Class of Photostable, Highly Efficient UV Dyes: 2-Phenylbenzoxazoles

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The photophysics and lasing properties of 2-phenylbenzoxazole,2-(4′-methoxyphenyl)benzoxazole and 2-(4′-diethylaminophenyl)-benzoxazole in nonpolar solvents are reported. This class of 2-phenylbenzoxazoles provides near-UV laser generation with a wide range of tunability (330–380 nm). The efficient laser output and extreme photostability of this class of dyes make their practical application feasible when pumped by a nitrogen laser (337 nm), XeCl excimer laser (308 nm), or Nd:YAG laser (fourth harmonic, 266 nm).

Index Headings: **UV dyes; Amplified spontaneous emission; Photostability.**

INTRODUCTION

There have been many articles that focus on the absorption and emission properties of 2-phenylbenzoxazole and its derivatives.[1–5] A recent study comparing 2-phenylbenzothiazole (BT) and 2-phenylbenzoxazole (BO) found that even though these two molecules have similar molecular geometries, the photophysical properties are significantly different.[6] In *n*-heptane, BT exhibits a broad, structureless S_0–S_1 absorption band at room temperature with a maximum at 302 nm, whereas BO has a resolved vibronic progression with a maximum at 300 nm. The emission for the two compounds shows a similar trend with BT having a broad, structureless emission with a low fluorescence yield ($\Phi_f \sim 5.0 \times 10^{-3}$) and BO exhibiting a structured emission with a much higher fluorescence yield ($\Phi_f \sim 0.75$). The photophysical differences in these two compounds are attributed to a dominant radiationless process for BT in the excited state, most likely the torsional motion about the C_1–$C_{1'}$ bond (see Fig. 1). This has been substantiated by semi-empirical calculations (AM1) which showed a significant difference in the energy associated with the torsional motion between BO and BT.[6] Because oxygen is less electronegative than sulfur, the structure of BO with a partial double bond between C_1–$C_{1'}$ is more favorable. It follows then that if electron-donating groups are placed in a resonance position on the phenyl ring, the double-bond character of the C_1–$C_{1'}$ bond will be enhanced even more. As the double-bond character is increased, the torsional motion becomes less likely and the fluorescence quantum yield increases. In addition, the extended delocalization of the π electrons along the C_1–$C_{1'}$ bond is expected to decrease the S_0–S_1 energy gap. Therefore, a broad spectral coverage should be achieved by varying the electron-donating functional group. On the basis of this reasoning, 2-(4′-diethylaminophenyl)benzoxazole (ABO) and 2-(4′-methoxyphenyl)benzoxazole (MBO) have been synthesized to study their comparative photophysics. A practical application for BO and the derivatives presented in this study is to serve as near-UV dyes, in many uses, such as biological probes,[7] scintillation counters,[8] and laser dyes.[5,9,10]

EXPERIMENTAL

Synthesis. The Schiff base was synthesized by refluxing the appropriately substituted benzaldehyde (5.6 mmol) with 2-aminophenol (5.0 mmol) in ethanol with several drops of acetic acid for 2 h.[11] The Schiff base was then oxidized with $BaMnO_4$ to ABO or MBO.[12] ABO was purified by column chromatography on silica gel (eluent 2:8 v/v hexanes: ethyl acetate) followed by preparative HPLC (eluent dichloromethane), giving a yield of 10%; m.p. 128–129 °C; characterization by 400 MHz ^1H NMR ($CDCl_3$).† MBO was similarly purified by column chromatography on silica gel with the same eluent but then washed with hot hexanes, giving a yield of 75%; m.p. 95–96 °C (lit. 100–101 °C);[13] characterization by 400 MHz ^1H NMR ($CDCl_3$).‡ The Exalite 398 (Exciton), BO (Aldrich), and reagent-grade hexanes (Baxter) were used as received.

Measurements. Steady-state absorption and emission spectra were recorded by a Perkin–Elmer Lambda 6 spectrophotometer and Perkin–Elmer LS50 fluorometer, respectively. The experimental setup for measuring the amplified spontaneous emission (ASE) includes a nitrogen laser or the fourth-harmonic Nd:YAG pulse focused on the dye cell in a horizontal line using a quartz cylindrical lens. The generated ASE is collected at 90°. The dye solution is stirred to prevent local heating and any other detrimental processes from occurring. The ASE is then passed through a pinhole and detected with a 0.25-m monochromator (0.01-mm slit width) coupled with a photomultiplier tube (Oriel, 77341). The lasing efficiency was measured with a nitrogen laser as the excitation source; a grating-tuned, multipass dye laser (LSI, DLMS-210); and a joule meter (Molectron, J3-05).

The lifetime data were measured with an Edinburgh FL 900 photon counting system with a hydrogen-filled flash lamp or a nitrogen lamp as the excitation source. The temporal resolution of the exciting pulse is ~200 ps after deconvolution. The data were analyzed with a non-

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† 400 MHz ^1H NMR data for 2-(4′-diethylaminophenyl)benzoxazole in $CDCl_3$: 8.10 (d, J = 9, 2H, H_2), 7.12 (t, J = 2, 8, 8, 1H, H_4), 7.10 (dd, J = 2, 8, 1H, H_4), 7.03 (dd, J = 2, 8, 1H, H_4), 6.91 (t, J = 2, 8, 8, 1H, H_4), 6.7 (d, J = 9, 2H, H_2), 3.45 (m, J = 7, 4H, CH_2), 1.2 (t, J = 6, 6H, CH_3).

‡ 400 MHz ^1H NMR data for 2-(4′-methoxyphenyl)benzoxazole in $CDCl_3$: 8.10 (d, J = 9, 2H, H_2), 7.12 (t, J = 2, 8, 8, 1H, H_4), 7.10 (dd, J = 2, 8, 1H, H_4), 7.03 (dd, J = 2, 8, 1H, H_4), 6.91 (t, J = 2, 8, 8, 1H, H_4), 6.70 (d, J = 9, 2H, H_2), 3.85 (s, 3H, CH_3).

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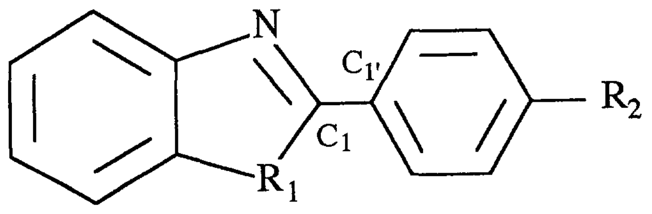

R_1	R_2	Abbreviation
S	H	BT
O	H	BO
O	$N(C_2H_5)_2$	ABO
O	OCH_3	MBO

FIG. 1. Structures of 2-phenylbenzothiazole (BT), 2-phenylbenzoxazole (BO), 2-(4'-diethylaminophenyl)benzoxazole (ABO), and 2-(4'-methoxyphenyl)benzoxazole (MBO).

linear least-squares procedure in combination with the deconvolution method.[14]

PHOTOPHYSICS

Absorption and emission spectra of ABO in hexanes are shown in Fig. 2a. In order to simplify the figure, the spectra for BO and MBO are not shown. The spectral data for all compounds are listed in Table I. It is interesting to note that all three compounds in nonpolar solvents exhibit absorption and emission spectra displaying vibronic structure accompanied by high fluorescence yields. With 2-phenylbenzoxazole in *n*-heptane as a reference, which has a fluorescence yield of 0.75 ± 0.09,[15] the fluorescence quantum yields for MBO and ABO in hexanes are 0.90 ± 0.09 and 0.95 ± 0.09, respectively. Also notable is that, in comparison to the results for 2-phenylbenzoxazole (λ_{max} = 298 nm), the maxima of the S_0–S_1 absorption bands for MBO (λ_{max} = 304) and ABO (λ_{max} = 334) show a significant red shift.

The distinct vibronic structure in the luminescence spectra of BO, according to the proposed mechanism by Chou et al.,[6] results from the partial double-bond character of the C_1–$C_{1'}$ bond, which limits torsional motion. The addition of electron-donating groups in the 4' position should increase the rigidity of the C_1–$C_{1'}$ bond because of the extended conjugation of double bonds resulting from charge transfer to the electron-accepting nitrogen atom in the benzoxazole ring. If this is the case, a red-shifted absorption and emission with a high fluorescence yield would be expected for MBO and ABO, which is in agreement with the experimental results. As the strength of the electron-donating group increases, the red shift relative to BO should increase. This is demonstrated by comparing the fluorescence maxima for MBO (342 nm) and ABO (377 nm) where $-N(C_2H_5)_2$ is a stronger electron-donating group than $-OCH_3$ (see Table I).

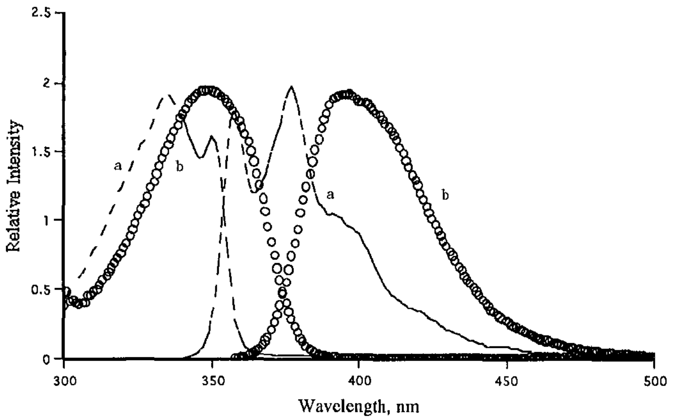

FIG. 2. Absorption and emission spectra of ABO (10^{-5} M) in (*a*) hexanes (----), (*b*) ethanol (ooo).

In a procedure to substantiate the spectroscopic evidence that charge transfer is increasing the double-bond character between C_1–$C_{1'}$, semi-empirical AM1 calculations were performed on various conformers of BO, MBO, and ABO. The dihedral angle between the benzoxazole group and the phenyl ring was constrained, while geometry optimization of the rest of the molecule was allowed. The dihedral angle was varied from 0°, where the molecule is planar, to 90°. For all three molecules, the heat of formation ranged from a minimum at 0° to a maximum at 90°. Energy differences between these two extremes were 2.54, 2.73, and 2.95 kcal/mol for BO, MBO, and ABO, respectively. The calculations show that the energy associated with the torsional motion increases as stronger electron-donating substituents are placed on the phenyl ring and, therefore, support the trends observed spectroscopically.

In protic solvents such as ethanol, the maxima of the absorption and emission spectra for all three compounds were shifted to longer wavelengths with a negligible change in the fluorescence yields (see Table I). However, the spectral features were changed dramatically. In contrast to the well-resolved vibronic structure observed in nonpolar solvents, in ethanol the absorption spectra are broad and gradually tail down to zero. The broadness of the spectra turns out to be critical in the efficiency of laser generation (*vide infra*). These experimental results agree with the charge transfer property, which attributes

TABLE I. The absorption, fluorescence, and ASE properties of BO, MBO, and ABO in hexanes and ethanol.

Dye	Solvent	λ_{ab} (nm)	log ϵ_{max}	λ_f (nm)	Φ_f	τ_{obs} (ns)	τ_r^b (ns)	λ_{ASE} (nm)
BO	Hexanes	298	4.45[a]	333	0.75[a]	1.27	1.69	333
	Ethanol	304	4.5	354	0.75	1.33	1.77	···
MBO	Hexanes	304	4.4	342	0.90	1.21	1.34	342
	Ethanol	308	4.4	365	0.96	1.08	1.13	···
ABO	Hexanes	334	4.8	377	0.95	1.21	1.51	377
	Ethanol	345	4.8	393	0.88	1.19	1.70	···

[a] See Ref. 15.

[b] τ_r = radiative lifetime calculated from τ_{obs}/Φ_f.

the broad structureless absorption band to the influences of solvent polarity and hydrogen-bonding effects.

LASING PROPERTIES

The near-unity fluorescence yield of BO and its derivatives draws our attention to their lasing properties in the UV (330–380 nm), a region in which there are few laser dyes. In this study, ASE, a necessary condition to achieve lasing action, was observed for BO, MBO, and ABO in nonpolar solvents. Figure 3a shows the ASE for ABO in hexanes with a maximum at 377 nm. The ASE maxima for BO and MBO in hexanes were 333 and 342 nm, respectively. Efforts to observe ASE for any of the three compounds in polar solvents like ethanol or methanol were unsuccessful. This result is in agreement with that reported by Cassard et al.[10] for BO in ethanol where no laser output was observed. They proposed that the photosynthesis of acetic or formic acid, which strongly absorb in the UV, might be a possible explanation. Another explanation could be a dominating triplet–triplet absorption in polar solvents, but this suggestion seems doubtful since the transient absorption for BO is reported to be in the region between 400 and 500 nm,[1] and the fluorescence quantum yield remains high, indicating negligible population in the triplet state. On the basis of the data reported here, a feasible explanation is the ground state reabsorption due to the broad absorption tail overlapping with the emission spectra. At the concentrations shown in Fig. 2, there is approximately the same degree of overlap in hexanes as in ethanol. However, there is a significant difference in the slope of the two absorption and emission spectra. In ethanol, the slope is more gradual than in hexanes. At the higher concentrations (10^{-3} M) necessary for lasing, the absorption tail in ethanol will overlap the region where lasing would occur.

The gain coefficient $\alpha(\lambda)$, which directly correlates with the conversion efficiency, can be calculated by measuring the intensity I_L of the ASE from the entire cell length L and the intensity $I_{L/2}$ from half the cell length according to the formula $\alpha(\lambda) = (2/L)\ln[I_L/I_{L/2}) - 1]$.[16] However, since it is difficult to optimize the lasing threshold, significant uncertainty is introduced. Alternatively, by measuring the power of the nitrogen laser pulse entering the dye laser (LSI, DLMS-210) and then measuring the power of the laser pulse resulting from a solution of ABO in hexanes (1.3×10^{-3} M), one can determine the conversion efficiency. In a typical experiment, 21 μJ of laser output was achieved at 377 nm when the dye was pumped by 260 μJ of a 337-nm pulse. This corresponds to a conversion efficiency of 8%. Under similar conditions, the lasing efficiency of a solution of Exalite 398 in *p*-dioxane (2.5×10^{-4} M) was measured as 10%. The tuning curve for ABO is shown in Fig. 3b. For solutions of BO and MBO in hexanes excited at 266 nm, the resulting dye laser pulse was too weak to measure. This is reasonable when the maxima for both compounds is ~300 nm. Unfortunately, for this study, a XeCl excimer laser was not available, but it would be ideal for exciting these two dyes. In fact, for BO in cyclohexane excited with a 308-nm pulse from a XeCl excimer laser, the laser output maximum has been reported at 336 nm with 11% conversion efficiency.[10] The literature also cites lasing maxima for BO in cyclohexane at 330 and 345 nm with the use of the fourth harmonic of a Nd^{3+} glass laser as the excitation source.[9] On the basis of MBO's fluorescence quantum yield of 0.90 (BO $\Phi_f \sim 0.75$) and strong ASE, it should lase at least as efficiently as BO with a XeCl excimer laser pulse for excitation. It is worth noting that the duration time (~10 ns) of our pump pulse is much longer than the decay of BO and its derivatives (~1–2 ns); therefore, a higher pumping threshold power is required. We believe that a higher conversion efficiency can be achieved by a shorter duration pump pulse.

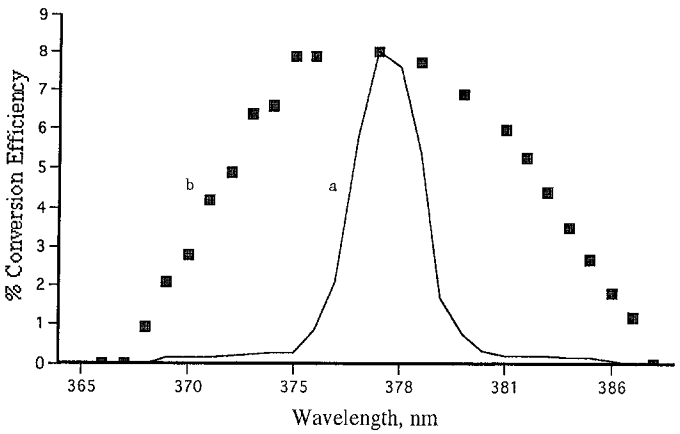

FIG. 3. (*a*) The ASE of ABO (10^{-3} M) observed in hexanes. (*b*) Tuning curve for ABO (10^{-3} M) in hexanes (λ_{ex} = 337 nm, 260 μJ).

PHOTOSTABILITY

To be a practical UV laser dye, these compounds must be photostable in solution.[17,18] A solution of ABO in hexanes (3×10^{-4} M) was irradiated with 337 nm at a repetition rate of 10 Hz (260 μJ) over a 1-h period while stirring. The dye laser output for ABO decreased by 17%. For comparison, a solution of Exalite 398 in *p*-dioxane (3×10^{-4} M) was irradiated under the exact same experimental conditions, and the dye laser output decreased by 18%, indicating that ABO can achieve a similar performance as commercially available laser dyes. Due to the inability to achieve the optimum excitation wavelength, similar photostability studies for BO and MBO could not be performed at this time.

In conclusion, this study of 2-phenylbenzoxazole,2-(4′-methoxyphenyl)benzoxazole and 2-(4′-diethylaminophenyl)benzoxazole has shown that all three compounds are potentially applicable as near-UV dyes that are conveniently excited with a N_2 laser, XeCl excimer laser, or a Nd:YAG laser. The transient absorption of BO in the region of 400–500 nm (see Ref. 1) and the high fluorescence yield point to little loss due to $T_1 \rightarrow T_n$ absorption. The ability to design other derivatives of 2-phenylbenzoxazole by varying the electron-donating substituent in the *ortho* and *para* positions that also lase efficiently could lead to a broad range of tunability. The unique advantage of these dyes is their extreme photostability, which is believed to make them commercially attractive in several applications.

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