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Excited-State Intramolecular Proton Transfer in Five-Membered Hydrogen-Bonding Systems: 2-Pyridyl Pyrazoles

Wei-Shan Yu,[†] Chung-Chih Cheng,[†] Yi-Ming Cheng,[†] Pei-Chi Wu,[‡] Yi-Hwa Song,[‡] Yun Chi,*,[‡] and Pi-Tai Chou*,[†]

Department of Chemistry, National Taiwan University, 106, Taipei, Taiwan R.O.C., and Department of Chemistry, National Tsing Hua University, 300, Hsinchu, Taiwan R.O.C.

Since the seminal studies on the excited-state intramolecular proton transfer (ESIPT) reaction in salicylic deivatives,[1] numerous ESIPT molecules have been discovered and investigated to shed light on their corresponding spectroscopy and dynamics.[2] Most ESIPT molecules possess six-membered ring types of a strong intramolecular hydrogen bond between O−H (or N−H) and C=O (or pyridinic nitrogen) groups, in which the intramolecular proton transfer in the $^1\pi\pi^*$ state[3] commonly reveals a negligible barrier in nonpolar solvents and may proceed during the period of low-frequency vibrational motions associated with the hydrogen bond.[4−7]

From the fundamental viewpoint, searching for the ESIPT reaction with a finite, well-defined barrier is of great importance to gain detailed insights into the reaction potential energy surface. To achieve this goal, conjugated pyrrole-pyridine systems such as 1-*H*-pyrrolo[3, 2-*h*]quinolines[8] possessing an N−H···N type of five-membered hydrogen bond have received much attention. Under similar proton donor/acceptor strengths, the intramolecular hydrogen-bonding (HB) strength is empirically on the order of 6 > 5 ≫ four-membered systems due to the steric and orientation effects. Unlike the O−H site that has certain rotational degrees of freedom, the orientation effect of the pyrrolic N−H site being restricted toward a specific direction becomes more critical for the HB formation. Furthermore, the photoacidity of the pyrrolic hydrogen is in general weaker than that of the phenolic hydrogen. As a result, ESIPT in five-membered HB pyrrole−pyridine systems may be associated with an appreciably large barrier. Unfortunately, to our knowledge, none of the five-membered N−H···H HB systems have yet been reported to exhibit intrinsic ESIPT. Instead, similar to the four-membered proton donor/acceptor systems such as the 7-azaindoles,[9] this class of molecules is well-known to undergo a guest molecule (including the protic solvents)-catalyzed excited-state proton-transfer reaction.[8]

In this study, we have alternatively designed and synthesized the conjugated 2-pyridyl pyrazole systems where the N(1)−H acidity is enhanced via the electron-withdrawing property of the proximal nitrogen atom (N(2), see Scheme 1) in the pyrazole ring. Scheme 1 shows the molecular drawings of 5-(2-pyridyl) 1-*H*-pyrazoles **1a−d**, possessing various substituents at the −3 position.[10] Both X-ray structural analyses and molecular modeling indicate that the N(1)−H····N(1′) HB isomer is the predominant species for **1a−d** in the ground state (see Supporting Information).

Prototypical absorption and emission spectra of **1a** in thoroughly dry cyclohexane are depicted in Figure 1. Upon $S_0 \rightarrow S_1$ ($\pi\pi^*$) excitation ($\lambda_{max} \approx 290$ nm, $\epsilon_{290} \approx 1.2 \times 10^4$ M^{-1} cm^{-1}), dual fluorescence was observed maximized at 320 nm (the F_1 band) and 585 nm (the F_2 band). The excitation spectra monitored at F_1 and
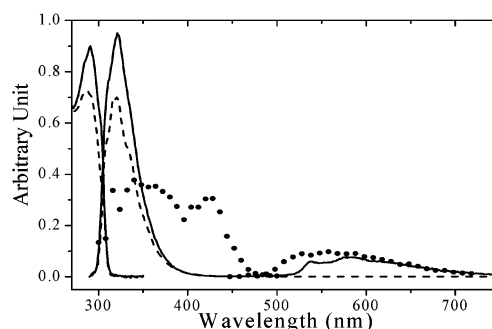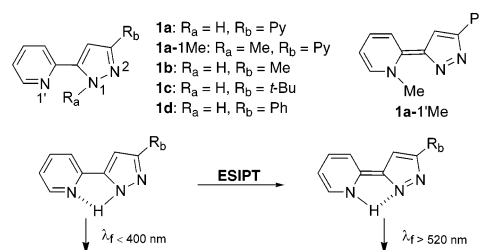

Figure 1. The absorption and emission spectra of (a) **1a** (−), 1.0×10^{-5} M), (b) **1a**-1Me (- - -) and (c) **1a**-1′Me (···) in cyclohexane. The excitation wavelength is 280 nm.

Scheme 1. Structures and Proposed ESIPT Mechanism for the Studied Systems

F_2 bands are identical, and are effectively the same as the $S_0 \rightarrow S_1$ absorption spectral feature, indicating that both emission bands originate from the same ground-state precursor. In a comparative study, **1a**-1Me (see Scheme 1), which serves as a nonproton-transfer model, exhibits a normal Stokes shifted emission maximum at ∼318 nm. Conversely, the proton-transfer tautomer analogue **1a**-1′Me reveals a single fluorescence maximum at ∼570 nm of which the spectral feature is similar to that of the F_2 band. We thus conclude that ESIPT takes place in **1a**, resulting in an anomalously large Stokes-shifted (>10 000 cm^{-1}) proton-transfer tautomer emission. Similar dual emissions were resolved in **1b−d**, of which the corresponding photophysical properties are listed in Table 1.

In contrast to the exclusive tautomer emission resulting from the ultrafast proton-transfer reaction for most ESIPT molecules,[4] the appearance of dual emissions in **1a−d** in which the normal fluorescence is prevailing is remarkable. It implies the existence of an appreciably high barrier associated with ESIPT so that the decay dynamics of the locally excited $S_1 \rightarrow S_0$ relaxation is competitive with the rate of proton transfer. Further insight into the reaction mechanism was gained from the dynamic studies. Single-exponential decay kinetics were resolved for the F_1 band of **1a**, and a lifetime was fitted to be ∼85 ps ($\chi^2 = 1.02$) at 298 K, while the F_2 band is apparently composed of rise and decay compo-

† Department of Chemistry, National Taiwan University, 106, Taipei, Taiwan R.O.C.
‡ Department of Chemistry, National Tsing Hua University, 300, Hsinchu, Taiwan R.O.C.

Table 1. Photophysical Parameters of **1a**−**d** Measured in Cyclohexane at 298 K

	$\lambda_{max}^{F_1}$ (Φ)^a	$\lambda_{max}^{F_2}$ (Φ)^a	$F_1{}^b$	$F_2{}^b$	ΔE^d
1a	320 (19)	585(1.5)	85	80 (-0.071)^c 275 (0.065)	2.03
1b	320 (21)	577(0.5)	115	120 (-0.017) 242 (0.021)	2.22
1c	320 (25)	577(0.2)	125	130 (-0.042) 213 (0.035)	2.62
1d	322 (9)	590(0.3)	74	76 (-0.070) 175 (0.061)	1.76

^{a} $\Phi \times 10^3$. ^{b} Picoseconds ^{c} Numbers in the parenthesis are preexponential factors of the fitting eq $F(t) = a_1\,e^{-k_1 t} + a_2\,e^{-k_2 t}$. ^{d} ΔE (in kcal/mol) measured in methylcyclohexane. λ in nm.
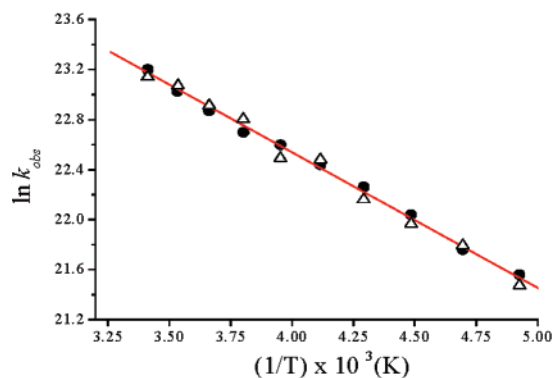
Figure 2. The plot for $\ln k_{obs}$ versus the reciprocal of temperatures in methylcyclohexane: **1a**-*h* (●) and **1a**-*d* (△) (monitored at the F_1 band).

nents that were fitted to be 80 and 275 ps, respectively ($\chi^2 = 1.01$). The rise time of the F_2 band, within experimental error, is identical with the decay time of the F_1 band, further supporting the precursor−successor type of reaction mechanism. ESIPT dynamics were also obtained for **1b**−**d** at 298 K and the results are listed in Table 1.

The rate constants of 70−130 ps^{-1} measured for **1a**−**d** are ∼2 orders of magnitude smaller than that reported for typical ESIPT molecules in nonpolar solvents.[4] Slower proton-transfer reaction may be in some way associated with its rather weak hydrogen-bonding strength, and hence a long HB distance. Thus, one might initially suspect that this is simply due to a larger barrier along the reaction coordinate with only the proton motion involved. To test this possibility, the ESIPT rates in deuterated (N(1)−D) versions of **1a**−**d** were investigated. If only proton motion is involved in the reaction coordinate, a large deuterium isotope effect would be predicted. However, as shown in Figure 2, within experimental errors, our results reveal a negligible isotope effect.

Accordingly, more than proton motion must be involved in the reaction coordinate. Molecular modeling of **1a** renders a relatively long N(1)H···N(1′) HB distance of ∼2.49 Å with an N−H···N angle of ∼93°.[11] These results, in combination with the restricted orientation of the pyrazole N−H bond, lead us to propose that the reaction coordinate does not couple directly with the N−H stretching mode. Rather, it involves other skeletal motions such as in-plane bending modes, which change the relative position of atoms associated with the hydrogen bond, and hence channel into the proton-transfer process. In this case, the resulting effective tunneling mass should be greatly increased so that the deuteration of amino proton results in only a very small fractional increase in the

tunneling mass. As a result, a negligible H/D isotope effect would be observed. We further carried out a series of temperature-dependent studies regarding reaction dynamics. As shown in Figure 2, the reaction rate for **1a** monitored by the decay dynamics of the F_1 band or equivalently the rise dynamics of the F_2 band revealed significant temperature dependence in the range of 298−203 K.[12] The logarithm plot for the ESIPT rate versus $1/T$ is sufficiently linear, from which a nearly deuterium isotope independent barrier ($\Delta E \approx 2.03$ kcal/mol) and frequency factor (∼3.8×10^{11} s^{-1}) were deduced. Negligible N−D isotope ESIPT dynamics were also observed for **1b**−**d**, and their corresponding ΔE are listed in Table 1. Upon increasing the electron-withdrawing ability in R$_b$ (see Scheme 1) the acidity of the N(1)−H proton should increase, and hence faster ESIPT dynamics is expected. In contrast, Table 1 shows a lack of correlation between ΔE and donating/accepting properties of R$_b$, indirectly supporting the skeletal reorganization facilitating ESIPT process. Further support was given by a similar Arrhenius plot for **1a** in dry CH$_3$CN, and ΔE was deduced to be ∼2.90 kcal/mol, consistent with that obtained in methylcyclohexane.

In conclusion, the results demonstrate a novel and unique system among ESIPT molecules where the intrinsic proton transfer is associated with a substantial energy barrier. The nature of the reaction potential surface in **1a**−**d** may be described by certain skeletal reorganization and hence is of a great theoretical challenge. This, in combination with the structural simplicity and diversity, makes the 5-(2-pyridyl)-1-*H*-pyrazole system an ideal model for probing ESIPT dynamics, which are believed to bring up a broad spectrum of interests in the proton-transfer field.

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(10) See Supporting Information for detailed syntheses and characterization.
(11) The calculation was based on the HF/6-31G(d′,p′) level. X-ray data were not applied here due to the dimeric structure in a single crystal.
(12) Further decreasing temperatures resulted in microcrystals interferences.

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