Effect of Formyl Group on Photoinduced Hydrogen Atom Transfer and *cis-trans* Isomerization of 2[2-(2-Pyrrolyl)ethenyl]pyridine

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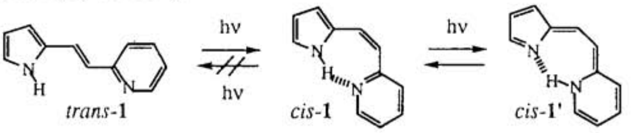
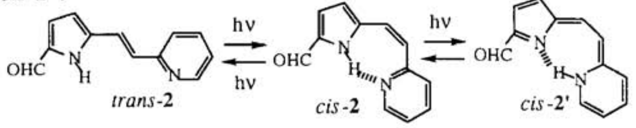
Formyl group as a substituent enhanced the hydrogen atom transfer in the excited singlet state as well as the intersystem crossing from the singlet to the triplet excited state of 2[2-(2-pyrrolyl)ethenyl]pyridine.

Hydrogen bonding can control the efficiency and the mode of photochemical isomerization. For example, olefin **1** with a pyrrole ring and a pyridine ring underwent one-way trans→cis isomerization.[1] In addition, *cis*-**1** exhibited intramolecular hydrogen atom transfer to give the tautomer *cis*-**1'** on photoirradiation. However, the singlet excited state of *cis*- and *trans*-**1** did not undergo intersystem crossing to the triplet state. The resulted excited singlet state of *cis*-**1'** gave fluorescence at the longer wavelength region (λ_{max}=570 nm in acetonitrile) compared to the absorption spectrum of *cis*-**1** (λ_{max}= 360 nm in acetonitrile); the quantum yield of fluorescence emission (Φ_f) in *cis*-**1** was very small (Φ_f=ca. 10^{-3}).[1]



In order to explore the effect of intramolecular hydrogen bonding in the excited triplet state we prepared an olefin **2** with introduction of the formyl group at the pyrrole ring of **1** to enhance the intersystem crossing. Thus, on direct irradiation both *cis*- and *trans*-**2** gave the triplet state after intersystem crossing from the excited singlet state as revealed by the observation of the T-T absorption spectra. Furthermore, very interestingly, the introduction of the formyl group increased the efficiency of hydrogen atom transfer to give the tautomer in the excited singlet state as observed by the considerably high quantum efficiency of fluorescence emission from the tautomer *cis*-**2'**.



The mixture of *cis*- and *trans*-**2** was prepared from a Wittig reaction of a ylide prepared by treatment of 2-bromopyridine with methylenetriphenylphosphorane and 2,5-diformylpyrrole.[2,3] *Cis*-**2** exhibited absorption maximum at the longer wavelelength than those of *trans*-**2** indicating the presence of intramolecular hydrogen bonding in *cis*-**2**; the longest maxima of the absorption spectra of *cis*-**2** appeared at 386, 382, and 379 nm in benzene, methanol, and acetonitrile, respectively, while those of *trans*-**2** at 376, 369, and 369 nm.

2 underwent mutual isomerization on direct irradiation at 366 nm light: the photostationary state trans-to-cis isomer ratio (([t]/[c])$_{pss}$) was 12/88, 21/79, and 26/74, respectively in benzene, acetonitrile, and methanol at [**2**]=1x10^{-4} M. The ([t]/[c])$_{pss}$ increased with the increasing of the concentration of **2**: for example, ([t]/[c])$_{pss}$=15/85 at [**2**]=3x10^{-4} M and 19/81 at [**2**]=6x10^{-4} M in benzene. Furthermore, the quantum yield of cis→trans isomerization ($\Phi_{c\to t}$) increased with increasing of the *cis*-**2** concentration from 0.082 ([*cis*-**2**]=1.2x10^{-4} M) to 0.18 ([*cis*-**2**]=7.0x10^{-4} M), while that of trans→cis isomerization ($\Phi_{t\to c}$) was almost constant and was 0.55±0.03 when [*trans*-**2**] = 1.2x10^{-4} and 7.0x10^{-4} M. The occurence of the cis→trans isomerization in **2** indicates the production of the triplet state even on direct irradiation. Furthermore, the effect of concentration on ([t]/[c])$_{pss}$ and $\Phi_{c\to t}$ indicates that the cis-to-trans isomerization took place as a quantum chain process in the excited triplet state.

On 308 nm laser excitation *trans*-**2** gave T-T absorption spectra (Figure 1a) with intense band at λ_{max}=420 nm and broad band tailing at 650 nm with the lifetime of 1.9 μs in benzene, acetonitrile, and methanol. These transients were quenched by oxygen with the rate constant of $4x10^{9}$ mol^{-1} dm^{3} s^{-1}. The transient spectrum observed on excitation of *cis*-**2** was weak in benzene and in methanol, but in acetonitrile rather intense transient absorption spectrum was observed as shown in Figure 1b. Thus, *cis*-**2** exhibited broad transient spectra at 400-600 nm under argon atmosphere with two-decay components of 1.9 μs and 200 ns. The profile of the transient absorption spectra under oxygen atmosphere was different from that observed under argon atmosphere as shown in Figure 1c; the absorption maximum

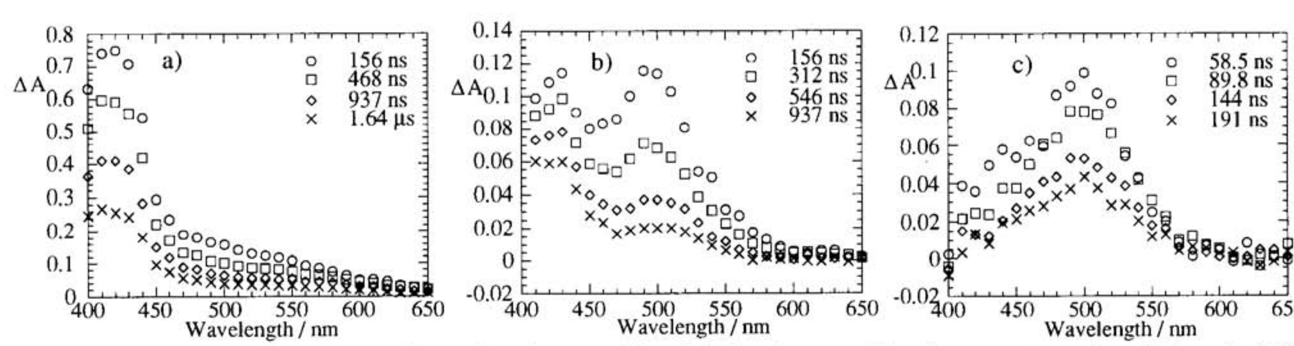


Figure 1. Transient absorption spectra of *trans*-**2** under argon (a) and *cis*-**2** under argon (b) and oxygen atmosphere (c) in acetonitrile.

(λ_{max}) appeared at 500 nm and the lifetime (τ) was 200 ns. Thus, the shorter wavelength component (400-450 nm) was quenched by oxygen with the rate constant of 3.4×10^9 M^{-1} s^{-1} and was assigned to the triplet state. The longer wavelength component with λ_{max}=500 nm and τ=200 ns was not quenched by oxygen and was assigned to the ground state.

The occurrence of the quantum chain process for cis-to-trans isomerization of **2** indicates that the most stable conformation in the excited triplet state is the planar trans form.[4] In fact, one can estimate the equilibration between the trans triplet ($^3t^*$) and the perpendicular triplet ($^3p^*$) with the equilibrium constant of ($[^3t^*]/[^3p^*]) \approx 40$ from the triplet lifetime, where the deactivation rate constant from $^3t^*$ and $^3p^*$ are estimated to be 2×10^4 s^{-1} and 2×10^7 s^{-1}, respectively.[4]

The tautomer *cis*-**2'** produced from the intramolecular hydrogen atom transfer in the excited state followed by the deactivation to the ground state may be a candidate for the ground state transient with λ_{max}=500 nm. If this is the case, one can observe the fluorescence emission from the tautomer.

Both *cis*- and *trans*-**2** show fluorescence emission at moderate quantum efficiency; Φ_f=0.115 and 0.034 in benzene and 0.018 and 0.042 in acetonitrile for *cis*- and *trans*-**2**, respectively. The fluorescence spectrum of the *trans*-**2** exhibited a mirror image with the absorption spectrum and the fluorescence excitation spectrum of *trans*-**2** and therefore it is assigned to the fluorescence from *trans*-**2**. However, the fluorescence emission from *cis*-**2** very much shifted to the longer wavelength region (λ_{max}=540 nm) compared to the absorption spectrum and the fluorescence excitation spectrum, although the fluorescence excitation spectrum and the absorption spectrum are similar with each other. The Stokes shift in acetonitrile was calculated as 2,400 cm^{-1} and 7900 cm^{-1} for *trans*- and *cis*-**2**, respectively and that in benzene was 960 cm^{-1} and 7400 cm^{-1} for *trans*- and *cis*-**2**, respectively. Thus, the observed fluorescence emission from *cis*-**2** was assigned not to the normal form *cis*-**2** (^{1}*cis*-**2***) but to the tautomer form *cis*-**2'** (^{1}*cis*-**2'***) produced by the adiabatic intramolecular hydrogen atom transfer in the excited singlet state.

It is noteworthy that the quantum yield of fluorescence emission of the tautomer in non-polar solvent is 100 times higher for *cis*-**2'** (Φ_f=0.115) than for *cis*-**1'**.[1] The formyl group was expected to enhance the intersystem crossing and to reduce the efficiency of hydrogen atom transfer in the excited singlet state. However, the experimental results are different. The formyl group enhanced not only the intersystem crossing to the triplet state, but also the efficiency of fluorescence emission from the tautomer in the excited singlet state. One can explain the above effect of formyl group that formyl group as an electron withdrawing group increase the acidity of the pyrrole NH resulting in the facile hydrogen atom transfer to give the tautomer.

In summary, introduction of the formyl group changed the photochemical behavior of **1**. While **1** underwent one-way trans→cis isomerization, **2** underwent photochemical two-way isomerization in the triplet state through the quantum chain process in cis-to-trans direction on direct irradiation after intersystem crossing to the triplet state. Thus, in the excited triplet state the intramolecular hydrogen bonding should become weaker to allow the isomerization around the double bond. Furthermore, *cis*-**2** underwent hydrogen atom transfer to give the tautomer in the excited singlet state with considerably high quantum efficiency.

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References and Notes

1 M. Obi, T. Arai, and H. Sakuragi, *Chem. Lett.*, **1998**, 169.

2 *trans*-**2** was obtained by column chromatography and purified by recrystallization from benzene. *cis*-**2** was prepared by photoirradiation of *trans*-**2** in benzene and recrystallized from hexane. The structures of *cis*- and *trans*-**2** were determined by NMR spectroscopy; *cis*-**2** exhibited a ^{1}H-NMR signal at δ=15.4 ppm for an intramolecularly hydrogen bonded N-H proton of pyrrole, while the N-H proton of *trans*-**2** appeared at a normal region of δ=9.96 ppm.

3 E. C. Taylor and S. F. Martin, *J. Am. Chem. Soc.*, **96**, 8095 (1974).

4 T. Arai and K. Tokumaru, *Chem. Rev.*, **93**, 23 (1993).