Excited State Proton Transfer in 3-Methyl-7-Azaindole Dimer. Symmetry Control

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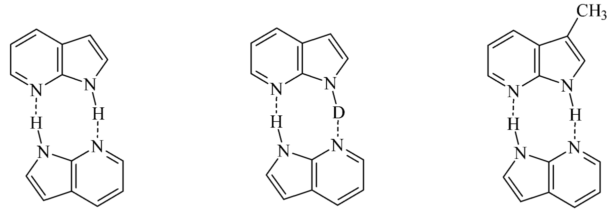
The concerted double proton transfer undergone by the C_{2h} dimer of 7-azaindole upon electronic excitation has also been reported to occur in 3-methyl-7-azaindole monocrystals and in dimers of this compound under free-jet conditions. However, the results obtained in this work for the 3-methyl-7-azaindole dimer formed in a 10^{-4} M solution of the compound in 2-methylbutane suggest that the dimer produces no fluorescent signal consistent with a double proton transfer in the liquid phase or in a matrix. In this paper, the spectroscopic behavior of the doubly hydrogen bonded dimer of 3-methyl-7-azaindole is shown to provide a prominent example of molecular symmetry control over the spectroscopy of a substance. This interpretation opens up a new, interesting research avenue for exploring the ability of molecular symmetry to switch between proton-transfer mechanisms. It should be noted that symmetry changes in the 3-methyl-7-azaindole dimer are caused by an out-of-phase internal rotation of the two methyl groups

Introduction

Kasha et al.[1] formulated two fundamental hypotheses in relation to the photophysics of the C_{2h} dimer of 7-azaindole (7AI), which is formed via a double hydrogen bond between the pyrrole and pyridine nuclei in two 7AI monomers, namely, (a) that the proton transfer in such a dimer is double and (b) that it takes place in a concerted manner. Both hypotheses have been verified thoroughly.[2−8] However, because most research on the dimer conducted over the past three decades has focused on these points, its basic spectroscopy has been largely ignored and remains unknown.

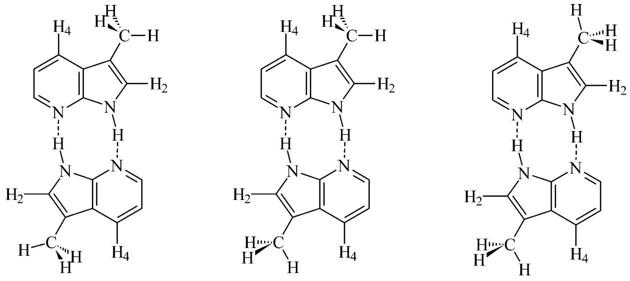
The basic concepts supporting the hypotheses of Kasha et al. revolve around the C_{2h} symmetry of 7AI dimer, which results in complete delocalization of the electronic excitation on its two halves and in the expected enhanced acidity and basicity associated with electronic excitation, which was used by Weller[9] to develop excited state intramolecular proton transfer (ESIPT) mechanisms. Electronic excitation of the C_{2h} dimer of 7AI results in complete and symmetric delocalization over the two halves and, more important, in a simultaneous marked increase in the acidity of the pyrrole proton and the basicity of the pyridine nitrogen—the two atoms involved in the hydrogen bonds.[4,10] As a consequence, the C_{2h} dimer can undergo a concerted double proton transfer upon electronic photoexcitation.

CHART 1



centrosymmetric dimer (C_{2h}) isotopomer dimer (Cs) heterodimer

CHART 2: Symmetry Heterodimers of 3-Methyl-7-azaindole



S4S4 *S4S2* *S2S2*

There is little spectroscopic information about the outcome of electronic excitation in the doubly hydrogen bonded dimer of 7AI when it loses its high centrosymmetry in the ground electronic state. The loss can result from the presence of some isotope in one of the monomer molecules (isotopomers; see Chart 1), interaction of the dimer with a polar molecule (complexes), the presence of a substituent in one of the monomers (heterodimers; see Chart 1), or a internal rotational movement in the dimer (symmetry heterodimers; see Chart 2). The first three situations have recently been examined. Thus, Sakota and Sekiya[11,12] studied deuterated 7AI dimers (viz., asymmetric isotopomers) under free-jet conditions and found them to exhibit localized electronic excitation and a concerted double proton transfer. Catalán and Pérez[13] found asymmetric isotopomers to exhibit localized electronic excitation and single proton transfers. Complexes formed between the doubly hydrogen bonded 7AI dimer and a polar molecule[14] have revealed that the loss of C_{2h} symmetry in the dimer produces a new electronic state A′ of lower energy than the ^1B_u and ^2A_g states in the C_{2h} dimer, and apparently red shifts the onset of the first electronic absorption band; also, it has allowed[15] the molecular structure producing the phosphorescence of 7AI with its onset at 430 nm originally detected by Kasha et al.[1] to be identified. Sekiya et al.[16] studied 3-methyl-7-azaindole−7-azaindole heterodimers under free-jet conditions and ascribed their results,

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based on excitation spectra, to a double proton transfer in the gas phase, but they pointed out that the corresponding emission spectrum could not be measured. Finally, Catalán et al. interpreted their results for the 4-methyl-7-azaindole−7-azaindole[8] and 3-methyl-7-azaindole−7-azaindole[17] heterodimers in 2-methylbutane as evidence for a single proton transfer in both heterodimers.

This paper examines in theoretical and experimental terms the fourth symmetry loss mechanism, which involves the transient formation of heterodimers via internal rotational vibrations leading to a C_{2h}, C_s, or even C_1 dimer. These conformers, which differ in the relative orientation of the two methyl groups, are designated “symmetry heterodimers” here (Chart 2). Chart 2 shows only three representative structures of these conformers, thus chosen to describe the global behavior of all the conformers generated by internal rotation of the methyl groups. As a matter of fact, from the C_{2h} dimer **S4S4**, the C_s dimer **S4S2** is generated by a 180° rotation of one of the methyl groups, and a subsequent new rotation of another methyl group produces a distinct C_{2h} dimer **S2S2**. The analysis of the three conformers will allows us to wholly realize the spectral behavior of the numerous dimers (quasi-degenerate) obtained by internal rotation of the methyl groups, many of which ought to exhibit C_1 symmetry. The paper also discusses previous results of Sekiya et al.[18] for 3-methyl-7-azaindole dimer in the gas phase and of Chou et al.[19] in the crystal phase, as well as their interpretation in the light of a double proton transfer in the first excited singlet state of the dimer.

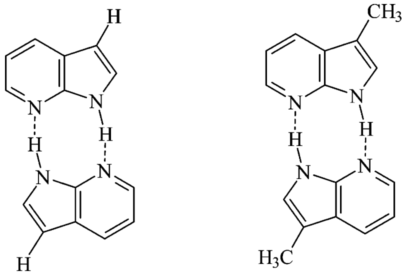
Theoretical and Experimental Section

All computations were done within the framework of the density functional theory (DFT) and time-dependent density functional theory (TDDFT), using the Turbomole v. 5.25 software package,[20] which was developed by the Quantum Chemistry Group of the University of Karlsruhe (Germany). Full geometry optimization of the ground and excited singlet electronic states was done by using the hybrid functional B3LYP[21−23] as implemented in Turbomole.[24] The TZVP basis set[25] was used for compatibility with previous studies by the authors and also because of the size of the system. Excited states were studied at the TDDFT level[26] as implemented in Turbomole.[27−29] Previous studies had shown this methodology to perform accurately with photoexcited molecules.[8,17,30,31] The free energy values in the ground state for the monomeric and dimeric forms of 3-methyl-7-azaindole (Chart 2) were performed using Gaussian 03.[32]

The 0−0 components of the $S_0 \rightarrow S_1$ electronic transitions were determined from the fully optimized geometry for each state, which was corrected for the zero point energy change, as computed from the vibrational frequencies for the corresponding molecular structures.

UV−visible spectra were recorded on a Cary-5 spectrophotometer, using a Suprasil quartz cell of 1 cm optical path. Spectroscopic emission measurements were made in Suprasil cylindrical quartz cells of 3 mm light path; as a result, the path length to the center of the cell, which governs the so-called filtering effects on fluorescence (a major factor with highly absorbing solutions), was less than 1.5 mm. The average path length ranged from 0 to 1.5 mm. Corrected fluorescence spectra were obtained by using a calibrated Aminco-Bowman AB2 spectrofluorimeter. The sample temperature was controlled via an Oxford DN1704 cryostat equipped with an ITC4 controller interfaced to the spectrophotometer. The cryostat was purged with nitrogen of purity greater than 99.99%.

CHART 3: Structures of 7-Azaindole and 3-Methyl-7-azaindole Dimers



3-Methyl-7-azaindole (3M7AI) was synthesized from 2-pyridylhydrazine and propionaldehyde to obtain the corresponding hydrazone. This hydrazone was refluxed with diethylene glycol in an inert atmosphere.[33] 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 of over 99%.

^{1}H NMR ($CDCl_3$): $\delta = 11.35$ (1 H, s, NH), 8.33 (1H,dd, $J = 1.6, 4.7$ Hz, H-6), 7.92 (1H, dd, $J = 1.6, 7.8$ Hz, H-4), 7.15 (1H, s, H-2), 7.08 (1H, dd, $J = 4.7, 7.8$ Hz, H-5), 2.34 (3 H, s, CH_3). MS, m/z: 132 (74) [M^+], 131 (100), 104 (15). $C_8H_8N_2$ (132.2): calcd C 72.68, H 6.10, N 21.19; found C 72.52, H 6.15, N 20.85.

The samples used consisted of 10^{-4} M solutions of 3M7AI in Uvasol grade 2-methylbutane (2MB) from Merck. All solutions were slowly cooled from room temperature to a low temperature in the cryostat.

Results and Discussion

Substituting the protons at C_3 in 7-azaindole dimer by two methyl groups converts the $7AI_2$ dimer into a $3M7AI_2$ dimer (Chart 3) and produces two structures seemingly identical in chemical terms which, however, as can be seen in this paper, exhibit rather disparate physical (spectroscopic) behavior.

This section initially describes the differences between the absorption and emission spectra of the two dimers, and then discusses their disparate behavior toward electronic excitation in structural terms.

Absorption Spectra. As shown by Catalán and Kasha,[2] changes in the absorption spectra for a 10^{-4} M solution of 7AI in 2MB as the temperature is lowered from 293 to 192 K provide a highly elegant description for the monomer-to-dimer conversion in 7AI. Thus, the spectrum at 293 K is determined by the monomer and exhibits outstanding peaks at 293, 287, and 282 nm. As the temperature is lowered, however, the spectrum for the monomer−dimer mixture becomes blurred. Finally, at a low enough temperature where only the dimer can exist the spectrum is clearly structured and exhibits well-defined peaks at 300, 293, and 286 nm; more importantly, it exhibits the 0−0 component (at 315 nm) and with onset at 320 nm.

The spectra for a 10^{-4} M solution of 3M7AI in 2MB are significantly different from those for a 7AI solution, even though at first both dimers possess C_{2h} symmetry and should therefore behave identically as the solution temperature is lowered. However, the spectrum for 3M7AI in 2MB at 293 K (Figure 1) is structured and exhibits two peaks at 295 and 289 nm in addition to a shoulder at 308 nm that might be the 0−0 component for the monomer and is highly consistent with the results of Sekiya et al.[18] under free-jet conditions. As the temperature is lowered, however, the spectrum rapidly becomes blurred and loses its structure altogether at 270 K (Figure 1). The fact that, below 270 K, the spectra cease to exhibit the

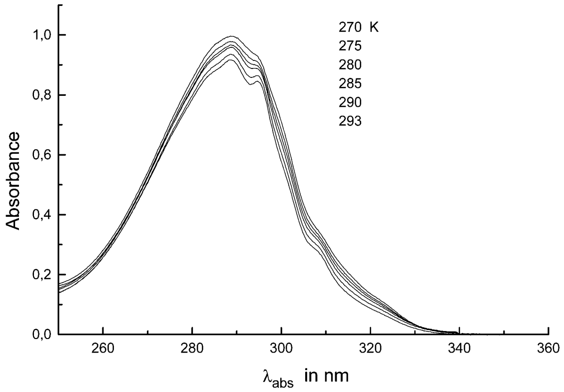


Figure 1. UV−visible spectra for a 10^{-4} M solution of 3M7AI in 2MB between 293 and 270 K.

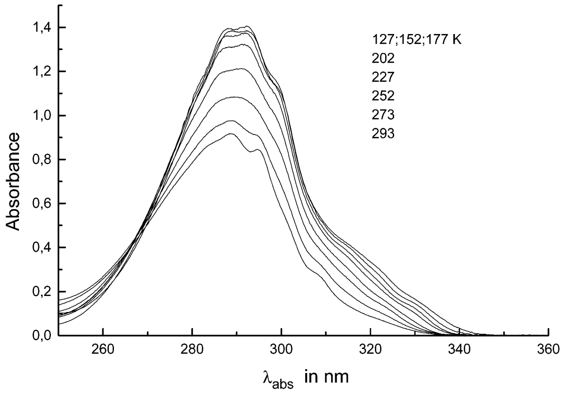


Figure 2. UV−visible spectra for a 10^{-4} M solution of 3M7AI in 2MB between 293 and 127 K.

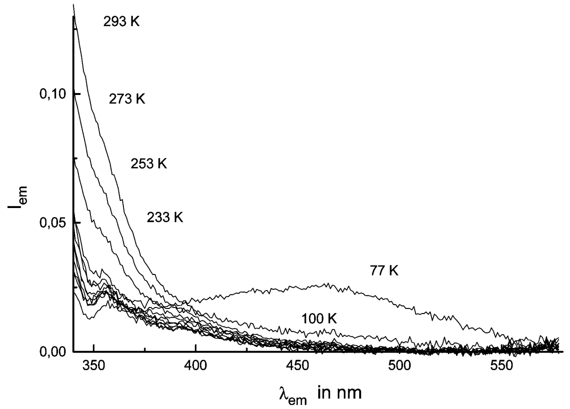


Figure 3. Emission spectra upon excitation at 315 nm of a 10^{-4} M solution of 3M7AI in 2MB between 293 and 77 K.

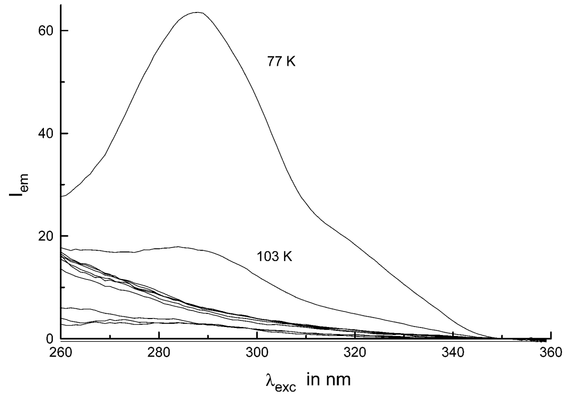


Figure 4. Excitation spectra for a 10^{-4} M solution of 3M7AI in 2MB by monitoring light at 480 nm between 293 and 77 K.

vibronic structure for the C_{2h} dimer to be expected based on the behavior of 7AI in 2MB is of a high spectroscopic significance.

This absence of vibronic structure together with the substantial shift in the onset of the first absorption band (Figure 2) for $3M7AI_2$ turns out to be very significant for the reason that it appears at 345 nm as the temperature decreases, in contrast to an identical $7AI_2$ sample that exhibits a constant offset at 320 nm. The shift in the onset for the 7AI dimer is known to be caused by a switch from the original C_{2h} symmetry to a lower one such as C_s.[13,14]

Based on the foregoing, the first absorption band for 3M7AI dimer in a 2MB solution must be structureless since the dimer behaves as if it were present as several very similar conformers, all doubly hydrogen bonded. In the 3M7AI dimer, such structures can only result from different internal rotational positions of its methyl groups leading to symmetry changes in the dimer. Chart 2 shows the three stationary structures potentially involved in the different steps of the internal rotational movement of the methyl groups, two of which (**S4S4** and **S2S2**) possess C_{2h} symmetry and one (**S4S2**) that possesses C_s symmetry; bear in mind that there would be many other inserted dimeric conformations between these three structures. These other structures, which ought to be of C_1 symmetry, will play a relevant role in the photophysics of the 3M7AI dimer.

The symmetry heterodimers produced by out-of-phase torsional movements of the two methyl groups, which are at symmetric positions in the dimer, must give rise to a potential energy curve involving only small energy barriers between the structures. As shown in the Theoretical Computations section, the true energy minimum in the ground electronic state corresponds to the **S4S4** structure of C_{2h} symmetry. However, the small magnitude of the barriers allows $3M7AI_2$ molecules to distribute between the different conformers, all of which will therefore contribute to the absorption. As a result, the spectrum will be blurred and exhibit a structureless band. We shall revisit this behavior in discussing the corresponding fluorescence excitation spectra below.

Emission Spectra. Figure 3 shows the changes observed in the emission spectra obtained by exciting light at 315 nm as the temperature was lowered from 293 to 77 K. Surprisingly, the band corresponding to the double proton transfer in the C_{2h} dimers of 7AI—which is centered in the 480 nm region and increases in intensity as temperature decreases—is absent from the spectra. In $3M7AI_2$, such a band should be red shifted as the 0−0 components under free-jet conditions differ 1650 cm^{-1} between $7AI_2$ and $3M7AI_2$. Only a new, broad fluorescence band between 375 and 560 nm, centered at 450 nm, is observed once the 2MB matrix is formed (i.e., when the sample becomes rigid). This fluorescence signal cannot be compared with that for the gas phase as it was not reported by Sekiya et al.;[18] clearly, however, it cannot be that observed in the crystal phase by Chou et al.[19]

The excitation spectra obtained by tuning light at 480 nm (Figure 4) additionally confirm that a 10^{-4} M solution of 3M7AI in 2MB does not give the emission corresponding to the double proton transfer; also, the excitation spectra obtained in the 2MB matrix are consistent with the absorption spectra recorded at low temperatures (Figure 2).

The emission detected below 400 nm over the temperature range 293−233 K can be assigned to 3M7AI monomers in solution, as confirmed by the excitation spectra obtained by tuning light at 380 nm (see Figure 5). Such spectra additionally

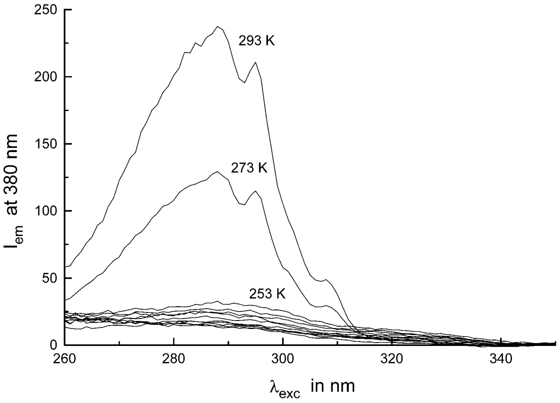


Figure 5. Excitation spectra for a 10^{-4} M solution of 3M7AI in 2MB by monitoring light at 380 nm between 293 and 113 K.

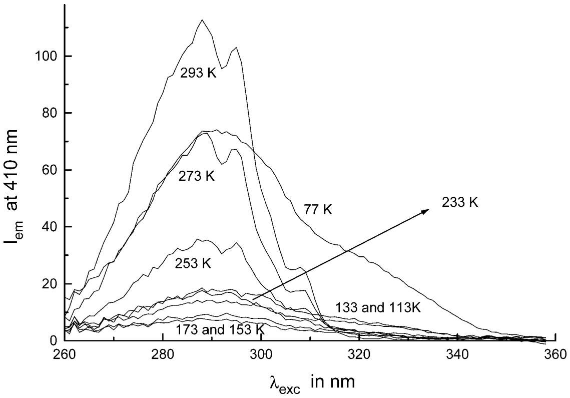


Figure 6. Excitation spectra for a 10^{-4} M solution of 3M7AI in 2MB by tuning light at 410 nm between 293 and 113 K.

confirm that the monomer concentration decreases with decreasing temperature, to undetectable levels below 230 K. This suggests that all 3M7AI is present in dimeric form below such a temperature. The excitation spectra of Figure 5 expose the spectral envelope of the first band for the monomer and reveal that the 0−0 component for the transition lies at 308 nm, as previously concluded from the absorption spectra and from the fact that the peaks at 295 and 289 nm obtained at 293 K are better resolved in the excitation spectra—the sample must thus be in dimeric form below such a temperature.

Interestingly, as the temperature where the 2MB matrix forms is approached, the sample begins to emit fluorescence centered at about 450 nm. Also, the corresponding excitation spectra obtained by tuning light at 410 nm (Figure 6)—where the signal corresponding to the double proton transfer cannot appear because its onset in 7AI is at 413 nm—appears to be produced by a mixture of $3M7AI_2$ forms (Chart 2) since its vibronic structure is not resolved along the absorption band. An identical conclusion is warranted by the excitation spectra obtained at the same temperatures (Figure 4).

Theoretical Computations. The optimized molecular structures in the ground electronic state of 3M7AI and the three doubly hydrogen bonded dimers it can form (Chart 2) confirm that only the monomer with its methyl group in staggered conformation pointing toward H_4 and the dimer having its two methyl groups identically arranged (**S4S4**) and possessing C_{2h} symmetry possess all real vibrational frequencies in the ground electronic state. The energy for the C_s dimer with its methyl groups in staggered conformation pointing, in each monomer, toward H_4 and H_2, respectively (**S4S2**), which may constitute the first step of an out-of-phase internal rotation of the methyl groups, is 1.1 kcal/mol higher than that for **S4S4**. The dimer C_{2h} with its two methyl groups in staggered conformation pointing toward H_2 (**S2S2**), which is 2.2 kcal/mol more unstable than **S4S4**, and hence the most unstable of the three, may constitute another torsional step. The last two dimeric structures, **S4S2** and **S2S2**, do not possess all real vibrational frequencies in their ground states.

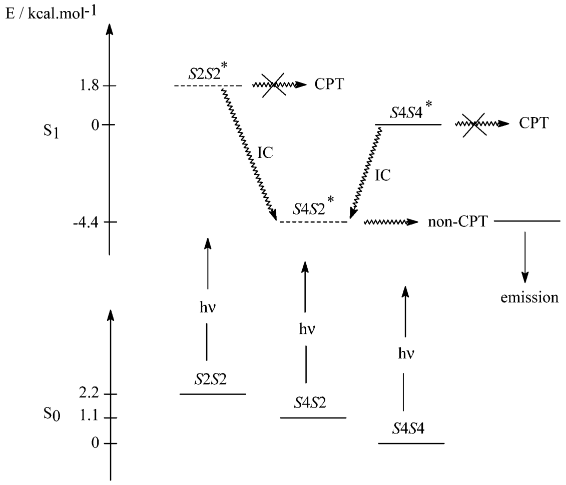


Figure 7. Photophysical diagram of the symmetry heterodimers of 3-methyl-7-azaindole [CPT, concerted proton transfer].

TABLE 1: Free Energy Values (in kcal·mol^{-1}) for S2S2, S4S4, and S4S2 Dimers in the Ground Electronic State at Several Temperatures

	$\Delta G°(298\ K)$	$\Delta G°(197\ K)$	$\Delta G°(127\ K)$
S2S2	−1.41	−5.31	−8.06
S4S4	−1.54	−5.35	−8.04
S4S2	−1.90	−5.62	−8.25

The free energies of these structures (Table 1) allowed us to determine the dimerization free energies for **S2S2**, **S4S4**, and **S4S2** dimeric structures. It is worth mentioning that the **S4S2** structure proves to be the most feasible and significant. As the temperature is lowered, the clearly dominant structures in solution are the hydrogen-bonded dimer structures.

It should be noted that, although the only stationary structure of 3-methyl-7-azaindole dimer in the ground electronic state is **S4S4**, where rotation of the methyl groups is unhindered and most probably out-of-phase, the sample behaves like a mixture of conformers represented by **S4S4**, **S4S2**, and **S2S2**. Because the energy differences between these conformers are small, and so are the intervening barriers by effect of the nonhindered internal rotation of a methyl group (see Figure 7), they are highly likely to undergo interconversion. This situation is bound to be complicated by the presence of such a fluid solvent as 2MB, the fluidity of which, however, decreases dramatically with decreasing temperature—thereby hindering or even slowing down the internal rotation of the methyl groups.

Table 2 shows the energies of the S_0 and S_1 electronic states and the corresponding 0−0 components of the most salient structures as determined at the TDDFT level and with the zero-point correction made. The data warrant the following spectroscopic comments:

(a) Because the energies of the three dimeric forms involved in the torsion of the methyl groups in the ground electronic state (viz., **S4S4**, **S4S2**, and **S2S2**) are so similar, the $3M7AI_2$ sample will include not only these three conformers but also many inserted dimers. Also, because the 0−0 components of their first electron transitions are not identical, they will overlap one another and conceal the vibrational structure as experimentally observed here (see Figure 2). The fact that lowering the

TABLE 2: Energies of S_0 and S_1 Electronic States, Energy Differences, and Corresponding 0−0 Components of the $S_0 \rightarrow S_1$ Transition As Determined at the TZPV Level

		E_T (a.u.)	ΔE (cm^{-1})	0−0 (cm^{-1})
7AI	S_0	−379.756 377	34 078	33 102
	S_1	−379.600 994		
3M7AI	S_0	−419.057 979	32 122	31 210
	S_1	−418.911 513		
7AI$_2$	S_0	−759.535 551	33 316	31 502
	S_1	−759.383 639		
S4S4	S_0	−838.138 303	31 513	29 510
	S_1	−837.994 614		
S4S2	S_0	−838.136 540	29 583	28 551
	S_1	−838.001 652		
S2S2	S_0	−838.134 781	31 377	29 370
	S_1	−837.991 711		

TABLE 3: Isotopic Effects and 0−0 Components from Experiments[6,11,18] and Theory for the $S_0 \rightarrow S_1$ Transitions of Several Isotopomers of 7AI and 3M7AI Dimers (All in cm^{-1})

	experimental		theoretical	
species	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$
7AI$_2$-*hh*	32 251	0	31 502	0
7AI$_2$-*hd*	32 303[a]	52[a]	31 394	45
7AI$_2$-*dd*	32 348	97	31 592	90
3M7AI$_2$-*hh*	30 600	0	29 510[b]	0
3M7AI$_2$-*hd*	30 648[a]	48[a]	29 538	28
3M7AI$_2$-*dd*	30 691	91	29 566	56

[a] Averaged values for the *h*d* and *d*h* structures. [b] The experimental data values have been estimated from the fluorescence excitation spectra; therefore, these data values have been obtained by taking into account the structure of the minimum energy for the ground electronic state (**S4S4**).

temperature does not restore the vibronic structure suggests that some of these forms continue to absorb simultaneously over the studied temperature range. Also, the shift in the onset as the temperature is lowered results in the increase of the presence of the C_s dimeric form **S4S2** at low temperatures.

(b) The free-jet spectroscopic data reveal that substituting the proton at position 3 in 7-azaindole by a methyl group causes an outstanding red shift of ca. 1207 cm^{-1}: the 0−0 component of 7-azaindole lies at 34 639 cm^{-1} [34] and that of 3-methylazaindole lies at 33 432 cm^{-1}.[18] Such a shift appears to be so great judging by the fact that an identical substitution in a similar molecule such as indole causes a shift of only 356 cm^{-1}—the 0−0 components of indole and 3-methylindole lie at 35 321 and 34 875 cm^{-1},[35] respectively—however, our theoretical calculations provide a red shift of 1892 cm^{-1}, confirming this special behavior caused in 7AI by a methyl group at position 3.

(c) The free-jet measurements also reveal that the 0−0 component of the C_{2h} dimer of 3M7AI is red shifted by 1652 cm^{-1} with respect to the 7AI dimer, i.e., from 32 252 cm^{-1} in 7AI$_2$[6] to 30 600 cm^{-1} in 3M7AI.[18] Such a shift also is consistent with the theoretical datum, which is 1992 cm^{-1}. Nevertheless, it is worth mentioning that the theoretical calculations indicate a first singlet excited state corresponding to the C_s dimer **S4S2**, below the corresponding S_1 excited state for the C_{2h} dimeric structures of **S4S4** and **S2S2**.

(d) The free-jet measurements also reveal that the 0−0 components of the $S_0 \rightarrow S_1$ transitions in the dimers of 7AI and 3M7AI are blue shifted owing to deuteration of one or both pyrrolic nitrogens, which are involved in the hydrogen bonds supporting the dimer structure of these compounds. The experimental data obtained by Sekiya et al.[6,11,18] as well as those obtained in this work for the dimers of 7AI and 3M7AI are gathered in Table 3. It is noteworthy, the excellent agreement found for the 7AI dimer, which preserves the C_{2h} symmetry and undergoes a concerted double proton transfer, but the data sets disagree for the 3M7AI dimer, in which the torsion of the methyl group can change the symmetry and, therefore, the 3M7AI dimer is not compelled to undergo a double proton transfer.

The energy values for the ground electronic state shown in Tables 1 and 2 are consistent with the simultaneous presence of several dimeric structures that could be electronically excited and will therefore produce a mixture of excited electronic forms potentially contributing to the fluorescence emission. Careful analysis of the energies for these structures in their first excited singlet state reveals that the most stable structure in such a state is **S4S2**, which possesses C_s symmetry. However, stability differences are more marked than in the ground state as the C_{2h} dimer **S4S4*** is more unstable than the C_s dimer **S4S2*** by 4.6 kcal/mol and the C_s dimer **S4S2*** is more stable than the C_{2h} dimer **S2S2*** by 6.2 kcal/mol . A careful analysis of the vibrational frequencies corresponding to the first excited singlet electronic state for these dimers shows that only the C_s dimer **S4S2** possesses all real vibrational frequencies. This new situation must undoubtedly dictate the photophysical evolution of the system (Figure 7) as the ease with which the methyl groups can rotate will facilitate the conversion of **S4S4*** and **S2S2*** into the more stable form **S4S2***—which will therefore govern the photophysics of the system.

At this point, we should examine the chemical properties of the three representative dimeric forms, which can no doubt be selectively populated. How do they behave upon electronic excitation? On one hand, the two C_{2h} structures (**S4S4** and **S2S2**) completely delocalize the excitation on their two halves (see Figure 8). On the other hand, the C_s structure, **S4S2**, has the excitation highly localized on one-half which, however, changes upon electronic excitation (see Figure 8).

From the molecular orbitals (MOs) shown in Figure 8, the actually important inference is that electronic excitation of the two C_{2h} dimers causes a large simultaneous increase in the acidity of the pyrrole groups and the basicity of the pyridine groups[4,10] that triggers a concerted double proton transfer via the two hydrogen bonds. In the C_s dimer, the acidity and basicity

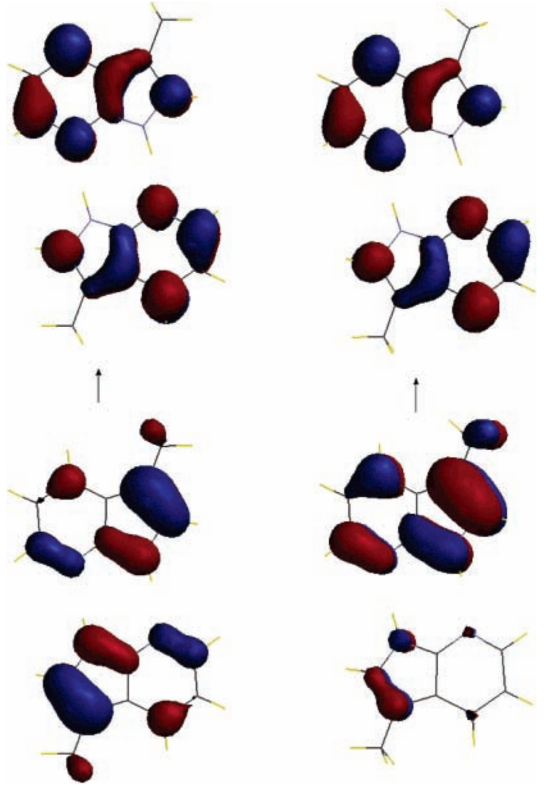


Figure 8. HOMO (below) and LUMO (above) orbitals involved in the description of the $S_0 \rightarrow S_1$ transition for the **S4S4**, **S2S2** (left), and **S4S2** (right) structures.

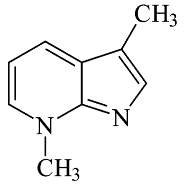
enhancement caused by electronic excitation occurs largely in a pyrrole and a pyridine group involved in the same hydrogen bond, so the outcome is a single proton transfer.

Photophysical Behavior of 3-Methyl-7-azaindole Dimer. The photophysics of the doubly hydrogen bonded dimer of 3M7AI can be conveniently explained by using a simplified Jablonski diagram including only the processes involved in the deactivation of the excited electronic states [viz., a first singlet excited state typical of the C_s structure triggering a single proton transfer, and a second excited singlet theoretically corresponding to the ^1B_u state in the C_{2h} dimers, but shared by the three forms and triggering a double proton transfer competing with both internal conversion (IC) and the torsional process leading to **S4S2**, of C_s symmetry (see Figure 7)].

In photoswitching to the ^1B_u state under a free collision regime in the gas phase, the system might undergo a double proton transfer, IC (via state A′), or internal rotation of the methyl groups to give the C_s dimer **S4S2**; ultimately, the IC and torsional processes induce the nonradiative conversion from S_2 to S_1. The occurrence of collisions in the gas phase would only favor the IC and torsional processes. The foregoing suggests that the likelihood of ^1B_u undergoing a double proton transfer is low relative to the other two processes. In fact, Sekiya et al.[18] found that, "The intensity of fluorescence from 3M7AI$_2$-*hh* and 3M7AI$_2$-*dd* was too weak to measure the dispersed fluorescent spectrum."

The increased intensity and structure observed in the fluorescence of a 3M7AI$_2$ monocrystal on lowering the temperature (see Figure 4 in ref 19) is consistent with the emission corresponding to the double proton transfer in 7AI dimer dissolved in 2MB.[2] We calculated the resulting Stokes shift from the corresponding absorption and fluorescence maxima (viz., 337 and 479 nm, respectively) in Figure 4 of the paper by Chou et al.[19] and found it to be 8800 cm^{-1}; the typical value for a

CHART 4: Structure of 3,7-Dimethyl-7-azaindole [(3MM(7)AI]



double proton transfer is 11 000 cm^{-1}. Unless the fluorescence produced by the double proton transfer in 3M7AI is affected in some unexpected way by the crystal field, such fluorescence emission should be red shifted with respect to a hypothetical fluorescence from 7AI centered at 480 nm. Based on the previous shift between the two dimers (1652 cm^{-1}), the emission should have been centered at 520 nm. Note that Chou et al.[19] found the model compound for the double proton transfer, 3MM(7)AI (see Chart 4), to exhibit fluorescence centered at ca. 510 nm in the crystal phase.

We should remark that the dimeric structure found by X-ray diffraction in 3M7AI by Chou et al.[19] presents, clearly, both methyl groups in staggered conformation in relation to H_4, in accordance with our theoretical results, thus showing the **S4S4** conformation as the most stable in the ground electronic state. Therefore, it seems feasible that this conformation may remain in the crystal phase and may produce the double proton transfer postulated by Chou et al., but taking into account the information mentioned above, this emission should be strongly influenced by the crystal structure.

The situation in solution becomes more interesting since the electronically excited structures **S4S4*** and **S2S2*** relaxed to **S4S2***, which is clearly the most stable form, and structure **S4S2***, which might have been electronically excited to its S_2 state via a rapid collisional mechanism, relaxed by IC and vibrationally to its A′ excited state—that is, if all excited states including **S4S4***, **S4S2***, and any other excited intermediate relaxed to a single excited structure: **S4S2***. Such a structure is the true energy minimum in the hypersurface for S_1, which possesses C_s symmetry and undergoes a single proton transfer. This reasoning is quite consistent with available experimental evidence for a 10^{-4} M solution of 3M7AI in 2MB at temperatures between 293 and 77 K.

In a recent paper,[10] we showed that the electronic excited state A′ undergoes a single proton transfer that causes the dimer to dissociate into a protonated half and a deprotonated half. These are the forms producing the emission when the medium hinders dissociation of the dimer (e.g., in a 2MB matrix). The possibility of systems involving multiple hydrogen bonds such as DNA bases undergoing proton transfer via only one of the hydrogen bonds has been proposed by Goodman[36] to account for mutational processes in DNA.

Conclusions

The relative orientation of two methyl groups at symmetric positions in 7AI dimer plays a central role in switching, via the specific molecular symmetry of the system, between the different possible proton-transfer mechanisms. This provides an interesting basis for undertaking new research into light-induced mutational processes.

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