Dimerization by Hydrogen Bonding and Photochemical Properties of Dipyridone

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Received: January 15, 2003; In Final Form: July 14, 2003

The ground state and the excited state of dipyridones are studied by various spectroscopic methods: absorption spectra, fluorescence spectra, time resolved fluorescence measurements, and nanosecond transient absorption spectra. In the system of 3-[(1,6-dihydro-6-oxo-2-pyridinyl)ethynyl]-2(1H)-pyridinone, the absorption and fluorescence spectra are assigned to the keto form in comparison to model compounds. The absorption spectra and the emission decay depend on the concentration in chloroform solution whereas they do not in methanol. This difference can be explained by the formation of a hydrogen-bonded dimer only in chloroform solution. The excited singlet states of the monomer and the dimer have different lifetimes even though they have same keto form. The origin of the fast nonradiative relaxation processes in the dimer system is discussed with the results of transient absorption spectroscopy. As an application of the formation of dimers by hydrogen bonding, the effect of the dimerization on photochemical isomerization is demonstrated in the system of 3-[2-(1,6-dihydro-6-oxo-2-pyridinyl)ehenyl]2(1H)-pyridinone.

1. Introduction

Hydrogen-bonded compounds have received considerable attention with a view toward application to material science, biological systems, and so forth. As for intermolecular hydrogen bonding compounds, DNA is very famous for its double helical structure using hydrogen bonding and other interactions. Many scientists have studied the excited-state behavior of intermolecular hydrogen bonding compounds as a prototype for the DNA misprinting system caused by photoirradiation. 7-Azaindole (7AI) is one of the most famous systems to form a hydrogen-bonded dimer in nonpolar solvent and produces excited-state double proton transfer (ESDPT).[1−3] In addition, its variable fluorescence properties have been studied.[4−8] Other compounds, such as purine, adenine, and 4-azabenzimidazole derivatives, have been studied as intermolecular hydrogen bonding compounds.[9−13]

The formation of the quadruple hydrogen-bonded dimer in 3-[(1,6-dihydro-6-oxo-2-pyridinyl)ethynyl]-2(1H)-pyridinone (**1)** has been reported by Wuest et al.[14] and is shown in Scheme 1. The photochemical character of compound **1** is interesting from the point of view of the investigation of the relationship between the hydrogen bonding and the dynamic process of the excited states. In the present paper, we have studied the association behavior by hydrogen bonding and the character of the photoexcited states by time-resolved fluorescence experiments and the transient absorption of **1** and its model compounds.

Even as a single molecule, **1** has the possibility to take keto and enol forms in the ground state and the excited states. Therefore, one of the essential problems is the determination of the structure of the excited states. To solve this problem, we prepared model compounds of keto and enol forms (compounds **2** and **3**, respectively) and compared the spectroscopic data. Another interesting point is the effect of solvents on hydrogen bonding. In the present paper, we have studied the behaviors of the present compounds both in chloroform and methanol solutions and have clarified that dimer formation can be controlled by changing solvents. In addition, we demonstrate a drastic change in the photochemical properties of 3-[2-(1,6-dihydro-6-oxo-2-pyridinyl)ehenyl]2(1H)-pyridinone (**4**) in Scheme 2 as an application of controlling hydrogen bonding by selecting different solvents.

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2. Experiments

Materials. Solvents chloroform and methanol are spectroscopic grade (Kanto Chem. Co. and Wako Chem. Co.) and were used as received. Compounds **1** and **2** were synthesized according to the literature.[14] Compound **3** was synthesized according to the procedure to obtain such methylated compounds.[18] Compound **4** was prepared by the hydrogenation of **3** with lithium alminium hydride followed by hydrolysis.

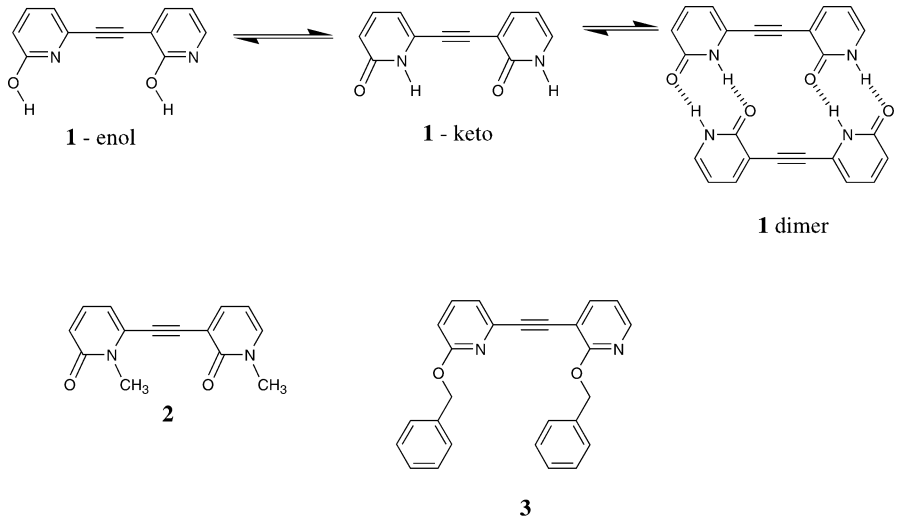
Equipment. UV−vis absorption spectra were measured with a JASCO Ubest-55 spectrophotometer. Sample cells with path length of 1 mm, 1 cm, and 10 cm were used to measure the concentration dependence of **1**. Fluorescence spectra were measured with a Hitachi F-4000 spectrofluorometer. Transient absorption spectra were measured with equipment previously reported.[19] Fluorescence lifetimes were measured with a picosecond mode-locked YAG laser (Continuum PY61-10, 40-ps fwhm: Third Harmonics 355 nm) as an excitation light source and a streak scope (Hamamatsu C4334, Hamamatsu C1808) connected to a monochromator (Jobin Evon CP200). Every data analysis and fitting was performed with an original software program (Igor Pro, Wavemetrics, Inc.).

3. Results and Discussion

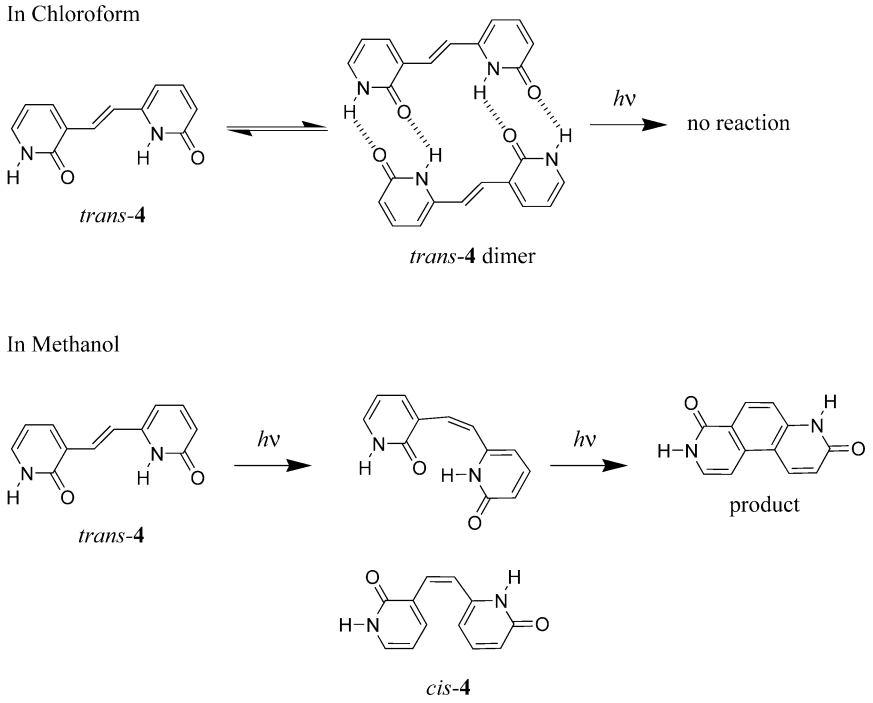
3.1. Ethynyl-Bridged Dipyridone (1). *(a) Absorption Spectra.* The absorption spectra of compounds **1**−**3** are shown in Figure 1. The absorption of **1** has been observed from 350−400 nm both in methanol and chloroform as shown in Figure 1a. The absorption spectra of **1** are similar to those observed

10.1021/jp034097y CCC: $25.00
Published on Web 10/31/2003

SCHEME 1: Possible Keto and Enol Structures and Dimerization of Ethynyl-Bridged Dipyridone 1 and Structures of the Model Compound of Keto Form 2 and Enol Form 3



SCHEME 2: Proposed Reaction Scheme of the Photochemical Reaction of Ethenyl-Bridged Dipyridone 4 in Chloroform and Methanol



for the model compound of the keto form (**2**) as shown in Figure 1a and b. In contrast, the model compound of the enol form (**3**) has an absorption band from 300−350 nm both in methanol and chloroform as shown in Figure 1c.

The wavelengths of the absorption peaks of compounds **1**−**3** are summarized in Table 1. The spectra of **1** are similar to the spectrum of model compound **2**. Therefore, **1** exists as the keto form in the ground state. This result contrasts with the fact that 2-pyridone takes the enol form in nonpolar solvent at low concentration.[16]

The absorption spectra of **1** observed at various concentrations in chloroform and methanol are shown in Figure 2a and b. Both of the spectra are presented on the scale of the molar extinction coefficient, ϵ_{obs}. The spectral profile and ϵ_{obs} in methanol do not depend on the concentration as shown in Figure 2a. The linear relationship of the absorbance to the applied concentration shows the accuracy of our experimental procedure for various concentrations. In contrast to this, the spectra in chloroform have a clear dependence on the concentration as shown in Figure 2b. At higher concentration, the spectrum has shifted to lower wavelength, and its extinction coefficient in the range of 325−425 nm has changed. Two isosbestic points at 380 and 400 nm can be recognized. These features of the absorption spectra indicate that the molecule **1** produces a dimer in chloroform and not in methanol. This fact can be rationalized if the hydrogen bond plays an important role in the association of a couple of molecules. Here we present the structure of the dimer of **1** as the hydrogen bonded species as shown in Scheme 1.

The averaged extinction coefficients in the wavelength range of 347−380 nm have been plotted by various concentrations of **1** and are shown in Figure 2c. To analyze the association feature of **1** in chloroform, we have used a simple association model in which the association constant K_a for the

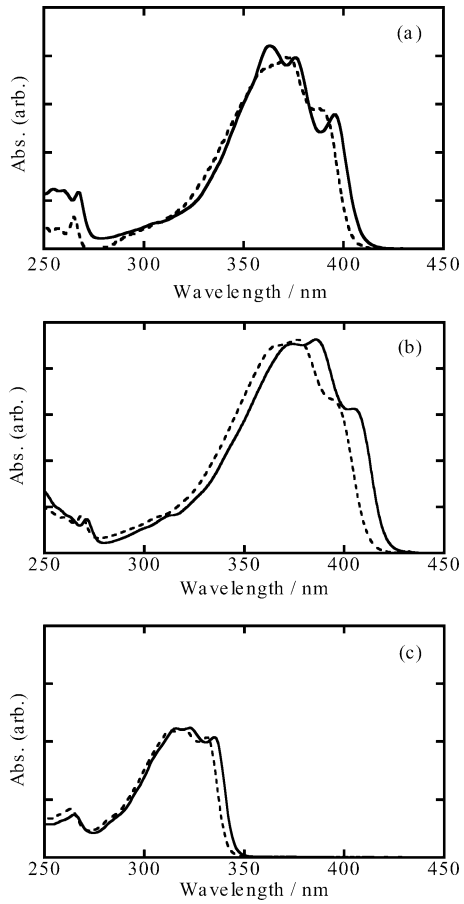


Figure 1. Absorption spectra of **1** (a), **2** (b), and **3** (c) in methanol (- - -) and chloroform (−).

formation of the dimer can be expressed by

$$K_a = \frac{[D]}{[M]^2} \tag{1}$$

where M and D represent the concentrations of dimer and monomer, respectively.

The total concentration C can be expressed by

$$C = [M] + 2[D] \tag{2}$$

The observed extinction coefficient ϵ_{obs} can be formulated by the solution of eqs 1 and 2 and can be described by

$$\epsilon_{obs} = \epsilon_M[M] + \epsilon_D[D] = \epsilon_M \cdot \frac{-1 + \sqrt{1 + 8K_aC}}{4K_a} + \epsilon_D \cdot \frac{1 + 4K_aC - \sqrt{1 + 8K_aC}}{8K_a} \tag{3}$$

where ϵ_D and ϵ_M are the molar extinction coefficients for the dimer and monomer, respectively.

The experimental results in Figure 2c can be fit by eq 3, and the association constant K_a was determined to be $(1.4 \pm 0.6) \times 10^5$ M^{-1} by curve fitting. The K_a for **1** obtained here is about 10 times larger than that for 2-pyridone ($\sim 10^4$).[17] The large value of the association constant for **1** can be attributed to quadruple hydrogen bonding.

(b) Fluorescence Spectra. The fluorescence and excitation spectra of **1**−**3** in methanol and chloroform are shown in Figure 3. The fluorescence spectra of **1** have been observed in the range of 400−600 nm in methanol as shown in Figure 3a. The spectra of **1** are similar to those of the model compound of keto form **2** shown in Figure 3b. In contrast to this, the spectra of the model compound of enol form **3** have been observed in the range of 330−450 nm as shown in Figure 3c. The similarity of the fluorescence spectra of **1** and **2** indicates that **1** takes the keto form in the excited singlet state. By the fluorescence and absorption spectra, we conclude that **1** takes the keto form both in the ground state and the excited singlet state. This fact is also supported by the small Stokes shift, which indicates a small adiabatic conformational change in the excited singlet state. We have also studied the fluorescence and excitation spectra in chloroform solution. However, there has been no noticeable spectral change from that in methanol solution except for the quantum yields of the fluorescence.

The emission maxima, the values of singlet energy, and the fluorescence quantum yields, Φ_f, of **1**−**3** in methanol and chloroform solutions are summarized in Table 1. Φ_f of **1** was determined to be 0.32 and 0.093 in methanol and chloroform, respectively. The values of Φ_f in model compound **2** and **3** are about 0.3 and 0.6, respectively, and have a small dependence on both solvents. The large difference in the fluorescence quantum yields of **1** between chloroform and methanol solutions seems to be due to dimer formation in chloroform solution as discussed in the previous section. In methanol, **1** exists as a solvated monomer, and in chloroform, **1** exists as a mixture of the monomer and the hydrogen-bonded dimer. This feature clearly appears in the time-resolved measurements of the fluorescence that is shown in the next section.

(c) Fluorescence Decay. The fluorescence time profiles of **1** in methanol are shown in Figure 4a. The decay curve has been analyzed by a single-exponential function, and the lifetime is 1.6 ns. In methanol, the lifetime does not depend on the concentration as shown on the right side of Figure 4a. However, in chloroform, the fluorescence decay depends on the concentration of **1** as shown in Figure 4b. The decay curves of **1** in chloroform have been analyzed by a double-exponential function, and the lifetimes of long and short components have been determined to be 0.3 and 1.8 ± 0.2 ns, respectively. The short-lifetime component increases with increasing concentration as shown on the right side of Figure 4b. This change in the decay kinetics by concentration happens on a similar scale (10^{-5} M) to the change in the absorption spectra shown in Figure 2. This result indicates that the concentration dependence on both the absorption and fluorescence decay is caused by dimerization with hydrogen bonding.

The fluorescence time profiles of the model compound of the keto form, **2**, in chloroform solution are shown in Figure 4c. The decay curve does not have a concentration dependence, and the lifetime has been determined to be 2.0 ns. Compound **2** does not produce the hydrogen-bonded dimer, in contrast to the fact that compound **1** produces the dimer, as shown by the absorption spectra. Thus, the short-lived component that is observed at higher concentrations of **1** in chloroform solution is due to the hydrogen-bonded dimer. Therefore, the hydrogen-bonded dimer of **1** has a fast nonradiative relaxation pathway. However, we cannot claim that only the hydrogen bonding enhances the nonradiative transitions because the fluorescence of **1** has a long lifetime in the alcohol solution. We conclude that dimerization via hydrogen bonding is essential to the short lifetime of the excited singlet state of **1**. This conclusion implies that the conformational holding to the planar structure by

TABLE 1: Summary of the Absorption and Fluorescence Spectra of Ethynyl-Bridged Dipyridone and Its Model Compounds

	solvent	compound **1**	compound **2**	compound **3**
absorption maxima/nm	MeOH	356, 372, 389	366, 376, 396	313, 320, 331
	$CHCl_3$	366, 377, 395[a]	372, 386, 405	316, 323, 325
fluorescence maxima/nm	MeOH	426	415, 435	346, 359
	$CHCl_3$	436[a]	420, 445	346, 359
singlet energy/kJ mol^{-1}	MeOH	300	296	354
	$CHCl_3$	296[a]	290	350
fluorescence quantum yield[b]	MeOH	0.32	0.33	0.66
	$CHCl_3$	0.093	0.36	0.64

[a] Concentration of the compound was $1-10^{-6}$ M. [b] Concentrations of the compounds were about 10^{-6} M. Except for a and b, the values ido not depend on the concentration in the range of $10^{-4}-10^{-6}$ M.

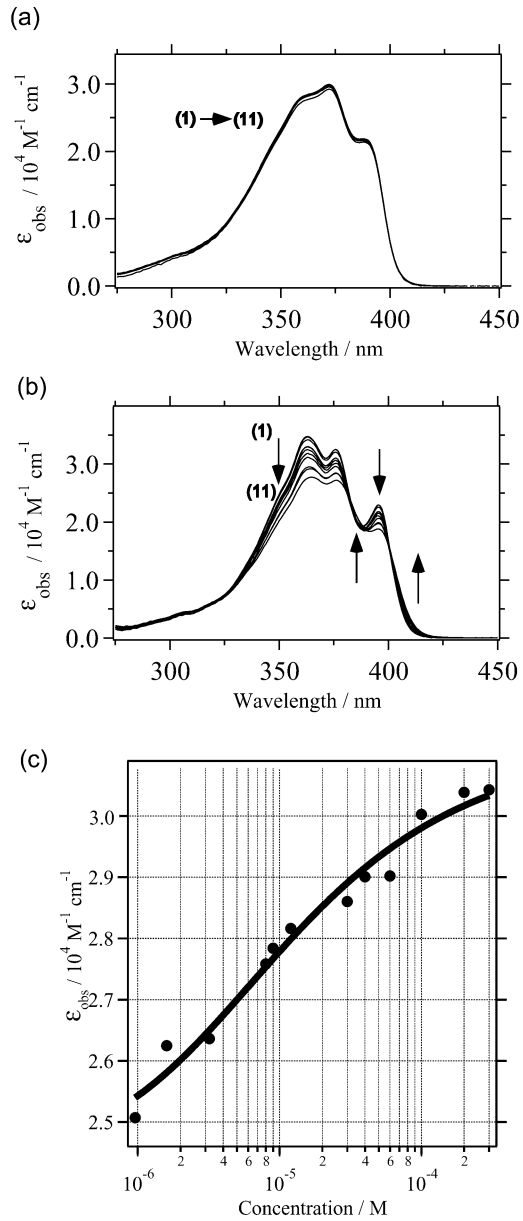


Figure 2. Absorption spectra of **1** in methanol (a), and in chloroform (b). The concentrations of the solutions are (1) 3.0×10^{-4}, (2) 2.0×10^{-4}, (3) 1.0×10^{-4}, (4) 6.0×10^{-5}, (5) 4.0×10^{-5}, (6) 3.0×10^{-5}, (7) 1.2×10^{-5}, (8) 8.0×10^{-6}, (9) 3.2×10^{-6}, (10) 1.6×10^{-6}, and (11) 9.6×10^{-7} M. (c) Concentration dependence of the averaged extinction coefficient in the chloroform solution of **1**. The solid line is theoretical curve obtained by eq 3 with $K_a = 1.4 \times 10^5$ M^{-1}.

hydrogen bonding is one of the important factors for the acceleration of the nonradiative transition process.

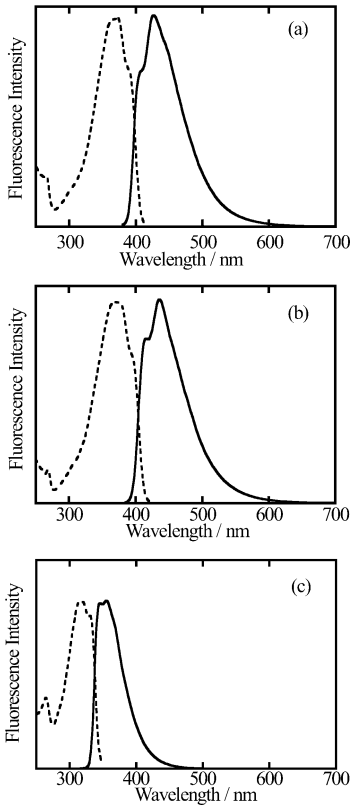


Figure 3. Fluorescence spectra (−) and excitation spectra (- - -). (a) Compound **1** in methanol solution: $\lambda_{ex} = 370$ nm for the fluorescence spectrum, and $\lambda_{em} = 425$ nm for the excitation spectrum. (b) Compound **2** in methanol solution: $\lambda_{ex} = 376$ nm, and $\lambda_{em} = 435$ nm. (c) Compound **3** in methanol solution: $\lambda_{ex} = 290$ nm, and $\lambda_{em} = 400$ nm.

(d) Transient Absorption of Triplet Excited States. Transient absorption spectra of **1**−**3** are shown in Figure 5. All observed absorption bands are assigned to the excited triplet state because they are quenched by oxygen. The T−T absorption of **1** was observed around 440 and 630 nm in methanol (Figure 5a) and decayed with a lifetime of 4.0 μs under an argon atmosphere. This absorption signal was quenched by oxygen with a rate constant of 2.0×10^9 M^{-1} s^{-1}. Similar T−T absorption was observed in chloroform, and its lifetime was 6.4 μs. The spectral shape of **1** is similar to that observed in the model compound of the keto form, **2** (Figure 5b), but is different from that observed in the model compound of the enol form, **3** (Figure 5c). By this, we assign the observed spectrum of **1** to the triplet state of the keto form.

The concentration for the observation of the T−T absorption spectra was 2×10^{-4} M, in which many of the molecules in chloroform are dimers. However, no noticeable difference between chloroform and methanol solutions has been observed

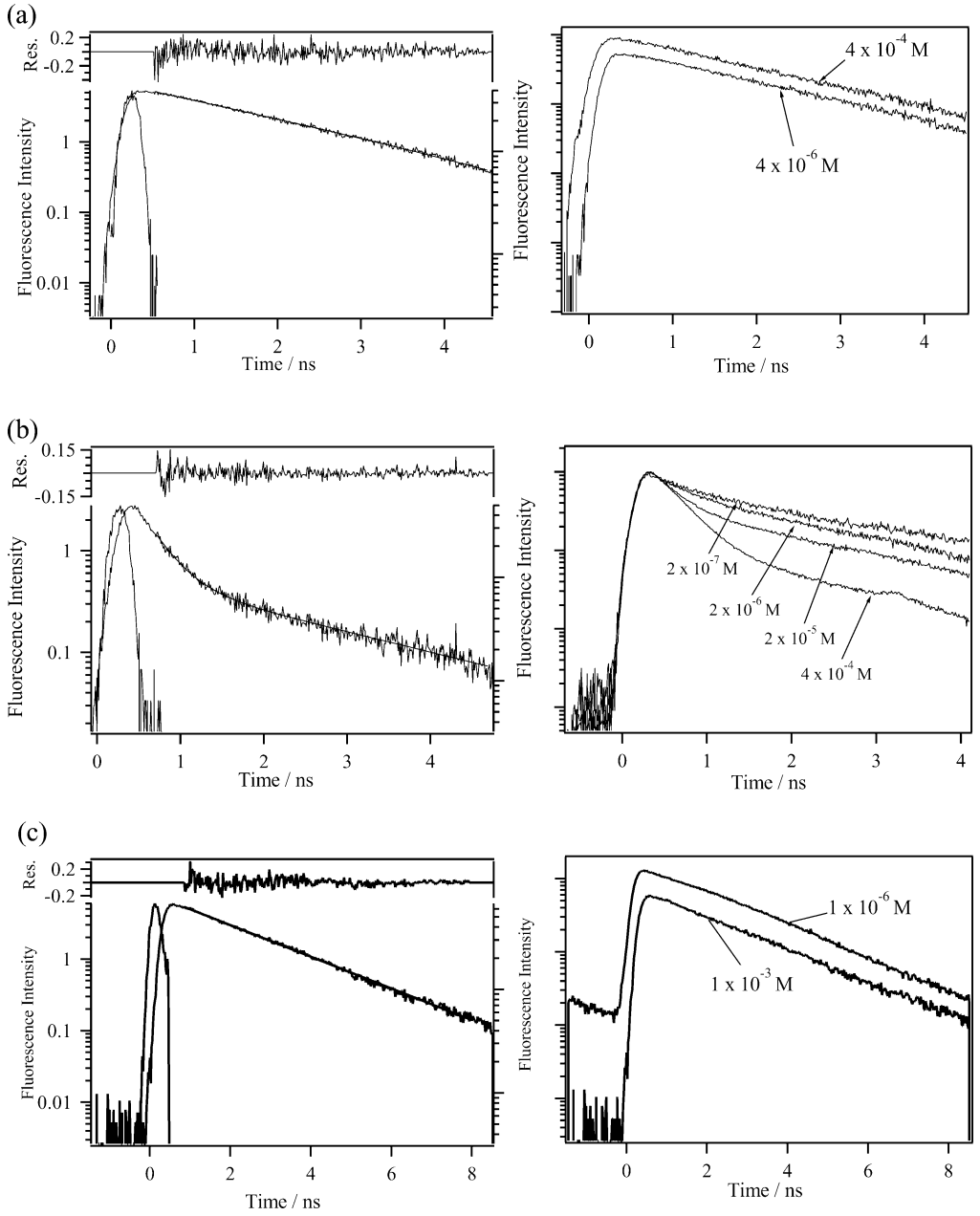


Figure 4. Fluorescence decay curves in the system of ethynyl-bridged dipyridons. (a) Compound **1** in methanol observed at a concentration of 4 $\times$ 10^{-6} M and simulation by convolution with a single-exponential function (left side) and the concentration dependence (right side). (b) Compound **1** in chloroform observed at 4 $\times$ 10^{-4} M and simulation by convolution with a double-exponential function (left side) and concentration dependence (right side). (c) Compound **2** in chloroform observed at 1 $\times$ 10^{-3} M and simulation by convolution with a single-exponential function (right side) and observed at two different concentrations, 1 $\times$ 10^{-6} and 1 $\times$ 10^{-3} M (right side).

with regard to the spectral shape, the absolute intensity, and the lifetime of the T−T absorption. Those results indicate that the character of the triplet excited states has not been affected by the dimerization of **1**. The similar intensity of the T−T absorption spectra also shows that the intersystem crossing (ISC) pathway is not the origin of the fast fluorescence decay kinetics of the dimer.

3.2. Ethenyl-Bridged Dipyridone (4). In this section, we demonstrate an application of the hydrogen-bonded dimer on the photochemical isomerization process. For this purpose, we synthesized a trans ethenyl-bridged dipyridone (*trans*-**4**) as shown in Scheme 2 and studied the photochemical behavior of it.

(a) Absorption Spectra and Chemical Isomerization. Absorption spectra of *trans*-**4** are shown in Figure 6a. The spectra in chloroform and methanol are not different each other and can be assigned to the keto form by the analogy of the results in the system of ethynyl-bridged dipyridone, **1**. The spectra do not have a large dependence on the solvent.

The time evolution of the absorption spectrum of *trans*-**4** under the photoirradiation in chloroform solution is shown in Figure 6b. The spectral shape hardly changed by irradiation. This result means that the *trans*-**4** is stable under light irradiation in chloroform solution. In contrast to this, the absorption spectrum in the methanol solution has been changed by light irradiation as shown in Figure 6c. The absorption band from 350 to 450 nm decreased in accordance with the increasing absorption band at around 320 nm. This feature is characteristic of the photoinduced isomerization from the trans to the cis isomer. However, these changes in the spectra do not have clear isosbestic points. Therefore, the following photochemical reaction process after isomerization to the cis isomer is expected.

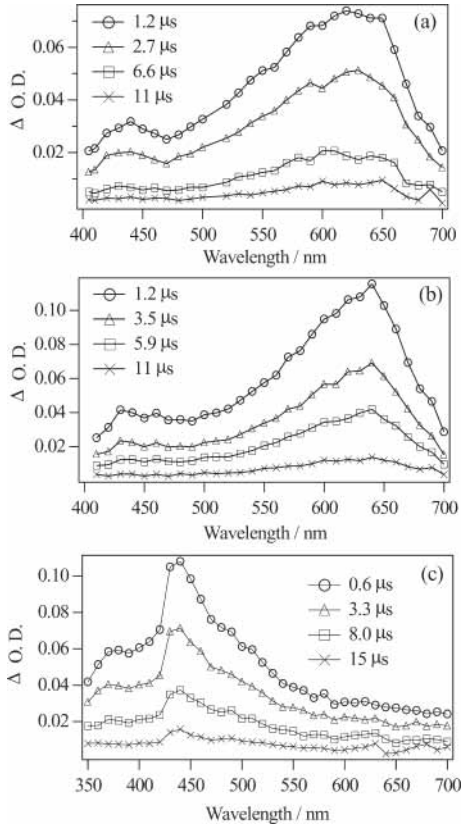


Figure 5. Transient absorption spectra observed by pulse excitation (308 nm) of **1** (a), **2** (b), and **3** (c) in methanol.

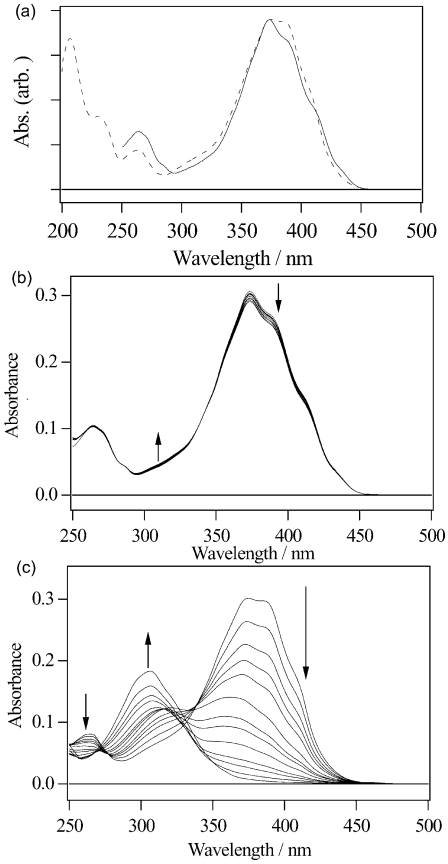


Figure 6. (a) Absorption spectra of *trans*-**4** in methanol (- - -) and chloroform (−). (b) Change in absorption spectra by irradiation with 374-nm light in the chloroform solution of *trans*-**4**. (c) Change in absorption spectra by irradiation with 374-nm light in the methanol solution of *trans*-**4**.

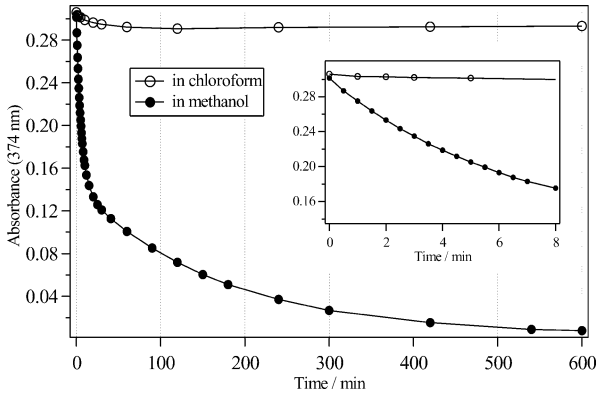


Figure 7. Time evolution of the absorbance observed at 374 nm by irradiation of the light at 374 nm. That on the short time scale is superimposed in the graph.

The time evolution of the absorbance observed at 375 nm is shown in Figure 7. This picture clearly shows the difference in the photochemical behavior of **4** in chloroform and in methanol solutions. The photochemical process in methanol solution has two stages: rapid process within 8 min and slower decay after 8 min. By this, we can expect two steps of the photochemical processes.

The intermediate and the product have been determined by NMR spectra recorded after photoirradiation. The dependence of the spectra on the irradiation time is shown in Figure 8. Before irradiation, the NMR spectrum shown in Figure 8a can be assigned to the trans isomer of **4**. The splitting by $J = 16.4$ Hz observed at $\delta = 7.41$ and 7.57 is characteristic of the olefin peaks of the trans isomers of olefines. One can notice that the olefin peaks of the cis isomer have appeared at $\delta = 6.48$ and 6.82 with a characteristic coupling constant ($J = 12.4$ Hz) after 10 min of irradiation and have disappeared by additional irradiation. After irradiation for 4.5 h, these peaks have disappeared. The time scale of the spectral change is coincident with the two stages of the absorption change in Figure 7. By the results of the NMR analysis, we propose the reaction scheme shown in Scheme 2. The intermediate and the product by irradiation are assigned to the cis isomer of **4** and the cyclized product, respectively. In chloroform solution, photoisomerization does not take place because dimerization by hydrogen bonding stabilizes the trans structure and prevents isomerization to the cis isomer.

(b) Fluorescense Spectra and Decay. The character and dynamics of the excited state of compound **4** are studied by fluorescence spectroscopy. The fluorescence spectra and excitation spectra (not shown) are similar in methanol and chloroform solutions. This result indicates that the ground and the excited singlet states of **4** take the keto form. However, the quantum yield in methanol ($\Phi = 0.036$) is much smaller than that in chloroform ($\Phi = 0.1$). This result is in contrast to the case of compound **1** and indicates that dimerization by hydrogen bonding is not essential to the fast nonradiative relaxation pathway. The small quantum yield of fluorescence emission in methanol is rationalized by the isomerization to the ground state of the cis isomer.

Fluorescence decay curves of *trans*-**4** in methanol and chloroform were fitted by monoexponential functions with lifetimes of 1.0 and 0.4 ns, respectively. It is remarkable that the nonradiative pathway of the excited singlet state is suppressed by hydrogen bonding in chloroform solution. The origin

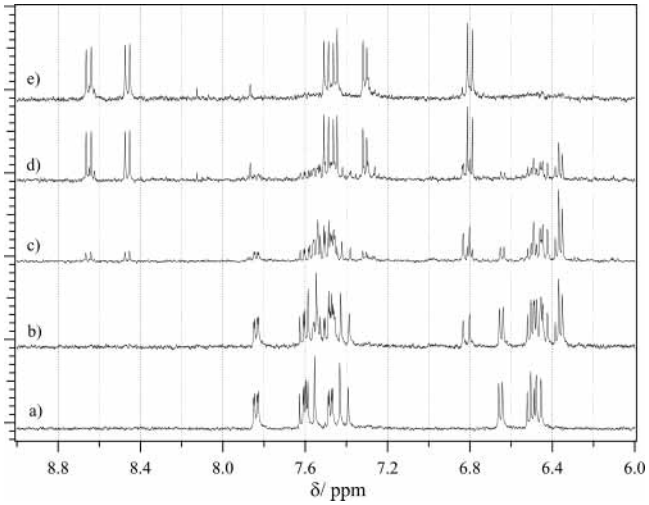


Figure 8. Change in the ^{1}H NMR spectra (400 MHz, CD_3OD) of **4** by light (366 nm) irradiation. NMR spectra are recorded (a) before irradiation and (b) 10, (c) 60, (d) 180, and (e) 270 min after the light irradiation. The assignments of the NMR peaks are as follows. *trans*-**4**: reactant observed before irradiation (a); ^{1}H NMR (400 MHz, CD_3OD): δ 6.47 (d, 1H, $J = 8.8$ Hz), 6.51 (t, 1H, $J = 6.8$ Hz), 6.65 (d, 1H, $J = 6.9$ Hz) 7.41 (d, 1H, $J = 16.4$ Hz), 7.48 (dd, 1H, $J = 6.8$, 1.6 Hz), 7.57 (d, 1H, $J = 16.4$ Hz), 7.61 (dd, 1H, $J = 8.8$, 7.2 Hz), 7.72 (dd, 1H, $J = 7.2$, 1.6 Hz). *cis*-**4**: intermediate observed strongly after 10 min of irradiation (b); ^{1}H NMR (400 MHz, CD_3OD): δ 6.36 (d, 1H, $J = 6.8$ Hz), 6.37 (t, 1H, $J = 6.8$ Hz), 6.44 (d, 1H, $J = 9.2$ Hz), 6.48 (d, 1H, $J = 12.5$ Hz), 6.82 (d, 1H, $J = 12.5$ Hz), 7.47 (dd, 1H, $J = 6.7$, 2.2 Hz), 7.51 (dd, 1H, $J = 9.1$, 6.9 Hz), 7.45 (dd, 1H, $J = 6.9$, 2.2 Hz broad). Cyclized product**:** final product observed after 270 min of irradiation (e); ^{1}H NMR (400 MHz, CD_3OD): δ 6.80 (d, 1H, $J = 9.8$ Hz), 7.31 (d, 1H, $J = 7.4$ Hz), 7.45 (d, 1H, $J = 7.4$ Hz), 7.50 (d, 1H, $J = 9.1$ Hz), 7.87 (s), 8.12 (s), 8.46 (d, 1H, $J = 9.1$ Hz), 8.65 (d, 1H, $J = 9.8$ Hz).

of the nonradiative transition in methanol should be a nonadiabatic transition to the ground state of *cis*-**4**.

4. Conclusions

The characteristics of the excited states of dipyridones have been studied by various spectroscopic methods. One of the essential problems is the formation of the hydrogen-bonded dimer. This formation causes two different features of the dynamics of the excited state. One is an opening special nonradiative pathway observed in the system of compound **1**. Unfortunately, we could not clearly obtain information about the origin of this pathway. Probable mechanisms are a nonadiabatic reaction process into a tautomer by intermolecular double or quadruple proton transfer and dissociation of the dimer into monomers. The ultrafast laser flash photolysis experiment or pump−probe techniques of the fluorescence measurement are promising for testing this problem.

The other characteristic of dimers is a restriction of the photoinduced isomerization in the system of compound **4**. Compound **4** shows a clear and drastic change in its photochemical properties by changing the solution from a protic solvent to an aprotic one. This is a simple demonstration that shows the application of the hydrogen-bonded dimer for controlling the photochemical reactions.

Acknowledgment. This work was supported by a Grant-in-Aid for Development of Scientific Research (no. 13740320) from the Japan Society for the Promotion of Science and a Grant-in-Aid for Scientific Research on Priority Areas (417) and the 21st Centrury COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government. K.M. is indebted to the Yazaki Memorial Foundation for Science & Technology, the Kao Foundation for Arts and Sciences, the Casio Science Promotion Foundation, and the Saneyoshi Foundation. T.A. is grateful for financial support from the Asahi Glass Foundation.

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