Photoisomerization and Photoinduced Hydrogen-Atom Transfer in 1-Chloro-4-(2-pyrrol-2-ylethenyl)phthalazine

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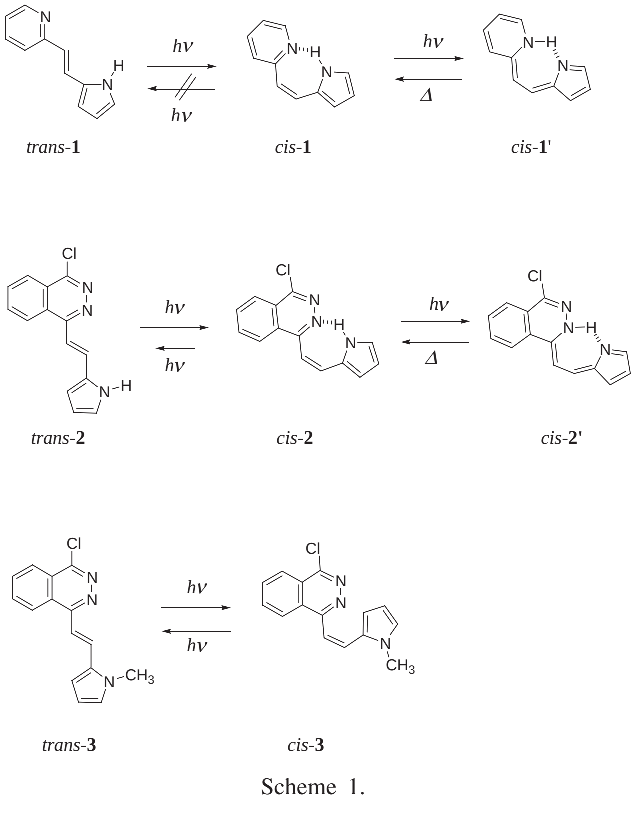
An olefin having a phthalazine ring and a pyrrole ring (**2**) exhibited a fluorescence spectrum with a large Stokes shift in the *cis*-isomer. The *cis*-isomer composition at the photostationary state was considerably high, so as give an isomer ratio at the photostationary state ($([\mathrm{cis}]/[\mathrm{trans}])_{\mathrm{PSS}}$ of 97/3 upon irradiation at 366 nm. These results indicate the occurrence of intramolecular hydrogen-atom transfer in the singlet excited state. The produced tautomer scarcely gave the *trans* isomer by a reverse hydrogen-atom transfer, and cis-to-trans isomerization was prevented by the existence of intramolecular hydrogen bonding in the *cis* isomer. Both *cis*-**2** and *trans*-**2** underwent intersystem crossing to give the same triplet excited state with a lifetime of 10 μs in benzene. Based on these results, the photochemical isomerization of **2** in the singlet excited state and in the triplet excited state is discussed.

Photochemical cis-trans isomerization is one of the basic photochemical reactions; the mode of isomerization can be controlled by a substituent on ethylenic carbon.[1]

Inter- or intramolecular hydrogen bonding also affects the mode of isomerization.[2–9] An olefin having a pyridine ring and a pyrrole ring (**1**) exhibited one-way trans-to-cis isomerization.[5,6] The *cis*-isomer underwent hydrogen atom transfer to give a tautomer, which exhibited fluorescence emission with a considerably large Stokes shift. The transient absorption spectra of the tautomer were observed by laser flash photolysis.

Among the compounds examined, we found that hemiindigo compounds having a pyrrole ring exhibited a color change between reddish orange and greenish yellow upon alternate irradiation of 366 nm and 546 nm.[8,9] However, we did not observed hydrogen-atom transfer in the excited state in hemiindigo compounds. Whether hydrogen-atom transfer takes place in the excited state or not should depend on the structure of the molecules; the normal form seems to have the lowest energy both in the ground state and the excited state.[8,9]

We have searched for compounds having different types of aromatic ring at one side of the C=C double bond, and a pyrrole ring at the other side to explore the structural effect on the photochromic behavior and photoinduced hydrogen-atom transfer. In this respect, we have prepared hydrogen-bonded compounds having a pyrrole ring and a phthalazine ring on the ethylenic carbon (olefin **2**). The pyrrole NH may form intramolecular hydrogen bonding with both the N atoms of a phthalazine ring, and may exhibit interesting photochemical properties. Thus, **2** exhibited fluorescence emission with a considerably large Stokes shift or underwent intersystem crossing to the triplet state, followed by isomerization around the double bond. Highly selective trans → cis isomerization in the excited singlet state was proposed (Scheme 1).



Scheme 1.

Experimental

Materials and Solvents. Olefins **2** and **3** were synthesized by a Wittig reaction[10] to yield only *trans*-isomers. *cis*-Isomers were obtained by isomerization of *trans*-isomers upon irradiation at 366 nm. Both *trans*- and *cis*-isomers were purified by column chloromatography on silica gel and recrystallized from benzene or hexane.

***trans*-1-Chloro-4-(2-pyrrol-2-ylethenyl)phthalazine (*trans*-2):** ^{1}H NMR (200 MHz, DMSO) δ 6.14 (m, 1H), 6.57 (m, 1H), 7.01 (m, 1H), 7.70 (d, 1H, $J = 15.8$ Hz), 7.89 (d, 1H, $J = 15.8$ Hz), 8.50 (m, 1H), 11.50 (br, 1H) ppm. ^{13}C NMR (50 MHz, DMSO) δ 155.03, 151.81, 133.96, 130.22, 127.57, 124.90, 124.47, 122.48, 113.39, 112.35, 109.99 ppm. Anal. Calcd for

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$C_{14}H_{10}ClN_3$: C, 65.76; H, 3.92; N, 16.43%. Found: C, 65.72; H, 3.72; N, 16.45%. ESI-MS calcd for $[M+Na]^+ = 278.0455$; found 278.0432. mp 195 °C. UV–vis (benzene) $\lambda_{max} = 392$ nm; $\varepsilon = 2.4 \times 10^4$ $M^{-1}\,cm^{-1}$.

***cis*-2:** ^1H NMR (200 MHz, DMSO) δ 6.35 (m, 1H), 6.62 (m, 1H), 6.73 (d, 1H, $J = 13.2$ Hz), 6.99 (d, 1H, $J = 13.2$ Hz), 7.20 (m, 1H), 7.96 (m, 2H), 8.31 (m, 2H), 13.70 (br) ppm. mp 104–105 °C UV–vis (benzene) $\lambda_{max} = 425$ nm; $\varepsilon = 1.9 \times 10^4$ $M^{-1}\,cm^{-1}$.

***trans*-1-Chloro-4-[2-(1-methylpyrrol-2-ylethenyl)]phthalazine (*trans*-3):** ^1H NMR (200 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.25 (t, 1H, $J = 3.4$ Hz), 6.74–6.84 (m, 2H), 7.37 (d, 1H, $J = 15.2$ Hz), 7.92–8.02 (m, 2H), 8.17 (d, 1H, $J = 15.2$ Hz), 8.25–8.35 (m, 2H) ppm. ^{13}C NMR (50 MHz, DMSO) δ 156.26, 154.57, 148.67, 133.54, 130.31, 126.23, 125.06, 124.49, 113.52, 110.33, 108.40, 33.47 ppm. Anal. Calcd for $C_{15}H_{12}ClN_3$: C, 66.79; H, 4.48; N, 15.60%. Found: C, 66.76; H, 4.54; N, 15.34%. ESI-MS calcd for $[M+Na]^+ = 292.0617$; found 292.0568. mp 163–164 °C UV–vis (benzene) $\lambda_{max} = 402$ nm; $\varepsilon = 2.5 \times 10^4$ $M^{-1}\,cm^{-1}$.

***cis*-3:** ^1H NMR (200 MHz, $CDCl_3$) δ 3.71 (s, 3H), 5.82–6.00 (m, 2H), 6.56 (t, 1H, $J = 4.0$ Hz), 6.72 (d, 1H, $J = 12.7$ Hz), 7.00 (d, 1H, $J = 12.7$ Hz), 7.82–7.88 (m, 2H), 8.15 (d, 1H, $J = 7.9$ Hz), 8.32 (d, 1H, $J = 7.9$ Hz) ppm. mp 139–140 °C. UV–vis (benzene) $\lambda_{max} = 390$ nm; $\varepsilon = 4.4 \times 10^3$ $M^{-1}\,cm^{-1}$.

In spectroscopy, Dotite Spectrosol or Luminasol was used as a solvent without further purification.

Measurement. Absorption and fluorescence spectra were measured on a JASCO Ubest-55 and on a Hitachi F-4000 fluorescence spectrometer, respectively. NMR spectra were measured on a Varian Gemini 2000.

Laser flash photolyses were performed by using an excimer laser (Lambda Physik LPX-100, 308 nm, 20 ns fwhm) as an excitation light source, and a pulsed xenon arc (Ushio UXL-159) was used as a monitoring light source. A photomultiplier (Hamamatsu R-928) and a storage oscilloscope (Iwatsu TS-8123) were used for detection.

The quantum yield of isomerization and the photostationary isomer ratio were determined with 366-nm light from a 150 W Xe lamp through a monochrometer with a bandwidth of 5 nm. The sample solution was deaerated by bubbling argon and irradiated for 5–15 min to keep the conversion within 10%. The light intensity was determined by tris(oxalato)ferrate(III) actinometory.[11] The concentration of each isomer was determined by high-performance liquid chromatography through a column (TOSO ODS-80TS) and eluting with acetonitrile/water = 4/1.

Results and Discussion

Absorption and Emission Spectra. The absorption spectra of **2** and **3** in benzene are shown in Figs. 1 and 2. The absorption maximum of *cis*-**3** ($\lambda_{max} = 390$ nm) appeared at a shorter wavelength region than that of *trans*-**3** ($\lambda_{max} = 402$ nm). The absorption maximum of *cis*-**2** ($\lambda_{max} = 425$ nm) appeared at a longer wavelength region than that of *trans*-**2** ($\lambda_{max} = 390$ nm). Usually, the *cis* isomers exhibit absorption maxima at shorter wavelength compared with that of the *trans* isomers, since the aromatic ring and the C=C double bond take an almost planar conformation in the *trans* isomers, while the single bonds connecting the aromatic ring and the double bond are twisted to some extent due to a steric hindrance in the *cis* isomers. The molar extinction coefficient (ε) should depend on the extent of the conjugation of the molecules. The smallest value of ε in *cis*-**3** can be explained by the less-planar conformation of *cis*-**3**. The intramolecular hydrogen bonding may increase the planarity of the molecule and the conjugation by way of intramolecular hydrogen bonding to induce a red shift of the absorption spectrum and the comparatively high value of ε in *cis*-**2**.

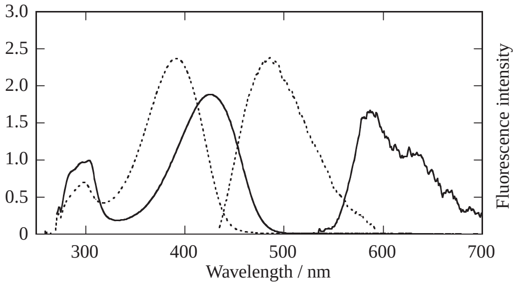

Fig. 1. Absorption and fluorescence spectra of *trans*-**2** (dashed line) and *cis*-**2** (solid line) at room temperature in benzene.

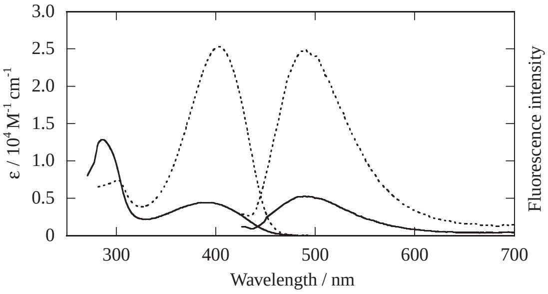

Fig. 2. Absorption and fluorescence spectra of *trans*-**3** (dashed line) and *cis*-**3** (solid line) at room temperature in benzene.

Olefins **2** and **3** exhibited fluorescence spectra, as shown in Figs. 1 and 2. The quantum yield of fluorescence emission was 5×10^{-3}, 1×10^{-3}, 5×10^{-3}, and 8×10^{-3} for *trans*-**2**, *cis*-**2**, *trans*-**3**, and *cis*-**3**, respectively. In addition, the Stokes shifts of the fluorescence emissions in benzene were 4700, 6300, 4500, and 5300 cm^{-1} for *trans*-**2**, *cis*-**2**, *trans*-**3**, and *cis*-**3**, respectively. The observed large Stokes shift indicates a change of the molecular structure or the electronic structure upon excitation to the excited state. Among the compounds examined in Figs. 1 and 2, only *cis*-**2** showed no spectral overlap between the absorption spectrum and the fluorescence spectrum. This result indicates the occurrence of a considerably large structural change upon the photoexcitation of *cis*-**2**. One of the candidates of a structural change is the production of a tautomer by way of hydrogen-atom transfer in the excited singlet state. Another possibility is photochemical isomerization to the *trans* isomer by an adiabatic process in the singlet excited state. However, the *trans*-isomer exhibited absorption and fluorescence spectra at a shorter wavelength region compared to that of the *cis*-isomer (Fig. 1). Therefore, the former mechanism that the tautomer produced by the intramolecular hydrogen atom transfer can explain the observed fluorescence emission at 580 nm upon excitation of *cis*-**2**. The fluorescence spectrum in acetonitrile of *cis*-**2** was similar to that in benzene. If the fluorescence emission of *cis*-**2** was assigned to fluorescence from

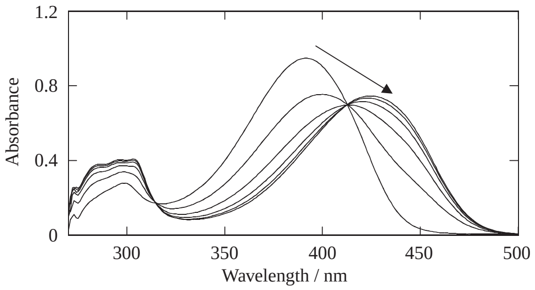

Fig. 3. Change of absorption spectrum of *trans*-**2** on irradiation at 366 nm.

the excited state having a charge-transfer character, the fluorescence in acetonitrile would exhibit at a longer wavelength region than that in benzene. Therefore, the observation of fluorescence spectra with large Stokes shift for only *cis*-**2** having an intramolecular hydrogen bonding indicates the occurrence of hydrogen-atom transfer in *cis*-**2** to give a *cis*-tautomer form in the singlet excited state.

The triplet energy of olefin **3** was estimated from the phosphorescence spectra in ethanol at 77 K to be 56 kcal mol^{-1} and 59 kcal mol^{-1} for *trans*-**3** and *cis*-**3**, respectively.

Photochemical Isomerization of Olefin 2. Olefin **2** underwent isomerization mutually between the *trans* and *cis* isomers upon photoirradiation, as revealed by a change of the absorption spectrum (Fig. 3).

The isomer ratio at the photostationaly state on irradiation of **2** at 366 nm was ([cis]/[trans])$_{\text{PSS}}$ = 97/3 and 83/17 at concentrations of 2.0×10^{-4} M and 1.0×10^{-3} M, respectively, under an argon atmosphere. The high composition of the *cis*-isomer at the photostationary state should be due to the presence of intramolecular hydrogen bonding in the *cis* isomer. The fact that the *trans* isomer composition at the photostationary state increased with increasing concentration of olefin **2** indicated that the quantum yield of cis-to-trans isomerization increased with increasing concentration.

One should mention here the effect of the substrate concentration on the cis-trans isomerization in the excited triplet state. In the triplet state, stilbene undergoes deactivation from the perpendicular triplet state (^{3}p*) as a unimolecular process. In addition, the triplet stilbene deactivates from the trans triplet state (^{3}t*) by energy transfer quenching with azulene. Thus, in the absence of a triplet quencher, stilbene undergoes mutual isomerization through the excited triplet state, deactivating from ^{3}p* to give *cis* and *trans* isomers, while in the presence of azulene as a triplet quencher, both the unimolecular deactivation from ^{3}p* giving *cis* and *trans* isomers and the bimolecular deactivation from ^{3}t* with azulene solely giving the *trans* isomer take place. The increase of the azulene concentration increased the *trans* isomer composition at the photostationary state in the triplet-state isomerization of stilbene.

The bimolecular process giving solely *trans* isomer could also take place by a quenching process between ^{3}t* and the ground state *cis* isomer to increase the *trans* isomer composition at the photostationary state, when the triplet excited state has a relatively long lifetime. In this process, the triplet energy transfer process between ^{3}t* and the cis ground state is dependent on the concentration of olefins, and regenerates the triplet state, resulting in the increase of the quantum yield of cis-to-trans isomerization and the *trans* isomer composition at the photostationary state. The concentration dependence on the isomer ratio at the photostationary state of olefin **2** can be explained by the above mechanism.

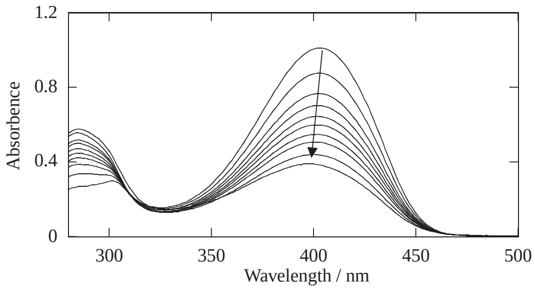

Fig. 4. Change of absorption spectrum of *trans*-**3** on irradiation at 366 nm.

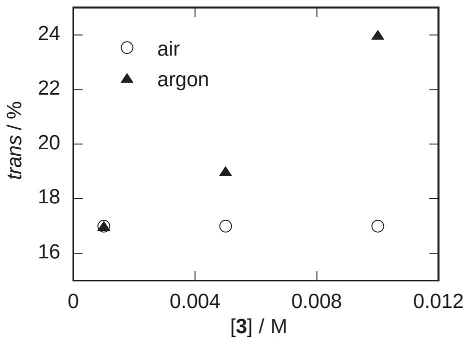

Fig. 5. Concentration dependence of the ratio of *trans* isomer at the photostationary state of **3** on irradiation at 366 nm.

Oxygen may affect the isomerization in the triplet excited state.[1,12] Actually, the isomer ratio at the photostationary state under an oxygen atmosphere was ([cis]/[trans])$_{\text{PSS}}$ = 97/3 and 91/9 at a concentration of 2.0×10^{-4} M and 1.0×10^{-3} M, respectively. These results indicate that isomerization occurs in the triplet excited state as well as in the singlet excited state.

Photochemical Isomerization of Olefin 3. Figure 4 shows the change of the absorption spectrum of *trans*-**3** upon irradiation at 366 nm. Since both the *cis* and *trans* isomers of **3** did not have intramolecular hydrogen bonding, one does not need to consider the effect of hydrogen bonding on the cis-to-trans isomerization in the excited state. The isomer ratio at the photostationary state upon irradiation at 366 nm was ([cis]/[trans])$_{\text{PSS}}$ = 83/17, 81/19, and 76/24 at concentrations of 1.0×10^{-3} M, 5.0×10^{-3} M, and 1.0×10^{-2} M, respectively, under an argon atmosphere (Fig. 5). On the other hand, the isomer ratio at the photostationary state under an oxygen atmosphere remained at the same value in the concentration range from 1.0×10^{-3} M to 1.0×10^{-2} M, that is [cis]/[trans] = 83/17. The concentration and oxygen dependence on the isomer ratio at the photostationary state indicate that the cis-trans isomerization took place in the triplet excited state as well as in the singlet excited state, as discussed concerning in the case of olefin **2**.

$\Phi_{\text{trans}\rightarrow\text{cis}}$ was determined to be 0.6 for **3**, and was independent of its concentration (1.0×10^{-3} M–1.0×10^{-2} M) under an argon atmosphere, determined by HPLC analyses with tris(oxalato)ferrate(III) actinometory. The isomer ratio at the photostationary state is related to the quantum yield of isomerization and the molar extinction coefficient of *trans* ($\varepsilon_{\text{trans}}$) and *cis* isomers ($\varepsilon_{\text{cis}}$) at the excitation wavelength,

$$([\text{cis}]:[\text{trans}])_{\text{PSS}} = (\varepsilon_{\text{trans}}/\varepsilon_{\text{cis}}) \times (\Phi_{\text{trans}\rightarrow\text{cis}}/\Phi_{\text{cis}\rightarrow\text{trans}}). \quad (1)$$

The molar extinction coefficients of *trans*-**3** and *cis*-**3** at 366 nm are 1.27×10^4 $\text{M}^{-1}\,\text{cm}^{-1}$ and 0.37×10^4 M^{-1}, respectively. Thus, the high proportion of *cis* isomer at the photostationary state upon irradiation at 366 nm should be due to the large difference of the molar extinction coefficient between *trans*-**3** and *cis*-**3**. From equation 1, one can calculate $\Phi_{\text{cis}\rightarrow\text{trans}}$ to be 0.42, 0.48, 0.65 at concentrations of 1.0×10^{-3} M, 5.0×10^{-3} M, and 1.0×10^{-2} M, respectively, under an argon atmosphere.

Upon camphor quinone ($E_{\text{T}} = 51.5$ kcal mol^{-1}) sensitization, only the *trans* isomer was detected at the photostationary state, indicating that compound **3** underwent highly selective isomerization to produce the *trans* isomer in the triplet excited state.

Transient Absorption Spectra. The transient absorption spectra of *trans*-**2** and *cis*-**2** observed in benzene under an argon atmosphere are shown in Figs. 6 and 7. In *trans*-**2** the transient spectrum with a $\lambda_{\text{max}} = 570$ nm decayed with a lifetime of 10 µs under an argon atmosphere without changing the spectral profile, while in *cis*-**2** the transient spectrum with the maximum wavelength of 510 nm just after laser excitation shifted to longer wavelength with $\lambda_{\text{max}} = 570$ nm at 1.6 µs after laser excitation. The lifetimes of the transients observed in *cis*-**2** were determined to be 200 ns and 10 µs under an argon atmosphere in benzene. The transient species with maximum of 570 nm observed for *cis*-**2** (10 µs) was quenched by oxygen in benzene with a quenching rate constant of 3×10^9 $\text{M}^{-1}\,\text{s}^{-1}$, and was assigned to the triplet state. On the other hand, the lifetime of the transient species with a maximum wavelength of 510 nm observed for *cis*-**2** (200 ns) was not affected by oxygen in benzene; therefore, this transient was assigned to the ground state tautomer produced by intramolecular hydrogen atom transfer in the singlet excited state.

The transient absorption of *trans*-**2** was observed at 570 nm with a lifetime of 10 µs, and was quenched by oxygen in a solvent with a quenching rate constant of 3×10^9 $\text{M}^{-1}\,\text{s}^{-1}$. Since the quenching rate constants by oxygen for *cis*-**2** and *trans*-**2** were the same, and nearly 1/9 of the diffusion controlled rate constant of oxygen in benzene, the observed transient can be assigned to the triplet state of *trans*-**2**.

Figures 8 and 9 show the transient absorption spectra of *trans*-**3** and *cis*-**3**. The transient absorption spectra of *trans*-**3** were similar to those of *cis*-**3**, and were quenched by oxygen with a rate constant of 2×10^9 $\text{M}^{-1}\,\text{s}^{-1}$. The lifetime of the triplet state was 8 µs under an argon atmosphere for *trans*-**3** and *cis*-**3**. Observations of the long lived triplet state under a degassed condition and the quenching rate constant by oxygen made the transient species possible to be assigned to be the trans planar form in the triplet excited state.

One could observe the cis triplet state ($^3\text{c}^*$), $^3\text{p}^*$, or $^3\text{t}^*$ by laser flash photolysis. Usually, the *cis* isomer has a more steric congestion compared to the *trans* isomer, and therefore the *trans* isomer is energetically more stable than the *cis* isomer in both the ground state and the excited state. Thus, the transient spectra should be assigned to either $^3\text{t}^*$ or $^3\text{p}^*$. Since the deactivation rate constant from $^3\text{p}^*$ is 3 orders of magnitude faster than that from $^3\text{t}^*$, the triplet lifetime changes from

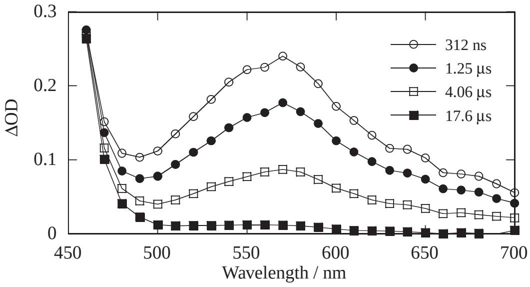

Fig. 6. Transient absorption spectra of *trans*-**2** in benzene under argon.

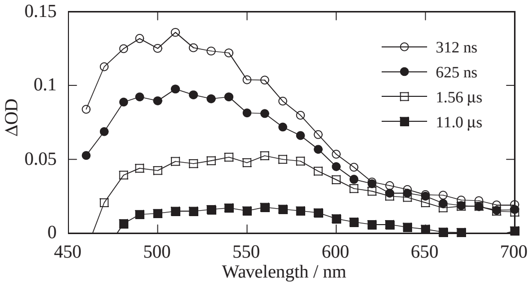

Fig. 7. Transient absorption spectra of *cis*-**2** in benzene under argon.

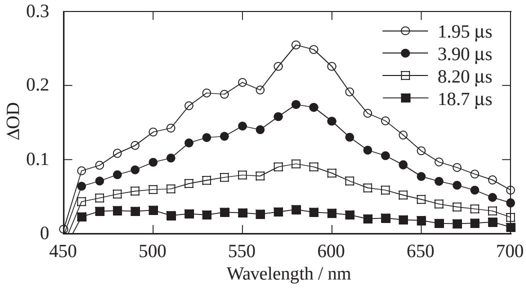

Fig. 8. Transient absorption spectra of *trans*-**3** in benzene under argon.

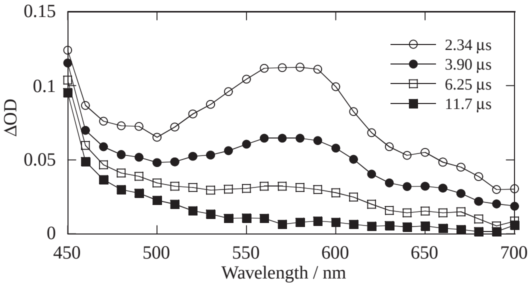

Fig. 9. Transient absorption spectra of *cis*-**3** in benzene under argon.

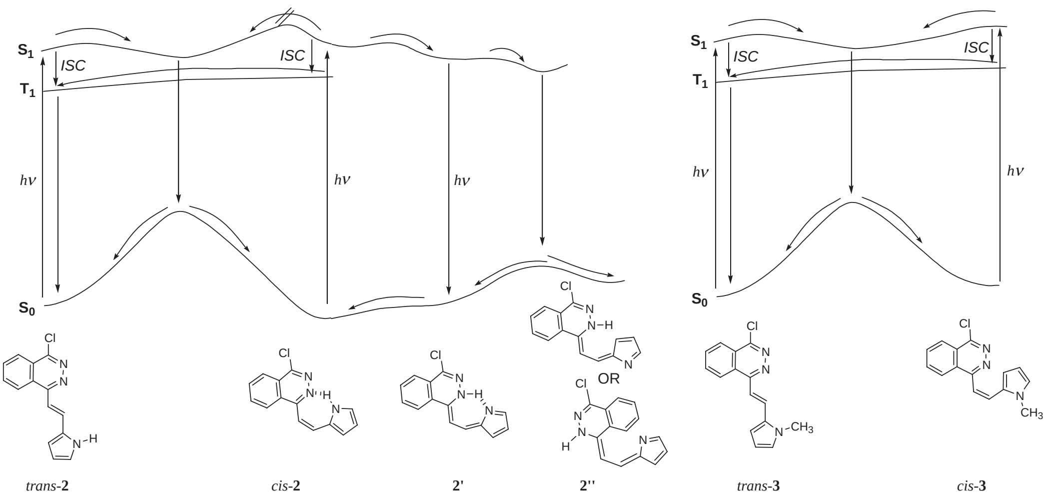

Fig. 10. Potential energy surfaces of isomerization for olefins **2** and **3**.

50 ns to tens of μs, depending upon the potential-energy surface of the triplet state. When the triplet state of olefin has a lifetime longer than 1 μs, one could assume that $^3t^*$ is far more stable than $^3p^*$, and the observed transient should be assigned to $^3t^*$.

Excited-State Intramolecular Hydrogen-Atom Transfer of 2. *trans*-**2** and *cis*-**2** exhibited fluorescence spectra with Stokes shifts of 4700 cm^{-1} and 6300 cm^{-1}, respectively, in benzene. The large Stokes shift observed in *cis*-**2** indicated that the conformation or electronic structure of *cis*-**2** in the singlet excited state was different from that in the ground state. The above results indicated that the excited state intramolecular hydrogen-atom transfer took place in *cis*-**2** to give a tautomer, which exhibited fluorescence with a large Stokes shift. A transient absorption spectrum assigned to the tautomer in the ground state was observed, and the absorption maximum appeared at 510 nm by laser flash photolysis.

The structure of the tautomer could be the *trans*-tautomer form (**2″** in Fig. 10) or the *cis*-tautomer form (**2′** in Fig. 10). Regarding the conformation of the tautomer, we have reported that the conformation of the tautomer produced by a photoinduced hydrogen-atom transfer in the singlet excited state of 2-(2-hydroxyphenyl)benzoxazole and 2-(2-hydroxyphenyl)benzothiazole is the *trans*-keto form, based on laser flash photolysis experiments.[13,14] In the same manner, it is considered that *cis*-**2** underwent excited-state hydrogen-atom transfer, followed by cis-to-trans isomerization to give the *trans*-tautomer (**2″** in Fig. 10). The maximum wavelengths of the absorption and fluorescence spectra of the tautomer are 510 nm and 570 nm, respectively, and the Stokes shift is 2000 cm^{-1}. The small Stokes shift compared with those of *trans*-**2**, *trans*-**3**, and *cis*-**3** supports the above discussion that the ground-state species observed in the transient absorption spectrum can be assigned to the tautomer **2″**.

Potential Energy Surface of Isomerization for Olefin 2 and 3. Based on the photoisomerization behavior and the observation of the long-lived triplet state assigned to the trans triplet state, the potential-energy surfaces of photoisomerization and the hydrogen-atom transfer are depicted as shown in Fig. 10. In olefin **2**, the *cis* isomer undergoes adiabatic intramolecular hydrogen-atom transfer to produce the tautomer in the excited singlet state. The isomerization around the double bond to produce the *trans* isomer in the excited singlet state is suppressed by the intramolecular hydrogen bonding in the *cis* isomer. The intersystem crossing to the triplet state should take place in *cis*-**2** competing with the hydrogen-atom transfer, and the cis-to-trans isomerization should take place efficiently in the excited triplet state. Actually, the triplet species with a maximum of 570 nm, which was assigned to be the *trans* planar form, was observed by laser flash photolysis. In olefin **3**, cis-trans mutual isomerization takes place in the excited singlet state and one-way cis-to-trans isomerization takes place in the excited triplet state.

Conclusion

Olefin **2** exhibited a color change from yellow to orange upon photoirradiation. In addition, *cis*-**2** exhibited fluorescence emission at a considerably long-wavelength region due to the intramolecular hydrogen-atom transfer in the singlet excited state. The effect of the presence of the adjacent nitrogen to the N···H–N intramolecular hydrogen bonding is not clear, but adiabatic intramolecular hydrogen atom transfer took place in *cis*-**2**. Furthermore, an intersystem crossing to the triplet state took place to produce the triplet state *cis*-**2**, which underwent one-way cis-to-trans isomerization. We should mention here that the present compounds **2** and **3** exhibited a quite long triplet lifetime compared to that of the olefins with a similar size aromatic ring, such as stylylnaphthalene ($\tau_T = 100$–200 ns).[1] Therefore, the present results concerning **2** and **3** should be very important not only from the view point of constructing molecules with photoinduced hydrogen-atom transfer and a color change, but also from basic interest concerning the potential-energy surface and the triplet lifetime of arylethenes.

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