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Synthesis of some Novel Oxygen-Containing Cyanine Dyes

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ABSTRACT

p-Substituted 2-phenyl-4,5-dihydrofurylium hexachloroantimonates and their 5-methyl analogues underwent acid-catalysed condensation with ethyl orthoformate, malonaldehyde tetraethyl acetal, and glutaconaldehyde potassium salt to give a facile synthesis of a series of novel cyanine dyes involving oxonium salt–enol ether resonance. X-ray crystallography of bis [2-(p-fluorophenyl)-4,5-dihydrofur-3-yl]methinecyanide hexachloroantimonate was studied.

1 INTRODUCTION

Cyanine dyes are well known as spectral sensitizers;[1] within this class of dyes those related to oxygen heterocycles are relatively few, but have been reported derived from pyrylium,[2] flavylium,[3] and dihydrofurylium salts.[4]

The neighbouring participation of a carbonyl group in solvolysis results in the formation of oxonium salts as intermediates,[5] among which the 2-phenyl-4,5-dihydrofurylium salt from 4-chlorobutyrophenone (**1c**) is notable for its stability and can be prepared as the crystalline hexachloroantimonate (**3c**). We report here that variously *p*-substituted **3** and **4** are highly reactive active methylene compounds and undergo acid-catalysed condensation with ethyl orthoformate, malonaldehyde tetraethyl acetal, as well as with glutaconaldehyde potassium salt, to give respectively highly

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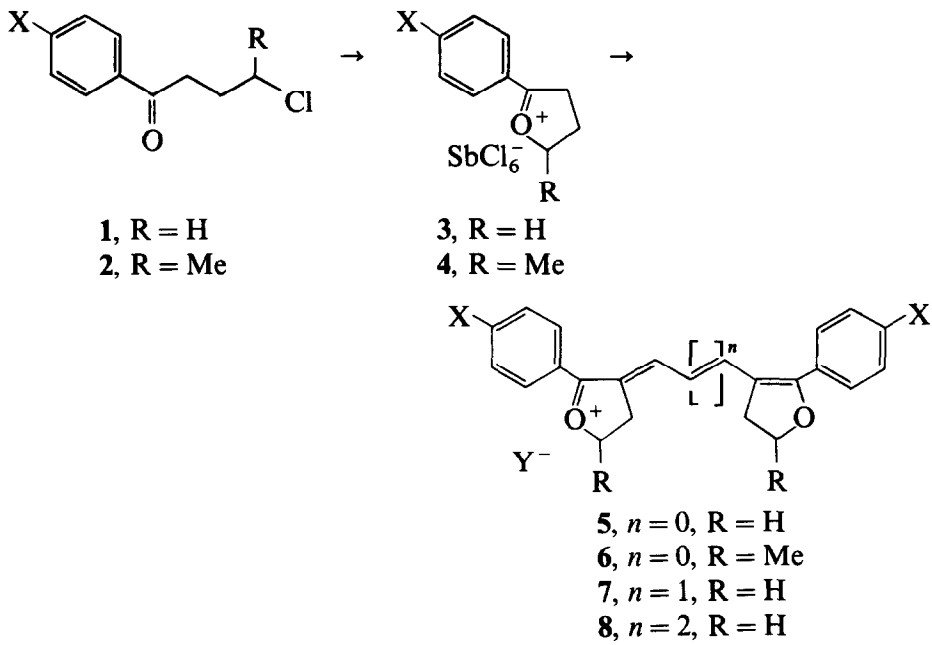
TABLE 1
Synthesis and Characterization of Cyanine Dyes[a]

Dye	*R*	*X*	*Y*	*Reaction* (°C/h)	*Yield* (%)	*M.p.* (*dec.*) (°C)	λ_{max} (*nm*)/$10^{-4}\varepsilon$ (*solvent*)	*Formula* (*mol. wt*)	*Analysis* (%)		
										Calcd	*Found*
5a	H	OH	Br	50/24	95	230–231	533/4·73 (MeOH)	$C_{21}H_{19}O_4Br.H_2O$ (433·1)	C: H:	58·2 4·9	58·5 5·2
5b	H	OMe	Br	50/24	30	158–159	528·5/3·65 (MeOH)	$C_{23}H_{23}O_4Br$ (441·1)	C: H:	62·3 5·2	62·0 5·2
5c	H	H	$SbCl_6$	20/50	75	170–171	490·5/5·02 (MeCN)	$C_{21}H_{19}O_2SbCl_6$ (638)	C: H:	39·5 3·0	39·3 2·9
5d	H	Ph	$SbCl_6$	15/50	70	192–193	518·5/3·76 (MeCN)	$C_{33}H_{27}O_2SbCl_6$ (790·1)	C: H:	50·2 3·4	50·4 3·4
5e	H	F	$SbCl_6$	20/50	71	169–170	493·5/5·88 (MeCN)	$C_{21}H_{17}O_2F_2SbCl_6$ (673·6)	C: H:	37·4 2·5	37·8 2·6
5f	H	Cl	$SbCl_6$	15/50	57	175–176	500·5/4·75 (MeCN)	$C_{21}H_{17}O_2SbCl_8$ (706·5)	C: H:	35·7 2·4	35·8 2·4
5g	H	Br	$SbCl_6$	15/50	66	182–183	502/5·17 (MeCN)	$C_{21}H_{17}O_2Br_2SbCl_6$ (795·4)	C: H:	31·7 2·2	31·9 2·1
5h	H	NO_2	$SbCl_6$	10/69	48	157–158	500·5/4·53 (MeCN)	$C_{21}H_{17}O_6N_2SbCl_6.CH_3CN$ (768·9)	C: H: N:	35·9 2·6 5·5	36·2 2·7 5·2
6a	Me	OH	TsO	50/48	97	228–230	525/7·2 (MeOH.HCl)	$C_{30}H_{30}O_7S$ (534·2)	C: H:	67·4 5·6	67·3 5·7
6b	Me	OBzl	TsO	50/48	53	155–156	525/— (MeCN.HCl)	$C_{44}H_{42}O_7S$ (714·3)	C: H:	73·9 5·9	74·0 6·2
6c	Me	H	$SbCl_6$	25/96	77	191–192	490/5·02 (MeCN.HCl)	$C_{23}H_{23}O_2SbCl_6$ (666)	C: H:	41·5 3·5	41·0 3·5

6d	Me	Me	$SbCl_6$	25/84	93	190–191	502/— (MeCN . HCl)	$C_{25}H_{27}O_2SbCl_6$ (704)	C: H:	42·6 3·9	42·7 3·9
6e	Me	F	$SbCl_6$	25/96	70	204–205	492/5·32 (MeCN . HCl)	$C_{23}H_{21}O_2F_2SbCl_6$ (702)	C: H:	39·3 3·0	38·8 3·0
6f	Me	Cl	$SbCl_6$	25/96	82	194–196	498/4·87 (MeCN . HCl)	$C_{23}H_{21}O_2SbCl_8$ (734·9)	C: H:	37·6 2·9	36·9 2·5
6g	Me	Br	$SbCl_6$	25/96	83	202–203	500/4·92 (MeCN . HCl)	$C_{23}H_{21}O_2Br_2SbCl_6$ (823·8)	C: H:	33·5 2·6	33·1 2·5
7a	H	OH	TsO	50/24	67	220–222	627/10·39 (MeOH . HCl)	$C_{30}H_{28}O_7S . \frac{1}{2}H_2O$ (541·2)	C: H:	66·7 5·6	66·5 5·3
7b	H	OMe	TsO	50/24	76	184–186	616/6·56 (MeCN . HCl)	$C_{32}H_{32}O_7S$ (560·3)	C: H:	68·6 5·7	68·5 5·7
7c	H	H	$SbCl_6$	25/48	50	151–153	585/— (MeCN . HCl)	$C_{23}H_{21}O_2SbCl_6$ (663·6)	MS, *m/e*: 329 ($M - SbCl_6$)		
7d	H	Ph	$SbCl_6$	25/24	68	167–169	613/9·78 (MeCN . HCl)	$C_{35}H_{29}O_2SbCl_6$ (815·7)	C: H:	51·5 3·6	51·6 3·5
7e	H	F	$SbCl_6$	25/56	32	168–170	587/— (MeCN . HCl)	$C_{23}H_{19}O_2F_2SbCl_6$ (699·6)	MS (FAB^+): 365 ($M - SbCl_6$)		
7f	H	Cl	$SbCl_6$	25/24	50	180–182	594/6·87 (MeCN . HCl)	$C_{23}H_{19}O_2SbCl_8$ (732·5)	MS (FAB^+): 397 ($M - SbCl_6$)		
7g	H	Br	$SbCl_6$	25/24	57	179–180	594/— (MeCN . HCl)	$C_{23}H_{19}O_2Br_2SbCl_6$ (821·4)	MS (FAB^+): 487 ($M - SbCl_6$)		
8a	H	OH	TsO	50/48	77	199–201	714/— (MeOH . HCl)	$C_{32}H_{30}O_7S$ (558·2)	C: H:	68·8 5·4	68·3 5·4
8b	H	OMe	TsO	50/48	39	116–119	708/— (MeCN . HCl)	$C_{34}H_{34}O_7S$ (586·3)	MS (EI): 416 ($M - TsO$)		
8c	H	H	$SbCl_6$	25/96	52	140–142	674/— (MeCN . HCl)	$C_{25}H_{23}O_2SbCl_6$ (689·6)	MS (EI): 355 ($M - SbCl_6$)		
8e	H	F	$SbCl_6$	25/96	70	204–206	674/— (MeCN . HCl)	$C_{25}H_{21}O_2F_2SbCl_6$ (725·6)	MS (EI): 391 ($M - SbCl_6$)		

[a] IR and PMR spectra are not reported.



Scheme 1. X and Y are defined in Table 1.

coloured methine (**5** and **6**), trimethine (**7**) and pentamethine (**8**) cyanine dyes with oxonium salt–enol ether resonance (Scheme 1).

2 RESULTS AND DISCUSSION

Both *p*-substituted 4-chlorobutyrophenones (**1**) and *p*-substituted 4-chlorovalerophenones (**2**) and their related hydroxy and bromo derivatives were prepared by Friedel–Crafts acylation,[6,7] except for *p*-nitro-4-chlorobutyrophenone (**1h**) which was prepared by hydrolytic decarboxylation of 2-(*p*-nitrobenzoyl)butyrolactone.[8] The cyclic oxonium hexachloroantimonates (**3** and **4**) were prepared by treating **1** and **2** with antimony pentachloride in dichloromethane[5] and were obtained as crystalline solids which were used directly without further purification.

Whilst the formation of most cyanine dyes is base-catalysed, the title cyanine dyes (Table 1) were formed directly from the hexachloroantimonates. Due to their strong electron-donating ability, the *p*-hydroxy and *p*-alkyloxy 4-halo and 4-hydroxy-ketones of **1** and **2** were capable of condensing with carbonyl components directly to give cyanine dyes in presence of *p*-toluenesulphonic acid. The stability of the oxygen cyanine dyes decreases with increasing number of methine groups, as is usually

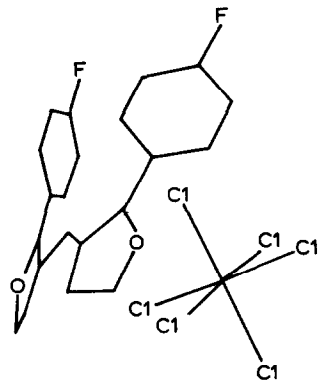


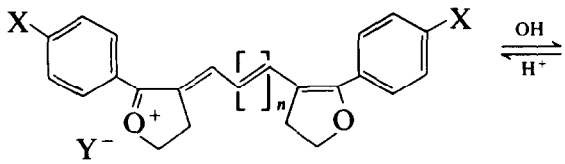
Fig. 1. Structure of **5e** determined in the Laboratory of X-ray Crystallography, Peking University, Beijing, People's Republic of China.

observed. The formation of the pentamethine cyanine dyes was thus somewhat sluggish and some of them refused to crystallize, whilst the heptamethine derivatives were too unstable to be isolated.

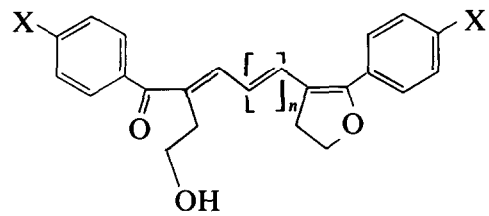
One of the methine dyes (**5e**) was subjected to single-crystal X-ray analysis and the result is shown in Fig. 1. The molecule is *trans*-oriented, with most of the bond lengths practically identical to normal values. The two C—O bond lengths are both 1·328 Å, intermediate between C=O double and C—O single bond lengths, indicating that the lone pair electrons of both oxygen participate in the resonance. Two dihydrofuran rings incline to each other at an angle of 28·9°, while the angle of inclination between the phenyl and heterocyclic rings is 31·5°.

Addition of dilute sodium hydroxide or sodium bicarbonate solution to a solution of the cyanine dyes **5** and **7** converted them to their yellow pseudo bases **9** and **10** respectively [eqn (1); Table 2]. Both **9** and **10** were crystalline solids and only moderately stable, slowly turning red on standing. Prolonged heating during recrystallization should be avoided since they usually separated from solution as oils. The pseudo bases **10b** and **10d** taken as examples, on treatment with an acid reverted back to the cyanine dyes **7b** and **7d**, respectively, and it is thus possible to prepare different salts of the dyes via their pseudo bases.

The colour changes observed with the *p*-hydroxylated cyanine dye **5a** on basification are similar to those of anthocyanidins.[9] Thus, acid and neutral solutions of **5a** in methanol were intensely red. With slow addition of sodium hydroxide or sodium bicarbonate solution, the colour of the solution changed to bluish violet at pH 7–8 and on standing decolorized. Further addition of sodium hydroxide rendered the colour of solution bluish green and, ultimately, yellow. The highly coloured intermediates were most likely



5, $n = 0$
7, $n = 1$

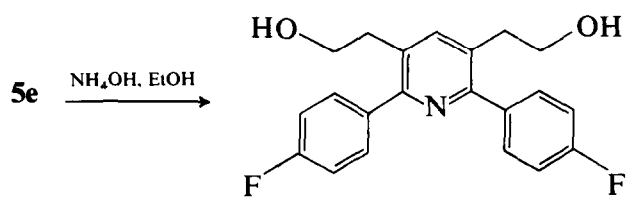


(1)

9, $n = 0$
10, $n = 1$

quinonoids, the colourless one a hemiketal and the yellow one a pseudo base. They were all not stable enough to be isolated.

With ammonium hydroxide, **5e** yielded a pyridine derivative shown by MS, PMR, and elemental analysis to be 2,6-bis(*p*-fluorophenyl)-3,5-bis(2-hydroxyethyl)pyridine (**11**):



11

The respective ranges of UV absorption maximum (nm) were

5	**6**	**7**	**8**
493–533	492–525	585–627	674–714

depending upon the *p*-substituents. A methyl substituent on C(5) of the dihydrofuran ring would affect very slightly the absorption. Some of the cyanine dyes were very difficult to dissolve and their extinction coefficients could not be accurately estimated.

TABLE 2
Pseudo Bases[a]

Pseudo base	*X*	*Yield* (%)	*M.p.* (°C)	λ_{max}[b] (*nm*)	*Formula* (*mol. wt*)		*Analysis* (%) *Calcd*	*Found*
9b	OMe	68	138–140	377	$C_{23}H_{24}O_5$ (380·2)	C:	72·6	71·8
						H:	6·4	6·9
9c	H	68	117–118	366	$C_{21}H_{20}O_3$ (320·2)	C:	78·7	78·7
						H:	6·3	6·4
9d	Ph	53	221–223	378[c]	$C_{33}H_{28}O_3$ (472·2)	C:	83·9	83·5
						H:	6·0	5·8
9e	F	71	129–130	364	$C_{21}H_{18}O_3F_2$ (356·2)	C:	70·8	71·1
						H:	5·1	5·2
9f	Cl	66	143–144	369	$C_{21}H_{18}O_3Cl_2$ (389·1)	C:	64·8	64·5
						H:	4·7	4·5
9g	Br	45	123–124	376	$C_{21}H_{18}O_3Br_2$ (478·0)	C:	52·6	53·0
						H:	4·0	4·1
9h	NO_2	73	134–135	394	$C_{21}H_{18}O_7N_2$ (410·2)	C:	61·5	62·1
						H:	4·4	4·7
						N:	6·4	6·6
10b	OMe	72	150–151	399[d]	$C_{25}H_{26}O_5$ (406·2)	C:	73·9	73·7
						H:	6·4	6·6
10d	Ph	86	187–189	405[d]	$C_{35}H_{30}O_3$ (498·2)	C:	84·3	84·1
						H:	6·1	6·0

[a] IR and PMR are not reported.
[b] Solvents other than methanol were: [c] MeOH–DMF, 10:1; [d] acetone.

3 EXPERIMENTAL

3.1 General

All melting and boiling points were uncorrected. All solvents were purified and redistilled. All evaporations were carried out by rotatory evaporator with the bath temperature at 40–45°C. IR spectra were recorded on a Specord-75 (Carl Zeiss) or a 5MX (Nicolet); PMR on a French RMN-250 or a Varian FT-80; MS on a ZAB-NS (VG); and UV on a Shimadzu UV-250. Chemical shifts are given in ppm from internal TMS.

3.2 Preparation of starting materials

This was as mentioned in Section 2, and below.

3.3 *p*-Nitro-4-chlorobutyrophenone (1h)

A mixture of 2-(*p*-nitrobenzoyl)butyrolactone[8] (5·0 g, 21·3 mmol), concentrated hydrochloric acid (50 ml), and glacial acid (15 ml) was heated at 120°C for 1 h with liberation of carbon dioxide. The cooled reaction mixture was poured into saturated brine (30 ml) with stirring. The solid was filtered, washed with saturated sodium carbonate solution and then water, and dried to give **1h** (3·15 g, 65% yield) with *m/e* 227 (M^+, $C_{10}H_{10}NO_3Cl$, mol. wt. 227·6). It was used directly without further purification.

Acidification of the sodium carbonate washings in the above yielded *p*-nitrobenzoic acid (0·9 g, 24% yield). The reaction temperature should not exceed 120°C and for no longer than 1 h. Thus, 5 h heating led only to the formation of *p*-nitrobenzoic acid in 61% yield.

3.4 2-(*p*-Substituted phenyl)-4,5-dihydrofurylium hexachloroantimonates (3)

Antimony pentachloride (10 mmol) was added to the *p*-substituted 4-chlorobutyrophenone (**1**, 10 mmol) in dichloromethane (25 ml). The formation of **3** took place with evolution of heat. The separated crystalline solid **3** was filtered, dried, and used directly. The yields and melting points (with decomposition) were:

3c (X = H), 95%; m.p. 123–125°C (lit.[5] 65%; m.p. 120–123°C).
3d (X = Ph), 84%; m.p. 112–114°C.
3e (X = F), 95%; m.p. 129–130°C.
3f (X = Cl), 80%; m.p. 119–120°C.
3g (X = Br), 91%; m.p. 115–116°C.
3h ($X = NO_2$), 51%; m.p. 123–125°C.

3.5 2-(*p*-Substituted phenyl)-5-methyl-4,5-dihydrofurylium hexachloroantimonates (4)

These were prepared by the same method as **3**:

4c (X = H), 63%; m.p. 132–133°C.
4d (X = Me), 91%; m.p. 128–130°C.
4e (X = F), 56%; m.p. 129–130°C.
4f (X = Cl), 50%; m.p. 124–126°C.
4g (X = Br), 36%; m.p. 123–124°C.

3.6 Bis[2-(*p*-hydroxyphenyl)-4,5-dihydrofur-3-yl]methinecyanine bromide (5a)

p-Hydroxy-4-bromobutyrophenone (1·1 g, 5 mmol) was dissolved in chloroform (22 ml) and ethyl orthoformate (4·2 ml, 26 mmol) and *p*-

toluenesulphonic acid (0·02 g) was added; the mixture was stirred at 50°C for 24 h. Four times the volume of anhydrous ether was added with stirring and the liquor kept in a refrigerator to crystallize. Compound **5a** was filtered, then washed with and recrystallized from chloroform.

Compound **5b** was similarly synthesized from *p*-methoxy-4-bromobutyrophenone, which was itself prepared by methylation of *p*-hydroxy-4-bromobutyrophenone (Table 1).

3.7 Bis[2-(*p*-hydroxyphenyl)-5-methyl-4,5-dihydrofur-3-yl]methinecyanine *p*-toluenesulphonate (6a)

To *p*,4-dihydroxyvalerophenone (1 g, 5·1 mmol, prepared by Fries rearrangement of phenyl 4-chlorovalerate in 33% yield) in acetonitrile (15 ml) was added ethyl orthoformate (4 ml, 25 mmol) and *p*-toluenesulphonic acid (1 g, 5·7 mmol) and the mixture stirred at 50°C for 48 h. Four times the volume of anhydrous ether was added with stirring and the mixture was kept in a refrigerator for crystallization. The red crystals were filtered, washed with a little anhydrous ether and recrystallized from acetonitrile–ether to give **6a**.

Compound **6b** was similarly synthesized from *p*-benzyloxy-4-hydroxyvalerophenone prepared by benzylation of *p*,4-dihydroxyvalerophenone (Table 1).

3.8 Bis[2-(*p*-substituted phenyl)-4,5-dihydrofur-3-yl]methinecyanine (5) and bis[2-(*p*-substituted phenyl)-5-methyl-4,5-dihydrofur-3-yl]methinecyanine hexachloroantimonates (6): general procedure

To each (10 mmol) of the compounds **3c–3h** and **4c–4g** dissolved in acetonitrile (10–15 ml) was added ethyl orthoformate (3·6 ml, 22 mmol) and the mixture was stirred at ambient temperature for 24–96 h, giving a dark-coloured solution which was worked up as in the preparation of **6a** to give the respective **5** and **6** compounds.

3.9 Bis[2-(*p*-hydroxyphenyl)-4,5-dihydrofur-3-yl]trimethinecyanine *p*-toluenesulphonate (7a)

p,4-Dihydroxybutyrophenone (1 g, 5·6 mmol) was dissolved in acetonitrile (20 ml). Malonaldehyde tetraethyl acetal[10] (4·4 g, 20 mmol) and *p*-toluenesulphonic acid (1·2 g, 7 mmol) were added and the mixture was stirred at 50°C for 24 h. The reaction mixture was worked up as for **5a** and the product was recrystallized from anhydrous methanol–ether to give **7a**.

Compound **7b** was similarly synthesized from *p*-methoxy-4-hydroxybutyrophenone, which was prepared by methylation of *p*,4-dihydroxybutyrophenone (Table 1).

3.10 Bis[2-(*p*-substituted phenyl)-4,5-dihydrofur-3-yl]trimethinecyanine hexachloroantimonates (7): general procedure

To each (5 mmol) of the compounds **3c–3g** dissolved in acetonitrile (12 ml) was added malonaldehyde tetraethyl acetal (2·2 g, 10 mmol) and the mixture was stirred at ambient temperature for 24–96 h. The usual work-up was followed to give the respective compounds **7**, which were recrystallized from acetonitrile (Table 1).

3.11 Bis[2-(*p*-hydroxyphenyl)-4,5-dihydrofur-3-yl]pentamethinecyanine *p*-toluenesulphonate (8a)

p,4-Dihydroxybutyrophenone (1 g, 5·6 mmol) was dissolved in acetonitrile (15 ml). Glutaconaldehyde potassium salt[11] (0·75 g, 5·5 mmol) and a solution of *p*-toluenesulphonic acid (2·1 g, 12 mmol) in acetonitrile (30 ml) were added successively. The mixture was stirred at 50°C for 48 h and, following the usual work-up, gave **8a**, which was recrystallized from acetonitrile.

p-Methoxy-4-hydroxybutyrophenone was used similarly to synthesize **8b** (Table 1).

3.12 Bis[2-(*p*-substituted phenyl)-4,5-dihydrofur-3-yl]pentamethinecyanine hexachloroantimonate (8)

To **3c** (2·4 g, 5 mmol) dissolved in acetonitrile (15 ml), glutaconaldehyde potassium salt (0·7 g, 5·2 mmol) and a solution of *p*-toluenesulphonic acid (1 g, 5·7 mmol) in acetonitrile (15 ml) were added successively. The mixture was stirred at ambient temperature for 96 h, the usual work-up giving **8c**, which was recrystallized from acetonitrile.

Compound **8d** was similarly synthesized from **3d** (Table 1).

3.13 3-(*p*-Substituted benzoyl)-4-[2-(*p*-substituted phenyl)-4,5-dihydrofur-3-yl]but-3-en-1-ol (9)

Each (2 mmol) of the cyanine dyes **5b–5h** was dissolved in acetone (30–50 ml) and 5% sodium bicarbonate was added slowly with stirring. The yellow solid **9** was collected and recrystallized from ethyl acetate–petroleum ether (Table 2).

3.14 3-(*p*-Substituted benzoyl)-6-[2-(*p*-substituted phenyl)-4,5-dihydrofur-3-yl]hexa-3,5-dien-1-ol (10)

The cyanine dyes **7b** and **7d** were converted to their pseudo bases **10b** and **10d** respectively, as for **5** (Table 2).

3.15 Conversion of a pseudo base to its cyanine dye

The pseudo base **10b** (30 mg) was dissolved in a little acetonitrile, and *p*-toluenesulphonic acid (14 mg) was added. The solution turned blue and a green crystalline solid (21 mg, 50% yield) was obtained on addition of anhydrous ether and keeping in a refrigerator. The product was identified by IR and PMR to be the **7b** *p*-toluenesulphonate.

3.16 2,6-Bis(*p*-fluorophenyl)-3,5-bis(2-hydroxyethyl)pyridine (11)

To **5e** (0·7 g, 1 mmol) suspended in ethanol (5 ml) was added 28% ammonium hydroxide (2 ml). The mixture was boiled for 3·5 h with further addition of ammonium hydroxide in small portions (totalling 4 ml). The reaction mixture was poured into water, extracted with ethyl acetate and, with the usual work-up, gave a yellow oil, which was chromatographed on silica gel H using ethyl acetate as eluent to yield a white solid (0·2 g, 55% yield). This was recrystallized from ethyl acetate–petroleum ether in colourless needles, m.p. 128–129°C. IR: ν_{max}^{KBr} 3400, 1610, 1515, 1420, 1235, 1069 cm^{-1}. PMR, δ ($CDCl_3$): 2·13 (s, 2H), 2·88 (t, 4H), 3·73 (t, 4H), 7·08 (m, 8H), 7·66 (s, 1H). MS, *m/e*: 355 (M^+). Analysis: Calcd for $C_{21}H_{19}O_2F_2N$: C, 71·0; H, 5·4; N, 3·9. Found: C, 71·0; H, 5·4; N, 4·2%.

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