

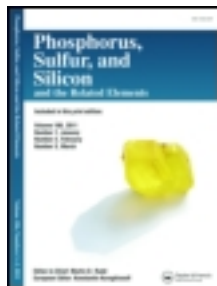
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SYNTHESIS AND APPLICATION OF 2-N-(THIAZOL-2-YL)BENZO/NAPHTHO [1,2-d]-1,2,3-TRIAZOLES

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The synthesis of a series of bright, intensely fluorescent brighteners based on 2-N-(thiazol-2-yl)benzo/naphtho[1,2-d]-1,2,3-triazoles is described. The absorption - emission spectra of the fluorescent brighteners were recorded and their dyeing properties were studied.

Keywords: Thiazol-2-yl benzo/naphtho[1,2-d]-1,2,3-triazoles; fluorescent brighteners; application; polyester fibres

INTRODUCTION

The last decade has seen a significant development and prominence in the contribution of heterocyclic compounds to the dyestuff chemistry. From the review of fluorescent compounds and 1,2,3-triazoles it has been found triazoles attached to conjugated systems seem to be well established for increasing the intensity of fluorescence. A fluorophoric heterocycle such as 1,2,3-triazole and its benzo and naphtho analogues have gained considerable attention because of their application as fluorescent brighteners, corrosion inhibitors and photo stabilizers. Many variations in the fused and pendant 1,2,3-triazoles find an important place in commercial fluorescent brighteners. During the course of our research work various fluorophoric systems based on carbocyclic and heterocyclic 1,2,3-triazoles have been

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generated to provide access to a range of fluorescent brighteners^[1-8] and few of them are illustrated in the Fig. 1.

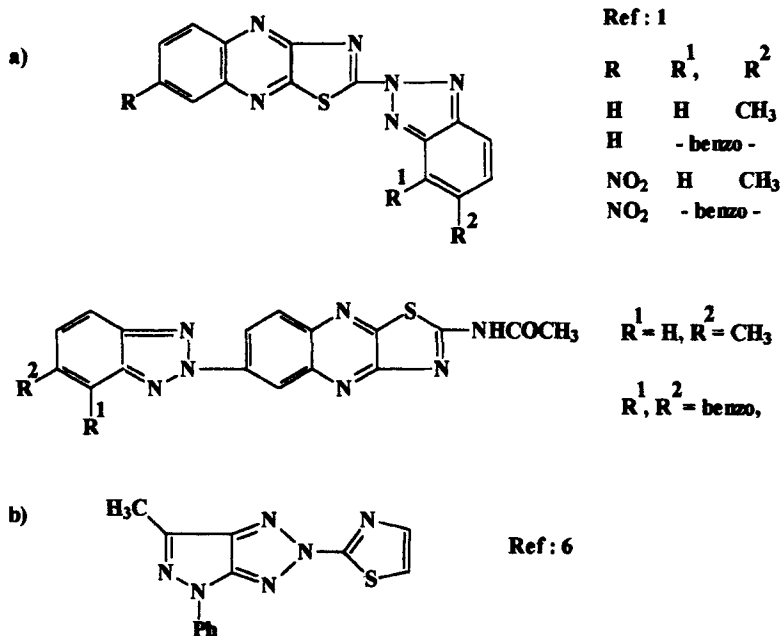


FIGURE 1

RESULTS AND DISCUSSION

In the present communication, we report the synthesis of 2-N-(thiazol-2-yl)benzo/naphtho[1,2-d]-1,2,3-triazoles **6a-6c** and **7a-7c**, and their use as moderately suitable fluorescent brighteners for the application to polyester fibres.

2-Amino-4-methyl-5-acetylthiazole^[9] (**1**) was prepared by the cyclocondensation of 3-chloro-2,4-pentane dione^[10,11] and thiourea in refluxing aqueous solution and ethyl 2-aminothiazole-4-acetic acid-5-carbonyl ester (**2**) was prepared by the cyclocondensation of diethyl acetone dicarboxylate with thiourea using iodine in refluxing ethanol. These 2-aminothiazoles (**1**) and (**2**) were diazotised and coupled with selected aromatic amines. The amines were selected in order to ensure the coupling occurred

in aryl moiety at the position ortho to the amino group. Thus, coupling with *p*-toluidine (**3a**), *p*-anisidine (**3b**), and 2-naphthylamine-1-sulfonic acid (**3c**) at 10–15°C and 6–6.5 pH yielded ortho amino arylazo dyes (**4a – 4c**) and (**5a – 5c**). Further aerial oxidation of the ortho amino arylazo dyes using copper acetate as an oxidizing agent in refluxing DMF yielded the corresponding benzo/naphtho [1,2-d]-1,2,3-triazoles (**6a – 6c**) and (**7a – 7c**). The reaction sequence is depicted in Figure 2.

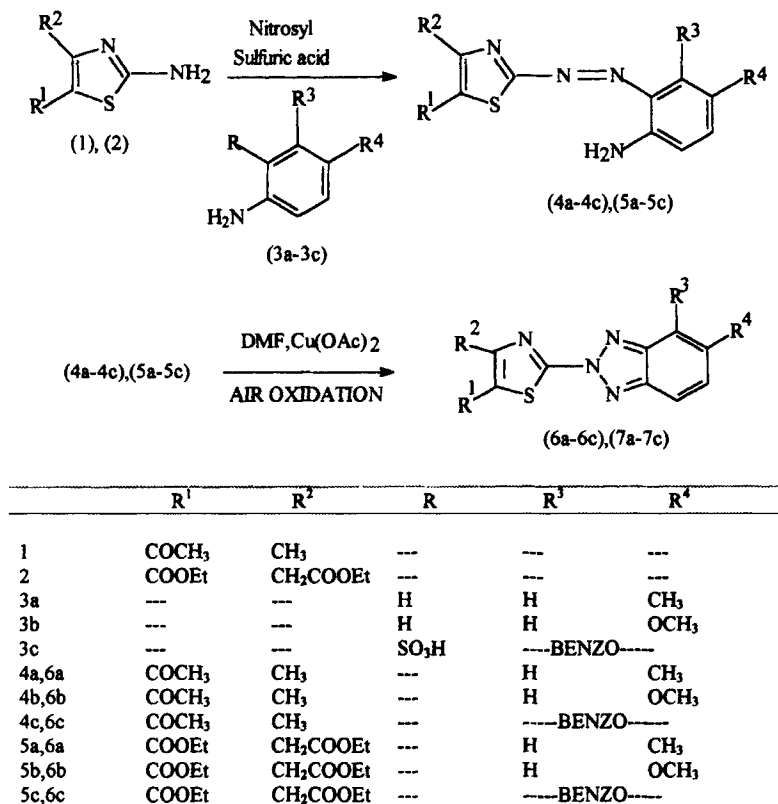


FIGURE 2

The compounds (**6a – 6c**) and (**7a – 7c**) were colorless to off white solids and they exhibited intense blue fluorescence in daylight in their DMF solutions. The absorption and emission spectra were recorded in DMF

solutions and are given in Table III. These compounds were applied on polyester fibres as fluorescent brighteners (0.1% shade).

TABLE I Physical and analytical data of 1,2,6a-6c and 7a-7c

Compd.	Yield %	<i>m.p</i> °C Solvent	Molecular Formula	Elemental analysis % (calcd. / found)			
				C	H	N	S
1	97	260 DMF	C ₆ H ₈ N ₂ OS	46.15	5.13	17.95	20.51
				46.21	4.89	17.50	19.95
2	92	122 CHCl ₃	C ₁₀ H ₁₄ N ₂ O ₄ S	46.51	5.43	10.85	12.40
				46.60	5.26	10.53	12.76
6a	72	>350 DMF-EtOH	C ₁₃ H ₁₂ N ₄ O ₂ S	57.35	4.41	20.59	11.76
				56.98	4.01	20.88	11.69
6b	66	>350 DMF-EtOH	C ₁₃ H ₁₂ N ₄ O ₂ S	54.17	4.17	19.44	11.11
				54.09	3.88	19.81	10.82
6c	68	>350 DMF-EtOH	C ₁₆ H ₁₂ N ₄ OS	62.34	3.70	18.18	10.39
				62.19	3.43	18.25	10.05
7a	58	>350 DMF-EtOH	C ₁₇ H ₁₈ N ₄ O ₄ S	54.55	4.81	14.97	8.56
				54.88	4.60	14.40	8.79
7b	65	>350 DMF-EtOH	C ₁₇ H ₁₈ N ₄ O ₅ S	52.30	4.62	14.36	8.21
				52.58	4.08	14.10	7.99
7c	63	>350 DMF	C ₂₀ H ₁₈ N ₄ O ₄ S	58.54	4.39	13.66	7.80
				58.85	4.00	13.90	7.92

TABLE II Spectral data of 1,2,6a-6c and 7a-7c

Compd	IR (Nujol) <i>cm</i> ⁻¹ Selected bands	¹ H-NMR (δ ppm) (a = DMSO-d ₆ , b = CDCl ₃)	MS (<i>m/z</i>)
1	3340, 3420 (NH ₂), 1660 (CO)	a. 2.05(s, 3H, CH ₃), 2.2 (s, 3H, COCH ₃), 7.5(s, 2H, NH ₂ , D ₂ O exchangeable)	156
2	3320, 3410 (NH ₂), 1670, 1725 (CO)	b. 1.1 – 1.58(s, 6H, 2CH ₃) 4–4.2 (m, 6H, 3CH ₂), 6.33 (m, 2H, NH ₂ , D ₂ O exchangeable)	258
6a	1680 (CO)	a. 2.2 – 2.5(m, 9H, 3CH ₃), 6.8 – 7.9 (m, 3H, arom).	272
6b	1670 (CO)	a. 2.1 – 2.6(m, 9H, 3CH ₃), 6.7 – 7.8 (m, 3H, arom)	288
6c	1675 (CO)	a. 2.2 – 2.4(m, 5H, 2CH ₃), 7.0 – 8.2 (m, 6H, arom).	---
7a	1650, 1780(CO)	a. 1.1 – 1.9(m, 9H, 3CH ₃), 4.0 – 4.8 (m, 6H, 3CH ₂), 6.8 – 7.7 (m, 3H, arom).	374
7b	1630, 1760(CO)	a. 1.2 – 2.0(m, 9H, 3CH ₃), 3.9 – 4.6 (m, 6H, 3CH ₂), 6.9 – 7.8 (m, 3H, arom)	390
7c	1660, 1740 (CO)	a. 1.1 – 1.7(m, 6H, 2CH ₃), 4.0 – 4.6 (m, 6H, 3CH ₂), 7.1 – 7.9 (m, 6H, arom)	---

TABLE III Fluorescence and dyeing data of 6a – 6c and 7a – 7c

Compd.	Fluorescence on dyed polyester fibres	Absorption max. (nm).	Emission max. (nm)	Log ϵ	Grade on polyester
6a	Weak Greenish blue	372	443	4.22	2
6b	Weak blue	369	439	4.16	2
6c	Weak blue	364	434	4.09	2
7a	Weak blue	361	438	3.96	2
7b	Weak blue	357	436	4.25	2
7c	Weak blue	368	429	4.45	2

Grades on polyester are based on standard grade 3 of 4-methyl-7,N,N-dimethyl coumarin on polyester.

4 = Excellent

3 = Good

2 = Moderate

1 = Poor

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded in Nujol mulls on a Bomem Hartmann and Braun FTIR spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on a 60 MHz Hitachi R-1200 RS-NMR spectrometer using TMS as internal standard and the chemical shifts are given in δ ppm. Mass spectra were recorded on a Varian Mat-311 instrument (70 eV). Absorption and fluorescence emission spectra in DMF solutions were recorded on a Beckmann Model – 25 spectrophotometer and Aminco Bowman spectrophotofluorimeter, respectively.

2-Amino-4-methyl-5-acetylthiazole (1)^[9] was prepared by cyclocondensation of 3-chloro-2,4-pentane dione^[10,11] and thiourea in aqueous medium and ethyl 2-amino thiazole-4-acetic acid-5-carboxy ester (2)^[12] by cyclocondensation of diethyl-1,3-acetone dicarboxylate and thiourea using iodine in refluxing ethanol. The results are given in Tables I-II.

2-N-(4,5-Disubstituted thiazole-2-yl)benzo or naphtho[1,2-d]-1,2,3-triazoles (6a – 6c) and (7a – 7c)(General Method)

2-Amino-4,5-disubstituted thiazole 1 or 2 (0.01 mol) was added in portions with stirring during 1/2 h to a cold solution of previously prepared

nitrosyl sulfuric acid by dissolving solid sodium nitrite (0.011 mol) in concentrated sulfuric acid (10 ml). The mixture was allowed to stir for 1 h at 10 – 15°C. The thick diazonium salt solution was diluted by the addition of acetic acid (15 ml) and water (5 ml). The excess nitrous acid was destroyed by the addition of urea (0.5 g). The mixture was filtered to give the clear diazonium solution.

Appropriate aromatic amines **3a** – **3c** (0.01 mol) was dissolved in acetic acid and cooled to 10–15°C. The cold diazonium salt solution was gradually run into the coupling solution in 1 h. Solid sodium acetate was added to the mixture in order to ensure the pH 6–6.5 during the coupling period. The mixture was stirred for 6 h and then neutralized. The precipitated ortho amino arylazo dye was filtered, washed with water and dried.

A mixture of ortho amino arylazo dye **4a-4c** and **5a-5c**, copper acetate (0.01 mol) and DMF (20 ml) was refluxed for 4 h. A continuous current of air was passed through the mixture to facilitate oxidation. The mixture was allowed to cool to room temperature and was poured over ice cold dilute hydrochloric acid (40ml, 5%) with constant stirring, when a crude solid of 1,2,3-triazole separated. The precipitated solid was filtered, washed with water and dried. The results are given in Tables I – II.

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