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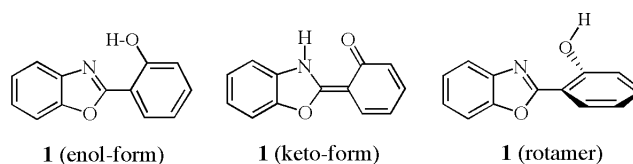
2-(3,4,5,6-Tetrafluoro-2-hydroxyphenyl)benzoxazole (**2**) emits the long wavelength fluorescence around 500 nm in nonpolar solvent *via* the intramolecular proton transfer process in the excited state of **2** (enol-form) and also emits the intermediate wavelength fluorescence around 440 nm in polar solvent, which is assumed to originate from the excited state of **2** (anion). The ease of formation of **2** (anion), compared to 2-(2-hydroxyphenyl)benzoxazole (**1**), is explained by the strongly inductive fluorine atoms. In a solvent with the intermediate polarity, **2** emits both fluorescences and their relative intensity is dependent on the concentration of **2**, which is supposed to be caused by the high sensitivity of the intermediate wavelength emission to the concentration quenching.

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The photophysics of 2-(2-hydroxyphenyl)benzoxazole (**1**) has been widely studied due to its dual emitting processes including the excited state intramolecular proton transfer (ESIPT)[1-6]. The excited state of the intramolecularly hydrogen bonded enol rapidly converts to the excited state of the keto-form, which emits fluorescence around 500 nm and may also decay thermally back to the enol-form. Second fluorescence around 360 nm is caused by the excited state of the rotamer which does not exhibit the intramolecular hydrogen bonding and thus is free to be linked by hydrogen bonds with the medium. Dual phosphorescence has been also observed at low temperature and is *via* the corresponding triplet states of the enol-form and the keto-form[7-12]. These interesting photophysical properties, particularly the large Stokes shifted fluorescence through ESIPT process, have been highly applied in the fields of laser dyes [13], scintillators [14], and devices [15].

The fluorescence of benzoxazole **1** depends largely on the nature of the solvent. In nonpolar solvent such as cyclohexane, **1** emits the long wavelength fluorescence (~500 nm) exclusively and the intensity of the short wavelength fluorescence (~360 nm) gradually increases as the polarity of the solvent is increased. This solvent effect is explained by the equilibrium of the ground states of the enol-form and the rotamer[16,17]. The third fluorescence, with intermediate wavelength (~440 nm), is described in a limited number of papers and those indicate this fluorescence is observed in protic solvents such as alcohol and water[18].

On the other hand, pentafluorophenol is rather acidic compared to phenol, with an approximate  $pK_a$  of 5.5 compared with that of 10.0 for phenol [19]. As a result, 2-(3,4,5,6-tetrafluoro-2-hydroxyphenyl)benzoxazole (**2**) is expected to have a high affinity to hydrogen bond. This plays an important role in the equilibrium between the enol- and keto-forms, thus leading to an unusual fluorescence characteristic of the benzoxazole **2**. In this paper, we will describe the solvent- and concentration-sensitive fluorescence of **2**.



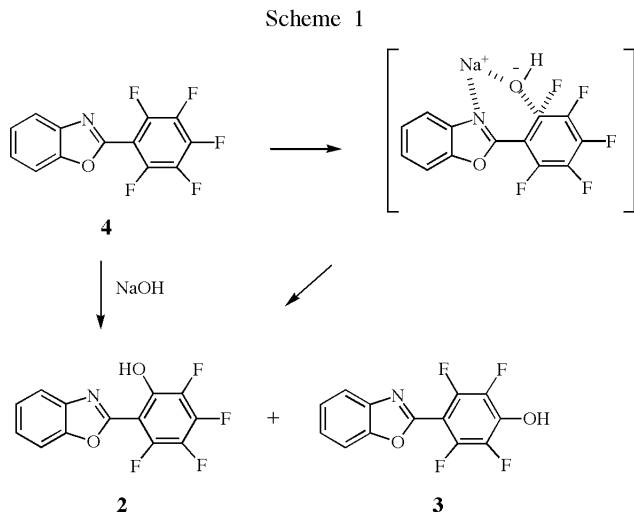
In a continuing research on the reactivity and function of polyfluorobenzene derivatives[20,21], it was found that benzoxazole **2** can be prepared by the reaction of 2-(2,3,4,5,6-pentafluorophenyl)benzoxazole (**4**) with sodium hydroxide. It was also found that the product ratio of **2** and its *para*-analogue **3** is dependent on the reaction conditions. When the reaction is carried out in dried dioxane, the *ortho*-substituted product **2** is produced selectively, whereas the *para*-analogue **3** is obtained by adding water or 18-crown-6 to the reaction mixture (Table 1). These results show the important role the counter cation (sodium cation) plays. The transition state is stabilized through coordination of the sodium cation with the oxazole-nitrogen atom and the attacking hydroxide anion, as shown in Scheme 1[22]. The position of the hydroxy group in **2** and **3** was unequivocally determined by the  $^{19}\text{F}$ -nmr analysis.

Table 1  
Product Yield and Ratio of Tetrafluorobenzoxazoles **2** and **3**

Solvent	Condition Temp/°C	Time/ hours	Total Yield/% [a]	Ratio of <b>2</b> / <b>3</b> [a]
dioxane	40	24	85	95 / 5
dioxane - water (9/1)	40	24	quant.	<1 / >99
dioxane - 18-crown-6	rt	100	quant.	<1 / >99

[a] Total yield and ratio of **2** and **3** based on  $^{19}\text{F}$ -nmr analysis.

In nonpolar solvents such as cyclohexane and toluene, the absorption and fluorescence spectra of tetrafluorobenzoxazole **2** are essentially the same as those of the benzoxazole **1**. Slightly blue-shifted absorptions ( $\lambda_{\text{ab}} = 295$  and



316 nm) and the reverse red-shifted fluorescence ( $\lambda_{em} = 509$  nm with shoulder), compared to those of **1**, are notable. Comparable absorption properties are found for the ethyl acetate solution of **2**. However, its fluorescence properties are quite different from those in nonpolar solvents. Excitation in the main absorption band ( $\lambda_{ex} = 295$  nm) gave rise to the clearly detectable emission in the 433.5 nm band, together with the long wavelength emission. The intermediate wavelength emission was exclusively observed in more polar solvents such as acetonitrile and dimethyl sulfoxide. In the absorption spectra of the acetonitrile solution of **2**, a weak plateau at around 360 nm is detected (Figure 1). It should also be noted that excitation at 360 nm only gave rise to the intermediate wavelength emission and moreover that the excitation spectra showed a correlation between the intermediate wavelength emission and the 360 nm absorption. A pronounced solvent polarity-dependence, of the intensity of the intermediate

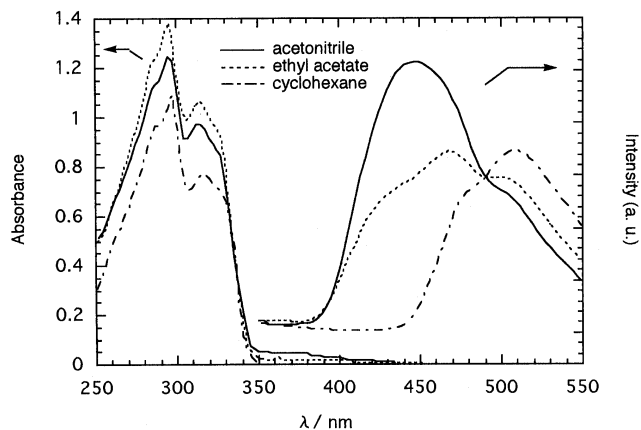


Figure 1. Absorption and Fluorescence Spectra of **2** in Cyclohexane, in Ethyl Acetate, and in Acetonitrile. Excitation Wavelength; 295 nm, Concentration;  $9.6 \times 10^{-5}$  M for Absorption Spectra and  $2.4 \times 10^{-5}$  M for Fluorescence Spectra.

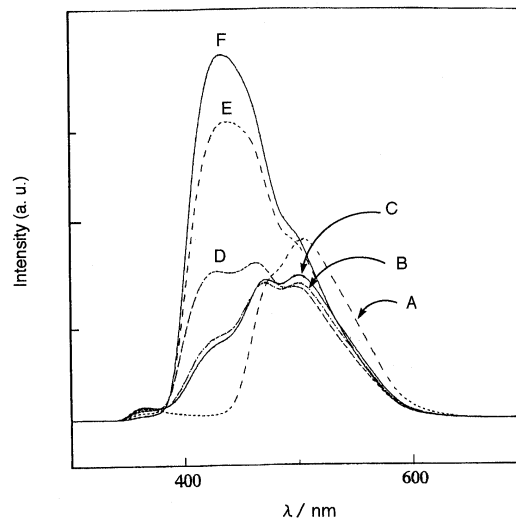


Figure 2. Fluorescence Spectra of **2** in a Mixture of Cyclohexane and Ethyl Acetate in the Volume Ratio of A, 10:0; B, 8:2; C, 6:4; D, 4:6; E, 2:8; F, 0:10. Excitation Wavelength; 295 nm, Concentration;  $6.4 \times 10^{-6}$  M.

and long wavelength emissions, was noticed in solutions consisting of various compositions of ethyl acetate and cyclohexane. As shown in Figure 2, the intensity of the intermediate wavelength emission increases as the ratio of ethyl acetate to cyclohexane increases, that is, as the solvent polarity increases. A characteristic of tetrafluorobenzoxazole **2** is that the shorter wavelength emission around 360 nm, which is detected in the case of the benzoxazole **1**, is not observed in these solvents. However the intermediate wavelength emission around 440 nm is clearly observed in aprotic solvents such as dimethyl sulfoxide, acetonitrile, and even in ethyl acetate.

2-(4,6-Difluoro-2-hydroxyphenyl)benzoxazole (**5**), prepared by the nucleophilic aromatic substitution of 2-(2,4,6-trifluorophenyl)benzoxazole (**6**) with sodium hydroxide, was then investigated in order to determine the electronic effects on absorption and fluorescence properties. Figure 3 indicates that the spectral properties, particularly the fluorescence behavior of **5**, are just intermediate between those of **1** and **2**, with the exception of the long wavelength emission around 470 nm with 500 nm shoulder. A shorter wavelength emission around 360 nm is definitely detected in ethyl acetate, which shows a similar trend to that of **1**, whereas in more polar solvent such as acetonitrile the intermediate wavelength emission is observed, similar to that of **2**.

The fluorescence quantum yields of benzoxazoles **2** and **5** measured in cyclohexane and in acetonitrile are summarized in Table 2. To determine the effect of the introduced fluorine atoms, quantum yields of benzoxazole **1** were also measured under similar conditions, to give  $\Phi = 0.019$  (cyclohexane) and 0.012 (acetonitrile), respectively. The introduction of fluorine atoms to the 2-phenyl group was found to bring about a decrease in fluorescence quantum

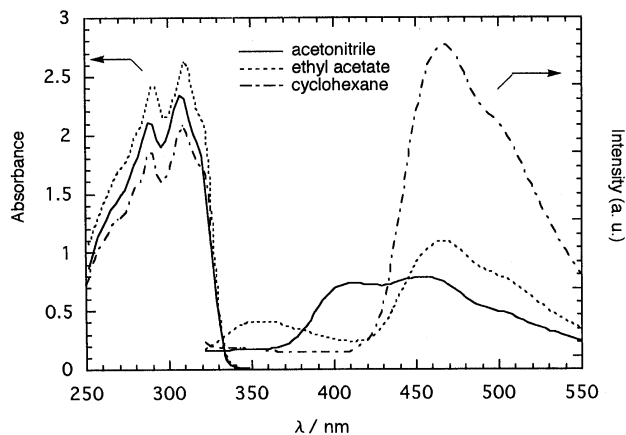


Figure 3. Absorption and Fluorescence Spectra of **5** in Cyclohexane, in Ethyl Acetate, and in Acetonitrile. Excitation Wavelength; 289 nm, Concentration;  $9.6 \times 10^{-5} M$  for Absorption Spectra and  $2.4 \times 10^{-5} M$  for Fluorescence Spectra.

yield. A similar trend is realized in the starting benzoxazoles; that is, **4** ( $\Phi = 0.152$  in cyclohexane) and **6** ( $\Phi = 0.056$  in cyclohexane) are substantially diminished, compared with 2-phenylbenzoxazole ( $\Phi = 0.786$  in cyclohexane)[23].

Table 2

Fluorescence Quantum Yield of 2-(2-Hydroxyphenyl)benzoxazoles **2** and **5**

Benzoxazole [b]	Quantum Yield/ $\Phi$ [a]	
	Cyclohexane	Acetonitrile
<b>2</b>	0.004	0.005
<b>5</b>	0.015	0.005

[a] Quantum yield was calculated on the basis of quinine in 0.5 M- $H_2SO_4$  aq ( $\Phi = 0.51$ ,  $\lambda_{ex} = 299$  nm); [b] Quantum yields of **1** were estimated to be  $\Phi = 0.019$  in cyclohexane and  $\Phi = 0.012$  in acetonitrile, respectively, under the similar conditions.

A concentration dependence for benzoxazole **2** on the spectral properties is very notable. The apparent validity of Beer's law is realized in nonpolar solvents, whereas the nonvalidity of Beer's law is noticed in acetonitrile, which is due to the additional absorption band around 360 nm that appears in acetonitrile. Its relative absorption compared to that of the short wavelength bands is considerably large in high dilution and diminishes gradually as the concentration increases, and the absorption spectra become essentially identical with those in nonpolar solvent (Figure 4)[24,25]. Concentration dependence of the emission-wavelength is not observed in cyclohexane and acetonitrile, but interestingly it is in ethyl acetate. The intermediate wavelength emission, which is main emission at high dilution, seems to be red-shifted gradually as the concentration is increased (Figure 5). However, the change in the fluorescence spectra may be interpreted by the difference in concentration dependence of the fluorescence quantum efficiency of the intermediate and long wavelength emissions. Indeed the

outstanding quenching of the intermediate wavelength emission, compared to that of the long wavelength emission, is observed in acetonitrile solution.

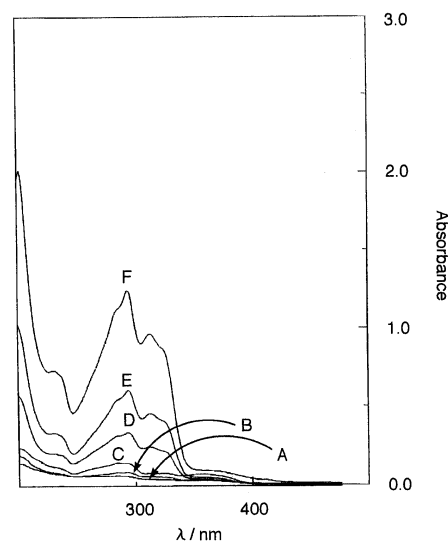


Figure 4. Concentration Dependence of Absorption Spectra of **2** in Acetonitrile. Concentration: A,  $3.0 \times 10^{-6} M$ ; B,  $6.0 \times 10^{-6} M$ ; C,  $1.2 \times 10^{-5} M$ ; D,  $2.4 \times 10^{-5} M$ ; E,  $4.8 \times 10^{-5} M$ ; F,  $9.6 \times 10^{-5} M$ .

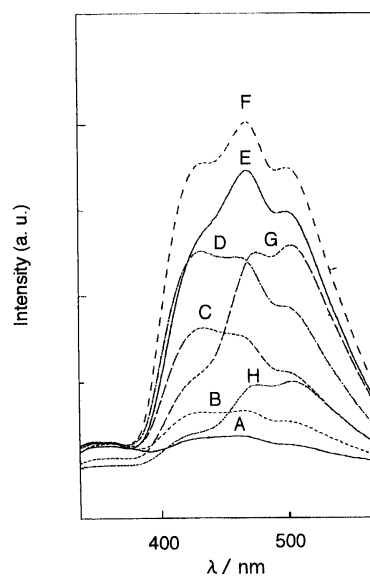


Figure 5. Concentration Dependence of Fluorescence Spectra of **2** in Ethyl Acetate. Excitation Wavelength; 295 nm, Concentration: A,  $1.5 \times 10^{-6} M$ ; B,  $3.0 \times 10^{-6} M$ ; C,  $6.0 \times 10^{-6} M$ ; D,  $1.2 \times 10^{-5} M$ ; E,  $2.4 \times 10^{-5} M$ ; F,  $4.8 \times 10^{-5} M$ ; G,  $9.6 \times 10^{-5} M$ ; H,  $1.9 \times 10^{-4} M$ .

The intermediate wavelength fluorescence emitted in aprotic polar solvents is characteristic of the fluorine substituted benzoxazole **2**. For benzoxazole **1**, a similar emission is found in protic solvents such as alcohols and water[16,18]. Species,

from which this emission originates, has been discussed for **1** and its keto isomer with *trans*-configuration of the quinone-carbonyl group toward the NH group has been suggested[26]. However, its possibility may be ruled out, because reported transient absorption spectroscopies show that the *trans*- and *cis*-keto isomers absorb around 430 nm[27,28].

The intermediate wavelength emission of **2** has the following features summarized as; a) its intensity is large in polar solvents, and the wavelength is red-shifted with increase in polarity as shown by the order of 433.5 nm in ethyl acetate, 437.0 nm in acetonitrile, and 441.0 nm in dimethyl sulfoxide, suggesting that it is the emission from the excited state of an ionic molecule; b) the emission is observed on excitation in the main absorption band of 295 nm and in the long wavelength absorption band of 360 nm; c) the relative absorption of the 360 nm band is large in high dilution in a polar solvent and diminishes gradually on increasing concentration of **2**, accompanied with a substantial emission quenching; and d) similar ionic entity absorbing in the 360 nm band is observed in the presence of large amount of diazabicyclo[2.2.2]octane (DABCO) even in nonpolar solvent and forms a 1:1 complex with DABCO. On the basis of these features, the phenolate anion **2** (anion) is assumed as the ionic molecule [29], because the fluorophenol moiety of **2** is rather acidic and is expected to be more acidic in the excited state [19]. Thus, the following scenario will be assumed; the isomer **2** (rotamer), which is hydrogen-bonded to solvent molecules under the polar environment, equilibrates with **2** (anion). The molecule **2** (anion) absorbs in the 360 nm band and its excited state **2**\* (anion)

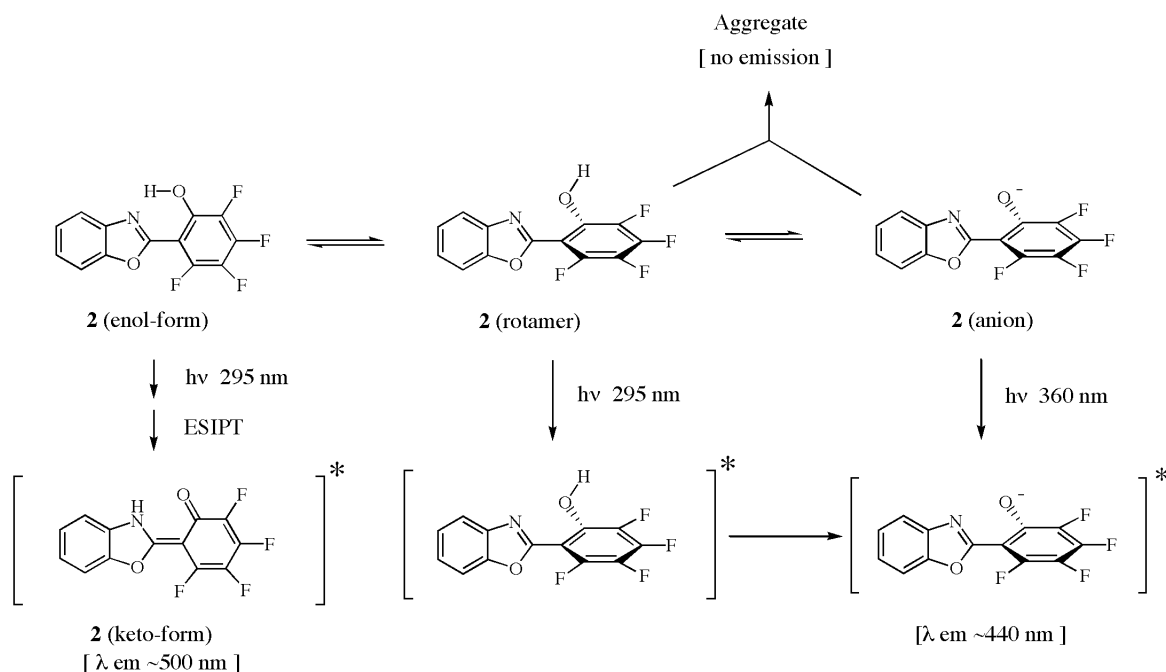
emits the intermediate wavelength fluorescence on excitation of the 360 nm band. The same excited state is formed from the excited state of **2** (rotamer). The ease of formation of **2** (anion) from **2** (rotamer) is due to the strongly inductive fluorine atoms and is the reason why the shorter wavelength emission from the excited state of **2** (rotamer) is not detected in the case of **2**. Concentration dependence of the fluorescence is assumed to be caused by the formation of an aggregate of **2** (rotamer) and **2** (anion). The aggregate has no fluorescence property and its formation is accelerated on increasing their concentration (Scheme 2). It should be added that the absorption spectra of **2** (enol-form), **2** (rotamer), and the aggregate are essentially identical and cannot be distinguished from each other.

In conclusion, the benzoxazole **2** emits the long wavelength fluorescence around 500 nm in nonpolar solvent *via* the ESIPT process in the excited state of **2** (enol-form) and also emits the intermediate wavelength fluorescence around 440 nm in polar solvent, which is assumed to originate from the excited state of **2** (anion). In a solvent with the intermediate polarity, **2** emits both fluorescences and their relative intensity is dependent on the concentration of **2**, which is supposed to be caused by the high sensitivity of the intermediate wavelength fluorescence to the concentration quenching.

## EXPERIMENTAL

The ir spectra were recorded on a JASCO A-100 spectrometer and samples were run as potassium bromide pellets. The  $^1\text{H}$ - and  $^{19}\text{F}$ -nmr spectra were measured with a JEOL JNM-LA400 (400

Scheme 2



MHz for  $^1\text{H}$  nmr and 376 MHz for  $^{19}\text{F}$  nmr) spectrometer in solutions of deuteriochloroform. The chemical shifts are given in  $\delta$ /ppm downfield from tetramethylsilane as an internal standard for  $^1\text{H}$ -nmr and from hexafluorobenzene as an external standard for  $^{19}\text{F}$ -nmr, respectively;  $J$  values are given in Hz. Product ratios were evaluated by  $^{19}\text{F}$ -nmr analysis. The uv-visible and fluorescence spectra were recorded with JASCO Ubest-50 spectrometer and JASCO FP-777 spectrometers, respectively. The ms spectra were acquired using a HITACHI M-80B mass spectrometer. Acetonitrile, ethyl acetate, cyclohexane, and dimethyl sulfoxide for spectroscopy were the highest quality from KOKUSAN Chemical Co. and were used without further purification.

#### Preparation of 2-(2,3,4,5,6-Pentafluorophenyl)benzoxazole (4).

Triethylamine (5.60 g, 55.4 mmol) was added dropwise to a solution of 2-aminophenol (5.00 g, 45.9 mmol) and pentafluorobenzoyl chloride (12.8 g, 55.5 mmol) in 100 mL of ethyl acetate and the mixture was stirred at room temperature for 7 hours. To the mixture was added 10 mL of aqueous sodium hydroxide (1 *M*) and the mixture was stirred at room temperature for 12 hours. The mixture was extracted with ethyl acetate and the extracts were washed with water and brine, dried over magnesium sulfate, and evaporated to leave a solid (14.0 g). The obtained crude solid (6.50 g) was mixed with diphosphorus pentoxide (7.59 g, 53.5 mmol) and the mixture was heated at 175 °C for 1 hour. After the mixture was cooled to room temperature, ice-water was added to the mixture. The mixture was extracted with ethyl ether and the extracts were washed with aqueous sodium hydroxide (0.25 *M*), water, and brine and dried over magnesium sulfate. The extracts were evaporated to leave a solid which was recrystallized from hexane to give white crystals (3.70 g, 61% yield based on 2-aminophenol) of **4**: mp 110-112 °C; ir: 1650  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_5$ );  $^1\text{H}$  nmr:  $\delta$  7.89 (1H, m), 7.65 (1H, m), and 7.45 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  25.49 (2F, ddd,  $J = 24.1, 10.5,$  and  $4.5$  Hz), 13.84 (1F, tt,  $J = 20.7$  and  $4.5$  Hz), and 2.03 (2F, m); uv: (cyclohexane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 287 nm (4.19). These spectral data are consistent with those previously reported [30].

#### Preparation of 2-(3,4,5,6-Tetrafluoro-2-hydroxyphenyl)benzoxazole (2).

Crushed sodium hydroxide was used for this reaction. A mixture of **4** (0.10 g, 0.35 mmol) and sodium hydroxide (0.07 g, 1.75 mmol) in 10 mL of dioxane, which was dried over calcium chloride, was stirred at 40 °C for 24 hours. The mixture was acidified with 1 *M* of hydrochloric acid and extracted with ethyl acetate. The extracts were washed with water and brine, dried over magnesium sulfate, and evaporated to leave a solid.  $^{19}\text{F}$  nmr analysis showed that the solid included 85% of total yield of **2** and **3** in a ratio of 95/5. Chromatography on silica gel (hexane/ethyl acetate, 10:1) of the solid produced a trace of **3** and 0.08 g (81%) of **2**, which was recrystallized from hexane/ethyl acetate.

Compound **2** has mp 180-182 °C ir: 3100-2600 (OH) and 1670  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_4$ );  $^1\text{H}$  nmr:  $\delta$  12.55 (1H, s), 7.77 (1H, m), 7.68 (1H, m), and 7.47 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  22.6 (1F, ddd,  $J = 22.0, 9.8,$  and  $5.3$  Hz), 12.8 (1F, ddd,  $J = 22.0, 20.3,$  and  $5.3$  Hz), 0.85 (1F, ddd,  $J = 20.3, 9.8,$  and  $3.8$  Hz), and -7.15 (1F, td,  $J = 22.0$  and  $3.8$  Hz).

Anal. Calcd for  $\text{C}_{13}\text{H}_5\text{NF}_4\text{O}_2$ : C, 55.12; H, 1.78; N, 4.95. Found: C, 55.08; H, 1.67; N, 4.88.

Using the same conditions as those above in the presence of water or 18-crown-6 (5 molar equivalents to 2-(pentafluorophenyl)benzoxazole) produced **3** exclusively, conditions and results are given in Table 1.

Compound **3** has mp 220 °C (dec.); ir: 3450 (OH) and 1650  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_4$ );  $^1\text{H}$  nmr:  $\delta$  7.76 (1H, m), 7.68 (1H, m), and 7.45 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  23.5 (2F, m) and 0.30 (2F, m); ms:  $m/z$  283 ( $\text{M}^+$ , 100%), 255 (10.6%), 92 (4.3%), 64 (12.0%), and 63 (12.3%).

Anal. Calcd for  $\text{C}_{13}\text{H}_5\text{NF}_4\text{O}_2$ : C, 55.12; H, 1.78; N, 4.95. Found: C, 54.76; H, 1.85; N, 4.94.

#### Preparation of 2-(2,4,6-Trifluorophenyl)benzoxazole (6).

A mixture of 2-aminophenol (0.31 g, 2.84 mmol) and 2,4,6-trifluorobenzoic acid (0.50 g, 2.84 mmol) in 25 g of polyphosphoric acid was stirred at 150 °C for 1 hour. After the mixture was cooled to room temperature, ice-water was added to the mixture. The mixture was extracted with ethyl ether and the extracts were washed with water and brine, and dried over magnesium sulfate. The extracts were evaporated to leave a solid which was chromatographed on silica gel (hexane/ethyl acetate, 10:1) and then purified by recrystallization from hexane to give a white solid (0.26 g, 37% yield) of **6**: mp 115-117 °C; ir: 3100 (CH) and 1630  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_3$ );  $^1\text{H}$  nmr:  $\delta$  7.87 (1H, m), 7.63 (1H, m), 7.42 (2H, m), and 6.87 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  60.78 (1F, tt,  $J = 9.0$  and  $9.0$  Hz) and 57.71 (2F, m); uv (cyclohexane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 285 nm (4.35).

Anal. Calcd for  $\text{C}_{13}\text{H}_6\text{NF}_3\text{O}$ : C, 62.64; H, 2.43; N, 5.62. Found: C, 62.67; H, 2.30; N, 5.59.

#### Preparation of 2-(4,6-Difluoro-2-hydroxyphenyl)benzoxazole (5).

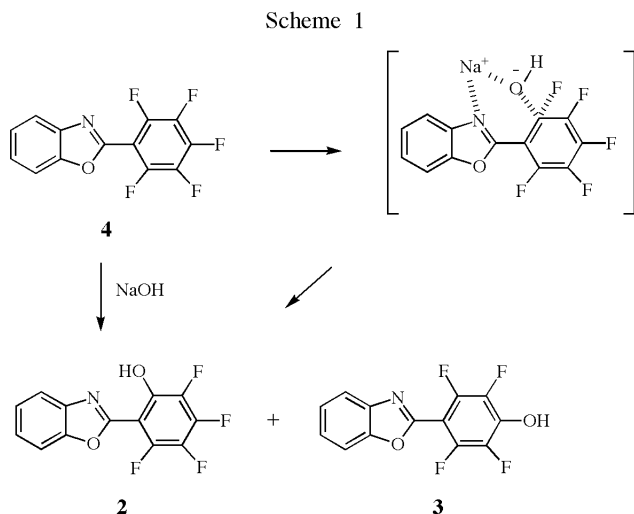
A mixture of **6** (0.10 g, 0.40 mmol) and crushed sodium hydroxide (0.08 g, 2.0 mmol) in dried dioxane (20 mL) was stirred at 40 °C for 2.5 hours and then refluxed for another 2.5 hours. By using a similar procedure as that described above, a crude solid was obtained that was chromatographed on silica gel (hexane/ethyl acetate, 20:3) to give 0.10 g (100%) of **5**. Purification was performed by recrystallization from hexane. Compound **5** has mp 144-146 °C; ir: 3100-2600 (OH), 3100 (CH) and 1640  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_2$ );  $^1\text{H}$  nmr:  $\delta$  12.63 (1H, s), 7.74 (1H, m), 7.67 (1H, m), 7.42 (2H, m), 6.66 (1H, dt,  $J = 10.0$  and  $2.2$  Hz), and 6.53 (1H, ddd,  $J = 10.7, 10.0,$  and  $2.2$  Hz);  $^{19}\text{F}$  nmr:  $\delta$  60.13 (1F, td,  $J = 10.0$  and  $10.7$  Hz) and 55.83 (1F, td,  $J = 10.7$  and  $2.2$  Hz).

Anal. Calcd for  $\text{C}_{13}\text{H}_7\text{NF}_2\text{O}_2$ : C, 63.15; H, 2.86; N, 5.67. Found: C, 63.02; H, 2.82; N, 5.61.

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316 nm) and the reverse red-shifted fluorescence ( $\lambda_{em} = 509$  nm with shoulder), compared to those of **1**, are notable. Comparable absorption properties are found for the ethyl acetate solution of **2**. However, its fluorescence properties are quite different from those in nonpolar solvents. Excitation in the main absorption band ( $\lambda_{ex} = 295$  nm) gave rise to the clearly detectable emission in the 433.5 nm band, together with the long wavelength emission. The intermediate wavelength emission was exclusively observed in more polar solvents such as acetonitrile and dimethyl sulfoxide. In the absorption spectra of the acetonitrile solution of **2**, a weak plateau at around 360 nm is detected (Figure 1). It should also be noted that excitation at 360 nm only gave rise to the intermediate wavelength emission and moreover that the excitation spectra showed a correlation between the intermediate wavelength emission and the 360 nm absorption. A pronounced solvent polarity-dependence, of the intensity of the intermediate

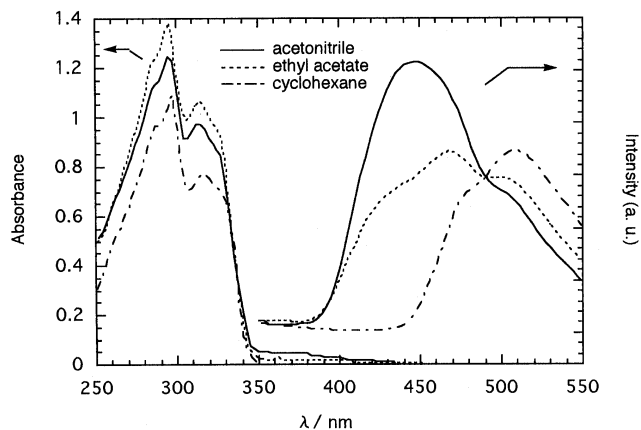


Figure 1. Absorption and Fluorescence Spectra of **2** in Cyclohexane, in Ethyl Acetate, and in Acetonitrile. Excitation Wavelength; 295 nm, Concentration;  $9.6 \times 10^{-5}$  M for Absorption Spectra and  $2.4 \times 10^{-5}$  M for Fluorescence Spectra.

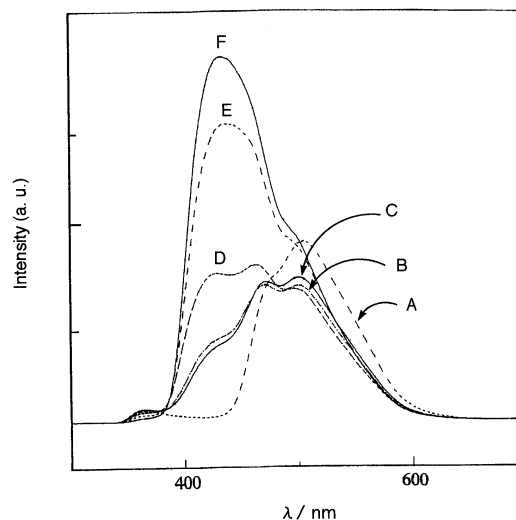


Figure 2. Fluorescence Spectra of **2** in a Mixture of Cyclohexane and Ethyl Acetate in the Volume Ratio of A, 10:0; B, 8:2; C, 6:4; D, 4:6; E, 2:8; F, 0:10. Excitation Wavelength; 295 nm, Concentration;  $6.4 \times 10^{-6}$  M.

and long wavelength emissions, was noticed in solutions consisting of various compositions of ethyl acetate and cyclohexane. As shown in Figure 2, the intensity of the intermediate wavelength emission increases as the ratio of ethyl acetate to cyclohexane increases, that is, as the solvent polarity increases. A characteristic of tetrafluorobenzoxazole **2** is that the shorter wavelength emission around 360 nm, which is detected in the case of the benzoxazole **1**, is not observed in these solvents. However the intermediate wavelength emission around 440 nm is clearly observed in aprotic solvents such as dimethyl sulfoxide, acetonitrile, and even in ethyl acetate.

2-(4,6-Difluoro-2-hydroxyphenyl)benzoxazole (**5**), prepared by the nucleophilic aromatic substitution of 2-(2,4,6-trifluorophenyl)benzoxazole (**6**) with sodium hydroxide, was then investigated in order to determine the electronic effects on absorption and fluorescence properties. Figure 3 indicates that the spectral properties, particularly the fluorescence behavior of **5**, are just intermediate between those of **1** and **2**, with the exception of the long wavelength emission around 470 nm with 500 nm shoulder. A shorter wavelength emission around 360 nm is definitely detected in ethyl acetate, which shows a similar trend to that of **1**, whereas in more polar solvent such as acetonitrile the intermediate wavelength emission is observed, similar to that of **2**.

The fluorescence quantum yields of benzoxazoles **2** and **5** measured in cyclohexane and in acetonitrile are summarized in Table 2. To determine the effect of the introduced fluorine atoms, quantum yields of benzoxazole **1** were also measured under similar conditions, to give  $\Phi = 0.019$  (cyclohexane) and 0.012 (acetonitrile), respectively. The introduction of fluorine atoms to the 2-phenyl group was found to bring about a decrease in fluorescence quantum

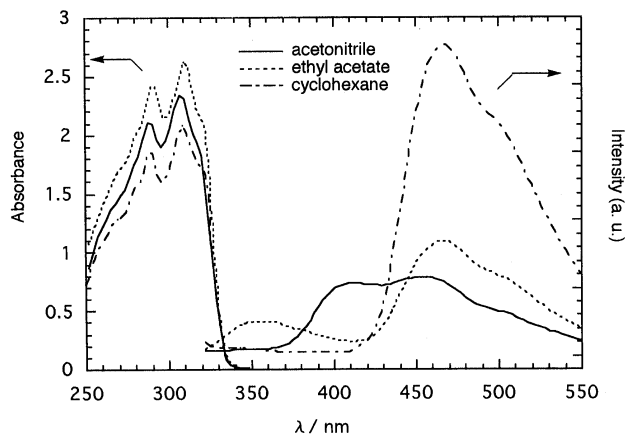


Figure 3. Absorption and Fluorescence Spectra of **5** in Cyclohexane, in Ethyl Acetate, and in Acetonitrile. Excitation Wavelength; 289 nm, Concentration;  $9.6 \times 10^{-5} M$  for Absorption Spectra and  $2.4 \times 10^{-5} M$  for Fluorescence Spectra.

yield. A similar trend is realized in the starting benzoxazoles; that is, **4** ( $\Phi = 0.152$  in cyclohexane) and **6** ( $\Phi = 0.056$  in cyclohexane) are substantially diminished, compared with 2-phenylbenzoxazole ( $\Phi = 0.786$  in cyclohexane)[23].

Table 2

Fluorescence Quantum Yield of 2-(2-Hydroxyphenyl)benzoxazoles **2** and **5**

Benzoxazole [b]	Quantum Yield/ $\Phi$ [a]	
	Cyclohexane	Acetonitrile
<b>2</b>	0.004	0.005
<b>5</b>	0.015	0.005

[a] Quantum yield was calculated on the basis of quinine in 0.5 M- $H_2SO_4$  aq ( $\Phi = 0.51$ ,  $\lambda_{ex} = 299$  nm); [b] Quantum yields of **1** were estimated to be  $\Phi = 0.019$  in cyclohexane and  $\Phi = 0.012$  in acetonitrile, respectively, under the similar conditions.

A concentration dependence for benzoxazole **2** on the spectral properties is very notable. The apparent validity of Beer's law is realized in nonpolar solvents, whereas the nonvalidity of Beer's law is noticed in acetonitrile, which is due to the additional absorption band around 360 nm that appears in acetonitrile. Its relative absorption compared to that of the short wavelength bands is considerably large in high dilution and diminishes gradually as the concentration increases, and the absorption spectra become essentially identical with those in nonpolar solvent (Figure 4)[24,25]. Concentration dependence of the emission-wavelength is not observed in cyclohexane and acetonitrile, but interestingly it is in ethyl acetate. The intermediate wavelength emission, which is main emission at high dilution, seems to be red-shifted gradually as the concentration is increased (Figure 5). However, the change in the fluorescence spectra may be interpreted by the difference in concentration dependence of the fluorescence quantum efficiency of the intermediate and long wavelength emissions. Indeed the

outstanding quenching of the intermediate wavelength emission, compared to that of the long wavelength emission, is observed in acetonitrile solution.

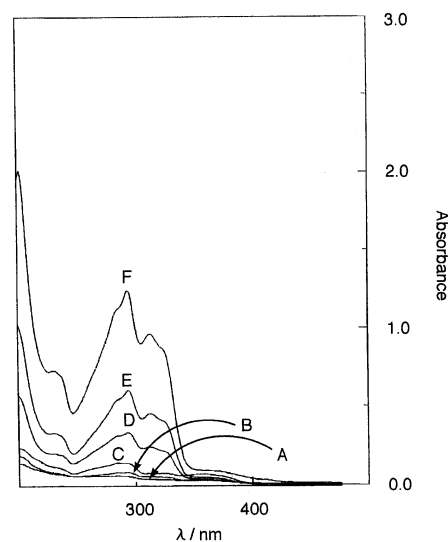


Figure 4. Concentration Dependence of Absorption Spectra of **2** in Acetonitrile. Concentration: A,  $3.0 \times 10^{-6} M$ ; B,  $6.0 \times 10^{-6} M$ ; C,  $1.2 \times 10^{-5} M$ ; D,  $2.4 \times 10^{-5} M$ ; E,  $4.8 \times 10^{-5} M$ ; F,  $9.6 \times 10^{-5} M$ .

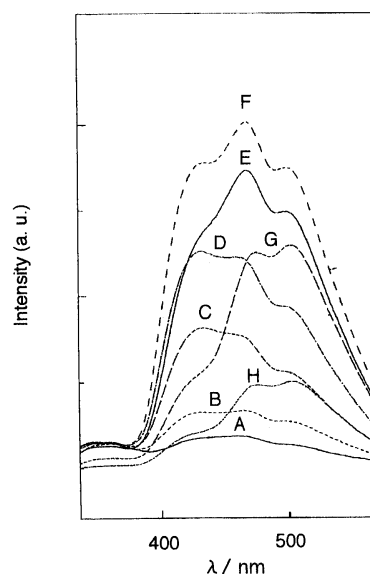


Figure 5. Concentration Dependence of Fluorescence Spectra of **2** in Ethyl Acetate. Excitation Wavelength; 295 nm, Concentration: A,  $1.5 \times 10^{-6} M$ ; B,  $3.0 \times 10^{-6} M$ ; C,  $6.0 \times 10^{-6} M$ ; D,  $1.2 \times 10^{-5} M$ ; E,  $2.4 \times 10^{-5} M$ ; F,  $4.8 \times 10^{-5} M$ ; G,  $9.6 \times 10^{-5} M$ ; H,  $1.9 \times 10^{-4} M$ .

The intermediate wavelength fluorescence emitted in aprotic polar solvents is characteristic of the fluorine substituted benzoxazole **2**. For benzoxazole **1**, a similar emission is found in protic solvents such as alcohols and water[16,18]. Species,



from which this emission originates, has been discussed for **1** and its keto isomer with *trans*-configuration of the quinone-carbonyl group toward the NH group has been suggested[26]. However, its possibility may be ruled out, because reported transient absorption spectroscopies show that the *trans*- and *cis*-keto isomers absorb around 430 nm[27,28].

The intermediate wavelength emission of **2** has the following features summarized as; a) its intensity is large in polar solvents, and the wavelength is red-shifted with increase in polarity as shown by the order of 433.5 nm in ethyl acetate, 437.0 nm in acetonitrile, and 441.0 nm in dimethyl sulfoxide, suggesting that it is the emission from the excited state of an ionic molecule; b) the emission is observed on excitation in the main absorption band of 295 nm and in the long wavelength absorption band of 360 nm; c) the relative absorption of the 360 nm band is large in high dilution in a polar solvent and diminishes gradually on increasing concentration of **2**, accompanied with a substantial emission quenching; and d) similar ionic entity absorbing in the 360 nm band is observed in the presence of large amount of diazabicyclo[2.2.2]octane (DABCO) even in nonpolar solvent and forms a 1:1 complex with DABCO. On the basis of these features, the phenolate anion **2** (anion) is assumed as the ionic molecule [29], because the fluorophenol moiety of **2** is rather acidic and is expected to be more acidic in the excited state [19]. Thus, the following scenario will be assumed; the isomer **2** (rotamer), which is hydrogen-bonded to solvent molecules under the polar environment, equilibrates with **2** (anion). The molecule **2** (anion) absorbs in the 360 nm band and its excited state **2**\* (anion)

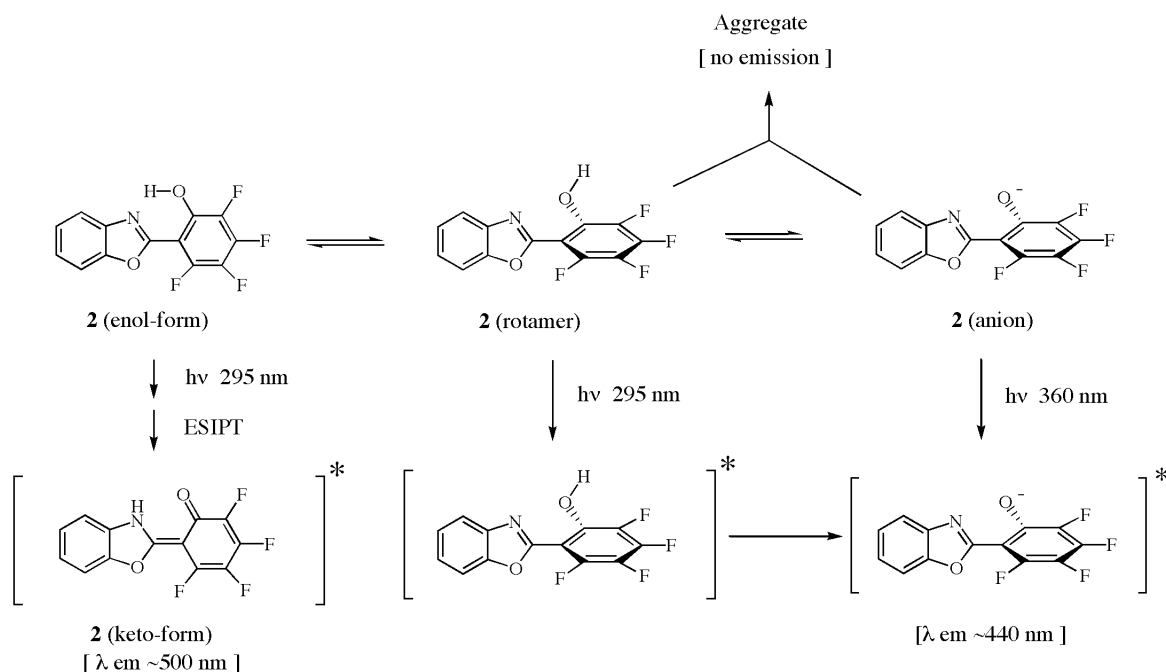
emits the intermediate wavelength fluorescence on excitation of the 360 nm band. The same excited state is formed from the excited state of **2** (rotamer). The ease of formation of **2** (anion) from **2** (rotamer) is due to the strongly inductive fluorine atoms and is the reason why the shorter wavelength emission from the excited state of **2** (rotamer) is not detected in the case of **2**. Concentration dependence of the fluorescence is assumed to be caused by the formation of an aggregate of **2** (rotamer) and **2** (anion). The aggregate has no fluorescence property and its formation is accelerated on increasing their concentration (Scheme 2). It should be added that the absorption spectra of **2** (enol-form), **2** (rotamer), and the aggregate are essentially identical and cannot be distinguished from each other.

In conclusion, the benzoxazole **2** emits the long wavelength fluorescence around 500 nm in nonpolar solvent *via* the ESIPT process in the excited state of **2** (enol-form) and also emits the intermediate wavelength fluorescence around 440 nm in polar solvent, which is assumed to originate from the excited state of **2** (anion). In a solvent with the intermediate polarity, **2** emits both fluorescences and their relative intensity is dependent on the concentration of **2**, which is supposed to be caused by the high sensitivity of the intermediate wavelength fluorescence to the concentration quenching.

## EXPERIMENTAL

The ir spectra were recorded on a JASCO A-100 spectrometer and samples were run as potassium bromide pellets. The  $^1\text{H}$ - and  $^{19}\text{F}$ -nmr spectra were measured with a JEOL JNM-LA400 (400

Scheme 2



MHz for  $^1\text{H}$  nmr and 376 MHz for  $^{19}\text{F}$  nmr) spectrometer in solutions of deuteriochloroform. The chemical shifts are given in  $\delta$ /ppm downfield from tetramethylsilane as an internal standard for  $^1\text{H}$ -nmr and from hexafluorobenzene as an external standard for  $^{19}\text{F}$ -nmr, respectively;  $J$  values are given in Hz. Product ratios were evaluated by  $^{19}\text{F}$ -nmr analysis. The uv-visible and fluorescence spectra were recorded with JASCO Ubest-50 spectrometer and JASCO FP-777 spectrometers, respectively. The ms spectra were acquired using a HITACHI M-80B mass spectrometer. Acetonitrile, ethyl acetate, cyclohexane, and dimethyl sulfoxide for spectroscopy were the highest quality from KOKUSAN Chemical Co. and were used without further purification.

#### Preparation of 2-(2,3,4,5,6-Pentafluorophenyl)benzoxazole (4).

Triethylamine (5.60 g, 55.4 mmol) was added dropwise to a solution of 2-aminophenol (5.00 g, 45.9 mmol) and pentafluorobenzoyl chloride (12.8 g, 55.5 mmol) in 100 mL of ethyl acetate and the mixture was stirred at room temperature for 7 hours. To the mixture was added 10 mL of aqueous sodium hydroxide (1 *M*) and the mixture was stirred at room temperature for 12 hours. The mixture was extracted with ethyl acetate and the extracts were washed with water and brine, dried over magnesium sulfate, and evaporated to leave a solid (14.0 g). The obtained crude solid (6.50 g) was mixed with diphosphorus pentoxide (7.59 g, 53.5 mmol) and the mixture was heated at 175 °C for 1 hour. After the mixture was cooled to room temperature, ice-water was added to the mixture. The mixture was extracted with ethyl ether and the extracts were washed with aqueous sodium hydroxide (0.25 *M*), water, and brine and dried over magnesium sulfate. The extracts were evaporated to leave a solid which was recrystallized from hexane to give white crystals (3.70 g, 61% yield based on 2-aminophenol) of **4**: mp 110–112 °C; ir: 1650  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_5$ );  $^1\text{H}$  nmr:  $\delta$  7.89 (1H, m), 7.65 (1H, m), and 7.45 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  25.49 (2F, ddd,  $J = 24.1, 10.5,$  and  $4.5$  Hz), 13.84 (1F, tt,  $J = 20.7$  and  $4.5$  Hz), and 2.03 (2F, m); uv: (cyclohexane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 287 nm (4.19). These spectral data are consistent with those previously reported [30].

#### Preparation of 2-(3,4,5,6-Tetrafluoro-2-hydroxyphenyl)benzoxazole (2).

Crushed sodium hydroxide was used for this reaction. A mixture of **4** (0.10 g, 0.35 mmol) and sodium hydroxide (0.07 g, 1.75 mmol) in 10 mL of dioxane, which was dried over calcium chloride, was stirred at 40 °C for 24 hours. The mixture was acidified with 1 *M* of hydrochloric acid and extracted with ethyl acetate. The extracts were washed with water and brine, dried over magnesium sulfate, and evaporated to leave a solid.  $^{19}\text{F}$  nmr analysis showed that the solid included 85% of total yield of **2** and **3** in a ratio of 95/5. Chromatography on silica gel (hexane/ethyl acetate, 10:1) of the solid produced a trace of **3** and 0.08 g (81%) of **2**, which was recrystallized from hexane/ethyl acetate.

Compound **2** has mp 180–182 °C ir: 3100–2600 (OH) and 1670  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_4$ );  $^1\text{H}$  nmr:  $\delta$  12.55 (1H, s), 7.77 (1H, m), 7.68 (1H, m), and 7.47 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  22.6 (1F, ddd,  $J = 22.0, 9.8,$  and  $5.3$  Hz), 12.8 (1F, ddd,  $J = 22.0, 20.3,$  and  $5.3$  Hz), 0.85 (1F, ddd,  $J = 20.3, 9.8,$  and  $3.8$  Hz), and  $-7.15$  (1F, td,  $J = 22.0$  and  $3.8$  Hz).

Anal. Calcd for  $\text{C}_{13}\text{H}_5\text{NF}_4\text{O}_2$ : C, 55.12; H, 1.78; N, 4.95. Found: C, 55.08; H, 1.67; N, 4.88.

Using the same conditions as those above in the presence of water or 18-crown-6 (5 molar equivalents to 2-(pentafluorophenyl)benzoxazole) produced **3** exclusively, conditions and results are given in Table 1.

Compound **3** has mp 220 °C (dec.); ir: 3450 (OH) and 1650  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_4$ );  $^1\text{H}$  nmr:  $\delta$  7.76 (1H, m), 7.68 (1H, m), and 7.45 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  23.5 (2F, m) and 0.30 (2F, m); ms:  $m/z$  283 ( $\text{M}^+$ , 100%), 255 (10.6%), 92 (4.3%), 64 (12.0%), and 63 (12.3%).

Anal. Calcd for  $\text{C}_{13}\text{H}_5\text{NF}_4\text{O}_2$ : C, 55.12; H, 1.78; N, 4.95. Found: C, 54.76; H, 1.85; N, 4.94.

#### Preparation of 2-(2,4,6-Trifluorophenyl)benzoxazole (6).

A mixture of 2-aminophenol (0.31 g, 2.84 mmol) and 2,4,6-trifluorobenzoic acid (0.50 g, 2.84 mmol) in 25 g of polyphosphoric acid was stirred at 150 °C for 1 hour. After the mixture was cooled to room temperature, ice-water was added to the mixture. The mixture was extracted with ethyl ether and the extracts were washed with water and brine, and dried over magnesium sulfate. The extracts were evaporated to leave a solid which was chromatographed on silica gel (hexane/ethyl acetate, 10:1) and then purified by recrystallization from hexane to give a white solid (0.26 g, 37% yield) of **6**: mp 115–117 °C; ir: 3100 (CH) and 1630  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_3$ );  $^1\text{H}$  nmr:  $\delta$  7.87 (1H, m), 7.63 (1H, m), 7.42 (2H, m), and 6.87 (2H, m);  $^{19}\text{F}$  nmr:  $\delta$  60.78 (1F, tt,  $J = 9.0$  and  $9.0$  Hz) and 57.71 (2F, m); uv (cyclohexane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 285 nm (4.35).

Anal. Calcd for  $\text{C}_{13}\text{H}_6\text{NF}_3\text{O}$ : C, 62.64; H, 2.43; N, 5.62. Found: C, 62.67; H, 2.30; N, 5.59.

#### Preparation of 2-(4,6-Difluoro-2-hydroxyphenyl)benzoxazole (5).

A mixture of **6** (0.10 g, 0.40 mmol) and crushed sodium hydroxide (0.08 g, 2.0 mmol) in dried dioxane (20 mL) was stirred at 40 °C for 2.5 hours and then refluxed for another 2.5 hours. By using a similar procedure as that described above, a crude solid was obtained that was chromatographed on silica gel (hexane/ethyl acetate, 20:3) to give 0.10 g (100%) of **5**. Purification was performed by recrystallization from hexane. Compound **5** has mp 144–146 °C; ir: 3100–2600 (OH), 3100 (CH) and 1640  $\text{cm}^{-1}$  ( $\text{C}_6\text{F}_2$ );  $^1\text{H}$  nmr:  $\delta$  12.63 (1H, s), 7.74 (1H, m), 7.67 (1H, m), 7.42 (2H, m), 6.66 (1H, dt,  $J = 10.0$  and  $2.2$  Hz), and 6.53 (1H, ddd,  $J = 10.7, 10.0,$  and  $2.2$  Hz);  $^{19}\text{F}$  nmr:  $\delta$  60.13 (1F, td,  $J = 10.0$  and  $10.7$  Hz) and 55.83 (1F, td,  $J = 10.7$  and  $2.2$  Hz).

Anal. Calcd for  $\text{C}_{13}\text{H}_7\text{NF}_2\text{O}_2$ : C, 63.15; H, 2.86; N, 5.67. Found: C, 63.02; H, 2.82; N, 5.61.

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