A comparative study. The photophysics of 2-phenylbenzoxazoles and 2-phenylbenzothiazoles

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The photophysical properties of 2-phenylbenzothiazole and 2-phenylbenzoxazole were compared. At room temperature 2-phenylbenzothiazole in *n*-heptane exhibits a broad, structureless absorption and a low fluorescence yield of ≈ 0.005 ($\tau_f < 200$ ps). In contrast, 2-phenylbenzoxazole shows a structured absorption and a high fluorescence yield, $\Phi_f \approx 0.78 \pm 0.05$ ($\tau_f \approx 1.5$ ns). These spectral differences arise from a drastic change in the dynamics of C_1–$C_{1'}$ torsional motion, as evidenced in the temperature-dependent studies, spectral properties of their derivatives and AM1 calculations.

1. Introduction

Recent studies of the excited-state intramolecular proton transfer molecules, 2-(2′-hydroxylphenyl) benzothiazole (HBT) and 2-(2′-hydroxylphenyl) benzoxazole (HBO), have shown unique relaxation processes. It has been widely accepted that HBT undergoes a rapid rate ($\approx 10^{13}$ s^{-1} [1,2]) of excited-state proton transfer to yield a cis–trans isomeric tautomer species (fig. 1, [3–6]). However, the cis–trans isomerization for HBO was not detected after rapid ESIPT [7,8]. This result suggests that the photophysical properties of 2-phenylbenzothiazole (BT) and 2-phenylbenzoxazole (BO) may be quite different although they have similar molecular structures (fig. 2). In this study, the photophysics of BT, BO and their derivatives were compared. The results unambiguously indicate a significant difference in dynamics of the C_1–$C_{1'}$ torsional motion between BO and BT in both ground and excited states. The difference becomes insignificant when the C_1–$C_{1'}$ double bond character is enhanced due to the charge transfer from electron donating substituents.

2. Experimental

BT and BO (Aldrich) were twice recrystallized with spectrophotometric methylcyclohexane and once by vacuum sublimation. 2-(4′-diethylaminophenyl) benzothiazole (**I**) and 2-(4′-diethylaminophenyl) benzoxazole (**II**) were synthesized by the reaction of 4-(diethylamino)benzaldehyde with 2-aminothiophenol or 2-aminophenol in the presence of sodium acetate in acetic acid [9]. 2-(3′-dimethylaminophenyl) benzothiazole (**III**) was obtained by the reaction of 3-dimethylamino benzaldehyde (**III′**) with 2-aminothiophenol using the same method as

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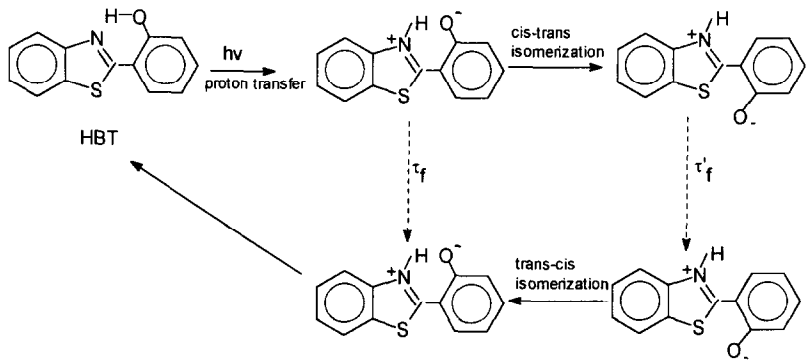
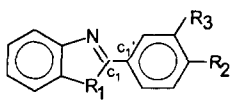


Fig. 1. The mechanism of excited-state proton transfer for HBT.



R_1	R_2	R_3	
O	H	H	BO
S	H	H	BT
S	$N(C_2H_5)_2$	H	I
O	$N(C_2H_5)_2$	H	II
S	H	$N(C_2H_5)_2$	III
NH	H	H	2-phenylbenzimidazole

Fig. 2. Molecular structures of various compounds in this study.

described above. III′ was synthesized by the treatment 3-dimethylaminobenzoic acid (Aldrich) with $SOCl_2$ and followed by the reduction of 3-dimethylaminobenzoyl chloride with $LiAlH(OBu\text{-}t)_3$. The final products were purified by column chromatography on silica gel (eluent 5:1 v/v hexanes:ethyl acetate) followed by recrystallization from methylcyclohexane. The purified solvents were obtained according to the previously reported method [10]. Quantum yields were measured using 2-phenylbenzoxazole in *n*-heptane as a reference, for which the fluorescence yield has been measured to be 0.75 ± 0.09 [11]. Steady-state absorption and emission spectra were recorded by an HP (model 8452A) spectrophotometer and a Shimadzu (model 5000) fluorometer, respectively. A detailed description of transient absorption and low temperature measurements have been published elsewhere [5]. The lifetime study was performed by an Edinburgh FL 900 photon counting system with a hydrogen filled flash lamp/or a nitrogen lamp as the excitation source. The temporal resolution after deconvolution of the exciting pulse is ≈ 200 ps. Data were analyzed with the nonlinear least square procedure in combination with the deconvolution method [12].

3. Results and discussion

Significant differences in the absorption and emission spectra between BT and BO were observed. BT exhibits a broad, diffuse S_0–S_1 ($\pi\pi^*$) absorption band with a maximum at 302 nm ($\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}) in *n*-heptane. On the other hand, the absorption spectrum of BO shows well-resolved vibronic progressions with a maximum at 300 nm ($\epsilon = 2.2 \times 10^4$ M^{-1} cm^{-1}, fig. 3). Also illustrated in fig. 3 are the emission spectra for both BT and BO at room temperature. A structureless emission band maximum at 350 nm was observed for BT with a very low fluorescence yield, $\Phi_f \approx (5.0 \pm 0.8) \times 10^{-3}$. The lifetime of fluorescence is shorter than our instrumental detection limit of 200 ps. In contrast, the results for BO signify a structured emission band which is a mirror image of the absorption spectrum. The fluorescence yield and lifetime of BO were measured to be 0.75 ± 0.05 and 1.5 ± 0.2 ns, respectively in *n*-heptane. However, despite drastic differences in the spectral features between BT and BO, their derivatives containing diethylamino substituents at the 4′ position have similar photophysical properties. Both

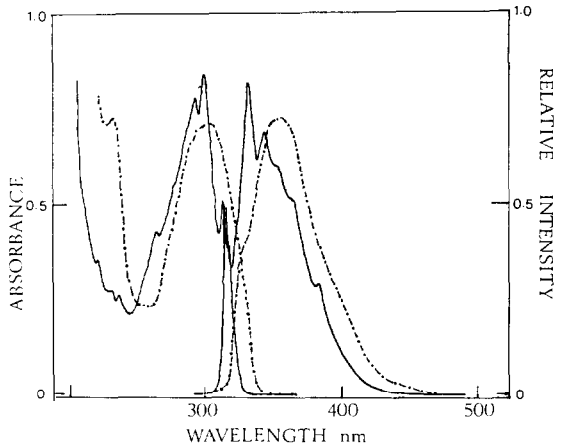


Fig. 3. Absorption and emission spectra of BO (——) and BT (-·-·-) in *n*-heptane. The emission spectra were obtained by 300 nm excitation.

I and **II** exhibit structured absorption and emission spectra in nonpolar solvents. The quantum yields were measured to be 0.83 ± 0.05 and 0.80 ± 0.05 for **I** and **II** in *n*-heptane, respectively.

One possible mechanism to account for the discrepancy in the fluorescence lifetime and yield between BT and BO is based on the differences in the energy levels of the lone pair electrons on the oxygen and sulfur atoms. This implies that for BT the lowest excited singlet state has an $n\pi^*$ configuration because of the higher energy of the lone pair electrons on the sulfur atom, while a $\pi\pi^*$ state is in the lowest excited singlet state for BO. Accordingly, upon excitation BT undergoes a dominant $S(n\pi^*)$–triplet state intersystem crossing, resulting in a small fluorescence yield. For BT this mechanism implies that the efficiency of the triplet state population is near 100%. However, only a weak triplet–triplet absorption maximum at 420–440 nm was detected at room temperature.

In addition, the comparative temperature-dependent fluorescence spectra of BT and BO in methylcyclohexane have been obtained. Only a slight change in the fluorescence yield from 0.75 (298 K) to 0.82 (77 K) was noteworthy for BO. On the other hand, the fluorescence yield of BT increases as the temperature decreases. Inn a 77 K methylcyclohexane glass, structured absorption and emission spectra were observed. The fluorescence yield was measured to be 0.3 ± 0.1, which is nearly two orders of magnitude higher as the yield at room temperature. Since the interconversion between $n\pi^*$ and $\pi\pi^*$ states is not likely to be strongly perturbed by viscosity and temperature, the possibility that the π^* state is the lowest singlet excited state for BT can be ruled out. The temperature-dependent study directly supports a dominant thermally activated radiationless process for BT in the excited state, most plausibly the torsional motion around the C_1–$C_{1'}$ bond.

The high quantum yield for **I** suggests that the electron donating 4′-diethylamino group enhances the partial C_1–$C_{1'}$ double bond character. Hence, the torsional frequency of **I** increases significantly in comparison to that of BT, resulting in a negligible contribution of C_1–$C_{1'}$ torsional motion to the radiationless pathways. This key factor of delocalization of π electrons induced by a para-electron donating effect was confirmed by the spectral study of compound **III**. Since the diethylamino group is in the meta position with respect to the benzothiazole ring (see fig. 2), no conjugation between the nitrogen atom in the benzothiazole ring and the dialkylamino group can be drawn for **III**. As was expected, a low fluorescence yield ($\Phi_f < 0.01$) was observed for **III**, in contrast to $\Phi_f \approx 0.83$ for **I**. This proposal can be further substantiated by protonating the 4′-diethylamino group of **I** in acidified ethanol so that charge transfer diminishes. As a result, a blue-shifted ($\lambda_{max} = 330$ nm), low quantum yield ($\approx 8.0 \times 10^{-3}$) fluorescence was observed for protonated **I**. This result is in contrast to the high fluorescence yield of 0.70 of **I** in ethanol.

The broad, structureless absorption spectrum for BT in comparison to the structured absorption spectrum for BO is intriguing as well. The molecular symmetries of BT and BO are not drastically different and cannot account for the spectral differences. The lifetime of BO in *n*-heptane was measured to be 1.5 ± 0.2 ns, and the radiative lifetime for BO was calculated to be ≈ 2.0 ns based on the measured fluorescence yield of 0.75. For BT, it is reasonable to assume the same order of the magnitude of radiative lifetime as BO since absorptivity and spectral frequencies are similar between BO and BT (see fig. 3). Thus, the nonradiative decay of BT ($\Phi_f \approx 5.0 \times 10^{-3}$) was estimated to be on the order of 10^{11} s^{-1} which is too slow to apply lifetime broadening as a possible explanation. Thus, we propose that similar to the ex-

cited-state dynamics, the barrier for the torsional motion of BT in the ground state is also significantly lower than that of BO.

The broad, structureless feature of the absorption spectrum of BT is a result of spectral overlap of various rotamers around the C_1–$C_{1'}$ bond at room temperature. To verify this proposal we have carried out AM1 calculations to obtain relative ground state energy levels of various conformers of BT and BO. This was achieved by calculating the heat of formation for various conformers by fixing the dihedral angle between the benzothiazole (or benzoxazole) moiety and the phenyl ring, followed by optimizing all bond lengths and angles. The dihedral angle was varied over a range of 0°, in which benzoxazole and phenyl rings are coplanar, to an angle of 90°. As a result, the energy level of BO varied from a minimum energy of 84.53 kcal/mol at 0° (conformer **a**) to a maximum energy of 90.19 kcal/mol at 90° (conformer **b**). The 5.8 kcal/mol energy difference should cause a negligible population of **b** at room temperature. On the other hand, for BT the energy varies from a minimum energy of 89.53 kcal/mol at 0.0° (conformer **a**) to a maximum energy of 90.19 kcal/mol at 90° (conformer **b**). The small difference of only 0.5 kcal/mol between **a** and **b** allows the existence of various conformers by thermal population at room temperature, supporting the proposed mechanism.

In conclusion, our results provide evidence for significant differences in the dynamics of C_1–$C_{1'}$ torsional motion between BO and BT. This discrepancy may be qualitatively explained by canonical structures **A** and **B** drawn for BT and BO (fig. 4). Since the chromophore which accounts for the S_0–S_1 transition is localized at the phenyl ring moiety [13], the canonical structures deduced from the benzene ring in benzoxazole or benzothiazole moiety were not considered. The presence of structure **A** increases the C_1–$C_{1'}$ double bond character, hence, the rigidity of the molecular frame. On the other hand, the single bond character is increased by the presence of structure **B**. Since the electron donating ability of the sulfur atom is stronger than that of the oxygen atom, structure **B** is more favorable in BT than in BO. As a result, there is more C_1–$C_{1'}$ single bond character in BT, consistent with the AM1 calculation. This qualitative molecular structure analysis can also be applied to the compound, 2-phenylbenzimidazole (fig. 2), in which the nitrogen atom in imidazole has an electronegativity similar to that of the oxygen in benzoxazole. In fact, the spectral features of 2-phenylbenzimidazole, such as structured absorption, emission in nonpolar solvents, and high quantum yield of fluorescence [14], are similar to BO. The spectral differences between derivatives of BO and BT decrease to a negligible amount when C_1–$C_{1'}$ double bond character is enhanced, such as in the case of **I** and **II**, due to the delocalization of π electrons induced by the charge transfer of the electron donating substituents.

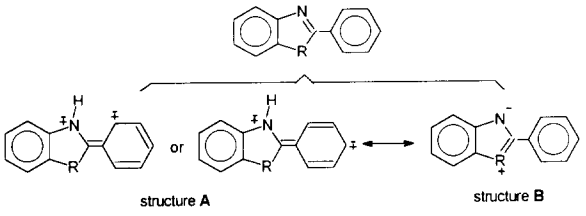


Fig. 4. The proposed two types of canonical structures for BO and BT.

The conclusion drawn for BT and BO may qualitatively explain the different relaxation mechanisms for HBT and HBO. Since the rate of excited-state proton transfer ($>10^{12}$ s^{-1}) is faster than the isomerization process, negligible cis–trans isomerization occurs in the normal form for both HBT and HBO (see fig. 5). The proton-transfer tautomer form can be depicted by either the zwitterionic or π-electron conjugated cis–keto form. However, at this stage, unless further detailed structural analysis based on the time-resolved Raman or IR studies [#1] can be performed, the definitive structure assignment is still ambiguous. Most likely, the electronic configuration of the proton-transfer tautomer is a hybrid mixture between these two structures. The contribution of each form will be solvent as well as substituent dependent [#2]. Similar to the conclusion drawn for BO and BT, the lower electronegativity of the sulfur atom of HBT should yield to a greater contribution

[#1] Although an elegant picosecond infrared absorption experiment has been studied by Elsaesser and Kaiser [15], only carbonyl stretching of the tautomer species was monitored.

[#2] Detailed dynamics study of cis–trans isomerization for derivatives of HBT in various solvents will be published.

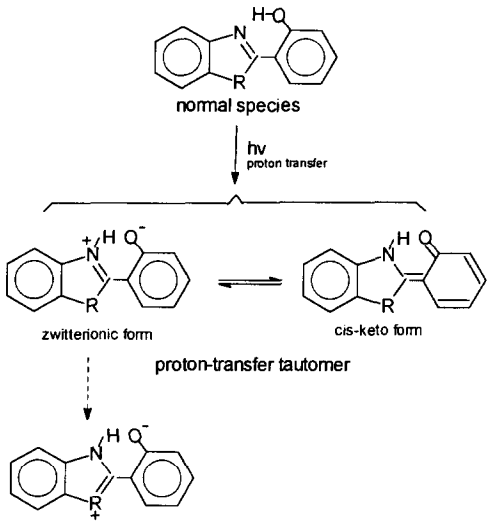


Fig. 5. The proposed canonical structures for the proton-transfer tautomer of HBT and HBO.

of the zwitterionic structure in comparison to that of HBO. In other words, there is more C_1–$C_{1'}$ single bond character in the HBT tautomer, resulting in a smaller C_1–$C_{1'}$ torsional barrier. Therefore, the observed cis–trans isomerization of the HBT tautomer [3–6] can be rationalized.

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