The Effect of *meta*-Substitution on the Photochemical Properties of Benzoxazole Derivatives

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The photochemistry of 2-(2-hydroxy-3-methoxyphenyl)benzoxazole (**3-MHBO**) and 2-(2-hydroxy-4-methoxyphenyl)benzoxazole (**4-MHBO**) have been investigated. The excited-state properties of **4-MHBO** were similar to those for the parent compound 2-(2-hydroxyphenyl)benzoxazole (**HBO**), whereas different properties were observed for **3-MHBO**. **4-MHBO** in benzene exhibited large Stokes-shifted fluorescence from the keto-form in the excited singlet state ($\mathbf{K}_E^*$) after excited-state intramolecular proton transfer (ESIPT), whereas **3-MHBO** emitted dual fluorescence from $\mathbf{E}^*$ and $\mathbf{K}_E^*$ species. Fluorescence due to $\mathbf{K}_E^*$ for **3-MHBO** ($\lambda_{max} = 525$ nm) occurred at a considerably longer wavelength than that of **4-MHBO** ($\lambda_{max} = 480$ nm). The fluorescence efficiency of **3-MHBO** ($\Phi_f = 0.002$) was much smaller than those of **4-MHBO** and **HBO** ($\Phi_f = 0.018$ and 0.02, respectively). These results are consistent with suppression of ESIPT, stabilization of $\mathbf{K}_E^*$ species, and acceleration of non-radiative decay, probably because of the formation of a hydrogen bond between phenol oxygen and methoxy hydrogen at 3-position in **3-MHBO**. Thus, **3-MHBO** displayed a *meta*-substituent effect involving the relaxation pathway of excited state **HBO** derivatives.

Excited-state intramolecular proton (or hydrogen atom)-transfer reactions (ESIPT) in hydrogen-bonded molecules have widely been investigated[1] from the view points of the development of new functional molecules, such as fluorescent metal probes,[2] laser dyes,[3] photostabilizers,[4] and organic light-emitting diodes.[5] Typical ESIPT molecules preferentially exist as enol form (**E**) in their ground state. ESIPT reaction is a photochemical tautomerization, which is triggered upon photoexcitation of the ground state **E** form, that yields an excited keto form ($\mathbf{K}^*$) on the subpicosecond time scale.[6] After decaying to the ground state, **K** reverts back to the original thermally stable **E** (Fig. 1). The structural difference between absorbing species **E** and emitting species **K** in this reaction cycle results in a large Stokes-shifted fluorescence, which is unusual emission at longer wavelength from a small molecule and therefore is not reabsorbed even in high concentrations of a chromophore. However, precise control of the fluorescence properties of ESIPT is required for specific applications.[7]

2-(2′-Hydroxyphenyl)benzoxazole (**HBO**) is known to undergo ESIPT. Due to its chemical stability, structural simplicity, and facility for chemical modification,[8] the photochemistry of many **HBO** analogues has been investigated experimentally and theoretically.[9] Nevertheless, to the best of our knowledge, the practically important spectral properties that are dependent on the substituent position in **HBO** analogues have not been investigated. In this paper, we report the effect of substitution on the photochemical properties, especially in the relaxation pathways, for benzoxazole derivatives 2-(2-hydroxy-3-methoxyphenyl)benzoxazole (**3-MHBO**) and 2-(2-hydroxy-4-methoxyphenyl)benzoxazole (**4-MHBO**). The UV-absorption and fluorescence spectra of **4-MHBO** were similar to those for the parent compound **HBO**, whereas different photochemical properties were observed for **3-MHBO**.

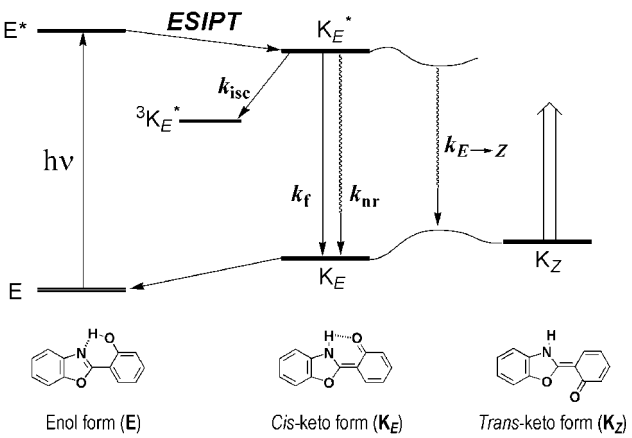

Fig. 1. Energy diagram of enol (**E**) and keto (**K**) tautomers of **HBO**.

Experimental

Materials. Schiff bases **1** and **2** were prepared by condensing *o*-aminophenol with 2-hydroxy-3-methoxybenzaldehyde for **1** and with 2-hydroxy-4-methoxybenzaldehyde for **2**, in refluxing ethanol for 24 h. After the solution was cooled to room temperature, the crude product was filtered off and washed with cold ethanol, followed by recrystallization from ethanol to give pure product.

2-Hydroxy-*N*-(3-methoxysalicylidene)aniline (1): ^{1}H NMR ($CDCl_3$, 200 MHz, Me_4Si) δ 12.58 (1H, brs, OH), 8.70 (1H, s, C*H*=N), 7.24–7.16 (2H, m, ArH), 7.08–7.01 (3H, m, ArH), 6.99–6.90 (2H, m, ArH), 5.97 (1H, brs, OH), 3.94 (3H, s, CH_3). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.93; N, 5.76%. Found: C, 69.09, H, 5.46, N, 5.61%.

2-Hydroxy-*N*-(4-methoxysalicylidene)aniline (2): ^{1}H NMR ($CDCl_3$, 200 MHz, Me_4Si) δ 12.69 (1H, brs, OH), 8.58 (1H, s,

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C*H*=N), 7.32 (1H, d, $J = 7.4$ Hz, ArH), 7.21–7.10 (2H, m, ArH), 7.02–6.93 (2H, m, ArH), 6.55–6.53 (2H, m, ArH), 5.87 (1H, brs, OH), 3.86 (3H, s, CH_3). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.93; N, 5.76%. Found: C, 69.15; H, 5.47; N, 5.63%.

2-(3-Methoxy-2-hydroxyphenyl)benzoxazole (3-MHBO): A mixture of **1** (198 mg, 0.814 mmol) and DDQ (430 mg, 1.89 mmol) in chloroform was stirred for 2 h at room temperature (Scheme 1). After evaporation to remove solvent, the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1 to 100% ethyl acetate) followed by recrystallization from ethyl acetate to give a white solid (82 mg, 42%).

^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si) δ 11.70 (1H, s, OH), 7.77–7.75 (1H, m, ArH), 7.65 (1H, d, $J = 8.0$ Hz, ArH), 7.63–7.60 (1H, m, ArH), 7.41–7.37 (2H, m, ArH), 7.05 (1H, d, $J = 8.0$ Hz, ArH), 6.97 (1H, t, $J = 8.0$ Hz, ArH), 3.97 (3H, s, CH_3). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81%. Found: C, 69.55; H, 4.93; N, 5.88%.

2-(4-Methoxy-2-hydroxyphenyl)benzoxazole (4-MHBO):[10] A mixture of **2** (211 mg, 0.868 mmol) and DDQ (203 mg, 0.895 mmol) in chloroform was stirred for 2 h at room temperature (Scheme 1). After evaporation to remove the solvent, the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1 to 100% ethyl acetate) followed by recrystallization from ethyl acetate to give a white solid (45 mg, 22%).

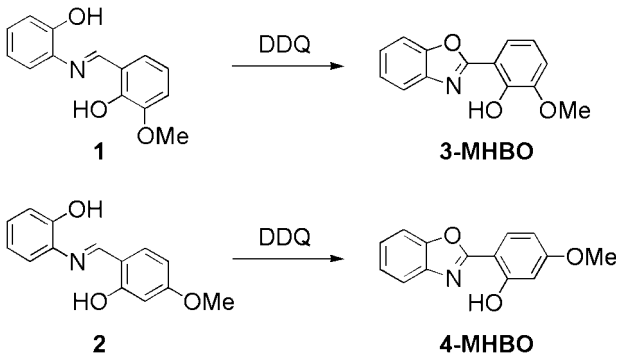
^{1}H NMR ($CDCl_3$, 400 MHz, Me_4Si) δ 11.64 (1H, s, OH), 7.92 (1H, d, $J = 8.8$ Hz, ArH), 7.70–7.67 (1H, m, ArH), 7.59–7.56 (1H, m, ArH), 7.37–7.34 (2H, m, ArH), 6.64–6.58 (2H, m, ArH), 3.87 (3H, s, CH_3).

Measurements. ^{1}H NMR spectra were measured with a Bruker ARX-400 (400 MHz for ^{1}H NMR) and Bruker AVANCE 500 (125 MHz for ^{13}C NMR) spectrometer in solution of $CDCl_3$ with tetramethylsilane as an internal standard. UV absorption and fluorescence spectra were recorded on a Shimadzu UV-1600 UV–visible spectrophotometer and on a Hitachi F-4500 fluorescence spectrometer, respectively. Fluorescence lifetimes were determined with Horiba NAES-1100 time-resolved spectrofluorometer. Laser flash photolysis was performed by using an excimer laser (Lambda Physik LPX-100, 308 nm, 20 ns fwhm) as excitation light sources, and a pulsed xenon arc (Ushio UXL-159) was used as a monitoring light source. A photomultiplier (Hamamatsu R-928) and a storage oscilloscope (Iwatsu TS-123) were used for the detection.

Results and Discussion

Steady-State Absorption Spectra. The shapes of the absorption spectra of **4-MHBO** resemble those of the parent compound **HBO**,[11] whereas those of **3-MHBO** were different from those of **4-MHBO** or **HBO**. Figure 2 shows the steady-state absorption spectra of **3-MHBO** and **4-MHBO**, measured in benzene, acetonitrile, and ethanol. For **4-MHBO** (Fig. 2b), the absorption band around 330–340 nm was assigned to the *syn*-enol form, and the absorption around 319–323 nm are due to *anti*-enol form.[12] The absorption spectrum of **3-MHBO** (Fig. 2a) is more complex.

The difference in the absorption spectra is obviously a consequence of the methoxy group at the 3′-position in **3-MHBO**, which changes the electronic structure, as seen from a comparison of the NMR spectra. In ^{1}H NMR spectra, the peak corresponding to the methoxy hydrogen (methoxy-H) appeared at 3.97 and 3.87 ppm for **3-** and **4-MHBO**, respectively. On the other hand, the hydrogen at 6′-position (6′-H) appeared



Scheme 1.

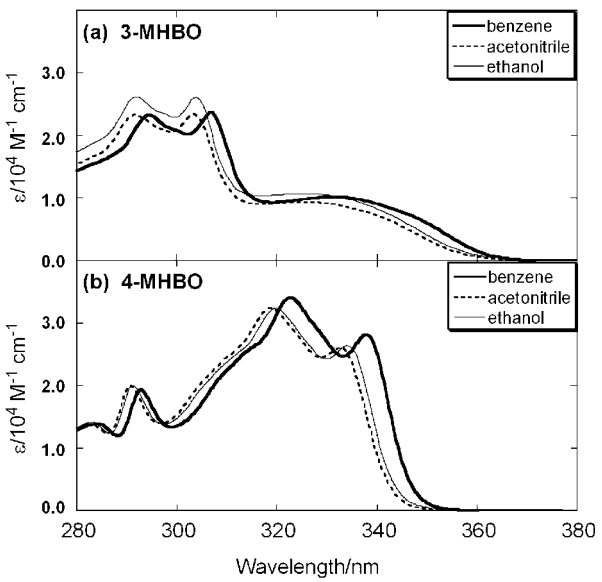
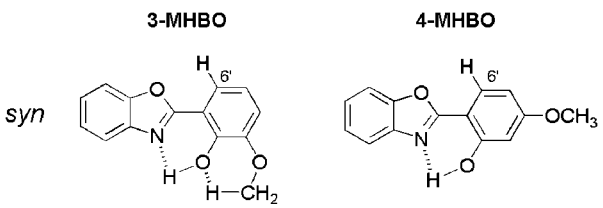


Fig. 2. UV absorption spectra of **3-MHBO** (a) and **4-MHBO** (b) in benzene, acetonitrile, and ethanol.



	^{1}H NMR ($CDCl_3$) δ(ppm)	
	3-MHBO	**4-MHBO**
OCH_3	3.97	3.87
6′-H	7.65	7.92

Fig. 3. Hydrogen bonds in **3-** and **4-MHBO**.

at 7.65 and 7.92 ppm for **3-** and **4-MHBO**, respectively (Fig. 3). The downfield shift of methoxy-H (0.10 ppm) and the upfield shift of 6′-H (0.27 ppm) in **3-MHBO** suggests that: 1) a hydrogen bond between the neighboring hydroxy groups at 2′-position formed and 2) mesomeric effect (electron-donating effect) of 3′-methoxy group on 6′-H. These effects on the electronic structure probably cause the considerable difference in the absorption spectra of **3-MHBO**.

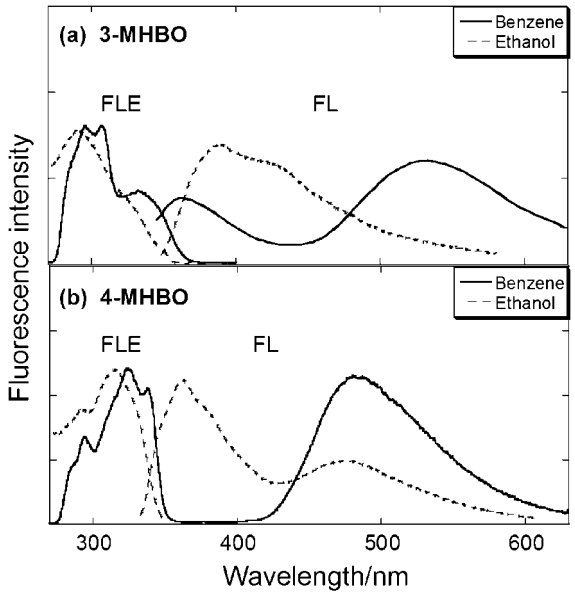


Fig. 4. (a) Fluorescence (FL) and fluorescence excitation spectra (FLE) of **3-MHBO** in benzene (solid line, $\lambda_{ex} = 307$ nm for FL, $\lambda_{em} = 525$ nm for FLE) and in ethanol (dotted line, $\lambda_{ex} = 304$ nm for FL, $\lambda_{em} = 388$ nm for FLE), (b) FL and FLE of **4-MHBO** in benzene (solid line, $\lambda_{ex} = 323$ nm for FL, $\lambda_{em} = 480$ nm for FLE) and in ethanol (dotted line, $\lambda_{ex} = 320$ nm for FL, $\lambda_{em} = 364$ nm for FLE).

Steady-State Fluorescence Spectra. The steady-state fluorescence spectrum of **4-MHBO** in benzene exhibited only large Stokes-shifted fluorescence with a maximum at 480 nm due to $\mathbf{K}_E^*$ (Fig. 4b), which was again fluorescence behavior similar to that of **HBO**. On the other hand, **3-MHBO** in benzene showed dual fluorescence at 365 and 525 nm (Fig. 4a). The 365 nm band is due to $\mathbf{E}^*$, while the band at 525 nm is assigned to $\mathbf{K}_E^*$ formed by ESIPT. The substituent effects of the methoxy group at the 3-position on the fluorescence properties of **HBO** cause fluorescence emission from $\mathbf{K}_E^*$, to occur at considerably longer wavelength than that for **4-MHBO** or **HBO** and the dual fluorescence in less-polar solvent, such as benzene. The fluorescence red-shift for $\mathbf{K}_E^*$ is probably because hydrogen bonding between carbonyl oxygen and methoxy hydrogen stabilized the $\mathbf{K}_E^*$ of **3-MHBO**. The dual fluorescence from **3-MHBO** indicates that the methoxy group at the 3-position works as an electron-donating group and makes intramolecular hydrogen bonding with OH group, which suppresses proton transfer in the excited singlet state in benzene.

The emission spectra of both **3-MHBO** and **4-MHBO** in ethanol were totally different from those in benzene. **3-MHBO** exhibited a fluorescence band at 387 nm. The shoulder around 425 nm probably originates from an anion species, observed only in protic solvents.[13] The peak with a large Stokes-shifted fluorescence for $\mathbf{K}_E$ was not observed in ethanol probably because ESIPT in **3-MHBO** is suppressed by the solvent molecules. The emission spectrum of **4-MHBO** in ethanol consists of two bands with the maxima at 360 and 473 nm, assigned to **E** and $\mathbf{K}_E$, respectively. The appearance of the emission band of **E** suggests that ESIPT partially inhibited in ethanol.

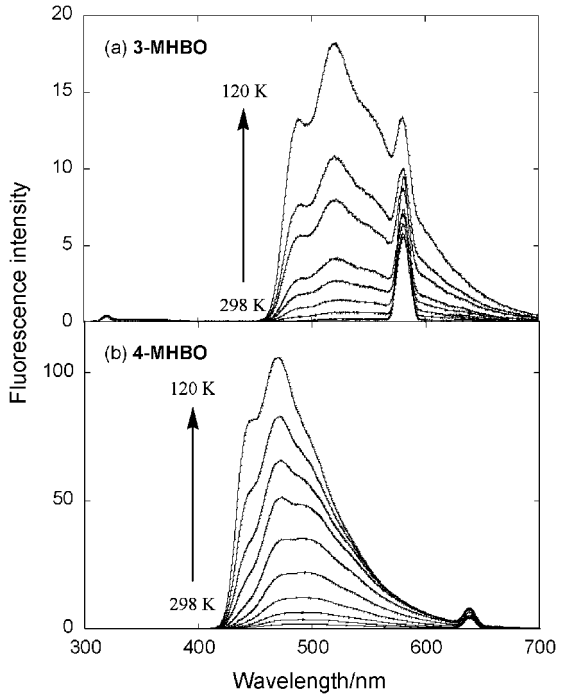


Fig. 5. Fluorescence spectra of **3-MHBO** (a) and **4-MHBO** (b) in methylcyclohexane at various temperatures. The peak at 584 nm in (a) and 632 nm in (b) are due to the excitation wavelength of 292 and 321 nm, respectively.

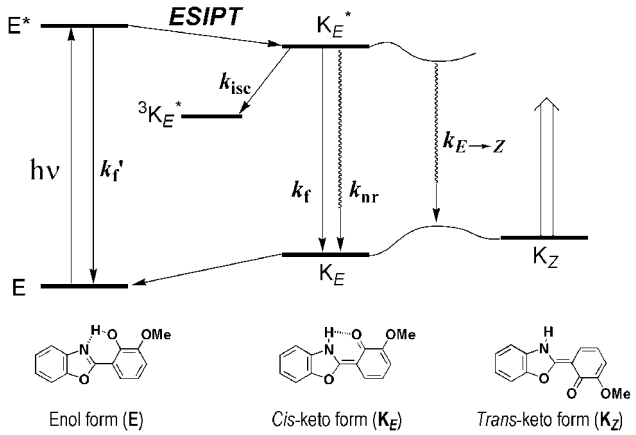


Fig. 6. Energy diagram of **E** and **K** tautomers of **3-MHBO**.

The fluorescence quantum yields in benzene were 0.002 and 0.018 for **3-MHBO** and **4-MHBO**, respectively. The value of the quantum yield for **3-MHBO** is determined as sum of dual fluorescence from **E** and $\mathbf{K}_E$. The lower fluorescence quantum yield of **3-MHBO** is probably because hydrogen bonding between phenol oxygen and methoxy hydrogen promotes nonradiative decay.

Figure 5 shows the temperature dependence of the fluorescence spectra in methylcyclohexane. The fluorescence intensity in the range of 480–700 nm for $\mathbf{K}_E$ of **3-MHBO** increased at lower temperature, whereas the intensity in the range of 350–400 nm for **E** was almost independent of temperature (Fig. 4a). Usually, the rate constants for fluorescence emission are not affected by temperature. Therefore, the lack of temperature effects on the fluorescence intensity of **E** indicates that the rate

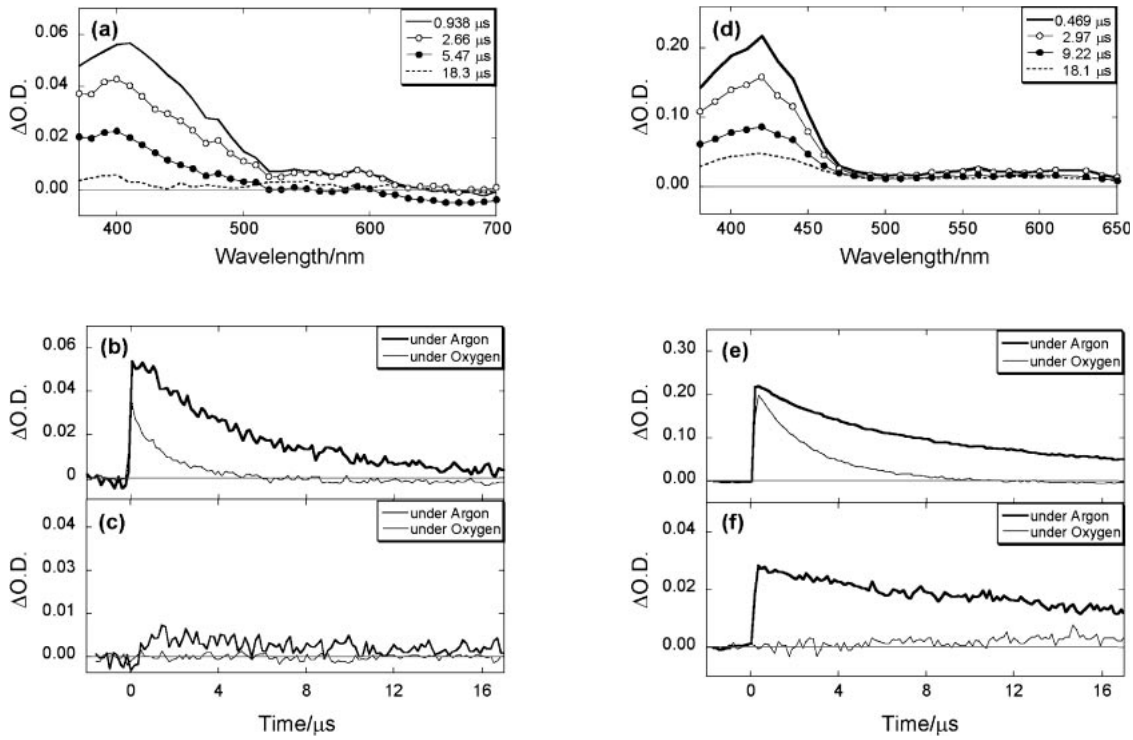


Fig. 7. Transient absorption spectra of **3-MHBO** (a), the decay curve at 420 nm (b) and at 560 nm (c) in benzene. Transient absorption spectra of **4-MHBO** (d), the decay curve at 420 nm (e) and at 560 nm (f) in benzene.

constant of ESIPT (Fig. 6) for $\mathbf{E}^*$ of **3-MHBO** is scarcely affected by changing temperature. On the other hand, the increase in the fluorescence intensity from $\mathbf{K}_E{}^*$ with a decrease in the temperature suggests that the relaxation pathways, especially, $k_{E\rightarrow Z}$ is affected by temperature, since this isomerization process is expected to have activation barrier.

The fluorescence spectra of **4-MHBO** had only the large Stokes-shifted fluorescence from $\mathbf{K}_E$ at all temperatures. This fluorescence emission from $\mathbf{K}_E{}^*$ also increased with a decrease in the temperature due to the suppression of the isomerization from $\mathbf{K}_E{}^*$ with activation barrier.

Transient Absorption Spectra. The laser transient absorption spectra of **3-MHBO** and **4-MHBO** in benzene after excitation with a 308 nm wavelength laser at room temperature under argon atmosphere are shown in Fig. 7. Both **3-MHBO** and **4-MHBO** had new absorption peaks at 410 nm and at 420 nm, respectively. Since they were not quenched by oxygen, they were ascribed to the ground state $\mathbf{K}_Z$ tautomer (Fig. 7b). In addition to the transient band for $\mathbf{K}_Z$, a broad signal over the entire spectral region was observed for both **3-MHBO** and **4-MHBO**, which was quenched by oxygen. Thus, it can be assigned to the excited triplet state (Fig. 7c). Because the decay curves for **3-MHBO** or **4-MHBO** under argon include both $\mathbf{K}_Z$ and the triplet state species, the curves did not fit single-exponential function. Thus, the lifetimes for $\mathbf{K}_Z$ were measured under oxygen and determined to be 1.6 and 1.7 μs for **3-MHBO** and **4-MHBO**, respectively.

The quantum yields of formation of $\mathbf{K}_Z$ ($\Phi_{E\rightarrow Z}$) on the excitation of **E** for **3-MHBO** and **4-MHBO** can be estimated in benzene by comparing the ΔO.D. values of the $\mathbf{K}_Z$ for **3-MHBO** and **4-MHBO** with that of the T–T absorption of an optically matched benzophenone (ε at 530 nm = 7220 $M^{-1}\,cm^{-1}$) solution at 308 nm. The molar extinction coefficients for $\mathbf{K}_Z$ of **3-MHBO** and **4-MHBO** at 420 nm were assumed to be the same as that of *Z*-6-[*N*-methyl-2(3*H*)-benzothiazolylidene]cyclohexa-2,4-dienone (*Z*-NBT) (ε at 420 nm = 7000).[14] Thus, the $\Phi_{E\rightarrow Z}$ values were estimated to be 0.04 and 0.31 for **3-MHBO** and **4-MHBO**, respectively. The $\Phi_{E\rightarrow Z}$ value for **3-MHBO** was much lower than that for **4-MHBO** suggesting that the photoisomerization from $\mathbf{K}_E{}^*$ to $\mathbf{K}_Z$ in **3-MHBO** is suppressed by the intramolecular hydrogen bond with methoxy hydrogen at the 3-position.

In order to measure the T–T absorption spectra, **3-** and **4-MHBO** were excited at 390 nm in the presence of Michler's ketone as a triplet sensitizer in benzene under argon (Fig. 8). The T–T abosorption spectra were observed in the region from 400–800 nm as broad spectra. The lifetimes of the triplet state were determined to be 3.4 and 2.3 μs for **3-MHBO** and **4-MHBO**, respectively. Previously, we have reported the equilibrium between $^3\mathbf{E}^*$ and $^3\mathbf{K}_E{}^*$ for **HBO**.[14] The existence of both $^3\mathbf{E}^*$ and $^3\mathbf{K}_E{}^*$ species has been clarified by using model compounds, i.e., 2-(2-methoxyphenyl)benzoxazole (**MBO**) and 2-phenylbenzoxazole (**PBO**), that do not undergo ESIPT.[15] On excitation in the presence of a triplet sensitizer, both **MBO** and **PBO** exhibit T–T absorption spectra of simple $^3\mathbf{E}^*$, whereas **HBO** exibit T–T absorption spectra for a mixture of $^3\mathbf{E}^*$ and $^3\mathbf{K}_E{}^*$, of which the absorption band was broadened in the range of 420–700 nm. The similarity of the T–T absorption spectra of **3-** and **4-MHBO** strongly indicate that the observed T–T absorption spectra of **3-** and **4-MHBO** in Fig. 8 are of a mixture of $^3\mathbf{E}^*$ and $^3\mathbf{K}_E{}^*$ species.

The quantum yields for intersystem crossing (Φ_{isc}) involving **3-** and **4-MHBO** can be estimated by the triplet–triplet energy transfer from **3-** or **4-MHBO** to β-carotene with an opti-

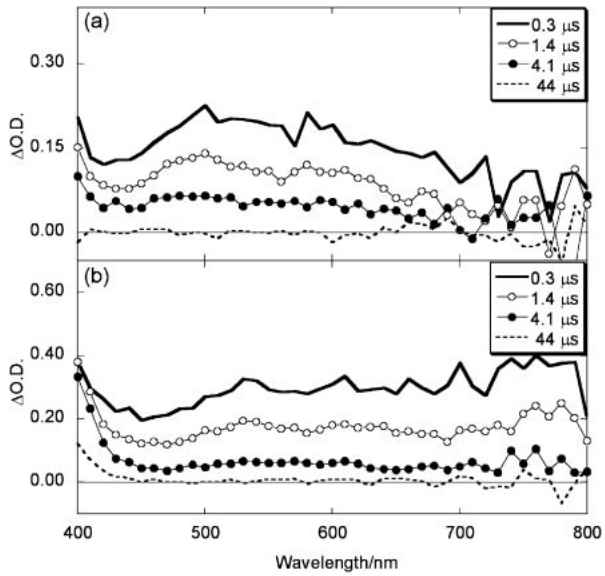


Fig. 8. Transient absorption spectra of **3-MHBO** (a) and **4-MHBO** (b) on excitation at 390 nm in the presence of Michler's ketone in benzene under argon.

Table 1. Observed and Calculated Spectroscopic Parameters for **3-MHBO** and **4-MHBO**

	fl. max (λ_{max})/nm	Φ_f	$\tau(^1\mathbf{K}_Z)$ /μs	$\Phi_{E\to Z}$	$\tau(^3\mathbf{K}_E{}^*)$ /μs	Φ_{isc}
3-MHBO	365, 525	0.002	1.6	0.04	3.4	0.02
4-MHBO	480	0.018	1.7	0.31	2.3	0.03

cally matched reference, i.e., a **HBO** ($\Phi_{isc} = 0.03$) solution, at 308 nm. Although β-carotene absorbs light at 308 nm, it did not produce any transient species upon the excitation at 308 nm on the micro-second timescale. Therefore, one can estimate the Φ_{isc} values by observing the intensity of T–T absorption spectra at 540 nm. The estimated values of the quantum yields of intersystem crossing Φ_{isc} were 0.02 and 0.03 for **3-** and **4-MHBO**, respectively.

The four pathways for relaxation from $\mathbf{K}_E{}^*$ are: fluorescence emission, isomerization, intersystem crossing, and non-radiative decay. From the estimated values of Φ_f, $\Phi_{E\to Z}$, and Φ_{isc} for **3-** and **4-MHBO**, the quantum yield for non-radiative decay (Φ_{nr}) was calculated to be 0.94 and 0.64, for **3-** and **4-MHBO**, respectively. The efficiency for non-radiative decay from $\mathbf{K}_E{}^*$ in **3-MHBO** is higher than that in **4-MHBO** suggesting that the existence of the neighbouring methoxy group at the 3-position promotes non-radiative decay by forming a hydrogen bond in the excited singlet state (Table 1).

In summary, the *meta*-substitution effects on the photochemical properties of benzoxazole derivatives were investigated. The photochemical properties of **4-MHBO** were similar to those for the parent compound, **HBO**, whereas different properties were observed for **3-MHBO**. The fluorescence peak due to $\mathbf{K}_E{}^*$ of **3-MHBO** ($\lambda_{max} = 525$ nm) appeared at considerably longer wavelength than that of **4-MHBO** ($\lambda_{max} = 480$ nm). The fluorescence quantum yield of **3-MHBO** ($\Phi_f = 0.002$) was much smaller than those of **4-MHBO** and **HBO** ($\Phi_f = 0.018$ and 0.02, respectively). These results may be a consequence of the stabilization of $\mathbf{K}_E{}^*$ species and non-radiative decay due to the formation of a hydrogen bond between phenol oxygen and methoxy hydrogen at 3-position in **3-MHBO**. Thus, **3-MHBO** displayed a *meta*-substituent effect with respect to the relaxation pathway of excited state HBO derivatives.

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