

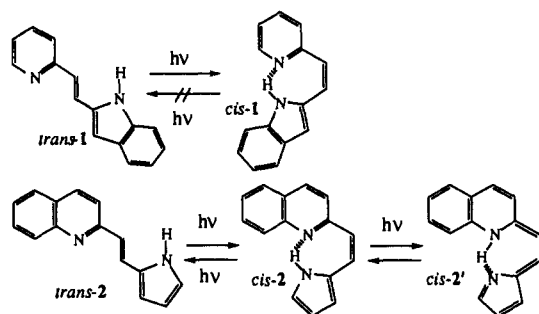
Novel Photoinduced Hydrogen Atom Transfer through Intramolecular Hydrogen Bonding Coupled with Cis–Trans Isomerization in *cis*-1-(2-Pyrrolyl)-2-(2-quinolyl)ethene

Tatsuo Arai,* Masaya Moriyama, and Katsumi Tokumaru*

Department of Chemistry
University of Tsukuba
Tsukuba, Ibaraki 305, Japan

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The effect of intramolecular hydrogen bonding on photoisomerization of unsaturated bonds has recently received attention.^{1–4} We recently found that intramolecular hydrogen bonding between an indole and a pyridine ring substituted on the *cis* side of an unsaturated bond (*cis*-1) completely suppressed the *cis*-to-*trans* isomerization in the singlet excited state, whereas reverse isomerization efficiently took place from the *trans*-to-*cis* isomer.^{3,4} The intramolecular hydrogen bonding works solely to accelerate deactivation of ¹(*cis*-1)* to the ground state, therefore leading to *trans*-to-*cis* one-way isomerization. This contrasts with the recently well-recognized *cis*-to-*trans* one-way isomerization occurring in an adiabatic way in the triplet state of ethylenes substituted with aromatic groups of low triplet excitation energies such as anthracene or perylene.⁵



We now report that substitution of a quinoline and a pyrrole ring on the *cis* side of an unsaturated bond results in unique photochemical behavior. Thus, on excitation of *cis*-1-(2-pyrrolyl)-2-(2-quinolyl)ethene (*cis*-2), the intramolecular hydrogen bonding allows the double bond to isomerize to *trans* and concurrently induces intramolecular hydrogen atom transfer, giving a tautomer (*cis*-2') in benzene.

The mixture of *cis*- and *trans*-2 was prepared from the Wittig reaction of a ylide prepared by treatment of 2-chloroquinoline with methylenetriphenylphosphorane and 2-pyrrolicarbaldehyde.⁶ *trans*-2 was obtained by flash column chromatography and recrystallized from hexane. *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

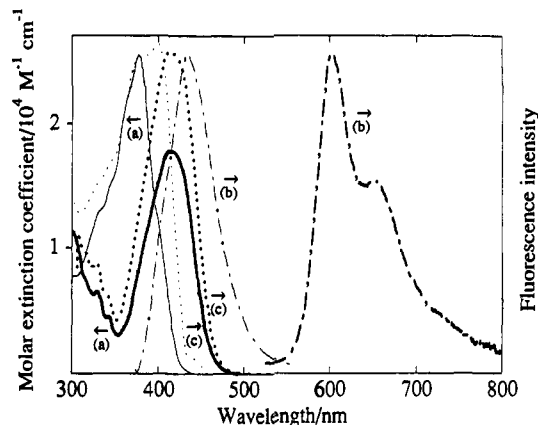


Figure 1. Electronic spectra of 2 in benzene at room temperature. (a) Absorption spectra of *cis* (bold solid line) and *trans* (light solid line). (b) Fluorescence spectra of *cis* (bold dash-dot line) and *trans* (light dash-dot line). (c) Fluorescence excitation spectra of *cis* (bold dotted line) and *trans* (light dotted line).

spectroscopy and elemental analysis.⁷ In brief, *cis*-2 exhibited a ¹H-NMR signal at $\delta = 15.1$ for a strongly hydrogen-bonded N–H proton, while the N–H proton of the pyrrole ring of *trans*-2 appeared at a normal region of $\delta = 8.72$.

Irradiation of *cis*- and *trans*-2 in benzene under N₂ with a xenon lamp at 399 nm,⁸ that is, at the isosbestic point of the absorption spectra of *cis*- and *trans*-2, afforded a photostationary mixture of the *cis* and *trans* compound in a ratio of 93.4:6.6. The quantum yield for *trans* → *cis* isomerization ($\Phi_{t \rightarrow c}$) was 0.67 when [*trans*-2] = 1.25 × 10⁻³ and 2.5 × 10⁻⁴ M on 405-nm irradiation, whereas $\Phi_{c \rightarrow t}$ remained at 0.06 when [*cis*-2] = 2.3 × 10⁻³ and 2.3 × 10⁻⁴ M on 436-nm irradiation.

Figure 1 depicts the absorption, fluorescence, and fluorescence excitation spectra of *cis*- and *trans*-2 in benzene. The absorption of *cis*-2 ($\lambda_{\max} = 414$ nm) is 37 nm shifted to longer wavelength than *trans*-2 ($\lambda_{\max} = 377$ nm) and is also much shifted from the spectra of *cis*- and *trans*-1. This is the reverse of the spectral features of many arylethylenes like stilbene.^{9,10} Moreover, *cis*-2 was quite different from *cis*-1, exhibiting fluorescence with a very large Stokes shift ($\lambda_{\max} = 600$ nm) and decaying with a lifetime of 73 ps, indicating that a remarkable conformational change takes place between the ground and the fluorescent states. On the contrary, *trans*-2 fluoresced with a small Stokes shift at $\lambda_{\max} = 440$ nm with a lifetime of 64 ps. The above facts suggest that the fluorescence observed on excitation of *cis*-2 arises not from its vertically excited state but from the singlet excited state of its tautomer, ¹(*cis*-2')*. Therefore, ¹(*cis*-2)* undergoes either adiabatic intramolecular hydrogen atom transfer to give the fluorescent tautomer, ¹(*cis*-2')*, or isomerization to *trans*-2 competing with fast unimolecular deactivation through the intramolecular hydrogen bond, as observed for 1.

Laser photolysis of *cis*-2 in benzene at 23 °C gave transient absorption with λ_{\max} at 580 nm, as shown in Figure 2, decaying with a lifetime of 300 ns to the ground state. This decay was not affected by the presence of oxygen. Deuterated *cis*-2 exhibited

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(7) *cis*-2: ¹H-NMR (270 MHz, CDCl₃) δ 6.36–6.53 (2H, pyrrole H), 6.27 (1H, d, $J = 12.8$ Hz, CH=CH), 6.75 (1H, d, $J = 12.8$ Hz, CH=CH), 7.16 (1H, pyrrole H), 7.26–8.12 (6H, quinoline H), 15.1 (1H, N–H); mp 88.5–89.7 °C. Anal. Calcd for C₁₅H₁₂N₂: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.65; H, 5.67; N, 12.57. *trans*-2: ¹H-NMR (270 MHz, CDCl₃) δ 6.27–6.87 (3H, pyrrole H), 6.96 (1H, d, $J = 16$ Hz, CH=CH), 7.26–8.01 (7H, quinoline H and CH=CH), 8.72 (1H, N–H); mp 135.5–136.5 °C. Anal. Calcd for C₁₅H₁₂N₂: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.72; H, 5.50; N, 12.72.

(8) Irradiation was performed in the cell room of a Hitachi F-4000 spectrofluorometer with an attached 150-W xenon lamp at 399 ± 2.5 nm.

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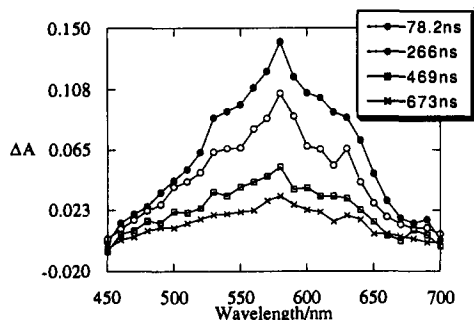


Figure 2. Transient absorption spectra observed on 308-nm laser excitation of *cis-2* in benzene at 23 °C.

the same transient absorption, but the lifetime increased by 20% to 360 ns, indicating a role of hydrogen atom transfer for the decay of the transient. This is contrasted with a broad T-T absorption observed at 500–700 nm on excitation of camphorquinone with a 480-nm laser in the presence of *cis-2* in benzene, which decayed with a lifetime of 190 ns and was effectively quenched by oxygen with a rate constant of $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Comparison of the above transient absorption observed on direct excitation with the fluorescence ($\lambda_{\text{max}} = 600 \text{ nm}$) suggests that the fluorescence arises from the excited state of the species showing absorption at 580 nm. Thus, $^1(\text{cis-2})^*$ undergoes intramolecular hydrogen atom transfer to give $^1(\text{cis-2}')^*$, which deactivates to *cis-2'* with 73-ps lifetime accompanied by emission of fluorescence at 600 nm; the resulting *cis-2'* with λ_{max} at 580 nm reverts to *cis-2* with a time constant of ca. 300 ns at room temperature. Therefore, the photoisomerization of **2** might be coupled with the intramolecular hydrogen atom transfer accompanied by lowering of the double bond character in the tautomer. The rate constant $k(\text{cis-2}' \rightarrow \text{cis-2})$ increased with increasing temperature from $2.1 \times 10^6 \text{ s}^{-1}$ at 15.8 °C to $7.7 \times 10^6 \text{ s}^{-1}$ at 39.5 °C. The Arrhenius plot gives an activation energy E_a and a frequency factor A for $\text{cis-2}' \rightarrow \text{cis-2}$ as $9.4 \text{ kcal mol}^{-1}$ and $2.8 \times 10^{13} \text{ s}^{-1}$, respectively.

In conclusion, the intramolecular hydrogen bonding in *cis-2* leads to the internal conversion of its excited singlet state to the ground state ($\text{cis-2}^* \rightarrow \text{cis-2}$) either through hydrogen bonding

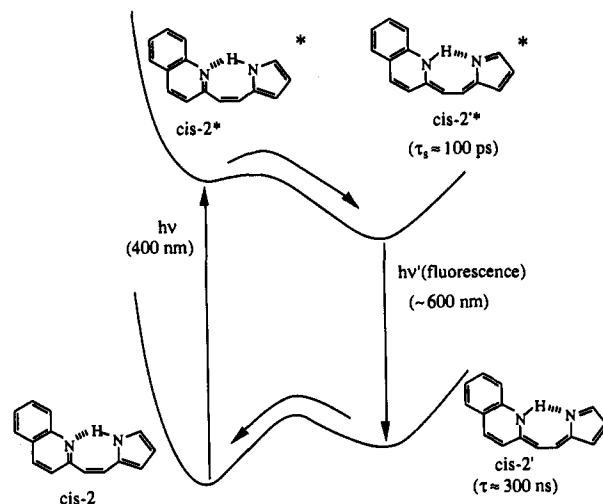


Figure 3. Potential energy surface of photoinduced hydrogen atom transfer of *cis-2* in benzene.

or through intramolecular hydrogen atom transfer, giving the tautomeric *cis-2'* in the excited singlet state. The resulting $^1(\text{cis-2}')^*$ deactivates with a lifetime of 73 ps to the ground state *cis-2'* or may undergo isomerization of the double bond to *trans-2*. Ground-state *cis-2'* reverts to the starting *cis-2* with an activation energy of $9.4 \text{ kcal mol}^{-1}$. Figure 3 depicts the potential energy surfaces of hydrogen atom transfer in *cis-2*.

Intramolecular proton or hydrogen atom transfer in the excited state has often been shown for the O—H...O or O—H...N system.¹¹ However, the present work demonstrates fast intramolecular hydrogen atom transfer taking place in the N—H—N system¹² between a pyrrole ring and a quinoline ring connected by a C=C double bond.

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