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Synthesis of Fluorescent 2,3-Fused Coumarin Derivatives

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ABSTRACT

7-Diethylamino-3-substituted coumarin-2-imine derivatives are utilised in the synthesis of a new range of fluorescent coumarin derivatives. The coumarin derivatives were applied to polyester and their properties evaluated. Visible absorption–emission characteristics of the compounds were studied.

1 INTRODUCTION

Fluorescent coumarin dyes for polyester ranging from orange to violet shades and obtained by reactions of coumarin-2-imine derivatives have been reported.[1-4] Cyanation of these derivatives to give deeper shades has been reported by Moeckli.[5]

We report here studies on the reactivity of the imino function of 7-diethylamino-3-substituted coumarin-2-imine derivatives when it is flanked by a suitably substituted group at the 3-position. We expected to obtain the 2,3-fused coumarin derivative by reacting the coumarin-2-imine derivatives with appropriate reactants. The heterocyclisation across the 2- and 3-positions was carried out with the intention of obtaining coumarin derivatives with enhanced fluorescence and better dyeing properties.

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TABLE 1

Physical and Spectral Data of 2,3-Fused Coumarin Derivatives

Compd	Molecular formula[a]	M.p.[b] (°C)	Yield (%)	Visible spectra data (MeOH)			IR data ν (cm^{-1})	PMR spectral data	
				Absorption λ_{max} (nm)	log e	Emission λ_{max} (nm)		Solvent	δ (ppm)
4c	$C_{28}H_{22}N_5O_2$	229(a)	60	420	4·5	—	(NH_2) 3 340 (CO) 1 680	CF_3COOH	1·48 (t, 6H, —$N(CH_3)_2$); 4·08 (q, 4H, —$N(CH_2)_2$); 7·7–8·5 (m, 7H, aromatic protons at 6-, 8-, 9-positions and four benzimidazolyl protons); 9·4 (s, 1H, 10-position proton)
4d	$C_{22}H_{20}N_4O_4$	255(a)	65	450	4·2	—	(NH_2) 3 340 (CO) 1 680	CF_3COOH	1·48 (t, 6H, —$N(CH_3)_2$); 4·08 (q, 4H, —$N(CH_2)_2$); 7·7–7·9 (m, 2H, protons *ortho* to —$N(Et)_2$); 7·9–8·38 (m, 3H, protons *meta* to —NO_2 and 9-position proton); 8·48 (d, 2H, protons *ortho* to —NO_2); 8·5 (s, 1H, 10-position proton)
5a	$C_{17}H_{17}N_3O_4$	218(b)	70	430	4·1	—	(NH) 3 340 (CO) 1 690	$CDCl_3$ DMSO-d_6	1·28 (t, 6H, —$N(CH_3)_2$); 4·08 (q, 4H, —$N(CH_2)_2$); 6·3–8·1 (m, 5H, one NH and four aromatic protons)
5e	$C_{18}H_{18}N_2O_4$	230(b)	35	425	4·2	—	(CO) 1 680 1 690	CF_3COOH	1·58 (t, 6H, —$N(CH_3)_2$); 3·08 (s, 3H, —$COCH_3$); 4·08 (q, 4H, —$N(CH_2)_2$); 7·6–8·2 (m, 3H, protons at 6-, 8-, 9-positions; 9·0 (s, 1H, proton at 10-position)

5f	$C_{21}H_{22}N_2O_6$	224(b)	30	425	4·0	—	(CO) 1 680 1 690	CF_3COOH	1·28 (m, 9H, —$N(CH_3)_2$ and —$COOCH_3$); 3·6 (q, 4H, —$N(CH_2)_2$); 4·3 (d, 2H, —$COOCH_2$); 7·8 (d, 2H, 6/8-position proton); 8·1 (d, 1H, 5-position proton); 8·9 (s, 1H, 10-position proton)
7a	$C_{14}H_{16}N_3O_3PS$	278(c)	45	410	3·9	430	(CO) 1 680		—
7b	$C_{20}H_{20}N_3O_3PS$	290(c)	40	440	3·8	476	(CO) 1 680	$CDCl_3$	1·28 (t, 6H, —$N(CH_3)_2$); 3·4 (q, 4H, —$N(CH_2)_2$); 7·0 (d, 2H, *ortho* to $N(Et)_2$); 7·2–7·8 (m, 6H, five aromatic and 6-position proton); 8·4 (s, 1H, at 5-position); 10·4 (s, 1H, —OH proton) (D_2O exchangeable)
9a	$C_{29}H_{32}N_5O$	266(d)	70	428	5·0	506	—	$CDCl_3$	1·2 (t, 6H, —$N(CH_3)_2$); 2·8 (s, 6H, —$N(CH_2)_2$); 3·2 (q, 4H, —$N(CH_2)_2$); 6·7 (d, 2H, *ortho* to $N(Et)_2$); 6·9–7·4 (m, 9H, aromatic protons); 8·1 (s, 1H, 6-position proton)
9b	$C_{28}H_{28}N_4O_2$	260(d)	78	438	4·8	512	—	$CDCl_3$	1·2 (t, 6H, —$N(CH_3)_2$); 3·2 (q, 4H, —$N(CH_2)_2$); 3·8 (s, 3H, —OCH_3); 6·9 (d, 2H, 2- and 4-position protons); 6·9–7·3 (m, 9H, aromatic protons); 8·1 (s, 1H, 6-position proton)
10	$C_{20}H_{19}N_4O_2PS$	305(c)	55	460	4·0	526	—	$CDCl_3$	1·2 (t, 6H, —$N(CH_3)_2$); 3·5 (q, 4H, —$N(CH_2)_2$); 6·9 (d, 2H, 2- and 4-position protons); 7·1–7·9 (m, 5H, benzimidazole protons and 1H at 5-position); 11·2 (s, 1H, —OH, exchanged with D_2O)

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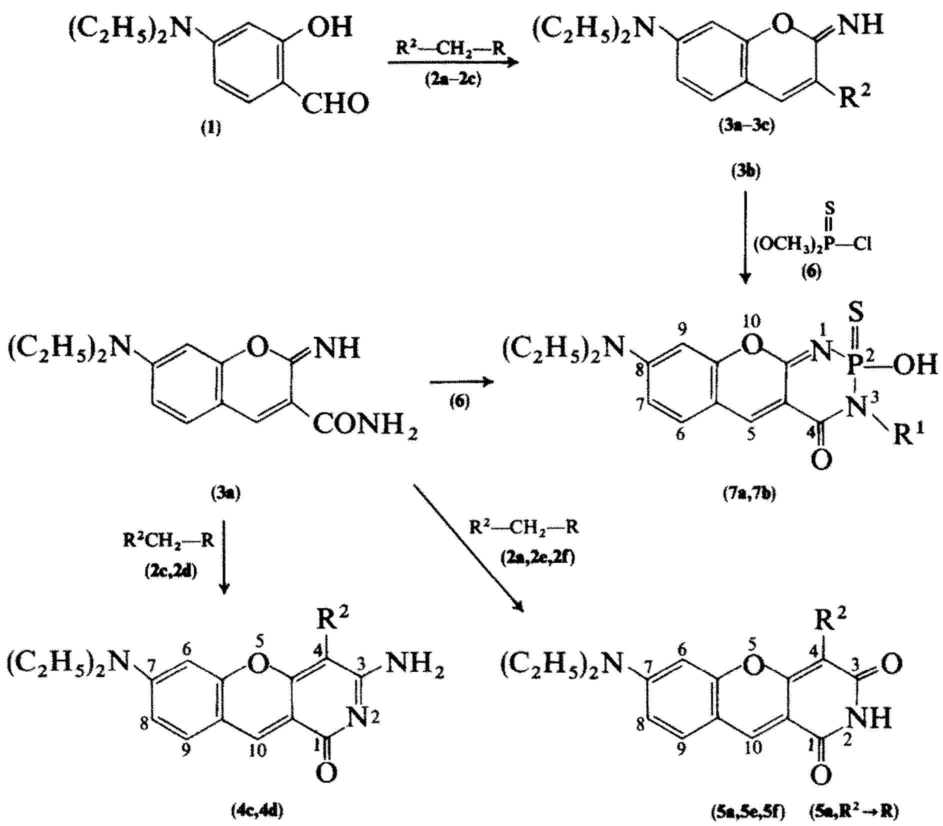
[a] All compounds showed satisfactory elemental analysis ±0·3%.

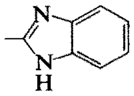
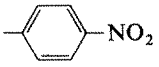
[b] Solvent of crystallisation: (a) chlorobenzene; (b) ethanol/dimethylformamide; (c) dimethylformamide; (d) ethanol.

2 RESULTS AND DISCUSSION

Reaction of the 3-carboxamide derivative **3a** with *p*-nitrobenzyl cyanide (**2d**) and with benzimidazo-2-acetonitrile (**2c**) gave bright orange and yellow compounds respectively. These compounds gave bright shades on polyester but suffered from poor lightfastness. The physical and spectral data of these derivatives are given in Table 1.

The above reaction was extended to the synthesis of a new series of 2,3-fused diones based on the coumarin system (Scheme 1). Reacting **3a** with

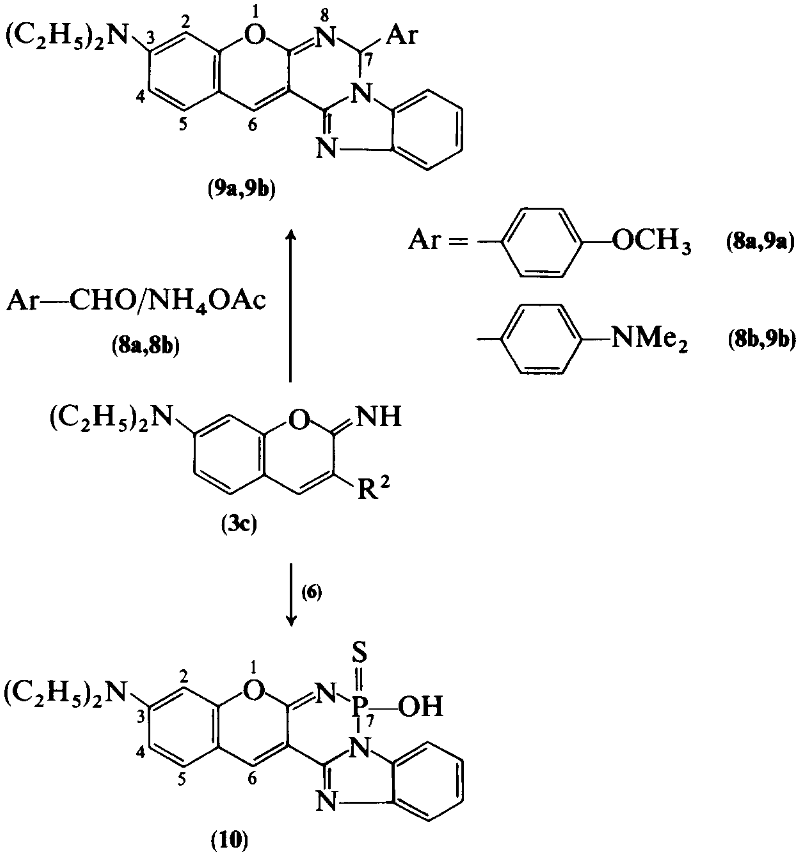


	a	b	c	d	e	f
R^2	$CONHR^1$	$CONHR^1$			$COCH_3$	$COCH_2COOC_2H_5$
R^1	H	Ph				
R	CN	CN	CN	CN	$COOC_2H_5$	$COOC_2H_5$

Scheme 1

esters such as ethyl acetoacetate (**2e**), diethylacetone dicarboxylate (**2f**) and with amides such as cyanoacetamide (**2a**) afforded compounds **5a**, **5e** and **5f**, the physical and spectral data of which are given in Table 1. Whilst **5e** and **5f** dyed polyester in weak shades, the product **5a** from cyanoacetamide gave bright yellow shades on polyester but had poor pick-up value.

Recent reports of fluorescent coumarin dyes containing a phosphorus atom in the ring[6] prompted us to investigate the possibilities of synthesising fused coumarin derivatives containing a phosphorus atom from 7-diethylamino-3-substituted coumarin-2-imine derivatives (**3a**–**3c**). The coumarin-2-imine derivatives **3a** and **3b** were reacted with dimethyl phosphorothiochloridate (**6**) to give the diazaphosphorino derivatives (**7a, 7b**). These derivatives were characterised by elemental analysis, IR and PMR spectra and visible absorption–emission spectral data which are given in Table 1. These compounds gave yellow shades on polyester with average tinctorial power but suffered from poor lightfastness.



Scheme 2

TABLE 2
Evaluation of Dyeings

Compd	*P.U.*[a]	*Xeno*[a]	*Thermo*[a]	*Shade on polyester*
4c	3	1	4	Yellow
4d	3	2	3	Bright orange
5a	1	2	2	Bright yellow
5e	2	2	2	Yellowish orange
5f	2	2	2	Cream
7a	2	2	3	Yellow
7b	1	2	3	Yellow
9a	4	3	4	Greenish yellow
9b	4	3	3	Greenish yellow
10	4	3	2	Yellowish orange

[a] Abbreviations: P.U., pick up; Xeno, lightfastness; Thermo, sublimation fastness.

7-Diethylamino-3-benzimidazolyl coumarin-2-imine (**3c**) also offered scope for a heterocyclisation reaction because of the suitably positioned imino —NH and benzimidazolyl —NH (Scheme 2). Reaction of **3c** with aromatic aldehydes (**8a, 8b**) in ethanol and ammonium acetate yielded the pyrimido(1,6-*a*)-benzimidazoles **9a** and **9b** respectively. These compounds were highly fluorescent and gave bright yellow shades on polyester with good lightfastness and tinctorial power.

Reactions of **3c** with dimethyl phosphorothiochloridate (**6**) yielded the diazaphosphorino derivative **10**, which had an intense green fluorescence in daylight and dyed polyester a bright yellowish orange shade with average tinctorial power but poor lightfastness.

It was apparent that in the case of compounds **9a**, **9b** and **10** rigidisation of the coumarin system by involving the benzimidazolyl —NH in the reaction yielded intensely fluorescent compounds.

The physical and spectral data of these derivatives are given in Table 1. Table 2 gives the dyeing evaluation data of all the fused coumarin derivatives.

3 EXPERIMENTAL PROCEDURES

All melting points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 397 spectrophotometer from Nujol mull, visible absorption spectra on a Kontron spectrophotometer and fluorescence spectra on a Aminco–Bowman spectrophotofluorimeter. The PMR spectra were recorded on a Varian EM-360L spectrophotometer using TMS as external standard and mass spectra were recorded on a Varian CH7 spectrometer.

Benzimidazo-2-acetonitrile (**2c**),[7] *p*-nitrobenzyl cyanide (**2d**),[8] cyanoacetamide (**2a**),[9] cyanoacetanilide (**2b**)[10] and 4-diethylaminosalicylaldehyde (**1**)[11] were prepared according to known methods. Commercial samples of ethyl acetoacetate (**2e**) and diethylacetone dicarboxylate (**2f**) were used.

3.1 General method for the preparation of 7-diethylamino-3-substituted coumarin-2-imine derivatives (3a–3c)

A mixture of 4-diethylaminosalicylaldehyde (0·01 mol) and the appropriate acetonitrile derivative **2a**–**2c** (0·01 mol) was refluxed in ethanol (20·0 ml) in the presence of piperidine as catalyst for 2 h. The solid product which deposited was filtered, washed with ethanol and dried. The compounds were recrystallised from dimethylformamide.

3a:	M.p. = 202°C	Lit.[12] m.p. = 202°C	Yield = 85%
3b:	M.p. = 215°C	Lit.[12] m.p. = 215°C	Yield = 65%
3c:	M.p. = 239°C	Lit.[13] m.p. = 239°C	Yield = 65%

3.2 General method for the preparation of compounds 4c, 4d

*Preparation of 3-amino-7-diethylamino-4-(*p*-nitrophenyl)-1*H*-[1]benzopyrano-[3,2-c] pyridin-1-one (**4d**) and 3-amino-4-(2-benzimidazolyl)-7-diethylamino-1*H*-[1]benzopyrano[3,2-*c*]pyridin-1-one (**4c**)*

A mixture of the coumarin derivative **3a** (0·005 mol) and the appropriate acetonitrile derivative (**2c, 2d**) (0·005 mol) was refluxed in dimethylformamide (10 ml) in the presence of piperidine as catalyst for 3 h. The solid product which separated out was filtered, washed with ethanol and dried. The compounds were recrystallised from dimethylformamide.

Yields, melting points and absorption–emission and PMR spectral data are given in Table 1.

3.3 General method for the preparation of compounds 5a, 5e, 5f

*Preparation of 4-acetyl-7-(diethylamino)-1*H*-[1]benzopyrano[3,2-*c*]pyridine-1,3-2*H*-dione (**5e**); ethyl-7-diethylamino-2,3-dihydro-1,3-dioxo-1*H*-[1]benzopyrano[3,2-*c*]pyridine-4-propionate (**5f**) and 7-diethylamino-2,3-dihydro-1,3-dioxo-1*H*-[1]benzopyrano[3,2-*c*]pyridine-4-carbpnitrile (**5a**)*

A mixture of 7-diethylamino-3-carboxamidocoumarin-2-imine **3a** (0·01 mol) and the appropriate ester (**2e, 2f**) or the amide (**2a**) (0·01 mol) was refluxed in dimethylformamide (5 ml) in the presence of piperidine as catalyst for 4 h. The solid which separated on addition of ethanol (20 ml) was filtered, washed with ethanol and dried. The compounds were recrystallised from ethanol/dimethylformamide (50:50).

The yields, melting points, absorption–emission data and PMR spectral data are given in Table 1.

3.4 General method for the preparation of the diazaphosphorino derivatives (7a, 7b)

*Preparation of 8-diethylamino-2,3-dihydro-2-hydroxy-4*H*-[1]benzopyrano[2,3-*d*]1,3,2-diazaphosphorin-4-one 2-sulphide (**7a**) and 8-diethylamino-2,3-dihydro-2-hydroxy-3-phenyl-4*H*-[1]benzopyrano[2,3-*d*]1,3,2-diazaphosphorin-4-one 2 sulphur (**7b**)*

A mixture of the appropriate coumarin-2-imine derivative (**3a, 3b**) (0·001 mol) and dimethyl phosphorothiochloridate (**6**) (0·001 mol) was refluxed in dimethylformamide/ethanol (4:1, 10 ml) in the presence of pyridine (0·001 mol) for 4 h. The product which separated was filtered, washed with dilute sodium sulphite solution and dried. The compounds were recrystallised from dimethylformamide/ethanol mixture (70:30).

The yields, melting points, absorption–emission spectral data and PMR spectral data are given in Table 1.

3.5 General method for the preparation of pyrimido(1,6-*a*)benzimidazole derivatives (9a, 9b)

*Preparation of 3-diethylamino-7-(*p*-dimethylaminophenyl)-7*H*-[1]benzopyrano-(2,3:4,5)pyrimido[1,6-*a*]benzimidazole (**9a**) and 3-diethylamino-7-(*p*-anisyl)-7*H*-[1]benzopyrano(2,3:4,5)pyrimido[1,6-*a*]benzimidazole (**9b**)*

A mixture of 7-diethylamino-3-benzimidazolyl coumarin-2-imine, **3c** (0·009 mol), the appropriate aldehyde (**8a, 8b**) (0·009 mol), and ammonium acetate (0·027 mol) was refluxed in ethanol (1 g/6 ml) for 4 h. On cooling, the yellow solid was filtered, washed with ethanol and recrystallised from ethanol. The yields, melting points, visible absorption–emission data and PMR spectral data are given in Table 1.

3.6 Preparation of 3-diethylamino-7-hydroxy-7*H*-[1]benzopyrano-[2′,3′,4,5]diazaphosphorino[1,6-*a*]benzimidazole 7-sulphide (10)

A mixture of 3-benzimidazolyl derivative **3c** (0·001 mol) and dimethyl phosphorothiochloridate (**6**) (0·001 mol) was heated in dimethylformamide (5 ml) in the presence of pyridine at 70°C for 4 h. The solid which separated on addition of alcohol (10 ml) was filtered, washed with dilute sodium sulphite solution and dried. The compound was recrystallised from dimethylformamide. Yield, melting point, visible absorption–emission data and PMR spectral data are given in Table 1.

4 CONCLUSION

The various 2,3-fused coumarin derivatives, in spite of the brilliance of their shades on polyester, did not possess good lightfastness. Further modifications of the structures are required to obtain dyes with improved dyeing properties.

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