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New Fluoran Leuco Dyes Having a Phenylenediamine Moiety at the 6-Position of the Xanthene Ring

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ABSTRACT

*New fluoran leuco dyes incorporating a p-(*N,N*-dibutylamino)phenylamino moiety at the 6-position of 2,3-dimethylxanthene (**1**) and of 2-chloro-3-methylxanthene (**2**) have been synthesized. The spectral characteristics of these compounds were quite different from those of conventional flouran dyes; remarkably broad absorption bands in the range ca. 500–850 nm (λ_{max}: 608 nm for **1**, 645 nm for **2**) were observed in m-cresol as a result of yielding zwitterions of **1** and **2**. Coloured anions of these compounds were also formed in a basic methanol solution. The molecular structures of the colourless lactones and the coloured zwitterions were identified by ^{13}C NMR spectroscopy. The new fluorans reported herein are promising compounds as a basic skeleton of new functional leuco dyes because of their unique spectral characteristics and colour properties in both acidic and basic media.* © *1997 Elsevier Science Ltd*

Keywords: fluoran leuco dye, phenylenediamine moiety, absorption spectrum, ^{13}C NMR spectrum, lactone structure, zwitterion structure.

INTRODUCTION

A large number of fluoran {spiro[isobenzofuran–1(3H), 9′-(9H)xanthene]-3-one} compounds, which form coloured zwitterions upon contact with Lewis

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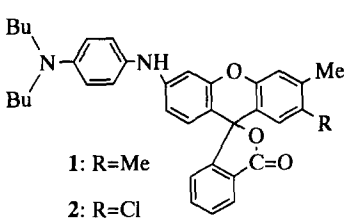
acids such as phenol-related compounds (Scheme 1), have been reported [1–6]. They are important as leuco dyes (so-called 'colour formers') for use in pressure- and thermo-sensitive recording systems [7–9]. Most of the conventional fluoran leuco dyes are designed based on a fluoran molecule carrying an *N,N*-dialkylamino group at the 6-position of the xanthene ring, and with the introduction of substituent groups at the 2- and 3-positions.

Research on new fluoran leuco dyes having interesting physical and chemical properties is still very active. Recently, such research has concentrated on the development of fluorans which possess novel spectral characteristics and unique coloured–colourless equilibria [10]. We have therefore designed some new functional dyes by means of structural modification of the fluoran molecule and have found that fluoran compounds incorporating a phenylenediamine [*p*-(*N,N*-dialkylamino)phenylamio] moiety at the 6-position of the xanthene ring (**1** and **2**) possess unique spectral characteristics which are quite different from those of the flouran compounds reported so far. Thus, in protic media such as *m*-cresol, **1** and **2** showed remarkably broad absorption bands in the range of *ca.* 500–850 nm and were dark green in colour. These compounds gave different absorption spectra in alkaline methanol solution, having a purple colour. We describe here the synthesis and the spectral characteristics of these new types of fluoran compounds, in comparison with those of the conventional fluoran (**3**) and structural analogs of **1** i.e., **4** and **5**. In this study, the structures of the colourless and the coloured species of the fluorans were determined using ^{13}C NMR spectroscopy.



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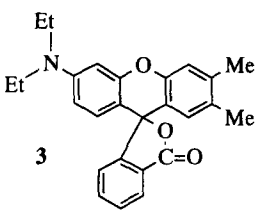
2: R=Cl



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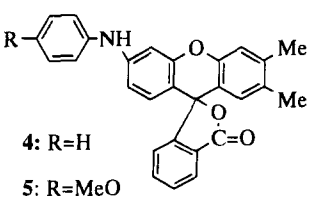
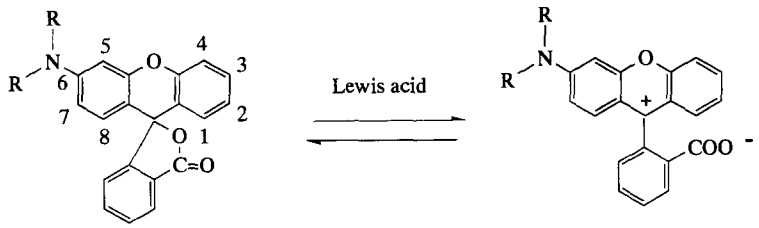


4: R=H

5: R=MeO



Colourless lactone form

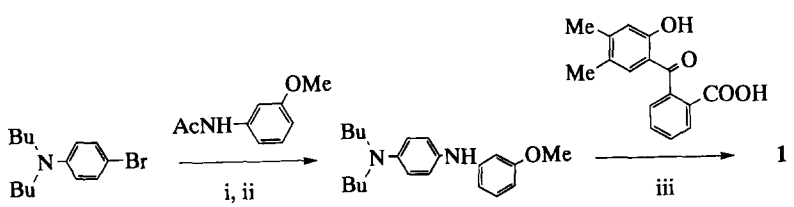
Coloured zwitterion form

Scheme 1

EXPERIMENTAL

Materials

2′,3′-Dimethyl-6′-{[4-(*N*,*N*-dibutylamino)phenyl]amino}-spiro[isobenzofuran-1(3H),9′-[9H]xanthene]-3-one (1): Compound **1** was synthesized using the method shown in Scheme 2. 4-(*N*,*N*-dibutylamino)bromobenzene (3.15 g, 15.8 mmol) was reacted with N-acetylanisidine (2.48 g, 15.0 mmol) in the presence of a copper catalyst (CuI, 0.029 g, 0.15 mmol) and potassium carbonate (4.15 g, 30 mmol) at *ca.* 200°C, followed by hydrolysis to yield the phenylenediamine derivative. This compound was then condensed in conc. H_2SO_4 (40 ml) with 2-(4,5-dimethyl-2-hydroxybenzoyl)benzoic acid (4.05 g, 15 mmol). The resultant compound was recrystallized from 2-propanol and the crystals were dried under reduced pressure to yield pure **1** (pale yellow crystals, yield 62%). The structure and the purity of this compound were confirmed by IR, NMR, MS, and elemental analysis: mp 165–166°C; IR(KBr) 3382 (NH), 1767(COO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C, $\delta_{TMS}=0$ ppm) $\delta=0.96$ (6H, *t*, Bu), 1.36 (4H, *m*, Bu), 1.56 (4H, *m*, Bu), 2.06 (3H, *s*, $ArCH_3$), 2.24 (3H, *s*, $ArCH_3$), 3.25 (4H, *t*, Bu), 5.56 (1H, *s*, NH), 6.40 (1H, *d* of *d*, xanthene), 6.43 (1H, *s*, xanthene), 6.53 (1H, *d* of *d*, xanthene), 6.62 (1H, *d* of *d*, xanthene), 6.63 (2H, *d*, $Bu_2NC_6H_4NH$), 6.99 (1H, *s*, xanthene), 7.04 (2H, *d*, $Bu_2NC_6H_4NH$), 7.15 (1H, *d* of *d*, benzolactone), 7.56–7.65 (2H, *m*, benzolactone), 8.00 (1H, *d* of *d*, benzolactone). Mass spectrum: M/Z 546 (M^+). Found: C, 79.14; H, 6.99; N, 5.10%. Calcd. for



Scheme 2. Reagents and conditions: i, CuI, K_2CO_3, 1,2,4-trimethylbenzene, 200°C, 5 h; ii, KOH, ethanol, reflux, 2 h (80% yield); iii, conc. H_2SO_4, 25°C, 12 h (78% yield).

$C_{36}H_{38}N_2O_3$: C, 79.09; H, 7.01; N, 5.12%. 1 gave another crystal form when recrystallized from toluene (mp 127-130°C).

2′-Chloro-3′-methyl-6′-{[4-(*N*,*N*-dibutylamino)phenyl]amino}-spiro[isobenzofuran-1(3H),9′-[9H]xanthene]-3-one (2): Compound **2** was synthesized by a method similar to that described for **1**. Pale yellow crystals (recrystallized from toluene-hexane mixed solvent); yield 60%; mp 115–118°C; IR(KBr) 3370 (NH), 1767 (COO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C, $\delta_{TMS}=0$ ppm) $\delta=0.96$ (6H, *t*, Bu), 1.36 (4H, *m*, Bu), 1.57 (4H, *m*, Bu) 2.34 (3H, *s*, $ArCH_3$), 3.25 (4H, *t*, Bu), 5.61 (1H, *s*, NH), 6.43 (1H, *d* of *d*, xanthene), 6.51 (1H, *d*, xanthene), 6.60 (1H, *d*, xanthene), 6.62 (2H, *d*, $Bu_2NC_6H_4NH$), 6.71 (1H, *s*, xanthene), 7.02 (2H, *d*, $Bu_2NC_6H_4NH$), 7.08 (1H, *s*, xanthene), 7.14 (1H, *d* of *d*, benzolactone), 7.59–7.64 (2H, *m*, benzolactone), 8.00 (1H, *d* of *d*, benzolactone). Mass spectrum: M/Z 567 (M^+). Found: C, 74.06; H, 6.18; N, 4.90%. Calcd. for $C_{35}H_{35}ClN_2O_3$: C, 74.13; H, 6.22; N, 4.94%. A different crystal form of **2** was obtained when recrystallized from toluene (mp 156–157°C).

2′,3′-Dimethyl-6′-(*N*,*N*-diethylamino)-spiro[isobenzofuran-1(3H),9′-[9H]xanthene]-3-one (3): Compound **3** was synthesized by a method similar to that described for **1**. Pale orange crystals (recrystallized from toluene-2-propanol mixed solvent), yield 64%; mp 207–208°C; IR(KBr) 1752 (COO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C, $\delta_{TMS}=0$ ppm) $\delta=1.17$ (6H, *t*, Et), 2.07 (3H, *s*, $ArCH_3$), 2.26 (3H, *s*, $ArCH_3$), 3.35 (4H, *q*, Et), 6.38 (1H, *d* of *d*, xanthene), 6.43 (1H, *d*, xanthene), 6.47 (1H, *s*, xanthene), 6.56 (1H, *d*, xanthene), 7.03 (1H, *s*, xanthene), 7.17 (1H, *d* of *d*, benzolactone), 7.57–7.66 (2H, *m*, benzolactone), 8.01 (1H, *d* of *d*, benzolactone). Mass spectrum: M/Z 399 (M^+). Found: C, 78.10; H, 6.26; N, 3.55%. Calcd. for $C_{26}H_{25}NO_3$: C, 78.17; H, 6.31; N, 3.51%.

2′,3′-Dimethyl-6′-phenylamino-spiro[isobenzofuran-1(3H),9′-[9H]xanthene]-3-one (4): 3-Phenylaminoanisole (1.00 g, 5.02 mmol) and 2-(4,5-dimethyl-2-hydroxybenzoyl)benzoic acid (2.30 g, 8.51 mmol) were heated with p-toluenesulfonic acid (0.04 g, 0.21 mmol) for 3 h at 200°C. The solid residue was purified on a silica gel column using a mixture of toluene and ethyl acetate as eluent. The product was recrystallized from toluene to yield **4** as a 1:1 (molar ratio) toluene adduct. To remove the solvated toluene, the crystals were refluxed with n-octane to yield pure **4** (white crystals, yield 30%). mp 220–223°C; IR(KBr) 3386 (NH), 1759 (COO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C, $\delta_{TMS}=0$ ppm) $\delta=2.06$ (3H, *s*, $ArCH_3$), 2.25 (3H, *s*, $ArCH_3$), 5.88 (1H, *s*, NH), 6.48 (1H, *s*, xanthene), 6.62 (2H, *s*, xanthene), 6.90 (1H, *s*, xanthene), 7.03 (1H, *t*, C_6H_5NH), 7.14 (2H, *d*, C_6H_5NH), 7.16 (1H, *d* of *d*, benzolactone), 7.23 (2H, *t*, C_6H_5NH), 7.56–7.68 (2H, *m*, benzolactone), 8.02 (1H, *d* of *d*, benzolactone). Mass spectrum: M/Z 419 (M^+). Found: C, 80.30; H, 5.02; N, 3.30%. Calcd. for $C_{28}H_{21}NO_3$: C, 80.17; H, 5.05; N, 3.34%.

2′,3′-Dimethyl-6′-(4-methoxyphenylamino)-spiro[isobenzofuran-1(3H),9′-[9H] xanthene]-3-one (5): Compound **5** was synthesized by a method similar to that described for **4**. Pale pink crystals (recrystallized from toluene), yield 29%. mp 232–233°C; IR(KBr) 3386 (NH), 1759(COO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25°C, $\delta_{TMS} = 0$ ppm) $\delta = 2.07$ (3H, *s*, $ArCH_3$), 2.26 (3H, *s*, $ArCH_3$), 3.81 (3H, *s*, MeO), 5.62 (1H, *s*, NH), 6.48 (1H, *d* of *d*, xanthene), 6.49 (1H, *s*, xanthene), 6.57 (1H, *d* of *d*, xanthene), 6.69 (1H, *d* of *d*, xanthene), 6.81 (2H, *d*, $MeOC_6H_4NH$), 7.01 (1H, *s*, xanthene), 7.12 (2H, *d*, $MeOC_6H_4NH$), 7.16 (1H, *d* of *d*, benzolactone), 7.58–7.67 (2H, *m*, benzolactone), 8.01 (1H, *d* of *d*, benzolactone). Mass spectrum: M/Z 449 (M^+). Found: C, 77.32; H, 5.20; N, 3.15%. Calcd. for $C_{29}H_{23}NO_4$: C, 77.49; H, 5.16; N, 3.12%.

Measurements

To obtain absorption spectra of the fluorans in phenolic solvents, *m*-cresol was mainly used. A methanol solution containing 0.5 M sodium methoxide was used as an alkaline solvent. Other solvents used were special grade or spectral grade. Absorption spectra were recorded with a Shimadzu UV-2200 spectrophotometer at 25°C.

The molecular structures of the colourless and the coloured species of the fluoran compounds were determined by ^{13}C NMR spectroscopy. $CDCl_3$ and phenol-d_6 were used as the solvents. The signals were assigned using 2D NMR techniques involving H, C-COSY (^1H, ^{13}C Chemical-shift Correlation Spectroscopy), COLOC (Correlated Spectroscopy by Long Range Coupling) and 2D NOE [NOESY (Nuclear Overhauser Effect Spectroscopy)]. The NMR spectrometer used was a Bruker AMX 400 (proton resonance frequency: 400 MHz).

RESULTS AND DISCUSSION

Absorption spectra of fluoran compounds in protic media

When dissolved in aprotic solvents such as chloroform, benzene, tetrahydrofuran and acetonitrile, compounds **1-5** showed no visible absorption. This indicates that in aprotic solvents these compounds substantially exist as the colourless lactone structure. On the other hand, these compounds developed coloured species upon contact with phenol-related compounds. Absorption spectra of **1-5** in *m*-cresol (pK_a in water: 10.1) [11] are shown in Fig. 1. The absorption maxima (λ_{max}) and the molar absorptivities (ε at the λ_{max}) of these compounds are listed in Table 1. Compound **3** showed two

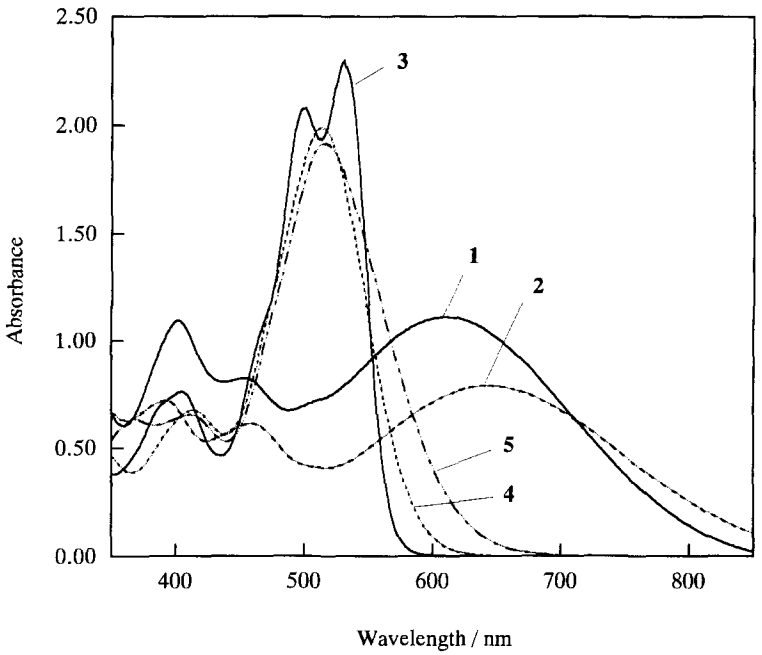


Fig. 1. Visible absorption spectra of **1–5** in *m*-cresol at 25°C. [Flourans]: 7.5×10^{-5} M. Light-path length: 1 cm.

TABLE 1
Visible Absorption Maxima (λ_{max}) and Molar Absorptivities (ε at λ_{max}) of **1–5** in *m*-Cresol and Alkaline Methanol at 25°C.

Compound	λ_{max}/nm	$(\varepsilon\times10^{-4}/M^{-1}cm^{-1})$
	m-Cresol	*MeOH Containing 0.5M MeONa*
1	402(1.46) 608(1.48)	440(0.89) 550(1.25)
2	393(0.96) 461(0.82) 645(1.05)	436(0.43) 561(0.55)
3	406(1.09) 501(2.97) 531(3.29)	ND[a]
4	415(0.90) 513(2.65)	486(1.19)
5	370(0.87) 411(0.90) 517(2.62)	494(1.25)

[a]not detected

narrow absorption bands at λ_{max} 531 nm and λ_{max} 501 nm with a shoulder band at λ_{max} *ca.* 400 nm, giving an orange colour. It is generally accepted that the conventional type of flouran compounds represented by **3** and rhodamines, which have an *N,N*-dialkylamino group at the 6-position of the xanthene ring, form coloured zwitterions in protic solvents such as alcohols and *m*-cresol (Scheme 1) [7–9, 12–14]. In contrast to **3**, **1** formed a remarkably broad absorption band in the range of *ca.* 500–850 nm (λ_{max} 608 nm) together with another band at λ_{max} *ca.* 400 nm, and showed a dark green colour. A spectrum similar to that of **1** was observed for **2** with a 37 nm bathochromic shift of the first (longest wavelength) absorption band (λ_{max} 645 nm). In all cases, the absorption spectra satisfied Lambert-Beer's law at concentrations of **1-5** below 1.0×10^{-4} M, and the spectral shapes were scarcely affected by the concentration change. This implies that these spectra do not stem from intermolecular aggregates such as intermolecular charge-transfer complexes.

In order to ascertain the molecular structure of the coloured species of **1** formed in *m*-cresol, the ^{13}C NMR spectra of **1** were measured in $CDCl_3$ and phenol-d_6 (Fig. 2). The chemical shifts (δ from $SiMe_4$) are listed in Table 2. In $CDCl_3$, the signal of the spiro carbon (No. 9 in Table 2) in **1** (δ 83.9 ppm) appeared in the typical C(sp^3, quaternary)-O region (75–85 ppm) [15], indicating that **1** substantially exists as the lactone structure (**1a** in Scheme 3). On the other hand, in phenol-d_6, the signal of the spiro carbon in **1** significantly shifted to a lower magnetic field [relative chemical shift ($\Delta\delta$) from the corresponding signal observed in $CDCl_3$, 77.8 ppm] and appeared in the sp^2-hybridization region (δ 161.8 ppm). A remarkable upfield shift was also

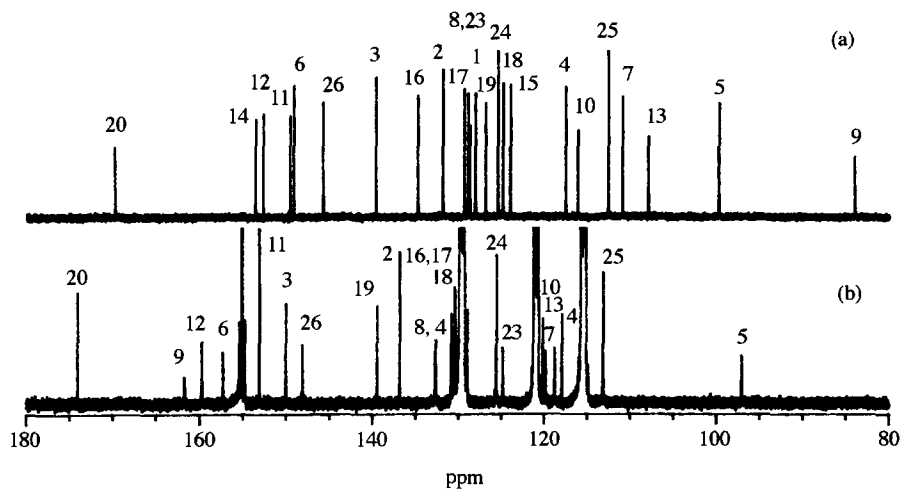
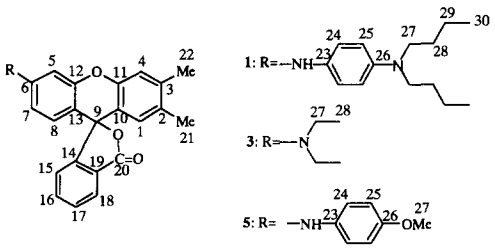


Fig. 2. Partial ^{13}C NMR spectra of **1** in $CDCl_3$ at 25°C (*a*) and in phenol-d_6 at 50°C (*b*). [**1**]: 0.1 M. Numbers attached to the signals: see Table 2.

TABLE 2

^{13}C NMR Chemical Shifts (δ in ppm from $SiMe_4$) of **1**,**3** and **5** in $CDCl_3$ at 25°C, and Relative Chemical Shifts ($\Delta\delta$ in ppm) of Each Carbon in Phenol–d_6 at 50°C [$\Delta\delta$ = (δ Observed in Phenol–d_6)–(δ Observed in $CDCl_3$), at Each Carbon]

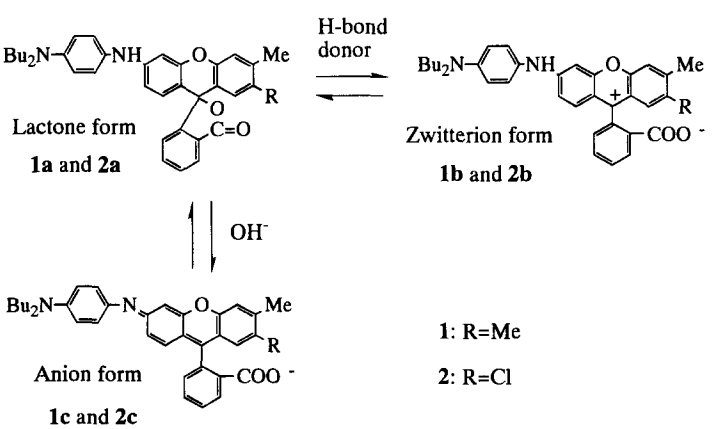


	1		*3*		*5*	
Carbon No.	*δ in $CDCl_3$*	*$\Delta\delta$ in Phenol–d_6*	*δ in $CDCl_3$*	*$\Delta\delta$ in Phenol–d_6*	*δ in $CDCl_3$*	*$\Delta\delta$ in Phenol–d_6*
1	128.1	0.9	128.2	0.8	128.1	0.8
2	131.9	5.0	131.7	4.8	132.0	4.8
3	139.7	10.3	139.6	10.2	139.8	10.3
4	117.5	0.4	117.5	0.2	117.5	0.4
5	99.8	–2.8	97.6	–1.9	100.6	–3.4
6	149.2	8.1	149.5	7.7	147.9	8.9
7	110.9	8.9	108.2	8.7	111.4	7.5
8	129.0	3.7	128.9	3.8	129.1	3.5
9	84.0	77.8	84.3	78.8	83.7	74.9
10	116.1	4.1	116.3	3.6	116.0	3.8
11	149.6	3.5	149.8	3.1	149.5	3.5
12	152.7	7.1	152.9	6.2	152.7	6.6
13	107.9	10.9	105.2	12.6	109.0	8.8
14	153.6	–20.9	153.6	–21.9	153.6	–19.8
15	124.0	5.3	124.0	5.0	124.1	4.8
16	134.8	–3.9	134.7	–4.0	134.9	–4.1
17	129.4	1.1	129.3	–0.7	129.5	1.2
18	124.8	5.6	124.8	5.6	124.9	5.2
19	126.9	12.6	127.1	12.7	126.8	11.6
20	169.8	4.3	169.8	4.4	169.7	4.0
21	19.0	–0.1	19.0	–0.3	19.0	–0.2
22	19.8	0.8	19.8	0.6	19.8	0.7
23	128.8	–4.0	—	—	134.0	–4.0
24	125.5	0.4	—	—	124.1	1.7
25	112.6	0.5	—	—	114.8	0.7
26	145.8	2.3	—	—	156.3	2.2
27	51.1	–0.1	44.5	1.4	55.6	0.0
28	29.4	0.1	12.5	–0.3	—	—
29	20.4	0.1	—	—	—	—
30	14.0	0.0	—	—	—	—

produced in a benzolactonic carbon atom (No. 14 in Table 2). In addition to this change, relatively large shifts (> 3 ppm) in the δ values were observed for most of the fluoran carbons. These results support the view that, in phenol-d_6, a cleavage of the C(spiro)-O bond in the lactone ring takes place, and the conjugation system of the xanthene ring significantly changes. As can be seen from Table 1, the similarity of the δ values and the $\Delta\delta$ values of **1** to those of **3** suggests that the coloured species of **1** formed in *m*-cresol would be its zwitterion (**1b** in Scheme 3). It has been reported that the chemical shift of the spiro carbon in the coloured species of 9-(diethylamino)-spiro[12H-benzo[a]xanthene-12,1′(3H)-isobenzofuran]-3′-one appears at at 162 ppm [16]. This also supports the belief that **1b** is produced in phenol-d_6. Similar changes in the $\Delta\delta$ values were observed for **5**. The coloured species of **1** would not be a cation in which protons are attached to the nitrogen atoms in the phenylenediamine moiety, because the $\Delta\delta$ values of the carbon atoms in the neighborhood of the nitrogen atoms are small.

Interestingly, the analogs of **1**, i.e., **4** which does not have the *N,N*-dibutylamino group in **1**, and **5** in which the *N,N*-dibutylamino group is replaced by a methoxyl group, showed spectra similar to that of **3** (Fig. 1). It is thus considered that the *N,N*-dibutylamino groups in the phenylenediamine moieties play an important role in the broad absorption bands observed in **1b** and **2b**. To reveal the electronic transition characteristics of **1b** and **2b**, investigations of the molecular orbital calculations are currently being conducted in this laboratory. The electronic transition characteristics of the conventional fluoran dyes have already been investigated using the PPPMO method [17].

The λ_{max} and ε values of **2** in various protic media are summarized in Table 3. Among the phenol-related compounds examined, a decrease in the ε value occurred in *o*-cresol and *o*-chlorophenol, and no visible absorption was



Scheme 3

TABLE 3
Visible Absorption Maxima (λ_{max}) of the First Absorption Bands and Molar Absorptivities (ε at λ_{max}) of **2** in Various Protic Media at 25°C

Solvent	λ_{max}/nm	$\varepsilon \times 10^{-4}/M^{-1}cm^{-1}$
o-Cresol	623	0.38
o-Chlorophenol	640	0.54
o-Methoxyphenol	Nd[a]	—
m-Methoxyphenol	648	1.13
m-Hydroxyacetophenone	ND	—
Salicylaldehyde	ND	—
Acetic Acid	637	0.11
Ethanol	ND	—
2,2,2-Trifluoroethanol	604	1.07

[a]not detected

observed in *o*-methoxyphenol, *o*-hydroxyacetophenone and salicylaldehyde. The formation of the zwitterion of the flouran compound in alcoholic and phenolic solvents is promoted by hydrogen-bonding interactions between the flouran (at the charged $-COO^-$ group) and the protic solvents [12, 18]. The interaction should be inhibited when the hydrogens in the phenolic OH groups become unavailable through ortho chelation (i.e., formation of intramolecular hydrogen bond) and steric effects. Similar phenomena were reported in the case of rhodamine B. [18]. The unexpected decrease in the ε value in a relatively strong acid, i.e., acetic acid (pK_a in water: 4.6) [11], may be attributed to the strong self-association of acetic acid, which causes loss of enthalpy in the formation of the solute-solvent interaction [12]. As for alcoholic solvents, ethanol, being a weak hydrogen-bonding donor compared with phenols, did not develop the coloured **2b**, while almost full colour development occurred in 2,2,2-trifluoroethanol, which is known to be a strong hydrogen-bonding donor [12] (pK_a in water: 12.4) [15].

Absorption spectra of flouran compounds in alkaline media

Compounds **1** and **2** developed different absorption spectra in alkaline methanol containing 0.5 M sodium methoxide (Fig. 3) and were purple in colour. Because **3** showed no absorption spectrum under the same conditions whereas **4** and **5** developed spectra, the colour development in the alkaline media is a property common to the fluorans having an -NH-phenyl group at the 6-position of the xanthene ring. Thus, the coloured species developed in the alkaline medium may be anions which are produced by the deprotonation of the -NH-groups (Scheme 3). Although we measured the NMR spectra of **1** under alkaline conditions in an effort to obtain spectroscopic evidence for the structure of **1c**, the anionic species could not be determined because of

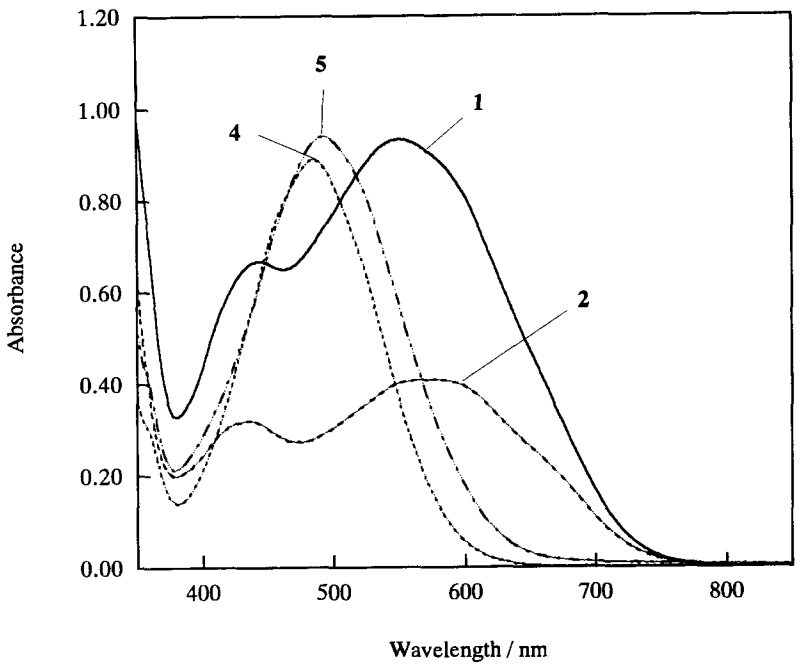


Fig. 3. Visible absorption spectra of **1–5** in methanol containing 0.5 M MeONa [Flourans]: 7.5×10^{-5} M. Light-path length: 1 cm. **3** showed no visible absorption.

signal broadening. The anions **1c** and **2c** (Scheme 3) have structures analogous to indoaniline-type dyes [19–21]. The formation of a coloured anion of the 3-arylphthalide derivative has been reported [22].

As noted in Table 1, the λ_{max} values of **1** and **2** showed *ca.* 50–60 nm bathochromic shifts compared with those of **4** and **5**. The large difference in the ε values of **1** and **2** under this particular condition (0.5 M MeONa) may be partially due to the positions of the lactone-anion equilibria. Compound **1** almost fully developed the anion in this condition, whereas the ε value of **2** (5.4×10^3 M^{-1} cm^{-1} in methanol containing 0.5 M MeONa) was raised to 7.00×10^3 M^{-1} cm^{-1} in methanol solution containing 1.0 M MeONa.

In conclusion, this paper has reported that the new flouran compounds having a *p*-(*N,N*-dibutylamino)phenylamino moiety at the 6-position of the xanthene ring have unique spectral characteristics and would be promising compounds as a basic skeleton of a new functional leuco dye.

REFERENCES

1. Gregory, P., *High Technology Applications of Organic Colorants.* Plenum Press, New York, 1991, p. 124.

2. Griffiths, J., *Developments in the Chemistry and Technology of Organic Dyes*. Blackwell Sci. Pub. Ltd, London, 1984, p. 26.
3. Nishimura, Y., Misawa, H., Sakuragi, H. and Tokumaru, K., *Chemistry of Functional Dyes (I)*. eds. Z. Yoshida & T. Kitao, 1989, p. 164, Mita Press, Tokyo.
4. Kubata, M., Yoshioka, H., Nakatsu, K., Matsumoto, M. and Sato, Y., *Chemistry of Functional Dyes (I)*, eds. Z. Yoshida & T. Kitao, 1989, p. 223, Mita Press, Tokyo.
5. Yamaguchi, T., Takakura, T., Murofushi, K. and Imamura, K., *Chemistry of Functional Dyes (I)*, eds. Z. Yoshida & T. Kitao, 1989, p. 397, Mita Press, Tokyo.
6. Minami, K. and Kitao, T , *Chemistry of Functional Dyes (I)*, eds. Z. Yoshida & T. Kitao, 1989, p. 524, Mita Press, Tokyo.
7. Sato, Y., *Shikizai Kyokaishi (J. Japan Soc. of Col. Mater.)*, **61** (1988) 292.
8. Hatano, Y., *Shikizai Kyokaishi (J. Japan Soc. of Col. Mater.)*, **62** (1989) 288.
9. Kaneko, T., *Shikizai Kyokaishi (J. Japan Soc. of Col. Mater.)*, **65** (1992) 21.
10. Mitsui, H., Nagao, Y., Abe, Y. and Misono, T., *Shikizai Kyokaishi (J. Japan Soc. of Col. Mater.)*, **68** (1995) 403.
11. Chem. Soc. Jpn. (ed.), *Kagaku Binran Kiso-hen II (Handbook of Chemistry, in Japanese)*, 1984, p. 340, Maruzen, Tokyo.
12. Hinckley, D. A., Seybold, P. G. and Borris, D. P., *Spectrochim. Acta*, **42A** (1986) 747.
13. Hinckley, D. A. and Seybold, P. G., *Spectrochim. Acta*, **44A** (1988) 1053.
14. Sueishi, Y., Sugiyama, Y., Yamamoto, S. and Nishimura, N., *Bull. Chem. Soc. Jpn.*, **67** (1994) 572.
15. Jpn. Sci. Anal. Chem. (ed.), *Bunseki Kagaku Data Book (Data Book of Anal. Chem.*, in Japanese), 1983, p. 180, Maruzene, Tokyo.
16. Ribs, G. and Weis, C. D., *Dyes and Pigments*, **15** (1991) 165.
17. Matsuoka, M., Ueda, K. and Kitao, T., *Shikizai Kyokaishi*, **55** (1982) 213.
18. Lundgren, H. P. and Binkley, C. H., *J. Polymer. Sci.*, **14** (1954) 139.
19. Tokita, S., Suzuki, T. and Nikaido, M., *J. Photopolym. Sci. Technol.*, **5** (1992) 533.
20. Tokita, S., Suzuki, T., Shimokashi, T., Kogo, Y. and Kafuku, K., *J. Photopolym. Sci. Technol.*, **4** (1991) 410.
21. Adachi, M., Murata, Y. and Nakamura, S., *J. Org. Chem.*, **58** (1993) 5238.
22. Nakai, Y., Nagao, Y., Abe, Y., Misono, T., Tsuchida, T. and Kondo, M., *Shikizai Kyokaishi*, **63** (1990) 463.