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LETTERS

# Novel Photochemical Behavior of Olefin with a Pyrrole Ring and a Phenanthroline Ring Controlled by Hydrogen Bonding

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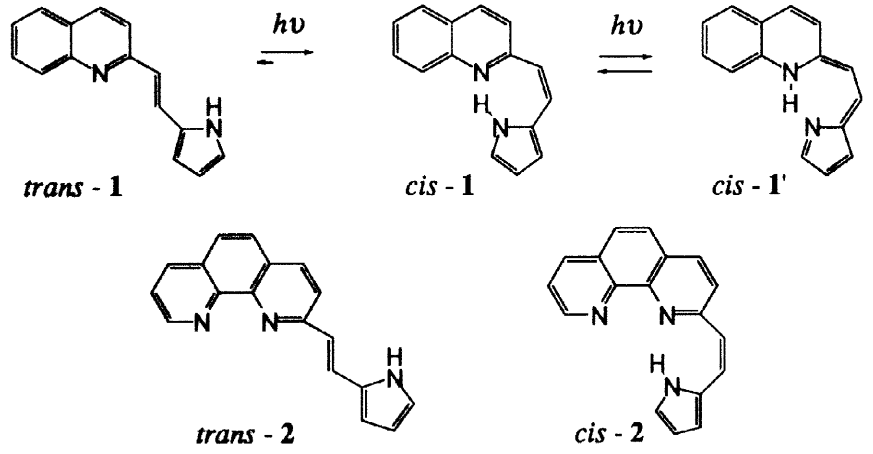
***Abstract:*** 2-(2-(2-Pyrrolyl)ethenyl)phenanthroline exhibited *trans*-to-*cis* one-way isomerization on photoirradiation. Furthermore, the *cis*-isomer underwent intramolecular hydrogen atom transfer in the excited singlet state. The *cis*-to-*trans* isomerization took place efficiently on addition of a metal ion.

In recent years, much attention has been directed to the effect of intramolecular hydrogen bonding on photoisomerization of unsaturated bonds.[1-3] We have reported a novel photochromism by way of intramolecular hydrogen bonding;[4-7] olefin **1**[5] with a quinoline and a pyrrole ring (Scheme 1), exhibited *trans*-*cis* isomerization and the *cis* isomer showed the intramolecular hydrogen atom transfer on N-H:N in the excited singlet state, giving a tautomer as a result. We wish to report here the effect of hydrogen bonding and the additives to control the photochemical isomerization as well as the intramolecular hydrogen atom transfer on olefin **2**.



Scheme 1

A mixture of *cis*- and *trans*-**2** was prepared from the Wittig reaction by the treatment of 2-chlorophenanthroline with methyltriphenylphosphonium bromide and pyrrole-2-carboxaldehyde (Scheme 2) in 12% yield. *Cis*-**2** was obtained by photoirradiation of *trans*-**2** in methanol followed by flash column chromatography. The structure of *cis*- and *trans*-**2** was confirmed by $^1$H NMR spectroscopy and elemental analysis.[8]

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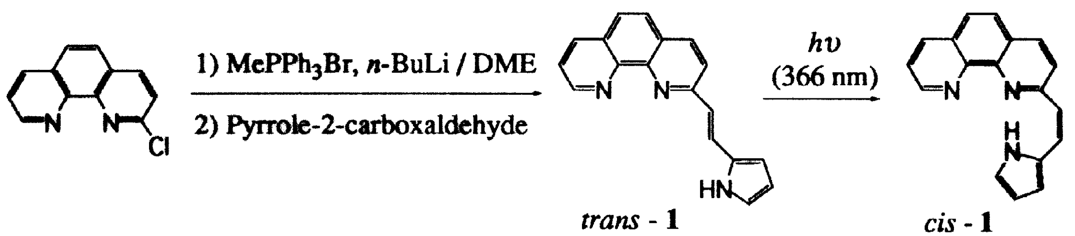


**Schem 2**

On irradiation with 366-nm light[9] from a high-pressure mercury lamp in the solvent such as benzene, methanol and acetonitrile under $N_2$ at room temperature, **2** underwent *trans*-to-*cis* one-way isomerization (Figure 1). The presence of intramolecular hydrogen bonding in *cis*-**2** may account for the *trans*-to-*cis* isomerization in the excited state. The quantum yield for *trans*→*cis* isomerization ($\Phi_{t\rightarrow c}$) was as high as 0.51 in benzene, but decreased to 0.21 in methanol when the concentration of *trans*-**2** is 1.65 x $10^{-4}$M and 1.2 x $10^{-4}$M, respectively. It is suggested that, due to the hydrogen bonding between *trans*-**2** and the solvent, the *trans*-to-*cis* isomerization proceeds more slowly in methanol than in benzene.

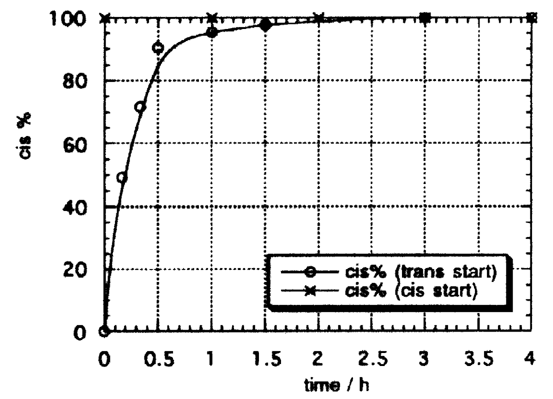


**Figure 1.** The ratio of a photostationary mixture of **2** in methanol on irradiation under $N_2$ with 366-nm light from a high-pressure mercury lamp.

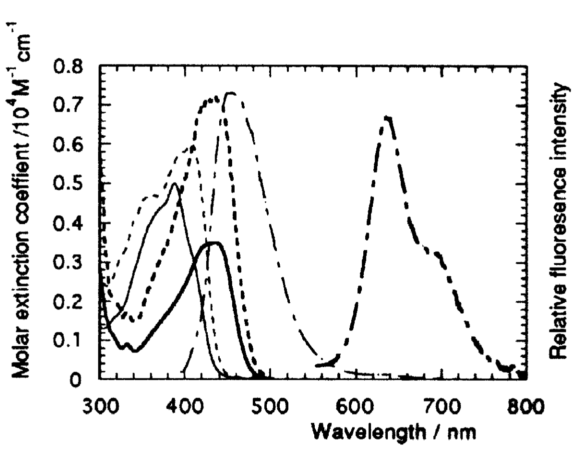
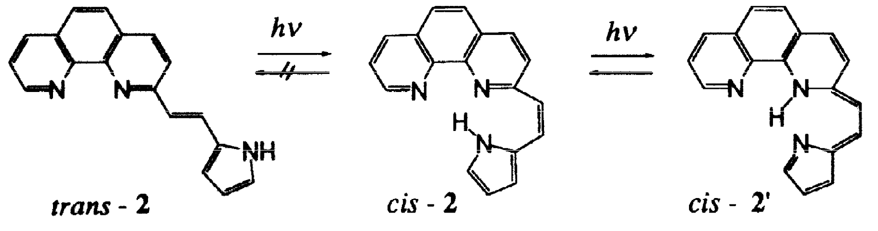


**Figure 2.** Electronic spectra of **2** in benzene at room temperature. (a) Absorption spectra of *cis* form (bold solid line) and *trans* form (light solid line). (b) Fluorescence spectra of *cis* form (bold dash-dot line) and *trans* form (light dash-dot line). (c) Fluorescence excitation spectra of *cis* form (bold dotted line) and *trans* form (light dotted line).

Electronic spectra of **2** in benzene, such as the absorption, fluorescence and fluorescence excitation spectra (Figure 2), were measured to study their behavior in the excited state. The absorption maximum of *cis*-**2** ($\lambda_{max}$ = 436 nm) appeared at a longer wavelength than *trans*-**2** ($\lambda_{max}$ = 388 nm) and the Stokes shift (7300 $cm^{-1}$) of *cis*-**2** is rather larger than the value of *trans*-**2** (4300 $cm^{-1}$). These results indicate that a marked conformational change took place by excitation from the ground to the fluorescent state in *cis*-**2**. The tautomer $^1$(*cis*-**2'**)$^*$ most probably was produced by the intramolecular hydrogen atom transfer in the excited state of



**Scheme 3**

$^1$(*cis*-**2**)$^*$. Therefore, the fluorescence observed on excitation of *cis*-**2** arises not from its vertical excited state but from the single excited state of its tautomer $^1$(*cis*-2')$^*$ (Scheme 3).

Protonation of the hetero atom of the phenanthroline ring could change the photochemical behavior of **2**. In this respect, the HCl solution was added to a methanol solution of the *cis* and *trans* forms. In the case of the *cis* form ($\lambda_{max}$ = 419 nm) almost no change was observed without irradiation, but some longer wavelength shift appeared after irradiation with 366-nm light from a UV lamp (Figure 3). On the contrary, the absorption maximum of the *trans* form ($\lambda_{max}$ = 386 nm) shifted to the longer wavelength ($\lambda_{max}$ = 462 nm) after the addition of the HCl solution. The *trans* form might be completely protonated due to the existence of two lone pairs of the nitrogen atoms of the phenanthroline. Under the same condition the absorption spectrum of the *trans* form changed nearly to that of the *cis* form on irradiation with 365-nm light. Therefore, it is suggested that the intramolecular hydrogen bonding of N-H:N in *cis* form is more stable than the intermolecular hydrogen bonding between the olefin and HCl, and as a result only *trans*-to-*cis* isomerization occurred (Scheme 4).

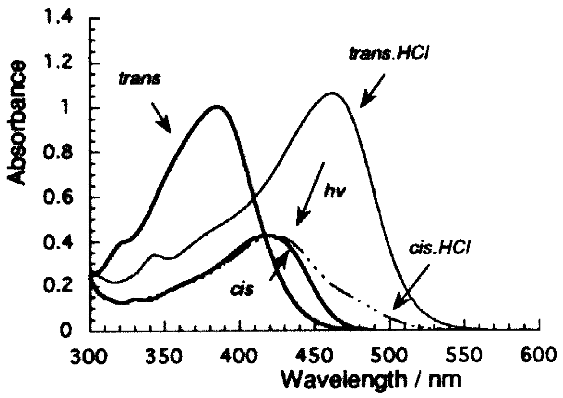
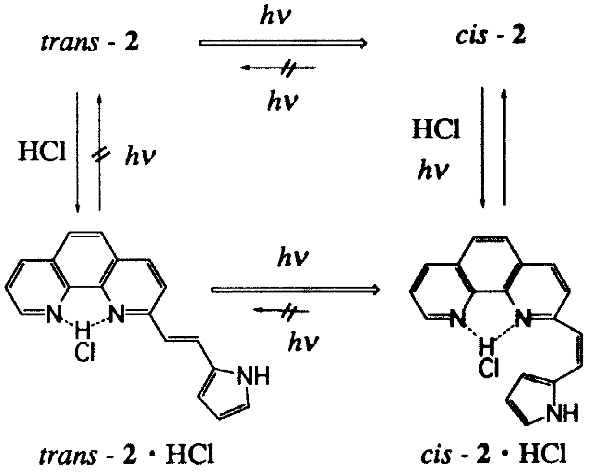


Figure 3. Absorption spectra of **2** in the presence or absence of HCl in methanol.



Scheme 4

The *trans* form which has no intramolecular hydrogen bonding tends to make a complex with the metal ion. If the complex is more stable than the complex of the *cis* form, we can use the metal ion to control the *cis*-*trans* isomerization.

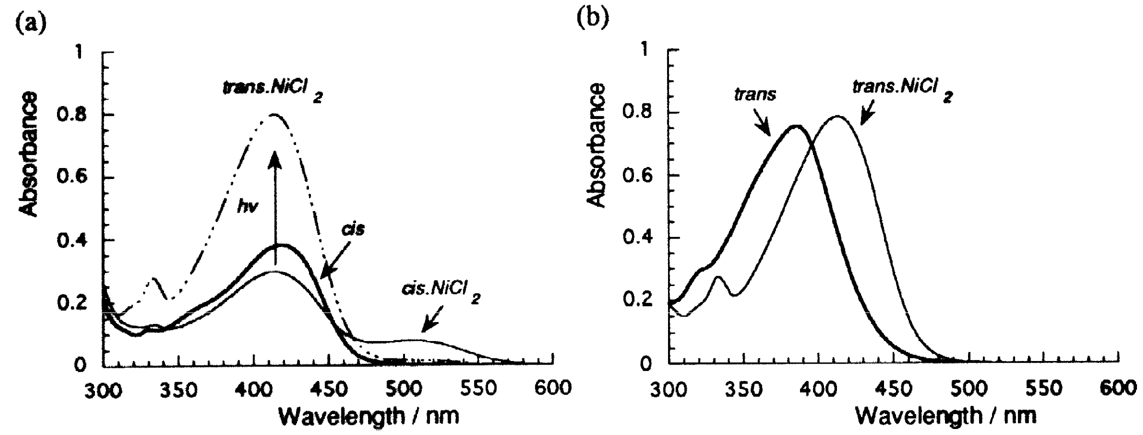
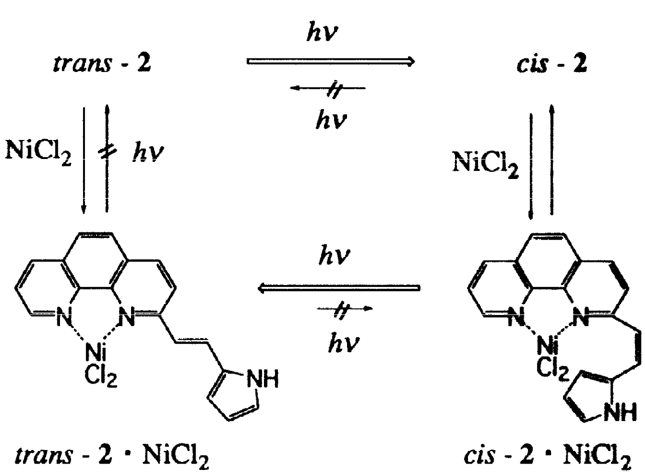


Figure 4. Absorption spectra of *cis* form (a) and *trans* form (b) in the presence of $NiCl_2$ in methanol ([*cis* form] = [*trans* form] = $2.59 \times 10^{-5}$ M, [$NiCl_2$] = $6.80 \times 10^{-4}$ M).

As shown in Figure 4 (a), the absorption of the *cis* form changed to give the absorption maximum at 414 and 508 nm after the addition of $NiCl_2$. The longer wavelength absorbance decreased and the absorbance at 414 nm increased after photoirradiation. In the case of the *trans* form (Figure 4 (b)), the addition of $NiCl_2$ immediately changed the absorption spectrum to give the absorption maximum at 414 nm. On photoirradiation with 365-nm light from a UV lamp, the *cis-trans* two-way isomerization occurred when the quantity of $NiCl_2$ is several equivalents of the olefin. For example, the photostationary mixture of the complex of the *trans* and *cis* compound was in a ratio of 71:29 in the presence of 3 equivalents of $NiCl_2$ to the *trans* form. When a large excess of $NiCl_2$ was added, the *cis*-to-*trans* one-way isomerization took place. Therefore, we can completely reverse the isomerization to only the *cis*-to-*trans* direction by use of complexation of the olefin with $NiCl_2$ (Scheme 5).



Scheme 5

In summary, the intramolecular hydrogen bonding in *cis*-2 resulted in *trans*-to-*cis* one-way isomerization and the intramolecular hydrogen atom transfer through the N-H:H bond in the excited state. Complexation with $Ni^{2+}$ changed the mode of isomerization of 2 to give a higher composition of the *trans* isomer.

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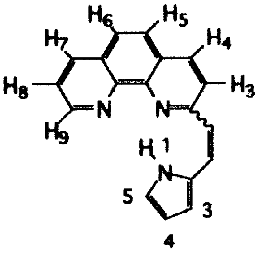
### *References and Notes*

1. (a) Lewis, F. D.; Howard, D. K.; Oxman, J. D.; Upthagrove, A. L.; Quillen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 5964. (b) Lewis, F. D.; Stern, C. L.; Yoon, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 3131.
2. (a) Lightner, D. A.; McDonagh, A. F. *Acc. Chem. Res.* **1984**, *17*, 417. (b) Kanna, Y.; Arai, T.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1482.
3. Eenkhoorn, J. A.; Osmund de Silva, S.; Snieckus, V., *Can. J. Chem.* **1973**, *51*, 792.
4. Arai, T.; Iwasaki, T.; Tokumaru, K. *Chem. Lett.* **1993**, 691.
5. Arai, T.; Moriyama, M.; Tokumaru, K. *J. Am. Chem. Soc.* **1994**, *116*, 3171.
6. Arai, T.; Maeda, Y. *Chem. Lett.* **1997**, 335.
7. Arai, T.; Norikane, Y. *Chem. Lett.* **1997**, 339.
8. 

*Cis* - **2**: $^1$H NMR (200MHz, $CDCl_3$) δ 6.22 (1H, d, J = 12.8 Hz, CH=CH), 6.41 (1H, m, pyrrole-$H_4$), 6.58 (1H, m, pyrrole-$H_5$), 6.81 (1H, d, J = 12.8 Hz, CH=CH), 7.41 (1H, m, pyrrole-$H_3$), 7.56 (1H, d, J = 8 Hz, phenanthroline-$H_3$), 7.67 (1H, d, $J_1$ = 8 Hz, $J_2$ = 4.6 Hz, phenanthroline-$H_8$), 7.75 (2H, d, J = 1.6 Hz, phenanthroline-$H_5$, $H_6$), 8.16 (1H, d, J = 8 Hz, phenanthroline-$H_4$), 8.27 (1H, dd, $J_1$ = 8 Hz, $J_2$ = 1.6 Hz, phenanthroline-$H_7$), 9.22 (1H, dd, $J_1$ = 4.6 Hz, $J_2$ = 1.6 Hz, phenanthroline-$H_9$). *Trans* - **2**: $^1$H NMR (200 MHz, $CD_3OD$) δ 6.19 (1H, m, pyrrole-$H_4$), 6.49 (1H, m, pyrrole-$H_5$), 6.91 (1H, m, pyrrole-$H_3$), 7.16 (1H, d, J = 16.4 Hz, CH=CH), 7.67 (1H, d, $J_1$ = 8 Hz, $J_2$ = 4.2 Hz, phenanthroline-$H_8$), 7.85 (2H, d, J = 2 Hz, phenanthroline-$H_5$, $H_6$), 7.86 (1H, d, J = 16.4 Hz, CH=CH), 7.91 (1H, d, J = 8.4 Hz, phenanthroline-$H_3$), 8.29 (1H, d, J = 8.4 Hz, phenanthroline-$H_4$), 8.27 (1H, dd, $J_1$ = 8.2 Hz, $J_2$ = 1.6 Hz, phenanthroline-$H_7$), 9.22 (1H, dd, $J_1$ = 4.6 Hz, $J_2$ = 1.6 Hz, phenanthroline-$H_9$). Anal. Calcd for $C_{18}H_{13}N_3$: C, 79.68; H, 4.83; N, 15.49. Found: C, 79.68; H, 4.83; N, 15.49.
9. The 366-nm light was isolated through L-35 and U-360 glass filters (Toshiba).