Photoinduced Proton Transfer

DOI: 10.1002/anie.200801350

Proton transfer with a twist? Femtosecond Dynamics of 7-(2-pyridyl)-indole in Condensed Phase and in Supersonic Jets**

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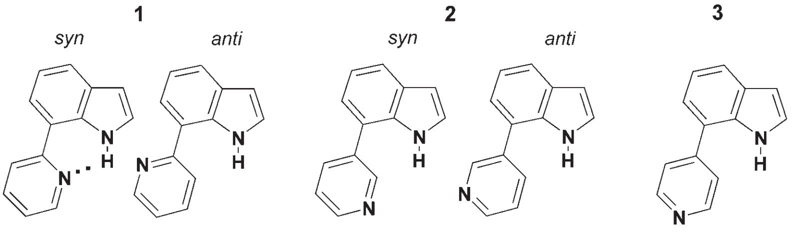
The results of spectral and photophysical studies strongly suggest that photoinduced proton transfer in 7-(2-pyridyl)indole (**1**) is accompanied by mutual twisting of the pyridyl and indole moieties. This conclusion is supported by the unusual finding that the photoreaction is faster in a cold, supersonic-jet-isolated molecule than in solutions at room temperature, and by the ultrafast repopulation of the ground state substrate. The twisting and the presence of S_1–S_0 conical intersection (CI) are also predicted by calculations. The phenomenon may be quite general for several classes of organic molecules with intramolecular hydrogen bonds.

Recent experimental and theoretical developments demonstrate that proton transfer—a fundamental chemical reaction—is by no means a one-dimensional process.[1] In particular, for tautomerization occurring along a hydrogen bond, coupling with modes that modulate the hydrogen bond strength may be crucial.[2] Much less explored is the possibility of large conformational changes accompanying proton/hydrogen transfer, although the role of torsional motion in the deactivation of phototautomerization products has been discussed in some depth.[3–9]

Compound **1** is a member of a series of three isomeric 7-pyridylindoles (Scheme 1), which were studied previously in solution.[10] Compounds **1** and **2** can exist in *syn* and *anti* rotameric forms. In **1** there is no doubt that the dominant species corresponds to the planar, intramolecularly H-bonded *syn* form. Calculations predict this *syn* rotamer to be about 5 kcal mol^{-1} more stable than the *anti* rotamer which lacks the intramolecular H-bond and is nonplanar because of steric repulsion between indolyl NH and pyridyl CH. In **2**, both rotamers should have a nonplanar structure and similar energies; calculations predict the *syn* form to be more stable, but only by less than 0.5 kcal mol^{-1}.



Scheme 1. The structure of three isomeric 7-pyridylindoles.

For compounds **2** and **3**, in which the indolyl moiety is respectively in the *meta* and *para* positions with respect to the pyridine nitrogen atom, strong fluorescence is observed at 293 K both in nonpolar and polar aprotic solvents.[10] This is not the case for **1**, which fluoresces extremely weakly. Moreover, fluorescence excitation spectra of **1** do not coincide with the absorption, being shifted to the blue by about 2×10^3 cm^{-1} (Figure 1). We therefore assign the fluorescence to a small fraction of *anti* rotamers. Such an assignment is corroborated by the fact that the fluorescence quantum yield in *n*-hexane is about ten times weaker than in acetonitrile (0.0005 and 0.006, respectively). Calculations predict a larger dipole moment for the *anti* form and, therefore, its population should increase with solvent polarity. The *anti* population can also be enhanced in alcohols, which can form two independent hydrogen bonds with **1**-*anti*, one to the indolyl NH and the other to the pyridyl nitrogen atom. Another strong argument for the assignment of the emitting species to the *anti* form is that the energy calculated for transition to the lowest excited singlet state for **1**-*anti* is 0.4 eV

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[**] The work was sponsored by a KBN grant 1T09A 016 30, EC Grant G5MA-CT-2002-04026, and NWO grant 048.021.2003.011. R.P.T. and A.S. thank the Robert A. Welch Foundation and the NSF. B.B. thanks the Deutsche Forschungsgemeinschaft for funding of the project.

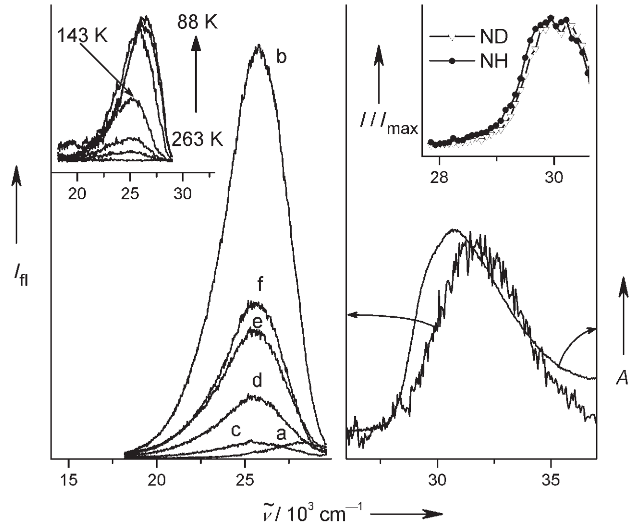


Figure 1. Left: fluorescence of **1** at 293 K: a) *n*-hexane, b) acetonitrile, c) methanol, d) ethanol, e) 1-propanol, f) 1-butanol; inset, temperature dependence measured in the 1:1 methanol:ethanol mixture. Right: room temperature absorption and fluorescence excitation of **1** in 1-propanol (monitored at 25 000 cm^{-1}); inset: one-color REMPI spectra of jet-cooled **1** and its ND isotopologue.

higher than that for **1**-*syn*.[9] This prediction is in excellent agreement with the observed difference between the maxima of the fluorescence excitation and absorption spectra.

The lack of detectable fluorescence from **1**-*syn* implies that nearly all the photoexcited molecules of **1**, that is, those corresponding to the *syn* form, decay very rapidly. This rapid decay was confirmed by transient absorption (TA) spectroscopy (Figure 2). The initially excited species reveals a characteristic TA spectrum, which decays in about 1.0 ± 0.2 ps. After that, no significant signal is observed throughout the whole available spectral range, except for a region around 360 nm, where a component is found decaying in a few ps. Since this region is close, but slightly to the red of the onset of stationary absorption, we assign this decay to cooling of the hot molecule in the ground state. Essentially the same spectra and similar decay time were observed in solvents differing in polarity and proticity: *n*-hexane, acetonitrile, CH_3OH, CH_3OD, 1-propanol, ethylene glycol, and decanol. In decanol and CH3OD the decay was somewhat slower, 1.7 and 1.9 ps, respectively.

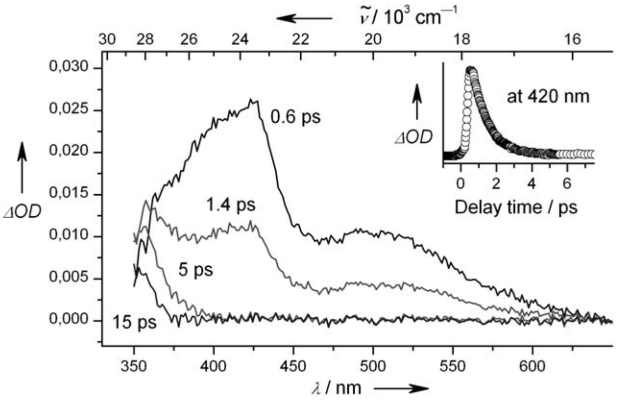


Figure 2. Transient absorption spectra of **1** in acetonitrile at 293 K; inset, decay of TA signal probed at 420 nm.

The explanation for the rapid decay of electronically excited **1**-*syn* is the excited state proton transfer, which occurs along the intramolecular hydrogen bond. Calculations predict that the reaction should be barrierless[9] and therefore should also occur in a cold, isolated molecule. Attempts to detect photoexcited **1** in a jet using nanosecond laser pulses were not successful, indicating that lowering the temperature does not stop a rapid depopulation of S_1. Therefore, the jet setup was modified by shortening the excitation/ionization pulses. In these experiments, molecules of **1** were ionized resonantly via S_1 by laser pulses of about 200 fs duration, using either one-color or two-color schemes. The resonance-enhanced multiphoton ionization (REMPI) signal onset was observed at about 29×10^3 cm^{-1}, similar to the room-temperature absorption (Figure 1). Figure 3 presents the kinetic profiles of the ion signals. Interestingly, the decay is not monotonic: a second small maximum is observed at about 1 ps after excitation and its intensity is higher in the deuterated molecule. Convolution of a Gaussian with a harmonically modulated monoexponential decay: $(1+a^*\cos(\omega t+\phi))^*\exp(-t/\tau)$, provided a satisfactory fit to the experimental data. A very fast decay of the ion signal, 280 fs, was extracted. In the N-deuterated molecule the lifetime of the initially excited species increases to 390 fs. The cosine frequency was about 34 cm^{-1} in both cases.

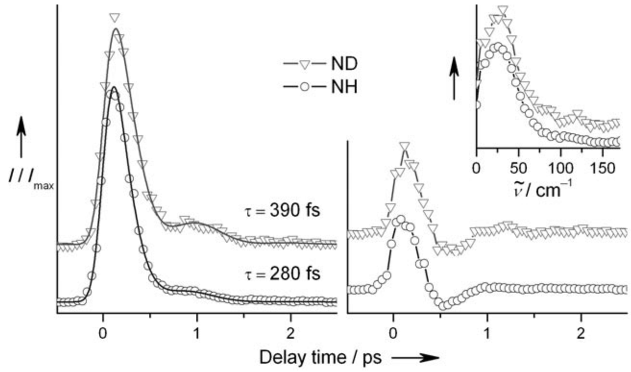


Figure 3. Left: pump-probe REMPI spectra (○) obtained in a supersonic jet for **1** and its N-deuterated analogue (▽); solid lines are the results of the fitting procedure. Right: oscillatory components of the data and their Fourier transforms (inset).

The *syn* structure of the absorbing species was confirmed by using the IR/fsMPI technique (IR absorption detected by femtosecond multiphoton ionization).[11,12] The IR/fsMPI spectrum of **1** reveals a band at 3412 cm^{-1}, assigned to the NH stretch of the *syn* form (Figure 4). This value indicates a fairly strong red shift assigned to an intramolecular hydrogen bond; the value for bare indole in the jet is 3525 cm^{-1}.[13]

For comparison, IR/R2PI spectra (IR absorption detected by resonance two-photon ionization) were also recorded, using ns laser pulses, for 2-(2-pyridyl)indole (**4**) and its bridged derivative, 3,3′-dimethylene-2-(2-pyridyl)indole (**5**). Both molecules should have intramolecular hydrogen bonds weaker than **1**, especially the bridged derivative. These

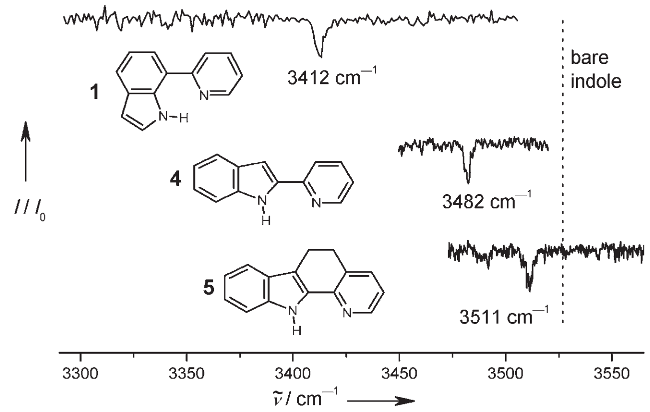


Figure 4. The ionization-detected absorption of three pyridylindoles.

expectations are fully confirmed by the higher NH stretching vibrational transition frequency (Figure 4).

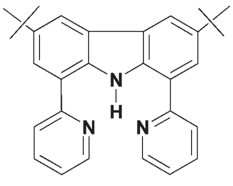
The observation that the photoexcited population of **1** decays in a cold molecule much faster than at room temperature may seem at first rather odd. However, it can be rationalized on the basis of both experiment and calculations. Analysis of the excited state potential energy profile obtained at the CC2/cc-pVDZ level reveals a barrierless hydrogen transfer coupled to the indole-pyridine torsional coordinate.[9] The initially excited structure is unstable with respect to torsion around the C–C bond joining the two moieties. A shallow excited state minimum has been calculated for the tautomeric species, corresponding to an indole–pyridine angle of 33°. At this geometry, the S_1–S_0 energy difference is only about 1 eV. Equally important is the finding of a S_1–S_0 CI at an indole–pyridine dihedral angle close to 90°. Finally, the back reaction, occurring in S_0, is also predicted to be barrierless.

These computational predictions are in excellent agreement with the photophysical behavior of **1** detected both in solution and a jet. Coupling of hydrogen transfer with twisting implies that tautomerization should be sensitive to changes in torsional potential. In the condensed phase, solvent molecules hinder torsion, thus slowing down the reaction. The barrierless character of tautomerization in a jet-isolated molecule is suggested by the deuterium isotope effect, which is equal, within experimental accuracy, to the square root of two. The same value was obtained from TA decay times measured in CH_3OH and CH_3OD.

The lowest vibrational mode of **1**, calculated at 29 cm^{-1} by DFT at the B3LYP/6-31G(d,p) level, corresponds to the torsional motion of the indole and pyridine moieties, occurring with a period of about 1 ps. The pump-probe REMPI spectra shown in Figure 3 reveal, for both NH and ND isotopologues, a second small maximum delayed by about 1 ps from the primary signal maximum. This feature is an indication of a coherent process. It is tempting to associate it with the torsional vibration, which is mandatory for a partial recurrence/reflection of the initial wave packet at the CI point back into the initially excited state. The next lowest frequency vibration should have a period shorter by a factor of 3, because it was calculated at 89 cm^{-1}.

The presence of a CI and the barrierless character of both forward and reverse tautomerization processes help to rationalize several other experimental findings. Firstly, TA spectra demonstrate a lack of detectable transient species along the decay route all the way down to the initial (possibly vibrationally hot) ground-state form. This result is consistent with the fact that no fluorescence from either **1**-*syn* or the phototautomer could be detected. Actually, calculations predict a small barrier between the tautomeric species and the CI geometry. The fluorescence of the phototautomer should then be expected in the near infrared, and thus outside our detection range. However, the TA data seem to exclude the possibile existence of a measurable fraction of the phototautomeric species.

In summary, experimental and computational evidence strongly suggest that the phototautomerization in 7-(2-pyridyl)indole is coupled with a twisting of the molecule, and that the twisting provides an efficient channel for ultrafast excited state deactivation. Moreover, the tautomerization is barrierless in both the lowest excited electronic singlet and the ground state. This pattern of excited-state tautomerization/deactivation may turn out to be quite general. It was predicted theoretically for 2-(2-hydroxyphenyl)benzotriazole,[7] methyl salicylate,[8] and salicylic acid.[6] Our recent studies of 2,9-(di-2-pyridyl)-4,7-di(*tert*-butyl)carbazole (**6**, Scheme 2), a molecule structurally related to **1**, revealed dual fluorescence, indicating phototautomerization.[14] Both emissions are very weak at 293 K in solution, but increase significantly upon lowering of temperature. On the contrary, neither fluorescence nor ion signals could be detected using nanosecond lasers for the molecule isolated in the jet. The situation is probably very similar to that of **1** and thus the elusive short-lived species can be detected only with femtosecond pulse excitation/ionization.



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Scheme 2. The structure of 2,9-(di-2-pyridyl)-4,7-di(*tert*-butyl)carbazole.

Experimental Section

Synthesis of **1** has been described elsewhere.[10] Stationary absorption and fluorescence spectra were recorded in spectral grade solvents on a Shimadzu UV 3100 spectrophotometer and on an Edinburgh FS 900 CDT or Jasny spectrofluorimeter, respectively.

The details of the setup employed for the femtosecond transient absorption experiments have been reported previously.[15] Briefly, a Hurricane (Spectra Physics) laser/amplifier system generated a pulse train (130 fs full width at half-maximum, 800 nm centre wavelength, 1 kHz repetition rate) that was separated into two parts. One part was employed to pump a Spectra Physics OPA 800, which generated pump pulses at 325 nm. The other part was focused on a calcium fluoride crystal to generate a white light continuum from 350 nm to 800 nm that was used for the probe pulse. The polarizations of the two beams were set at the magic angle. The probe beam was coupled into a 400 μm optical fiber after passing the sample and was detected with a CCD spectrometer (Ocean Optics, PC 2000). A chopper (83 Hz, Rofin Ltd) placed in the excitation beam provided I and I_0 depending on the status of the chopper (open or closed). The total instrumental response was about 200 fs (FWHM). The excitation power was kept as low as approximately 5 μJ per pulse using a pump spot diameter of about 1 mm. Apart from using a relatively low excitation intensity, thermal effects and photodegradation were also taken care of by stirring the solution. Photodegradation was not substantial as shown by comparing absorption spectra taken before and after the transient absorption experiment. All experiments were performed at ambient temperature.

Femtosecond multiphoton ionization (fsMPI), fsMPI-detected infrared (IR/fsMPI) and femtosecond pump-probe photoionization spectra were measured for jet-cooled molecules. The principle and the setup for the IR/fsMPI experiment have been described previously.[11] The sample/nozzle temperature was typically maintained at 343 K. REMPI signals were generated using the tunable output of an optical parametric converter (TOPAS, Light Conversion) pumped by a femtosecond chirped-pulse amplified Ti:sapphire laser system (1 kHz, 260 fs FWHM autocorrelation at 800 nm). The applied set of dielectric mirrors allowed for a scanning range from 330 to 360 nm with nearly constant energy of 15 μJ per pulse. The tunable UV laser was employed for excitation (pump) and the second harmonic of the Ti:sapphire fundamental for the ionization (probe) of the electronically excited intermediate in the time-resolved pump-probe measurements by the $1\times\mathrm{UV}+2\times400$ nm process. Both the UV and 400 nm (80 $\mu\mathrm{J\,pulse^{-1}}$) beams were quasi-collinearly introduced into the detection chamber and overlapped in the ionization region of the mass spectrometer. Each of the beams alone did not produce any ions, so the observed ion signal was purely two-color. Time separation between the pump and probe pulses was controlled by means of an optical delay stage. Partial deuteration was performed by adding a few drops of heavy water to the sample compartment, and subsequent evaporation of the water under vacuum. This procedure resulted in fully resolved mass peaks of the ND and NH species with the ratio between 1:1 and 3:1. Contamination of the ND signal by ^{13}C isotopologues of the NH species did not exceed 20%. Details of measurements of infrared spectra detected by resonance two-photon ionization (IR/R2PI) were described elsewhere.[16]

Received: March 20, 2008

Keywords: conical intersection · excited state proton transfer · femtochemistry · photochemistry · tautomerism

[1] *Hydrogen-Transfer Reactions* (Eds.: J. T. Hynes, J. P. Klinman, H. H. Limbach, R. L. Schowen), Wiley-VCH, Weinheim, **2007**.

[2] M. Kijak, Y. Nosenko, A. Singh, R. P. Thummel, J. Waluk, *J. Am. Chem. Soc.* **2007**, *129*, 2738.

[3] D. O'Connor, G. W. Scott, D. R. Coulter, A. Gupta, S. P. Webb, S. Yeh, J. H. Clark, *Chem. Phys. Lett.* **1985**, *121*, 417.

[4] G. Goeller, J. Rieker, A. Maier, J. J. Stezowski, E. Daltrozzo, M. Neureiter, H. Port, M. Wiechmann, H. E. A. Kramer, *J. Phys. Chem.* **1988**, *92*, 1452.

[5] C. A. S. Potter, R. G. Brown, F. Vollmer, W. Rettig, *J. Chem. Soc. Faraday Trans.* **1994**, 59.

[6] A. L. Sobolewski, W. Domcke, *Phys. Chem. Chem. Phys.* **2006**, *8*, 3410.

[7] A. L. Sobolewski, W. Domcke, C. Hättig, *J. Phys. Chem. A* **2006**, *110*, 6301.

[8] J. D. Coe, B. G. Levine, T. J. Martinez, *J. Phys. Chem. A* **2007**, *111*, 11302.

[9] A. L. Sobolewski, W. Domcke, *J. Phys. Chem. A* **2007**, *111*, 11725.

[10] G. Wiosna, I. Petkova, M. S. Mudadu, R. P. Thummel, J. Waluk, *Chem. Phys. Lett.* **2004**, *400*, 379.

[11] Y. Nosenko, M. Kunitski, R. P. Thummel, A. Kyrychenko, J. Herbich, J. Waluk, C. Riehn, B. Brutschy, *J. Am. Chem. Soc.* **2006**, *128*, 10000.

[12] Y. Nosenko, M. Kunitski, C. Riehn, R. P. Thummel, A. Kyrychenko, J. Herbich, J. Waluk, B. Brutschy, *J. Phys. Chem. A* **2008**, *112*, 1150.

[13] J. R. Carney, T. S. Zwier, *J. Phys. Chem. A* **1999**, *103*, 9943.

[14] G. Wiosna-Sałyga, J. Dobkowski, M. S. Mudadu, I. Sazanovich, R. P. Thummel, J. Waluk, *Chem. Phys. Lett.* **2006**, *423*, 288.

[15] G. Balkowski, A. Szemik-Hojniak, I. H. M. van Stokkum, H. Zhang, W. J. Buma, *J. Phys. Chem. A* **2005**, *109*, 3535.

[16] O. Krauß, B. Brutschy, *Chem. Phys. Lett.* **2001**, *350*, 427.