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Short communication

Synthesis of coumarin dyes containing *N*-alkylsulfonamide groups

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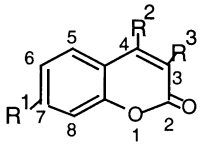
Abstract

Coumarins containing *N*-alkylsulfonamide groups built into benzoxazolyl, benzothiazolyl, or benzimidazolyl systems were synthesized and then reacted with NaCN to give fluorescent red compounds. Results from a determination of the spectral properties and dyeing characteristics of these new dyes suggest that they are potential commercial solvent dyes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Coumarin; *N*-alkylsulfonamide; Electronic spectra; Dyeing characteristics; Bathochromic shift; Hyperchromic effect

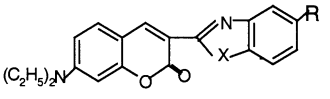
1. Introduction

While coumarin (**I**, $R' = R^2 = R^3 = H$) is a colorless compound, when R^1 is an electron-donor and R^2 or R^3 is an electron-acceptor, the resultant coumarin exhibits color and intense fluorescence. Coumarins containing benzoxazolyl, benzothiazolyl and benzimidazolyl systems were reported in 1958 [1]. Such coumarins have been reported to be useful in solar collection and lasers [2–9].



I

The yellow colorant CI Disperse Yellow 232 [6,7] has been shown to have a type **II** structure ($R = Cl$, $X = O$). This dye has better properties than those having $R = H$ or CH_3. Cyanation of type **II** coumarins according to Fig. 1 gives fluorescent red dyes [8].



II (X=N, O, S; R=H, CH_3, Cl)

In the present paper, the synthesis of coumarins containing *N*-alkylsulfonamide groups is reported (cf. **III** and **IV**). The properties of these new dyes are compared with those of dyes **V,** which were obtained using previously reported methods [2–5,9].

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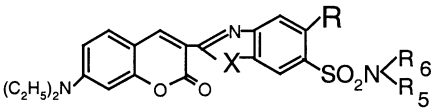
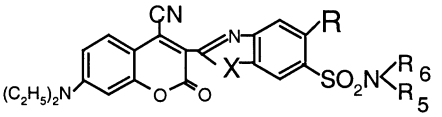


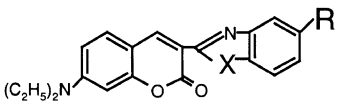
III

a: X=O, R=H, R_5=R_6=C_2H_5; **b**: X=O, R=H, R_5=H, R_6=$(CH_2)_3OCH_3$
c: X=S, R=H, R_5=R_6=C_2H_5; **d**: X=S, R=H, R_5=H, R_6=$(CH_2)_3OCH_3$
e: X=NH, R=H, R_5=R_6=C_2H_5; **f**: X=NH, R=H, R_5=H, R_6=$(CH_2)_3OCH_3$
g: X=O, R=CH_3, R_5=R_6=C_2H_5; **h**: X=O, R=CH_3, R_5=H, R_6=$(CH_2)_3OCH_3$



IV

a: X=O, R=H, R_5=R_6=C_2H_5; **b**: X=O, R=H, R_5=H, R_6=$(CH_2)_3OCH_3$
c: X=S, R=H, R_5=R_6=C_2H_5; **d**: X=S, R=H, R_5=H, R_6=$(CH_2)_3OCH_3$
e: X=NH, R=H, R_5=R_6=C_2H_5; **f**: X=NH, R=H, R_5=H, R_6=$(CH_2)_3OCH_3$
g: X=O, R=CH_3, R_5=R_6=C_2H_5; **h**: X=O, R=CH_3, R_5=H, R_6=$(CH_2)_3OCH_3$



V

a: X=O, R=H; **b**: X=S, R=H; **c**: X=NH, R=H;
d: X=O, R=CH_3 **e**: X=O, R=Cl; **f**: X=O, R=NO_2

2. Experimental

2.1. General

All melting points are uncorrected. UV–visible spectra were recorded on a SHIMADZU UV-3100 instrument and IR spectra on an FT/IR-430 instrument. ^{1}H NMR spectra were recorded on Jeol FX-90Q instrument in $CDCl_3$ and chemical shifts were expressed in ppm. Mass spectra were recorded on a HP1100MSD instrument and fluoresence spectra on a SHMADZU RF-5000 instrument.

The procedure used to dye polyester fabric was as follows: dye dissolved in DMF was added to water with rapid stirring to reduce the particle size. Polyester microfiber fabric (1 g) was dyed in a 1% (o.w.f.) dye bath at pH 4–5 for 45 min at 130 °C. The dyed fabric was given a reduction clear in $NaOH/Na_2S_2O_4$ solution for 15 min at 70 °C. Wash fastness, sublimation fastness, and light fastness were assessed according to ISO

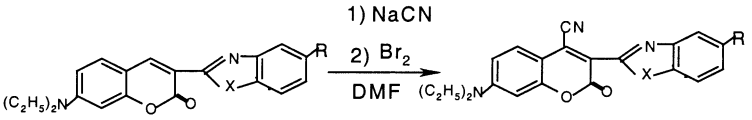


Fig. 1. Synthesis of 4-cyano coumarins (X = N, 0, S; R = H, CH_3, Cl).

methods 105-C03-1989, 105-P01-1993, 105-B02-1994, respectively [10].

2.2. Synthesis of type *III* coumarins

A mixture of 3-benzoxazolyl-7-diethylamino-2H-1-benzopyran-2-one (4.0 g, 0.011 mol) and chlorosulfonic acid (30 g, 0.26 mol) was stirred for 3.5 h at 130 °C. The reaction mixture was cooled to 10 °C and poured into cold water (200 g). The precipitate was collected and washed with cold water until the washings were about pH 5. The filter cake was transferred to a 3-necked flask along with 5 ml water (as solvent) and diethylamine (1.56 g, 0.02 mol) was added, keeping the temperature below 10 °C. The reaction mixture was kept for 2 h at room temperature, then filtered off and washed with water until the washings were colorless. The product was dried in vacuo at 60 °C for 8 h to give dye **IIIa** (4.26 g, 85%), m.p. 168–170 °C. M^+ 469, IR: ν 2971, 2926, 1711, 1611, 1509, 1351, 1162, 1130, 1079, 1028 cm^{-1}; elemental analysis: calcd: C, 61.41; H, 5.76; N, 8.96; S, 6.82%; anal.: C, 61.0; H, 5.70; N, 8.90; S. 6.84%; ^{1}H NMR: δ1.2 (*t*, 12H), 3.4 (*q*, 8H), 6.6 (*d*, 2H), 7.5(*d*, 1H), 7.8 (*d*, 2H), 8.4 (*s*, 1H), 8.9 (*s*, 1H).

Dyes **IIIb–g** were synthesized by the procedure given above for **IIIa.** Relevant data on yield and m.p. are given below.

b: Amine/yield = $CH_3O(CH_2)_3N/H_2$/75%. m.p. 205–207 °C, M^+ 485, IR: ν 2972, 2928, 1712, 1612, 1510, 1352, 1162, 1130, 1079, 1029 cm^{-1}; elemental analysis: calcd: C, 59.38; H, 5.57; N, 8.66; 5, 6.60%; anal.: C, 59.11; H, 5.48; N, 8.59; S, 6.51%; ^{1}H NMR: δ 1.1 (*t*, 6H), 1.5 (*p*, 2H), 2.8 (*s*, 3H), 3.1 (*q*, 8H), 4.6 (*t*, 1H), 6.0 (*d*, 2H), 6.6 (*d*, 1H), 7.2 (*d*, 2H), 7.6 (*s*, 1H), 8.0 (*s*, 1H).

c: Amine/yield = $C_2H_5)_2$NH/86%. m.p. 232–234 °C, M^+ 485, IR: ν 2973, 2929, 1710, 1612, 1510, 1350, 1161, 1130, 1078, 1029 cm^{-1}; elemental analysis: calcd: C, 59.38; H, 5.57; N, 8.66; S, 13.20%; anal.: C, 59.11; H, 5.50; N, 8.59; S, 13.09%; ^{1}H NMR: δ 1.2 (*t*, 12H), 3.4 (*q*, 8H), 6.6 (*d*, 2H), 7.5 (*d*, 1H), 7.8 (*d*, 2H), 8.4 (*s*, 1H), 8.9 (*s*, 1H).

d: Amine/yield = $CH_3O(CH_2)_3NH_2$/75%. m.p. 217–219 °C, M^+ 501, IR: ν 2971, 2927, 1712, 1612, 1510, 1352, 1162, 1131, 1080, 1029 cm^{-1}; Elemental analysis: calcd: C, 57.49; H, 5.39; N, 8.38; S, 12.77%; anal.: C, 57.39; H, 5.32; N, 8.31; S, 12.68%; ^{1}H NMR: δ 1.2 (*t*, 6H), 1.5 (*p*, 2H), 2.8 (*s*, 3H), 3.1 (*q*, 8H), 4.6(*t*, 1H), 6.0 (*d*, 2H), 6.6 (*d*, 1H), 7.2 (*d*, 2H), 7.6 (*s*, 1H), 8.0 (*s*, 1H).

e: Amine/yield = $(C_2H_5)_2$NH/89%. m.p. 243–244 °C, M^+ 468, IR: ν 2973, 2932, 1702, 1619, 1527, 1354, 1182, 1135, 1079, 1029 cm^{-1}; elemental analysis: calcd: C, 61.54; H, 5.98; N, 11.97; S, 6.84%; anal.: C, 61.18; H, 5.89; N, 12.02; S, 6.77%; ^{1}H NMR: δ 1.2 (*t*, 12H), 3.4 (*q*, 8H), 6.6 (*d*, 2H), 7.5 (*d*, 1H), 7.8 (*d*, 2H), 8.1 (*s*, 1H), 8.2 (*s*, 1H), 9.1 (*s*, 1H).

f: Amine/yield = $CH_3O(CH_2)_3NH_2$/77%. m.p. 241–243 °C; M^+ 484; IR: ν 2972, 2928, 1712, 1617, 1520, 1352, 1162, 1130, 1079, 1029 cm^{-1}; elemental analysis: calcd: C, 59.50; H, 5.79; N, 11.57; S, 6.61%; anal.: C, 59.38; H, 5.68; N, 11.62; S, 6.58%; ^{1}H NMR: δ 1.2 (*t*, 6H), 1.6 (*p*, 2H), 2.8 (*s*, 3H), 3.3 (*q*, 8H), 4.6 (*t*, 1H), 6.0 (*d*, 2H), 6.6 (*d*, 1H), 7.2 (*d*, 2H), 7.6 (*s*, 1H), 8.0 (*s*, 1H), 9.0 (*s*, 1H).

g: Amine/yield = $(C_2H_5)_2$NH/85%. m.p. 144–146 °C; M^+ 483; IR: ν 2972, 2930, 1741, 1618, 1506, 1353, 1162, 1135, 1080, 1029 cm^{-1}; elemental analysis. calcd: C, 62.11; H, 6.00; N, 8.70; S, 6.63%; anal. C, 61.88; H, 5.70; N, 8.34; S, 6.52%; ^{1}H NMR: δ 1.2 (*t*, 12H), 2.6 (*s*, 3H), 3.4 (*q*, 8H), 6.6 (*d*, 2H), 7.4 (*d*, 1H), 7.6 (*d*, 1H), 8.3 (*s*, 1H), 8.7 (*s*, 1H).

h: Amine/yield = $CH_3O(CH_2)_3NH_2$/76%. m.p. 180–182 °C, M^+ 499, IR: ν 2974, 2929, 1743, 1620, 1505, 1353, 1162, 1135, 1085, 1080, 1029 cm^{-1}; Elemental analysis: calcd: C, 60.12; H, 5.81; N, 8.42; 5, 6.41%; anal. C, 59.9; H, 5.71; N, 8.31; S, 6.35%; ^{1}H NMR: δ 1.1 (*t*, 6H), 1.5 (*p*, 2H), 2.5 (*s*, 3H), 2.8 (*s*, 3H), 3.1 (*q*, 8H), 4.7 (*t*, 1H), 6.0 (*d*, 2H), 6.6 (*d*, 1H), 6.9 (*s*, 1H), 7.4 (*s*, 1H), 7.7 (*s*, 1H).

2.3. Synthesis of type *IV* coumarins

The target coumarins were prepared with the aid of a published method [8]. The procedure used to prepare **IVa** is as follows: NaCN (1.0 g, 0.02 mol) was added to a solution of dye **IIIa** (4.7 g, 0.01 mol) in DMF (32 ml) in a 100 ml three-necked flask. The reaction mixture was stirred at 45 °C for 1 h, cooled to 0 °C, and Br_2 (1.4 g, 0.011 mol) was added dropwise over 2 h. The product was collected by filtration, washed with ethanol, and dried to give compound **IVa.**

Yield = 72%; m.p. 196–198 °C, M^+ 494; IR: *v* 2974, 2927, 2229, 1733, 1621, 1508, 1355, 1162, 1148, 1078 cm^{-1}; elemental analysis: calcd: C, 60.73; H, 5.26; N, 11.34; S, 6.48%; anal. C, 60.98; H, 5.30; N, 11.02; S, 6.21%; ^{1}H NMR: δ 1.2 (*t*, 12H), 3.3 (*q*, 8H), 6.6 (*d*, 2H), 7.7 (*d*, 1H), 7.9 (*d*, 2H), 8.3 (*s*, 1H).

Compounds **IVb–h** were prepared according to the method reported above for **IVa.**

b: Amine/yield = $CH_3O(CH_2)_3NH_2$/68%; m.p. 238–240 °C, M^+ 510; IR: v 2969, 2926, 2228, 1734, 1621, 1520, 1352, 1146, 1145, 1075 cm^{-1}; elemental analysis: calcd: C, 58.82; H, 5.10; N, 10.98; S, 6.27%; anal. C, 58.61; H, 5.15; N, 10.83; S, 6.32%; ^{1}H NMR: δ1.1 (*t*, 6H), 1.2 (*p*, 2H), 2.5 (*s*, 3H), 3.5 (*q*, 8H), 3.9 (*t*, 1H), 6.6 (*d*, 2H), 7.1 (*d*, 1H), 7.7 (*d*, 2H), 8.2 (*s*, 1H).

c: Amine/yield = $(C_2H_5)_2NH$/70%; m.p. 228–230 °C, M^+ 510; IR: *v* 2969, 2927, 2230, 1734, 1621, 1508, 1355, 1148, 1146, 1078 cm^{-1}; elemental analysis: calcd: C, 58.82; H, 5.10; N, 10.98; S. 12.55%; anal. C, 58.47; H, 5.17; N, 10.61; S, 12.01%; ^{1}H NMR: δ 1.1 (*t*, 12H), 3.3 (*q*, 8H), 6.6 (*d*, 2H), 7.7 (*d*, 1H), 7.9 (*d*, 2H), 8.3 (*s*, 1H).

d: Amine/yield = $CH_3O(CH_2)_3NH_2$/71%; m.p. 236–238 °C, M^+ 526; IR: v 2969, 2927, 2230, 1734, 1621, 1508, 1355, 1148, 1146, 1079, 1078 cm^{-1}; elemental analysis: calcd: C, 57.03; H, 4.94; N, 10.65; S, 12.17%; anal.: C, 56.96; H, 4.91; N, 10.55; S, 12.08%; ^{1}H NMR: δ 1.1 (*t*, 6H), 1.2 (*p*, 2H), 2.5 (*s*, 3H), 3.5 (*q*, 8H), 3.9 (*t*, 1H), 6.6 (*d*, 2H), 7.1 (*d*, 1H), 7.7 (*d*, 2H), 8.2 (*s*, 1H).

e: Amine/yield = $(C_2H_5)_2NH$/70%; m.p. 243–245 °C, M^+ 493; IR: *v* 2976, 2929, 2227, 1702, 1619, 1527, 1354, 1182, 1135, 1079, 1029 cm^{-1}; elemental analysis: calcd: C, 60.85; H, 5.48; N, 14.20; S, 6.54%; anal. C, 60.34; H, 5.54; N, 13.97; S, 6.12%; ^{1}H NMR: δ 1.1 (*t*, 12H), 3.3 (*q*, 8H), 6.6 (*d*, 2H), 7.8 (*d*, 1H), 7.9 (*d*, 2H), 8.3 (*s*, 1H), 9.2 (*s*, 1H).

f: Amine/yield = $CH_3O(CH_2)_3NH_2$/48%; m.p. 278–280 °C, M^+ 509; IR: *v* 2974, 2928, 2227, 1704, 1618, 1523, 1353, 1190, 1148, 1079, 1029 cm^{-1}; elemental analysis: calcd: C, 58.94; H, 5.30; N, 13.75; S, 6.29%; anal.: C, 58.88; H, 5.40; N, 13.31; S, 6.32%; ^{1}H NMR: δ 1.1 (*t*, 6H), 1.2 (*p*, 2H), 2.5 (*s*, 3H), 3.5 (*q*, 8H), 3.9 (*t*, 1H), 6.6 (*d*, 2H), 7.1 (*d*, 1H), 7.7 (*d*, 2H), 8.2 (*s*, 1H), 9.1 (*s*, 1H).

g: Amine/yield = $(C_2H_5)_2NH$/72%; m.p. 177–179 °C, M^+ 508; IR: *v* 2974, 2927, 2229, 1733, 1621, 1508, 1355, 1148, 1141, 1078 cm^{-1}; elemental analysis: calcd: C, 61.42; H, 5.51; N, 11.02; S, 6.30%; anal.: C, 61.12; H, 5.42; N, 10.60; S, 6.01%; ^{1}H NMR: δ 1.2 (*t*, 12H), 2.6 (*s*, 3H), 3.4 (*q*, 8H), 6.6 (*d*, 2H), 7.5 (*d*, 1H), 7.6 (*d*, 1H), 8.3 (*s*, 1H).

h: Amine/yield = $CH_3O(CH_2)_3NH_2$/69%; m.p. 170–172 °C, M^+ 524; IR: *v* 2969, 2926, 2228, 1734, 1621, 1520, 1353, 1146, 1145, 1075 cm^{-1}; elemental analysis: calcd: C, 59.54; H, 5.34; N, 10.69; S, 6.11%; anal.: C, 59.49; H, 5.41; N, 10.60; S, 6.15%; ^{1}H NMR: δ 1.1 (*t*, 6H), 1.5 (*p*, 2H), 2.5 (*s*, 3H), 2.8 (*s*, 3H), 3.1 (*q*, 8H), 4.7 (*t*, 1H), 6.0 (*d*, 2H), 6.6 (*d*, 1H), 7.4 (*s*, 1H), 7.7 (*s*, 1H).

3. Results and discussion

3.1. Coumarin dye synthesis

Representative results from the preparation of coumarin dyes are given in Tables 1 and 2. Varying heteroatom X and substituent R in type **V** coumarins required the reaction conditions shown in Table 1, to optimise the chlorosulfonation step. Chlorosulfonation was easier when R was not a ring-deactivating group but it did not take place when R was NO_2. Following the chlorosulfonation step condensation with different *N*-alkyl amines gave yields in the 58–86% range (Fig. 2, Table 2). As would be expected, the reaction yields decreased as the size of the alkylamine increased.

Cyanation of coumarins with NaCN (cf. Fig. 1) was carried out in DMF according to a published method [8]. In order to optimize the reaction conditions, the influence of solvent type, temperature, and amount of NaCN on product formation was

Table 1
Reaction conditions for the chlorosulfonation of coumarins **V**[a]

Coumarin	X	R	Reaction temperature (°C)	Reaction time (h)	Yield (%)
Vc	NH	H	120	2.0	98
Vb	S	H	120	2.5	98
Va	O	H	130	3.5	98
Vd	O	CH_3	120	3.0	98
Ve	O	Cl	154	10	40
Vf	O	NO_2	Reflux	No reaction	–

[a] Reaction was followed by TLC (silica gel), using benzene:acetone:ethanol:hexane (7:1:1:1).

Table 2
Reaction yields and melting points for type **VI** coumarins

Dye	R_5	R_6	Yield (%)	m.p. (°C)
VIa	CH_3	CH_3	85	252–254
VIa	C_2H_5	C_2H_5	86	232–234
VIa	H	$(CH_2)_3OCH_3$	73	217–219
VIa	H	$(CH_2)_3OCH(CH_3)_2$	70	180–182
VIa	H	$(CH_2)_3O(CH_2)_5CH(CH_3)_2$	58	176–178

Table 3
Effects of NaCN levels on the cyanation of type **V** coumarins

NaCN/coumarin ratio	Yield (%)	Purity (% HPLC)
1.5	62	91.5
2.0	72	98.9
2.5	72	98.8

studied by TLC and HPLC. It was found that the amount of NaCN had the principal effect on yield and that the optimum NaCN to coumarin ratio was 2:1 (cf. Table 3). We also found that product quality decreased when the reaction temperature exceeded 70 °C.

3.2. Electronic spectra

All of the dyes exhibited typical coumarin absorption at 270–288 nm and a separate absorption in the visible region. Electronic spectral data for dyes **III–V** are shown in Table 4.

Comparing the λ_{max} and molar extinction coefficients (ε_{max}) of dye **Va** with **IIIa** and **b,** dye **Vb** with **IIIc** and **d,** dye **Vc** with **IIIe** and **f,** and dye **Vd** with **IIIg** and **h,** it can be seen that the presence of an *N*alkylsulfonamide group afforded a bathochromic shift of ~10 nm and a significant hyperchromic effect. Comparisons involving **IIIa** with **IIIb, IIIc** with **IIId, IIIe** with **IIIf,** and **IIIg** with **IIIh** indicated that the nature of alkyl groups R_5 and R_6 had little effect on λ_{max} and ε_{max}, as would be expected. Similar results were obtained when coumarin dyes that have a CN group in the 4-position were compared. Comparing dyes **Va–d** with **Ve** and **II** indicated that an electron-attracting group does not produce a bathochromic effect. In fact, the dye with a NO_2 group was not fluorescent.

3.3. Emission spectra

Fluorescence spectra were recorded by exciting dye solutions at their λ_{max} in the visible region. The relative fluorescence intensities were evaluated at dye concentration of 10^{-7} mol/l, using the intensity of dye **IIIa** as the reference value (1.0). Comparing the λ_{ex} and λ_{em} for dyes **Va–d** with dyes **IIIa–h** , it can be seen that the *N*-alkylsulfonamide substituent caused a 10-nm bathochromic shift but had little effect on fluorescence intensity.

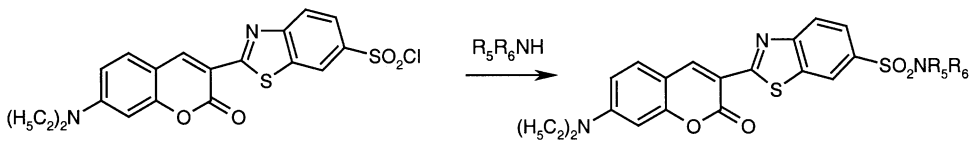


Fig. 2. Synthesis of type **VI** coumarins.

Table 4
Electronic spectra of dyes **III–V** in chloroform

Dye	λ_{max} (nm)	ε_{max} (l mol$^{-1}\times10^{9}$ cm^{-1})	λ_{ex}[a] (nm)	λ_{em}[a] (nm)	Relative fluourescence intensity
Va	448	5.3	450	477	1.0
Vb	465	5.2	467	489	1.4
Vc	457	4.8	467	494	1.1
Vd	450	5.0	450	479	1.1
Ve	453	5.6	458	480	0.96
Vf	453	3.6	–	–	–
IIIa	458	6.1	462	483	1.1
IIIb	459	6.0	462	484	1.1
IIIc	474	6.4	468	497	1.5
IIId	474	6.3	468	497	1.4
IIIe	461	5.8	483	501	1.2
IIIf	461	5.9	462	499	1.0
IIIg	460	5.9	462	499	1.1
IIIh	460	5.8	462	499	1.0
IVa	516	4.1	541	572	1.0
IVb	517	3.0	540	570	1.0
IVc	546	4.4	553	580	1.2
IVd	547	4.1	553	580	1.1
IVe	541	3.8	547	573	1.0
IVf	541	4.3	547	573	0.95
IVg	516	4.5	541	572	1.0
IVh	515	3.8	541	572	1.0

[a] em = emission; ex = excitation.

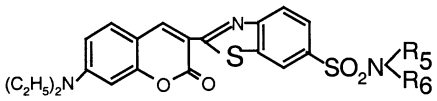
3.4. Coumarin solubility

Dye solubility was measured in 50 ml of solvent (methanol, $CHCl_3$) at room temperature. Using dye **Vb** as the reference compound, the effects of *N*-alkylsulfonyl group size on solubility are shown in Table 5. As expected, the compounds with the longer carbon chain lengths had greater solubility in $CHCl_3$ than CH_3OH. Results were essentially the same for the others series coumarins.

3.5. Dyeing and fastness properties

The application of coumarin dyes to polyester fabric (0.4 denier) gave greenish-yellow to orange shades. The associated % exhaustion and fastness

Table 5
Type **VI** coumarin solubiliy as a function of *N*-alkyl group size versus coumarin **Vb**[a]



VI

Solvent	**Vb**	CH_3 $^2CH_3$[b]	C_2H_5 $^2C_2H_5$[b]	H $^2(CH_2)_3O$ CH_3[b]	H $^2(CH_2)_3O$ C_2H_5[b]	H $^2(CH_2)_3O$ C_4H_9[b]	H $^2(CH_2)_3O$ C_4H_9[b]	H $_2(CH_2)_3O$ C_8H_{17}[b]
CH_3OH	0.01	0.05	0.06	0.01	0.02	0.02	0.1	6.8
$CHCl_3$	0.4	0.8	0.98	0.2	0.65	2.5	4	14.8

[a] Values are g dye/50 ml solvent.
[b] R_5 and $^2R_6$ for type **VI** coumarins.

Table 6
Exhaustion (Exh.). (%) and fastness properties of dyes **IIIa–h** and **Va–d**

Dye	Exh.	Fastness properties												
		Boiling in soap solution			Acid perspiration			Alkali perspiration			Sublimation at 180 °C			
		Loss in depth	Staining of adjacent fibre		Loss in depth	Staining of adjacent fibre		Loss in depth	Staining of adjacent fibre		Loss in depth	Staining of adjacent fibre		Light
			Polyester	Cotton		Polyester	Cotton		Polyester	Cotton		Polyester	Cotton	
Va	98.4	4–5	4–5	4–5	4–5	4	4–5	4–5	4–5	4	3–4	3	3–4	3
Vb	47.6	4–5	4–5	4–5	4	4	4	4	4	4–5	3–4	3–4	4	3
Vc	92.8	4–5	4–5	4–5	4	4	4–5	4–5	4–5	4	3–4	3–4	4	2
Vd	94.7	4–5	4–5	4–5	4–5	4–5	4	4–5	4	4–5	3	3	3	3
IIIa	83.0	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4	4
IIIb	45.7	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4
IIIc	84.2	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4–5	4
IIId	90.5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4
IIIe	41.8	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4
IIIf	48.4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4
IIIg	91.2	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4	3–4
IIIh	95.0	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4	4–5	4–5	4

properties are given in Table 6. The sublimation and light fastness of dyes were enhanced 1–2 units by adding an *N*-alkylsulfonamide group.

4. Conclusion

Introducing an *N*-alkylsulfonamide group into the 3-position of coumarin dyes produces bathochromic and hyperchromic effects and enhances fastness to light and sublimation. It is likely that improving their solubility in organic solvents would enhance their commercial utility.

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