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# Excited-state intramolecular proton transfer followed by *cis*–*trans* isomerization of (1-hydroxy-2-naphthyl)-s-triazine derivatives

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## Abstract

The excited-state intramolecular proton transfer (ESIPT) reactions of 2,4-dimethoxy-6-(1-hydroxy-2-naphthyl)-s-triazine (NTR) and 2,4-dimethoxy-6-(1-hydroxy-2-naphthyl)-1,3-pyrimidine (NPR) were studied by laser photolyses and fluorescence measurements with the aid of MO calculations. Large Stokes-shifted fluorescences ( $\Delta\bar{\nu} = 6400$  and  $7300\text{ cm}^{-1}$ ) originating from ESIPT were observed for NTR and NPR. Laser photolyses of NTR and NPR gave long-lived transients which could be attributed to their *trans*-keto tautomers ( $^1\text{K}_{tr}$ ) produced by *cis*–*trans* isomerization of the proton-transferred *cis*-keto form ( $^1\text{K}_{cis}^*$ ) in the  $S_1$  state. Temperature effects on the fluorescence lifetime and fluorescence quantum yield of  $^1\text{K}_{cis}^*$  and relative formation yield of  $^1\text{K}_{tr}$  showed that another temperature-dependent nonradiative deactivation process competing with the *cis*–*trans* isomerization was involved in the relaxation processes of  $^1\text{K}_{cis}^*$ . A lower apparent activation energy ( $12\text{ kJ mol}^{-1}$ ) for the total nonradiative deactivation rate of NTR including *cis*–*trans* isomerization was obtained in comparison with that ( $18\text{ kJ mol}^{-1}$ ) of NPR. Remarkable viscosity effects were observed on the fluorescence lifetimes of  $^1\text{K}_{cis}^*$  of NTR and NPR at 293 K, indicating that the main deactivation pathway from  $^1\text{K}_{cis}^*$  was the *cis*–*trans* isomerization  $^1\text{K}_{cis}^* \rightarrow ^1\text{K}_{tr}$ . The results of MO calculations on the ground and excited states of NTR and NPR supported a relaxation scheme including ESIPT followed by *cis*–*trans* isomerization. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

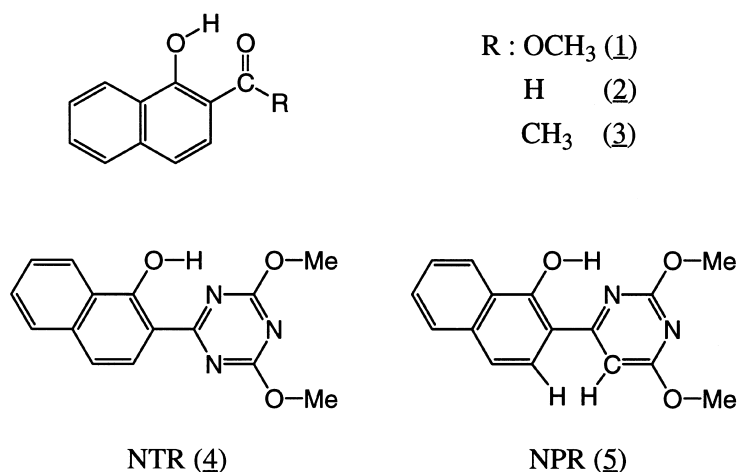
Since the original work of Weller [1], on the excited-state intramolecular proton transfer (ESIPT) of methyl salicylate, ESIPT has received much attention because of its importance in fundamental aspects of reaction dynamics [2–11] and also because of the various possibilities for applications, as in e.g., photostabilizer [12–15], proton

transfer laser [16–19], information storage device at a molecular level [20], luminescent solar concentrator [21], and fluorescence probe for biomolecules [22]. Such a variety of applications are based on unique photophysical properties of ESIPT systems, i.e., large radiationless deactivation efficiency, a four-level relaxation scheme, spectral sensitivity to environment, large Stokes-shifted fluorescence, etc.

We have recently studied the ESIPT of 1-naphthol derivatives as shown in Scheme 1 by means of the laser photolysis method, time-resolved thermal lensing method, and time-resolved

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Scheme 1.

fluorometry [23]. Because of relatively small exothermicities for the ESIPT reactions of 1-naphthol derivatives compared to those for phenol analogues, the occurrence of ESIPT depends strongly on the electronic nature of the substituent R. As the electron-donating substituent destabilizes the  $S_1$  state of the proton-transferred keto-form, ESIPT is not observed for compound **1**, while the compounds **2** and **3** show large Stokes-shifted fluorescences originating from ESIPT. The ESIPT has also been found for a triazine derivative **4** [24] which is a naphthalene analogue of (hydroxyphenyl)-s-triazine [25]. The transient absorption spectra of **2–4** exhibit a long-lived transient which can be assigned to the ground-state *trans*-keto tautomer produced by *cis–trans* isomerization following ESIPT [23,24]. The relaxation scheme including ESIPT of compounds **2–4** is depicted in Scheme 2.

The *cis–trans* isomerization following ESIPT has also been reported for other proton transfer systems such as *o*-hydroxyphenylbenzazoles [26–29], 2-(2'-hydroxyphenyl) oxazole [30], 2,2'-bipyridin-3-ol [31], and photochromic salicylideneaniline [32]. *Cis–trans* isomerization is sensitive to the environments, and the ground-state *trans*-keto tautomer has a large activation energy for back proton transfer. As a result, the ESIPT followed by *cis–trans* isomerization systems have possibilities for the various applications, e.g., a

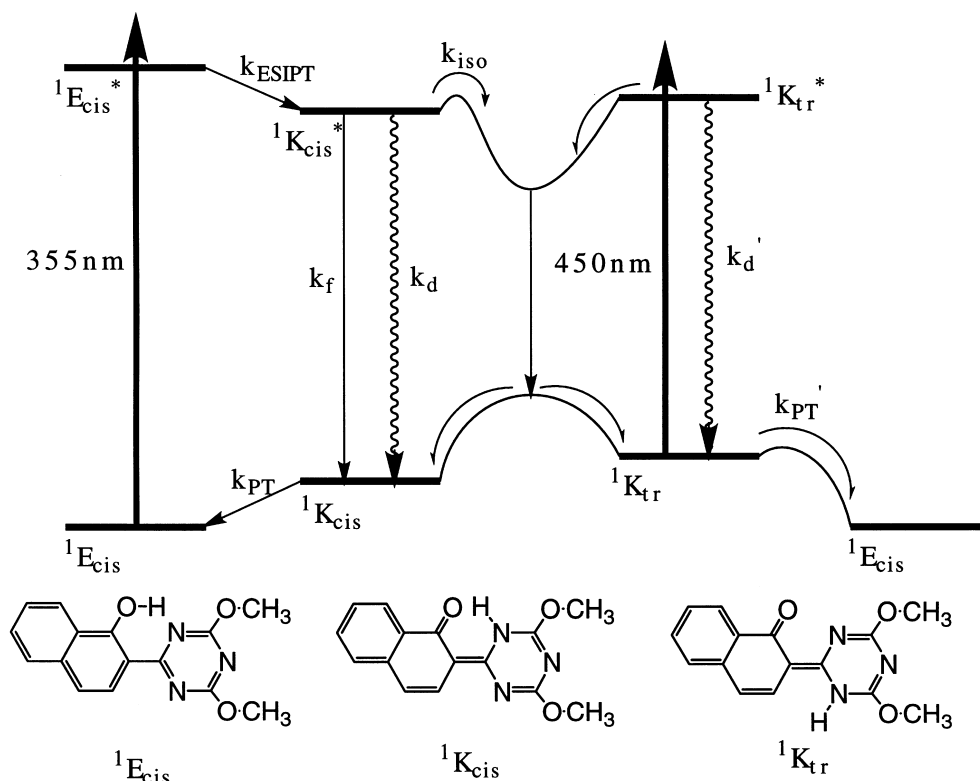
new information storage device at a molecular level [30] and fluorescence probe for lipid bilayers [33]. Therefore, elucidation of reaction dynamics of ESIPT followed by *cis–trans* isomerization are of essential importance for designing new molecular devices.

The aim of this article is to clarify relaxation pathways of the proton-transferred *cis*-keto tautomer including *cis–trans* isomerization and the reason why *cis–trans* isomerization occurs just after ESIPT. Spectral and photophysical properties of 2,4-dimethoxy-6-(1-hydroxy-2-naphthyl)-s-triazine (NTR) are compared with those of 2,4-dimethoxy-6-(1-hydroxy-2-naphthyl)-1,3-pyrimidine (NPR), which involves intramolecular H–H repulsion as shown in Scheme 1.

## 2. Experimental and MO calculations

### 2.1. Materials

Synthesis of NTR was described previously [24]. NPR was synthesized by photochemical rearrangement [34] of 2,4-dimethoxy-6-(1-naphthoxy)-1,3-pyrimidine, which was synthesized by the reaction of 1-naphthol with 6-chloro-2,4-dimethoxy-1,3-pyrimidine (Aldrich, 99 at.%) according to the reported procedure [35]. The product was purified by column chromatography followed by



Scheme 2.

recrystallizations twice from acetonitrile and was identified by mass spectrometry and NMR spectra. Potassium hydroxide (Kanto), polystyrene (PS; Aldrich, average MW ca. 280,000), 3-methylpentane (3MP; Wako, special grade), methylcyclohexane (MCH; Aldrich, spectrophotometric grade), and *n*-pentane (Kanto, Uvasol) were used as received. *n*-Hexadecane (Kanto, special grade) was purified by column chromatography. Ethanol (EtOH; Wako, spectro-sol) and acetonitrile (Kishida) were purified by fractional distillation.

## 2.2. Methods

Absorption and fluorescence spectra were recorded on a UV/VIS spectrophotometer (JASCO, Ubest-50) and a spectrofluorometer (Hitachi, F-4010), respectively. Fluorescence lifetime ( $\tau_f$ ) was obtained with a time-correlated single-photon counting fluorometer (Edinburgh Analytical In-

struments, FL900). Fluorescence lifetimes less than  $\sim 200$  ps were determined by using a picosecond laser system which was based on a mode-locked Ti:sapphire laser (Spectra-Physics Tsunami; 800 nm; 82 MHz; FWHM,  $\sim 70$  fs) pumped by a diode laser (Spectra-Physics Millennia V; 532 nm; 4.5 W). The repetition rate was adjusted to 4 MHz by using a pulse-picker (Spectra-Physics Model 3980), and the third harmonic (266 nm; FWHM,  $\sim 250$  fs) was used for the excitation source. The monitoring system consisted of a microchannel plate-photomultiplier tube (Hamamatsu, R3809U-51) cooled at  $-20^\circ\text{C}$  and a single-photon counting module (Becker and Hickl, SPC-530). The fluorescence was detected through a polarizer placed at "magic angle" with respect to the polarization direction of the excitation source. Fluorescence quantum yields were determined relative to quinine bisulfate in 1 N  $\text{H}_2\text{SO}_4$  [36]. NMR spectra were recorded on a

JEOL Alpha-500 FT NMR spectrometer. Chemical shifts ( $\delta$ ) in ppm were measured in  $\text{CDCl}_3$  referred to trimethylsilane as internal standard.

Nanosecond laser flash photolysis experiments were carried out by using the third harmonic (355 nm) of an  $\text{Nd}^{3+}$ -YAG laser (Spectra Physics, GCR-130, pulse width 5 ns) as excitation source. The monitoring system for the transient species consisted of a 150 W short gap xenon lamp (Hamamatsu, L2274), a monochromator (JOBIN YVON, HR320), and a photomultiplier tube (Hamamatsu, R928). The transient signals were recorded on a digitizing oscilloscope (Tektronix, TDS-540) and transferred to a personal computer (NEC, PC-9801 BX3) to analyze the data.

All measurements were carried out under de-aerated condition unless otherwise noted. All measurements except for temperature effect experiments were carried out at 293 K. In the temperature effect experiments, the temperature of the sample was controlled by using an Oxford DN-1704 cryostat.

Molecular orbital calculations were performed by use of the PM3 method (MOPAC ver. 6.01) [37] and the INDO/S-CI method on an IBM RS/6000 workstation (model 41T). Within the CI scheme, all singly excited configurations involving the 10 highest occupied and the 10 lowest unoccupied orbitals were included.

### 3. Results and discussion

#### 3.1. Ground-state geometries of NTR and NPR

In order to obtain an insight into the ground-state geometry of NTR and NPR, their NMR spectra were measured. The chemical shift ( $\delta$ ) of the hydroxyl proton in the NMR spectra of NTR ( $\delta = 13.9$  ppm) and NPR ( $\delta = 14.7$  ppm) showed remarkable increases in comparison with that ( $\delta = 5.4$  ppm [38]) of 1-naphthol, indicating that a strong intramolecular hydrogen bond is involved in the ground state of NTR and NPR, and the intramolecular hydrogen bond in NPR is stronger than that in NTR [39].

Fig. 1 shows the optimized molecular structures for the enol form of NTR and NPR obtained by

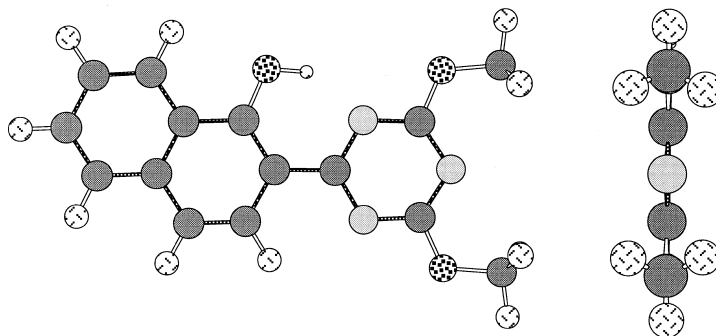
PM3 calculations. In both compounds, the naphthalene and heteroaromatic rings are coplanar to each other, inspite of the steric repulsion between two hydrogen atoms in the *ortho* position of the two aromatic rings in NPR. The equilibrium torsional angle of biphenyl has been reported to be  $\sim 40^\circ$  [40,41], while in 2-(2'-hydroxyphenyl)pyridine [42], two aromatic rings have been calculated to be almost coplanar. The coplanarity in 2-(2'-hydroxyphenyl)pyridine has been explained on the basis of counterbalance among the H-H repulsion in the *ortho* position of two aromatic rings, the hydrogen-bond stabilization, and electron delocalization effects. As in the case of the above compound, destabilization originating from the H-H repulsion in NPR is considered to be compensated by stabilization due to the strong hydrogen bond and also the electron delocalization effects.

#### 3.2. Spectral properties of NTR and NPR

Fig. 2 shows the absorption and fluorescence spectra of NTR and NPR in MCH at 293 K. From the relatively large extinction coefficients, all the ultraviolet absorption bands can be assigned to  $(\pi, \pi^*)$  transitions. It is clear from Fig. 2 that the absorption spectra of NTR and NPR cannot be described as a simple superposition of the absorption spectra of 1-naphthol and heteroaromatic moieties. This shows that there exists strong electronic interaction between two chromophores, consistent with their coplanarity obtained by MO calculations. The first absorption band at around  $\sim 27,000 \text{ cm}^{-1}$  corresponds to the pseudo  $(\pi, \pi^*)$  transition associated with the intramolecular hydrogen bond. The first and second ( $\sim 33,000 \text{ cm}^{-1}$ ) absorption bands of NTR and NPR are similar in shape and intensity except for a slight shift of the peak wavelength. The third absorption band at  $\sim 36,000 \text{ cm}^{-1}$  of NTR is shifted to a lower energy for NPR ( $\sim 35,000 \text{ cm}^{-1}$ ), and the extinction coefficient of the band of NPR decreases significantly. These spectral properties can be explained on the basis of MO calculations as described below.

Excited state properties of NTR and NPR were calculated by the INDO/S-CI method at

NTR



NPR

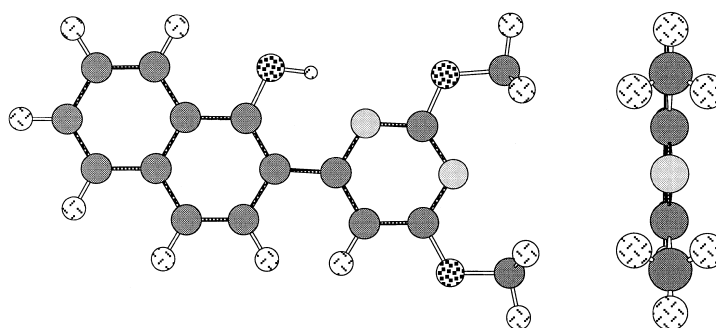


Fig. 1. Optimized molecular structures for the enol form of NTR and NPR.

the ground-state geometries optimized by the PM3 method. The calculated oscillator strengths for each absorption band (A–D) are shown in Fig. 2. The calculated energy and oscillator strength for the  $S_n \leftarrow S_0$  transitions of NTR and NPR coincide well with the observed absorption spectra except for the lowest energy transition A. As the first absorption band corresponds to the pseudo ( $\pi, \pi^*$ ) transition due to intramolecular hydrogen bond, we could not obtain satisfactory results by MO calculations at an INDO/S–CI level. The MO calculations show that transition C lies close in energy to transition D in NTR, while in NPR transitions C and D are far apart. This is consistent with the fact that the third absorption band is broadened in NPR compared with NTR.

Fig. 3 shows molecular orbitals of NTR and NPR obtained by INDO/S–CI calculations. Based on these orbitals, CI expansions of the wave

functions for the transitions (A–D) are given by the following equations:

## NTR

$$\phi(A) = 0.79\chi(1-1) + 0.33\chi(1-2), \quad (1)$$

$$\phi(B) = -0.59\chi(2-1) + 0.52\chi(1-1) - 0.47\chi(1-2), \quad (2)$$

$$\phi(C) = 0.37\chi(5-1) - 0.51\chi(1-2) + 0.44\chi(1-3), \quad (3)$$

$$\phi(D) = -0.37\chi(5-1) - 0.56\chi(1-2) - 0.36\chi(1-3), \quad (4)$$

## NPR

$$\phi(A) = -0.75\chi(1-1) + 0.39\chi(1-2), \quad (5)$$

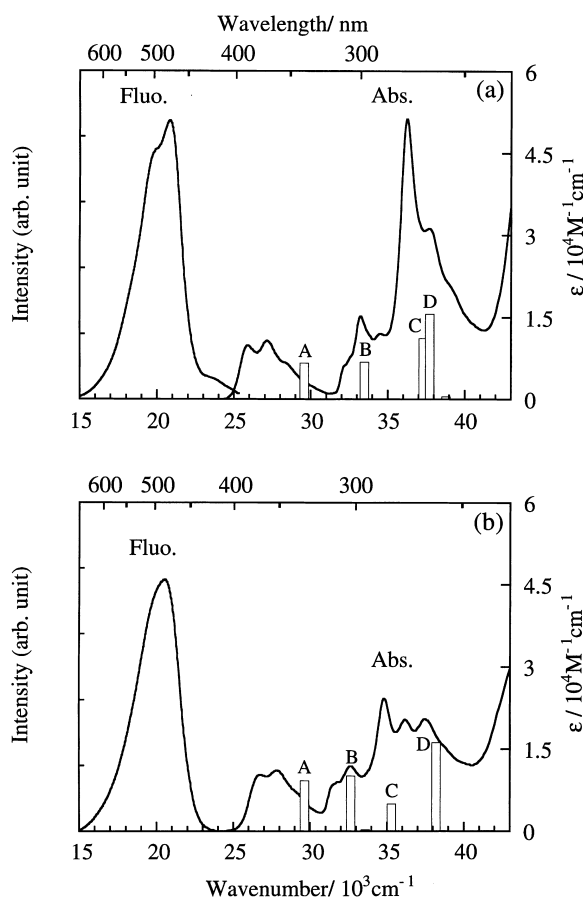


Fig. 2. Absorption and fluorescence spectra, and calculated oscillator strengths for the  $S_n \leftarrow S_0$  transitions of (a) NTR and (b) NPR in MCH at 293 K. The calculated values for the oscillator strength are 0.24, 0.24, 0.39, and 0.55 for transitions A–D of NTR, and 0.30, 0.33, 0.16, and 0.53 for transitions A–D of NPR.

$$\begin{aligned} \phi(B) = & 0.63\chi(2-1) - 0.50\chi(1-1) \\ & - 0.34\chi(1-2), \end{aligned} \quad (6)$$

$$\begin{aligned} \phi(C) = & 0.46\chi(3-1) + 0.60\chi(1-2) \\ & - 0.28\chi(1-3), \end{aligned} \quad (7)$$

$$\begin{aligned} \phi(D) = & 0.39\chi(3-1) - 0.51\chi(1-2) \\ & + 0.42\chi(1-4), \end{aligned} \quad (8)$$

where  $\chi(x-y)$  denotes the one-electron transition from an occupied orbital  $x$  to an unoccupied or-

bital  $-y$ . The CI expansions for transitions A and B of NTR are similar to those of NPR, which is consistent with the similarity between the lowest two absorption bands of NTR and NPR. The differences in shape and intensity of the third absorption band for NTR and NPR would be associated with the differences in the CI expansions for transitions C and D of NTR and NPR. It should be noted here that the first absorption band corresponds mainly to the LUMO $\leftarrow$ HOMO transition which has intramolecular charge transfer character from the naphthalene moiety to the heteroaromatic ring both for NTR and NPR. This intramolecular charge transfer in the  $S_1$  state of NTR and NPR would facilitate ESIPT because of an increase of the acidity of OH group and the basicity of the nitrogen atom in the heteroaromatic ring.

In Fig. 2, moderately large Stokes-shifted fluorescences can be seen for both compounds. The fluorescence spectra have no mirror image relationship with respect to the first absorption band. The fluorescence excitation spectra taken at the fluorescence maxima coincided well with the corresponding absorption spectra. These observations are indicative of the occurrence of ESIPT in NTR [24] and NPR, which is also confirmed from transient absorption measurements as described below. The Stokes shift ( $\Delta\bar{\nu} = 7300 \text{ cm}^{-1}$ ) observed for NPR is greater than that ( $\Delta\bar{\nu} = 6400 \text{ cm}^{-1}$ ) of NTR. These differences can be attributed to an increase in the stabilization energy accompanying ESIPT in NPR (see Section 3.5).

### 3.3. *Cis-trans isomerization following ESPIT of NTR and NPR*

Fig. 4(a) shows the transient absorption spectra obtained by 355 nm laser photolysis of NPR in degassed MCH at 293 K. A broad absorption band around 470 nm is seen in addition to ground-state bleaching around 360 nm. The recovery of the parent enol molecule is found to occur with a decay of the transient at 470 nm. A remarkable feature is that the transient absorption band at 470 nm is not quenched by dissolved oxygen, indicating the transient to be a ground-state species. As an NPR anion produced by proton ejection of

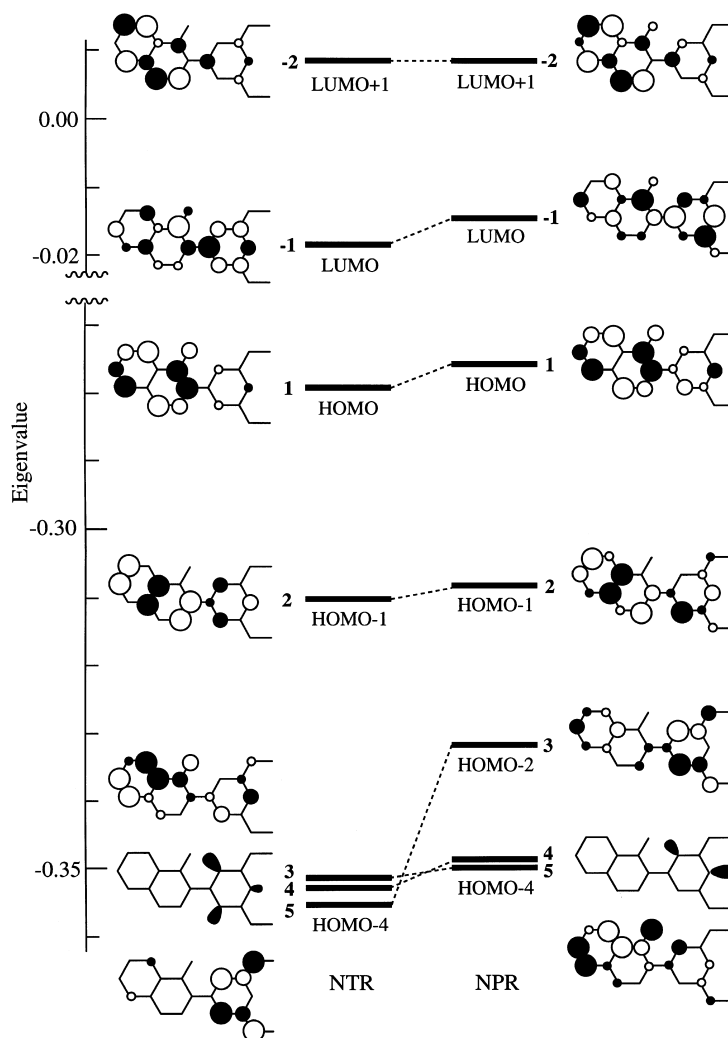


Fig. 3. Molecular orbitals for the enol form of NTR and NPR.

NPR upon laser excitation would be a possible candidate for such a transient, we compared the transient absorption spectra in Fig. 4(a) with the difference absorption spectra obtained by subtracting a steady-state absorption spectrum of NPR in EtOH from the absorption spectrum of NPR in a  $10^{-2}$  M KOH/EtOH solution. However, an agreement in the spectral profiles was not obtained.

The transient absorption spectra of NPR depended strongly on environment as shown in Fig. 4. In polystyrene (PS) films at 293 K, the

transient absorption spectra taken by 355 nm laser photolysis of NPR consist, almost exclusively, of the  $T_n \leftarrow T_1$  absorption bands, and the 470 nm band due to the keto form almost disappears. This indicates that large structural changes are included in the course of the formation of the long-lived transient. In general, the ESIPT process does not subject solvent-viscosity effects; therefore, the structural change would occur after the ESIPT. From these facts, the transient at 470 nm can be attributed to the *trans*-keto tautomer ( $^1K_{tr}$ ) produced by *cis*–*trans* isomerization of the *cis*-keto



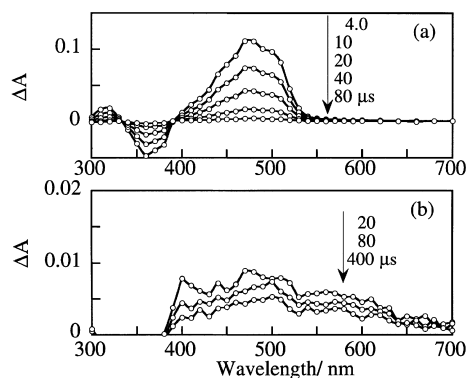


Fig. 4. (a) Transient absorption spectra obtained by 355 nm laser photolysis of NPR in MCH at 293 K. (b) Transient absorption spectra obtained by 355 nm laser photolysis of NPR in PS films at 293 K.

tautomer ( $^1K_{cis}^*$ ) following ESIPT as in the case of NTR. Hence, similar relaxation pathways including ESIPT followed by *cis*–*trans* isomerization can be seen both for NTR and NPR as shown in Scheme 2. The increase in the  $T_n \leftarrow T_1$  absorption intensity relative to that of the keto form in PS film suggests that the formation of the keto form competes with intersystem crossing to the triplet state.

### 3.4. Temperature effects on the photorelaxation properties of NTR and NPR

Fig. 5 shows plots of the initial absorbance ratio ( $\Delta A(T)/\Delta A(293\text{ K})$ ) measured at the transient absorption maxima (450 and 470 nm for NTR and NPR, respectively), the relative fluorescence quantum yield ( $\Phi_f(T)/\Phi_f(77\text{ K})$ ), and the relative fluorescence lifetime ( $\tau_f(T)/\tau_f(77\text{ K})$ ) of NTR and NPR in 3MP as a function of  $T^{-1}$ . Here the  $\Delta A(T)$  value is proportional to the *trans*-keto formation yield, and the value of  $\Delta A(T)/\Delta A(293\text{ K})$  corresponds to the relative yield of the *trans*-keto form, normalized at 293 K. It can be seen that the relative formation yield of the *trans*-keto form decreases with decreasing temperature. In contrast, the relative fluorescence lifetime and fluorescence quantum yield increase with a decrease in temperature, and become almost temperature-independent below  $\sim 125$  and  $\sim 143\text{ K}$  for NTR and NPR, respectively. The significant increases in fluorescence lifetime and quantum yield while

decreasing the keto formation yield is also a manifestation of the *cis*–*trans* isomerization reaction [43,44] following ESIPT. Similar temperature effects have also been reported for other ESIPT followed by *cis*–*trans* isomerization systems, 2-(2'-hydroxyphenyl)-benzothiazole [27] and 2-(2'-hydroxyphenyl)-3-H-indole [28].

On the basis of Scheme 2, the observed fluorescence quantum yield  $\Phi_f$  can be written as

$$\begin{aligned}\Phi_f &= \Phi_{PT}\phi_f \\ &= \Phi_{PT} \frac{k_f}{k_f + k_d + k_{iso}} \\ &= \Phi_{PT}k_f\tau_f,\end{aligned}\quad (9)$$

where  $\Phi_{PT}$  and  $\phi_f$ , respectively, are the quantum yield of intramolecular proton transfer from the *cis*-enol form to the *cis*-keto form ( $^1E_{cis}^* \rightarrow ^1K_{cis}^*$ ) and the fluorescence quantum efficiency of  $^1K_{cis}^*$ ,

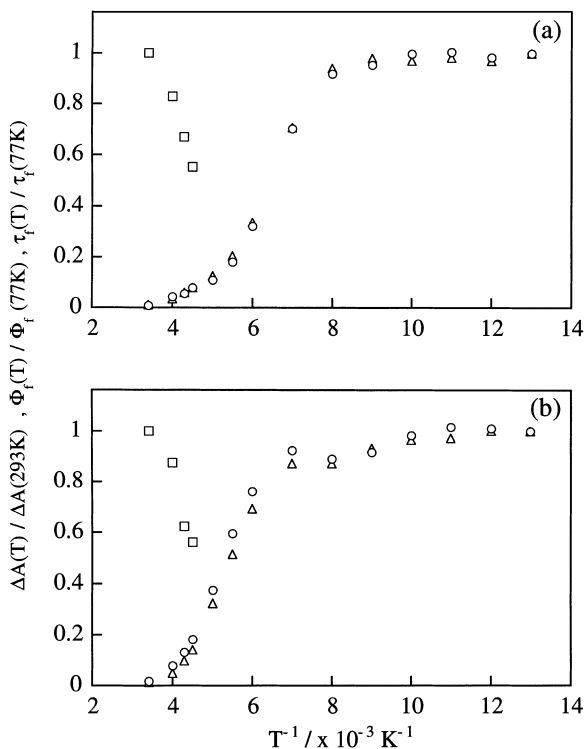


Fig. 5. Plots of the initial absorbance ratio  $\Delta A(T)/\Delta A(293\text{ K})$  ( $\square$ ), fluorescence quantum yield ratio  $\Phi_f(T)/\Phi_f(77\text{ K})$  ( $\triangle$ ), and fluorescence lifetime ratio  $\tau_f(T)/\tau_f(77\text{ K})$  ( $\circ$ ) of (a) NTR and (b) NPR in 3MP as a function of  $T^{-1}$ .

and  $k_f$ ,  $k_{iso}$ , and  $k_d$  are the rate constants for fluorescence, *cis*–*trans* isomerization, and nonradiative deactivation process (except for the *cis*–*trans* isomerization), respectively. From Eq. (9), one can examine the temperature dependence of the ESIPT process. We calculated the  $\Phi_f/\tau_f$  value for each temperature from the data in Fig. 5, and obtained almost constant values for the whole temperature range investigated. Since the  $k_f$  value can be assumed to be insensitive to temperature change, the value of  $\Phi_{PT}$  is found to be independent of temperature. These observations show that the ESIPT processes of NTR and NPR have no potential barrier, and that there are no nonradiative processes competing with intramolecular proton transfer from the  $S_1$  state of the parent *cis*-enol form ( ${}^1E_{cis}^*$ ) probably due to the ultra-fast nature of ESIPT processes in NTR and NPR. From these results, the value of  $\Phi_{PT}$  can be assumed to be unity, and therefore  $\Phi_f/\tau_f$  corresponds to  $k_f$ . The  $k_f$  values are summarized in Table 1 together with the  $\Phi_f$  and  $\tau_f$  values at 293 and 77 K. At 293 K, the  $\Phi_f$  and  $\tau_f$  values of NTR and NPR are very small in 3MP, on the contrary the  $\tau_f$  values of NTR and NPR in PS films are much larger than those in 3MP. These results indicate that the main deactivation pathway from the  $S_1$  state of the *cis*-keto form in fluid media at room temperature is the *cis*–*trans* isomerization which requires large amplitude motions.

On the basis of Scheme 2, the nonradiative deactivation rate  $k_{nr}(T)$  of the  ${}^1K_{cis}^*$  and the quantum yield  $\Phi_{iso}(T)$  for *cis*–*trans* isomerization ( ${}^1K_{cis}^* \rightarrow {}^1K_{tr}$ ) at temperature  $T$  can be written as

$$k_{nr}(T) = k_{iso}(T) + k_d(T) \\ = \{\tau_f(T)\}^{-1} - \{\tau_f(77\text{ K})\}^{-1}, \quad (10)$$

$$\Phi_{iso}(T) = \Phi_{PT} \frac{k_{nr}(T) - k_d(T)}{\{\tau_f(77\text{ K})\}^{-1} + k_{nr}(T)} \\ = C\Phi_{PT}\Delta A(T), \quad (11)$$

where  $k_{iso}(T)$  and  $k_d(T)$  denote the *cis*–*trans* isomerization rate and the temperature-dependent nonradiative deactivation rate other than *cis*–*trans* isomerization, and  $\tau_f(77\text{ K})$  is the fluorescence lifetime at 77 K. Since the initial absorbance  $\Delta A(T)$  of  ${}^1K_{tr}$  observed at 450 nm (for NTR) or 470 nm (for NPR) should be proportional to the isomerization yield  $\Phi_{iso}(T)$ , the relation in Eq. (11) can be obtained. From Eq. (10), one can calculate the  $k_{nr}(T)$  value from those of  $\tau_f(T)$  and  $\tau_f(77\text{ K})$ . If the  $k_d(T)$  value is negligibly small, the value of  $\Phi_{iso}(T)$  is obtained from Eq. (11) based on the calculated value of  $k_{nr}(T)$  because  $\Phi_{PT}$  can be assumed to be unity. Therefore, if  $k_d(T)$  is negligible, the ratio of the isomerization yields at temperatures  $T$  and 293 K should be equal to that of the initial absorbances at temperatures  $T$  and 293 K. Table 2 shows the calculated value of  $\Phi_{iso}(T)/\Phi_{iso}(293\text{ K})$  based on Eq. (11) and the ratio of the observed initial absorbance,  $\Delta A(T)/\Delta A(293\text{ K})$ . It can be seen from Table 2 that the calculated values of  $\Phi_{iso}(T)/\Phi_{iso}(293\text{ K})$  tend to become larger than  $\Delta A(T)/\Delta A(293\text{ K})$  at lower temperatures both for NTR and NPR. These indicate that in addition to the *cis*–*trans* isomerization, another temperature-dependent nonradiative deactivation process such as internal conversion is involved in the relaxation processes of  ${}^1K_{cis}^*$ . The involvement of nonradiative deactivation via an  $(n,\pi^*)$  excited state competing with *cis*–*trans* isomerization following ESIPT has been reported for 2-(2'-hydroxyphenyl)pyridine [42]. The nonradiative decay process, which is induced by out-of-plane bending and/or

Table 1  
Photophysical properties of NTR and NPR in 3MP and PS films at 293 and 77 K

Sample	$\Phi_f$		$\tau_f$ (ns)			$k_f$ ( $s^{-1}$ ) <sup>a</sup>
	293 K <sup>a</sup>	77 K <sup>a</sup>	293 K <sup>a</sup>	293 K <sup>b</sup>	77 K <sup>a</sup>	
NTR	$6.4 \times 10^{-3}$	0.57	0.053	1.7 (24%) 4.4 (76%)	5.9	$9.7 \times 10^7$
NPR	$4.4 \times 10^{-3}$	0.33	0.080	1.4 (32%) 3.3 (68%)	4.7	$7.0 \times 10^7$

<sup>a</sup> In 3MP.

<sup>b</sup> In PS films, two components were observed.

Table 2

Initial  $\Delta A$  ratio and calculated  $\Phi_{\text{iso}}$  ratio for NTR and NPR<sup>a</sup>

Sample		293 K	250 K	233 K
NTR	$\Delta A(T)/\Delta A(293 \text{ K})^b$	1.0	0.76	0.59
	$\Phi_{\text{iso}}(T)/\Phi_{\text{iso}}(293 \text{ K})^c$	1.0	0.97	0.95
NPR	$\Delta A(T)/\Delta A(293 \text{ K})^b$	1.0	0.81	0.56
	$\Phi_{\text{iso}}(T)/\Phi_{\text{iso}}(293 \text{ K})^c$	1.0	0.94	0.87

<sup>a</sup> Since at temperatures below  $\sim 220 \text{ K}$ , precipitation of the solute occurred in sample solutions in the transient absorption measurements, the values of  $\Delta A(T)/\Delta A(293 \text{ K})$  were determined above 233 K.

<sup>b</sup> Absorbances at lower temperatures were corrected for solvent contraction.

<sup>c</sup> Calculated values based on Eq. (11), assuming that  $k_d(T)$  was negligible.

torsional motion involving the carbonyl group, is a possible candidate for the nonradiative process [45,46].

In order to evaluate the activation energy for the temperature-dependent nonradiative deactivation process, the value of  $\ln(\tau_f(T)^{-1} - \tau_f(77 \text{ K})^{-1})$  was plotted as a function of  $T^{-1}$  as shown in Fig. 6. Linear relations are seen both for NTR and NPR, and the activation energies are obtained to be 12 and 18  $\text{kJ mol}^{-1}$  for NTR and NPR, respectively. As described above, these activation energies involve contribution from not only *cis-trans* isomerization but also from other nonradiative processes. Further, the dynamics of *cis-trans* isomerization usually depend on viscosity and temperature [47–50], so that the activation energy obtained by the plot in Fig. 6 would reflect the effects of both temperature and viscosity.

Viscosity effects on the fluorescence lifetimes of NTR and NPR were examined at 293 K in several alkanes which have different viscosity as shown in Table 3. As the viscosity of the solvent becomes larger (*n*-pentane to *n*-hexadecane), the fluores-

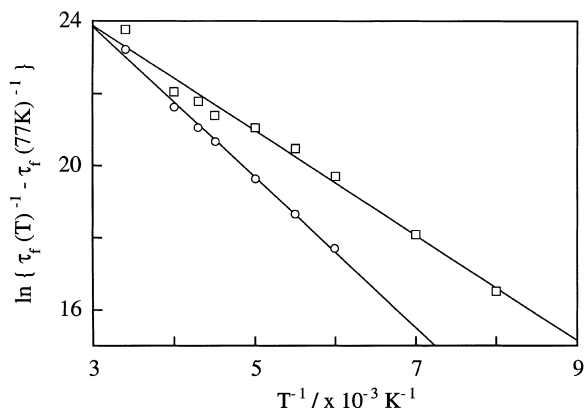


Fig. 6. Arrhenius plots of nonradiative deactivation rates for NTR ( $\square$ ) and NPR ( $\circ$ ) in 3MP.

cence lifetime of NTR and NPR increases significantly. This remarkable viscosity effect on the fluorescence lifetime supports the conclusion that the main deactivation path from the  $S_1$  state of the *cis*-keto form is *cis-trans* isomerization ( $^1K_{cis}^* \rightarrow ^1K_{tr}$ ) which requires large structural changes at ambient temperature. In order to separate the effects of temperature and viscosity, further studies by using a series of *n*-alkanes will be needed in future.

### 3.5. Theoretical considerations for the intramolecular proton transfer cycle of NTR and NPR

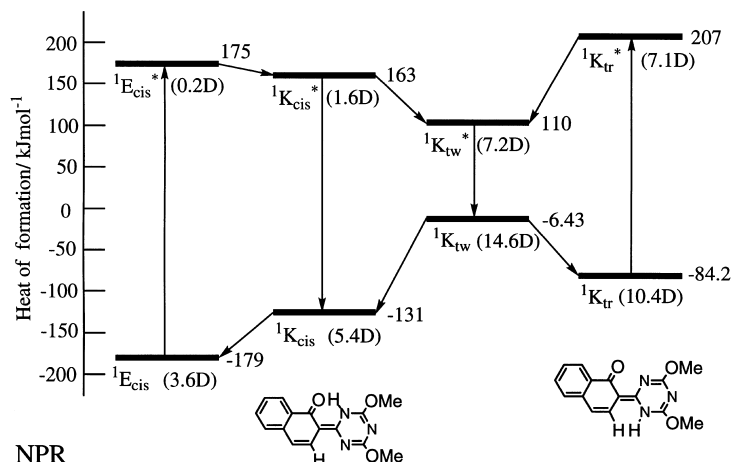
The energy state diagram calculated for the relaxation processes of excited NTR and NPR is shown in Fig. 7. Here the ground-state structures are optimized by the PM3 method, and the energy difference between ground and excited states are derived by the INDO/S-CI calculations. The electronic character of the lowest excited singlet

Table 3

Fluorescence lifetimes of NTR and NPR in various solvents at 293 K

Solvent	Dielectric constant	$\eta/\text{cP}$	$\tau_f$ (NTR)/ps	$\tau_f$ (NPR)/ps
<i>n</i> -Pentane	1.84 [52]	0.234 (20°C) [53]	44	80
3-Methylpentane	1.90 [52]	0.307 (25°C) [52]	53	80
Methylcyclohexane	2.02 [52]	0.734 (20°C) [52]	58	83
<i>n</i> -Hexadecane	2.05 [54]	3.474 (20°C) [53]	172	155
Acetonitrile	37.5 [52]	0.375 (15°C) [52]	22	22

## NTR



## NPR

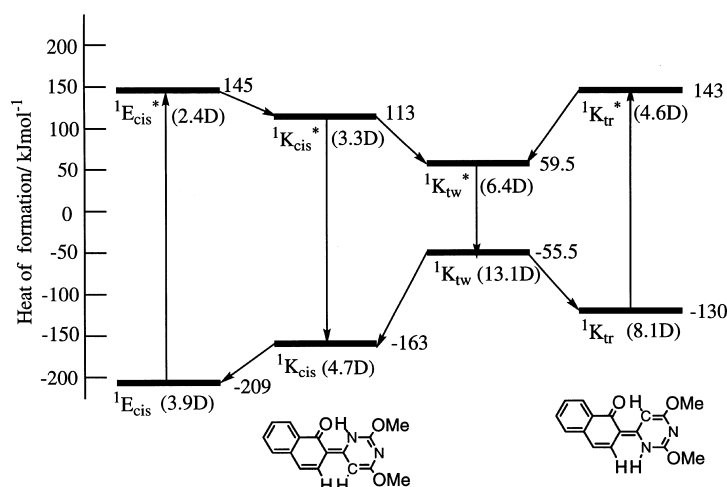


Fig. 7. Calculated energy-state diagram for the intramolecular proton transfer cycle of NTR and NPR. The calculated dipole moment in Debye is shown in parentheses for each state.

state of NTR and NPR is calculated to be  $(\pi, \pi^*)$  both for  ${}^1E_{cis}$  and  ${}^1K_{cis}$ . The energy level of  ${}^1K_{cis}^*$  is located at a slightly lower energy relative to that of  ${}^1E_{cis}^*$  both in NTR and NPR, which is consistent with the occurrence of the ESIP. The stabilization energy ( $22 \text{ kJ mol}^{-1}$ ) accompanying ESIP of NPR is larger than that ( $12 \text{ kJ mol}^{-1}$ ) of NTR, whereas, the destabilization energy in the Franck–Condon ground state is almost the same. This result supports the larger Stokes shift observed for NPR. The  $S_1 \leftarrow S_0$  transition energies for  ${}^1K_{cis}$  and  ${}^1K_{tr}$  of NPR are smaller than those of NTR, which is in agreement with the experimental results in the

fluorescence spectra of  ${}^1K_{cis}^*$  and transient absorption of  ${}^1K_{tr}$ . It is worth noting here that the energy difference between the *cis*-keto form and *trans*-keto form of NPR is much smaller than that of NTR in both ground and excited states. This difference can be explained as follows: In NTR, *cis*–*trans* isomerization ( ${}^1K_{cis}^* \rightarrow {}^1K_{tr}$ ) results in steric hindrance between the *ortho* hydrogen atoms and electronic repulsion between the lone pair of orbitals on the carbonyl oxygen and the nitrogen atom, whereas in NPR, steric hindrance between the *ortho* hydrogen atoms already exists in the *cis*-keto form.

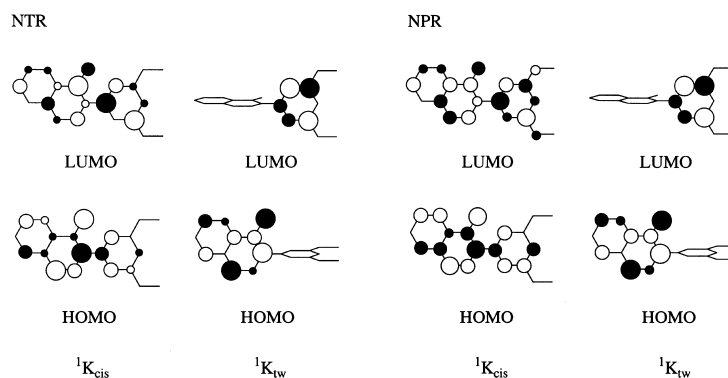


Fig. 8. Molecular orbitals for the  $^1K_{cis}$  and  $^1K_{tw}$  forms of NTR and NPR.

Fig. 8 shows the HOMO and LUMO of  $^1K_{cis}$  and its  $90^\circ$  twisted state ( $^1K_{tw}$ ) for NTR and NPR, calculated by the INDO/S–CI method. As described in Section 3.2, the  $S_1 \leftarrow S_0$  transition of  $^1K_{cis}$  is mainly due to the LUMO  $\leftarrow$  HOMO transition. The LUMO of the  $^1K_{cis}$  form possesses antibonding character on the central C–C bond as shown in Fig. 8, which is favorable for the *cis*–*trans* isomerization in  $^1K_{cis}^*$ . The bond orders of the central C–C bond of  $^1K_{cis}$  of NTR were calculated to be 1.50 and 1.15 for the  $S_0$  and  $S_1$  states, respectively. For the  $^1K_{cis}$  of NPR, the bond orders were obtained to be 1.43 and 1.17 for the  $S_0$  and  $S_1$  states, respectively. The significant decrease in the bond order in the  $S_1$  state is also consistent with the occurrence of *cis*–*trans* isomerization following ESIPT.

The calculated dipole moment of each species is shown in Fig. 7. The  $^1K_{tw}$  form has a large dipole moment (14.6 and 13.1 Debye for NTR and NPR, respectively) originating from intramolecular charge transfer from the heteroaromatic ring to the naphthalene moiety. The electronic transitions to  $^1K_{tw}^*$  cause a charge migration to an opposite direction, leading to a decrease in the dipole moment (7.2 and 6.4 Debye for NTR and NPR, respectively). These dipole moments of  $^1K_{tw}^*$  are still higher than those of  $^1K_{cis}^*$ . The more polar nature of  $^1K_{tw}^*$ , compared to  $^1K_{cis}^*$ , was consistent with the decrease of fluorescence lifetime in going from nonpolar MCH ( $\tau_f = 58$  and 83 ps for NTR and NPR) to polar acetonitrile ( $\tau_f = 22$  ps both for NTR and NPR, Table 3). Potter et al., have re-

ported the role of twisted intramolecular charge-transfer states in the decay of 2-(2'-hydroxyphenyl)benzothiazole following ESIPT [51]. LeGourri rec et al., have suggested the presence of a weakly polar biradicaloid  $^1K_{tw}^*$  state in the course of ESIPT followed by *cis*–*trans* isomerization of 2-(2'-hydroxyphenyl)pyridine [42]. In the *cis*–*trans* isomerization following ESIPT of NTR and NPR, intramolecular charge transfer character is partly retained in  $^1K_{tw}^*$ , thus facilitating the *cis*–*trans* isomerization in polar media.

## References

- [1] A.Z. Weller, *Elektrochemie* 60 (1956) 1144.
- [2] E.M. Kosower, D. Huppert, *Ann. Rev. Phys. Chem.* 37 (1986) 127.
- [3] P.F. Barbara, P.K. Walsh, L.E. Brus, *J. Phys. Chem.* 93 (1989) 29.
- [4] S.J. Formosinho, L.G. Arnaut, *J. Photochem. Photobiol. A* 75 (1993) 21.
- [5] M. Kasha, J. Heldt, D. Gormin, *J. Phys. Chem.* 99 (1995) 7281.
- [6] T. Elsaesser, in: J. Manz, L. W ste (Eds.), *Femtosecond Chemistry*, VCH, Weinheim, 1994.
- [7] S. Nagaoka, J. Kusunoki, T. Fujibuchi, S. Hatakenaka, K. Mukai, U. Nagashima, *J. Photochem. Photobiol. A* 122 (1999) 151.
- [8] J.L. Herek, S. Pedersen, L. Ba ares, A.H. Zewail, *J. Chem. Phys.* 97 (1992) 9046.
- [9] A. Douhal, F. Lahmani, A.H. Zewail, *Chem. Phys.* 207 (1996) 477.
- [10] M. Kasha, *J. Chem. Soc. Faraday Trans.* 82 (1986) 2379.
- [11] A. Douhal, *Science* 276 (1997) 221.
- [12] J. Keck, H.E.A. Kramer, H. Port, T. Hirsch, P. Fischer, G. Rytz, *J. Phys. Chem.* 100 (1996) 14468.

- [13] G. Goeller, J. Rieker, A. Maier, J.J. Stezowski, E. Daltrozzo, M. Neureiter, H. Port, M. Wiechmann, H.E.A. Kramer, *J. Phys. Chem.* 92 (1988) 1452.
- [14] J. Catalán, F. Fabero, M.S. Guijarro, R.M. Claramunt, M.D.S. María, M.C. Foces-Foces, F.H. Cano, J. Elguero, R. Sastre, *J. Am. Chem. Soc.* 112 (1990) 747.
- [15] G.J. Stueber, M. Kieninger, H. Schettler, W. Busch, B. Goeller, J. Franke, H.E.A. Kramer, H. Hoier, S. Henkel, P. Fischer, H. Port, T. Hirsch, G. Rytz, J.-L. Birbaum, *J. Phys. Chem.* 99 (1995) 10097.
- [16] A.U. Khan, M. Kasha, *Proc. Natl. Acad. Sci. USA* 80 (1983) 1767.
- [17] P. Chou, D. McMorro, T.J. Aartsma, M. Kasha, *J. Phys. Chem.* 88 (1984) 4596.
- [18] J. Catalán, J.L.G. de Paz, J.C. del Valle, M. Kasha, *J. Phys. Chem. A* 101 (1997) 5284.
- [19] A. Douhal, F.A. Guerri, M.P. Lillo, A.U. Acuña, *J. Photochem. Photobiol. A* 78 (1994) 127.
- [20] R.W. Munn, *Chem. in Britain* (1984) 518.
- [21] F. Vollmer, W. Rettig, *J. Photochem. Photobiol. A* 95 (1996) 143.
- [22] A. Sytnik, M. Kasha, *Proc. Natl. Acad. Sci. USA* 91 (1994) 8627.
- [23] S. Tobita, M. Yamamoto, N. Kurahayashi, R. Tsukagoshi, Y. Nakamura, H. Shizuka, *J. Phys. Chem. A* 102 (1998) 5206.
- [24] M. Moriyama, Y. Kawakami, S. Tobita, H. Shizuka, *Chem. Phys.* 231 (1998) 205.
- [25] H. Shizuka, M. Machii, Y. Higaki, M. Tanaka, I. Tanaka, *J. Phys. Chem.* 89 (1985) 320.
- [26] W.E. Brewer, M.L. Martinez, P.-T. Chou, *J. Phys. Chem.* 94 (1990) 1915.
- [27] W. Al-Soufi, K.H. Grellmann, B. Nickel, *Chem. Phys. Lett.* 174 (1990) 609.
- [28] J.S. Stephan, C.R. Rodríguez, K.H. Grellmann, K.A. Zachariasse, *Chem. Phys.* 186 (1994) 435.
- [29] J.S. Stephan, K.H. Grellmann, *J. Phys. Chem.* 99 (1995) 10066.
- [30] V. Guallar, M. Moreno, J.M. Lluch, F.A. Guerri, A. Douhal, *J. Phys. Chem.* 100 (1996) 19789.
- [31] K. Tokumura, O. Oyama, H. Mukaihata, M. Itoh, *J. Phys. Chem. A* 101 (1997) 1419.
- [32] S. Mitra, N. Tamai, *Chem. Phys. Lett.* 282 (1998) 391.
- [33] C.R. Mateo, A. Douhal, *Proc. Natl. Acad. Sci. USA* 95 (1998) 7245.
- [34] H. Shizuka, T. Kanai, T. Morita, Y. Ohoto, K. Matsui, *Tetrahedron* 27 (1971) 4021.
- [35] J.T. Thurston, J.R. Dudley, D.W. Kaiser, I. Hechenbleikner, F.C. Schaefer, D. Holm-Hansen, *J. Am. Chem. Soc.* 73 (1951) 2981.
- [36] W.H. Melhuish, *J. Phys. Chem.* 65 (1961) 229.
- [37] J.J.P. Stewart, *J. Comput. Chem.* 10 (1989) 209, 221.
- [38] C.J. Pouchert, J. Behnke, *The Aldrich Library of <sup>13</sup>C and <sup>1</sup>H FT NMR Spectra*, First ed., Aldrich Chemical Company, WI, 1993.
- [39] T. Schaefer, *J. Phys. Chem.* 79 (1975) 1888.
- [40] Y. Takei, T. Yamaguchi, Y. Osamura, K. Fuke, K. Kaya, *J. Phys. Chem.* 92 (1988) 577.
- [41] F. Momicchioli, M.C. Bruni, I. Baraldi, *J. Phys. Chem.* 76 (1972) 3983.
- [42] D. LeGourriérec, V. Kharlanov, R.G. Brown, W. Rettig, *J. Photochem. Photobiol. A* 117 (1998) 209.
- [43] J. Saltiel, J.L. Charlton, in: P. de Mayo (Ed), *Rearrangements in Ground and Excited States*, vol. 3, Academic Press, New York, 1980.
- [44] M. Sumitani, N. Nakashima, K. Yoshihara, S. Nagakura, *Chem. Phys. Lett.* 51 (1977) 183.
- [45] S. Nagaoka, N. Hirota, M. Sumitani, K. Yoshihara, E.L. Kochany, H. Iwamura, *J. Am. Chem. Soc.* 106 (1984) 6913.
- [46] S.R. Flom, P.F. Barbara, *J. Phys. Chem.* 89 (1985) 4489.
- [47] D.H. Waldeck, *Chem. Rev.* 91 (1991) 415.
- [48] Y.-P. Sun, J. Saltiel, N.S. Park, E.A. Hoburg, D.H. Waldeck, *J. Phys. Chem.* 95 (1991) 10336.
- [49] A.C. Benniston, A. Harriman, *J. Chem. Soc. Faraday Trans.* 90 (1994) 2627.
- [50] A. Harriman, *J. Photochem. Photobiol. A* 65 (1992) 79.
- [51] C.A.S. Potter, R.G. Brown, F. Vollmer, W. Rettig, *J. Chem. Soc. Faraday Trans.* 90 (1994) 59.
- [52] J.A. Riddick, W.B. Bunger, *Organic Solvents*, Third ed., Wiley Interscience, New York, 1970.
- [53] D.E. Gray, *American Institute of Physics Handbook*, Third ed., McGraw-Hill, New York, 1982.
- [54] D.R. Lide, *CRC Handbook of Chemistry and Physics*, 78th ed., CRC Press, New York, 1997.