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Excited-state proton phototransfer in the (3-methyl-7-azaindole)-(7-azaindole) heterodimer

Javier Catalán *, Cristina Díaz, José L.G. de Paz

Departamento de Química Física Aplicada, Facultad de Ciencias, C-II-203, Grupo de Quimica Cuantica Organic, Universidad Autónoma de Madrid, Cantoblanco, ES-28049 Madrid, Spain

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Abstract

A molecule of 7-azaindole and another of 3-methyl-7-azaindole form a doubly hydrogen bonded heterodimer of C_s symmetry with a first electronic excited state a′ where the electronic excitation is highly localized on one of the molecular halves. Also, because the electronic excitation only increases the acidity of the pyrrole nucleus and the basicity of the pyridine nucleus in one of the two hydrogen bonds, the heterodimer undergoes single rather than double proton transfer.

1. Introduction

The two fundamental proposals of Kasha et al. [1] in relation to the photophysics of the C_{2h} dimer of 7-azaindole (7AI) which results from a double hydrogen bonding interaction between the corresponding pyrrole and pyridine units in two 7AI monomers, viz. that the proton transfer is double and that it takes place in a concerted manner, have been verified beyond doubt [2–7]. However, because research in this field has focussed on these two points over the past three decades, most of the basic spectroscopy of 7AI dimer has been ignored and remains unknown.

The basic concepts supporting the hypotheses of Kasha rely on the C_{2h} symmetry of 7AI dimer; this entails complete delocalization of the electronic excitation on its two halves and the change in its acid/base properties to be expected from electronic excitation which was used by Weller [8] to establish Excited State Intramolecular Proton Transfer (ESIPT) mechanisms. Electronic excitation in the C_{2h} dimer of 7AI causes complete delocalization of the excitation on its two halves; more important, it induces a simultaneous marked increase in acidity in the pyrrole proton and basicity in the pyridine nitrogen, the atoms involved in the hydrogen bonds of the dimer [4,9]. As a result, the C_{2h} dimer can undergo concerted double proton phototransfer.

One scarcely explored question is what happens upon electronic excitation of the doubly hydrogen bonded dimer of 7AI if it loses its high centrosymmetry in the ground state. The symmetry loss can be induced by the presence of isotopes in one of the 7AI molecules forming the dimer (isotopomers), through interaction of the dimer with a polar molecule (complexes) or by some substituent present in one of the monomers (heterodimers).

There has been some recent research into these three symmetry loss mechanisms. Thus, Sakota and Sekiya [10,11] found asymmetric deuterated isotopomers of 7AI dimer to exhibit localized electronic excitation and concerted double proton transfer under free-jet conditions. Also, Catalán and Pérez [12] found such isotopomers to exhibit localized electronic excitation and single proton transfers in the condensed phase. Complexes formed between the doubly hydrogen bonded dimer of 7AI and a polar molecule [13] have revealed that, on losing its C_{2h} symmetry, the dimer produces an excited electronic state of lower energy than the 1Bu and 2Ag states in the C_{2h} dimer; this appears to red-shift the onset of the first

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* Corresponding author. Fax: +34 91 497 4785.
E-mail address: Javier.Catalan@uam.es (J. Catalán).

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absorption band. Such complexes [14] have also allowed the identification of the molecular structure responsible for the phosphorescence of 7AI with its onset at 430 nm, which was first detected by Kasha et al. [1]. Sekiya et al. [15] studied heterodimers between 3-Me-7-azaindole and 7-azaindole under free-jet conditions and interpreted their results as evidence for a double proton transfer in the gas phase. On the other hand, Catalán and de Paz [7] interpreted the results for the heterodimer of 4-Me-7-azaindole and 7AI in the condensed phase as evidence of a single proton transfer.

This paper analyses in theoretical and experimental terms the dimer symmetry loss mechanism involving the formation of heterodimers and rationalizes reported information about the topic. Specifically, it deals with the heterodimer formed by one molecule of 7-azaindole and another of 3-methyl-7-azaindole, which was previously studied under free-jet conditions by Sekiya et al. [15]. Their conclusions raise three pivotal questions, namely:

(a) If the spectroscopic behaviour of (3M7AI-7AI) dimer is so similar to that of $7AI_2$ dimer, how can simply substituting a proton at position 3, possibly shift the 0–0 component of the $S_0 \rightarrow S_1$ transition by as much as $1666\ cm^{-1}$?
(b) If the electronic excitation is delocalized on the two molecular halves of the C_{2h} dimer of 7AI, but only on one in (3M7AI-7AI), how can both dimers undergo an identical double proton transfer process?
(c) According to Sekiya et al., "the fluorescence intensity of (3M7AI-7AI) was too weak to measure the dispersed fluorescence (DF) spectrum" Why?

2. Theoretical and experimental section

All computations were done within the framework of the Density Functional Theory (DFT) and the Time Dependent Density Functional Theory (TDDFT), using the software Turbomole v. 5.26, which was developed by the Quantum Chemistry Group of the University of Karlsruhe (Germany) [16]. Full geometry optimization of the ground and excited electronic states was done by using the hybrid functional B3LYP [17–19] as implemented in Turbomole [20]. The TZVP basis set [21] was used. Excited states were studied at the TDDFT level [22] as implemented in Turbomole [23–27]. Previous studies had shown this methodology to be accurate with photoexcited molecules [7,9,28].

The 0–0 components for the $S_0 \rightarrow S_1$ electronic transitions were calculated from the fully optimized geometry for each state, which was corrected for the zero point energy as computed from the vibrational frequencies for the compound.

UV–visible spectra were recorded on a Cary-5 spectrophotometer and corrected fluorescence spectra were obtained by using a calibrated Aminco-Bowman AB2 spectro fluorimeter, using a Suprasil quartz cell of 1 cm light path. The sample temperature was controlled by an Oxford DN1704 cryostat equipped with an ITC4 controller interfaced to the spectrophotometer. The cryostat was purged with dried nitrogen 99.99% pure.

7-Azaindole was obtained in 99% purity from Sigma and recrystallized in spectroscopic-grade cyclohexane twice. 3-methyl-7-azaindole was synthesized from 2-pyridylhydrazine and propionaldehyde to obtain the corresponding hydrazone. This hydrazone was refluxed with diethylene glycol in an inert atmosphere [29]. The resulting residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate 6/4 and dichloromethane/ethyl acetate 6/4) yielding 3-methyl-7-azaindole (23%) with a purity over 99%. All samples used were obtained from freshly made 2-methylbutane (2 MB) solutions containing a 10^{-4} M concentration of indole residue. The 2 MB solvent was Uvasol-grade and supplied by Merck.

3. Results and discussion

This section initially examines the theoretical data available for the heterodimer (3M7AI-7AI) in order to confirm whether the electronic excitation is localized and its implications on the proton transfer process in the excited heterodimer. Then, it deals with its absorption and emission spectra in relation to the type of proton transfer it undergoes.

3.1. The 0–0 components of the $S_0 \rightarrow S_1$ transition

Sekiya et al. [15] obtained fluorescence excitation (FE) spectrum for (3M7AI-7AI) heterodimer near the 0–0 region of the $S_0 \rightarrow S_1$ transition (specifically, from 30 560 to $31\,100\ cm^{-1}$) by tuning only the emission visible through a Toshiba Y45 glass filter. Based on such spectrum and, by analogy with those for $7AI_2$, they assigned the 0–0 component of the (3M7AI-7AI) to the peak at $30\,585\ cm^{-1}$.

The theoretical value for the 0–0 component of the $S_0 \rightarrow S_1$ transition in (3M7AI-7AI) as computed at the TDDTF level and corrected for the zero-point energy is $28\,457\ cm^{-1}$. This value is located at much lower energy, $2100\ cm^{-1}$, than the experimental value obtained under free-jet conditions [15], $30\,585\ cm^{-1}$. This great disagreement between the theoretical and experimental results, for the heterodimer 3M7AI-7AI appears to be remarkable if we bring about the small deviation of only $900\ cm^{-1}$ for the C_{2h} 7AI dimer, when comparing the experimental ($32\,252\ cm^{-1}$) and the theoretical values ($31\,349\ cm^{-1}$).

As recently shown by the authors [7], the C_s dimer of 7-azaindole produces a first excited electronic state a′ with its 0–0 component $484\ cm^{-1}$ below that of the 1Bu state in the C_{2h} dimer. Such a state is responsible for the above-described red shift in the onset of the first absorption band seemingly occurring in 7-azaindole dimer [12,13]. As shown below, this is also the case for the (3M7AI-7AI) heterodimer, and probably, what Sekiya et al. have reported might be the excitation spectra of the sample to a higher excited electronic state.

3.2. Localization of the electronic excitation and proton transfer

Fig. 1 shows the molecular orbitals (MO) involved in the first electronic transition in the following systems: (a) the dimer of 7AI corresponding to the energy minimum in the ground electronic state of C_{2h} symmetry; and (b) that corresponding to the energy minimum in the ground electronic state of the (3M7AI-7AI) heterodimer of C_s symmetry. As can be seen, electronic excitation in the C_{2h} dimer is completely, symmetrically delocalized on the two halves of the dimer. Also, upon photoexcitation the MO suggest a large simultaneous acidity increase in both pyrrole nuclei and basicity in the two pyridine nuclei. The principal outcome is that the dimer undergoes a concerted double proton transfer.

The situation in the C_s heterodimer is rather different. In fact, the electronic excitation is strongly localized (Fig. 1) on one half of the initial MO (HOMO) and in another half of the final MO (LUMO). In this case, the MO suggest an increase of pyrrole acidity and pyridine basicity, but only at one of the hydrogen bonds. As a result, electronic excitation triggers a single proton transfer.

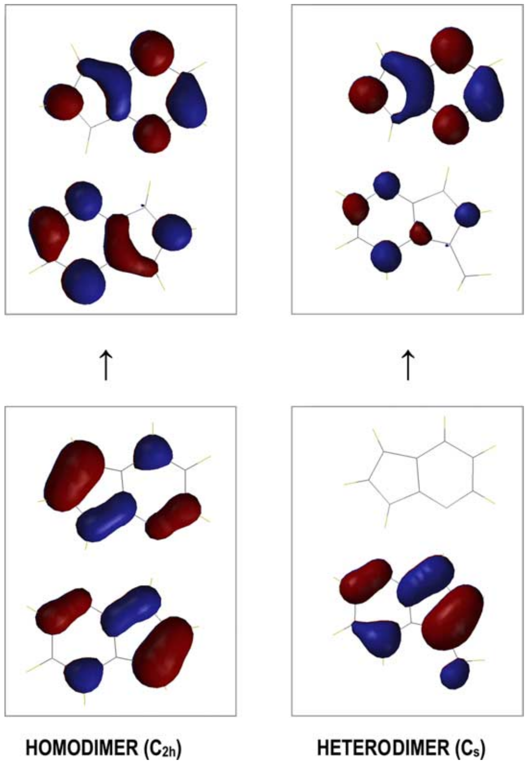

Fig. 1. HOMO (below) and LUMO (above) orbitals involved in the description of the $S_0 \rightarrow S_1$ transition for the 7AI homodimer and for the 3M7AI -7AI heterodimer.

3.3. Absorption and emission spectra of (3M7AI-7AI) in 2 MB

Fig. 2 shows the variation of the UV–visible absorption spectrum for a solution containing a 5×10^{-5} M concentration of both 7AI and 3M7AI in 2 MB with temperature. As can be clearly seen, the absorption spectrum expands above 315 nm, that is, beyond the 0–0 component of the C_{2h} dimer (at 315 nm)[2]. This onset at longer wavelengths facilitates the analysis of the emission of the heterodimer and its photoselection at 325 nm.

Fig. 3 shows the fluorescence emission obtained by excitation at 325 nm where only the (3M7AI-7AI) heterodimer absorbs. As can be clearly seen, the emission spectrum, which is structureless, for the a′ state in the heterodimer peaks in the 430 nm region. It must be reminded that the emission for the double proton transfer of the C_{2h} dimer peaks at 480 nm and exhibits structure at low temperature.

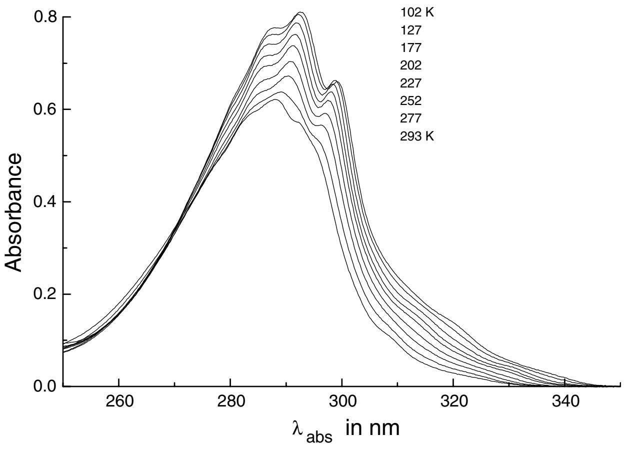

Fig. 2. UV–visible spectra for a 5×10^{-5} M solution of both 7AI and 3M7AI in 2 MB between 293 and 102 K.

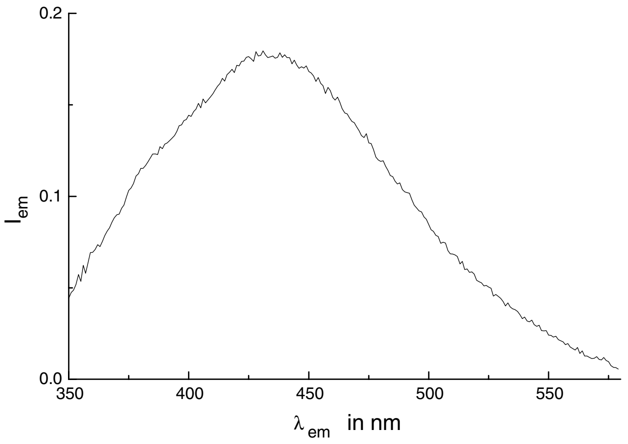

Fig. 3. Emission spectrum for the heterodimer upon excitation at 325 nm of a 5×10^{-5} M solution of both 7AI and 3M7AI in 2 MB at 102 K.

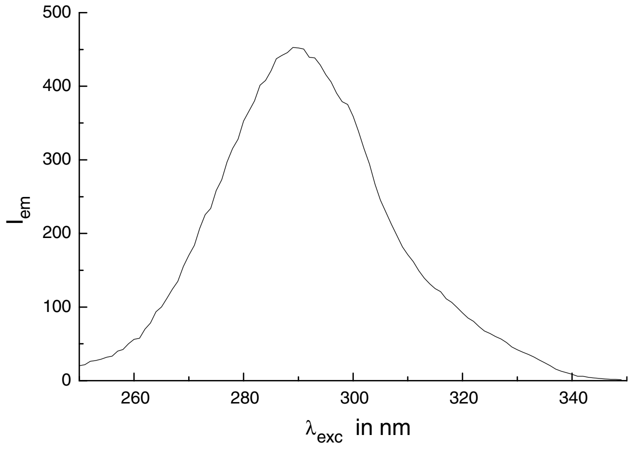

Fig. 4. Excitation spectrum for the heterodimer by monitoring light at 430 nm, for a 5×10^{-5} M solution of both 7AI and 3M7AI in 2 MB at 102 K.

Fig. 4 shows the fluorescence excitation spectra obtained by tuning light at 430 nm, which clearly allows one to ascribe this emission to the heterodimer of C_s symmetry.

These spectroscopic results provide conclusive answers to the questions raised by the interesting experiments of Sekiya et al. [15], namely:

(a) The large shift observed (1667 cm^{-1}) when the proton at C_3 is substituted by a methyl group, in one of the halves of the C_{2h} dimer of 7AI, is not a result of an electronic effect of the substituent, but rather of the electronic excitation causing a change in the electronic state S_1 involved in the $S_0 \rightarrow S_1$ transition, which switches from a C_{2h} dimer, where S_1 is a 1Bu state with the excitation strongly delocalized on both halves, to a C_s heterodimer where S_1 is an a′ state with the excitation completely localized on one half.

(b) The strong delocalization of the electronic excitation on both halves of the C_{2h} dimer and the strong localization on one in the C_s dimer results in the increased pyrrole acidity and pyridine basicity affecting both hydrogen bonds – and hence leading to a double proton transfer in the former and only one of them – and leading to a single proton transfer – in the latter.

(c) Sekiya et al. were unable to measure the DF for the double proton transfer in (3M7AI-7AI) under free-jet conditions simply because such a process is highly unlikely owing to heterodimer decays by IC to the first excited electronic state as it is mentioned above, and hence, this molecular system undergoes a single proton transfer. In condensed phase, the IC process would be the main photophysical step and consequently the emission spectrum for the heterodimer exhibits only the fluorescence centered at 430 nm.

4. Conclusions

The interesting experiments on the double proton transfer in (3M7AI-7AI) heterodimer recently reported by Sekiya et al. [15] should be revisited in the light of the fact that the heterodimer undergoes a single proton transfer only. This conclusion is supported by both the theoretical and experimental data reported in this work, the latter of which were obtained in a 2 MB solution.

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