Confirmation of Biprotonic Phototautomerism in 7-Azaindole Hydrogen-Bonded Dimers[1]

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Abstract: The spectral properties of 7-azaindole are compared with those of its N-methyl derivatives. The effect of temperature on the fluorescence of a concentrated solution of 7-azaindole is also investigated. The results offer strong support for the occurrence of an intermolecular double proton-transfer reaction in the lowest excited singlet electronic state of 7-azaindole hydrogen-bonded dimers. It appears that, at very low temperatures, proton tunneling may be an important mechanism for the reaction.

B iprotonic phototautomerism was first discovered by Taylor, El-Bayoumi, and Kasha[2] when they examined the fluorescence spectrum of 7-azaindole in 3-methylpentane as a function of concentration. It was known from earlier work by El-Bayoumi[3] that in carbon tetrachloride an appreciable fraction of the 7-azaindole molecules is present in the form of doubly hydrogen-bonded self-dimers. By investigating the effect of concentration on the infrared spectrum, an equilibrium constant of 118 l./mol was determined for the dimerization in carbon tetrachloride at room temperature. This value would be expected to be similar in other nonpolar, non-hydrogen-bonding solvents.

In Figure 1, the room-temperature fluorescence spectrum of 7-azaindole in 3-methylpentane is seen to consist of two fluorescence bands. The first band, F_1, has a maximum at about 325 nm and is attributed to the normal fluorescence of the monomer with possibly a small contribution from the dimer. The second band, F_2, has a maximum at about 480 nm and an intensity relative to F_1 which depends on concentration, excitation wavelength, and temperature. This second band was attributed[2] to fluorescence from a new tautomeric species which forms in the excited state of the dimer by the simultaneous intermolecular transfer of the two indolic protons, as shown in Figure 1. Great care was taken to eliminate alternative explanations of F_2 such as impurities, excimers, and photodecomposition products.

In this paper we wish to present some results which we have obtained in our laboratory as part of a continuing investigation of the 7-azaindole system. In particular, we have synthesized two N-methyl derivatives of 7-azaindole and compared their spectral behavior with that of the parent compound. In addition, we report some initial results from a study on the dependence of the relative intensity of F_2/F_1 on temperature. When taken together, these results confirm the occurrence of biprotonic phototautomerism in 7-azaindole H-bonded dimers. Our experiments also suggest that proton tunneling could be an important mechanism for this process at very low temperatures ($<200°$K).

Experimental Section

7-Azaindole, purchased from Aldrich Chemical Co., was recrystallized and washed extensively with cyclohexane and then dried at 65 °C for 24 hr. The solvents were purified by methods described previously.[2] The absorption spectra were obtained on a Cary 15 spectrophotometer. The fluorescence spectra (uncorrected) were obtained using conventional techniques with the exception that the exciting light was chopped at 41 cps and the amplifier was of the lock-in variety. Since the chopping speed was fast compared to the phosphorescence lifetime of 7-azaindole ($\sim$2.3 sec in 3MP at 77°K), the low-temperature spectra contained no contribution from the phosphorescence.

Both N^1-methyl-7-azaindole and 7-methyl-7H-pyrrolo[2,3-b]-pyridine (*i.e.*, the N^7-methyl stabilized tautomer of 7-azaindole pictured in Figure 2) were prepared according to the method of Robison and Robison.[4] The N^1-methyl derivative was purified by vacuum distillation and the N^7-methyl tautomer by paper chromatography.

In the study of F_2/F_1 as a function of temperature, cold N_2 was blown into the optical dewar which contained the sample and a pentane thermometer for monitoring the temperature. The sample was degassed using the freeze–pump–thaw technique.

Results and Discussion

N^1-**Methyl-7-azaindole.** This molecule is similar to 7-azaindole except for the replacement of the indolic hydrogen by a methyl group. Consequently, it is not able to form H-bonded dimers and serves as a convenient control on the experiments with 7-azaindole. As would be expected, the absorption spectrum of this compound occurs in about the same region as that of 7-azaindole, except for a relatively small red shift due to the perturbing action of the $-CH_3$ group.[5] It was found that the absorption spectrum follows Beer's law up to concentrations greater than 10^{-2} M, indicating, as expected, no tendency to self-associate.

The fluorescence spectrum of N^1-methyl-7-azaindole exhibits only the normal fluorescence analogous to F_1 in the 7-azaindole system. No long-wavelength fluorescence was detected at any concentration in any of the solvents used. This demonstrates the role of the proton in the process giving rise to F_2 and also supports the contention that F_2 is not excimer fluorescence. If excimers were easily formed in solution of 7-azaindole, one would expect to at least detect their presence in similar solutions of the N^1-methyl derivative.

7-Methyl-7H-pyrrolo[2,3-b]pyridine. This molecule, pictured in Figure 2, is the N^7-methyl stabilized tautomer of 7-azaindole. It has an electronic structure

(1) Supported by U. S. Atomic Energy Commission Contract No. AT(11-1)2039.

(2) C. A. Taylor, M. A. El-Bayoumi, and M. Kasha, *Proc. Nat. Acad. Sci. U. S.*, **63**, 253 (1969).

(3) M. A. El-Bayoumi, Ph.D. Thesis, Florida State University, 1961.

(4) M. M. Robison and B. L. Robison, *J. Amer. Chem. Soc.*, **77**, 6554 (1955).

(5) C. A. Taylor, M. A. El-Bayoumi, and M. Kasha, manuscript in preparation.
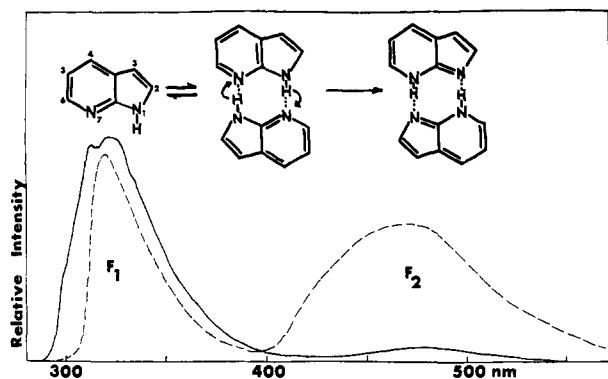
Figure 1. Room-temperature fluorescence of 7-azaindole in 3-methylpentane at 10^{-4} M (———) and 10^{-2} M (-----). The excitation wavelength was 285 nm. The reduced intensity at 10^{-2} M on the short-wavelength side of F_1 is due to self-absorption.
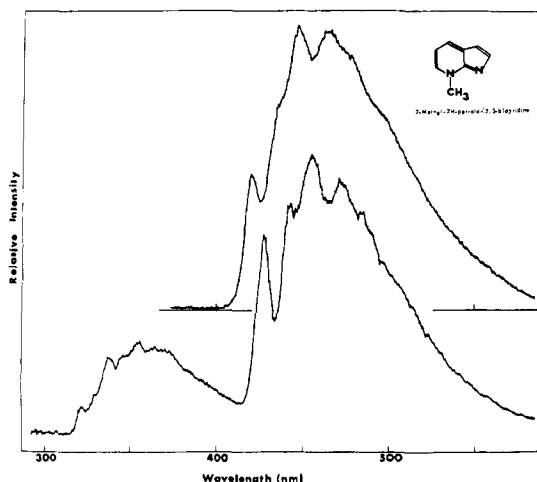

Figure 2. A comparison of the fluorescence spectrum of a 10^{-2} M solution of 7-azaindole (lower curve) with that of a 10^{-4} M solution of 7-methyl-7H-pyrrolo[2,3-b]pyridine. The solvent in both cases was 3-methylpentane and the temperature was 77°K. The excitation wavelength was 285 nm for the lower curve and 360 nm for the upper curve.

similar to that of the species to which F_2 in the 7-aza-indole solutions has been attributed. Consequently, it shoud have a fluorescence in the same region as F_2. The two emissions at 77°K are compared in Figure 2. One observes that the two emissions do indeed occur in the same region. In fact, even the band contours are similar. We offer this similarity as strong support for the occurrence of biprotonic phototautomerism in 7-azaindole H-bonded dimers.

Low-Temperature Fluorescence of 7-Azaindole. The fluorescence spectrum of 7-azaindole shown in Figure 2 indicates that F_2 is strong, even at 77°K. We have also obtained the fluorescence spectrum at 4°K of the same solution and it is very similar. The quantitative evaluation of F_2/F_1 in low-temperature glasses is complicated by problems of glass cracking, microcrystal formation, and the presence of trace amounts of water,[6] all of which interfere with the ability to obtain reproducible monomer–dimer equilibration. However, the prominence of F_2 at low temperature in 10^{-2} M solutions is established and suggests that the barrier to
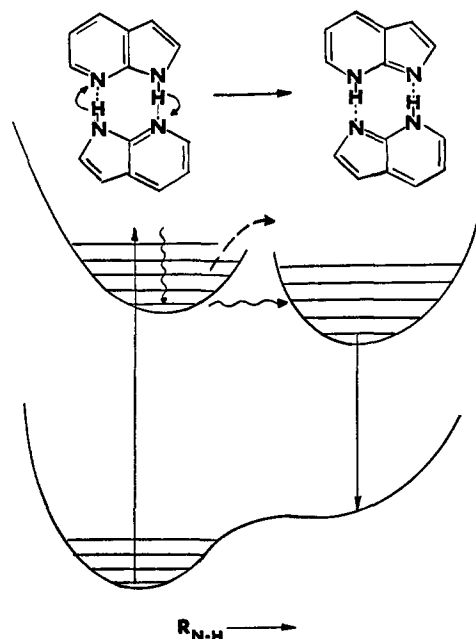

Figure 3. Qualitative potential energy diagram describing the energetics of biprotonic phototautomerism in 7-azaindole hydrogen-bonded dimers.

the proton-transfer process is quite small. It also lends additional support for the contention that excimers are not responsible for F_2. Excimer formation is expected to be diffusion controlled[7] and thus should not occur in a rigid glass at 77°K.

Dependence of F_2/F_1 on Temperature. In principle, by exploring the effect of temperature on the relative intensity of F_2 and F_1, a quantitative estimate of the barrier could be obtained. However, such an experiment is difficult to interpret because of the various parameters which change with temperature. These include changes in the absolute quantum yields of F_1 and F_2, shifts in the monomer–dimer equilibrium, changes in the viscosity of the solvent, and a change in the Boltzmann population of the low-frequency vibrational levels associated with the hydrogen bonds in the dimer.

A potential energy diagram which qualitatively describes the energetics of the double proton-transfer process is shown in Figure 3. The ordinate in this diagram can be imagined as a reaction coordinate associated with the simultaneous motion of the two protons in the dimer. In the ground state, the tautomer is pictured as being unstable. This is compatible with the fact that no tautomer absorption could be detected after prolonged illumination of a concentrated 7-aza-indole solution at 77°K. In the excited state, we envision an activation barrier to the double proton-transfer reaction to form the tautomer. As indicated in Figure 3, there are two possible mechanisms for the reaction: (a) a thermal mechanism (dashed arrow), and (b) a tunneling mechanism (solid arrow). The size and shape of the barrier determine the relative importance of these two mechanisms.

Some initial results illustrating the effect of temperature on the relative intensities of F_2 and F_1 are shown in Figure 4. The numbers along the ordinate are

(6) C. M. Chopin and J. H. Wharton, *Chem. Phys. Lett.*, **3**, 552 (1969).

(7) C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968, p 350.

simply the ratio F_2/F_1 measured from the relative intensities of the corresponding band maxima. No correction was made for differences in instrument response at the two wavelengths. In addition, changing the excitation wavelength would also change this scale. However, these changes would only have the effect of multiplying the vertical scale by a constant and would not alter the tentative interpretation which follows.

At high temperatures there is very little F_2 because the monomer–dimer equilibrium constant is small. As the temperature is lowered, the equilibrium constant increases and more dimers are formed. Consequently, there is an increase in the relative concentration of species which are capable of biprotonic phototautomerism, accompanied by a corresponding increase in F_2. If there were no barrier, all of the excited dimers would produce tautomers, and further lowering the temperature would cause a continued increase in F_2 until essentially all of the molecules were dimerized. However, this is not observed. Rather, the curve proceeds through a sharp maximum near 200°K ($kT \sim 140$ cm^{-1}). This maximum can be explained by postulating the existence of a small barrier to the proton-transfer reaction. Then, as the temperature is further lowered, the Boltzmann distribution is such that the contribution from the thermal mechanism rapidly diminishes.

If the thermal mechanism were the only one, the curve in Figure 4 would be expected to approach zero at very low temperatures. As mentioned in the previous section, there are inconsistencies in the results at temperatures where the solvent forms a rigid glass. However, there is no question about the prominence of F_2 in 10^{-2} M solution, even at 4°K. Thus, at these temperatures, the proton-tunneling mechanism must be important.

We are currently extending this study of the temperature dependence of F_2/F_1 to determine the effects of concentration, excitation wavelength, and solvent.
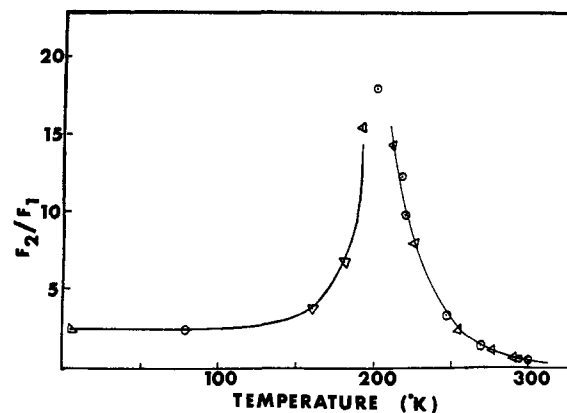

Figure 4. Relative intensity of tautomer fluorescence (F_2) and normal fluorescence (F_1) as a function of temperature. Excitation wavelength, 285 nm. The different symbols indicate data obtained on different days with the same sample. The solvent was 3-methylpentane and the concentration 10^{-2} M.

These initial results are presented here because they are in qualitative agreement with the interpretation of F_2 as being due to biprotonic phototautomerism, and thus serve as additional support for that interpretation.

Conclusion

By comparing the spectral properties of N^1-methyl-7-azaindole and its N^7-methyl tautomer with those of 7-azaindole, we have provided strong support for the occurrence of biprotonic phototautomerism in 7-azaindole H-bonded dimers. Initial results pertaining to the temperature dependence of F_2/F_1 are compatible with the model and thus provide additional support. The prominence of F_2 in a 10^{-2} M solution of 7-azaindole in 3-methylpentane, even at 4°K, implicates tunneling as a mechanism for the proton-transfer process at very low temperatures.