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Molecular design and synthesis of *N*-arylsulfonated coumarin fluorescent dyes and their application to textiles

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Abstract

A series of new coumarin fluorescent dyes derived from arylsulfonation of the parent benzothiazole, benzimidazole and benzoxazole dyes have been synthesized in high yield. The dyes were successfully applied to polyester fabrics to give highly fluorescent greenish-yellow shades. Improvements in fastness to sublimation, washing and perspiration (both acidic and alkaline) were observed but there was no general improvement in lightfastness compared with the parent compounds. Molecular modeling studies (AM1, MM2, ZINDO calculations) were used to investigate relationships between the chemical structures, spectral properties and technical performance.

Keywords: Fluorescent; Coumarin; Arylsulfonamide; UV–visible absorption; Molecular modeling; Lightfastness; Quantum yield

1. Introduction

Coumarin derivatives provide a range of organic materials which owe their commercial exploitation in a broad range of applications to their intense fluorescence. They are of special interest as yellowish-green fluorescent dyes. The most important coumarin fluorescent dyes contain benzothiazole (e.g., coumarin 6, **1a**), benzimidazole (e.g., coumarin 7, **1b**) or benzoxazole substituent in the 3-position. Initially these dyes were developed for the colouration of synthetic fibres such as polyester, and subsequently their uses have extended to include daylight fluorescent pigments, and functional applications such as dye lasers, solar collector systems, organic light emitting diodes (LED) and numerous biological applications [1–5]. Despite a reasonable set of all-round technical properties, these coumarin derivatives do not have adequate photostability for more demanding applications where prolonged exposure to light is involved. This paper is the first in a series aimed at the design and synthesis of coumarin dyes for improved technical properties which, in this case, describes the synthesis of heterocyclic coumarin derivatives into which is incorporated an arylsulfonamide group, their application as disperse dyes to polyester fabric and an evaluation of their technical performance.

2. Experimental

2.1. General

Melting points were determined as peak temperatures using a Mettler (DSC12E) Differential Scanning Calorimeter with a scanning speed of 10 °C/min. Infrared spectra were recorded as KBr discs with a Nicolet Protégé 460 Fourier Transform spectrophotometer. UV–visible spectra were measured on a Perkin–Elmer Lamda 2 Spectrometer for solutions in acetonitrile. One-dimensional ^{1}H NMR spectra were recorded in Bruker AC 200 (^{1}H at 200 MHz) using solutions of compounds of DMSO-d_6 containing TMS (tetramethylsilane) as the internal standard. Mass spectra were obtained on a Kratos Concept 1S Spectrometer operating in Electron Impact (EI) mode with low resolution. Fluorescence spectra were obtained using a Perkin–Elmer LS-3 Fluorescence Spectrophotometer. An Exeter CE-440 Elemental Analyser was used for elemental analysis.

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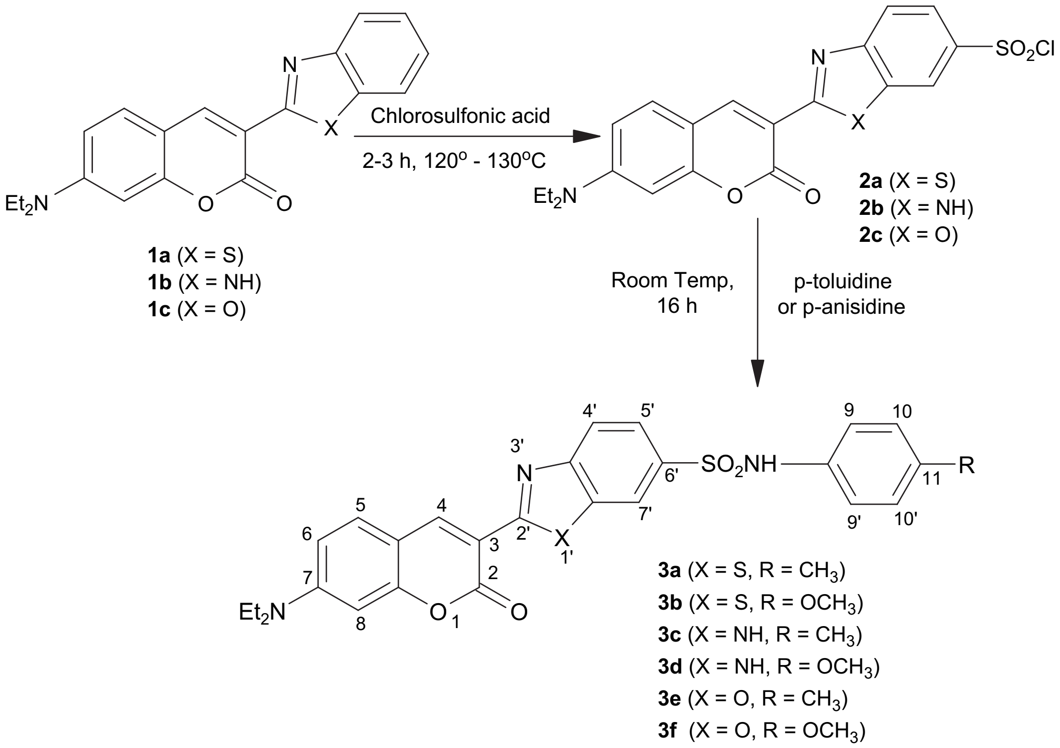


Scheme 1. Synthesis of coumarin derivatives **3a**–**f**.

Molecular modeling studies were carried out using CAChe Worksystem Version 6.1. For the geometry optimisation, MOPAC 6.1 and an augmented MM2 (Molecular Mechanics 2) force field were used.

2.2. Conformational analyses

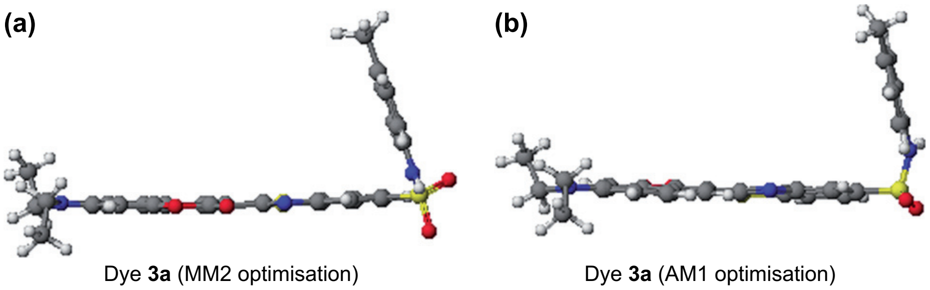
The structures of all compounds were refined by performing a geometry optimisation calculation in molecular mechanics using augmented MM2 parameters. To determine the lowest energy conformation, dihedral angles were changed prior to MM2 minimisations. Once the lowest energy conformation was found, MM2 calculations were followed by AM1 (Austin Model 1) to further optimise the structure. The UV–visible electronic transitions were calculated with ZINDO using INDO/1 parameters and a fixed geometry for the AM1 optimised structures.

2.3. Quantum yield measurement

Quantum yields were measured from emission spectra for solutions in acetonitrile. It is commonly accepted that this results in a 10–15% error [6–9]. The λ_{max} values from UV–visible absorption spectra were used as the excitation wavelengths for fluorescence measurements. Relative quantum yields were obtained from the emission curve areas using the method of Parker–Rees with coumarin 6 (**1a**) as the standard [6].

2.4. Polyester dyeing

Stock dispersions of dyes were prepared by overnight ball milling of a mixture of fluorescent dye (1.0 g), dispersing agent (Setamol WS, 1.0 g), ceramic balls (250 g) and water (100 cm^3). The dyes were applied to 100% polyester (PET) pre-scoured fabric, free of titanium dioxide, with the fluorescent dye (1.0% depth on weight of fibre), Matexil DA-AC



Dye **3a** (MM2 optimisation) Dye **3a** (AM1 optimisation)

Fig. 1. Conformation of dye **3a** after MM2 and AM1 optimisations.

Table 1
Calculated angles between the chromophore and arylsulfonamide planes for coumarin dyes

Dye	Angle (°) between chromophore and arylsulfonamide planes	
	MM2 optimisation	AM1 optimisation
3a	57.51	71.59
3b	58.36	71.83
3c	59.38	68.19
3d	58.99	68.08
3e	59.01	67.22
3f	57.91	67.25

(1.0 g/l), and Eulysin DBC (2.5 g/l) with a liquor ratio of 20:1 using a Zeltex Polycolor High Temperature High Pressure (HTHP) tube dyeing machine. The dyebaths were held at 60 °C for 20 min, the temperature raised to 130 °C at 2 °C/min and maintained at this temperature for 60 min. After cooling to 50 °C, the bath was drained off, and the dyed fabric reduction cleared with an aqueous solution of sodium hydroxide (2.0 g/l) and sodium dithionite (2.0 g/l) at 70 °C for 20 min to remove surface dye. Finally the samples were neutralised with dilute acetic acid (1.0%) and dried.

2.5. Fastness properties

Fastness to washing, perspiration (acidic and alkaline), sublimation and light of dyed polyester samples were carried out according to British Standard methods [10–13].

2.6. Synthesis of new coumarin derivatives

2.6.1. Intermediates

Coumarin derivatives **1a–c** were synthesized according to processes described elsewhere [14–16].

2.6.2. Dyes *3a–f*

The method for the synthesis of dye **3a** is described. For dyes **3b–f** essentially the same procedure was followed. However, for dyes **3c** and **d**, chlorosulfonation was carried out at 120 °C for 2 h, while for dyes **3e** and **f** the condition was 130 °C for 3.5 h.

A mixture of 3-(2-benzothiazolyl)-7-diethylaminocoumarin (0.63 g, 0.0018 mol) and chlorosulfonic acid (5.0 g) was stirred for 2.5 h at 120 °C. The mixture was cooled to 10 °C and poured into cold water (33 cm^3). The resulting precipitate was collected, washed with cold water until the washings were about pH 5. The filter cake was transferred to a flask with water (10 cm^3) and *p*-toluidine (0.35 g, 0.0033 mol) was added, keeping the temperature below 10 °C [17–19]. The mixture was stirred for 16 h at room temperature, filtered, washed with water until washings were colourless and dried in the vacuum oven. Dye **3a** was obtained as orange needles (from DMF–water). Yield (0.87 g, 84%); m.p. 305 °C, ν_{max} (KBr)/cm^{-1} 3173 (NH), 2973 (alkyl CH), 1685 (C=O), 1611 and 1575 (Ar C–C), 1510, 1481, 1347 (SO_2NH), 1259, 1193, 1159 (SO_2NH), 1080; *m/z* (EI): 519 (M^+, 100%), 504 (86), 491 (9), 382 (33), 349 (96), 321 (19), 306 (33), 277 (12), 106 (87), 79 (25), 63 (19); found C, 62.21; H, 4.87; N, 8.06; $C_{27}H_{25}N_3O_4S_2$ requires C, 62.41; H, 4.85; N, 8.09; δ_H ppm (200 MHz, DMSO-d_6): 1.13 (6H, t, $J = 7.0$ Hz, $N(CH_2CH_3)_2$), 2.14 (3H, s, Ar–CH_3), 3.67 (4H, q, $J = 6.6$ Hz, $N(CH_2CH_3)_2$), 6.65 (1H, d, $J_{8,6} = 2$ Hz, 8-H), 6.84 (1H, dd, $J_{6,5} = 9.2$ Hz and $J_{6,8} = 2.0$ Hz, 6-H), 6.94–7.05 (4H, m, 9,9′-H and 10,10′-H), 7.73–7.84 (2H, m, 4′-H and 5′-H), 8.05 (1H, d, $J_{5,6} = 8.6$ Hz, 5-H), 8.55 (1H, d, $J_{7',5'} = 2$ Hz, 7′-H), 9.02 (1H, s, 4-H) 10.21 (1H, s, Ar–SO_2NH).

Dye **3b** was obtained as yellowish-red needles. Yield (0.89 g, 92%); m.p. 304 °C, ν_{max} (KBr)/cm^{-1} 3159 (NH), 2975 (alkyl C–H), 1678 (C=O), 1610 and 1574 (Ar C–C), 1509, 1481, 1348 (SO_2NH), 1259, 1160 (SO_2NH), 1084; *m/z* (EI): 535 (M^+, 98%), 520 (17), 456 (9), 382 (18), 367 (27), 349 (68), 334 (38), 305 (13), 122 (100), 108 (33), 95 (14), 73 (35), 63 (13), 44 (32); found C, 60.38; H, 4.78; N, 7.75; $C_{27}H_{25}N_3O_5S_2$ requires C, 60.54; H, 4.7; N, 7.84; δ_H (200 MHz, DMSO-d_6): 1.13 (6H, t, $J = 7.0$ Hz, $N(CH_2CH_3)_2$) 3.48 (4H, q, $J = 6.8$ Hz, $N(CH_2CH_3)_2$) 3.62 (3H, s, Ar–OCH_3) 6.72 (1H, d, $J_{8,6} = 2.2$ Hz, 8-H) 6.85 (1H, dd, $J_{6,5} = 8.8$ Hz and $J_{6,8} = 2.4$ Hz, 6-H) 6.73–7.02 (4H, m, 9,9′-H and 10,10′-H) 7.71–7.82 (2H, m, 4′-H and 5′-H) 8.05 (1H, d, $J_{5,6} = 8.6$ Hz, 5-H) 8.48 (1H, d, $J_{7',5'} = 1.8$ Hz, 7′-H) 9.01 (1H, s, 4-H), 10.22 (1H, s, Ar–SO_2NH).

Table 2
Experimental and calculated (AM1/ZINDO) UV–visible spectral data for dyes **1a–c** and **3a–f**

Dye	λ_{max} (nm) (experimental) (acetonitrile)		λ_{max} (nm) (calculated) (AM1/ZINDO)	
	$\{\varepsilon_{max}$ (l mol^{-1} × 10^4 cm^{-1})$\}$		$\{\varepsilon_{max}$ (l mol^{-1} × 10^4 cm^{-1})$\}$	
	UV	Visible	UV	Visible
1a	214 (4.9)	458 (6.5)	205 (13.6)	391 (8.7)
3a	221 (4.9), 198 (7.2)	469 (5.9)	208 (10.2), 190 (14.5)	396 (8.7)
3b	221 (4.2), 196 (5.8)	469 (5.4)	207 (10.3), 190 (14.6)	396 (8.7)
1b	210 (5.1)	435 (5.0)	207 (14.3)	393 (8.4)
3c	214 (5.5), 198 (5.2)	451 (5.3)	210 (11.0), 190 (13.2)	394 (8.2)
3d	216 (5.5), 196 (5.9)	451 (5.3)	210 (10.9), 190 (13.2)	395 (8.2)
1c	201 (4.3)	438 (5.3)	204 (11.7)	391 (8.4)
3e	199 (6.9)	447 (5.4)	205 (10.5), 188 (14.6)	394 (8.6)
3f	197 (6.3)	448 (5.4)	205 (10.2), 190 (14.6)	395 (8.6)

Dye **3c** was obtained as reddish-yellow needles. Yield (0.80 g, 89%); m.p. 312 °C, ν_{max} (KBr)/cm^{-1} 3311 (NH), 2972 (alkyl CH), 1699 (C=O), 1618 and 1587 (Ar C–C), 1526, 1427, 1349 (SO_2NH), 1302, 1251, 1186, 1135 (SO_2NH), 1074; *m/z* (EI): 502 (M^+, 23%), 332 (29), 318 (20), 256 (14), 129 (23), 106 (64), 97 (30), 83 (37), 57 (81), 43 (100); found C, 64.40; H, 5.24; N, 11.10; $C_{27}H_{26}N_4O_4S$ requires C, 64.53; H, 5.21; N, 11.15; δ_H (200 MHz, DMSO-d_6): 1.15 (6H, t, $J = 7.0$ Hz, $N(CH_2CH_3)_2$) 2.14 (3H, s, Ar–CH_3) 3.50 (4H, q, $J = 7.0$ Hz, $N(CH_2CH_3)_2$) 6.73 (1H, d, $J_{8,6} = 2$ Hz, 8-H) 6.82 (1H, dd, $J_{6,5} = 9.2$ Hz and $J_{6,8} = 2.4$ Hz, 6-H) 6.96–7.10 (4H, m, 9,9′-H and 10,10′-H) 7.55 (1H, dd, $J_{5',4'} = 8.6$ Hz and $J_{5',7'} = 1.8$ Hz, 5′-H) 7.65–7.76 (2H, t, $J_{5,6} = 9.0$ Hz, 5-H and 7′-H) 7.95 (1H, s, 4′-H) 8.95 (1H, s, 4-H).

Dye **3d** was obtained as brownish-yellow needles. Yield (0.77 g, 82%); m.p. 310 °C, ν_{max} (KBr)/cm^{-1} 3312 and 3247 (NH), 2968 (alkyl CH), 1699 (C=O), 1619 and 1591 (Ar C–C), 1526, 1427, 1351 (SO_2NH), 1251, 1148 (SO_2NH), 1064; *m/z* (EI): 518 (M^+, 22%), 332 (24), 318 (14), 149 (13), 122 (44), 97 (21), 83 (30), 69 (46), 57 (100); found C, 62.41; H, 5.08; N, 10.75; $C_{27}H_{26}N_4O_5S$ requires C, 62.53; H, 5.05; N, 10.8; δ_H (200 MHz, DMSO-d_6): 1.15 (6H, t, $J = 7.0$ Hz, $N(CH_2CH_3)_2$) 3.48 (4H, q, $J = 7.2$ Hz, $N(CH_2CH_3)_2$) 3.63 (3H, s, Ar–OCH_3) 6.67 (1H, d, $J_{8,6} = 2.2$ Hz, 8-H) 6.74–7.02 (4H, m, 9,9′-H and 10,10′-H) 6.81 (1H, dd, $J_{6,5} = 8.6$ Hz and $J_{6,8} = 2.4$ Hz, 6-H) 7.51 (1H, dd, $J_{5',4'} = 8.4$ Hz and $J_{5',7'} = 1.8$ Hz, 5′-H) 7.67 (1H, d, $J_{7',5'} = 2.0$ Hz, 7′-H) 7.73 (1H, d, $J_{4',5'} = 9.0$ Hz, 4′-H) 7.92 (1H, d, 5-H) 8.95 (1H, s, 4-H), 9.84 (1H, s, Ar–SO_2NH).

Dye **3e** was obtained as reddish-yellow needles. Yield (0.85 g, 94%); m.p. 303 °C, ν_{max} (KBr)/cm^{-1} 3158 (NH), 2979 and 2925 (alkyl CH), 1732 (C=O), 1616 and 1588 (Ar C–C), 1506, 1459, 1351 (SO_2NH), 1318, 1280, 1191, 1153 (SO_2NH), 1083; *m/z* (EI): 503 (M^+, 100%), 488 (56), 351 (16), 333 (53), 318 (46), 290 (8), 261 (14), 227 (5), 199 (5), 106 (65), 77 (15), 43 (15), found C, 64.24; H, 5.02; N, 8.32; $C_{27}H_{25}N_3O_5S$ requires C, 64.4; H, 5; N, 8.34; δ_H (200 MHz, DMSO-d_6): 1.15 (6H, t, $J = 7.0$ Hz, $N(CH_2CH_3)_2$) 2.16 (3H, s, Ar–CH_3) 3.50 (4H, q, $J = 6.6$ Hz, $N(CH_2CH_3)_2$) 6.62 (1H, d, $J_{8,6} = 2$ Hz, 8-H) 6.83 (1H, dd, $J_{6,5} = 9.0$ Hz and $J_{6,8} = 2.0$ Hz, 6-H) 6.95–7.06 (4H, m, 9,9′-H and 10,10′-H) 7.66–7.78 (2H, m, 4′-H and 5′-H) 7.88 (1H, d, $J_{5,6} = 8.4$ Hz, 5-H) 8.01 (1H, d, $J_{7',5'} = 1.8$ Hz, 7′-H) 8.84 (1H, s, 4-H).

Dye **3f** was obtained as reddish-yellow needles. Yield (0.81 g, 87%); m.p. 293 °C, ν_{max} (KBr)/cm^{-1} 3157 (NH), 2977 (alkyl CH), 1732 (C=O), 1617 and 1588 (Ar C–C), 1510, 1457, 1352 (SO_2NH), 1283, 1153 (SO_2NH), 1082; *m/z* (EI): 519 (M^+, 19%), 351 (4), 319 (7), 122 (65), 108 (32), 95 (2), 73 (78), 57 (8), 44 (100); found C, 62.28; H, 4.87; N, 8.06; $C_{27}H_{25}N_3O_6S$ requires C, 62.42; H, 4.85; N, 8.09; δ_H (200 MHz, DMSO-d_6): 1.15 (6H, t, $J = 7.0$ Hz, $N(CH_2CH_3)_2$) 3.50 (4H, q, $J = 6.8$ Hz, $N(CH_2CH_3)_2$) 3.64 (3H, s, Ar–OCH_3) 6.62 (1H, d, $J_{8,6} = 2$ Hz, 8-H) 6.82 (1H, dd, $J_{6,5} = 9.4$ Hz and $J_{6,8} = 2.2$ Hz, 6-H) 6.75–7.04 (4H, m, 9,9′-H and 10,10′-H) 7.65–7.75 (2H, m, 4′-H and 5′-H) 7.87 (1H, d, $J_{5,6} = 8.4$ Hz, 5-H) 7.95 (1H, d, $J_{7',5'} = 1.8$ Hz, 7′-H) 8.85 (1H, s, 4-H) 10.1 (1H, s, Ar–SO_2NH).

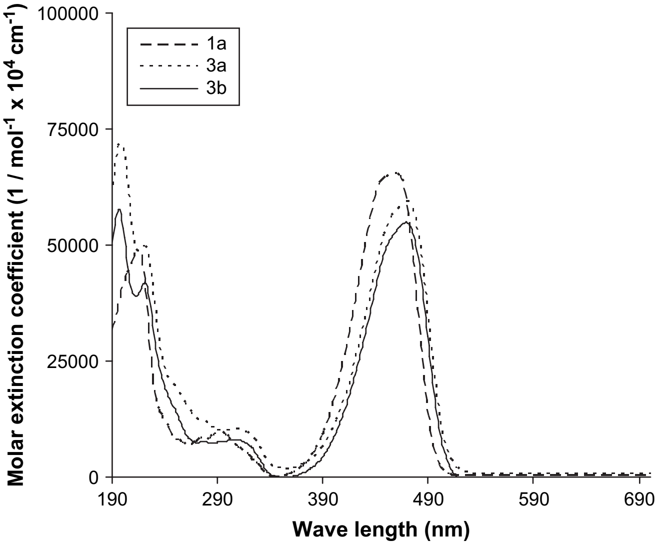


Fig. 2. UV–visible absorption spectra of coumarin derivatives **1a**, **3a** and **3b**.

3. Results and discussion

3.1. Molecular modeling

It has been suggested that, in the case of some textile reactive dyes, the incorporation of an arylsulfonamide ring provides the capability to act as a UV filter which leads to improved lightfastness properties [20]. It is significant that the group is not in the same plane as, and hence not conjugated with, the chromophore so that energy transfer from the UV filter to the chromophore is minimised. Incorporation of arylsulfonamide groups into acid dyes has also been reported to lead in some cases to improved dyeing properties, including lightfastness, on polyamide and wool [21]. The orientation of the aryl ring acting as the UV filter as an ‘open lid’ over the chromophoric system may also be a factor in improving lightfastness. Based on our recent X-ray crystallographic study of CI Pigment Yellow 97, which contains a phenylsulfonamide group, we have proposed that this may be an important factor in improving its technical performance, including lightfastness [22].

Dyes **3a–f** were prepared from the appropriate parent coumarins **1a–c** according to Scheme 1. The synthetic

Table 3
Fluorescence spectral data for dyes **1a–c** and **3a–f**

Dye	Maximum wavelength (nm)		Stokes’ shift (nm)	Quantum yield
	Excitation	Emission		
1a	458	510	52	0.78 [23][a]
3a	469	519	50	0.71
3b	469	519	50	0.68
1b	435	497	62	0.74
3c	451	497	46	0.70
3d	451	497	46	0.68
1c	438	493	55	0.68
3e	447	503	56	0.53
3f	448	505	57	0.49

[a] Literature value for coumarin 6 in ethanol.

Table 4
Colouristic data for compounds **1a**–**c** and **3a**–**f** dyed on 100% polyester woven fabrics

Dye	Maximum reflectance value (%)	L	a^*	b^*
1a	148.09	100.93	−20.38	127.24
3a	143.59	99.46	−24.01	113.81
3b	148.92	97.96	−22.46	110.84
1b	139.33	99.65	−28.58	116.7
3c	131.65	97.5	−30.02	92.11
3d	135.14	97.68	−35.17	98.02
1c	138.59	99.98	−31.39	114.27
3e	126.90	95.98	−33.68	90.97
3f	130.77	96.83	−33.82	95.69

methodology had been previously established [17–19] for the synthesis of some *N*-alkylsulfonamide coumarin fluorescent dyes and worked well in our hands adapted to the arylsulfonamides, giving yields of 82–94%. We carried out molecular modeling on dyes **3a**–**f** using the CAChe system obtaining optimised molecular geometries by MM2 alone and by MM2 followed by AM1 procedures. Fig. 1 shows the calculated molecular conformations for dye **3a** as an example. Similar geometries were obtained for the other dyes. In both MM2 and AM1 optimised structures, the coumarin and heterocyclic ring systems are essentially planar and the aryl group on the sulfonamide is in an ‘open-lid’ configuration. MM2 calculations suggest a slightly smaller angle between the planes (57–60°) compared with the results of the AM1 calculations (67–72°) (Table 1). Our crystallographic determination of CI Pigment Yellow 97 demonstrated that there is an angle of 52° between the planes given by the azo chromophore and the phenylsulfonamide groups [20].

3.2. UV–visible and fluorescence spectral data analysis

The experimental UV–visible spectra of coumarin derivatives (**3a**–**f**) together with the parent compounds were obtained using acetonitrile as the common solvent, selected for its relatively low absorption in the UV region of the spectrum (to 190 nm). The spectra showed absorption bands in the UV and visible regions as shown in Table 2. The spectra of dyes **1a**, **3a** and **3b** are reproduced in Fig. 2 as an example. In the visible region, the absorption band in the arylsulfonated derivatives **3** experiences a small bathochromic shift (9–16 nm) compared to the corresponding parent compound **1**, and gives similar molar extinction coefficients. Dyes **1a**–**c** show a major UV absorption in the range 201–214 nm. It is of interest that dyes **3a**–**f** show much more intense UV absorption than the parent compounds, with a new lower wavelength band appearing just below 200 nm (not resolved in the case of dyes **3e** and **f**, although the higher intensity of the band compared with **1c** suggests its presence). We have commonly used the PPP-MO approach for the prediction of the spectral properties of a range of dyes and pigments [3,4]. However, the approach is inappropriate for these new dyes because they deviate significantly from planarity. We have instead applied ZINDO calculations to these dyes, using geometry optimised by AM1 and the results are also given in Table 2. The calculation method predicts the observed bathochromic shifts of the visible bands, although underestimating the $\lambda_{\max}$ values. However, it gives a reasonable correlation with the spectra in the UV region and successfully predicts the presence of the new low wavelength absorption band, a factor of considerable importance for the underlying molecular design concept. The fluorescence spectral properties (Table 3) of dyes **3** are broadly similar to those of the parent dyes **1**. They give Stokes’ shifts ranging from 46 to 62 nm, in most cases slightly smaller than the parent compounds, and reasonable quantum yields (0.49–0.71).

3.3. Dyeing and fastness properties

Preliminary dyeing experiments with acetic acid, sodium acetate and traditional polyester dyeing auxiliaries (wetting and dispersing agents) gave uneven dyeings where some areas of the fabrics were dull and red and others fluorescent green. A solution to this problem proved to be the use of Eulysin DBC (a commercially available product described as a phosphate-free aqueous solution of dispersing agents, complexing agents

Table 5
Fastness to sublimation, washing and light of polyester dyed with compounds **1a**–**c** and **3a**–**f**

Dye	Fastness properties										
	Sublimation			Washfastness							Lightfastness
	Colour change	Staining on		Colour change	Staining on						
		PET	Cotton		Dicell	Cotton	Nylon	PET	Acrylic	Wool	
1a	4–5	3	3–4	5	4	4–5	3–4	4–5	4–5	4–5	4
1b	4–5	3–4	3–4	4–5	3–4	4–5	3	5	4–5	4–5	3
1c	4–5	2–3	3	4–5	4	4–5	3–4	4–5	4–5	4–5	4
3a	5	5	5	5	5	5	4–5	5	5	5	3–4
3b	5	5	5	5	5	5	4–5	5	5	5	3–4
3c	5	5	5	5	5	4–5	4–5	5	5	5	3
3d	5	5	5	5	4–5	4–5	4–5	5	5	5	3–4
3e	5	5	5	5	5	4–5	5	5	4–5	5	3
3f	5	5	5	5	5	5	5	5	5	5	3

Table 6
Perspiration fastness (acidic/alkaline) of polyester dyed with compounds **1a–c** and **3a–f**

Dye	Colour change	Staining of adjacent fabric					
		Dicell	Cotton	Nylon	Polyester	Acrylic	Wool
1a	5/5	4–5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4–5/4–5
1b	5/5	4/4	4–5/4–5	4/4	4–5/4–5	4–5/4–5	4/4
1c	4–5/4–5	2/2	3–4/3–4	2/2	3/3	4–5/4–5	3/3
3a	5/5	4–5/5	5/5	4–5/5	5/5	4–5/5	4–5/5
3b	5/5	4–5/4–5	5/5	4–5/4–5	5/5	4–5/4–5	5/5
3c	5/5	4–5/4–5	5/5	4–5/5	5/5	5/5	5/5
3d	5/5	4–5/4–5	5/5	4–5/4–5	5/4–5	4–5/4–5	5/5
3e	5/5	4–5/4–5	5/4–5	4–5/4–5	5/5	4–5/4–5	5/5
3f	5/5	4/4	4–5/4–5	4/4	4–5/4–5	4–5/4–5	4–5/4–5

and an acid buffer system) during dyeing. The use of this agent led to even dyeings showing excellent fluorescence properties. All of the dyes applied to polyester fabrics by high-temperature dyeing techniques, were found to impart attractive greenish-yellow fluorescent shades on polyester fabrics. Colouristic data obtained by reflectance measurements are given in Table 4. By visual judgement, fabrics dyed with **3a** and **b** appeared the most highly fluorescent, even better than that dyed with the corresponding benzothiazole parent compound **1a**. This is supported by maximum reflectance values, which suggest that **3b** is the most highly fluorescing of all. Fabrics dyed with benzimidazole derivatives **3c** and **d** appeared less fluorescent and the benzoxazole derivatives **3e** and **f** showed lowest visual fluorescence, agreeing in qualitative terms with measured maximum reflectance values. Thus, the new dyes containing arylsulfonamide groups are at least as interesting as the parent dyes in terms of their ability to provide fluorescence, both in solution and when applied to polyester fabrics.

The fastness to light, sublimation, perspiration (both acidic and alkaline) and washing were evaluated according to British Standard methods and the data are given in Tables 5 and 6. In general, it was found that the incorporation of arylsulfonamide group into the parent dye structure **1a–c** did not lead to a general improvement in the lightfastness properties. Dye **3d** showed a minor improvement (from 3 to 3–4), dye **3c** remained unchanged, while the remaining dyes showed a slight deterioration. However, in all cases the introduction of the arylsulfonamide group gave a significant improvement in the sublimation fastness, washfastness and perspiration fastness. An especially marked improvement was achieved for dyes **3e** and **f**. These improvements are probably associated with the larger molecular size compared with the parent dyes.

4. Conclusion

Introduction of an arylsulfonamide group covalently into heterocyclic coumarins gave a range of dyes which were highly fluorescent both in solution and after application to polyester fibre. Molecular modeling studies suggest that the arylsulfonamide group is at an angle in an 'open-lid' arrangement with respect to the plane of the coumarin chromophoric system. The dyes applied to polyester, showed significant improvements in fastness to washing, perspiration and sublimation compared with the parent coumarin dyes. The electronic spectra of the dyes showed higher UV absorption than the parent dyes, successfully predicted by AM1/ZINDO calculations. However, the additional UV absorption is at low wavelengths, in the UVC region which is filtered out of sunlight and is not significant in the xenon-arc lamp used for lightfastness testing. It is conceivable that fine tuning of this absorption may provide the UV-protecting properties required to improve the lightfastness of the dyes. We will report on how this concept has been applied, making use of the molecular design and synthetic methodology described in this paper, in future publications.

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