



# The Photoinduced Hydrogen Atom Transfer and *trans*–*cis* Isomerization of the C=C Double Bond in 1-(1-Hydroxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one and Related Compounds Studied Using Nanosecond Time-Resolved Infrared Spectroscopy

Kaoru Kaneda, Shin Sato,<sup>1</sup> Hiro-o Hamaguchi,<sup>1</sup> and Tatsuo Arai\*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

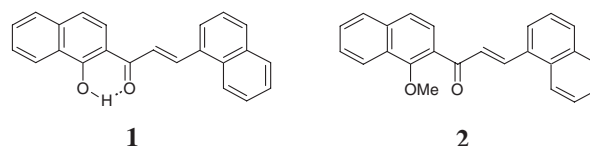
<sup>1</sup>Department of Chemistry, School of Science, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033

Received February 12, 2004; E-mail: arai@chem.tsukuba.ac.jp

The mechanism and intermediates of photoinduced hydrogen atom transfer and photoisomerization in 1-(1-hydroxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (**1**) and 1-(1-methoxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (**2**) have been investigated using nanosecond time-resolved infrared spectroscopy. For compound **1**, a bleach signal was observed at 1575 cm<sup>−1</sup> just after the laser excitation and recovered within 2 ms. The transient absorption at 1500 cm<sup>−1</sup> decayed with two components of 1 μs and 2 ms, which are due to the triplet state and the ground state tautomer, respectively. On the basis of these results, the potential energy surface of hydrogen atom transfer in compound **1** was deciphered. Upon laser excitation of compound **2**, the transient absorption signals at 1528 cm<sup>−1</sup> and 1392 cm<sup>−1</sup> assigned to the triplet state were observed in addition to the bleach signals at 1664 cm<sup>−1</sup> and 1600 cm<sup>−1</sup>. The bleach signal at 1600 cm<sup>−1</sup> remained as a permanent bleaching after the fast recovery with the 1.2 μs time constant. This result indicates that compound **2** underwent *trans*-to-*cis* isomerization upon laser excitation. By utilizing the data obtained in stationary and transient IR spectroscopy, we have directly determined the quantum yield of *trans*-to-*cis* isomerization to be 0.23 ± 0.01 from the difference in the IR signals.

Hydrogen bonding interactions and tautomerization by way of intramolecular hydrogen bonding are basic and important subjects in fundamental chemistry. In particular, photochemical hydrogen atom transfer has attracted considerable interest to observe ultrafast hydrogen atom transfer processes in both forward and reverse directions.<sup>1–16</sup> We have been interested in studying the cooperative effect of photoinduced hydrogen atom transfer and the photochemical *cis*–*trans* isomerization around the C=C double bond in compounds having both hydrogen bonding and the isomerizable C=C double bond.<sup>8,9,13–16</sup>

In the course of our research, we have been studying the hydrogen atom transfer and the *cis*–*trans* isomerization in 2'-hydroxychalcone and related compounds.<sup>8,9,12,17</sup> We found that 2'-hydroxychalcone underwent photochemical one-way *cis*-to-*trans* isomerization due to the ultrafast intramolecular hydrogen atom transfer both in the excited singlet and the triplet states to give the excited state tautomer.<sup>8,9</sup> The potential energy surface of the excited state tautomer produced as the triplet manifold may resemble one-way *cis*-to-*trans* isomerization, since the tautomer has a polyene-like electronic configuration.<sup>8,9</sup> However, in this compound it was difficult to observe any evidence of adiabatic intramolecular hydrogen atom transfer due to the inefficient fluorescence emission of the tautomer. We have recently found that the naphthyl analogue 1-(1-hydroxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (**1**) also underwent intramolecular hydrogen atom transfer in the excited state and we easily observed the fluorescence emission from the tautomer.<sup>12</sup> We have also prepared 1-(1-methoxy-2-naph-



Scheme 1.

thyl)-3-(1-naphthyl)-2-propen-1-one (**2**) as a model compound of **1** without intramolecular hydrogen bonding (Scheme 1). On the basis of the fluorescence spectroscopy and the transient UV–vis absorption spectroscopy, the potential energy surface of hydrogen atom transfer of compound **1** has been proposed.<sup>12</sup>

We wish to report here further studies of hydrogen atom transfer in compound **1** and the photochemical behavior of compound **2** by nanosecond time-resolved infrared spectroscopy in addition to the photoisomerization behavior of compound **2**. Time-resolved infrared spectroscopy has been shown to be useful in obtaining detailed information on the small structural differences both in the excited and ground states.<sup>18–29</sup>

Although benzene was used as the solvent in the previous report, the transient IR spectra could not be detected in benzene but was detected in CCl<sub>4</sub>. We have therefore briefly studied the absorption, transient absorption, and fluorescence spectra in CCl<sub>4</sub>, and these results are also included in this paper.

## Experimental

**Materials and Solvents.** *trans*-1-(1-Hydroxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (*trans*-**1**) was prepared from 1'-hy-

droxy-2'-acetonaphthone and 1-naphthaldehyde by aldol condensation.<sup>12</sup> *trans*-1-(1-Methoxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (*trans*-2) was prepared from *trans*-1 by the reaction with dimethyl sulfate in THF in the presence of aqueous NaOH.<sup>12</sup> *cis*-1-(1-Methoxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (*cis*-2) was obtained from *trans*-2 by irradiating with sunlight. Each of the compounds was purified by column chromatography and recrystallized from ethyl acetate and hexane.

Anhydrous CCl<sub>4</sub> (Wako) was used without further purification.

***trans*-1-(1-Hydroxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (*trans*-1):** mp 173–174 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (1H, d, *J* = 8.8 Hz), 7.54–7.58 (3H, m), 7.60–7.67 (2H, m), 7.78 (1H, d, *J* = 8.0 Hz), 7.84 (1H, d, *J* = 15.2 Hz), 7.87–7.97 (4H, m), 8.32 (1H, d, *J* = 8.4 Hz), 8.52 (1H, d, *J* = 8.4 Hz), 8.84 (1H, d, *J* = 15.2 Hz), 14.9 (1H, s).

***trans*-1-(1-Methoxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (*trans*-2):** mp 77–78 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.00 (3H, s), 7.54–7.58 (3H, m), 7.59–7.62 (2H, m), 7.70 (1H, d, *J* = 8.4 Hz), 7.72 (1H, d, *J* = 15.6 Hz), 7.79 (1H, d, *J* = 8.4 Hz), 7.89–7.95 (4H, m), 8.26–8.31 (2H, m), 8.62 (1H, d, *J* = 15.6 Hz).

***cis*-1-(1-Methoxy-2-naphthyl)-3-(1-naphthyl)-2-propen-1-one (*cis*-2):** mp 72–73 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.00 (3H, s), 7.17 (1H, d, *J* = 10.4 Hz), 7.26–7.28 (1H, m), 7.40–7.54 (7H, m), 7.61–7.66 (2H, m), 7.72–7.76 (2H, m), 8.00 (1H, d, *J* = 8.8 Hz), 8.11 (1H, d, *J* = 8.8 Hz).

**Measurements.** UV–vis and IR absorption spectra were measured on a SHIMADZU UV-1600 spectrometer and JASCO FT/IR-670plus spectrometer, respectively. Fluorescence spectra were obtained on a Hitachi F-4500 fluorescence spectrometer. Laser flash photolysis for transient UV–vis spectroscopy was performed by using an excimer laser (Lambda Physik LPX-100, wavelength 308 nm, 20 ns fwhm). A pulsed xenon arc (Ushio UXL-159) was used as a monitoring light source. In time-resolved IR spectroscopy,<sup>30–32</sup> the third harmonic of a diode-laser pumped Nd:YLF laser (Spectra Physics TFR, wavelength 349 nm, 10 ns fwhm) was used as an excitation light source. Continuous wave infrared light source (JASCO, MoSi<sub>2</sub>) was used as a probe beam. Changes in IR intensity induced by photoexcitation were detected by a photovoltaic mercury–cadmium–telluride (MCT) detector (Kolmar Technologies). An AC-coupled low noise preamplifier/amplifier system was used to amplify the signal which was finally averaged on a digital oscilloscope. Time resolution of the system was 50 ns.

## Results and Discussion

**Absorption, Transient Absorption, and Fluorescence Spectra of Compound 1 and 2.** *trans*-1 and *trans*-2 exhibited absorption spectra with maxima at 390 nm and 350 nm, respectively, in CCl<sub>4</sub>, which were very similar to those observed in benzene (Fig. 1).<sup>12</sup> The red-shift of the absorption spectrum of *trans*-1 compared with that of *trans*-2 indicates that the hydroxynaphthyl group and carbonyl group in *trans*-1 take a planar conformation due to the presence of the intramolecular hydrogen bonding in the CCl<sub>4</sub> solution. Furthermore, *trans*-1 exhibited a large Stokes shifted fluorescence in CCl<sub>4</sub> as well as in benzene (Fig. 2).<sup>12</sup> This indicates that *trans*-1 undergoes hydrogen atom transfer in the excited singlet state in CCl<sub>4</sub> also.

Upon laser flash photolysis of *trans*-1, transient absorption spectra were observed from 450 to 750 nm with the initial absorption maxima at 660 nm and 480 nm (Fig. 3). The transient absorption spectrum changed within a 10 μs time scale to give the absorption maximum only at 480 nm. The decay profile at

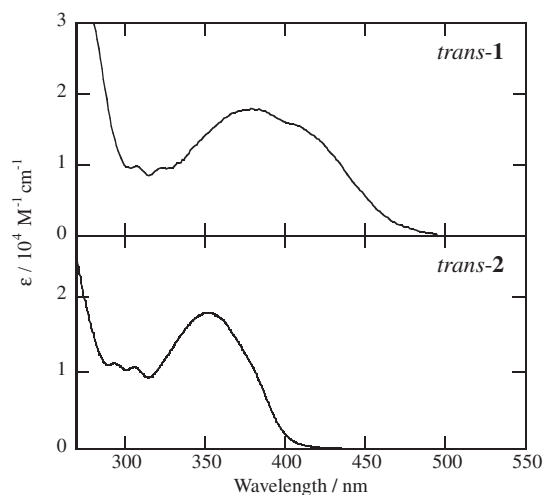


Fig. 1. Absorption spectra of *trans*-1 and *trans*-2 in CCl<sub>4</sub>.

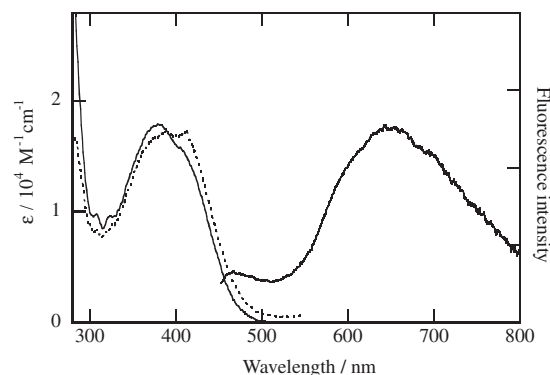


Fig. 2. Absorption, fluorescence, and fluorescence excitation spectra of *trans*-1 in CCl<sub>4</sub>.

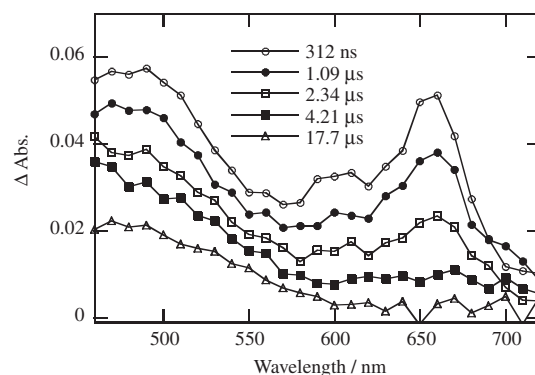


Fig. 3. Transient absorption spectra of *trans*-1 in CCl<sub>4</sub> (0.20 mM, Abs.<sub>308nm</sub> = 1.9) under Ar.

660 nm shows a time constant of only 2 μs, while that at 480 nm shows two components of 2 μs and 100 μs. The shorter lived transient of 2 μs both at 660 nm and 480 nm was quenched by oxygen, while the longer-lived transient of 100 μs was not quenched by oxygen. Therefore, the shorter and longer lived transients can be assigned to the triplet state tautomer and ground state tautomer, respectively, as previously proposed, in benzene solution.<sup>12</sup>

The transient absorption spectrum of *trans*-2 is quite differ-

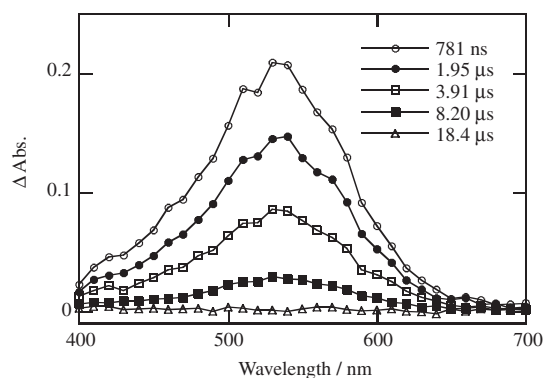


Fig. 4. Transient absorption spectra of *trans*-2 in  $\text{CCl}_4$  (0.059 mM,  $\text{Abs.}^{308\text{nm}} = 0.59$ ) under Ar.

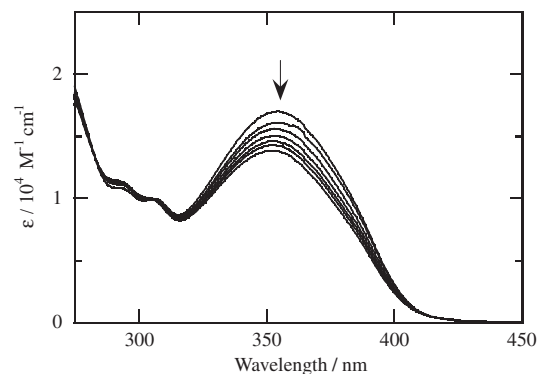


Fig. 5. Change of the absorption spectra of *trans*-2 on irradiation at 365 nm in benzene.

ent from that of *trans*-1 and exhibited an absorption maximum at 540 nm with a lifetime of 3  $\mu\text{s}$  in  $\text{CCl}_4$  (Fig. 4). The transient spectrum was quenched by oxygen and was assigned to the triplet state, which was similar to the result observed in benzene.<sup>12</sup> The considerably long lifetime indicates that the planar *trans* triplet and the perpendicular triplet state were equilibrated in the excited triplet state with an equilibrium very much shifted to the *trans* side.<sup>12</sup>

The quantum yield of intersystem crossing of *trans*-2 was estimated from the laser flash photolysis using benzophenone and *trans*-2 as sensitizers and  $\beta$ -carotene as an energy acceptor. Since the quantum yield of intersystem crossing from the singlet excited state to the triplet state of benzophenone is 1, the relative ratio of the T–T absorption spectra of  $\beta$ -carotene observed upon benzophenone sensitization and *trans*-2 sensitization gave the  $\Phi_{\text{isc}}$  value of *trans*-2. Thus,  $\Phi_{\text{isc}}$  of *trans*-2 was determined to be  $0.59 \pm 0.06$ .

**Photochemistry of Compound 2.** Upon photoirradiation with 365 nm light in benzene or  $\text{CCl}_4$ , *trans*-2 underwent *trans*–*cis* isomerization as revealed from the decrease of absorbance at 350 nm, while *trans*-1 was stable upon photoirradiation (Fig. 5).

Since the photoisomerization behavior in benzene was similar to that in  $\text{CCl}_4$ , the detailed photochemical experiments of *trans*-2 were performed in benzene. As shown in Fig. 6, the photostationary state *trans*-to-*cis* isomer ratio ( $[t]/[c]_{\text{pss}}$ ) upon 365 nm irradiation under an argon atmosphere increased with increasing concentration of *trans*-2, while that under air is

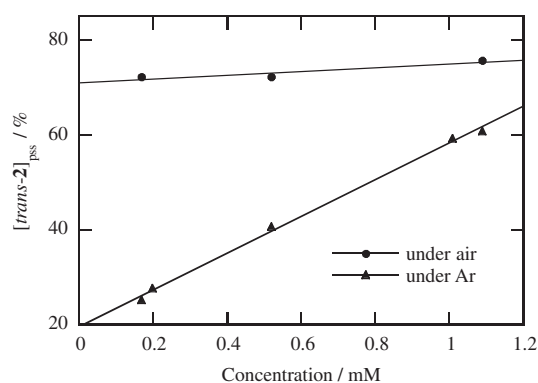


Fig. 6. Concentration dependence of the photostationary state isomer ratios of compound 2 under Ar and air.

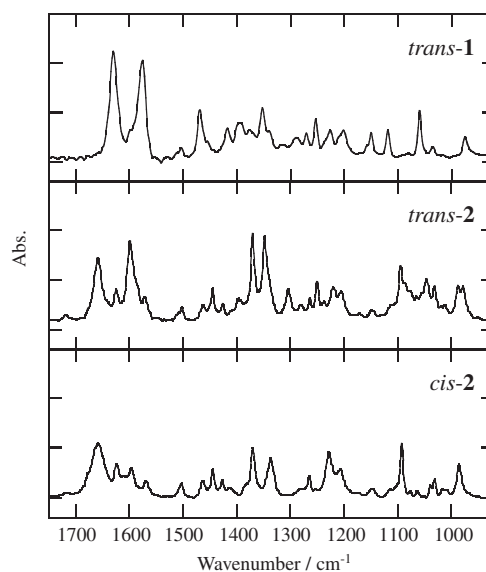


Fig. 7. Infrared spectra of *trans*-1, *trans*-2, and *cis*-2 in  $\text{CCl}_4$ .

almost constant. These results indicate that the isomerization proceeded mainly in the excited triplet state.

The quantum yield of *trans*  $\rightarrow$  *cis* isomerization was determined with irradiation at 365 nm. The  $\Phi_{t \rightarrow c}$  value was  $0.20 \pm 0.03$  and  $0.020 \pm 0.001$  under argon and air, respectively, and these values are independent of the concentration of *trans*-2. The quantum yield of *cis*-to-*trans* isomerization increased with increasing concentration under argon atmosphere from 0.34 at the concentration of  $1.7 \times 10^{-4}$  M to 0.50 at  $5.2 \times 10^{-4}$  M, while the value is almost constant under air,  $\Phi_{c \rightarrow t} = 0.30$ . These results also support the theory that the isomerization proceeds in the triplet state.

**IR Spectra in the Ground State.** Figure 7 shows the IR spectra of *trans*-1, *trans*-2, and *cis*-2 in  $\text{CCl}_4$  in the ground state at room temperature. Characteristic absorption peaks appeared at 1630, 1576, and 1201  $\text{cm}^{-1}$  for *trans*-1. The 1630  $\text{cm}^{-1}$  peak can be assigned to the C=O stretching vibration, and 1576  $\text{cm}^{-1}$  to the C=C stretching vibration. The low C=O stretching frequency of 1630  $\text{cm}^{-1}$  indicates the formation of strong intramolecular hydrogen bonding for *trans*-1.

Both *cis*- and *trans*-2 exhibited IR absorption at 1660 and 1600  $\text{cm}^{-1}$  due to the C=O and C=C stretching vibration, re-

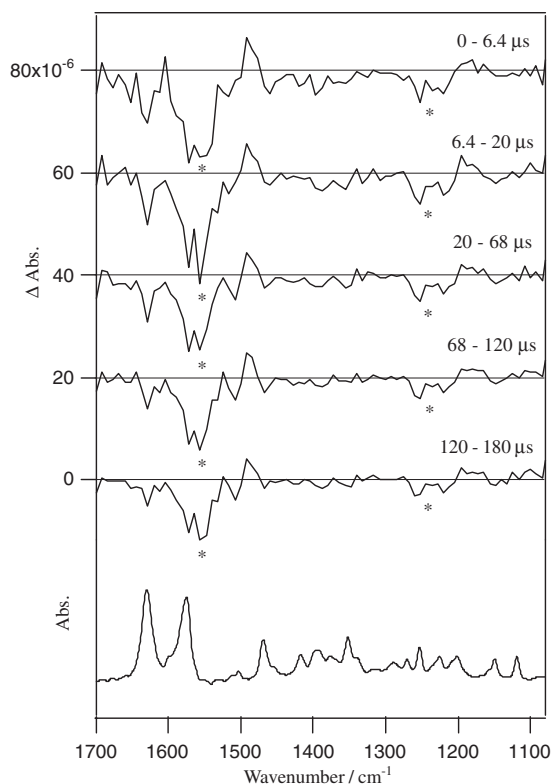


Fig. 8. Transient and ground state infrared spectra of *trans*-**1** in  $\text{CCl}_4$  (20 mM). The asterisked depletions at  $1550\text{ cm}^{-1}$  and  $1210\text{--}1270\text{ cm}^{-1}$  are due to the solvent.

spectively. The peak observed at  $980\text{ cm}^{-1}$  for *trans*-**2** can be assigned to the *trans*-olefinic CH out-of-plane bending vibration, since the band was not observed for *cis*-**2**.

**Transient IR of Compound 1.** Figure 8 shows the transient IR spectra, where we observed several bleaching signals in addition to the positive transient signals at  $1500$  and  $1176\text{ cm}^{-1}$ . As mentioned in the previous section, the bleaching signals observed at  $1630\text{ cm}^{-1}$  and  $1575\text{ cm}^{-1}$  were assigned to the C=O and C=C stretching vibration, respectively. The time profile of the recovery of the bleach at  $1575\text{ cm}^{-1}$  is shown in Fig. 9. This bleaching signal recovered with a time constant of 2 ms. A similar value was obtained from the bleach signal observed at  $1630\text{ cm}^{-1}$ . These results indicate that *trans*-**1** can undergo some conformational change upon photoirradiation, but the starting compound was reproduced within a ms time scale. However, this conformational change is not a permanent one, but rather is a transient change similar to photoinduced hydrogen atom transfer to produce the tautomer, which decayed to the ground state tautomer followed by reverse hydrogen atom transfer to produce the starting *trans*-**1**.

The positive transient signal observed at  $1500\text{ cm}^{-1}$  (Fig. 10) was composed of two components, one of them decaying with a time constant of  $1\text{ }\mu\text{s}$  under argon atmosphere and the other decaying with a time constant of 2 ms. The shorter lived component was quenched by oxygen and was assigned to the triplet state. The longer lived component was not quenched by oxygen and was assigned to the ground state species. The ground state transient could be assigned to either the *cis*-keto tautomer or the *trans*-keto tautomer. The temperature effect on the transient

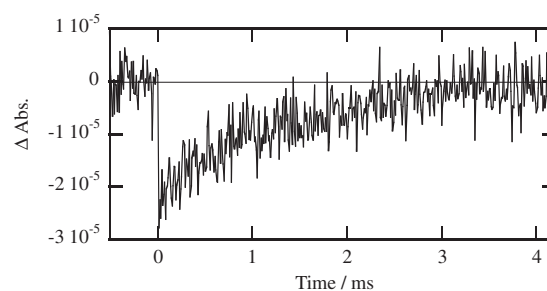


Fig. 9. Time profile of the transient infrared signal of *trans*-**1** in  $\text{CCl}_4$  detected at  $1575\text{ cm}^{-1}$ .

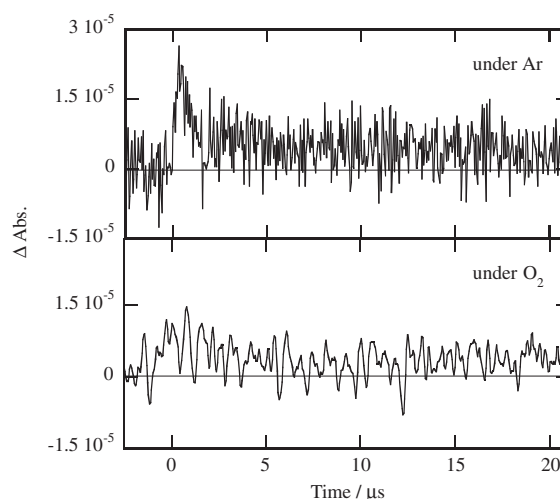


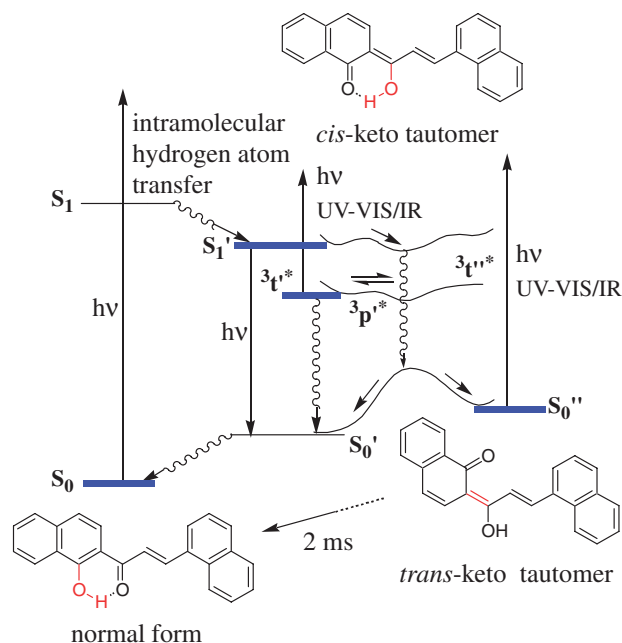
Fig. 10. Time profiles of the transient infrared signal of *trans*-**1** in  $\text{CCl}_4$  at  $1500\text{ cm}^{-1}$  under Ar and  $\text{O}_2$ .

spectra indicates that the *cis*-keto tautomer undergoes ultrafast reverse hydrogen atom transfer to give the starting form.<sup>12</sup> Since the observed transient ground state has a moderately long lifetime of 2 ms, it can be assigned to the *trans*-keto tautomer. The positive transient signal at  $1176\text{ cm}^{-1}$  was not quenched by oxygen and was also assigned to the long lived transient species produced by intramolecular hydrogen atom transfer in the excited state (*trans*-keto tautomer).

The above spectroscopic evidence indicates that *trans*-**1** undergoes photoinduced hydrogen atom transfer in the excited state followed by deactivation to produce the tautomer with a lifetime in the  $\mu\text{s}$  to ms time scale, which also undergoes reverse hydrogen atom transfer to give the starting *trans*-**1**.

The above discussion is well in accordance with our previous report mainly based on fluorescence and transient absorption spectroscopy.<sup>12</sup> In transient absorption spectroscopy, we have observed two transient species with a  $2\text{ }\mu\text{s}$  lifetime assigned to the triplet state and more than a  $100\text{ }\mu\text{s}$  lifetime assigned to the ground state tautomer.

When we combine the results of both the UV-vis absorption and fluorescence spectroscopy with the results of the IR spectroscopy, the transient IR observed for *trans*-**1** (shorter lived component of  $2\text{ }\mu\text{s}$ ) due to the triplet state can be assigned to the triplet state tautomer of *trans*-**1** (*cis*-keto form) and the longer lived ground state tautomer (2 ms) of *trans*-**1** can be assigned to the ground state *trans*-keto form. Since the OH group



Scheme 2.

exists on the phenyl ring in the normal form and in the olefinic chain in the tautomer, the signal of the CO stretching vibration of the tautomer should appear at a lower energy than the CO stretching of the phenolic OH group. In fact, the normal form and the tautomer form exhibited signals at  $1201\text{ cm}^{-1}$  and  $1176\text{ cm}^{-1}$ , which are assignable to the CO stretchings of the phenolic and olefinic OH groups, respectively. These results also support the above discussion of the photoinduced hydrogen atom transfer in the excited state followed by deactivation to the ground state to produce the *cis*-keto form.

We have determined the lifetime of the ground state tautomer to be 2 ms in those experiments, which could not accurately be determined in our transient absorption measurements by laser flash photolysis.<sup>12</sup> On the basis of these findings and the previous results, we can slightly modify the potential energy surface of the photoinduced hydrogen atom transfer in compound **1** (Scheme 2).

The intramolecular hydrogen atom transfer that produces the *cis*-keto tautomer takes place in the excited singlet state. The *cis*-keto tautomer undergoes non-radiative deactivation to give the ground state *trans*-keto form by twisting around the newly produced quasi-double bond or intersystem crossing to the triplet state. In addition, the *cis*-keto tautomer in the excited singlet state gives a fluorescence emission at a longer wavelength. In the ground state, the *trans*-keto tautomer undergoes isomerization around the quasi-double bond followed by reverse hydrogen atom transfer to give the starting form, while the *cis*-keto tautomer quickly reverts to the normal form.

**Transient IR of Compound 2.** Figure 11 shows the transient IR spectra observed upon laser excitation of *trans*-**2** in  $\text{CCl}_4$ . Bleaching signals similar to *trans*-**1** were observed for *trans*-**2** at  $1600\text{ cm}^{-1}$  and  $1664\text{ cm}^{-1}$  due to the C=C and C=O stretching vibration. Very interestingly, positive transient absorption signals at  $1528\text{ cm}^{-1}$  and  $1392\text{ cm}^{-1}$  were observed (Fig. 12). The former absorption decayed with the time constants of 390 ns and  $1.8\text{ }\mu\text{s}$  and were quenched by oxygen.

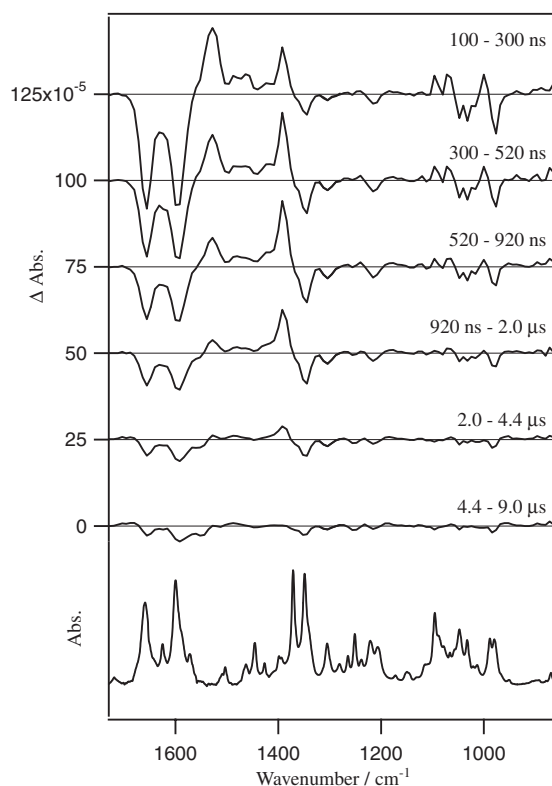


Fig. 11. Transient and ground state infrared spectra of *trans*-**2** in  $\text{CCl}_4$  (20 mM).

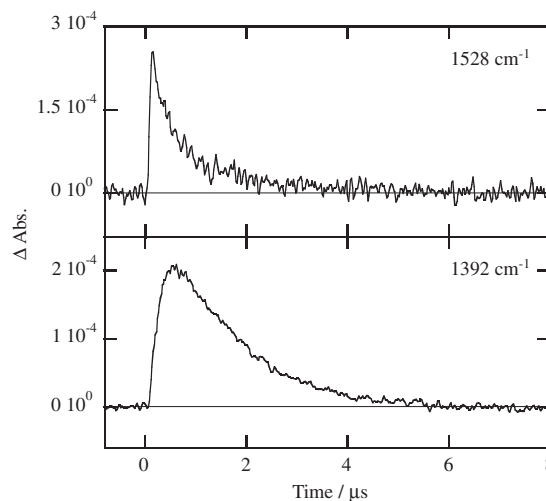


Fig. 12. Time profiles of the transient infrared signal of *trans*-**2** in  $\text{CCl}_4$  detected at  $1528\text{ cm}^{-1}$  and  $1392\text{ cm}^{-1}$ .

The latter absorption have rising (260 ns) and decaying components ( $1.4\text{ }\mu\text{s}$ ) and were also quenched by oxygen. Therefore, these absorption signals were assigned to the triplet excited states. The bleaching signal at  $1664\text{ cm}^{-1}$  recovered with a time constant of  $1.2\text{ }\mu\text{s}$ , but the signal at  $1600\text{ cm}^{-1}$  did not recover on this time scale (Fig. 13). Since compound **2** undergoes photochemical *trans*-*cis* isomerization mutually, these differences in the recovery of the signals may well be due to the *trans*-to-*cis* photoisomerization. *trans*-**2** undergoes *trans*-to-*cis* isomerization upon photoirradiation either in the excited singlet state



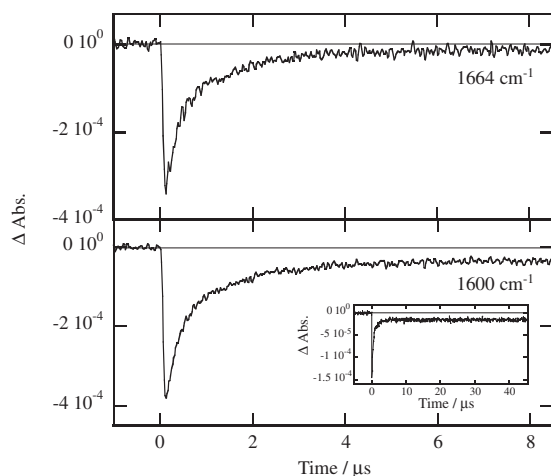


Fig. 13. Time profiles of the transient infrared signal of *trans*-2 in CCl<sub>4</sub> detected at 1664 cm<sup>-1</sup> and 1600 cm<sup>-1</sup>.

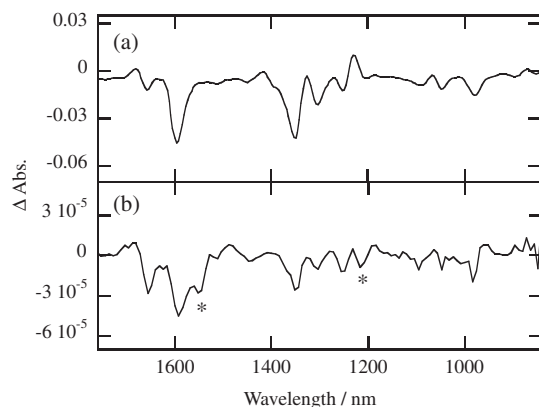
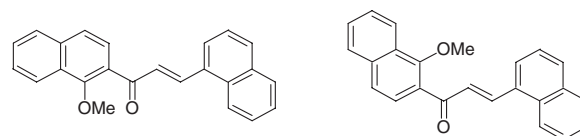


Fig. 14. Difference spectrum obtained by subtracting the infrared absorption spectrum of *trans*-2 from that of *cis*-2 (a), and the non-decaying permanent infrared spectrum observed by transient infrared spectroscopy (b). The asterisked bands at 1550 cm<sup>-1</sup> and 1210 cm<sup>-1</sup> are due to the solvent.

or in the triplet state and, therefore, the starting isomer would not be fully recovered and the permanent signals were observed in the transient IR spectra. The difference in the IR spectra between *trans*- and *cis*-2 almost reproduces the permanent IR spectra observed by transient IR spectroscopy (Fig. 14).

Since the changes in the signal intensities at 1528 cm<sup>-1</sup> and at 1392 cm<sup>-1</sup> were assigned to the triplet state, which exhibited producing and decaying dynamics, the above two components both at 1528 cm<sup>-1</sup> and 1392 cm<sup>-1</sup> indicate the occurrence of the conformational change in the excited triplet state. Usually, in the excited state, the double bond and the single bond in the ground state become a quasi-single bond and a quasi-double bond. Thus, the single bond connecting the methoxynaphthyl group and carbonyl group may have some double bond character that increases the rotation barrier around this bond. The rotation around this bond may cause a large geometrical change in compound 2 and may result in a change of the vibrational frequency. Thus, the rising component of 260 ns at 1392 cm<sup>-1</sup> and the fast decaying component of 390 ns at 1528 cm<sup>-1</sup> should be assigned to the rotation around the quasi-double bond from



Scheme 3.

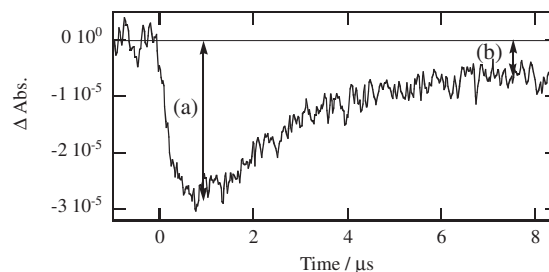


Fig. 15. Time profile of the transient infrared signal of *trans*-2 in CCl<sub>4</sub> detected at 1304 cm<sup>-1</sup>. The absolute value of the signal intensity at 1 μs indicated as (a) and 7.5 μs indicated as (b) correspond to the disappearance of *trans*-2 and the formation of *cis*-2, respectively.

the initially produced triplet state to the rotational isomer (Scheme 3).

As shown in the ground state IR spectra, there are some signals (1304, 1251, and 980 cm<sup>-1</sup>) that were observed only for the *trans*-isomer. By using the transient IR data at 1304 cm<sup>-1</sup>, one could determine the quantum yield of *trans*-*cis* isomerization very easily and accurately (Fig. 15). In fact we have succeeded in determining the quantum yield of *trans*-*cis* isomerization to be 0.23, which is very close to the value obtained by conventional methods using [tris(oxalate)]ferrate(III) actinometry.

## Conclusion

We have observed a bleach signal at 1575 cm<sup>-1</sup> and a transient absorption signal at 1500 cm<sup>-1</sup> for *trans*-1 by nanosecond time-resolved infrared spectroscopy. From the analyses of these signals, we have determined the lifetimes of the triplet state and the ground state tautomer of *trans*-1 produced by photoirradiation. In *trans*-2, the triplet state signals were observed at 1528 cm<sup>-1</sup> and 1392 cm<sup>-1</sup> as transient absorption with the ground state bleach signals at 1664 cm<sup>-1</sup> and 1600 cm<sup>-1</sup>. Thus, the triplet state intermediate can be discussed. In addition, we have succeeded in determining the quantum yield of the *trans*-to-*cis* isomerization of compound 2 for the first time to be 0.23 ± 0.01 from the permanent signal observed at 1304 cm<sup>-1</sup>.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) and the 21 Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), by University of Tsukuba Research Projects, and by the Asahi Glass Foundation.

## References

- 1 M. Kasha, *J. Chem. Soc., Faraday Trans. 2*, **82**, 2379 (1986).
- 2 P. F. Barbara, P. K. Walsh, and L. E. Brus, *J. Phys. Chem.*, **93**, 29 (1989).

- 3 S. J. Formosinho and L. G. Arnaut, *J. Photochem. Photobiol., A*, **75**, 1 (1993).
- 4 S. J. Formosinho and L. G. Arnaut, *J. Photochem. Photobiol., A*, **75**, 21 (1993).
- 5 M. Kasha, J. Heldt, and D. Gormin, *J. Phys. Chem.*, **99**, 7281 (1995).
- 6 J. Catalán, J. Palomar, and J. L. G. de Paz, *J. Phys. Chem. A*, **101**, 7914 (1997).
- 7 W. S. Yu, C. C. Cheng, Y. M. Cheng, P. C. Wu, Y. H. Song, Y. Chi, and P. T. Chou, *J. Am. Chem. Soc.*, **125**, 10800 (2003).
- 8 T. Arai and Y. Norikane, *Chem. Lett.*, **1997**, 339.
- 9 Y. Norikane, N. Nakayama, N. Tamaoki, T. Arai, and U. Nagashima, *J. Phys. Chem. A*, **107**, 8659 (2003).
- 10 M. Ikegami and T. Arai, *Chem. Lett.*, **2000**, 996.
- 11 M. Ikegami and T. Arai, *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1296.
- 12 K. Kaneda and T. Arai, *Photochem. Photobiol. Sci.*, **2**, 402 (2003).
- 13 M. Obi, H. Sakuragi, and T. Arai, *Chem. Lett.*, **1998**, 169.
- 14 Y. Y. Yang and T. Arai, *Tetrahedron Lett.*, **39**, 2617 (1998).
- 15 T. Arai and Y. Hozumi, *Chem. Lett.*, **1998**, 1153.
- 16 T. Arai, M. Moriyama, and K. Tokumaru, *J. Am. Chem. Soc.*, **116**, 3171 (1994).
- 17 K. Kaneda and T. Arai, *Org. Biomol. Chem.*, **1**, 2041 (2003).
- 18 T. Yuzawa, H. Takahashi, and H. Hamaguchi, *Chem. Phys. Lett.*, **202**, 221 (1993).
- 19 M. Ito, T. Yuzawa, H. Mukaihata, and H. Hamaguchi, *Chem. Phys. Lett.*, **233**, 550 (1995).
- 20 K. Tokumura, M. Natsume, T. Nakagawa, M. Hashimoto, T. Yuzawa, H. Hamaguchi, and M. Itoh, *Chem. Phys. Lett.*, **271**, 320 (1997).
- 21 K. Kobayashi, M. Iguchi, T. Imakubo, K. Iwata, and H. Hamaguchi, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1993.
- 22 Y. Wang, T. Yuzawa, H. Hamaguchi, and J. P. Toscano, *J. Am. Chem. Soc.*, **121**, 2875 (1999).
- 23 S. Tanaka, C. Kato, K. Horie, and H. Hamaguchi, *Chem. Phys. Lett.*, **381**, 385 (2003).
- 24 K. Iwata and H. Takahashi, *J. Mol. Struct.*, **598**, 97 (2001).
- 25 S. Srivastava, P. H. Ruane, J. P. Toscano, M. B. Sullivan, C. J. Cramer, D. Chiapperino, E. C. Reed, and D. E. Falvey, *J. Am. Chem. Soc.*, **122**, 8271 (2000).
- 26 Y. Wang and J. P. Toscano, *J. Am. Chem. Soc.*, **122**, 4512 (2000).
- 27 E. M. Tippmann and M. S. Platz, *J. Phys. Chem. A*, **107**, 8547 (2003).
- 28 M.-L. Tsao, N. Gritsan, T. R. James, M. S. Platz, D. A. Hrovat, and W. T. Borden, *J. Am. Chem. Soc.*, **125**, 9343 (2003).
- 29 C. B. Martin, X. Shi, M.-L. Tsao, D. Karweik, J. Brooke, C. M. Hadad, and M. S. Platz, *J. Phys. Chem. B*, **106**, 10263 (2002).
- 30 K. Iwata and H. Hamaguchi, *Appl. Spectrosc.*, **44**, 1431 (1990).
- 31 T. Yuzawa, C. Kato, M. W. George, and H. Hamaguchi, *Appl. Spectrosc.*, **44**, 684 (1994).
- 32 M. Hashimoto, T. Yuzawa, C. Kato, K. Iwata, and H. Hamaguchi, "Handbook of Vibrational Spectroscopy," ed by J. M. Chalmers and P. R. Griffith, John Wiley & Sons Ltd., Chichester, UK (2002).