthermore, Figure 4 depicts a clear-cut isosbestic point.

On the Emission of a 2×10^{-2} M Solution of 7AI Excited at Its Red Edge. As can be seen from Figure 5, the fluorescence emissions obtained by exciting the red edge of the first absorption band for a 2×10^{-2} M solution can still be assigned to the tautomer form (T*) of the dimer. The weak bands obtained can be ascribed to the low intensity of the excitation source (a 150 W xenon lamp) and to the fact that the excitation slit was only 2 nm wide. Figure 6 shows the fluorescence excitation spectra normalized at the maximum by recording light along the emission band peaking at 480 nm (specifically, it shows the spectra obtained by monitoring light at 440, 480, 520, and 540 nm). Note that these spectra are virtually superimposable and that their onsets lie between 335 and 340 nm. This result is quite consistent with the information derived from the corresponding UV spectra (see Figures 1 and 3) and thus confirms that the new 7AI aggregate form β emits the same fluorescence as dimer D. Also, these excitation spectra differ from those for 2×10^{-3} and 1×10^{-4} M 7AI solutions (see Figure 7 and Figure 8, respectively). The spectra obtained in *n*-Hx have been excluded from Figures 5−8 as they were virtually identical to those recorded in 3MP.

On the Photophysical Implications of Exciting a 2×10^{-2} M Solution of 7AI at 320 nm with a Femtosecond Laser. In light of the steady-state photophysical evidence for a 2×10^{-2} M solution of 7AI, one can draw several interesting conclusions in relation to the potential consequences of exciting such highly concentrated solutions at 320 nm by using strong light sources. Because two different aggregates (or two different strains of dimer D) for 7AI exist in this spectral region, both of which emit fluorescence centered at 480 nm, the nonconcerted double-proton phototransfer mechanism should be reconsidered in the light of the new evidence, which no doubt raises crucial questions. In fact, the two structures D and β must obviously exhibit a different proton-transfer kinetics in their first excited electronic states. Evidence obtained in this work suggests that avoiding the presence of the new aggregate β in these experiments would entail using 7AI concentrations not larger than 10^{-4} M.

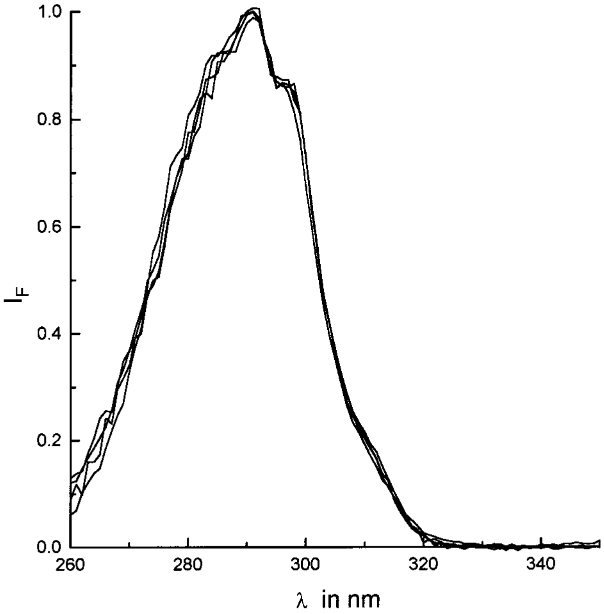

Figure 8. Fluorescence excitation spectra monitoring at 440, 480, 520, and 540 nm for a 0.0001 M 3-methylpentane solution of 7AI at room temperature. These spectra are drawn normalized at their peak maxima.

Conclusions

Upon excitation at 320 nm of a 7AI (2×10^{-2} M) in 3-methylpentane solution, three emissions from aggregates are reported. The 7AI aggregate α emits at 350 nm and does not undergo proton phototransfer. The other two 7AI aggregates D (Scheme 1) and β emit fluorescence centered at 480 nm and must possess different proton phototransfer kinetics. As a result, the interpretation that fosters a nonconcerted mechanism for the double proton phototransfer of the 7AI dimer D cannot be deemed conclusive. The original assumption that the double-proton phototransfer in dimer D of 7AI is concerted, as proposed by Kasha and co-workers and supported by the recent femtosecond spectroscopy experiments of Takeuchi and Tahara,[13] should continue to be held as true.

Acknowledgment. This paper is dedicated to Prof. Michael Kasha on the occasion of his 80th birthday, in admiration of his great chemical and physical intuition and his vast and solid scientific foundations. We are greatly indebted to Dirección General de Investigación Cientifica y Tecnica (Spain) for the support project PB98-0063. Prof. T. Tahara is gratefully acknowledged for a preprint of reference 13 and for a private communication.

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