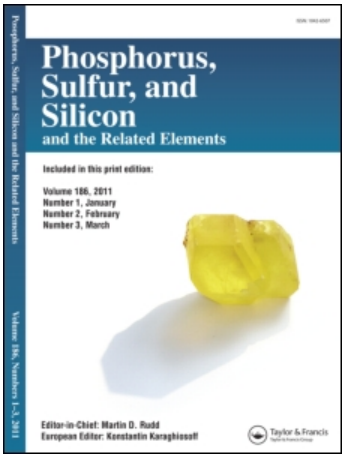

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SYNTHESIS AND APPLICATION OF 4-(COUMARIN-3-YL)-THIOPHENES

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SYNTHESIS AND APPLICATION OF 4-(COUMARIN-3-YL)-THIOPHENES

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A facile synthesis of 4-(coumarin-3-yl)thiophenes (**6a–6j**) was achieved by the condensation of ethyl 2-acetamido-3, 5-dicarbethoxythiophene-4 acetate (**4**) with selected o-hydroxyaldehydes (**5a–5j**) in the presence of piperidine. The key intermediate, ethyl 2-acetamido-3, 5-dicarbethoxythiophene-4-acetate (**4**) was synthesized by cyclocondensation of diethyl acetonedicarboxylate (**1**), sulfur and ethyl cyanoacetate (**2**) by a Gewald synthesis followed by acetylation. 4-(Coumarin-3-yl)thiophenes (**6a–6j**) were applied on polyester fibers as fluorescent disperse dyes and their fluorescence and dyeing properties were studied.

Key words: 4-(Coumarin-3-yl)thiophenes; synthesis; application; polyester fibers; fluorescent disperse dyes.

INTRODUCTION

Many novel heterocyclic compounds have been synthesized and investigated as fluorescent dyes and fluorescent brighteners in the recent past. A fluorophoric heterocycle such as coumarin pendant to another heterocycle in a suitable position finds an exceedingly important place in commercial dyes illustrated in the patent literature.[1–3] Compounds with coumarin ring systems attract special attention on account of their wide application in the field of biomedicine.[4] We have recently reported the synthesis of novel heterocyclic dyes and fluorescent brighteners such as quinoxalines,[5–6] coumarins,[7] and benzo(b)thiophenes[8–10] and study of their biomedical and textile applications. The versatility of thiophenes in the dyestuff field[11–13] was demonstrated by us. The results of this study have encouraged us to explore the utility of thiophenes in developing a variety of fluorescent heterocyclic compounds. Several current reports[14,15] describe the synthesis and technical importance of thiophene dyes. Thiophene moieties have been extensively studied in the field of medicine[16] and fungicides.[17]

RESULTS AND DISCUSSION

In this communication, we wish to report a facile synthesis of a few hitherto unknown 4-(coumarin-3-yl)-thiophenes (**6a–6j**) by a novel method and their use as fluorescent disperse dyes on polyester fibers. The dyes derived from a thiophene moiety offer many advantages such as a color deepening effect as an intrinsic

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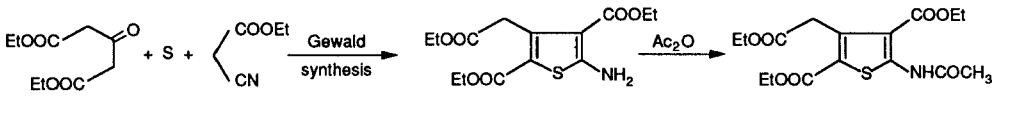
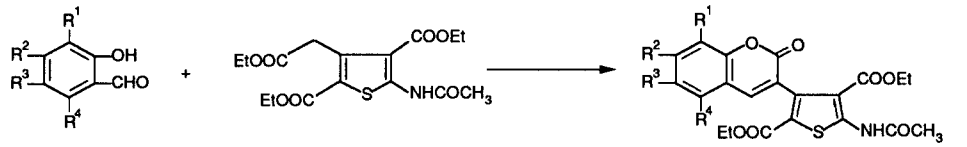
property of the thiophene ring, small molecular structure leading to better dyeability and heterocyclic nature of the thiophene ring resulting in good sublimation fastness of the dyed fibers. Presence of an electron withdrawing group such as carbethoxy at the 3- and 5-position of thiophene nucleus results in deepening of dye hues on polyester fibers.

The object of present study was the synthesis of novel, fluorescent heterocycles. It was therefore planned to develop a fluorophore such as coumarin pendant to a thiophene nucleus at the 4-position by a simple method and study of the fluorescent properties of various (coumarin-3-yl)-thiophenes. The cyclocondensation reaction of diethyl acetone dicarboxylate (**1**), sulfur and ethyl cyanoacetate (**2**) in the presence of base following Gewald synthesis[18] resulted in ethyl 2-amino-3,5-dicarbethoxythiophene-4-acetate (**3**).[12] Ethyl 2-acetamido-3,5-dicarbethoxythiophene-4-acetate (**4**) a versatile key intermediate in the synthesis of various heterocyclic systems, was synthesized by acetylation of (**3**). In connection with our interest to study fluorescent properties of (**6a–6j**), we have devised a route for the efficient synthesis of (**6a–6j**). The sequence involved in the present synthesis consists of the condensation of (**4**) with selected o-hydroxyaldehydes (**5a–5j**) in refluxing N,N-di-



(1) (2) (3) (4)



(5a - 5j) (4) (6a - 6j)

(5,6)	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	OH	H	H
c	H	H	OH	H
d	H	OCH_3	H	H
e	H	H	OCH_3	H
f	H	H	Cl	H
g	H	H	NO_2	H
h	OCH_3	H	NO_2	H
i	H	OCH_3	H	OCH_3
j	H	NEt_2	H	H

methylformamide under strictly anhydrous conditions using piperidine as condensing agent.

The compounds (**6a–6j**) were yellow to red and they exhibited intense bluish-green fluorescence in daylight in most organic solvents. The absorption and emission maxima of (**6a–6j**) were recorded in DMF solution and are given in Table III. The absorption and emission maxima of (**6a–6j**) were in the range of 371–396 nm and 506–524 nm respectively. These compounds (**6a–6j**) were applied on polyester fibers as fluorescent disperse dyes (1% shade). Volume (100 ml) of dispersion corresponding to 1% shade of a dye (1 g) was based on the weight of the fabric (2 g) taken. The hues of the dyed polyester fibers were yellow, orange and red. Their promising fluorescence and dyeing properties are given in Table III.

EXPERIMENTAL

All the melting points are uncorrected. IR spectra were recorded in Nujol mulls on a Perkin Elmer Model-397 spectrophotometer. ^{1}H-NMR spectra were recorded on a varian-670 MHz instrument EM-

TABLE I

Physical data of **4** and **6a–6j**

Compd.	Yield %	m.p.°C Solvent	Molecular formula	Elemental analysis % (calcd./found) C	H	Cl	N	S
4	77	154-5 EtOH	$C_{16}H_{21}NO_7S$	51.75 51.71	5.66 5.62		3.77 3.74	8.62 8.60
6a	72	129 EtOH	$C_{21}H_{19}NO_7S$	58.74 58.70	4.42 4.45		3.26 3.21	7.45 7.42
6b	76	149 EtOAc	$C_{21}H_{19}NO_8S$	56.62 56.64	4.26 4.21		3.14 3.13	7.19 7.14
6c	73	163-4 EtOAc	$C_{21}H_{19}NO_8S$	56.62 56.60	4.26 4.23		3.14 3.11	7.19 7.16
6d	68	279 DMF	$C_{22}H_{21}NO_8S$	57.51 57.52	4.57 4.53		3.05 3.02	6.97 6.93
6e	64	166 DMF	$C_{22}H_{21}NO_8S$	57.51 57.50	4.57 4.52		3.05 3.09	6.97 6.99
6f	79	287-8 DMF	$C_{21}H_{18}ClNO_7S$	54.42 54.46	3.88 3.84	7.55 7.53	3.02 3.06	6.91 6.88
6g	66	291 DMF	$C_{21}H_{18}N_2O_9S$	53.16 53.13	3.79 3.77		5.90 5.93	6.75 6.72
6h	68	329 DMF	$C_{22}H_{20}N_2O_{10}S$	58.32 58.29	3.96 3.92		5.55 5.51	6.34 6.30
6i	78	284-5 DMF	$C_{23}H_{23}NO_9S$	56.44 56.41	4.70 4.72		2.86 2.83	6.54 6.51
6j	83	>360 DMF	$C_{25}H_{28}N_2O_7S$	60.00 60.03	5.60 5.18		5.60 5.32	6.40 6.27

TABLE II

Spectral data of **4** and **6a–6j**

Compd.	IR(nujol) cm-1 Selected bands	^{1}H-NMR(DMSO-d_6-TMS)(δ)	MS (m/z)
4	3380(NH),1680(CO) 1720(COOEt),1675(CH_2COOEt)	7.23(s,1H,NH),2.26(s,3H,CH_3),1.32(t,9H,3CH_3) 3.5-4.8(m,8H,4CH_2)	371
6a	3385(NH),1680(CO) 1720(COOEt),1705(CO)	7.23(s,1H,NH),2.27(s,3H,CH_3),1.36(t,6H,2CH_3) 4.1-4.5(m,4H,2CH_2),7.31-7.55(m,5H,arom.)	429
6b	3330(NH),1685(CO),1050(OH) 1720(COOEt),1710(CO),3450(OH)	7.27(s,1H,NH),2.22(s,3H,CH_3),1.39(t,3H,2CH_3) 4.0-4.45(m,4H,2CH_2),7.4-7.8(m,4H,arom),11.5(s,1H,OH)	445
6c	3340(NH),1680(CO),1050(OH) 1720(COOEt),1705(CO),3400(OH)	7.24(s,1H,NH),2.25(s,3H,CH_3),1.28(t,6H,2CH_3) 4.0-4.55(m,4H,2CH_2),7.4-7.9(m,4H,arom),11.4(s,1H,OH)	445
6d	3370(NH),1685(CO),1250(OCH_3) 1725(COOEt),1700(CO)	7.30(s,1H,NH),2.23(s,3H,CH_3),1.36(t,6H,2CH_3) 4.1-4.6(m,4H,2CH_2),7.4-7.6(m,4H,arom),3.95(s,3H,OCH_3)	459
6e	3380(NH),1680(CO),1260(OCH_3) 1720(COOEt),1710(CO)	7.25(s,1H,NH),2.26(s,3H,CH_3),1.34(t,3H,2CH_3) 4.21-4.5(m,4H,2CH_2)7.3-7.6(m,4H,arom),3.95(s,3H,OCH_3)	459
6f	3350(NH),1685(CO) 1730(COOEt),1705(CO)	7.31(s,1H,NH),2.25(s,3H,CH_3),1.39(t,6H,2CH_3) 4.1-4.4(m,4H,2CH_2),7.4-7.7(m,4H,arom)	463
6g	3380(NH),1680(CO),1350,1570(NO_2) 1725(COOEt),1710(CO)	7.22(s,1H,NH),2.27(s,3H,CH_3),1.37(t,6H,2CH_3) 4.2-4.7(m,4H,2CH_2),7.35-7.8(m,4H,arom)	474
6h	3380(NH),1685(CO),1340,1550(NO_2) 1720(COOEt),1705(CO),1250(OCH_3)	7.23(s,1H,NH),2.28(s,3H,CH_3),1.34(t,6H,2CH_3) 4.1-4.4(m,4H,2CH_2),7.3-7.7(m,3H,arom),4.0(s,3H,OCH_3)	504
6i	3370(NH),1680(CO),1260(OCH_3) 1725(COOEt),1710(CO)	7.26(s,1H,NH),2.29(s,3H,CH_3),1.37(t,6H,2CH_3) 4.2-4.5(m,4H,2CH_2)7.35-7.7(m,3H,arom)4.1(s,6H,2OCH_3)	489
6j	3380(NH),1680(CO) 1720(COOEt),1705(CO)	7.23(s,1H,NH),2.30(s,3H,CH_3)1.1-1.5(m,12H,4CH_3) 3.8-4.7(m,8H,4CH_2),7.4-7.9(m,4H,arom)	500

TABLE III

Fluorescence and dyeing data of **6a–6j**

Compd.	Color on dyed polyester fibre	Absorption max.(nm)	Emission max.(nm)	logϵ	Pick-up	Light fastness	Sublimation fastness
6a	Yellow	374	510	4.42	2	4	3
6b	Yellow	371	506	4.29	3	3	4
6c	Yellow	373	509	4.31	3	3	3
6d	Orange	385	517	4.54	3	4	4
6e	Orange	382	514	4.51	3	4	4
6f	Orange red	389	519	4.58	4	5	5
6g	Yellow	377	511	4.49	3	3	3
6h	Yellow	382	514	4.52	3	3	3
6i	Orange red	386	516	4.56	3	5	5
6j	Red	396	524	4.63	4	5	5

Pick-up: Pick-up values are based on standard depths.
5 = 1 Standard depth (commercial)
4 = ½ Standard depth (commercial)
3 = ¼ Standard depth (commercial)
2 = ⅛ Standard depth (commercial)
1 = 1/12 Standard depth (commercial)

Light fastness:
8 = Outstanding
7 = Excellent
6 = Very good
5 = Good
4 = Fairly good
3 = Fair
2 = Poor
1 = Very poor

Sublimation fastness:
5 = Excellent
4 = Good
3 = Fair
2 = Poor
1 = Very poor

360-L using TMS as internal standard and the chemical shifts are given in δ ppm. Mass spectra were recorded on a Varian Mat-311 instrument (70eV). Absorption and fluorescence emission spectra in DMF solution were recorded on a Beckman Model-25 spectrophotometer and Aminco Bowman spectrophotofluorimeter, respectively.

Ethyl 2-amino-3,5-dicarbethoxythiophene-4-acetate (**3**) was prepared[12] following the visual procedure for a Gewald synthesis.[18]

Ethyl 2-acetamido-3,5-dicarbethoxythiophene-4-acetate (**4**). A mixture of ethyl 2-amino-3,5-dicarbethoxythiophene-4-acetate **3** (0.01 mole) and an excess of acetic anhydride (10 ml) was refluxed for 1 hr. The reaction mixture was then cooled to room temperature; shiny white product separated. It was separated by filtration and dried. The results are given in Tables I and II.

2-Acetamido-3,5-dicarbethoxy-4-(coumarin-3-yl)thiophenes (**6a–6j**) (*General method*): A mixture of ethyl 2-acetamido-3,5-dicarbethoxythiophene-4-acetate **4** (0.01 mole), o-hydroxyaldehyde **5a–5j** (0.01

mole), piperidine (1 ml) and N,N-dimethylformamide (10 ml) was refluxed for 5 hrs. The reaction mixture was then cooled to room temperature and poured over crushed ice (100 gm); product precipitated. It was separated by filtration, washed with water and dried. The results are given in Tables I–III.

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