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Polycyclic Compounds Part VI. Structural Features of C.I. Disperse Yellow 232*

N. R. Ayyangar, K. V. Srinivasan & Thomas Daniel

National Chemical Laboratory, Pune 411 008, India

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ABSTRACT

*The chemical constitution of C.I. Disperse Yellow 232 [Intrasil Brilliant Yellow 10GF] was elucidated as 3-(5'-chloro-2'-benzoxazolyl)-7-diethylamino-2H-1-benzopyran-2-one (**1**). The structure of the dye was confirmed by synthesis from commercially available starting materials. The relative merits of different methods for the preparation of **1** are also discussed.*

1 INTRODUCTION

The structure of C.I. Disperse Red 303 has been shown by us in a previous communication to be an isomeric mixture of 1-methoxy-2-phenyl-3*H*-naphtho[2,1,8-*mna*]thioxanthen-1-one and 3-methoxy-2-phenyl-1*H*-naphtho-[2,1,8-*mna*]thioxanthen-1-one, the orange and the red components respectively in almost equal amounts.[1] In continuation of our efforts to deduce the chemical constitution of commercial fluorescent systems which may have applications as dye-lasers and luminescent solar concentrators, we discuss in this present paper the structural features of C.I. Disperse Yellow 232 (Intrasil Brilliant Yellow 10GF; Crompton–Knowles Corporation), **1**. This dye has been reported to have a brilliant greenish–yellow hue on polyester with good light (4–5), sublimiation (5) and washing (5) fastness properties.[2] Although described to have an azo constitution,[2] we found the dye to possess an aryloxazole and a coumarin ring, contributing to the fluorescence

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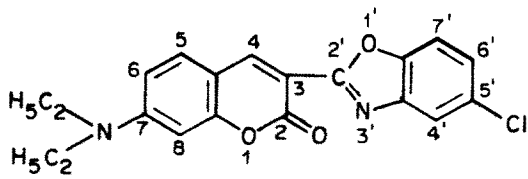

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exhibited by the dye. A detailed study of the spectral and elemental analyses aided by literature survey of similar compounds established the structure of the dye as 3-(5′-chloro-2′-benzoxazolyl)-7-diethylamino-2*H*-1-benzopyran-2-one (**1**). Further the structure of the dye was unambiguously established by synthesis from readily available starting materials.

2 EXPERIMENTAL

2.1 General

Melting points recorded are uncorrected. The UV–visible spectra were recorded on a Perkin–Elmer 350 spectrophotometer, IR spectra on a Perkin–Elmer 137B spectrophotometer and the IR frequencies are expressed in cm^{-1}. The ^{1}H-NMR spectra were run on Varian T-60 and Bruker WH-90 FT spectrometers in chloroform-d containing 0·1% TMS as internal standard. The chemical shifts δ are expressed in ppm. Mass spectra were recorded on a CEC 21-110B or Finnigan MAT-1020 automated GC/MS mass spectrometer at minimum source temperature.

2.2 Isolation and purification of the commercial Disperse Yellow 232(1)

The commercial dye (5 g) was dried at 50°C under reduced pressure and the dry sample was extracted with chloroform (500 ml) for 24 h. Removal of the solvent from the chloroform extract yielded a brown solid (0·88 g), TLC of which on silica gel showed a single brilliant greenish–yellow spot with an R_f value of 0·5 when eluted with chloroform. The extracted dye (0·88 g) was purified by chromatography through a silica-gel column using chloroform petroleum ether (4:1) as eluent. The chromatographed dye was recrystallised from acetone: m.p., 195°C; λ_{max}(DMF), 282 nm (ε, 4121), 452 nm (ε, 61618); ν_{max}(Nujol), 1720, 1620, 1520, 1450, 1340, 1240, 1180, 1140 cm^{-1}; ^{1}H-NMR ($CDCl_3$), 1·16 (6H, t, N—CH_2—$C\underline{H}_3$), 3·37 (4H, q, N—$C\underline{H}_2$—CH_3), 6·42 (1H, d, $J = 2$Hz, 8H), 6·75 (1H, d of d, 6-H), 7·15 (1H, q, 6′-H), 7·22 (1H, d, $J = 9$ Hz, 7′-H), 7·40 (1H, d, $J = 10$ Hz, 5-H);

MS: *m/z* 368 (M^+, 33%), 353 (76), 325 (23), 213 (37), 177 (88), 149 (83), 135 (96), 119 (94), 111 (53), 97 (52), 69 (38), 55 (100).

Calculated for $C_{20}H_{17}ClN_2O_3$; C, 65·2; H, 4·6; N, 7·6; Cl, 9·6.
Found: C, 65·3; H, 5·2; N, 7·75; Cl, 9·1%.

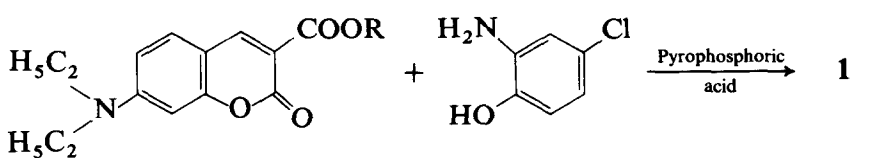
2.3 Synthesis of 3-(5′-chloro-2′-benzoxazolyl)-7-diethylamino-2*H*-1-benzopyran-2-one (1) (Intrasil Brilliant Yellow 10 GF)

2.3.1 Method I

The dye was synthesised by the condensation of 7-diethylamino-2-oxo-2*H*-1-benzopyran-3-carboxylic acid or its ethyl ester (**2a, 2b**) with 4-chloro-2-aminophenol (**3**) (Scheme 1). The benzopyran-2-one (**2**) was synthesised starting from diethyl-*m*-aminophenol (DEMAP) (**4**) in five steps (Scheme 2) or in a single step (Scheme 3).

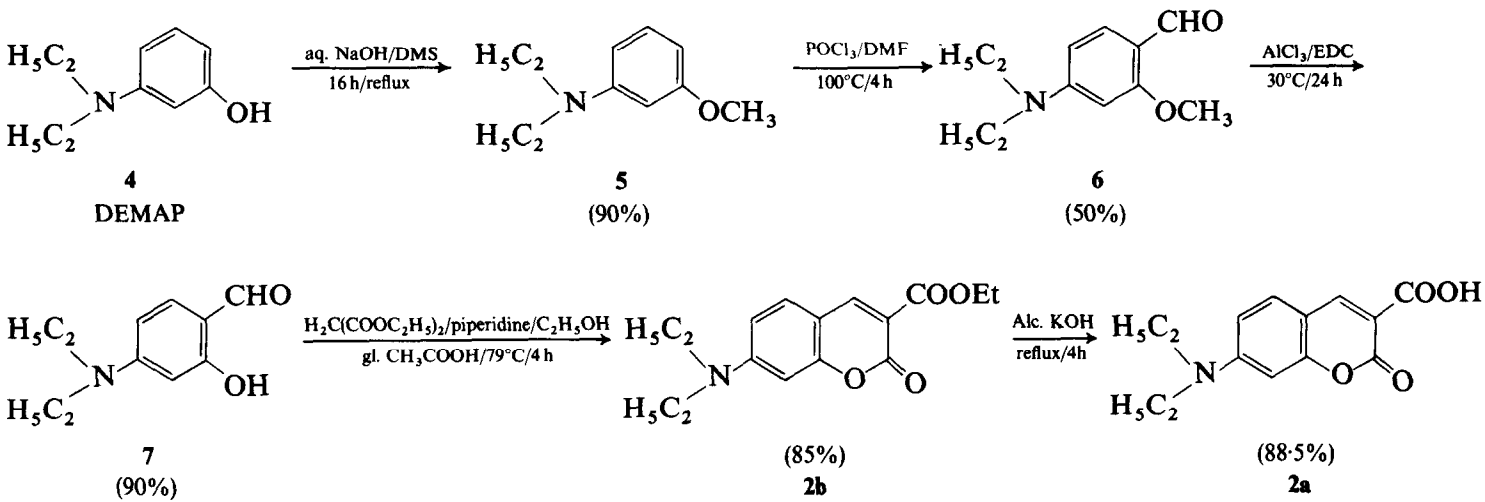
Preparation of DEMAP methyl ether (***5***). To a solution of DEMAP (16·5 g, 0·1 mol) in aqueous sodium hydroxide (5% w/v) (100 ml), dimethyl sulphate (27·7 g, 0·22 mol) was added dropwise with stirring over 1 h. The reaction mixture was heated at 95–98°C for 5 h and then poured into ice-cold water. The aqueous mixture was extracted with chloroform, then the chloroform layer repeatedly washed with water and dried. Removal of chloroform gave the methyl ether **5** as a colourless liquid, $b.p._{14}$ 147–148°C (lit.[3] $b.p._{14}$ 146–148°C); yield, 90%.

*Preparation of 4-diethylamino-2-methoxybenzaldehyde (**6**).* Phosphorous oxychloride (18·4 g, 0·12 mol) was slowly added over 1 h into cooled dimethylformamide (36·5 g, 0·5 mol) at 0°C and the mixture was stirred a further 1 h at 0°C. Then DEMAP methyl ether (**5**) (17·9 g, 0·10 mol) was added dropwise over 1 h and the mixture heated on a boiling water bath for 4 h. It was then cooled and poured into ice-cold water. The pH of the slurry was adjusted to 4–4·5 and filtered. The separated solid product was dried. M.p. 76°C, (lit.[4] m.p. 73–76°C); yield, 10·3 g (50%). It was characterised as **6** by



2a R=H
2b R=C_2H_5

Scheme 1



4
DEMAP

5
(90%)

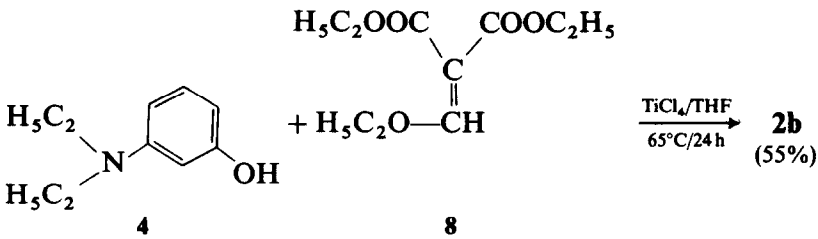
6
(50%)

7
(90%)

(85%)
2b

(88·5%)
2a

Scheme 2



Scheme 3

spectral and elemental analysis; ν_{max}(Nujol), 2670, 1640, 1470, 1400, 1360, 1270, 1220 cm^{-1}; ^{1}H-NMR ($CDCl_3$), 1·16 (6H, t, N—CH_2—$C\underline{H}_3$), 5·33 (4H, q, N—$C\underline{H}_2$—CH_3), 5·93 (1H, m, 5-H), 6·13 (1H, d, J = 3Hz, 3-H), 7·46 (1H, d, J = 9 Hz, 6-H), 9·9 (1H, s, —C$\underline{H}$O); MS: *m/z* 207 (M^+, 52%), 192 (100), 164 (33), 136 (15), 121 (9), 108 (7), 91 (3), 77 (3).

Calculated for $C_{12}H_{17}NO_2$: C, 69·6; H, 8·2; N, 6·8.
Found: C, 69·4; H, 8·1; N, 6·7%.

Preparation of 4-diethylaminosalicylaldehyde (7). 4-Diethylamino-2-methoxybenzaldehyde **6** (4·14 g, 0·02 mol) was stirred into ethylene dichloride (60 ml) and powdered aluminium chloride (2·66 g, 0·4 mol) was then added rapidly. Care was taken to effect the reaction under strictly anhydrous conditions. The reaction mixture was stirred at room temperature for 24 h and the product was isolated by pouring into water, extraction with chloroform and removal of the solvent. M.p. 67°C (lit.[5] m.p. 65–67°C); yield, 3·2 g (89%). The compound was characterised by spectral and elemental analysis: ν_{max}(Nujol), 2360, 1620, 1550, 1520, 1450, 1340, 1240, 1120 cm^{-1}; ^{1}H-NMR ($CDCl_3$), 1·20 (6H, t, N—CH_2—$C\underline{H}_3$), 3·40 (4H, q, N—$C\underline{H}_2$—CH_3), 6·12 (1H, d of d, 5-H), 6·33 (1H, d, J = 3·5 Hz, 3-H), 7·28 (1H, d, J = 9 Hz, 6-H), 9·53 (1H, s, C$\underline{H}$O), 11·64 (1H, broad s, OH, exchangeable with D_2O); MS: *mz* 193 (M^+ 34%), 178 (100), 162 (5), 150 (67), 136 (7), 122 (9), 104 (4), 94 (8), 77 (3) and 64 (4).

Calculated for $C_{11}H_{15}NO_2$: C, 68·4; H, 7·8; N, 7·25.
Found: C, 68·5; H, 8·0; N, 7·1%.

*Preparation of 7-diethylamino-2-oxo-2H-1-benzopyran-3-carboxylic acid ethyl ester (**2b**).* To a mixture of the aldehyde **7** (2·89 g, 0·015 mol), diethyl malonate (2·40 g, 0·015 mol) and piperidine (1·27 g, 0·015 mol) in ethanol (40 ml), a drop of glacial acetic acid was added. The reaction mixture was refluxed for 4 h and ethanol was then removed by distillation. The residual mass was poured into ice-cold water and the pH of the aqueous slurry was adjusted to 4·5–5·0 by careful addition of concentrated hydrochloric acid.

The solid product which separated was filtered and dried. The crude product was dissolved in acetone, adsorbed on silica gel and chromatographed through a column of silica gel using acetone/petroleum ether (1:10 v/v) as the eluting solvent to give pure **2b**; m.p. 87°C (lit.[6] m.p. 87°C); ν_{max}(Nujol), 1710, 1630, 1610, 1520, 1450, 1380, 1240, 1200, 1140, 1120, 1030, 930, 830 cm^{-1}; ^{1}H-NMR ($CDCl_3$), 1·26 (9H, m, N—CH_2—$C\underline{H}_3$ and O—CH_2—$C\underline{H}_3$), 3·43 (4H, q, N—$C\underline{H}_2$—CH_3), 4·36 (2H, q, O—$C\underline{H}_2$—CH_3), 6·40 (1H, m, 6-H), 6·63 (1H, d, $J = 3$ Hz, 8-H), 7·30 (1H, d, $J = 9$ Hz, 5-H), 8·33 (1H, s, 4-H); MS: *m/z* 289 (M^+, 45%), 274 (100%), 246 (14), 200 (8), 188 (4), 174 (6), 160 (5), 144 (4), 116 (5), 77 (3), 43 (3).

Calculated for $C_{16}H_{19}NO_4$: C, 66·4; H, 6·6; N, 4·8.
Found: C, 66·4; H, 6·4; N, 4·5%.

*Preparation of 7-diethylamino-2-oxo-2*H*-1-benzopyran-3-carboxylic acid (**2a**).* The ethyl ester **2b** (1·44 g, 0·005 mol) was added to a solution of potassium hydroxide (0·35 g, 0·006 mol) in ethanol (100 ml) and the mixture refluxed on a water bath for 4 h. Ethanol was removed by distillation and the residual mass was poured into ice-cold water, the pH of the resulting slurry adjusted to 2–3 by addition of dilute hydrochloric acid (10% w/v) and then subjected to extraction with chloroform. Further work-up in the usual manner after the removal of chloroform yielded **2a**: m.p. 220°C; Yield: 1·15 g (88·5%); ν_{max}(Nujol), 1730, 1600, 1560, 1490, 1440, 1390, 1260, 1180, 1120, 1070, 1000, 795 cm^{-1}; ^{1}H-NMR ($CDCl_3$), 1·06 (6H, t, —CH_2—$C\underline{H}_3$), 2·93 (4H, q, —$C\underline{H}_2$—CH_3), 5·53 (1H, m, 6-H), 5·7 (1H, d, $J = 2$ Hz, 8-H), 6·30 (1H, d, $J = 9$ Hz, 5-H), 7·36 (1H, s, 4-H); MS: *m/z* 261 (M^+, 55%), 246 (100), 202 (15), 174 (33), 145 (14), 116 (16), 89 (23), 77 (19), 63 (21), 45 (30).

Calculated for $C_{14}H_{15}NO_4$: C, 64·4; H, 5·75; N, 5·4.
Found: C, 64·7; H, 5·9; N, 5·0%.

*One-step preparation of benzopyran-2-one (**2b**).* To a cooled solution (2°C) of a mixture of DEMAP (7·95 g, 0·05 mol) and diethyl ethoxymethylene-malonate (11·80 g, 0·055 mol) in dry tetrahydrofuran (40 ml), titanium tetrachloride (6 ml) was added rapidly. The temperature was slowly raised to 65°C over 0·5 h and the mixture stirred for 24 h at 65°C. The crude material, obtained after pouring into ice and extraction with chloroform, was subjected to column chromatography through silica gel using chloroform as eluent to afford **2b** in 55% yield.

*Preparation of 3-(5′-chloro-2′-benzoxazolyl)-7-diethylamino-2*H*-1-benzo-pyran-2-one(**1**).*[8] A mixture of the benzopyran-2-one-3-carboxylic acid **2a** (0·261 g, 0·001 mol), or its ethyl ester **2b** (0·289 g, 0·001 mol), 4-chloro-2-

aminophenol (0·143 g, 0·001 mol) and pyrophosphoric 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 by sodium carbonate solution (10%, w/v) and extracted with chloroform (300 ml). The chloroform layer was washed with water and dried over anhydrous sodium sulphate. After removal of chloroform by distillation, the residual crude dye was purified by column chromatography as described in Section 2·2: m.p. 195°C; yield, 0·276 g (75%).

The dye synthesised as above was identical in all respects (IR, NMR, mass and elemental analysis) with the isolated commercial dye **1**. The mixed m.p. remained undepressed.

2.3.2 Method II

Alternative synthesis of **1** *(Disperse Yellow 232).*[9] A mixture of ethyl cyanoacetate **9** (1·13 g, 0·01 mol), 3-methoxypropylamine (0·89 g, 0·01 mol) and glacial acetic acid (0·1 ml) was heated with stirring at 95°C for 4 h in an inert atmosphere (nitrogen). The liquor was cooled to 29°C and 4-chloro-2-aminophenol (1·43 g, 0·01 mol) was added. They were heated at 180°C for 6 h with stirring under nitrogen, then cooled to 29°C, 4-diethylaminosalicylaldehyde **7** (1·93 g, 0·01 mol) in isopropanol (25 ml) was added and the mixture was refluxed for 20 h, maintaining the nitrogen atmosphere. The reaction mixture was poured into ice-cold water (200 ml) and the pH of the slurry adjusted to 3 by dilute hydrochloric acid (10%, w/v). The precipitated crude dye was filtered and further purified by column chromatography as described in Section 2.2: yield, 2·5 g (70%). The dye was identical in all respects to the dye prepared as described in Section 2.3.2, and isolated commercial dye (Section 2.2).

3 RESULTS AND DISCUSSION

The anthraquinone or the azo constitution for the dye was discounted by subjecting it to vatting treatment using alkaline sodium dithionite when neither decolorisation nor any colour change was observed. This prompted us to look for other structures such as coumarins, naphthalimides, benzoxazoles, and other heterocycles which normally exhibit fluorescence in daylight. On the basis of elemental analysis and molecular weight obtained from the mass spectrum, the molecular formula of the dye was derived as $C_{20}H_{17}ClN_2O_3$. The detailed spectral analysis of the dye aided by a literature survey based on the derived molecular formula led to the elucidation of its chemical constitution as the coumarin derivative, 3-(5′-chloro-2′-benzoxazolyl)-7-diethylamino-2*H*-1-benzopyran-2-one (**1**).

The electronic spectrum of **1** in the UV region revealed a characteristic wavelength maximum of low intensity at 282 nm corresponding to a coumarin nucleus. The high-intensity wavelength maximum at 452 nm was indicative of the brilliant greenish-yellow colour of the dye. The IR spectrum revealed a strong carbonyl stretching frequency at 1720 cm^{-1} attributable to the α,β-unsaturated cyclic lactone of the dye molecule.

The ^{1}H-NMR spectrum revealed a triplet and a quartet centred at 1·16 and 3·37 respectively, corresponding to the methyl and methylene protons of the diethylamino substituent. A *meta* coupled doublet at 6·42 ($J = 2$ Hz) integrating for one proton was assigned to 8-H, taking into consideration the proximity of the electron-donating nitrogen and oxygen atoms at *ortho* positions. The doublet of a doublet centred at 6·75 was indicative of a 6-H proton *ortho* to the diethylamino substituent. The *ortho* coupled doublet at 7·22 ($J = 9$ Hz) was ascribed to the more shielded 7′-H proton of the benzoxazole ring, whereas the doublet at 7·40 ($J = 10$ Hz) was assigned to the deshielded 5-H of the coumarin skeleton. The 6′-H proton of the benzoxazole ring appeared as a quartet (doublet of doublets) centred at 7·15. The magnetic resonance due to 4′-H appeared as a *meta* coupled doublet at 7·64 ($J = 2$ Hz). The most deshielded proton in the NMR spectrum at 8·5, which appeared as a singlet, was attributed to the 4-H proton of the coumarin nucleus which is in conjugation with the electron-withdrawing —C═O and —C═N linkages.

The mass spectrum showed the molecular ions at 368 (M^+) and 370 (M + 2) corresponding to the ^{35}Cl and ^{37}Cl isotopes present in the dye. The first facile loss of a methyl group from the dialkylamino substituent to give a peak at 353 in good relative abundance was in agreement with such a fragmentation reported for 7-diethylamino-4-methylcoumarin.[7] The fragment ions at 325 (M—CH_3—CO), 318 (M—CH_3—Cl), 311 (M—C_2H_5—CO), 296 (M—CH_3—CO—COH), 282 (M—C_2H_5—CO—COH), 269 (M—CH_3—2CO—C_2H_4) and 268 (M—CH_3—CO—COH—C_2H_4) were in good agreement with the fragmentation pattern of the dye.

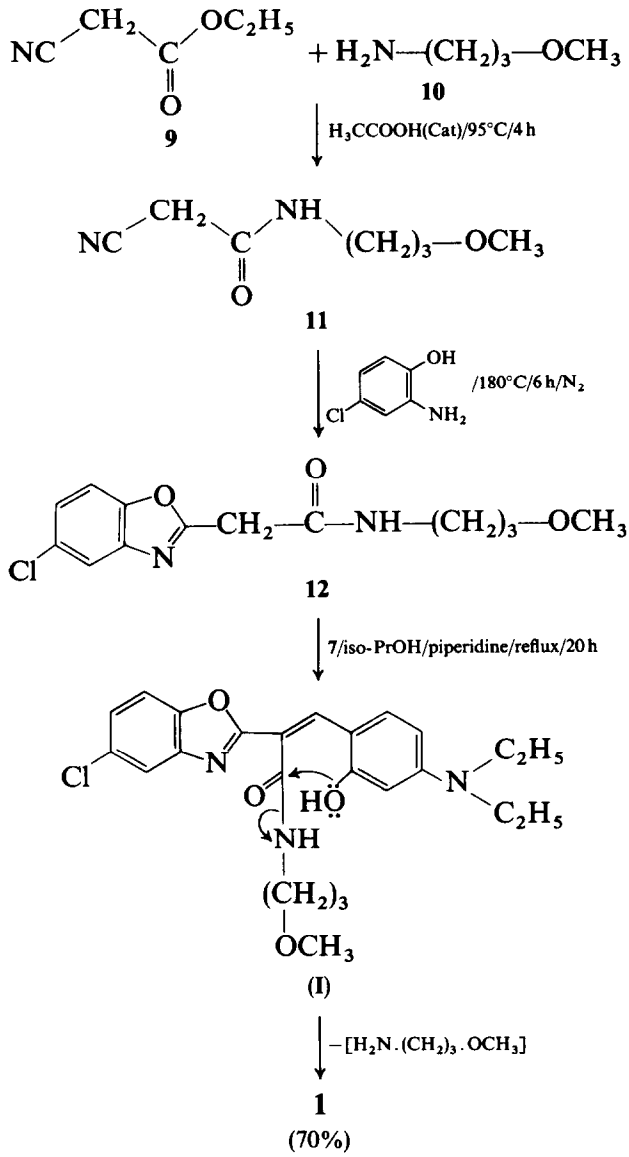
The elucidated structure of the dye was confirmed by an unambiguous synthesis involving

(a) Condensation of the benzopyran-2-one (**2a**, **2b**) with 4-chloro-2-aminophenol (Scheme 1).[8] The benzopyran-2-one **2** was prepared from the commercially available diethyl -*m*-aminophenol either by the multi-step process as in Scheme 2 or by a reported[9] single-step process (Scheme 3).

(b) N-(3-Methoxypropyl)cyanoacetamide (**11**) prepared by the condensation of the ethyl cyanoacetate (**9**) with 3-methoxypropylamine (**10**) was reacted with **3** to yield the benzoxazolylacetamide **12**. The

acetamide **12** was condensed with 4-diethylaminosalicylaldehyde **7** as prepared in Scheme 2 in the presence of catalytic amounts of piperidine to yield the dye **1**. The process is illustrated in Scheme 4.[10]

The condensations involving *o*-aminophenol **3** were performed in an atmosphere of nitrogen to suppress its autoxidation to undesired products. The key intermediate in the synthesis of the dye **1** by Method (a) is the



Scheme 4

benzopyran-2-one ethyl ester **2b**. Although we had hydrolysed **2b** to the new carboxylic acid **2a** in good yield, we found that both **2a** and **2b** react with 4-chloro-2-aminophenol to give **1** in equivalent yields (75%). The compound **2b** could be synthesised in four steps (Scheme 2) or in one step (Scheme 3). However, we prefer to synthesise **2b** by Scheme 2, since ethoxymethylene-malonate and titanium tetrachloride in the latter process are much more expensive as compared with diethyl malonate and other reagents employed in the previous method. Moreover, titanium tetrachloride poses a material handling problem in scale-up operations for a commercial process. The relative importance of Scheme 2 is also enhanced by the fact that it allows the synthesis of diethylaminosalicylaldehyde (**7**) which can be utilised for the alternative synthesis of **1** by Method (b). A salient feature of Method (b) is that it enables us to recover and re-use one of the reactants, viz. 3-methoxypropylamine (**10**). The process economics can be further improved if ethylamine or propylamine can be used instead of **10**. The structure of the dye **1** was in conformity with X-ray crystallographic analysis carried out in our laboratory, reported elsewhere.[11]

The solution of dye **1** in chloroform, when excited at 452 nm, gave a fluorescent spectrum with an emission λ_{max} at 473 nm. Consequently, the dye was tested for its laser properties. It exhibited optimum lasing in the wavelength range 523·2–534·5 nm when pumped by a pulsed nitrogen laser at $\lambda = 337$ nm. The laser characteristics of the dye **1** and similar dyes will form the subject matter of a separate communication.

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