Adiabatic Intramolecular Hydrogen Atom Transfer in 2-[2-(2-Pyrrolyl)ethenyl]pyridine

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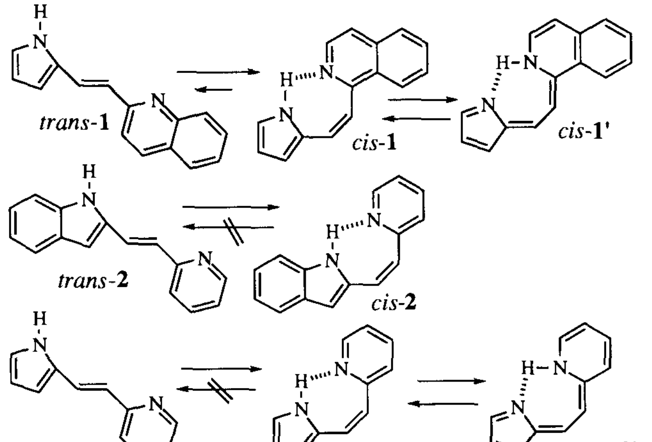
2-[2-(2-Pyrrolyl)ethenyl]pyridine (**3**) forms an intramolecular hydrogen bond between the pyridine and pyrrole ring and undergoes one-way trans→cis isomerization on direct irradiation. Furthermore, cis isomer undergoes intramolecular hydrogen atom transfer to give a tautomer in the excited singlet state. Based on the experimental findings, effects of intramolecular hydrogen bond and the solvent on the photochemical behaviors of **3** were discussed.

The effects of intramolecular hydrogen bonding on the cis-trans isomerization as well as intramolecular hydrogen atom transfer in the excited singlet state for 1-(2-pyrrolyl)-2-(2-quinolyl)ethene (**1**)[1] and 2-[2- (2-pyridyl)ethenyl] indole (**2**)[2-4] have been studied. On photoirradiation of **1** cis-trans mutual isomerization took place. In addition, hydrogen atom transfer through an intramolecular hydrogen bond took place in *cis*-**1** in the excited singlet state.[1] On the other hand, **2** underwent trans→cis one-way isomerization, but no evidence of intramolecular hydrogen atom transfer was observed.[2-4]



It seems that the hydrogen bonded compound undergoing mutual isomerization between trans and cis isomers exhibits a tautomer fluorescence produced by an adiabatic intramolecular hydrogen atom transfer in the excited singlet state, while one-way isomerizing hydrogen bonded compound gives no tautomer fluorescence. In order to shed light on the factors controlling the adiabatic intramolecular hydrogen atom transfer of N-H:N systems, we prepared 2-[2-(2-pyrrolyl)ethenyl]-pyridine (**3**) with a pyrrole and a pyridine ring.

We now wish to report that **3** underwent one-way trans→cis isomerization in addition to the intramolecular hydrogen atom transfer in the excited singlet state. Furthermore, novel solvent effects on the forward and reverse hydrogen atom transfer are discussed.

The mixture of *cis*- and *trans*-**3** was synthesized from the Wittig reaction of a ylide prepared by treatment of 2-bromopyridine with methyltriphenylphosphorane and 2-pyrrolecarboaldehyde.[5] *Trans*-**3** was obtained by flash column chromatography and recrystallized from hexane. *Cis*-**3** was prepared by photoirradiation of *trans*-**3** in benzene and recrystallized from hexane. *Cis*-**3** forms an intramolecular hydrogen bond like *cis*-**1** and *cis*-**2**, showing a characteristic ^{1}H-NMR signal of N-H at 14.1 ppm.

Figure 1 shows the absorption and fluorescence spectrum of *cis*- and *trans*-**3** in acetonitrile. The absorption maximum (λ_{max}) in acetonitrile appeares at 360 and 341 nm for *cis*- and *trans*-**3**, respectively; λ_{max} shifts to the shorter wavelength with increasing solvent polarity. Fluorescence spectrum of *trans*- and *cis*-**3** was observed at 400-500 and 550-700 nm, respectively in hexane, acetonitrile and methanol; λ_{max}=430 nm and 570 nm for *trans*- and *cis*-**3**, respectively, in acetonitrile. The large Stokes-shifted fluorescence observed on excitation of *cis*-**3** indicates that a considerable structural change takes place adiabatically in the excited singlet state of *cis*-**3**. The Φ_f of *cis*-**3'** is slightly larger in non-polar solvents such as hexane (1.6×10^{-3}) than that in polar solvents (6×10^{-4} in ethanol and acetonitrile). While τ_s is almost constant in all the solvents employed (~70 ps).

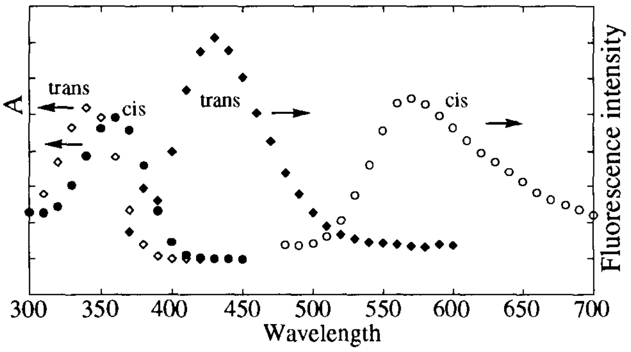


Figure 1. Absorption and fluorescence spectra of *cis*-2-[2-(2-pyrrolyl)ethenyl]pyridine (**3**) in acetonitrile.

On direct irradiation **3** underwent one-way trans→cis isomerization in protic as well as in aprotic solvents. The quantum yield of trans→cis isomerization ($\Phi_{t\rightarrow c}$) of **3** was determined as high as 0.7 in benzene, acetonitrile, and methanol with irradiation at 366 nm with a high pressure mercury lamp. Since T-T absorption spectrum was not observed on direct irradiation with 308 nm laser pulse as described later, the trans→cis isomerization took place in the excited singlet state.

Transient absorption spectrum attributable to the tautomer *cis*-**3'** with λ_{max} =530 nm was observed by laser flash photolysis with a 308 nm excimer laser as shown in Fig. 2; Fig. 2 compared the fluorescence and absorption spectra attributable to *cis*-**3'**. The observed transient was not quenched by oxygen and decayed with single exponential suggesting that the observed transient is not assigned to the T-T absorption spectrum, but is assigned to the ground state. Actually, on benzil sensitization the T-T absorption spectra was observed with λ_{max} shorter than 430 nm and the lifetime of 2 μs under argon atmosphere.

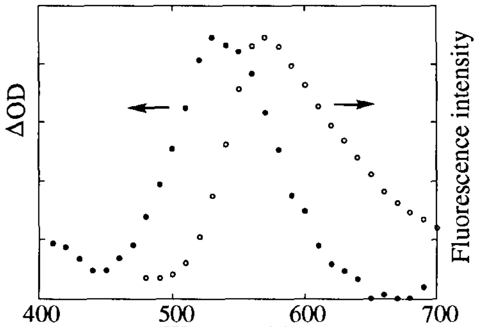


Figure 2. Transient absorption spectrum and fluorescence spectrum assigned to *cis*-**3'** observed on excitation of *cis*-**3** in acetonitrile.

The lifetime of *cis*-**3'** in the ground state ($\tau_{cis\text{-}3'}$), i.e., the inverse of the rate constant for *cis*-**3'**→*cis*-**3** conversion, changes with solvents; $\tau_{cis\text{-}3'}$ is 200 ns in hexane, 180 ns in benzene, 85 ns in THF and 70 ns in acetonitrile. Thus, with increasing of the solvent polarity $\tau_{cis\text{-}3'}$ becomes shorter.

The lifetime of the transient absorption observed on 308 nm excitation suffers the deuterium isotope effect on the nitrogen atom in the pyrrole ring, i.e., 180 and 220 ns for N-H and N-D, respectively, in benzene solution. However, the fluorescence spectra of normal form was not detected even at 77 K in the mixed solvent of methylcyclohexane and 2-methylpentane (3:1). These results indicate that *cis*-**3** does not undergo isomerization around the double bond but undergoes tautomerization to the *cis*-**3'** in the excited singlet state, which returns to *cis*-**3** of the ground state.

The decay constants, $1/\tau_{cis\text{-}3'}$, decreased with the decrease of temperature; $2.2\text{x}10^6$ s^{-1} at 250K to $1.2\text{x}10^6$ s^{-1} at 238K in acetonitrile and $4.8\text{x}10^6$ s^{-1} at 276K to $3.4\text{x}10^6$ s^{-1} at 268K in hexane. From the Arrhenius plots, activation energy for *cis*-**3'**→*cis*-**3** conversion in the ground state was determined to be 6.3 and 5.7 kcal mol^{-1} in hexane and acetonitrile, respectively.

Transient absorption spectrum attributable to the ground state tautomer was not observed in ethanol and methanol probably due to its very short lifetime, although large Stokes-shifted fluorescence spectra were observed. The lifetime $\tau_{cis\text{-}3'}$ decreased on addition of methanol in acetonitrile solution from 70 ns in pure acetonitrile to 25 ns in the presence of $4\text{x}10^{-4}$ M of methanol (Fig. 3). Therefore, methanol interact with the ground state tautomer *cis*-**3'** to accelerate the reversion to the ground state normal form *cis*-**3** as shown below.

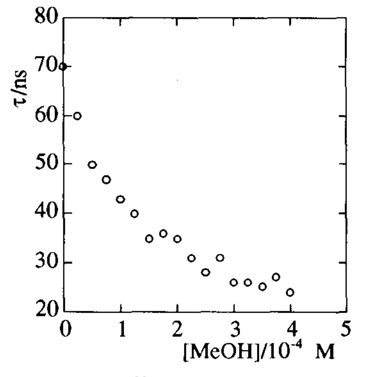
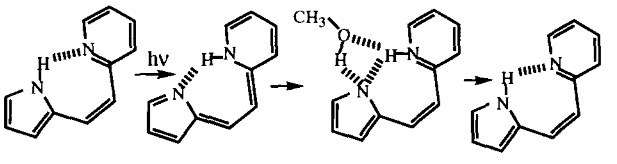


Figure 3. Effect of methanol on the lifetime of *cis*-**3'** in acetonitrile.



The present results indicate that the intramolecular hydrogen atom transfer prevails over the isomerization around the double bond in the excited singlet state of *cis*-**3**. In addition, solvents scarcely affect the forward hydrogen atom transfer process in the excited singlet state as well as the behavior of the excited state tautomer, but strongly accelerate the reversion from the ground state tautomer to the ground state normal form probably by making intermolecular hydrogen bonds.

References

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