bound to the n electrons of the substituent and to the π system of the ring, thus attaining a high degree of stability via charge delocalization.

The case for the formation of electrostatic adducts between aniline and gaseous carbenium ions is considerably strengthened by recent mass spectrometric observations. In fact, analysis of the high-energy dissociation spectra of the ions formed from the attachment of Et[+] to aniline has allowed Cooks and co-workers[3] to identify a *non-covalent* adduct, characterized as a weakly bound $C_6H_5NH_2 \cdot Et^+$ complex, regarded by the authors as a proton-bound dimer of aniline and ethylene.[20] The mass, properties, and stability (lifetime exceeding 10^{-6} s) of the observed adduct correspond to those expected for a species such as **5** (R, X = H), which differs from a conventional proton-bound dimer exclusively in the additional stabilization of the Et[+] cation arising from its electrostatic interaction with the π system.

Conclusion

The radiolytic and CI results suggest that attack of a purely alkylating cation, such as Me_2F^+, is characterized by an appre-

ciable kinetic bias for the N atom of anilines. The correlation between the apparent k_N/k_{ring} ratio and the absolute yields suggests that the N atom is also kinetically preferred by gaseous carbenium ions such as Et[+] and *i*-Pr[+], which, however, react predominantly as Brønsted acids, protonating the amino group.

As to positional selectivity, aside from the usual orienting effects of substituents, the alkylation of anilines displays a typical feature of gas-phase aromatic substitution, namely the enhanced reactivity of the ring positions ortho to an n-type substituent. The effect is traced to the increased local concentration of the electrophile caused by the preliminary formation of an electrostatic adduct with the anilines,[4a,b] in agreement with independent evidence from CID spectrometry.[3]

(20) A $[C_6H_5NH_2 \cdot Me_2F]^+$ adduct (of unknown structure) has been observed in the MeF CI spectrum of aniline, ref. 2.

Transient Absorption and Two-Step Laser Excitation Fluorescence Studies of Photoisomerization in 2-(2-Hydroxyphenyl)benzoxazole and 2-(2-Hydroxyphenyl)benzothiazole

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Contribution from the Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan. Received July 5, 1984

Abstract: The transient absorption spectra of 3-methylpentane solutions of 2-(2-hydroxyphenyl)benzoxazole (HBO) and -thiazole (HBT) exhibit transient absorption bands at 390–450 and 420–480 nm, respectively. The absorption band of HBO shows a single exponential decay ($\tau = 260$ ns), while that of HBT shows a double exponential decay ($\tau = 9.4$ and 53.3 μs) at room temperature. Both absorption bands may be attributable to their respective ground-state phototautomers generated by the intramolecular excited-state proton transfer and the fluorescence relaxation in HBO and HBT. The two-step laser excitation (TSLE) fluorescence spectra of the direct excitation of their transient absorption bands are identical with the large Stokes-shifted fluorescence spectra (λ_{max} 490 nm for HBO and 515 nm for HBT). The decay kinetics of the ground-state phototautomers by the transient absorption and the TSLE fluorescence variable delay technique suggest that there are two phototautomers in the ground state of HBT and only one phototautomer for HBO. Two types of ground-state phototautomers in HBT were tentatively ascribed to planar and twisted conformers about the C_1–C_7 bond between two aromatic moieties.

Recently we have investigated the reaction kinetics and dynamics of the proton transfer and isomerization in the ground and excited states of several hydrogen-bonding systems by the time-resolved fluorescence and transient absorption spectra and by the two-step laser excitation (TSLE) fluorescence, which has been developed by us as one of recent advances of laser spectroscopy.[1–4] The first laser excitation of the intra- and intermolecular hydrogen-bonding system induces the excited-state proton transfer followed by the fluorescent or nonfluorescent relaxation to the ground-state phototautomer. The second laser excitation of the

transient absorption band due to this ground-state phototautomer within the lifetime affords the two-step laser excitation fluorescence spectra and lifetime which should be identical with those of the ordinary fluorescence. Recently our investigations of the transient absorption and the TSLE fluorescence including the variable delay technique have revealed the intervention of the unexpectedly long-lived ground-state intermediate (phototautomer) in the excited-state isomerization and relaxation of 3-hydroxyflavone and 3-hydroxychromone in nonpolar solvents.[4,5] Recently, in the methanol solution of 7-hydroxyflavone (7-HF), two phototautomers have been suggested to be involved both in the ground and excited states by time-resolved TSLE fluorescence spectra and

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(2) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1984,** *106,* 850.
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lifetimes,[3] which are observed in the second laser excitation of the phototautomer at variable delay times from the first pulse.

Cohen and Flavian[6] proposed the photochromic proton transfer for the large Stokes-shifted luminescence of 2-(2-hydroxy-phenyl)benzothiazole (HBT). It was suggested that the stable ground-state conformer of HBT had the proton predominantly on the phenol oxygen (enol form) whereas the excited state had the proton on the nitrogen atom (keto form). Barbara et al.[7] have reported picosecond fluorescence spectroscopy of HBT in aprotic solvent and proposed two different cis-keto phototautomers generated by the intramolecular excited-state proton transfer which exhibit two exponential fluorescence decay kinetics at 293–200 K. The decay processes may involve angular motion about the C_1–C_7 bond in the excited state, though no particular conformation has been presented for these two cis-keto phototautomers. Further these authors[7] and Ding et al.[8] have reported the very short-lived fluorescence ($\tau = 7 \pm 2$ ps, at 460–520 nm) in addition to the 500–600-nm fluorescence at 4 K. Both reports have suggested that the short wavelength fluorescence may be attributable to the fluorescence relaxation from the higher vibrational states of cis-keto phototautomer generated from the Franck–Condon enol phototautomer. On the other hand, the occurrence of a similar excited-state proton transfer from the hydroxyl group to the nitrogen atom in a 2-(2-hydroxyphenyl)benzoxazole (HBO) is well documented. Recently Woolfe et al.[9] have reported that HBO consists of two rotomeric species of cis and trans enols in equilibrium in the ground state and that the excited-state proton transfer takes place only in the former. In spite of these investigations, the phototautomeric and rotomeric isomerizations of these compounds both in the ground and excited states are not obvious. Especially, kinetics and dynamics of the ground- and excited-state tautomers to the parent molecules are completely obscure. Therefore, this paper is concerned with these kinetics and dynamics of relaxation processes of the excited-state tautomer to the parent molecule.

This paper describes transient absorption and TSLE fluorescence studies of 3-methylpentane solutions of HBO and of HBT at 300–200 K. The solutions were observed to show transient absorption bands at 390–450 nm for HBO and at 420–480 nm for HBT at room temperature. The former exhibits a single exponential decay, while the latter shows a double exponential decay. These transient absorption bands were attributable to the ground-state phototautomers generated by the photoisomerization followed by the energy dissipation of their excited state phototautomers. The TSLE fluorescence including the variable delay technique confirms these assignments. However, the phototautomer of HBT was suggested to consist of two keto conformers in the ground state as well as in the excited state. By means of
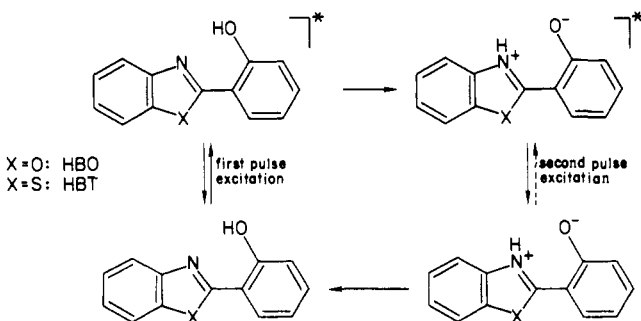
the temperature dependence of transient absorption and TSLE fluorescence (variable delay), kinetics and dynamics of the two keto phototautomers in the ground state are discussed in terms of angular rotation about the C_1–C_7 bond and the reverse proton

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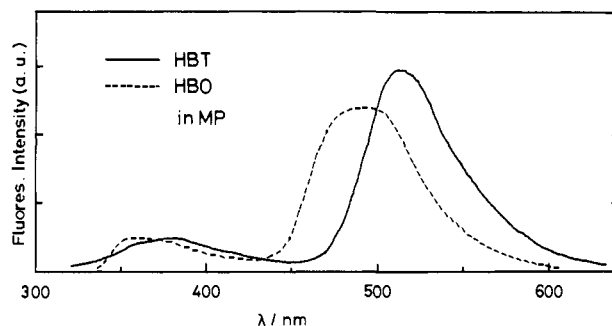

Figure 1. Non-time-resolved fluorescence spectra of deaerated MP solutions of HBT (–) and HBO (- - -) at room temperature. Excitation wavelength is 308 nm.

transfer to the parent molecule of HBT.

Experimental Section

Materials. 2-(2-Hydroxyphenyl)benzothiazole (Eastman Kodak Co.) was purified by recrystallization several times from aqueous ethanol. 2-(2-Hydroxyphenyl)benzoxazole (Tokyo Kasei Co.) was purified by recrystallization several times from aqueous ethanol and by sublimation, mp 127 °C. The purity of these compounds was confirmed both spectroscopically and by melting point determination. The solvent, 3-methylpentane (MP) (Aldrich Chemical Co.), was rendered free of fluorescent impurities by redistillation. The deuterium substitution of the 2-hydroxyl hydrogen atom was performed by CH_3OD (CEA, deuterium grade 99%) in a vacuum system. After CH_3OD was removed, MP pretreated by potassium mirror was added through a vacuum system. The solutions of samples in a rectangular quartz cell with graded seals were degassed by freeze–pump–thaw cycles.

Spectra and Lifetime and Transient Absorption Measurements. Absorption and fluorescence spectra were determined with a Hitachi 323 spectrophotometer and MPF 4 spectrofluorometer, respectively. Nanosecond fluorescence lifetimes were determined by a time-correlated single-photon counting system (Ortec) with a nanosecond light pulser (PRA Model 510) through a monochromator (Ritsu MC-10N). The fluorescence decay curves were analyzed by a computer-simulated convolution. Picosecond lifetimes were determined by using a forth harmonic pulse (266 nm) of a mode-locked Nd:YAG laser and a streak camera (Hamamatsu C979) system. Transient absorption spectra were determined by using an excimer laser (Lambda Physik EMG50E, XeCl 308 nm) and a monitoring Xe steady-light system.

Two-Step Laser Excitation Fluorescence Spectra and Variable Delay Technique. An excimer laser (fwhm ~ 10 ns, average power 6 W and repetition rate 2 Hz, 308 nm) was used for the first laser excitation, and a N_2 laser-pumped dye laser (Molectron UV12 and DL14) was used as the second laser.[3,4] The TSLE fluorescence was determined by a monochromator (Ritsu MC-10N)–photomultiplier (1P28)–oscilloscope (Tektronix Model 7904) system, where the oscilloscope was triggered by the second laser pulse detected by a biplanar phototube (HTV R617-02). The lifetimes of the ground-state phototautomers were determined from the fluorescence intensities at variable delay times between the two pulses.

Results and Discussion

Fluorescence and Transient Absorption. Figure 1 shows the fluorescence spectrum of the MP solution of HBO at room temperature. The spectrum at 490 nm may be attributable to the excited-state phototautomer, while the 370-nm band to the different hydrogen-bonding conformer which does not give rise to the proton transfer, as pointed out by Woolfe et al.[9] The fluorescence of the 490-nm band exhibits a single exponential decay throughout 300–77 K. An activation energy of the nonradiative process of the excited-state phototautomer was obtained to be 5.5 kcal/mol from the temperature dependence of fluorescence lifetimes by assuming temperature independence of the radiative rate constant and a constant fluorescence lifetime at 170–77 K.[10] Figure 1 also shows the large Stokes-shifted fluorescence of the MP solution of HBT at room temperature. The spectrum is attributable to the excited-state phototautomer by the excited-state proton transfer as suggested previously. Barbara et al.[7] have reported that this phototautomer fluorescence exhibits a double exponential decay in isopentane solution at

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Table I. Fluorescence Decay Times of a Deaerated MP Solution of HBT through 294–173 K[a]

temp, K	τ_{short}, ps	τ_{long}, ps
294	91 (62%)	247 (38%)
274	160 (77%)	551 (23%)
263	334 (94%)	1940 (6%)
251	486 (99%)	2470 (1%)
223	1064	
198	1918	
173	3463	

[a] Data in parentheses are fractions of components.
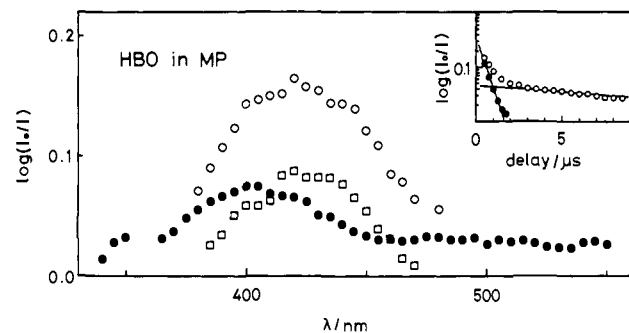
Figure 2. Transient absorption spectra of deaerated (O), (●) and aerated (□) MP solutions of HBO at room temperature. Delay times following excitation at 308 nm are 250 ns (O), 1500 ns (●), 200 ns (□). Transient absorption decay curve in the inset was obtained at 430 nm on deaeration. The concentration is 1.9×10^{-4} M.

293–200 K by picosecond spectroscopy. In this paper, a double exponential decay was observed in MP at 294–251 K by nano- and picosecond spectroscopies (Table I). Both lifetimes show remarkable increase, and the ratio of the long- and short-lived components decreases with decreasing temperature. The long-lived one remains much less than 1% at 251 K, and a single exponential decay was observed below 230 K. Now we tentatively propose the cis-keto form for I* and the twisted-keto form for II*, and the short- and long-lived fluorescence were tentatively ascribed to fluorescence from I* and II*, respectively, as suggested previously.[7] According to this assumption, the excited-state proton transfer takes place from the coplanar cis-enol form (N) to afford the phototautomer I*. The phototautomer II* seems to be generated by a rotation around the C_1–C_7 bond of I*. Since no long-lived component of decay was observed in the 515-nm fluorescence below 230 K, the rotational transition from I* to II* may be negligible within their lifetimes. This means that the formation of the ground-state phototautomer II from II* may be negligible below 230 K.

Transient absorption spectra of the deaerated MP solutions of HBO and HBT were measured by an excimer laser excitation. The transient absorption spectra exhibit strong absorption bands at λ_{max} 420 nm for HBO and at λ_{max} 450 nm for HBT, as shown in Figures 2 and 3, respectively. The decay curves of transient absorption bands are shown in the insets of these figures. Although the transient absorption (λ_{max} 420 nm) of HBO exhibits a double exponential decay of $\tau = 260$ ns and 10.9 μs at room temperature, the long-lived component (λ_{max} 400 nm) remarkably decreases both in intensity and decay time on aeration of the solution. Therefore, the long-lived absorption band seems to be attributable to the $T_n \leftarrow T_1$ absorption, while the short-lived one seems to be ascribed to the ground-state phototautomer of HBO as will be mentioned later. On the other hand, the decay of the HBT transient absorption band at 465 nm shows a typical double exponential. In addition to the 465-nm transient absorption band, a weak absorption band was observed at 360 nm. The intensity and two decay times of the 450-nm band of HBT are almost independent of the monitored wavelengths (440–470 nm) and of aeration and deaeration of the solution. However, the shorter wavelength absorption band (λ_{max} 360 nm) considerably decreases in the intensity on aeration. The band seems to be attributable to the $T_n \leftarrow T_1$ absorption or some reaction products. Nakagaki
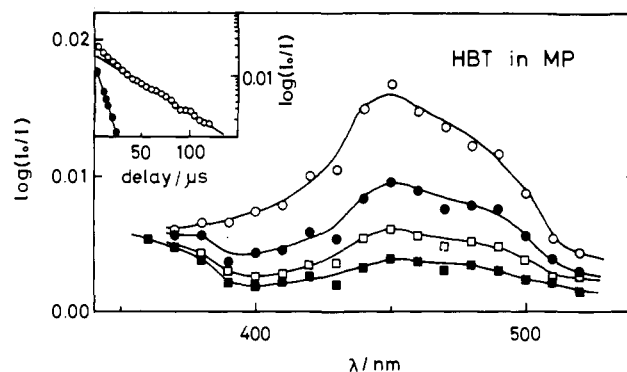
Figure 3. Transient absorption spectra of the deaerated MP solution of HBT at room temperature. Delay times following excitation at 308 nm are 2 μs (O), 20 μs (●), 40 μs (□), and 60 μs (■). Transient absorption decay curve in the inset was obtained at 465 nm on deaeration. The concentration is 2.2×10^{-5} M.
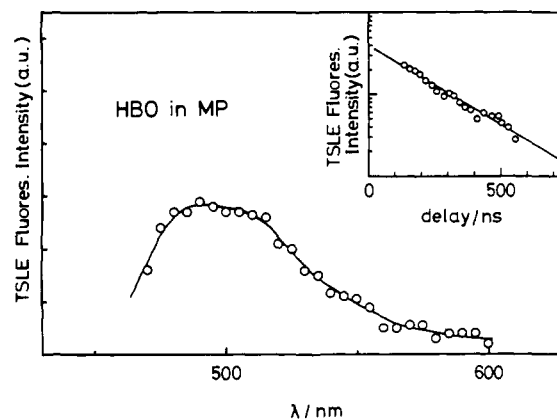
Figure 4. TSLE fluorescence spectrum of the deaerated MP solution of HBO at room temperature. Delay time after the first excimer laser excitation (308 nm) is 200 ns. The second laser wavelength is 406 nm. The concentration is 1.9×10^{-4} M.

et al.[11] reported a transient absorption band in the almost same wavelength region in the isopentane/methylcyclohexane solution of HBT with a double exponential decay as "photochromic colored species". Since the lifetimes of the singlet excited-state photo-tautomers are subnanosecond and/or at most a few nanoseconds, the transient absorption bands at λ_{max} 420 nm ($\tau = 260$ ns) of HBO and at λ_{max} 450 nm ($\tau = 9.4 \mu$ and 53.3 μs) of HBT may be ascribed to the ground-state phototautomer generated by the excited-state proton transfer and the relaxation. It is noteworthy that there seems to be a double exponential decay component involved in the photoisomerization of HBT (Table II).

In the photoisomerization of 7-hydroxyflavone in the methanol solution reported previously,[3] two ground-state phototautomers exhibiting two different fluorescence spectra and decay times were observed. Therefore, these phototautomers were confirmed to exhibit their respective fluorescence spectra by the TSLE time-resolved fluorescence. In the transient absorption spectra of HBT, however, no significant evidence of two transient absorption bands superimposed was obtained, though two following possibilities are considered: the observed transient absorption shown in Figure 3 may consist of a transient absorption band exhibiting two exponential decay or two absorption bands due to two ground-state phototautomers, which shows that completely identical absorption maxima are superimposed. However, the former possibility may be more reasonable than the latter from experimental results by the TSLE fluorescence variable delay technique.

Two-Step Laser Excitation Fluorescence. The TSLE fluorescence spectrum of the MP solution of HBO was measured, as shown in Figure 4. The TSLE fluorescence spectrum and decay

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Table II. Decay Times of the Ground-State Photoautomers of HBO and HBT in Deaerated MP Solvents[a]

| | HBO | | temp, K | HBT | | | |
| | abs[b] | TSLE[c] | | abs[b] | | TSLE[c] | |
				τ_{short}	τ_{long}	τ_{short}	τ_{long}
OH	260 ns	176 ns	300	9.4 μs (37%)	53.5 μs (63%)	8.0 μs (38%)	36.2 μs (62%)
			200	41.3 μs (36%)	264 μs (37%)	47.8 μs (44%)	269 μs (56%)
OD	2.05 μs	3.85 μs	300	15.5 μs (55%)	83.4 μs (45%)	10.4 μs (31%)	58.3 μs (69%)
			200	143 μs (83%)	2.78 ms (17%)	95.5 μs (53%)	2.24 ms (47%)

[a] Data in parentheses are fractions of components. [b] Determined by the transient absorption technique. [c] Determined by the variable delay technique of the TSLE fluorescence.
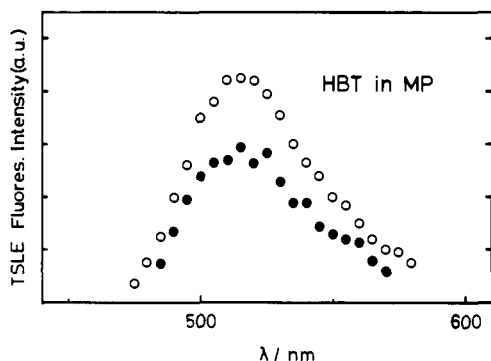

Figure 5. TSLE fluorescence spectra of the deaerated MP solution of HBT at room temperature. Delay time after the first excimer laser excitation (308 nm) is 800 ns (O) and 20 μs (●). The second laser wavelength is 440 nm. The concentration is 2.2 × 10⁻⁵ M.

Figure 6. Plot of TSLE fluorescence intensities vs. delay time between the first and second laser excitations in the deaerated MP solution of HBT at room temperature. The monitored wavelength is 540 nm. The concentration is 2.2 × 10⁻⁵ M.

are in good agreement with those obtained by an ordinary pulse excitation of the parent molecule. A single exponential decay of the ground-state phototautomer was obtained by plots of the TSLE fluorescence intensities vs. variable delay times between two laser pulses, whose decay time (τ = 176 ns) is in fair agreement with that of the transient absorption within experimental error. However, the transient absorption (λ_{max} 400 nm) in HBO attributable to the $T_n \leftarrow T_1$ absorption may be superimposed on the transient absorption due to the phototautomer in almost the same wavelength region, and then the second laser light is absorbed by the $T_n \leftarrow T_1$ absorption band. Therefore, the measurement of TSLE fluorescence is rather difficult in HBO, and the data by the TSLE fluorescence have less accuracy than those of transient absorption.

On the other hand, for HBT, if the fluorescence spectrum at λ_{max} 515 nm and the transient absorption at 450 nm are both attributable to phototautomer as mentioned above, the TSLE fluorescence obtained by the second laser excitation of the 450-nm band should be identical with the large Stokes-shifted fluorescence (λ_{max} 515 nm) obtained by the excitation of the parent molecule (normal form). The TSLE fluorescence spectra were measured at variable delay times. The spectra are independent of the delay time and identical with the ordinary fluorescence spectrum (Figure 1) at 300–160 K. Figure 5 shows the TSLE fluorescence spectra of HBT at the delay times of 800 ns and 20 μs from the first laser pulse at room temperature. Further, the double exponential decay curves of the TSLE fluorescence spectra were obtained at two different delay times. However, two exponential decay curves are almost identical with each other within the experimental error through 300–160 K, though the long-lived component in these double exponential decays was only a few percent of the short-lived one below 230 K. The TSLE fluorescence intensities were plotted vs. delay times between the first and second excitation pulses, as shown in Figure 6. As reported in previous papers,[2–4] a slope of these plots indicates the decay of the ground-state phototautomer excited by the second laser pulse. The plots shown in Figure 6 suggest two exponential decays of the ground-state phototautomer of HBT. These two decay times of the ground-state phototautomers of HBT were obtained to be 8.0 and 36.2 μs at room temperature, which are consistent with the short and long lifetimes determined by the transient absorption spectroscopy. Hence, we denote tentatively these ground-state phototautomers
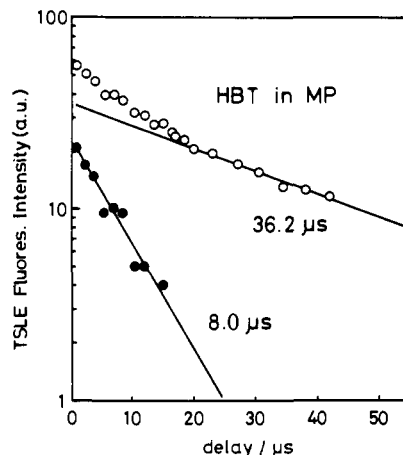
as the phototautomer I and II corresponding to I* and II*. However, since the transient absorption has less accuracy than the TSLE fluorescence, these two decay times obtained by the TSLE fluorescence spectroscopy have better reliability than by the transient absorption spectroscopy. This double exponential decay of the ground-state phototautomers were obtained below 230 K, where fluorescence decay of the excited-state phototautomers was single exponential as shown in Table I. If these two decay times of the ground-state phototautomers obtained by the TSLE fluorescence variable delay technique are attributable to two noninterchangeable ground-state phototautomers, two fluorescence spectra with respective lifetimes corresponding to the ground-state phototautomers (I and II) should be observed. However, a single exponential fluorescence decay was observed below 230 K by the ordinary pulse excitation as well as by TSLE fluorescence as mentioned above. Further, it is unlikely that fluorescence spectrum and lifetime of I are completely identical with those of II, respectively. Therefore, kinetics of the ground-state phototautomers I and II were considered to follow the reaction scheme

$$I^* \xrightarrow{\quad\times\quad} II^*$$
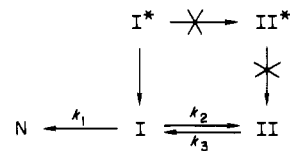
Then, we thought that the generation of II from II* may be negligible at this temperature, because the short lifetime component was observed to be dominant in the TSLE fluorescence decay and the long one was much less than 5% below 230 K. Taking account of this fact, the contribution of the ground-state phototautomer II to the TSLE fluorescence intensity may be approximately negligible in comparison with that of I. Hence, assuming the reaction scheme as mentioned above, the TSLE fluorescence intensities [F] at various delay times are expressed as follows: $[F] \propto [I] \, \epsilon_I \Phi_I$, where ϵ_I and Φ_I are the molar extinction coefficient and fluorescence quantum yield of I, respectively.

Transient Absorption and TSLE Fluorescence Studies
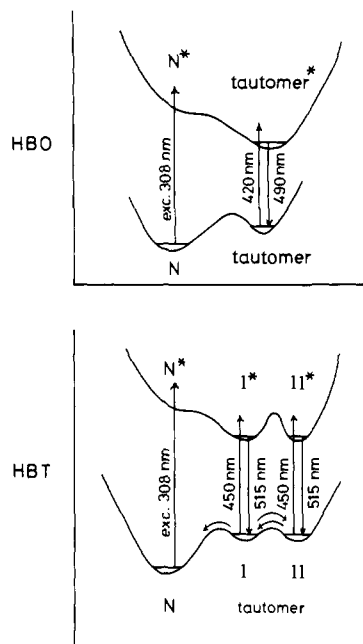
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Figure 7. Schematic energy diagram of the proton transfer in HBO and HBT.

Table III. Rate Constants in HBT's Proton-Transfer Reaction in the Ground State[a]

$$N \xleftarrow{k_1} I \underset{k_3}{\overset{k_2}{\rightleftharpoons}} II$$

	k_1, s^{-1}	k_2, s^{-1}	k_3, s^{-1}
OH	5.84×10^3	5.46×10^3	13.4×10^3
OD	0.90×10^3	4.85×10^3	5.17×10^3

[a] N is the normal enol form. I and II are the keto forms.

According to the reaction scheme and assumptions as mentioned above, the time-dependent concentrations of I and II are expressed as

$$[I] = \frac{[I]_0}{\beta - \alpha} [(k_3 - \alpha) \exp(-\alpha t) + (\beta - k_3) \exp(-\beta t)]$$

$$[II] = \frac{[I]_0 k_2}{\beta - \alpha} [\exp(-\alpha t) - \exp(-\beta t)]$$

where

$$\alpha, \beta = \frac{1}{2}[k_1 + k_2 + k_3 \pm [(k_1 + k_2 + k_3)^2 - 4k_1 k_3]^{1/2}$$

where $[I]_0$ is the concentration at $t = 0.$[12]

The ratio (r) of the short and long decay components of the ground-state phototautomer I obtained by this TSLE fluorescence variable delay technique is

$$r = (k_3 - \alpha)/(\beta - k_3)$$

The decay constants α and β afford $\alpha + \beta = k_1 + k_2 + k_3$, and $\alpha\beta = k_1 k_3$. From the observed ratio (r) of the decay components and the decay constants in the TSLE variable delay curve, the reaction rate constants, k_1, k_2, and k_3, were obtained. The reaction rate constants were also obtained for the deuterium-substituted HBT of the hydroxyl hydrogen atom. These data are summarized in Table III.

The time-dependent concentrations of I and II at 200 K were simulated by using obtained rate constants $k_1 - k_3$ as shown in Figure 8. If the contribution of [II] in the TSLE fluorescence
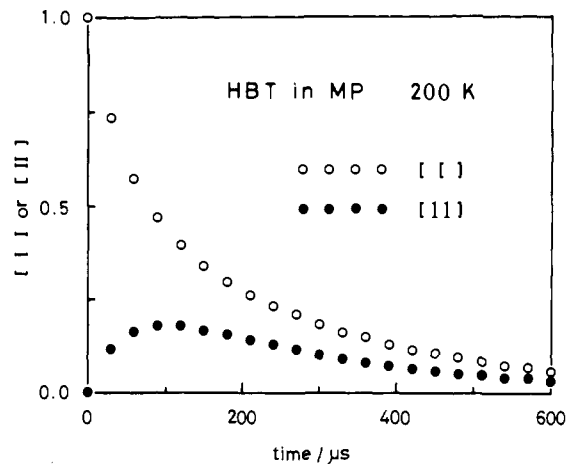
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(12) The lifetimes of excited- and ground-state phototautomers are of the order of nanosecond and microsecond, respectively. Then, we assumed that [I] was produced in proportion to the δ function.

Figure 8. Normalized time-dependent concentrations of the ground-state phototautomers I (O) and II (●), which were calculated with k_1, k_2, and k_3 values of the deaerated MP solution of HBT at 200 K.

is not negligible compared with that of [I], the long-lived component of the TSLE fluorescence decay should be observed to some extent in the decay curve. However, a very small amount of the long-lived fluorescence (~5%) was observed in the TSLE fluorescence decay curves irrespective of the delay times between the two laser pulses, as mentioned above, though [II] is small but not negligible in comparison with [I] as shown in Figure 8. Therefore, the molar extinction coefficient (ϵ_{II}) of the ground-state phototautomer II at the second laser wavelength seems to be much smaller than that of I (ϵ_I). This interpretation is consistent with the fact that transient absorption spectra (λ_{max} 450 nm) of the ground-state phototautomers are independent of the delay times at 200 K.

Among the rate constants, k_1 means that the rate constant of the reverse proton transfer is from the coplanar cis-keto phototautomer (I) to the parent molecule (N). The rate constants k_2 and k_3 reflect the torsional motion about the C_1–C_7 bond from I to II. The reverse proton transfer from I to the parent molecule of HBT exhibits a remarkable deuterium substitution effect of the 2-hydroxyl group, while the rate constants k_2 and k_3 of the C_1–C_7 torsional transitions between I and II show only a small isotope effect. Since the O–H (O–D) stretching vibration may take an important role in the reverse proton transfer from I to N, the experimental results of the deuterium substitution effect of the 2-OH group to these rate constants are in good consistency with the anticipation from the proposed reaction scheme. On the other hand, HBO was reported to consist of cis- and trans-enol conformers.[9] The excited state of the former exhibits the excited-state proton transfer to afford the phototautomer with cis-keto conformer. In this paper, this phototautomer was confirmed to have only one conformer in the excited state as well as in the ground state. However, it was demonstrated in this paper that there are two phototautomers both in the ground and excited states of HBT. The structure of the phototautomer II in HBT was tentatively proposed to be a twisted conformer about C_1–C_7, though it is not decided at the present stage whether the conformer II may be attributable to a really twisted conformer or a trans-keto amine. The structural difference of the phototautomers between HBO and HBT seems to be ascribed to the size and electronic character of oxygen and sulfur atoms in HBO and HBT.

Registry No. HBO, 835-64-3; HBT, 3411-95-8.