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Polycyclic Compounds Part VII. Synthesis, Laser Characteristics and Dyeing Behaviour of 7-Diethylamino-2H-1-benzopyran-2-ones*

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ABSTRACT

Several new 3-substituted benzoxazolyl/benzimidazolyl-7-diethylamino-2H-1-benzopyran-2-one laser dyes have been synthesized and their lasing characteristics evaluated. The spectral properties and dyeing characteristics of the new dyes are also discussed. The dyes **3b**, **3d** *and* **3g** *showed great promise as efficient laser dyes with strong possibilities of commercial exploitation. Moreover, the new dyes imparted brilliant greenish yellow shades on polyester, with moderate to good fastness properties, making them suitable for use as disperse dyes.*

1 INTRODUCTION

In a recent communication, we have established the structure of C.I. Disperse Yellow 232 as 3-(5′-chloro-2′-benzoxazolyl)-7-diethylamino-2H-1-benzopyran-2-one (**3g**)[1] and have also described the laser spectral properties of this fluorescent system. Substituted coumarin derivatives constitute a group of widely used laser dyes emitting in the blue-green region[2] and some members of this class are among the most efficient of currently known laser dyes. The presence of heterocyclic substituents such as those in dye **3g** may give rise to dyes with a wider range of optimum lasing wavelengths. In this communication, we report the synthesis of several new analogues **3a**–**f** of dye **3g** and their evaluation as laser dyes. The spectral properties and dyeing characteristics of the dyes are also discussed.

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2 EXPERIMENTAL

2.1 General

Melting points are uncorrected. UV-visible spectra were recorded on a Perkin-Elmer 350, and IR spectra on a Perkin-Elmer 137B (Connecticut, USA). ^{1}H-NMR spectra were run on Varian T-60 and Bruker WH-90 FT spectrometers in chloroform-D using 0·1% TMS (tetramethyl silane) as internal standard. The chemical shifts are expressed in ppm. Mass spectra were recorded on a CEC 21-110B (California, USA) or Finnigan MAT-1020 (Manchester, UK) automated GC/MS mass spectrometer at minimum source temperature. Fluorescence spectra were recorded on an SFM-25 Kontron (Zurich, Switzerland).

2.2 Preparation of the dyes 3—general procedure

A mixture of 7-diethylamino-2-oxo-2H-1-benzopyran-3-carboxylic acid ethyl ester (**1**) (0·001 mol) (previously described[1]), the appropriate 4-substituted *o*-aminophenol or *o*-phenylene diamine (0·001 mol), and polyphosphoric acid (1·0 g) was stirred at 180°C for 3 h in an inert atmosphere (nitrogen). The mixture was poured into ice-cold water (50 ml), the pH adjusted to 8·5 with 10% sodium carbonate solution, and the liquor extracted with chloroform (300 ml). The chloroform layer was washed with water and dried over anhydrous sodium sulphate. After removal of chloroform, the crude dye was purified by column chromatography.

2.3 Characterization and identification of dyes 3

3-(1H-benzimidazol-2′-yl)-7-diethylamino-2H-1-benzopyran-2-one, **3a**
Yellow needles from acetone: m.p. 240°C: yield, 84%; ν_{max} (cm^{-1}) (Nujol) 3370, 1690, 1610, 1590, 1530, 1430, 1350, 1250, 1150; ^{1}H-NMR (CDCl$_3$): 1·20 (6H, t, N—CH$_2$—CH$_3$), 3·40 (4H, q, N—CH$_2$—CH$_3$), 6·55 (1H, d, J = 2 Hz, 8-H), 6·66 (1H, d of d, 6-H), 7·20–7·32 (2H, m, 6′-H and 7′-H), 7·44 (2H, d, J = 9 Hz, 5′-H and 6′-H), 8·91 (1H, s, 4-H), 11·28 (1H, bs, NH exchangeable with D$_2$O); MS: *m/z* 333 (M$^+$, 92%), 318 (100), 303 (6), 289 (71), 261 (32),.233 (12), 205 (14), 167 (9), 159 (12). $C_{20}H_{19}N_3O_2$ requires C 72·07, H 5·71, N 12·61. Found: C 71·92, H 5·60, N 13·01.

3-[5′-Benzoyl(1H-benzimidazol-2′-yl)]-7-diethylamino-2H-1-benzopyran-2-one, **3b**

Yellow needles from chloroform: m.p. 265°C; yield 85%; ν_{max}(cm^{-1}) (Nujol), 3360, 1720, 1625, 1540, 1390, 1250, 1150; ^{1}H-NMR (CDCl$_3$): 1·24 (6H, t, N—

CH_2—$\mathbf{CH_3}$), 3·83 (4H, q, N—$\mathbf{CH_2}$—CH_3), 6·48 (1H, d, J = 2 Hz, 8-H), 6·68 (1H, d of d, 6-H), 7·00–8·17 (9H, m, Ar—H), 8·93 (1H, s, 8-H), 11·24 (1H, bs NH, exchangeable with D_2O); MS; *m/z* 437 (M^+, 100), 422 (94), 393 (27), 317 (70), 288 (24), 261 (22), 105 (64), 77 (63). $C_{27}H_{23}N_3O_3$ requires C 74·14, H 5·26, N 9·61. Found: C 73·92, H 5·45, N 9·62.

3-[5′-Chloro(1H-benzimidazol-2′-yl)]-7-diethylamino-2H-1-benzopyran-2-one, **3c**

Yellow needles from chloroform; m.p. 271°C; yield, 88%; ν_{max} (cm^{-1}) (Nujol), 3370, 1680, 1610, 1530, 1460, 1370, 1280, 1150; ^{1}H-NMR ($CDCl_3$): 1·20, (6H, t, N—CH_2—$\mathbf{CH_3}$), 3·40 (4H, q, N—$\mathbf{CH_2}$—CH_3); 6·53 (1H, d, J = 2 Hz, 8-H), 6·64 (1H, d of d, 6-H), 7·13 (1H, q, 6′-H), 7·40–7·71 (3H, m, 4′-H, 7′-H and 5-H), 8·84 (1H, s, 4-H), 11·24 (1H, bs, NH exchangeable with D_2O); MS: *m/z* 367 (M^+, 54%), 369 (M^+ + 2, 18), 352 (100), 339 (6), 323 (36), 295 (8). $C_{20}H_{18}N_3O_2Cl$ requires C65·39, H 4·99, N 11·44, Cl 9·53. Found: C 65·50, H 4·80, N 11·36, Cl 9·42.

3-[5′-Methyl(1H-benzimidazol-2′-yl)]-7-diethylamino-2H-1-benzopyran-2-one, **3d**

Yellow needles from methanol; m.p. 235°C; yield, 95%; ν_{max}(cm^{-1}) (Nujol) 3350, 1690, 1620, 1600, 1540, 1470, 1380, 1260, 1100; ^{1}H-NMR ($CDCl_3$): 1·24 (6H, t, N—CH_2—$\mathbf{CH_3}$), 2·46 (3H, s, Ar—CH_3), 3·44 (4H, q, N—$\mathbf{CH_2}$—CH_3), 6·48 (1H, d, J = 2 Hz, 8-H). 6·70 (1H, d of d, 6-H), 7·11 (1H, q, 6′-H), 7·20–7·62 (3H, m, 4′-H, 7′-H and 5-H), 9·28 (1H, s, 4-H), 11·20 (1H, bs, NH exchangeable with D_2O); MS: *m/z* 347 (M^+, 100%), 332 (89), 303 (50), 275 (8), 174 (13), 166 (43), 152 (69), 138 (20), 109 (12). $C_{21}H_{21}N_3O_2$ requires C 72·62, H 6·05, N 12·1. Found: C 72·54, H 6·24, N 11·7.

3-(2′-Benzoxazolyl)-7-diethylamino-2H-1-benzopyran-2-one, **3e**

Yellow needles from acetone; m.p. 170°C; yield 82%; ν_{max}(cm^{-1}) (Nujol) 1730, 1605, 1580, 1490, 1370, 1280, 1180, 1120; ^{1}H-NMR ($CDCl_3$): 1·20 (6H, t, N—CH_2—$\mathbf{CH_3}$), 3·42 (4H, q, N—$\mathbf{CH_2}$—CH_3), 6·46 (1H, d, J = 2 Hz, 8-H), 6·66 (1H, d of d, 6-H), 7·20–7·95 (5H, m, Ar—H), 8·73 (1H, s, 4-H); MS: *m/z* 334 (M^+, 72%), 319 (100), 291 (33), 262 (16), 234 (7), 206 (6), 159 (9). $C_{20}H_{18}N_2O_3$ requires C 71·86, H 5·38, N 8·38. Found: C 71·53, H 5·55, N, 8·01.

3-(5′-Benzoyl-2′-benzoxazolyl)-7-diethylamino-2H-1-benzopyran-2-one, **3f**

Yellow needles from chloroform; m.p. 188°C; yield, 72%; ν_{max} (cm^{-1}) (Nujol), 1740, 1660, 1590, 1520, 1450, 1380, 1250, 1190, 1130; ^{1}H-NMR ($CDCl_3$): 3·42 (6H, t, N—CH_2—$\mathbf{CH_3}$), 3·42 (4H, q, N—$\mathbf{CH_2}$—CH_3) 6·46

(1H, d, J = 2 Hz, 8-H), 6·66 (1H, d of d, 6-H), 7·20–8·20 (9H, m, Ar—H), 8·55 (1H, s, 4-H); MS: *m/z* 438 (M^+, 68%), 423 (100), 410 (6), 395 (17), 105 (10). $C_{27}H_{22}N_2O_4$ requires C 73·97, H 5·02, N 6·39. Found: C 73·64, H 5·14, N 6·22.

2.4 Evaluation of laser properties

The solution containing the dyes **3** was excited (or pumped) by a pulsed nitrogen laser; output power 60 kW; pulse duration 15 nsec, pulse repetition frequency 1 Hz. The schematic diagram of the experimental setup is shown in Fig. 1. The output from the nitrogen laser was line-focussed on the cuvette containing the dye solution (2×10^{-2}M) with the help of a cylindrical lens and the fluorescence of the dye was expanded using a beam expander and allowed to fall on the diffraction grating held in a Littrow position. The grating selects a particular wavelength to pass through the dye cell, depending upon the grating angle. The reflecting mirror or the output coupler partially reflects the beam back into the cell and partially transmits it. This forms the laser oscillator cavity. Once oscillation had been achieved, a laser output was obtained from the output coupler.

The lasing ranges of the dyes were monitored using a grating monochromator (Model 218, McPherson, Acton, MA, USA). The laser output was allowed to fall on the entrance slit of the monochromator and detected at the exit slit by a photo-diode. The intensity of the laser output was plotted against wavelength to give the tuning curve of the dye.

3 RESULTS AND DISCUSSION

Dyes **3a–g** were synthesized in good yield by the reaction of 3-carbethoxy-7-diethylamino-2H-1-benzopyran-2-one (**1**) with the corresponding 4-

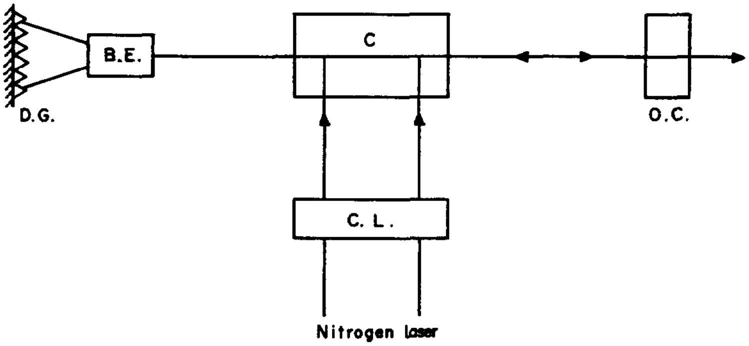
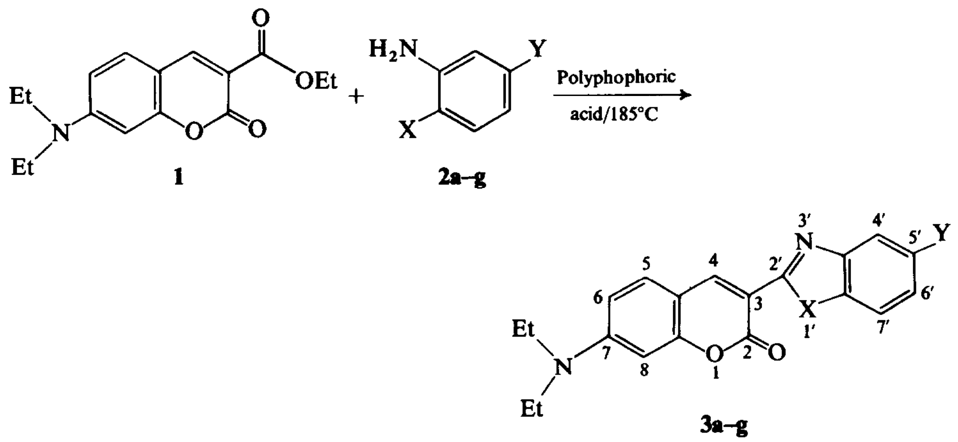


Fig. 1. Experimental set-up for evaluation of laser spectral characteristics. DG, Diffraction grating; BE, beam expander; C, cuvette; CL, cylindrical lens; OC, output coupler.



3a X = NH, Y = H
3b X = NH, Y = COPh
3c X = NH, Y = Cl
3d X = NH, Y = CH_3
3e X = O, Y = H
3f X = O, Y = COPh
3g X = O, Y = Cl

Scheme 1

substituted *o*-phenylenediamine or *o*-aminophenol derivative (**2a–g**) (Scheme 1). The coumarin derivative **1** was prepared from commercially available diethyl-*m*-aminophenol as per the method previously reported by us.[1] The absorption and fluorescence were measured in methanol (Table 1) and the laser spectra (Table 2) were recorded in chloroform except for **3b** which had poor solubility in most of the solvents; this dye was, however, soluble in a 1:1 mixture of ethylene dichloride and ethanol.[3]

TABLE 1
Electronic Spectra of Dyes 3 (in Methanol)

Dye no.	*λ_{max}(nm)*			
	Absorption		*Emission fluorescence*	*Relative intensity of fluorescence*
	UV	*VIS*		
3a	286 (13 105)[a]	437 (43 934)	492	1·6
3b	274 (24 320)	456 (55 670)	495	1·1
3c	288 (11 927)	442 (43 673)	493	1·8
3d	288 (13 295)	438 (43 873)	494	1·6
3e	278 (7 314)	444 (35 022)	490	1·2
3f	270 (14 292)	450 (45 887)	493	0·5
3g	278 (11 103)	452 (48 739)	493	1·0

[a] Numbers in parentheses: ε (litre mol^{-1} cm^{-1}).

TABLE 2
Laser properties of dyes 3[a]

Dye no.	*Lasing region (nm)*	*Bandwidth (nm)*	*Lasing maximum (nm)*	*Relative intensity (arbitrary scale where for* **3a***, intensity is 1)*
3a	523–531	8	526	1·0
3b	540–570	30	550	1·1
3c	517–524	7	520	1·1
3d	500–540	40	520	1·1
3e	—	—	No lasing	—
3f	—	—	No lasing	—
3g	523–534	11	528	0·7

[a] Chloroform was used as the solvent except for **3b**, for which ethylene dichloride: ethanol (1:1) was used.

3.1 Absorption spectra characteristics

All the dyes showed typical coumarin absorption at 270–288 nm and in the visible region, the absorption maxima ranged from 437–456 nm. The presence of the electron-withdrawing benzoyl and chloro substituents in dyes **3b** and **3c** resulted in bathochromic shifts of 19 and 5 nm, respectively, compared to the unsubstituted dye **3a**. A similar behaviour was apparent in the benzoxazole dyes **3e–g**. The benzoyl group also brought about a marked increase in the tinctorial strength of dyes **3b** and **3f** in comparison to the unsubstituted dyes **3a** and **3e**, respectively, as indicated by the molar extinction coefficient values (Table 1). Although this is not apparent for the chloro-substituted benzimidazole dye **3c**, a considerable increase in the ε-value for the chlorobenzoxazole dye **3g** compared to **3e** was observed.

3.2 Emission spectral characteristics

The fluorescence spectra were recorded by exciting the solutions of the dyes **3** at their respective absorption wavelength maxima in the visible region. The dyes exhibited fluorescence emission wavelength maxima ranging from 490–495 nm, depending upon the substituent. The relative intensities of fluorescence of the dyes were evaluated under identical concentrations of dye solutions (using a reference dye **3g** as **1**). In general, dyes **3a–d** in the benzimidazole series had better fluorescence intensities compared to those in the benzoxazole series.

3.3 Laser spectral properties

Solutions of dyes **3** at concentrations of the order of 2×10^{-2} M were pumped by a pulsed nitrogen laser at 337 nm. The optimum lasing wavelength range (bandwidth), lasing maxima and relative intensities (on an arbitrary scale using **3a** as standard) are recorded in Table 2. Generally, the benzimidazole dyes **3a–d** exhibited superior laser properties compared to the benzoxazole dyes **3e–g**. Dyes **3b** and **3d**, which contained the electron-withdrawing benzoyl group and the electron-donating methyl group, respectively, had a longer lasing wavelength tunability range of 30–40 nm compared to a range of 8 nm for dye **3a** which is a known commercial laser dye.[4] In addition, the dyes **3b** and **3d** exhibited greater relative intensities in comparison to **3a**, making them more efficient laser dyes. The benzoxazole dyes **3e** and **3f** did not lase, although they showed intense fluorescence. The coumarin dyes **3a–d** in the benzimidazole series showed more or less similar relative intensities of lasing and were better than the chlorobenzoxazole dye **3g** (Table 3).

3.4 Dyeing characteristics

The dyes were applied to polyester by high-temperature dyeing techniques and were found to impart greenish yellow to orange hues. The pick-up and fastness properties are recorded in Table 3. All the dyeings showed depths comparable to that of standard 1% lemon yellow and orange shades on polyester except for the dye **3d**, which was weaker. The light fastness was determined on an Atlas Fadeometer, Ohio, USA, and fading assessed using standard procedures.[5]

TABLE 3
Fastness Properties of Dyes **3a–g** on Polyester (1% Shade)

Dye no.	*Reference depth*	*Light fastness Xeno test*	*Sublimation fastness at 200°C for 1 min*		
			Loss in depth	*Change in tone*	*Staining of adjacent fibre*
3a	1/1	2	3	3	2–3
3b	1/1	3	3–4	3	4
3c	1/1	3	3–4	3–4	2–3
3d	1/3	3	3–4	3	3
3e	1/1	3	3	3	2
3f	1/1	3	3	3	3–4
3g	1/1	3	3	3	2–3

For sublimation fastness determinations, the dyed polyester fibre was stitched between two pieces of undyed polyester fibres and treated at 200°C for 1 min. Staining of the undyed material and changes in tone or loss in depth were assessed on the following ratings: 1—poor; 2—fair; 3—moderate; 4—good. From Table 3, it can be seen that all the dyes had moderate light-fastness and moderate to good sublimation-fastness properties.

4 CONCLUSION

Dyes **3b**, **3d** and **3g** show promise as efficient laser dyes. The dyes **3** also give rise to brilliant greenish yellow shades on polyester with moderate to good fastness properties.

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