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Photoinduced intramolecular hydrogen atom transfer in 2-(2-hydroxyphenyl)benzoxazole and 2-(2-hydroxyphenyl)-benzothiazole studied by laser flash photolysis

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2-(2-Hydroxyphenyl)benzoxazole (HBO) and 2-(2-hydroxyphenyl)benzothiazole (HBT) underwent hydrogen atom transfer to give the tautomer in both the singlet excited state and the triplet excited state. In the singlet excited state, the keto form produced by excited state hydrogen atom transfer underwent isomerization around the quasi-double bond to give the *trans*-keto form. In the triplet excited state, HBO and HBT were equilibrated between the enol form and the *cis*-keto form and the equilibrium constant was determined by triplet sensitization and quenching experiment by using laser flash photolysis in benzene at room temperature. From these results, we have revealed the energy diagram of the hydrogen atom transfer reaction of HBO and HBT both in the singlet excited state and the triplet excited state.

Introduction

The excited state intramolecular proton or hydrogen atom transfer (ESIPT) reaction has received considerable attention from the viewpoint of reaction dynamics and the possibility of the applications of photostabilizers, proton transfer laser, *etc.*[1–5] The mechanism of the ESIPT reaction is usually described by a four level scheme involving the singlet excited state of the normal form and the tautomer form and those forms in the ground state.

The ESIPT reaction of 2-(2-hydroxyphenyl)benzoxazole (HBO) and 2-(2-hydroxyphenyl)benzothiazole (HBT) (Fig. 1) was extensively investigated.[6–19] HBO and HBT underwent intramolecular hydrogen atom transfer not only in the singlet excited state but also in the triplet excited state.[14–16]

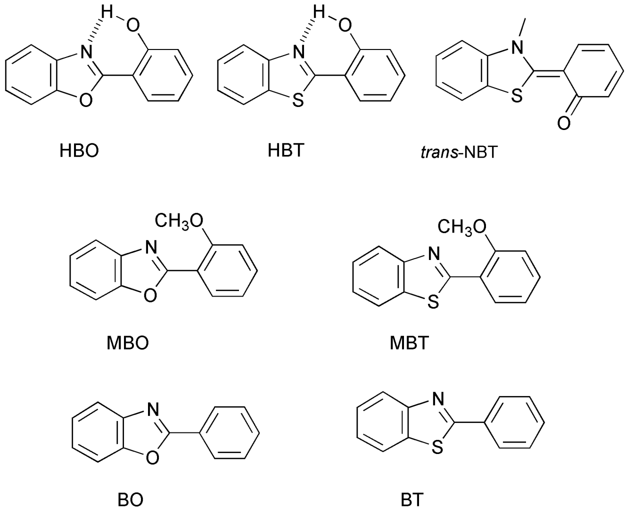

Fig. 1 Compounds investigated in this study.

In the singlet excited state, HBO and HBT gave a tautomer exhibiting fluorescence emission with a large Stokes shift, where the maximum wavelength was observed at 500 and 520 nm for HBO and HBT, respectively in non-polar solvents.[10–14] In addition, HBO and HBT exhibited transient absorption spectra with a maximum wavelength of 430 and 460 nm, respectively.[6,8,11]

From the results of two-step laser excitation (TSLE) fluorescence and the effect of temperature on the intensity of tautomer emission, the observed transient species in the ground state was assigned to the *trans*-keto form, which was produced by *cis*-to-*trans* isomerization of the *cis*-keto form in the singlet excited state.[10–14]

As to the photochemical behavior in the triplet excited state, HBO exhibited T–T absorption in non-polar solvents. In addition, dual phosphorescence spectra were observed in HBO and HBT at cryogenic temperatures.[13,16,17] In HBO, the observation of a nearly temperature-independent ratio of two phosphorescences was explained by the approximately isoenergetic relation of the enol and keto form in the triplet excited state.[16]

However, the potential energy diagram of ESIPT of HBO and HBT at room temperature was still uncertain.

In this study, the equilibrium constant between the enol and keto form in the triplet excited state of HBO and HBT was estimated by laser flash photolysis on triplet sensitization and quenching method. In addition, we have synthesized a model compound of the tautomer of HBT, and its photochemical behavior was examined. Thus, we can clearly observe the *cis*–*trans* isomerization of the keto form of HBO and HBT in the excited state and can estimate the quantum yield of formation of the *trans*-keto form in the ground state. Furthermore, we have revealed the potential energy diagram of hydrogen atom transfer (Fig. 2) of HBO and HBT.

Experimental

Materials and solvents

2-(2-Hydroxyphenyl)benzoxazole (HBO) and 2-(2-hydroxyphenyl)benzothiazole (HBT) were obtained from TCI (Tokyo Kasei) and purified by silica gel column chromatography and recrystallization from ethanol.

2-(2-Methoxyphenyl)benzoxazole (MBO) and 2-(2-methoxyphenyl)benzothiazole (MBT) were prepared from HBO and HBT by reaction with dimethyl sulfate in dioxane in the presence of aqueous NaOH.

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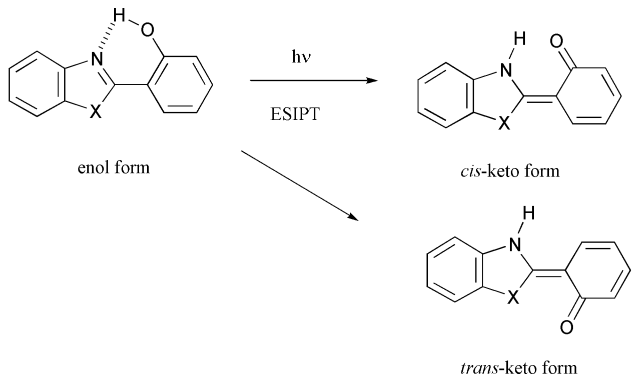
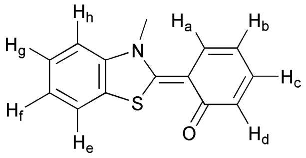


Fig. 2 Excited state intramolecular hydrogen atom transfer of HBO and HBT.

2-Phenylbenzoxazole (BO) and 2-phenylbenzothiazole (BT) were purchased from Aldrich and purified by silica gel column chromatography and recrystallization from ethanol.

trans-6-[*N*-Methyl-2(3*H*)-benzothiazolylidene]cyclohexa-2,4-dienone (*trans*-NBT) was synthesized according to a procedure similar to that reported by Nagaoka *et al.*[18] *trans*-NBT: ^{1}H NMR (methanol-d$_4$, 600 MHz) δ 4.29 (s, 3H; N-CH$_3$), 6.66 (m, 1H; H$_b$), 6.86 (d, 1H, $J = 8.6$ Hz; H$_d$), 7.39 (m, 1H; H$_c$), 7.67 (m, 1H; H$_f$), 7.70 (d, 1H, $J = 8.2$ Hz; H$_a$), 7.80 (m, 1H; H$_g$), 8.05 (d, 1H, $J = 8.5$ Hz; H$_h$), 8.13 (d, 1H, $J = 7.8$ Hz; H$_e$) ppm.



In spectroscopy, Dotite Spectrosol and Luminasol were used as solvents without further purification.

Measurement

Absorption and fluorescence spectra were measured on a JASCO Ubest-55 and on a Hitachi F-4000 fluorescence spectrometer, respectively. Quantum yields of fluorescence were determined by using anthracene ($\Phi_f = 0.27$)[21] as an emission standard.

Laser flash photolysis was performed by using an excimer laser (Lambda Physik LPX-100, 308 nm, 20 ns fwhm) or excimer laser pumped dye laser (Lambda Physik LEXtra-100, 308 nm, 20 ns fwhm and Lambda Physik Scanmate; Lambda Physik LPX-100, 308 nm, 20 ns fwhm and Lambda Physik FL-3002, 10 ns fwhm). Stilbene 3, DMQ, and QUI were used as laser dyes to obtain a 425, 366 and 390 nm laser pulse, respectively. A pulsed xenon arc (Ushio UXL-159) was used as a monitoring light source.

Results

Absorption and fluorescence spectra

Absorption and fluorescence spectra of HBO and HBT in benzene are shown in Fig. 3. The quantum yield of the tautomer fluorescence was determined to be 0.02 and 5 × 10^{-3} in benzene for HBO and HBT, respectively.

The effect of temperature on the quantum yield of fluorescence emission in benzene was examined. The fluorescence quantum yield of the tautomer emission increased with decreasing temperature in benzene from 0.013 at 40 °C to 0.035 at 7 °C indicating that the deactivation pathway with activation energy exists in the singlet excited state of the tautomer. The temperature effect on the fluorescence intensity was also reported in some hydrocarbon solvents.[7,8]

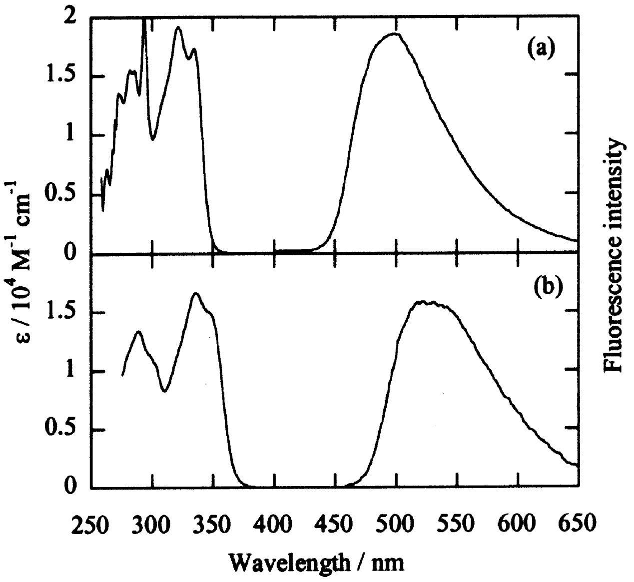


Fig. 3 Absorption and fluorescence spectra of HBO (a) and HBT (b) in benzene.

Transient absorption spectra on direct irradiation

HBO and HBT exhibited transient absorption spectra with a maximum wavelength of 430 and 465 nm, respectively on 308 nm excitation as shown in Fig. 4. The transient absorption spectra of HBO shifted to the shorter wavelength with time and the maximum wavelength appeared around 400 nm at 1.87 μs after the laser pulse, which had a lifetime of 2.5 μs at room temperature and was not quenched by oxygen. Therefore, this transient species can be assigned to the tautomer form. We have observed a negative temperature effect on the lifetime of this transient in methylcyclohexane as shown in Fig. 5. Thus, the lifetime increased with increasing temperature. In addition, a transient absorption with a maximum of 400 nm was observed in benzene (Fig. 4a), which was assigned to the triplet state by oxygen quenching experiments, where the quenching rate constant was determined to be 3 × 10^9 M^{-1} s^{-1}. The spectra and the lifetimes of transient absorption were similar to those in other hydrocarbon solvents.[6]

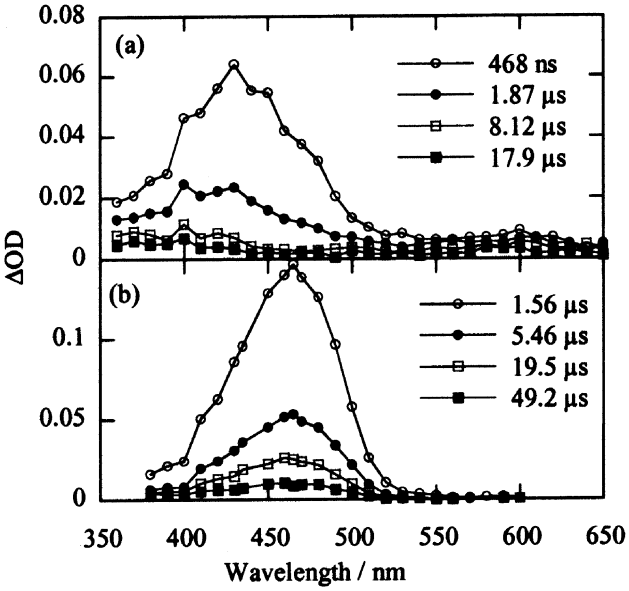


Fig. 4 Transient absorption spectra of HBO (a) and HBT (b) in benzene on direct irradiation.

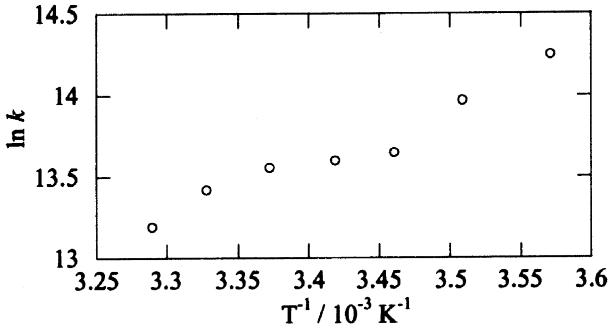


Fig. 5 Arrhenius plot for decay constants of HBO tautomer in methylcyclohexane.

Conformation and absorption spectrum of NBT, a model tautomer compound

In order to assign the conformation of the model compound NBT, COSY and NOESY spectra were measured in methanol-d_4. The two peaks at 8.05 and 7.70 ppm showed NOE with N-CH_3 proton (4.29 ppm) indicating that NBT exists in the *trans* conformation in the ground state.

The absorption spectrum of *trans*-NBT appeared with the maximum wavelength at 466 nm with a molar extinction coefficient of 7000 in benzene as shown in Fig. 6. *trans*-NBT did not give fluorescence emission in benzene at room temperature.

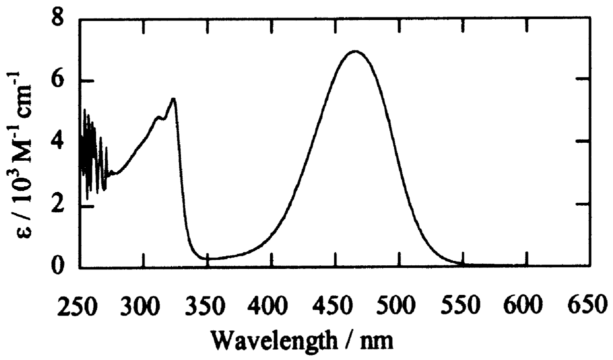


Fig. 6 Absorption spectrum of *trans*-NBT in benzene at room temperature.

Laser photolysis of *trans*-NBT

Laser flash photolysis of *trans*-NBT was performed in benzene. Immediately after excitation with a 308 nm laser pulse, bleaching of the absorption maximum at 465 nm and an intense absorption band at 510 nm were observed as shown in Fig. 7. The recovery at 465 nm and the decay at 510 nm gave the same time constant of 110 ns. This result indicates that *trans*-NBT underwent *trans*-to-*cis* isomerization photochemically followed by reverse *cis*-to-*trans* isomerization thermally in benzene with a time constant of 110 ns.

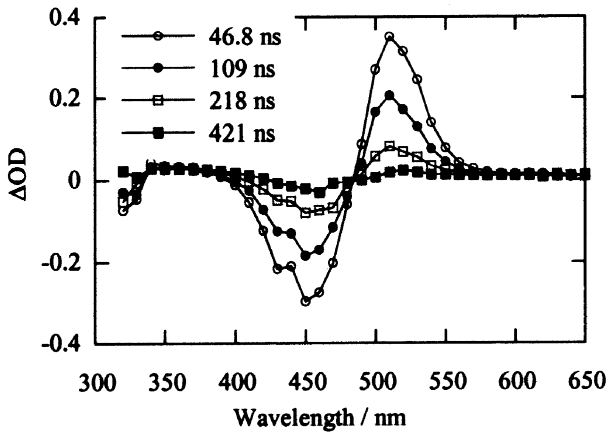


Fig. 7 Transient absorption spectra of *trans*-NBT in benzene at room temperature.

Two step laser excitation of HBO

After we produced the tautomer of HBO by 308 nm laser pulse with laser flash photolysis, the second laser pulse of 425 nm was irradiated with an appropriate delay time. In the time profile of transient absorption, we can observe the bleaching of the *trans*-keto form at 430 nm, with the concomitant recovery of the enol form at 344 nm under argon as shown in Fig. 8.

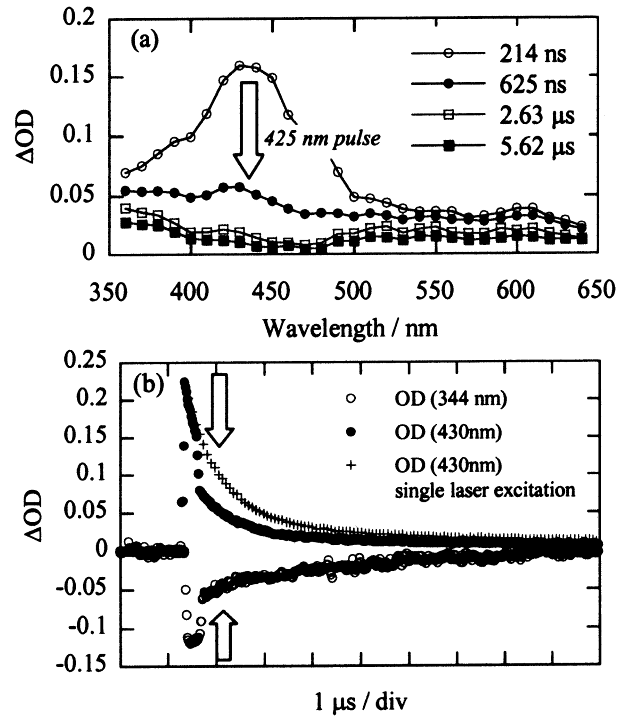


Fig. 8 Transient absorption spectra (a) and time profiles (b) observed by two step laser excitation (308 and 425 nm) monitored at 344 (○) and 430 nm (•) and by single laser excitation (308 nm) monitored at 430 nm (+) of HBO in benzene.

Determination of the quantum yield of formation of the tautomer form

The quantum yield of formation of the tautomer form was estimated in benzene by comparing the ΔOD value of the tautomer form of HBO and HBT with ΔOD of the T–T absorption of optically matched benzophenone solution at 308 nm, assuming that the molar extinction coefficient of the tautomer was the same as that of *trans*-NBT. The molar extinction coefficient of benzophenone in the triplet excited state at 530 nm was reported to be 7220.[20] Thus, the quantum yield of formation of the tautomer was estimated to be 0.2 and 0.4 for HBO and HBT, respectively at room temperature in benzene.

Transient absorption spectra of BO, BT, MBO, MBT and quantum yield of intersystem crossing

Transient absorption spectra of BO, BT, MBO, and MBT are summarized in Fig. 9. The intense band was observed at around 400 nm and the lifetimes of transient absorption spectra were determined to be 10 μs under argon atmosphere. The transient absorption spectra were assigned to the enol forms, since they could not undergo tautomerization.

The triplet energies of these compounds were estimated by the rate constant of the triplet energy transfer from sensitizer to quencher. The rate constants (k_q) from Michler's ketone

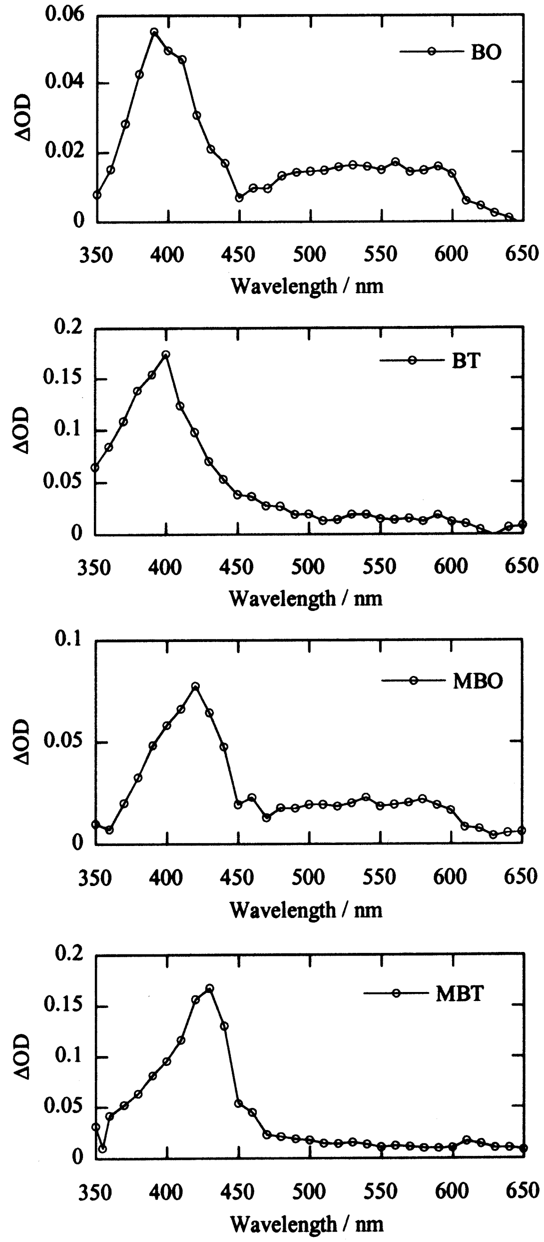


Fig. 9 Transient absorption spectra of BO, BT, MBO and MBT in benzene.

(E_T = 65.8 kcal mol^{-1})[21] to HBO and MBO were determined to be 3.7 × 10^9 and 3.6 × 10^9 M^{-1} s^{-1}, respectively, thus the triplet energy was estimated to be 66 kcal mol^{-1} for both HBO and MBO by using the Sandros equation (eqn. (1)),[28] which can be applied in the case that the energy transfer process is iso-energetic or slightly endothermic. The value of ΔE_a stands for the energy difference between the sensitizer and the quencher and the k_{diff} was estimated to be 6.3 × 10^9 M^{-1} s^{-1} in the case.[15,22–27]

$$k_q = k_{diff}\exp(-\Delta E_a/RT)/[1 + \exp(-\Delta E_a/RT)] \quad (1)$$

The triplet state of Michler's ketone was quenched by BO, MBT and HBT with a diffusion controlled rate constant. However, the lifetime of biacetyl triplet (E_T = 56 kcal mol^{-1})[21] was not affected by BO, MBT and HBT. On the basis of these results, the triplet energy of the enol form of HBT was estimated to be *ca.* 60 kcal mol^{-1}.

The quantum yields of intersystem crossing (Φ_{isc}) were estimated by comparing ΔOD of the T–T absorption spectrum of an optically matched solution on benzophenone sensitization (λ_{ex} = 360 nm). The concentration of quencher was 0.01 M and one can expect that triplet energy transfer occurred within the laser pulse of 20 ns. Triplet energies and quantum yields of intersystem crossing are summarized in Table 1.

Table 1 Photochemical properties of benzoxazole and benzothiazole derivatives at room temperature in benzene

	Φ_f [a]	τ_f/ns	Φ_{isc}	E_S [b]	E_T [b]
BO	0.66	1.5	0.13	89	(60) [d]
MBO	0.51	1.2	0.16	85	66 [c]
BT	0.01		0.57	87	60 [21]
MBT	0.05		0.69	83	(60) [d]
HBO	0.02		0.03	84	66 [c]
HBT	5 × 10^{-3}			80	(60) [d]

[a] 2-Phenylbenzoxazole (Φ_f = 0.75 in cyclohexane)[9] used as a fluorescence standard. [b] In kcal mol^{-1}. [c] From the quenching rate constant of 4,4′-bis(dimethylamino)benzophenone (**1**) (E_T = 65.8 kcal mol^{-1})[21] triplet by MBO and MBT. [d] Triplet state of **1** was quenched by BO, MBT and HBT with a diffusion controlled rate constant. However, the lifetime of biacetyl triplet (E_T = 56 kcal mol^{-1}) was not affected by BO, MBT and HBT.

We should mention the previous reports about the lack of intersystem crossing for HBT and BT. Thus, both HBO and HBT underwent hydrogen atom transfer to give the *cis*-keto form in the excited singlet state. The *cis*-keto form of HBT did not undergo intersystem crossing to the triplet state,[8] while HBO underwent intersystem crossing to the triplet state at room temperature. It was reported that only a weak T–T absorption spectrum with a maximum at 420–440 nm was detected at room temperature on direct irradiation of BT.[9] Therefore, the lack of intersystem crossing in HBT was explained in connection with the low efficiency of intersystem crossing in BT by the importance of torsional motion around the single bond to the radiationless deactivation.[8,9] However, we have observed the T–T absorption spectra (λ_{max} = 400 nm) of BT with quantum efficiency as high as 0.6.

Transient absorption spectra of HBO and HBT on triplet sensitization and the quenching rate constant

The transient absorption spectra observed on benzophenone and Michler's ketone sensitization of HBO and HBT on excitation at 366 and 390 nm, respectively at room temperature under argon atmosphere in benzene are shown in Fig. 10. In this sensitization experiment, the concentration of HBO and HBT was adjusted to 0.01 M and that of benzophenone and Michler's ketone was adjusted to 0.03 and 0.006 M, respectively. In these experimental conditions, the triplet energy transfer should take place within the duration of the laser pulse and just after the laser pulse we can observe the triplet state of HBO and HBT. The lifetime of the triplet state was determined to be 7.4 and 7.5 μs for HBO and HBT, respectively under argon atmosphere in benzene. These transient absorption spectra were quenched by oxygen with the rate constant of 3 × 10^9 M^{-1} s^{-1}.

The spectral profiles of MBO and MBT are similar to those of BO and BT, but the absorption maximum slightly shifted to a longer wavelength and appeared at 420 nm. However, the T–T absorption spectra of HBO and HBT observed on triplet sensitization (Fig. 10) are different from those of MBO and MBT (Fig. 9) indicating that the observed triplet states for HBO and HBT are not simply the enol triplet, but a mixture of the enol form ($^3E^*$) and the *cis*-keto form ($^3K^*$). The observed transient absorption spectra can be assigned to either the enol form or the *cis*-keto form in the triplet state.

The quenching rate constants for the HBO triplet by *cis*- (E_T = 54.3 kcal mol^{-1}) and *trans*-stilbene (E_T = 49.2 kcal mol^{-1}) are determined to be 3.3 × 10^9 and 4.7 × 10^9 M^{-1} s^{-1}, respectively for HBO. The quenching rate constants for HBT by *cis*- and *trans*-stilbene are 3.2 × 10^8 and 1.7 × 10^9 M^{-1} s^{-1}, respectively and are lower than the values for HBO.

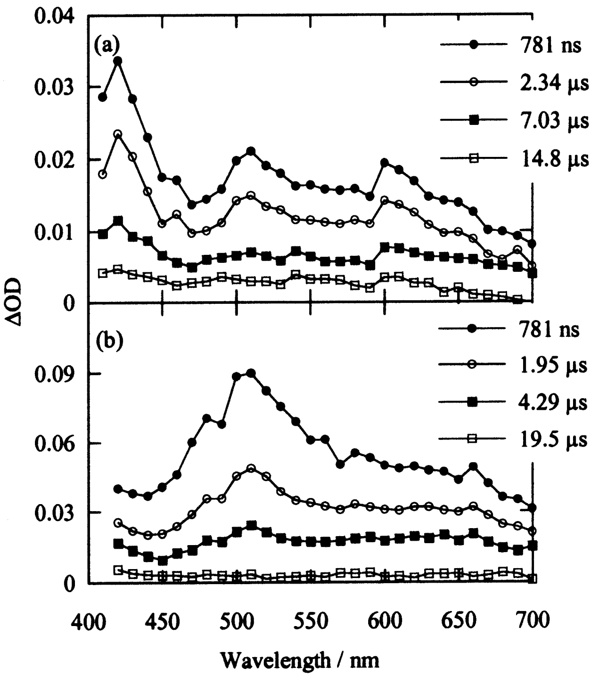


Fig. 10 Transient absorption spectra of HBO (a) and HBT (b) on triplet sensitization in benzene.

Discussion

Photochemistry of *trans*-NBT, as a model compound for the tautomer of HBT

The result of laser flash photolysis of *trans*-NBT (Fig. 7) indicates that *trans*-NBT underwent photochemical *trans*-to-*cis* isomerization followed by reverse *cis*-to-*trans* isomerization thermally in benzene with the time constant of 110 ns.

The absorption maximum of *cis*-NBT appeared at 510 nm which is longer than that of *trans*-NBT by 50 nm. The change of the absorption maximum may be due to the change of the dipole between *cis*- and *trans*-NBT and/or change of conjugation character of the N-CH_3 group between *cis*- and *trans*-NBT by steric effect.

The potential energy surface of isomerization of *trans*-NBT is shown in Fig. 11. The absorption spectrum of the ground state transients observed on laser excitation appearing at 465 nm (Fig. 4) is quite similar to that of *trans*-NBT. These results strongly indicate that HBT gave the *trans*-keto form by excited state hydrogen atom transfer in the singlet excited state followed by *cis*-to-*trans* isomerization.

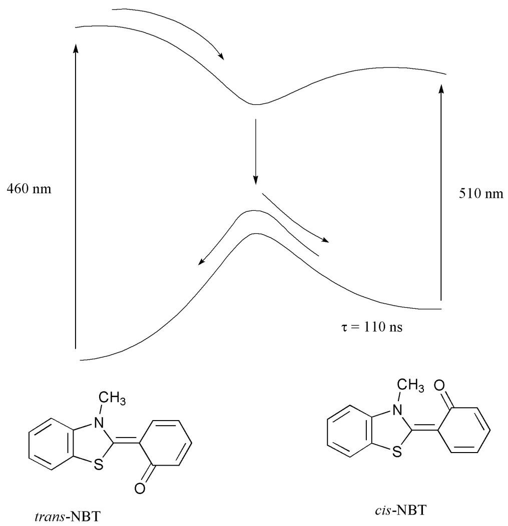


Fig. 11 Potential energy surfaces of isomerization of *trans*-NBT in benzene at room temperature.

Conformation of the tautomer

Since the absorption maximum of *trans*-NBT, the model compound of the *trans*-keto form, was observed at 466 nm and was shorter than that of *cis*-NBT, the transient observed on laser excitation of HBT (Fig. 4b) with the maximum at 465 nm was reasonably assigned to the *trans*-keto form. We can also assign the 430 nm transient observed for HBO (Fig. 4a) to the *trans*-keto form of HBO. Two step laser excitation also supports the assignment of the transient species to the *trans*-keto form in the ground state. The *cis*-keto form could not be observed since fast reverse hydrogen atom transfer can take place within our time resolution of 20 ns in the *cis*-keto form due to the presence of intramolecular hydrogen bonding. The quantum yield of *trans*-keto tautomer formation was thus estimated to be 0.2 and 0.4 for HBO and HBT, respectively.

Equilibrium constant between enol form and *cis*-keto form in the triplet excited state

We can estimate the equilibrium constant (K = [^{3}K*]/[^{3}E*]) by measuring the rate constant of energy transfer from the transient species to several quenchers.

The triplet energies of the enol form and the *cis*-keto form for HBO are estimated to be 63.8 and 50.0 kcal mol^{-1} and those for HBT are estimated to be 59.3 and 49.2 kcal mol^{-1}, respectively from the phosphorescence spectra.[13,16] These values were consistent with the triplet energies estimated from the quenching rate constant of the triplet excited state of HBO and HBT as shown in Table 1. Thus, the triplet energies of the enol forms of HBO and HBT are higher than those of *cis*- and *trans*-stilbene, while those of the *cis*-keto form are comparable to the triplet energy of *trans*-stilbene.

The observed quenching rate constants of HBT triplet by *trans*-stilbene ($k_q = 1.7 \times 10^9$ M^{-1} s^{-1}) as well as *cis*-stilbene ($k_q = 0.32 \times 10^9$ M^{-1} s^{-1}) were smaller than the diffusion controlled rate constant, while the values for HBO quenched by *cis*-stilbene are nearly 1/2 of the diffusion controlled rate constant ($k_{diff} = 6.3 \times 10^9$ M^{-1} s^{-1}). Since *cis*-stilbene can quench the triplet enol form with nearly the diffusion controlled rate constant, but can scarcely quench the triplet *cis*-keto form, we can estimate the equilibrium constant between the enol form and the *cis*-keto form (K = [^{3}K*]/[^{3}E*]) by using eqn. (2). Thus, K is estimated to be 0.91 and 20 for HBO and HBT, respectively.

$$k_q = k_{diff}[^3E^*]/([^3E^*] + [^3K^*]) = k_{diff}/(1 + K) \qquad (2)$$

Potential energy surfaces of hydrogen atom transfer of HBO and HBT

HBO and HBT exhibited fluorescence spectra with a large Stokes shift of 10000 cm^{-1}, which were assigned to the tautomer produced by hydrogen atom transfer in the singlet excited state. In addition, transient absorption spectra with a maximum wavelength of 430 and 465 nm respectively were observed in benzene. The fluorescence quantum yield of the tautomer emission increased with decreasing temperature. This result indicates that the deactivation pathway with activation energy exists in the singlet excited state of the tautomer, therefore the *cis*-keto form would undergo *cis*-to-*trans* isomerization to give the *trans*-keto form.

As to the deactivation from the triplet state, one can expect the *cis*–*trans* isomerization of the *cis*-keto form to give the *trans*-keto form as well as in the singlet excited state. If the *trans*-keto form was produced through the deactivation processes, one could observe its absorption spectra with the absorption maximum at 430 nm and the lifetime of 7.5 μs. However, we have observed only the T–T absorption spectra under oxygen atmosphere as well as argon atmosphere in benzene at room temperature. Therefore, the deactivation of the triplet state of HBO and HBT took place to give the enol form or the *cis*-keto form: the *cis*-keto form underwent fast reverse hydrogen atom transfer within our time resolution (~20 ns) to give the enol form. Thus, the diabatic as well as adiabatic *cis*–*trans* isomerization around the double bond in the *cis*-keto form did not take place in the triplet state. These results are summarized in Fig. 12.

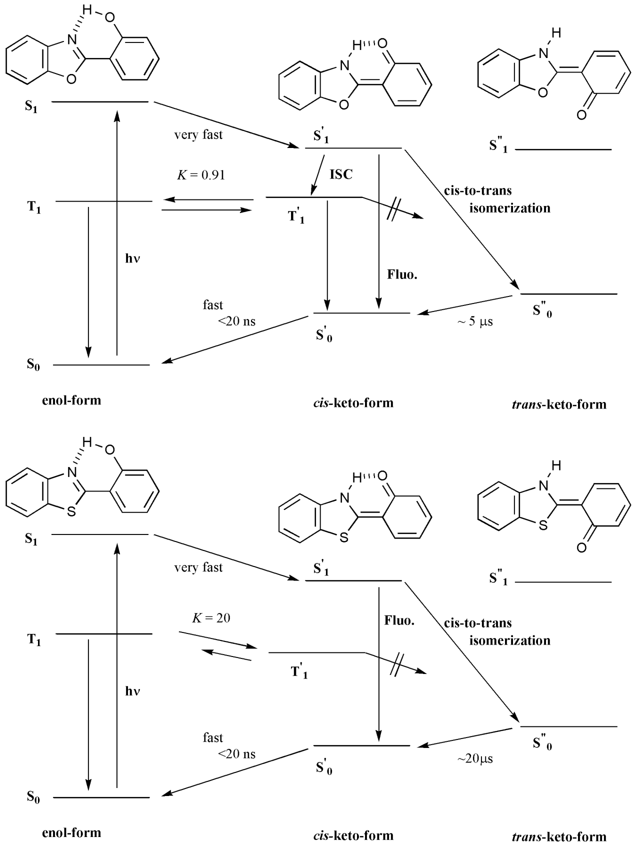


Fig. 12 Energy diagram of hydrogen atom transfer of HBO (above) and HBT (below).

Conclusion

HBO and HBT underwent excited state intramolecular hydrogen atom transfer followed by *cis*-to-*trans* isomerization in the singlet excited state to give the *trans*-keto tautomer with the quantum yield of 0.2 and 0.4 for HBO and HBT, respectively. On the other hand, *cis*–*trans* isomerization did not occur in the *cis*-keto form in the triplet excited state. These results indicate that intramolecular hydrogen bonding is broken in the singlet excited state, but may be present in the triplet excited state.

The *trans*-keto form produced by ESIPT followed by *cis*–*trans* isomerization in the ground state isomerizes thermally to the *cis*-keto form, which undergoes reverse hydrogen atom transfer within 20 ns. This reverse hydrogen atom transfer to give the enol form in the ground state was also supported by the effect of temperature on the lifetime of the ground state tautomer exhibiting negative Arrhenius activation energy in methylcyclohexane.

In conclusion, we have revealed the potential energy surface of hydrogen atom transfer of HBO and HBT in the excited state.

Acknowledgements

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