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Synthesis and Study of 6-Arylazo Coumarin Derivatives

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ABSTRACT

Alternative routes to arylazo coumarin derivatives from 4-diethylaminosalicaldehyde are reported. A new series of styryl and azostyryl derivatives from 4-diethylamino-2-methoxybenzaldehyde is also reported. These derivatives were studied for their application properties on polyester and their fastness properties were evaluated. The visible absorption–emission characteristics of the compounds were studied.

1 INTRODUCTION

Fluorescent coumarin dyes are of interest due to their brilliance of shade and intense fluorescence. However, these dyes often show poor tinctorial power and fastness properties. Various structural modifications to obtain coumarin dyes with better application properties have been widely documented in patent literature.

The object of this present work was to study the effect of an azo chromophore on the properties of a coumarin fluorophore when the azo group is directly linked to the coumarin moiety. Since the fluorescing property of a coumarin derivative is essentially due to the presence of an *N,N*-dialkylamino group at the 7-position and an electron-withdrawing group at the 3-position, we aimed at preparing azo coumarin derivatives containing an *N,N*-dialkylamino group at the 7-position and an electron-withdrawing group at the 3-position of the coumarin ring.

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The presence of an azo function was expected to diminish the fluorescence but increase the colour value and yield dyes with better dyeing properties. Literature reports of such azo coumarin derivatives are based on 7-amino and 4-hydroxy coumarin derivatives.[1]

2 RESULTS AND DISCUSSION

Two different approaches to the arylazo coumarin derivatives starting from 4-diethylaminosalicylaldehyde (**1**) were investigated.

The first method involved the formation of 4-diethylamino-2-methoxybenzaldehyde (**2**) from 4-diethylaminosalicylaldehyde (**1**). The methoxy aldehyde derivative (**2**) was converted to the styryl derivatives (**4a–4e**) by reacting with various acetonitrile derivatives (**3a–3e**). The coupling behaviour of these styryl derivatives was studied with different aromatic diazo compounds. It was observed that only very reactive diazo compounds coupled with the styryl derivatives.

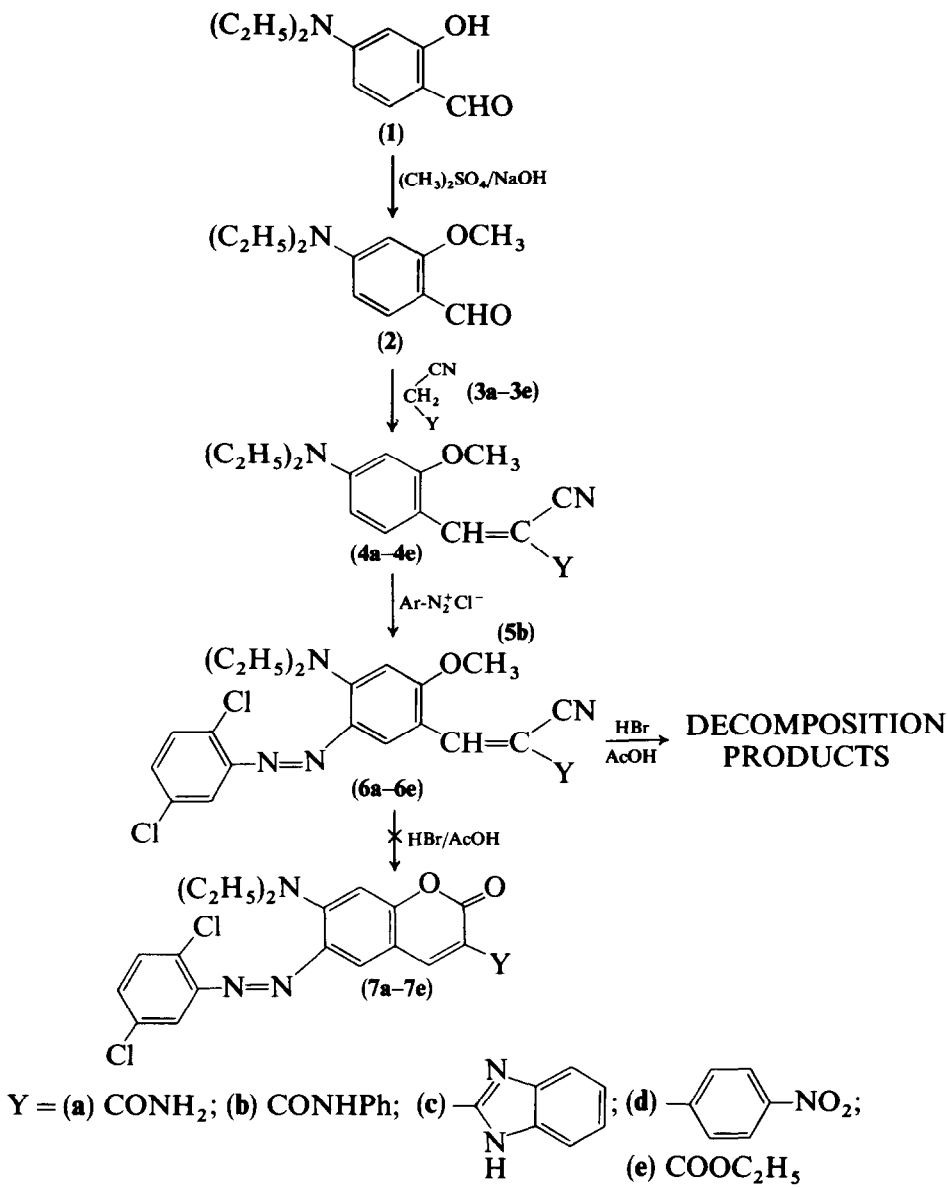
A series of azostyryl derivatives (**6a–6e**) was prepared by coupling **4a–4e** with diazotised 2,5-dichloroaniline (**5b**). The azostyryl derivatives, as well as the styryl derivatives, were characterised by elemental analysis, IR and visible absorption spectra. The physical and spectral data of the styryl and azostyryl derivatives are given in Table 1.

The dyes were applied to polyester and gave bright yellow to red shades with good tinctorial power and lightfastness. The azostyryl derivatives, however, showed average tinctorial power and lightfastness. Dyeing evaluation data are given in Table 4.

Attempts to cyclise the azostyryl derivatives with 40% hydrobromic acid in acetic acid did not yield the expected product **7**, the products isolated having no colour value. The loss in colour was attributed to cleavage of the azo function during demethylation with hydrobromic acid. Hence, attempts to synthesise arylazo coumarin derivatives through azostyryl formation failed to yield the desired products.

The next approach was through the formation of the Schiff base **8**, of 4-diethylaminosalicylaldehyde (**1**). Compound **8** was coupled with diazotised arylamines (**5a,5b**) to give the arylazo derivatives (**9a,9b**). These were reacted with acetonitrile derivatives (**3a–3e**) to give the 6-arylazo coumarin-2-imine derivatives (**10a–10f**). These compounds were characterised by elemental analysis, IR, PMR and visible absorption–emission spectral data. Physical and spectral data are given in Table 2. The dyes gave dull shades on polyester with average lightfastness and poor tinctorial power. Evaluation data of the dyeings are given in Table 4.

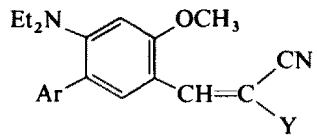
The coumarin-2-imine derivatives **10a–10f** were hydrolysed with

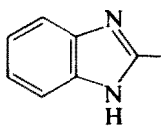


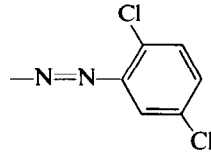
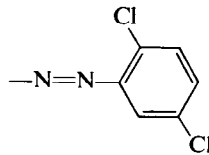
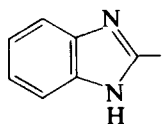
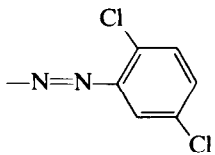
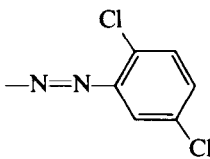
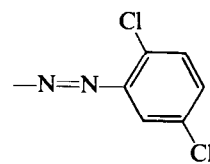
hydrochloric acid (5%) to give the arylazo coumarin derivatives (**11a–f**). These showed brighter fluorescence compared with compounds **10a–10f**. The compounds **11c,11f** gave the most intense fluorescence. The fluorescence intensities of all the arylazo coumarin derivatives were very weak compared with the standard 7-diethylamino-3-benzimidazolyl coumarin.

The 6-arylazo coumarin derivatives gave very weak shades on polyester and were not evaluated for their dyeing properties. The compounds were

TABLE 1
Physical and Spectral Data of Styryl Derivatives (**4a–4e** and **6a–6e**)

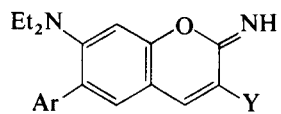


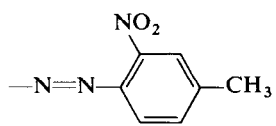
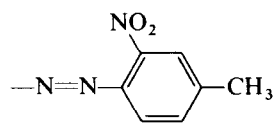
Compd	*Y*	*Ar*	*Molecular formula*[a]	*M.p.*[b] (°C)	*Yield* (%)	*Visible (MeOH)*			*IR* ν (cm^{-1})
						Absorption λ_{max} (*nm*)	*log* ε	*Emission* λ_{max} (*nm*)	
4a	$CONH_2$	H	$C_{15}H_{19}N_3O_2$ (279)	210(a)	48	440	4·1	—	2 220 (—CN) 3 340 (—NH_2) 1 680 (—C=O)
4b	CONHPh	H	$C_{21}H_{23}N_3O_2$ (349)	142(b)	65	450	4·2	—	2 220 (—CN) 3 150 (—NH) 1 680 (—CO)
4c		H	$C_{21}H_{22}N_4O$ (346)	195(b)	65	450	4·4	—	2 220 (—CN) 3 150 (—NH)
4d	Ph—NO_2—*p*	H	$C_{20}H_{21}N_3O_3$ (357)	155(a)	60	460	4·2	—	2 220 (—CN)
4e	$COOC_2H_5$	H	$C_{17}H_{22}N_2O_3$ (302)	128(b)	60	460	4·2	—	2 220 (—CN) 1 690 (—CO)

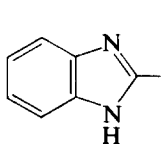
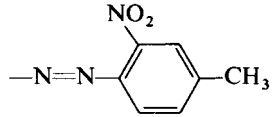
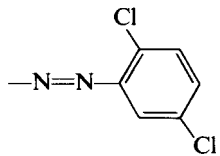
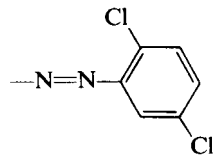
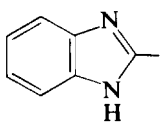
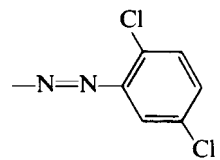
6a	$CO—NH_2$		$C_{21}H_{21}N_5Cl_2O_2$ (446)	190(a)	45(a)	408 500	4·1 3·8	—	2 220 (—CN) 3 340 ($—NH_2$) 1 680 (—CO)
6b	CO—NHPh		$C_{27}H_{25}N_5Cl_2O_2$ (522)	168(a)	45(a)	450 500	4·2 4·0	—	2 220 (—CN) 3 150 (—NH) 1 680 (—CO)
6c			$C_{27}H_{24}N_6Cl_2O$ (519)	165(a)	50	410 490	4·3 4·0	—	2 220 (CN) 3 150 (—NH)
6d	$Ph—NO_2—p$		$C_{26}H_{23}N_5Cl_2O_3$ (524)	172(a)	46	410 500	4·2 3·8	—	2 220 (—CN)
6e	$COOC_2H_5$		$C_{23}H_{24}N_4Cl_2O_3$ (475)	160(a)	50	410 510	4·0 3·9	—	2 220 (—CN) 1 690 (—CO)

[a] All the compounds showed satisfactory elemental analysis ±0·3%.
[b] Solvent of crystallisation: (a), DMF; (b), DMF + ethanol.

TABLE 2
Physical and Spectral Data of Azo Coumarin-2-imine Derivatives (**10a–10f**)

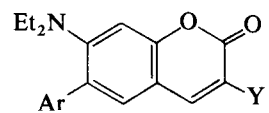


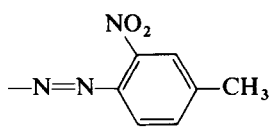
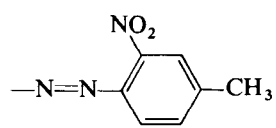
Compd	*Y*	*Ar*	*Molecular formula*[a]	*M.p.*[b] (°C)	*Yield* (%)	*Visible (MeOH)*			*IR* ν (cm^{-1})
						Absorption λ_{max} (*nm*)	*log* ε	*Emission* λ_{max} (*nm*)	
10a	$CONH_2$		$C_{21}H_{22}N_6O_4$ (422)	170(a)	50	460	4·1	464	3 150 (—NH) 1 680 (—CO) 3 340 ($—NH_2$)
10b	CONHPh		$C_{27}H_{26}N_6O_4$ (498)	210(a)	45	480	4·1	500	1 680 (—CO) 3 150 (—NH)

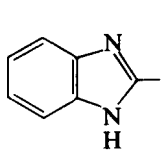
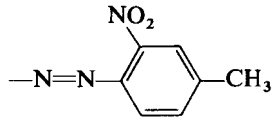
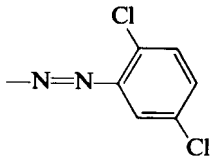
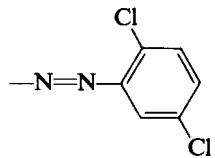
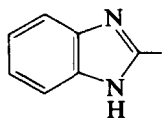
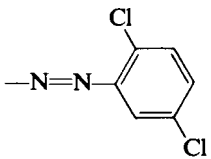
10c			$C_{27}H_{25}N_7O_3$ (495)	232(b)	50	480	4·6	508	3 150 (—NH)
10d	$CONH_2$		$C_{20}H_{19}N_5Cl_2O_2$ (432)	190(a)	50	420	4·0	460	3 150 (—NH) 1 680 (—CO) 3 340 (—NH_2)
10e	CONHPh		$C_{26}H_{23}N_5Cl_2O_2$ (508)	208(b)	45	400	4·0	460	1 680 (—CO) 3 340 (—NH) 3 150 (—NH)
10f			$C_{26}H_{22}N_6Cl_2O$ (505)	225(b)	55	480	4·6	518	3 150 (—NH)

[a] All compounds showed satisfactory elemental analysis.
[b] Solvent of crystallisation: (a) DMF; (b) DMF–ethanol.

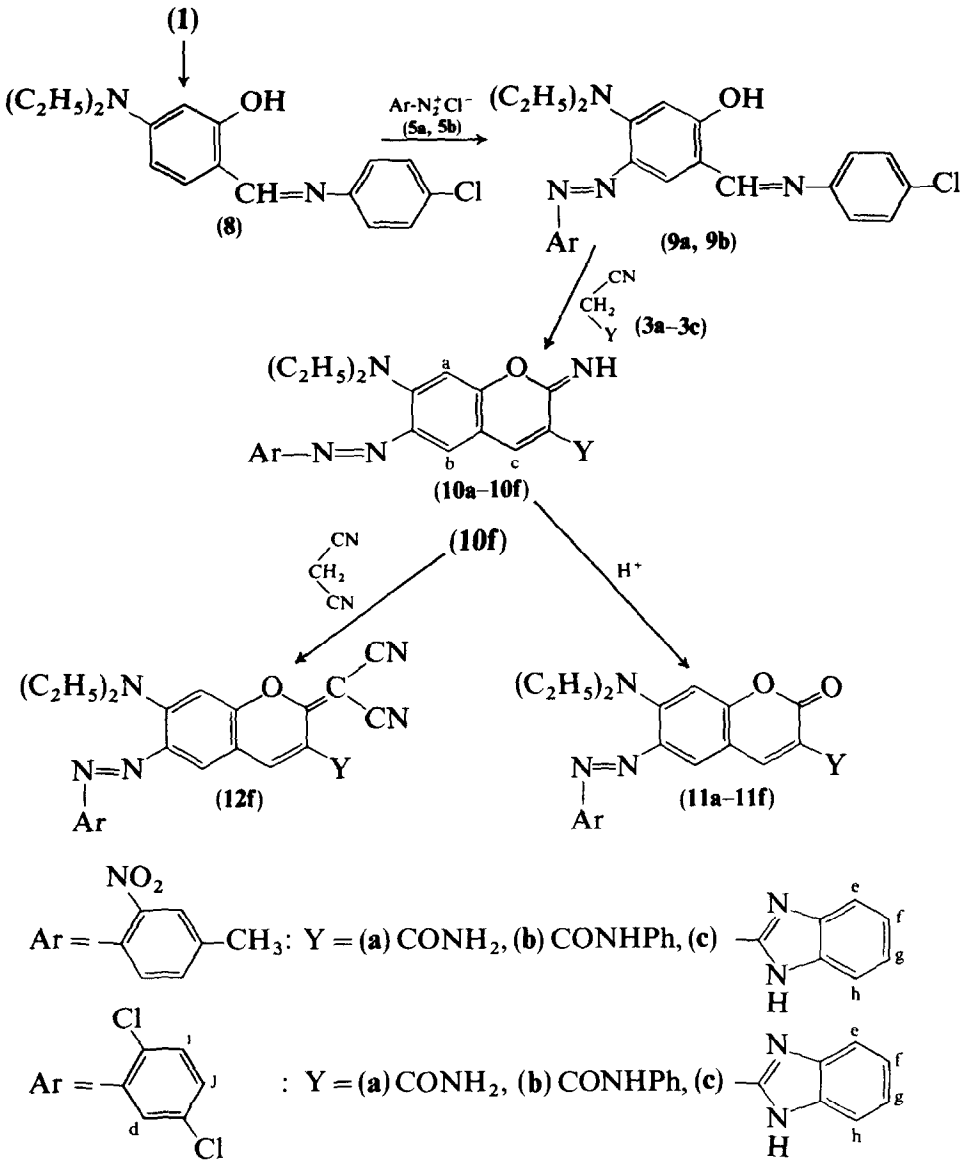
TABLE 3
Physical and Spectral Data of Azo Coumarin Derivatives (**11a–11f**)



Compd	*Y*	*Ar*	*Molecular formula*[a]	*M.p.*[b] (°C)	*Yield* (%)	*Visible (MeOH)*			*IR* ν (cm^{-1})
						Absorption λ_{max} (*nm*)	*log* ε	*Emission* λ_{max} (*nm*)	
11a	$CONH_2$		$C_{21}H_{21}N_5O_5$ (423)	185(a)	45	426	4·1	440	1 720 (CO)
11b	CONHPh		$C_{27}H_{25}N_5O_5$ (499)	230(a)	45	390	4·0	480	1 720

11c			$C_{27}H_{24}N_6O_4$ (496)	240(b)	50	404	4·2	480	1 720
11d	$CONH_2$		$C_{20}H_{18}N_4Cl_2O_3$ (433)	205(a)	45	390	3·9	440	1 720
11e	CONHPh		$C_{26}H_{22}N_4Cl_2O_3$ (509)	232(a)	40	360	4·0	450	1 720
11f			$C_{26}H_{21}N_5Cl_2O_2$ (506)	250(b)	50	440	4·2	482	1 720

[a] All compounds showed satisfactory elemental analysis ±0·3%.
[b] Solvent of crystallisation: (a), DMF; (b), DMF–ethanol.



characterised by elemental analysis, IR and visible absorption spectra. The physical and spectral data of the arylazo coumarin derivatives are given in Table 3.

Compound **10f**, in view of its intense fluorescence, was reacted with malonitrile under non-basic conditions and yielded the exocyclic dicyano derivative **12f**. Similar reactions have been reported by Wolfgang *et al.*[2] on coumarin-2-imine derivatives.

TABLE 4
Evaluation of Dyeings

Compd	*PU*[a]	*Xeno*[a]	*Thermo*[a]	*Shade on polyester*[b]
4a	1	3	2	Yellow
4b	4	4	2–3	Yellow
4c	4	1–2	2–3	Yellowish orange
4d	4	2–3	2	Red
4e	4	4	1	Yellow
6a	2	3	3	Yellow
6b	2	3–4	2–3	Orange
6c	1	3	3–4	Yellow
6d	4	2–3	2	Reddish orange
6e	2	3	2–3	Yellow
10a	1	3	4	Khaki
10b	2	2	3–4	Khaki
10c	2	2	2–3	Greenish yellow
10d	1	3	3–4	Greenish yellow
10e	1	3	2–3	Brown
10f	1	2	4–5	Khaki
13	2	3	4	Pale pink

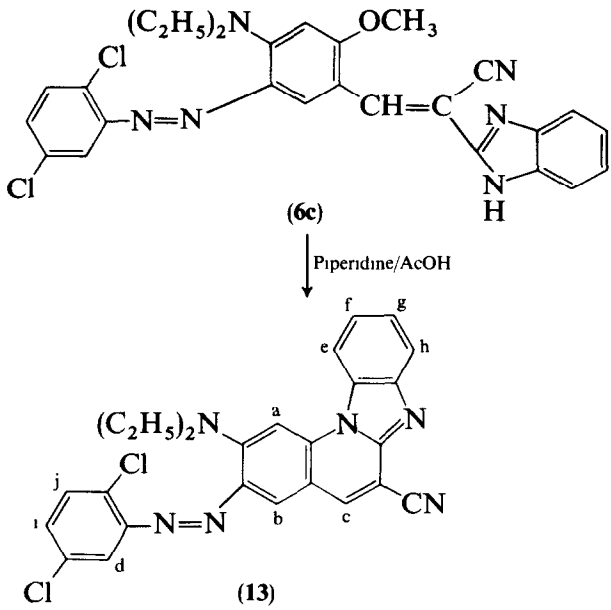
[a] Abbreviations: PU, pick up; Xeno, lightfastness; Thermo, sublimation fastness.
[b] Dyeing by HTHP method.

Compound **12f**, however, did not give a good dyeing on polyester.

The synthesis of a range of benzimidazo(1,2-*a*)quinoline derivatives[3] has been patented. A new synthesis of arylazobenzimidazo quinoline was devised by us.

The azostyryl derivative **6c** was subjected to a thermal cyclisation in *o*-dichlorobenzene, giving the arylazo benzimidazo(1,2-*a*)quinoline derivative **13**, which exhibited a faint greenish yellow fluorescence in daylight. The compound was characterised by elemental analysis, IR (CN at 2220 cm^{-1}) and PMR spectra and visible absorption–emission spectral data. It gave a pink shade on polyester with average lightfastness and good sublimation fastness. Evaluation data on the dyeing are given in Table 4.

The fluorescence of compound **13** was very weak compared with the benzimidazo(1,2-*a*)-quinoline derivative without the azo function. This is attributed to the presence of the azo function which acts as a quencher. The colour shift of **13** compared with the arylazo coumarin-2-imine derivative **10f** containing a pendant benzimidazolyl group is attributed to the rigidisation of the structure due to the participation of the benzimidazolyl —NH in the heterocyclisation.



3 EXPERIMENTAL PROCEDURES

All melting points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer spectrophotometer from a Nujol mull. Visible absorption–emission spectra were recorded on a Kontron spectrophotometer and fluorescence spectra on an Aminco–Bowman spectrofluorimeter. The PMR spectra were recorded on a Varian EM-360L spectrophotometer using TMS as external standard.

3.1 Preparation of starting materials

Cyanoacetamide,[4] cyanoacetanilide,[5] benzimidazo-2-acetonitrile,[6] *p*-nitrobenzyl cyanide,[7] 4-diethylaminosalicylaldehyde[8] and 4-diethylamino-2-methoxybenzaldehyde[9] were prepared by known methods. The ethyl cyanoacetate and malononitrile were commercial samples.

3.2 Preparation of the styryl derivatives (4a–4e)

A mixture of 4-diethylamino-2-methoxybenzaldehyde (**2**) (2·07 g, 0·01 mol) and the appropriate acetonitrile derivative (**3a–3e**) (0·01 mol) was refluxed in ethanol (10 ml) with pyridine as catalyst. The solid products separating out after 2 h of refluxing were filtered, washed with ethanol and dried. The

compounds were recrystallised from suitable solvents. The physical and spectral data of the compounds are given in Table 1.

3.3 Preparation of arylazostyryl derivatives (6a–6e)

To a solution of the styryl derivative (**4a–4e**) (0·01 mol) in acetic acid (10 ml) was added a diazotised solution of 2,5-dichloroaniline [prepared from 2,5-dichloroaniline (0·01 mol) and sodium nitrite (0·01 mol)] at 0–5°C slowly over 15 min. The pH was adjusted to 4–5 by sodium acetate solution.

The reaction mixture was then stirred at 10–15°C for 5 h until the reaction mixture showed the absence of diazo compound on spotting with a test coupler (H-acid). The azostyryl derivatives were filtered, washed with water and the dyes were crystallised from dimethylformamide.

Physical and spectral data of the azostyryl derivatives are given in Table 1.

3.4 Preparation of the Schiff base derivative (8)

A mixture of 4-diethylaminosalicylaldehyde (**1**) (1·93 g, 0·01 mol) and *p*-chloroaniline (1·27 g, 0·01 mol) was refluxed in ethanol (10 ml) in the presence of catalytic amounts of acetic acid. On cooling the reaction mixture a yellow solid was obtained which was filtered, washed with ethanol and dried. The solid was crystallised from dimethylformamide–ethanol mixture. Yield, 2·8 g (90%); m.p. 110°C (Table 5).

3.5 Preparation of arylazo Schiff base derivatives (9a, 9b)

To a solution of the Schiff base derivative (**8**) (3·1 g, 0·01 mol) in acetic acid (10 ml) was added a diazotised solution of an aromatic amine (**5a, 5b**) [prepared from the appropriate amine (0·01 mol), sodium nitrite (0·01 mol) and hydrochloric acid (0·03 mol)] at 0–5°C in 15 min.

The pH of the reaction mixture was adjusted to 6–7 by addition of saturated sodium acetate solution. The reaction mixture was stirred at 10–15°C for 5 h until it showed the absence of diazo compound on spotting

TABLE 5
Molecular formula: $C_{17}H_{19}N_2ClO$ (302·5)

	Elemental analysis (%)			
	C	*H*	*N*	*Cl*
Calculated	71·2	6·6	9·7	12·3
Found	71·1	6·8	9·5	12·5

TABLE 6
Physical Data of Arylazo Schiff Base Derivatives (**9a, 9b**)

Compd	*Molecular formula*	*M.p.* (°C)	*Yield* (%)	*Elemental analysis* (%)				
					C	*H*	*N*	*Cl*
9a	$C_{23}H_{21}N_4Cl_3O$ (475·5)	140	60	Calc.	58·0	4·4	11·7	22·3
				Found	58·3	4·5	11·8	22·0
9b	$C_{23}H_{24}N_5ClO_3$ (465·5)	165	60	Calc.	61·8	5·1	15·1	7·6
				Found	61·6	5·4	14·8	7·9

with a test coupler (H-acid). The solid products were filtered and dried. The products were crystallised from ethanol–dimethylformamide mixture (Table 6).

3.6 Preparation of 6-arylazo-7-diethylamino-3-substituted coumarin-2-imine derivatives (10a–10f)

A mixture of arylazo Schiff base derivative (**9a, 9b**) (0·01 mol) and the appropriate acetonitrile derivative (**3a–3c**) (0·01 mol) was refluxed in dimethylformamide (5 ml) in the presence of catalytic amounts of pyridine for 4 h. The reaction mixture on cooling and diluting with ethanol (5 ml) yielded the products. The solid products were filtered and recrystallised from suitable solvents. The physical and spectral data of the compounds are given in Table 2.

The PMR spectrum of a representative compound (**10f**) recorded in $CDCl_3$ and trifluoroacetic acid gave the following signals.

1.2 (t, 6H, —$N(CH_3)_2$); 3·3 (q, 4H, —$N(CH_2)_2$); 7·1–7·8 (m, 7H, protons at a and e–j positions); 8·0 (s, 1H, proton at position b); 8·05 (s, 1H, proton at position d); 8·1 (s, 1H, proton at position c).

3.7 Hydrolysis of arylazo coumarin-2-imine derivatives (10a–10f) (preparation of 6-arylazo-7-diethylamino-3-substituted coumarin derivatives (11a–11f)

A mixture of the coumarin-2-imine derivatives (**10a–10f**) (0·001 mol) and hydrochloric acid (15 ml, 5%) was refluxed for 6 h. The product isolated was recrystallised from dimethylformamide and characterised by elemental analysis and IR and visible spectra. Physical and spectral data are given in Table 3.

TABLE 7
Molecular formula $C_{29}H_{21}N_7Cl_2O$ (554)

	Elemental analysis (%)			
	C	*H*	*N*	*Cl*
Calculated	62·7	3·7	17·6	12·8
Found	62·3	3·4	17·4	12·5

IR, 1 730 cm^{-1} (coumarin —C=O).

3.8 Preparation of the exocyclic dicyano derivative (12f)

A mixture of the coumarin-2-imine derivative (**10f**) (0·01 mol) and malononitrile (0·011 mol) was refluxed in dimethylformamide (5 ml) for 6 h. The product obtained on cooling and diluting with ethanol (5 ml) was filtered and washed with ethanol. The solid product was crystallised from dimethylformamide. Yield, 45%; m.p. 240°C (Table 7).

Visible absorption–emission data, λ_{max} (abs) 464 nm (log ε 4·00);
λ_{max} (emi) 472 nm.

3.9 Preparation of arylazo benzimidazo(1,2-*a*)quinoline derivative (13)

A mixture of the azostyryl derivative **6c** (0·001 mol), piperidine (0·2 ml) and acetic acid (0·8 ml) was refluxed in *o*-dichlorobenzene (10 ml) for 5 h. On cooling the reaction mixture to room temperature and diluting with benzene (5 ml), a solid product was obtained. This was filtered, washed with alcohol and recrystallised from dimethylformamide. Yield, 0·28 g (50%); m.p. 280°C (Table 8).

Visible absorption–emission data, $\lambda_{max(abs)}$ 490 nm (log ε 3·90);
$\lambda_{max(emi)}$ 526 nm

TABLE 8
Molecular formula $C_{26}H_{20}N_6Cl_2$ (487)

	Elemental analysis (%)			
	C	*H*	*N*	*Cl*
Calculated	64·0	4·1	17·2	14·5
Found	64·2	4·2	17·4	14·8

IR, 2 220 cm^{-1} (—CN peak).

PMR spectrum ($CDCl_3$–trifluoroacetic acid):

1·3 (t, 6H, —$N(CH_3)_2$; 3·8 (g, 4H, —$N(CH_2)_2$; 7·2 (s, 1H, proton at position a); 7·3–8·0 (m, 6H, protons at positions e–j); 8·0 (s, 1H, proton at position d); 8·1 (s, 1H, proton at position b); 8·3 (s, 1H, proton at position c).

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