Synthesis of 2-(Alkyl and Aryl)thiazolo[4,5-*b*]quinoxaline Derivatives and Study of Their Fluorescent Properties

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Synthesis of 2-(alkyl and aryl)thiazolo[4,5-*b*]quinoxaline derivatives has been achieved by reacting 2, 3-dichloroquinoxaline derivatives with various thiocarboxylic acid amides. The resulting compounds have been studied for their fluorescent properties. Some of these compounds have been applied as fluorescent dyes on polyester fiber having fair dyeing properties.

In the recent years newer heterocyclic compounds are being synthesised and investigated as dyes and fluorescent brighteners. Quinoxaline derivatives have been described in literature as useful reactive dyes,[1] cyanine dyes,[2] azo dyes,[3] fluorescent dyes,[4,5] and pigments.[6] With the exception of a report of application of 1,4-oxazino[2,3-*b*]quinoxaline as fluorescent brighteners described,[7] there has been no investigation of quioxaline derivatives in the field of fluorescent brighteners.

We report here the synthesis of 2-(alkyl and aryl)-thiazolo[4,5-*b*]quinoxaline derivatives and the study of their fluorescent properties. The 2-(alkyl and aryl)-thiazolo[4,5-*b*]quinoxaline derivatives were synthesized by the reaction of 2,3-dichloroquinoxaline derivative with appropriate thiocarboxylic acid amides in refluxing *N*,*N*-dimethylformamide. The compounds **IIIa** and **IIIb** were obtained from thioacetamide and 4-methoxythiobenzamide, respectively. The products obtained were characterized by elemental anlyses and superimposable infrared spectra. The compound **IIIa** was further confirmed by recording its mass spectrum which showed molecular ion peak (*m*/*z*) at 201 corresponding to the molecular weight of **IIIa**. The compound **IIIb** was further confirmed by recording its ^{1}H NMR in trifluoroacetic acid: singlet at δ 3.95 (3H) corresponding to $-OCH_3$ group and multiplet δ 7.6—8.05 (4H) corresponding to all the aromatic protons.

The compounds **IIIa** and **IIIb** did not possess strong fluorescence. In order to obtain compounds which have stronger fluorescence, it was intended to prepare derivatives of **IIIa** and **IIIb** and observe the changes in the fluorescence properties. It is known that incorporation of certain groups in a given compound increases its possibility of enhancing fluorescence. An amino group in appropriate position is many a times helpful. It was, therefore, proposed to synthesise compounds with an amino group at the 7-position of the thiazolo[4,5-*b*]quinoxaline.

The 7-amino derivatives of **IIIa** and **IIIb** were prepared via its 7-nitro derivatives. The 7-nitro derivatives **IIIc** and **IIId** were prepared by reaction of 2,3-dichloro-6-nitroquinoxaline with thioacetamide and 4-methoxythiobenzamide, respectively, in refluxing *N*,*N*-dimethylformamide. The nitro derivatives were characterized by their elemental

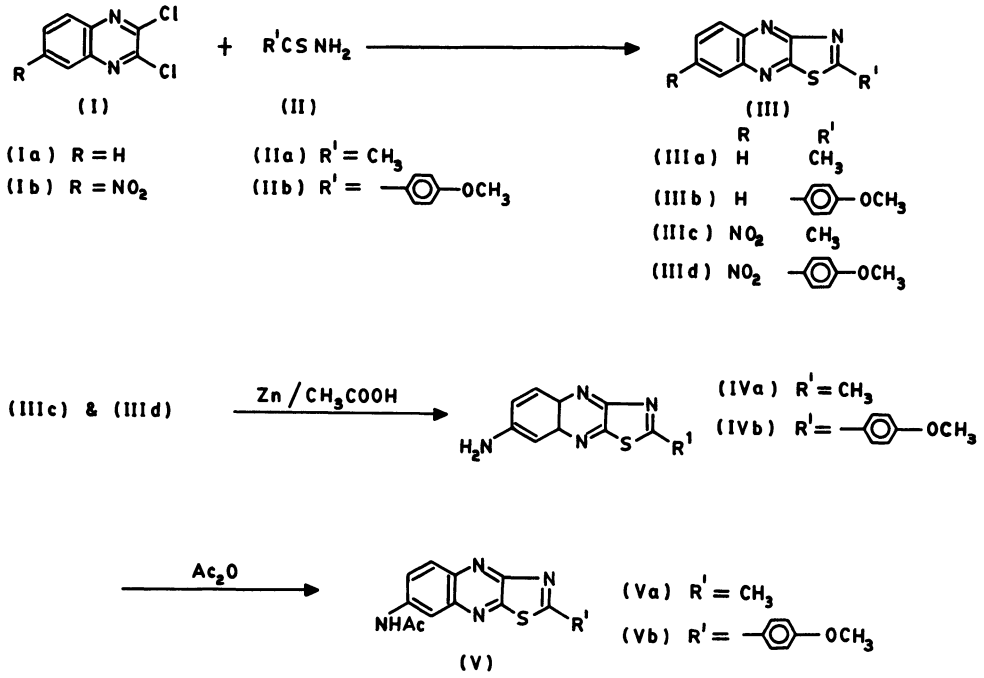

Table 1. Physical Data of 2-(Alkyl and Aryl)thiazolo[4,5-*b*]quinoxaline Derivatives

Compound No.	Yield %	Mp θ_m/°C	Recrystallization Solvent	λ_{max}/nm Absorption	log ε	λ_{max}/nm Emission	Elemental Analysis	C	H	N	S
IIIa	75	355	DMF	384	4.1535	448	Calcd	59.70	3.50	20.90	15.90
							Found	59.95	3.31	21.12	15.79
IIIb	72	357	DMF	385	4.3038	443	Calcd	65.50	3.70	14.30	10.90
							Found	65.39	3.62	14.51	10.73
IIIc	71	220—221	DMF	405	4.1703	471	Calcd	48.80	2.40	22.80	13.00
							Found	49.00	2.27	22.96	13.15
IIId	69	292	DMF	412	4.3102	469	Calcd	56.80	2.90	16.50	9.50
							Found	57.01	2.79	16.63	9.38
IVa	67	336	DMF	376	4.05	447	Calcd	55.60	3.70	25.90	14.80
							Found	55.38	3.63	25.79	14.70
IVb	65	343	DMF	380	4.2945	459	Calcd	62.30	3.90	18.20	10.40
							Found	62.57	3.78	18.06	10.23
Va	78	>360	DMF	368	4.0351	439	Calcd	51.30	4.30	23.90	13.70
							Found	51.12	4.18	23.80	13.56
Vb	73	>360	DMF	359	4.2630	442	Calcd	61.70	4.00	16.00	9.10
							Found	61.56	4.10	16.09	8.96

analyses and their superimposable infrared spectra. The nitro derivatives **IIIc** and **IIId** were subsequently reduced by zinc dust and acetic acid to yield the 7-amino derivatives **IVa** and **IVb**. The compounds **IVa** and **IVb** were characterised by their elemental analyses and infrared spectra (two peaks at 3280 and 3220 cm^{-1} corresponding to the amino group). The absorption maxima showed a shift to the lower wavelength (see Table 1). In order to shift the fluorescent towards the blue region which is desired in the case of fluorescent brighteners, the amino derivatives **IVa** and **IVb** were converted to the *N*-acetyl derivatives **Va** and **Vb** by refluxing in acetic anhydride. The compounds **Va** and **Vb** were characterized by their elemental analyses and infrared spectra (absence of two peaks corresponding to amino group, presence of a peak at 3300 cm^{-1} corresponding to -NH group, and a peak at 1720 cm^{-1} corresponding to the carbonyl group). The emission maxima of these derivatives shifted towards the blue region(see Table 1).

All the compounds synthesised in general showed fluorescence in greenish blue region (439 to 471 nm) (see Table 1). As the compounds were coloured, some of these were applied on polyester fibers as fluorescent dyes. The compounds **IIIc** dyed the fiber in orange red shade whereas **IIIb** and **Va** gave light greenish yellow and pale yellow shades with fair dyeing properties.

Experimental

All melting points are uncorrected. The IR sprctra were recorded on Perkin Elmer-397 spectrophotometer in Nujol mull. The UV and fluorescence spectra were recorded on Beckman Model-25 spectrophotometer and Aminco Bowman spectrophotofluorometer, respectively. The ^1H NMR spectra was recorded on Varian-60 MHz.

2,3-Dichloroquinoxaline,[8] 2,3-dichloro-6-nitroquinoxaline,[9] and 4-methoxythiobenzamide[10] were prepared by the methods reported.

General Procedure of Synthesising Thiazolo[4,5-*b*]-quinoxaline Derivatives (IIIa and IIIb). In a 50 ml R.B. flask were placed 2,3-dichloroquinoxaline derivatives (**Ia** and **Ib**) (0.005 mol), appropriate thiocarboxylic acid amides (**IIa** and **IIb**) (0.005 mol), and *N*,*N*-dimethylformamide (5—7 ml). The reaction mixture was refluxed till the reaction was complete (4—5 h) (checked by TLC). The reaction mixture was slowly added to ice water mixture when the product precipitated. The yield, mp, and recrystallization solvents are given in the Table 1.

General Procedure of Synthesising 7-Aminothiazolo[4,5-*b*]-quinoxaline Derivatives (IVa and IVb). In a 50 ml R.B. flask was placed 7-nitrothiazolo[4,5-*b*]quinoxaline (**IIIa** and **IIIb**) (0.005 mol). Acetic acid (10 ml) and concentrated hydrochloric acid (0.5—1 ml) were subsequently added. The reaction mixture was stirred and slowly heated so that the temperature was 80 °C. To this hot reaction mixture, zinc dust (0.006 mol) was added in portions over a period of 30—45 min. At the end of the addition the contents were refluxed (115—112 °C) under stirring for 3—4 h, till the reaction was complete (checked by TLC). The reaction mixture was then filtered hot and after cooling the filtrate was slowly added to a stirred ice-water mixture. The product was filtered, washed thoroughly with water, and dried. The yield, mp, and recrystallization solvents are given in the Table 1.

General Procedure of 7-Acetamidothiazolo[4,5-*b*]quinoxaline Derivatives (Va and Vb). The 7-aminothiazolo[4,5-*b*]-quinoxaline (**IVa** and **IVb**) (0.005 mol) was placed in a R.B. flask, and to this acetic anhydride (2—3 ml) and acetic acid (1—2 ml) were added. The reaction mixture was heated in an oil bath so that it gently refluxed. The reaction mixture was refluxed for 3—4 h till the reaction was complete (checked by TLC). On cooling the reaction mixture was slowly poured over ice-water mixtuer with continuous stirring when product precipitated. The compound was filtered, washed with water, and dried. The yield, mp, and recrystallization solvents are given in Table 1.

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