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The Influence of Chain Length and Electron Acceptor Residues in 3-Substituted 7-*N*,*N*-Diethylaminocoumarin Dyes

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ABSTRACT

*Several 7-*N,N*-diethylaminocoumarin dyes with vinylogously extended electron acceptor groups in the 3-position have been prepared by condensing the 3-aldehyde with various active methylene compounds. Structures vary according to both the nature of the electron withdrawing moiety and the length of the conjugation pathway between the 7-amino group and the electron acceptor residue. Dyes with colours ranging from red to cyan have been prepared, and their light absorption properties are discussed in terms of the electron acceptor and the extent of conjugation. Steric factors play a major role in influencing the colour properties, and this was exemplified in one extreme case where lengthening the conjugation chain by one vinyl unit caused a hypsochromic shift due to increased steric interactions. In general, the vinylogous donor–acceptor coumarin dyes were not as fluorescent as the more conventional 7-dialkylaminocoumarins which have a shorter conjugation path between the amino group and the 3-acceptor group. Two cationic dyes have been prepared by condensation of the coumarin aldehyde with enamines, and these show typical cyanine dye characteristics, with intense long wavelength absorption.*

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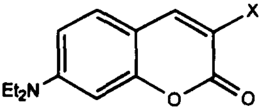

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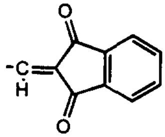

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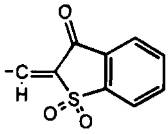

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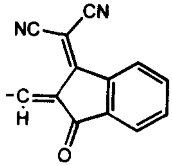

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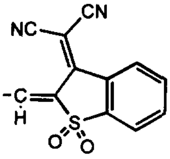

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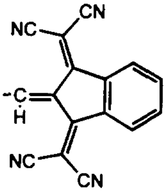

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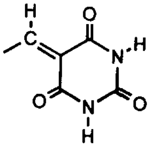

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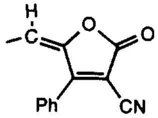

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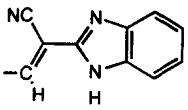

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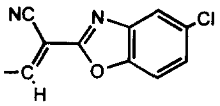

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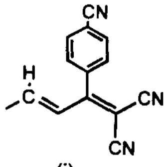

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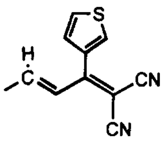

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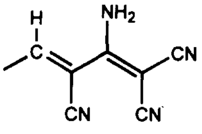

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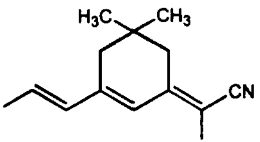
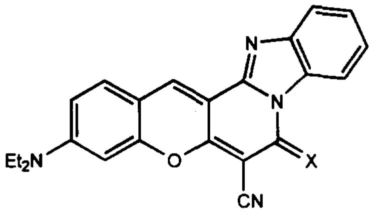


(m)

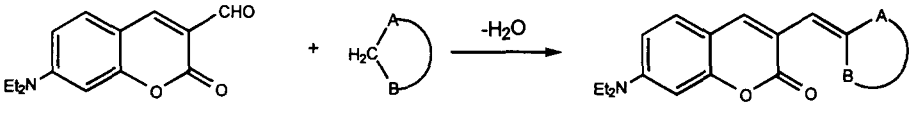
1 INTRODUCTION

7-Aminocoumarins **1**, in which *X* is an electron withdrawing group, are an important group of fluorescent dyes which can be regarded conveniently as styryl dyes in which the vinyl group has been 'rigidised' by inclusion in a fused six-membered lactone ring. It is well known that the effects of such rigidisation on λ_{max} values are relatively small, but that there is a pronounced increase in fluorescence efficiency. The absorption band width is also small, and thus the coumarins are intrinsically bright dyes even without the added effect of fluorescence. The absorption colour of compounds **1** where *X* is a simple acceptor residue is usually yellow, and the dyes show green fluorescence. Dyes with more bathochromic absorption colours can be produced by extending the conjugation length of *X*, but these have received much less attention. Although examples have been described in the patent literature, structure–spectra relationships have not been investigated. Commercial dyes of this type are rare, and at present it appears that the two red dyes **2a** and **2b** (CI Disperse Red 374 and 277 respectively) have been the only ones to achieve commercial importance. Even these can only loosely be regarded as coumarins, having in fact a more extended polycyclic chromophoric system than implied by structure **1**.



2 a, X = O
b, X = NH

Dyes **1** are typical donor–acceptor chromophores and as such should show a pronounced dependence of λ_{max} on both the electron withdrawing strength of group *X* and on the length of the conjugation pathway between the amino donor group and *X*. Thus bathochromic shifts should be readily obtained by increasing both variables. However, there are likely to be secondary effects from such structural changes, particularly an increase in absorption band width if there is greater molecular flexibility, and a corresponding loss of fluorescence efficiency, which would negate the intrinsic brightness advantages of the system. It was therefore of interest to examine a range of dyes of type **1** in which the electron withdrawing strength and the degree of conjugation of group *X* were progressively increased, in order to evaluate the influence of these variables on colour properties. Some coumarin cyanine-type chromophores were also examined, in which *X* carries a formal positive charge shared with the 7-amino group of the coumarin residue.



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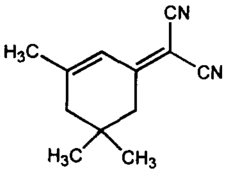
Scheme 1

2 RESULTS AND DISCUSSION

2.1 Synthesis of intermediates and dyes

The donor–acceptor dyes **1a–m** were synthesised by condensing 7-*N*,*N*-diethylamino-3-formylcoumarin **3** with the appropriate active methylene compound as shown in Scheme 1. The aldehyde **3** was prepared by Vilsmeier formylation of 7-*N*,*N*-diethylaminocoumarin. In most instances the reactions with **3** could be effected smoothly in refluxing ethanol containing a small amount of piperidine/acetic acid as catalyst, but in some cases best results were obtained with no acetic acid, or with no catalyst at all. A few reactions could not be carried out successfully in ethanol, and the dyes were prepared by using acetic anhydride as the reaction medium. The vinylogous dye **1m** was obtained by condensing the active methylene compound **4** with **3**. The requisite intermediate **4** was obtained from isophorone and malononitrile.[1] The basic dye **5** was obtained by condensation of the azaindole active methylene intermediate **6**[2] with **3**. All dyes were purified either by recrystallisation from ethanol, or by column chromatography over silica with dichloromethane as eluent. Reaction conditions, yields and characterisation data are summarised in Table 1. Dyes **1b** and **1d** have been described previously by Shenoy *et al.*,[3] but as microanalytical results were not reported, these are now given in Table 1.

The synthesis of cationic cyanine-type dyes was effected by condensing the coumarin aldehyde **3** with suitably nucleophilic unsaturated systems containing amino functionality. The quaternary salt **7** was synthesised by



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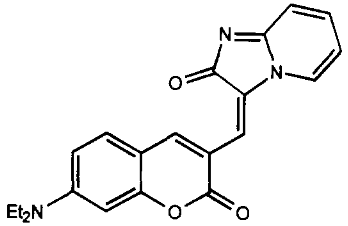

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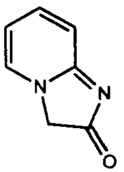

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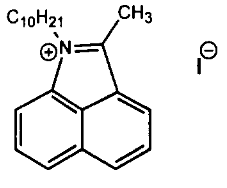
TABLE 1
Preparative and Characterisation Data for Coumarin Dyes

Dye	*Method*[a]	*Yield (%)*	*M.p. (°C)*	*Characterisation data*
1a	A	89	224–225	Found: C, 74·2; H, 5·25; N, 3·55%. $C_{23}H_{19}NO_4$ requires C, 74·0; H, 5·1; N, 3·75%
1b	B	86	228–229	Found: C, 64·5; H, 4·6; N, 3·3%. $C_{22}H_{19}NO_5S$ requires C, 64·5; H, 4·7; N, 3·4%
1c	A	69	213–215	Found: C, 73·5; H, 4·4; N, 10·1%. $C_{26}H_{19}N_3O_3$ requires C, 74·1; H, 4·5; N, 10·0%
1d	A	57	205–206	Found: C, 65·3; H, 4·2; N, 9·1%. $C_{25}H_{19}N_3O_4S$ requires C, 65·6; H, 4·2; N, 9·2%
1e	C	48	204–206	Found *m/z* = 470 (M + 1). Calculated $C_{29}H_{19}N_5O_2$ *m/z* = 469.
1f	D	88	252–253	Found: C, 60·8; H, 4·8; N, 11·6%. $C_{18}H_{17}N_3O_5$ requires C, 60·9; H, 4·8; N, 11·8%
1g	D	94	278–279	Found: C, 72·1; H, 4·8; N, 6·6%. $C_{25}H_{20}N_2O_4$ requires C, 72·8; H, 4·9; N, 6·8%
1h	C	93	264–265	Found: C, 71·8; H, 5·0; N, 14·6%. $C_{23}H_{20}N_4O_2$ requires C, 71·8; H, 5·2; N, 14·5%
1i	B	82	267–270	Found: C, 65·6; H, 4·4; N, 10·0%. $C_{28}H_{18}N_3O_3Cl$ requires C, 65·6; H, 4·6; N, 10·0%
1j	A	79	249–251	Found: C, 74·2; H, 4·7; N, 13·5%. $C_{26}H_{20}N_4O_2$ requires C, 74·3; H, 4·8; N, 13·3%
1k	A	82	253–254	Found: C, 68·8; H, 4·8; N, 10·6%. $C_{23}H_{19}N_3O_2S$ requires C, 68·8; H, 4·8; N, 10·5%
1l	A	87	246–247	Found: C, 66·8; H, 4·7; N, 19·6%. $C_{20}H_{17}N_5O_2$ requires C, 66·9; H, 4·7; N, 19·5%
1m	E	60	204–205	Found: C, 75·4; H, 6·6; N, 10·2%. $C_{26}H_{27}N_3O_2$ requires C, 75·5; H, 6·6; N, 10·2%
5	C	89	259–260	Found: C, 63·0; H, 5·2; N, 10·6%. $C_{21}H_{20}N_3O_3Cl$ requires C, 63·4; H, 5·0; N, 10·4%
8[b]	A	76	169–170	Found *m/z* = 536 (M + 1). Calculated for $C_{36}H_{43}N_2O_2$ *m/z* = 535.
9[c]	B	79	—	Found: C, 79·6; H, 7·6; N, 7·3%. $C_{38}H_{43}N_3O_2$ requires C, 79·4; H, 7·7; N, 7·3% Found *m/z* = 573. Calculated *m/z* = 573.

[a] See experimental section for details.

[b] As the iodide salt.

[c] As the *leuco* base.



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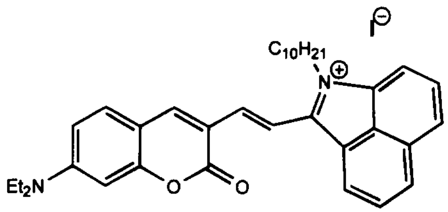

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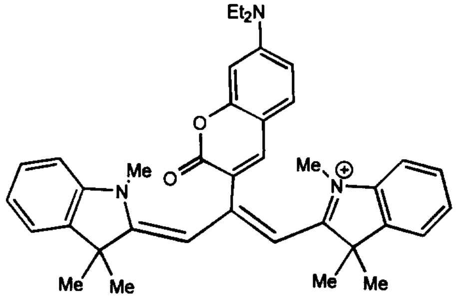

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N-alkylation of naphthostyril with 1-bromodecane under phase transfer conditions, followed by reaction with methylmagnesium iodide.[4] Reaction of the quaternary salt **7** with **3** in ethanol using a small amount of piperidine/acetic acid as catalyst gave the cationic dye **8**. However, in an attempt to produce an analogous cyanine dye from **3** and Fischer's base only the trinuclear cyanine dye **9** could be isolated, even when **3** was present in excess. The dye was initially isolated as the yellow *leuco* base, but was rapidly air-oxidised in acidic solution to the green cationic form **9**. Preparative and characterisation data for the cationic dyes are summarised in Table 1.

2.2 Light absorption and fluorescence properties

The visible absorption spectra of the neutral donor–acceptor dyes **1a–m** were measured in dichloromethane and in toluene in order to assess the degree of solvatochromism in these chromophores (Table 2). Fluorescence spectra were measured in dichloromethane, and emission maxima (uncorrected) are also summarised in Table 2. In general the dyes had low fluorescence efficiency in comparison with typical commercial coumarin fluorescent dyes, and a qualitative assessment of their relative fluorescence efficiencies is given, based on observed emission intensities under approximately equal excitation conditions. None showed strong fluorescence in daylight, but in most cases fluorescence could readily be detected instrumentally. A few dyes showed extremely weak fluorescence.

TABLE 2
Light Absorption and Emission Properties of Coumarin Dyes **1a–m**

Dye	λ_{max} (CH_2Cl_2) (nm)	ε_{max} (CH_2Cl_2) ($l\ mol^{-1}\ cm^{-1}$)	$\Delta\lambda_{1/2}$ (CH_2Cl_2) (nm)	λ_{max} (toluene) (nm)	$\Delta\lambda$ (CH_2Cl_2/toluene) (nm)	λ_{max} (fluorescence) (CH_2Cl_2) (nm)	*Relative fluorescence efficiency*
1a	545	83100	64	535	+10	587	moderate
1b	546	80500	62	536	+10	589	moderately high
1c	602	58200	90	583	+19	631	low
1d	624	57100	102	604	+20	652	very low
1e	601	50700	102	588	+13	642	moderate
1f	544	76400	56	526	+18	603	low
1g	574	43800	97	564	+10	625	moderate
1h	507	56500	85	492	+15	588	low
1i	532	49700	92	506	+26	576	moderate
1j	539	43800	92	527	+12	602	moderate
1k	529	35700	94	514	+15	529	moderate
1l	531	42800	104	513	+18	546	moderately high
1m	515	34400	112	509	+6	614	moderate

Consideration of the absorption λ_{max} values (Table 2) shows that for the neutral donor–acceptor chromophores **1a–g** which have the same conjugation pathlength between the donor and the acceptor groups, and in which the acceptor unit forms a five- or six-membered ring, the λ_{max} value is influenced strongly by the nature of the electron acceptor residue itself in a predictable manner. Thus dye **1a** containing the relatively weak 1,3-indandione acceptor residue is purple (λ_{max} 545 nm in dichloromethane), and as the 1,3-indandione residue is replaced by progressively stronger electron withdrawing residues (**1b**, **1c** and **1d**), the λ_{max} value is shifted bathochromically, giving ultimately the cyan dye **1d** (λ_{max} 624 nm in the same solvent). Shenoy *et al.*[4] have reported λ_{max} 628 nm for this dye in DMF. It is perhaps surprising that dye **1e** with an even stronger electron acceptor residue absorbs at shorter wavelengths than **1d**. However, modelling clearly shows the greater steric crowding in **1e** resulting in reduced molecular planarity, and as a consequence the dye has a lower extinction coefficient than **1d** and the band is displaced to shorter wavelengths.

There is a clear correlation between the steric requirement of the acceptor groups in dyes **1a–g** and molar extinction coefficient, and those dyes which on the basis of molecular modelling are the most planar, i.e. **1a**, **1b** and **1f** have values in the range 76400–83100 $l\ mol^{-1}\ cm^{-1}$, which compare favourably with typical values for analogous unhindered coumarin and styryl dyes with one less vinyl group. The same pattern is found for half-band widths (Table 2), and the less planar the dye, the larger the half-band width. Fluorescence efficiency does not appear to be simply related to the molar absorption coefficient, as exemplified by comparing **1b** with **1j**, **1k** and **1l**. Although dye **1b** with one of the highest ε_{max} values is perhaps the most fluorescent dye listed in Table 2, dyes **1j**, **1k** and **1l** are almost equally fluorescent and yet have ε_{max} values only about one half that of **1b**. Nor does a narrow band width seem to be a prerequisite for high fluorescence efficiency, as **1j**, **1k** and **1l** have much larger half-band widths than **1b**.

As might be expected, the neutral donor–acceptor dyes **1a–m** show a modest bathochromic shift of the absorption band between the solvents toluene and dichloromethane, i.e. a positive solvatochromism, which indicates an increased dipolar character of the chromophores in the excited state. The solvatochromic effect increases with increasing strength of the electron acceptor residue.

The neutral donor–acceptor dyes **1h–m** differ from **1a–g** in that the electron accepting units have greater flexibility, and in the event of steric interactions can move out of conjugation with the main 3-vinylcoumarin system by facile rotation about a single bond. Thus the molecules will be more responsive to steric crowding. In addition, the molecules can exist in various *cis–trans* conformations in solution, and the combined effect of these possibilities should lead to lower molar absorption coefficients, reduced bathochromic shifts, and lower fluorescence efficiency. Consideration of the data in Table 2 confirms these predictions, with the possible exception of dye **1h**, and dyes **1i–l** have ε_{max} values in the range 35700–49700 l mol^{-1} cm^{-1}, significantly lower than the values for dyes **1a–f**. However, absorption half-band widths of the second series are in general of similar magnitude to those of the hindered dyes of the first series, and it was rather surprising therefore to find that the dyes **1g–l** in general had similar or higher fluorescence efficiencies than dyes **1a–f**.

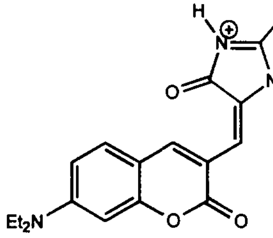
The higher ε_{max} value for the benzimidazole dye **1h** compared with the closely related benzoxazole dye **1i** is notable, but this may be attributed to the narrower absorption band of **1h**. The dyes **1h–l** show a more restricted colour range than the first series, and colours range from red to purple (λ_{max} 507–531 nm in dichloromethane), but they show a positive solvatochromism of similar magnitude.

It is interesting to compare the dyes **1j** and **1k** with dye **1l**. All three have the same number of vinyl groups in the chromophoric chain, and also have a dicyanovinyl acceptor residue at the end of the chain. However, whereas **1j** and **1k** have an aromatic residue attached to the dicyanovinyl group, which is known to have a minimal effect on colour, dye **1l** has an amino group in that position. The amino group would be expected to cause a large hypsochromic shift of the absorption band, as it will reduce the electron withdrawing effectiveness of the dicyanovinyl group. However, the λ_{max} value for dye **1l** (531 nm in dichloromethane) is very close to the values for **1j** and **1k** (539 and 529 nm respectively). The ε_{max} values also do not differ significantly. It can be concluded therefore that the electron withdrawing effect of the additional cyano group in the chromophoric chain of dye **1l** compensates completely for the electron donating effect of the amino group attached to the dicyanovinyl group.

Further information about the effect of increased chain length between the coumarin ring and the acceptor residue was obtained from dye **1m**. In this case the dicyanovinyl group is separated from the coumarin ring by two conjugated double bonds. To minimise chain flexibility one of the double bonds is included in a six membered ring. Dye **1m** can be compared directly with dyes **1j** and **1k** which contain one fewer double bond, as the aryl residues in these dyes attached to the dicyanovinyl group have only a minimal effect on λ_{max}. Dye **1m** has an absorption band at slightly *shorter* wavelengths than both **1j** and **1k**, (λ_{max} in dichloromethane 515 nm compared with 539 and 529 nm, respectively), and has a lower ε_{max} value and larger half-band width (Table 2). Clearly there is considerable additional steric crowding in **1m**, which can be attributed to the dimethylcyclohexane ring system. Thus, although this chain-bridging ring introduces some measure of rigidity, models show that it also results in significant twisting of the polymethine chain. Combined with the very small vinylene shift to be expected for donor–acceptor dyes with such a large chain length, the overall result is a small hypsochromic shift relative to **1j** and **1k**.

The basic dye **5** showed an interesting dependence of its absorption spectrum on pH. When isolated from basic solution with the neutral structure shown, it was red in colour (λ_{max} 522 nm in dichloromethane, ε_{max} 38200 l mol^{-1} cm^{-1}). In ethanol the λ_{max} was displaced to 518 nm and on addition of acid a blue colour developed (λ_{max} 585 nm). The large halochromic shift can be attributed to the formation of the protonated species **10**. The positive charge, which is not directly conjugated with the coumarin amino group, increases the electron withdrawing strength of the heterocyclic acceptor unit and so induces a large bathochromic shift. The dye **1h** also shows halochromism, although stronger acid conditions are needed to bring this about. Thus the red solution in ethanol (λ_{max} 497 nm) turned violet (λ_{max} 560 nm) on addition of a small amount of hydrochloric acid.

The 'ultimate' electron acceptor group *X* that could be introduced into



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a dye of general structure **1** would have a positively charged nitrogen atom in direct conjugation with the 7-amino group of the coumarin residue. This would result in a cyanine-type chromophore, where the positive charge would be more or less equally shared by the two nitrogen atoms. The resultant increase in electronic symmetry should in theory provide a large bathochromic shift, a narrow absorption band, and a high molar absorption coefficient. The dipolar character of the chromophore should also disappear and thus solvatochromism should be minimal. Cyanine-type dyes with 7-aminocoumarin residues do not appear to be known and thus syntheses of representative examples were examined.

The reactive salt **7** was first used to produce the dye **8**. The benz[*cd*]indole residue is known to be one of the most effective terminal groups for producing bathochromic shifts in cyanine dyes,[5,6] and the resultant dye **8** did in fact prove to be the most bathochromic of those made, with a λ_{max} of 696 nm in dichloromethane. The electronic symmetry of this chromophore was indicated by the minimal solvatochromism of the dye (a hypsochromic shift of 2 nm from toluene to dichloromethane). Also in accord with expectation, the dye had a high molar absorption coefficient and a narrow half-band width (75100 $l\ mol^{-1}\ cm^{-1}$ and 78 nm respectively in dichloromethane).

When synthesis of the corresponding cyanine dye derived from **3** and Fischer's base was attempted, only the trinuclear cyanine **9** could be isolated. This was insoluble in toluene but gave a green solution in dichloromethane (λ_{max} 600 nm, half-band width 102 nm), with a secondary weaker band at 400 nm. The chromophore cannot be planar and could adopt one or more conformations to minimise steric crowding. The intense absorption band at 600 nm is not consistent with a nearly planar chromophore involving the two indoline rings alone, as the analogous symmetrical trimethine dye from Fischer's base has a λ_{max} value of only 545 nm in ethanol. It thus appears more likely that the aminocoumarin residue is strongly conjugated with one of the indoline rings, the additional conjugation length providing the observed bathochromic shift. The second

TABLE 3
Photostability of Dyes **1a–m** in Cellulose Diacetate Film[a]

Dye	*Extent of photodegradation*[b] *(%)*
Standard[c]	6
1a	84
1b	37
1c	62
1f	25
1g	56
1i	11
1j	38
1k	47
1l	12
1m	100

[a] Dyes **1d** and **1e** decomposed in the film on storage in the dark. Dye **1h** underwent facile protonation during film preparation (colour change red to blue) and could not be tested in the neutral form.

[b] After 72 h exposure in a Microscal fadeometer.

[c] 2-(4'-*N*,*N*-diethylaminophenylazo)-5-nitrothiazole.

indoline residue would then be twisted partly out of conjugation with the main chromophore.

2.3 Stability properties of the dyes

None of the coumarin dyes synthesised were suitable for textile applications, and under typical aqueous dyeing conditions they tended to undergo a reverse Knoevenagel reaction with gradual loss of colour. The potential of the dyes as colorants for plastics was also examined, as aqueous stability is unimportant for such applications. To obtain information about photochemical stability in polymers, transparent films of cellulose diacetate were cast containing the dyes in sufficient concentration to give absorbance values (at λ_{max}) in the range 0·7–2·0. The absorbance values were measured before and after 72 h exposure in a Microscal fadeometer under ambient conditions. As a reference standard the blue azo dye 2-(4'-*N*,*N*-diethylaminophenylazo)-5-nitrothiazole was used, which was similarly dissolved in cellulose acetate film to give an absorbance value of 0·82. The extent of degradation in each case was determined, and the results are summarised in Table 3. In almost every case the lightfastness of the dyes was significantly inferior to that of the standard azo dye, which itself is not an exceptionally fast dye for coloration of plastics. Only the benzoxazole dye **1i** and dye **1l** had fastness values approaching that of the azo dye.

3 EXPERIMENTAL

3.1 Measurement of spectra

Visible absorption spectra were measured with a Perkin-Elmer Lambda 15 spectrophotometer. Fluorescence spectra were measured with a Perkin-Elmer LS5 spectrofluorimeter, using a red-sensitive detector, and are uncorrected. Relative fluorescence efficiencies were assessed by comparing emission intensity data, and taking into account the relative absorbances of each dye solution at the excitation wavelength. Efficiencies were graded arbitrarily as *high*, *moderately high*, *moderate*, *low* and *very low*. Using this assessment procedure, conventional fluorescent dyes such as **2a** and **2b** were classed as having high fluorescence efficiency.

3.2 General procedures for synthesis of coumarin dyes 1a–m, 5, 8 and 9

Method A

Equimolar amounts of 7-diethylamino-3-formylcoumarin **3** and the appropriate active methylene compound were heated in a small volume of ethanol under reflux in the presence of a few drops of piperidine/acetic acid catalyst (1:5 by volume). When the reaction was judged complete by thin layer chromatography the solvent was evaporated under reduced pressure and the product purified by recrystallisation from ethanol, or by column chromatography (silica/dichloromethane).

Method B

As for Method A but using piperidine alone as the catalyst.

Method C

Equimolar amounts of the coumarin aldehyde **3** and the active methylene compound were heated in a small volume of acetic anhydride on a water bath at 100°C until reaction was complete. The solution was added to water, stirred until the acetic anhydride had hydrolysed and the product was then filtered off and purified as in Method A.

Method D

As for Method A but without addition of catalyst.

Method E
As for method A, using methanol in place of ethanol.

Yields and characterisation data are summarised in Table 1.

3.3 Photostability measurements

Cellulose diacetate (1·0 g) was added to a mixture of dichloromethane (9 ml) and methanol (1 ml) with sufficient dye to give an absorbance in the final film in the range 0·7–2·0 at the λ_{max} of the dye. The mixture was stirred until a clear solution was obtained and the solution was applied to a clean glass plate using a TLC spreader providing a nominal wet film thickness of 0·5 mm. Immediately after coating the plate, a larger glass plate was placed over it, maintaining an air gap of *c.* 2 mm with the aid of microscope glass slide spacers. The top plate was heated with a hair dryer until a clear dry film was obtained, which could be peeled intact from the lower glass plate.

Small squares of the films (*c.* 2 × 2 cm) were taken and the absorbance values at λ_{max} of the dye recorded. They were then placed in a Microscal fadeometer at a fixed distance of 18 cm from the lamp and irradiated for 72 h. The absorbance values were then re-recorded and percentage degradation calculated from the decrease in absorbance value. In each experiment a film containing the blue dye 2-(4'-*N*,*N*-diethylaminophenylazo)-5-nitrothiazole was simultaneously irradiated as a reference standard. Relative degradation rates taken as an average of several determinations are shown in Table 3.

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