Novel Solvent Effect on Highly Selective Photochemical Isomerization of 2-[2-(2-Pyrrolyl)ethenyl]quinoxaline

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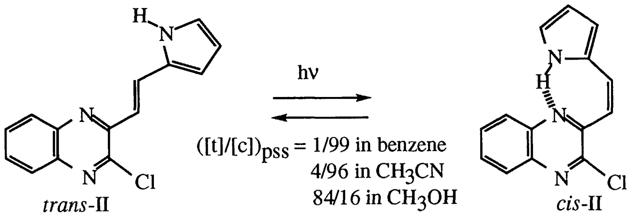
2-[2(2-Pyrrolyl)ethenyl]quinoxaline (**II**) underwent one-way trans→cis isomerization in benzene, while in methanol **II** underwent isomerization giving higher composition of trans isomer at the photostationary state.

Photochemical cis-trans isomerization has been extensively studied from the view points of mechanistic interests as well as of application.[1] A large number of arylethenes were synthesized and investigated to find the effects of aryl group on the ethylenic carbon to control the efficiency and the mode of isomerization.[1] Recently, much attention has been paid for the effect of hydrogen bonding on the photoisomerization of C=C double bond.[2-4] For example, 2-(2-(2-pyridyl)ethenyl)indole (**I**) underwent one-way trans→cis isomerization due to the presence of intramolecular hydrogen bonding in cis isomer. Furthermore, 2-(2-(2-pyrrolyl)ethenyl)quinoline underwent mutual isomerization between cis and trans isomers, while cis isomer exhibited intramolecular hydrogen atom transfer to give the tautomer.



We wish to report here a novel co-operative effect of intramolecular hydrogen bonding and solvent to control the efficiency and the selectivity of photoisomerization of **II**. The mixture of *cis*- and *trans*-**II** was prepared from a Wittig reaction of a ylide prepared by treatment of 2,3-dichloroquinoxaline with methylenetriphenylphosphorane and 2-pyrrolecarbaldehyde.[5,6]

Figure 1 shows absorption and fluorescence spectra of **II** in benzene. Usually, the absorption maximum of the cis isomer is appeared at the shorter wavelength than that of the trans isomer. However, the absorption maximum of the *cis*-**II** (λ_{max}=458 nm) appeared at the longer wavelength than that of *trans*-**II** (λ_{max}=423 nm) indicating an importance of intramolecular hydrogen bonding in *cis*-**II**. The absorption maximum of the *cis*-**II** shifted to the shorter wavelength (λ_{max}=452 nm) in methanol, but that of the *trans*-**II** shifted to the longer wavelength (λ_{max}=428 nm) in methanol. Fluorescence spectra of the trans isomer were observed in benzene (λ_{max}=500 nm) and in methanol (λ_{max}=583 nm), with Stokes shifts of 3640 cm^{-1} and 6210 cm^{-1}, respectively. This fact indicates an importance of intramolecular charge transfer in the excited singlet state of *trans*-**II**. The quantum yields of the fluorescence emission (Φ_f) of *trans*-**II** were determined as 0.035 and 0.012 in benzene and in methanol, respectively. *cis*-**II** exhibited weak fluorescence at λ_{max}= 640 nm with a Stokes shift of 6210 cm^{-1} assigned to the tautomer emission in benzene. Fluorescence spectrum of *cis*-**II** was not observed in acetonitrile or in methanol. These results greatly differ from the solvent effect on the proton transfer in O-H:O compounds. For example, methyl salicylate (**III**) exhibited only tautomer emission in non-polar solvent such as methylcyclohexane, while in methanol normal emission as well as tatomer emission was observed.

Photoirradiation of **II** (7.82×10^{-4} M) was performed at the isosbestic point (=453 nm) in several solvents. In benezene **II** underwent almost one-way trans→cis isomerization giving a photostationary mixture of $([c]/[t])_{pss}$=99/1. In acetonitrile, **II** gave photostationary mixture of $([c]/[t])_{pss}$=96/4. However, in methanol the photostationary state mixture very much shifted to the trans side giving $([c]/[t])_{pss}$=16/84.

Solvent methanol may interact with cis and trans isomers to increase the efficiency of cis→trans isomerization and to decrease the efficiency for trans→cis isomerization. In fact, the quantum yield of cis→trans isomerization ($\Phi_{c \to t}$) very much increased from 0.005 in benzene to 0.12 in methanol, while that of trans→cis isomerization ($\Phi_{t \to c}$) very much decreased from 0.44 in benzene to 0.020 in methanol. Thus, $\Phi_{c \to t}$ increased more than 20 times and $\Phi_{t \to c}$ decreased less than 1/20 by changing the solvent from benzene to methanol. In acetonitrile, $\Phi_{c \to t}$ (=0.010) and $\Phi_{t \to c}$ (=0.25) are respectively larger and smaller than those in benzene by a factor of ca. 2. Thus, the important properties of solvent to change the photostationary state isomer ratio more than 400 time in **II** is not the polarity of the solvent but the ability of forming or breaking the hydrogen bonding.

As to the solvent effect on the photoisomerization, it was reported that 1-styrylpyrene underwent one-way cis→trans isomerization in benzene on direct irradiation through an adiabatic

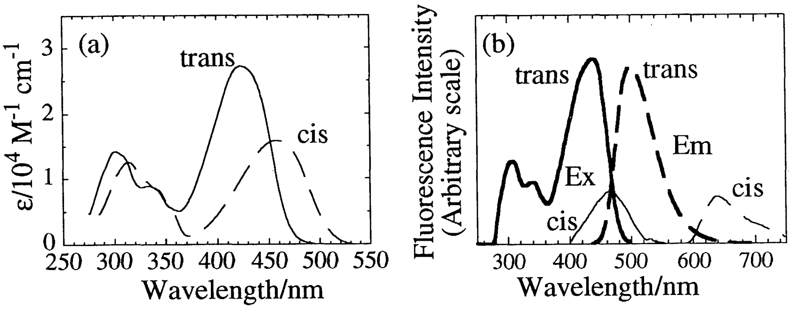


Figure 1. Electronic spectra of **II** in benzene at room temperature. (a) Absorption spectra of *cis*- and *trans*-**II**. (b) Fluorescence (Em; dashed line) and fluorescence excitation spectra (Ex; solid line) of *cis*- (light line) and *trans*-**II** (bold line).

conversion from cis ($^1c^*$) to the trans isomer ($^1t^*$) in the singlet excited state.[7] However, in acetonitrile the diabatic isomerization deactivating from the perpendicular singlet state ($^1p^*$) becomes important. This solvent effect is explained by the effect of solvent polarity to stabilize the $^1p^*$ state as reported for tetraphenylethene based on the results obtained by transient spectroscopy.[8]

Photochemical cis-to-trans isomerization of **I** does not take place in polar protic solvent as well as in non-polar solvent.[2a] Thus, irradiation of **I** results in the photostationary state isomer mixture containing >99% *cis*-**I** in benzene, ethanol and DMSO. The absence of cis→trans isomerization has been attributed to the considerably high barrier for isomerization induced by intramolecular hydrogen bonding; the intramolecular hydrogen bonding must be present even in ethanol and in DMSO. In the photoisomerization of **II** the $([c]/[t])_{pss}$ value decreased dramatically by changing the solvent from benzene (=99/1) to methanol (16/84). Thus, protic solvent changes the efficiency of cis→trans and trans→cis isomerization of **II** in different direction by forming intermolecular hydrogen bonding and/or breaking intramolecular hydrogen bonding.

The strength of intramolecular hydrogen bonding and the effect of solvent on the photochemical behavior of hydrogen bonded compounds were different among the compounds studied. However, the present findings indicate that the co-operative effect of intramolecular hydrogen bonding and intermolecular hydrogen bonding with solvent may control the efficiency and the direction of photochemical processes. We are now studying on this line to improve the selectivity of the photoisomerization by the co-operative effect of intramolecular and intermolecular hydrogen bonding.

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6 *trans*-**II** was obtained by column chromatography and purified by recrystallization from benzene. *cis*-**II** was prepared by photoirradiation of *trans*-**II** in benzene and recrystallized from hexane. The structures of *cis*- and *trans*-**II** were determined by NMR spectroscopy; *cis*-**II** exhibited a ^{1}H-NMR signal at δ=13.9 ppm for an intramolecularly hydrogen bonded N-H proton of pyrrole, while the N-H proton of *trans*-**II** appeared at a normal region of δ=8.71 ppm.

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