

**Comment on “On the Doubly Hydrogen Bonded Dimer of 7-Azaindole (0.1 M)
as a Model for DNA Base Pairs in Acetonitrile Solutions at Rt”**

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Catalán, the author of the above mentioned title, has been disregarding previous studies, which provided understanding for the nature of ultrafast double-proton transfer in dimers of 7-azaindole (7-AI). The latest, after what we thought to be a final comment (1, 2), was his questioning of the steady-state data on 7-AI in polar solvents (3). This is pertinent to the issue of whether the reaction is concerted or not and this subject has already been *fully* addressed and summarized in refs 2, 4, and references therein.

The most recent claim in a web publication by Catalán is that the steady-state spectra of 7-AI in polar solvents, e.g., acetonitrile (ACN), are lacking of the signature of the dimer formation

(3), which would be contradictory to previous observations important to interpretation of dynamics in the condensed phase (4). The data presented by Catalán (and the language used) in his document are seriously improper for scientific publication. Our prime concern here is that his specious results may give misleading information to readers in this and related fields of science. We have repeated several key emission measurements and here wish to provide evidence (including unpublished data) confirming our previous results. A plausible cause of his misleading results is experimentally verified and we plan to publish a general comment on these issues elsewhere.

Figure 1 displays representative emission spectra of 7-AI in several polar solvents upon photoexcitation at 320 nm at room temperature. With 7-AI concentration ≥ 0.05 M in ACN (see Figure 1A), a typical dual fluorescence feature is readily reproduced. The UV- and green-wavelength bands are assigned to the fluorescence of monomer (and possibly some oligomers) and that of tautomer generated by proton transfer, respectively (4). The absence of the collision-induced dimer formation (bimolecular exciplex) in the excited state, at least on the timescale of tautomerization, has already been addressed (4). With the increase of 7-AI concentration, the tautomer fluorescence intensifies, as already reported (4), that is in great contrast to the reported results by Catalán, claiming the absence of any trace amount of tautomer in his spectra (3). Furthermore, in Figure 1B, pronounced tautomeric fluorescence around 500 nm is undoubtedly

evident in diethyl ether and dichloromethane as well, which is asserted by Catalán to be unobservable (3). Even in 1,4-dioxane at $[7\text{-AI}] = 0.1 \text{ M}$, tautomer fluorescence is readily observed as displayed in Figure 1B; in this solvent ($[7\text{-AI}] = 0.2 \text{ M}$), the proton-transfer rate is obtained to be $(2.1 \text{ ps})^{-1}$ by femtosecond fluorescence upconversion measurements (data not shown). With the same apparatus, we have also repeated the experiment but replacing the solvent with *n*-propanol ($[7\text{-AI}] = 1.0 \times 10^{-4} \text{ M}$) and reproduced the results obtained by Maroncelli (5), both the band position and relative height.

One possible explanation for Catalán's results is the contamination of polar solvents by ambient water moisture. Because water molecules can efficiently compete with host hydrogen-bonding 7-AI monomers to form hetero-dimers, the use of anhydrous solvents (especially when dealing with hygroscopic polar solvents) is requisite to this type of experiments; this point is reminiscent of difficulty in the precise measurements of kinetic isotope effects for the reaction (4). Indeed, upon addition of 2% (v/v) water to 7-AI (0.1 M) in ACN, the intensity of the tautomer emission band decreases dramatically (see Figure 2), which is a strong indication for the inhibition of the homo-dimerization process of 7-AI in the presence of water moisture. We note that the UV emission band exhibits ~10-nm red-shift in the presence of 2% water. It is worth mentioning that in bulk water, 7-AI has a single fluorescence band with maximum around 390 nm; almost the entire population of the 7-AI molecules are solvated, i.e., the formation of

hetero-dimers (5, 6). In this case, proton-transfer processes occur by hydrogen-bonding interactions with water molecules, giving rise to short-lived tautomers. Another possible explanation may be the inaccurate calibration of the wavelength-dependent sensitivity of an instrument or the excitation wavelength, although Catalán described that the spectrometer used in his study was “calibrated.” These can cause a bias in the relative intensities observed.

In summary, the steady-state spectra reported in the recent web publication by Catalán are at fault and do not support his claim. Our results call for caution due to artifacts that could lead to such misleading results. As clearly summarized (2, 4), his assertion of concertedness from time-averaged low-resolution data is therefore unreliable, ignoring valuable experimental findings from careful time-resolved experiments (ref 4 and references therein) and high-level theory (7) at odd with his claim. Catalán uses highly inappropriate language with claims that regrettably cannot be substantiated, and has published a number of “comments,” “revisits,” and “reappraisals” on this and related subjects, but unfortunately not displaying care and scholarship, especially to works performed by other researchers (8, 9). This approach has to stop, as it is beneficial neither to him nor to the scientific community.

Experimental Section

The 7-AI (98%) was purchased from Sigma-Aldrich and either recrystallized twice in

cyclohexane or used as received. All the solvents used are of the most anhydrous grade available and freshly used as purchased. Steady-state fluorescence spectra were measured using a FluoroMax-2 fluorimeter (ISA-Spex) with 10-mm (or 3-mm for highly concentrated solutions) rectangular quartz cuvettes. Fluorescence spectra were collected in a right-angle geometry and carefully corrected for the spectral sensitivity of the instrument. The excitation wavelength used is 320 nm unless specified otherwise. All the measurements reported here are collected at room temperature.

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References

1. Catalán, J. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, E78.
2. Kwon, O.-H.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, E79.
3. Catalán, J. *Nat. Preced.* **2008**. Available from *Nature Precedings*,
<http://hdl.handle.net/10101/npre.2008.1926.1>.
4. Kwon, O.-H.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 8703.
5. Chapman, C. F.; Maroncelli, M. *J. Phys. Chem.* **1992**, *96*, 8430.

6. Kwon, O.-H.; Jang, D.-J. *J. Phys. Chem. B* **2005**, *109*, 20479.
7. Serrano-Andrés, L.; Merchán, M. *Chem. Phys. Lett.* **2006**, *418*, 569.
8. Catalán, J. *J. Phys. Chem. A* **2007**, *111*, 8774.
9. Catalán, J.; de Paz, J. L. G. *J. Phys. Chem. A* **2008**, *112*, 904.

Figure Captions

Figure 1. (A) Normalized steady-state emission spectra of 7-AI in ACN with $[7\text{-AI}] = 1 \times 10^{-5}$ M (black), 0.05 M (green), 0.1 M (red), and 0.2 M (cyan). Excitation wavelength for the 1×10^{-5} M solution is 290 nm. Note the increase of the tautomer emission (500 nm) with increase of the 7-AI concentration. (B) Normalized steady-state emission spectra of 7-AI in diethyl ether (green), dichloromethane (red), and 1,4-dioxane (black). The concentrations of 7-AI are 0.05 M in diethyl ether, 0.1 M in dichloromethane, and 0.1 M in 1,4-dioxane. Excitation wavelength for the 7-AI solution in dichloromethane is 335 nm. Asterisks denote Raman scatters. As noted in the text, we also confirmed the behavior in *n*-propanol which is consistent with the results of ref 5.

Figure 2. Normalized emission spectra of 7-AI (0.1 M) in anhydrous ACN (red) and in ACN with 2% (v/v) water (blue).

Figure 1

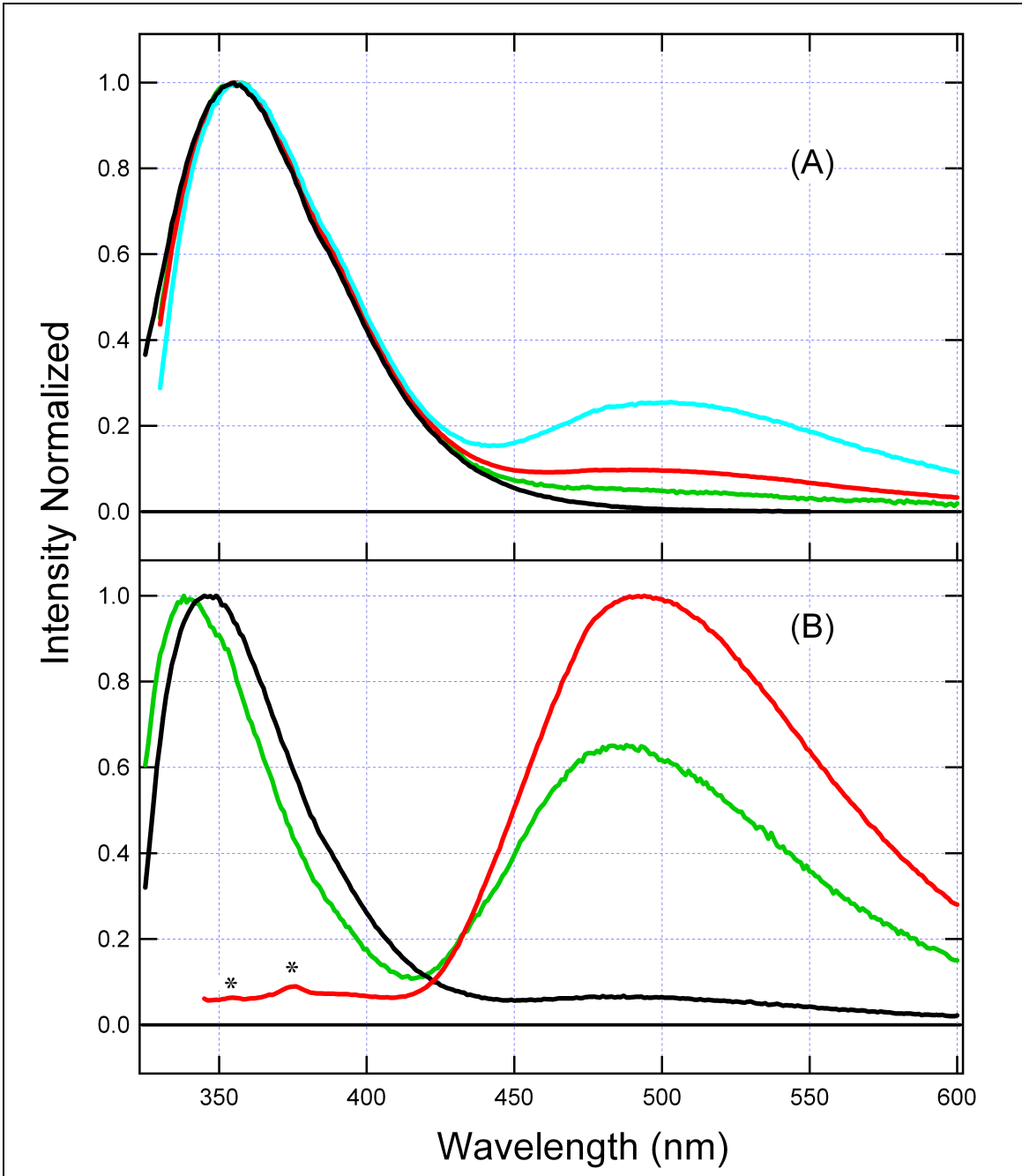


Figure 2

