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The synthesis and properties of benzoxazole fluorescent brighteners for application to polyester fibers

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Abstract

Fluorescent brighteners based on dicarboxylic acid derivatives are compounds of the benzoxazole type, synthesized by a simple reaction using polyphosphoric acid. The obtained compounds (**4a–c**, **6a–c**, **8a–c**) were characterized by the analysis of proton NMR spectrum and confirmed by UV spectrum. The physical properties of the compounds (**4a–c**, **6a–c**, **8a–c**) were performed by fastness test and whiteness measurement.

Keywords: Benzoxazole; Fluorescent brighteners; Whiteness; Fastness; Polyphosphoric acid

1. Introduction

As one type of functional dye, fluorescent brightener was used for making the chemically bleached matters such as fiber, paper, pulp, plastic, etc [1–3]. A typical fluorescent brightener can absorb light in ultraviolet region (330–380 nm) and emit visible blue lights (400–450 nm) [4]. Fluorescent brighteners are substances which normally have a system of conjugated double bonds and electron-donating groups to show the high fluorescence activity [5]. As for the kind of fluorescent brighteners, there are imidazole, triazole, coumarin, naphthalimide, stilbene and benzoxazole systems [6].

Many commercial fluorescent brighteners for application to polyester fibers contain a benzoxazole group and disperse type structure. The concern with benzoxazole derivatives has been growing because these compounds have a number of optical applications such as fluorescence compounds and dyes [7,8].

In this study, I tried to develop an efficient synthetic method for new benzoxazole compound as fluorescent brighteners. Dicarboxylic acid derivatives which were symmetrically substituted with various aminophenol derivatives were synthesized as the symmetrical benzoxazole fluorescent brighteners (**4a–c**, **6a–c**, **8a–c**) using polyphosphoric acid (PPA). The chemical structures of the synthesized compounds (**4a–c**, **6a–c**, **8a–c**) were characterized by the analysis of proton NMR spectrum and confirmed by UV spectrum. The physical properties were performed by various fastness test and whiteness measurement.

2. Results and discussion

2.1. Synthesis of dyes

The polyester fluorescent brighteners that contain a benzoxazole group are usually prepared from appropriate *o*-aminophenol and carboxylic acid or one of its derivatives. The reaction proceeds via an intermediate amide form and it can be an advantage to start from an acid derivative such as the acyl chloride [9]. The benzoxazole product was prepared by cyclization of an intermediate of amide form using thionyl chloride as acid catalyst [10,11]. The reaction route is given in Fig. 1.

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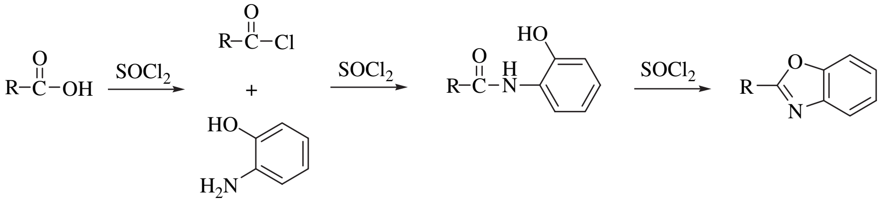


Fig. 1. The synthesis of benzoxazole compound by using thionyl chloride.

The problem in using thionyl chloride in this reaction is that the intermediate of amide form experiences difficulty in cyclization and the yield is very low. So I didn't use thionyl chloride but used polyphosphoric acid (PPA) instead and carried out the synthesis of benzoxazole compound.

Polyphosphoric acid (PPA) is a good solvent for many organic compounds and polymers. Also it has been used extensively in organic and polymer synthesis. It is one of the most effective reagents for acylation, alkylation and cyclization reactions [12].

2,6-Dicarboxylic acid pyridine (**1**) and *o*-aminophenol (**2a**) reacted in polyphosphoric acid (PPA) to produce an intermediate compound *N*,*N*-bis(2-hydroxyphenyl)pyridine-2,6-dicarboxylamide (**3a**) at 60–120 °C. When the intermediate compound was further heated at 200 °C for 3 h, the compound was totally converted into 2,6-di(benzoxazol-2-yl)pyridine, as shown in Scheme 1.

As mentioned above, by using polyphosphoric acid (PPA), benzoxazole fluorescent brighteners (**4a**–**c**, **6a**–**c**, **8a**–**c**) were synthesized. Therefore, the reaction route is given in Scheme 2 and the relevant data in Table 1.

2.2. Colour assessment and various fastnesses

The synthesized compounds (**4a**–**c**, **6a**–**c**, **8a**–**c**) were applied at concentrations of 0.05%, 0.1%, 0.3%, 0.5%, and 1% relatively to the weight of polyester fiber. The degree of whiteness and CIE $L^*a^*b^*$ coordinates were determined. The obtained data are presented in Table 2. The value of whiteness increased in the range of 0.05–0.5% and decreased after 0.5%. The whiteness of synthesized compounds was in the range of 54–137. The whiteness in synthesized compounds increased in the following order: **4b** < **6b** < **8b** < **4c** < **6c** < **8c** < **4a** < **6a** < **8a**. The data of chlorinated water fastness, rubbing fastness, washing fastness and light fastness, of the synthesized compounds are shown in Table 3. The results from chlorinated water fastness, rubbing fastness, washing fastness and light fastness tests showed that all the compounds (**4a**–**c**, **6a**–**c**, **8a**–**c**) appeared to have excellent fastnesses.

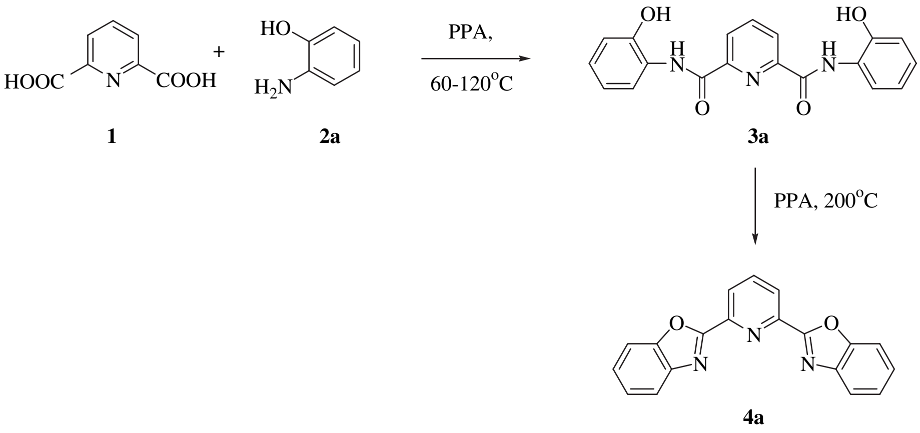
3. Conclusion

The symmetrically substituted benzoxazole fluorescent brighteners (**4a**–**c**, **6a**–**c**, **8a**–**c**) were synthesized by using polyphosphoric acid (PPA) as a solvent and as a catalyst in good yield. Also the synthesized compounds (**4a**–**c**, **6a**–**c**, **8a**–**c**) showed excellent dyeing properties in various fastnesses. Especially, the compounds (**4a**, **8a**) showed a high degree of whiteness and superior properties for polyester.

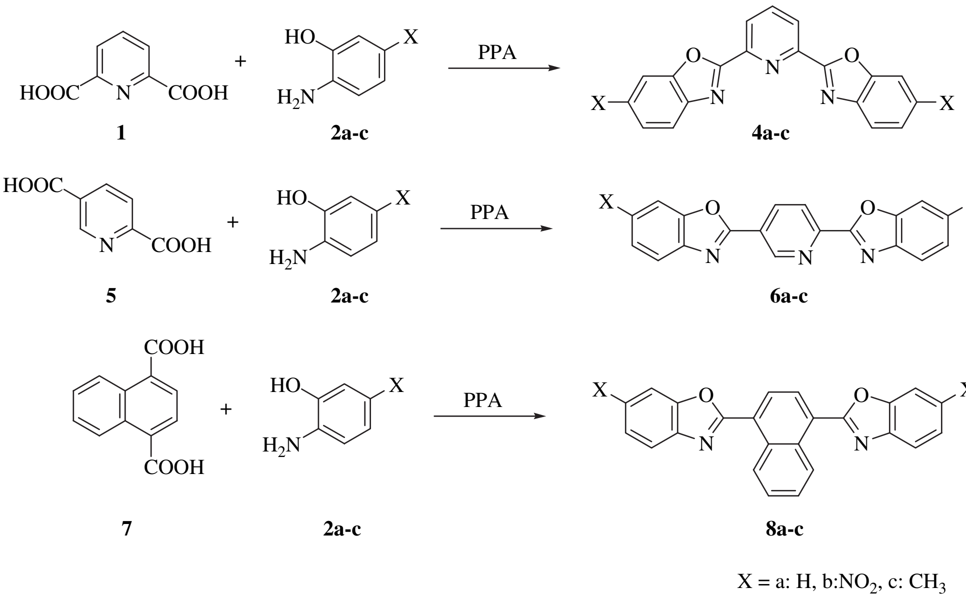
4. Experimental

4.1. Materials and analysis

All chemicals, which were purchased from commercial sources (Aldrich, Merck, Duksan, Yakuri, Junsei, etc.), were of analytical grade. The solvents were purified by distillation and the other reagents were used without further purification. The ^{1}H NMR spectrum was measured at 300 MHz using a Varian Mercury 300. The UV spectrum was obtained on a Shimadzu UV-2401PC. TLC was carried out using Merck silica gel plates (F254) with distilled solvents. Light fastness results were obtained on a Xenotest 150S. Washing fastness and chlorinated water fastness were tested on an Atras LP2. Rubbing



Scheme 1. The synthesis of benzoxazole compound by using PPA.



Scheme 2. The synthesis of benzoxazole fluorescent brighteners by using PPA.

fastness results were obtained on an Atras CM-5. The computer color matching (CCM) data were obtained on an SF600 Data color.

4.2. General method for the synthesis of dye compounds

Dicarboxylic acid derivatives (10 mmol) and *o*-aminophenol derivatives (**2a–c**, 20 mmol) were stirred in polyphosphoric acid (40 g) at 60 °C for 1 h and then heated at 120 °C for 3 h and again heated at 200 °C for 3 h under nitrogen. The reaction mixture was allowed to cool to 120 °C. The mixture was quenched with ice water and then extracted with diethyl ether. The organic layer was dried with anhydrous magnesium sulfate and evaporated to give dye compounds as solid.

4.2.1. Synthesis of 2,6-di(benzoxazol-2-yl)pyridine (4a)

Yields 90%; white solid; ^{1}H NMR (DMSO-d_6) δ: 7.45 (d, 4H, ArH), 7.79 (d, 1H, ArH), 7.85 (t, 4H, ArH), 8.12 (d, 1H, ArH), 8.90 (s, 1H, ArH).

Table 1
Characterization data of benzoxazole fluorescent brighteners (**4a–c**, **6a–c**, **8a–c**)

Entry	X	Yield (%)	UV (nm)
4a	H	90	282, 356
4b	NO_2	93	282, 355
4c	CH_3	84	282, 365
6a	H	95	272, 355
6b	NO_2	94	278, 354
6c	CH_3	94	276, 363
8a	H	90	289, 355
8b	NO_2	93	274, 353
8c	CH_3	91	280, 360

4.2.2. Synthesis of 2,6-di(6-nitrobenzoxazol-2-yl)pyridine (4b)

Yields 93%; yellow solid; ^{1}H NMR (DMSO-d_6) δ: 7.49 (d, 2H, ArH), 7.74 (d, 1H, ArH), 8.10 (d, 1H, ArH), 8.25 (s, 2H, ArH), 8.50 (d, 2H, ArH), 8.92 (s, 1H, ArH).

4.2.3. Synthesis of 2,6-di(6-methylbenzoxazol-2-yl)pyridine (4c)

Yields 84%; white solid; ^{1}H NMR (DMSO-d_6) δ: 2.27 (s, 6H, ArH), 7.05 (d, 2H, ArH), 7.38 (s, 2H, ArH), 7.51 (d, 2H, ArH), 7.70 (d, 1H, ArH), 8.08 (d, 1H, ArH), 8.90 (s, 1H, ArH).

4.2.4. Synthesis of 2,5-di(benzoxazol-2-yl)pyridine (6a)

Yields 95%; yellow solid; ^{1}H NMR (DMSO-d_6) δ: 7.34 (d, 4H, ArH), 7.52 (d, 2H, ArH), 7.73 (t, 4H, ArH), 7.84 (t, 1H, ArH).

Table 2
Colour fastness of polyester fiber dyed with compounds (**4a–c**, **6a–c**, **8a–c**)

Entry	o.w.f (%)	Whiteness	Entry	o.w.f (%)	Whiteness	Entry	o.w.f (%)	Whiteness
4a	0.05	98.02	**6a**	0.05	110.93	**8a**	0.05	120.62
	0.1	101.92		0.1	121.32		0.1	127.12
	0.3	101.46		0.3	127.84		0.3	136.11
	0.5	101.21		0.5	130.06		0.5	137.35
	1	94.65		1	124.40		1	130.67
4b	0.05	70.91	**6b**	0.05	77.53	**8b**	0.05	77.21
	0.1	70.75		0.1	77.27		0.1	79.35
	0.3	63.83		0.3	74.11		0.3	82.82
	0.5	60.64		0.5	68.98		0.5	83.47
	1	54.82		1	63.80		1	86.25
4c	0.05	90.99	**6c**	0.05	96.23	**8c**	0.05	99.71
	0.1	92.75		0.1	99.16		0.1	103.01
	0.3	97.52		0.3	97.19		0.3	91.10
	0.5	96.73		0.5	93.71		0.5	88.97
	1	94.05		1	97.11		1	78.72

Table 3
Various fastnesses of polyester fiber dyed with compounds (**4a–c**, **6a–c**, **8a–c**)

Compound	Washing fastness	Chlorinated water fastness	Light fastness	Rubbing fastness	
				Dry	Wet
4a	5	3	5	4–5	5
4b	4–5	3–4	5	4–5	4–5
4c	4–5	3–4	5	4–5	4–5
6a	4–5	3–4	5–6	4	5
6b	4	4	5	4–5	5
6c	4–5	4	5–6	4–5	4–5
8a	4–5	3	5–6	4	4–5
8b	4–5	3	5	4–5	5
8c	4–5	3–4	5	4–5	5

*4.2.5. Synthesis of 2,5-di(6-nitrobenzoxazol-2-yl)pyridine (**6b**)*

Yields 94%; yellow solid; ^{1}H NMR (DMSO-d_6) δ: 7.45 (d, 2H, ArH), 7.51 (d, 2H, ArH), 7.83 (t, 1H, ArH), 8.15 (s, 2H, ArH), 8.44 (d, 2H, ArH).

*4.2.6. Synthesis of 2,5-di(6-methylbenzoxazol-2-yl)pyridine (**6c**)*

Yields 94%; yellow solid; ^{1}H NMR (DMSO-d_6) δ: 2.45 (s, 6H, ArH), 7.10 (d, 2H, ArH), 7.45 (s, 2H, ArH), 7.55 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.85 (t, 1H, ArH).

*4.2.7. Synthesis of 1,4-di(benzoxazol-2-yl)naphthalene (**8a**)*

Yields 90%; yellow solid; ^{1}H NMR (DMSO-d_6) δ: 7.33 (t, 2H, ArH), 7.38 (d, 4H, ArH), 7.61 (d, 2H, ArH), 7.72 (t, 4H, ArH), 8.55 (d, 2H, ArH).

*4.2.8. Synthesis of 1,4-bis(6-nitrobenzoxazol-2-yl) naphthalene (**8b**)*

Yields 93%; yellow solid; ^{1}H NMR (DMSO-d_6) δ: 7.32 (t, 2H, ArH), 7.53 (d, 2H, ArH), 7.61 (d, 2H, ArH), 8.18 (s, 2H, ArH), 8.42 (d, 2H, ArH), 8.55 (d, 2H, ArH).

*4.2.9. Synthesis of 1,4-bis(6-methylbenzoxazol-2-yl) naphthalene (**8c**)*

Yields 91%; white solid; ^{1}H NMR (DMSO-d_6) δ: 2.21 (s, 6H, $-CH_3$), 7.14 (d, 2H, ArH), 7.33 (t, 2H, ArH), 7.42 (s, 2H, ArH), 7.49 (d, 2H, ArH), 7.63 (d, 2H, ArH), 8.57 (d, 2H, ArH).

4.3. Dyeing properties

4.3.1. Dyeing procedure

Dyeing of polyester fiber was carried out precisely at 130 °C for 1 h. It was prepared with a paste of finely powdered dye, 0.1% *aqueous* acetic acid solution and water at 40 °C, after adding polyester fiber, the temperature was increased to 130 °C at the rate of 1 °C/min.

4.3.2. Colour fastness test

The light fastness test was assessed by using Xenon arc lamp method in accordance with ISO 105-B02. The rubbing fastness test was carried out using crock meter method in accordance with ISO 105-X12 and the wash fastness test in accordance with ISO 105-C01 and chlorinated water fastness test in accordance with KS K 0725. The results are given in Tables 2 and 3.

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