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Analogs of Disperse Red 167 Containing a Built-in Photostabiliser Moiety‡

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ABSTRACT

The effects of incorporating a benzophenone stabilizer into the structure of Disperse Red 167 have been investigated. In this study, four different substituents in the parent dye structure were substituted sequentially to build the desired stabilizer moiety into the backbone of the prototype dye. Although the lightfastness of the dyes prepared was not superior to that of the parent dye, each possessed better sublimation fastness than the prototype and served as a useful probe of the requirements for high lightfastness on polyester.

The structure of each new compound was confirmed by [^{1}H] NMR, elemental analysis, and mass spectrometry. In addition, the detailed structure of one of the analogs was determined from X-ray diffractometer data.

INTRODUCTION

In previous reports from these laboratories, we described[1–3] results from the incorporation of benzophenone and benzotriazole groups into the backbone of the automotive disperse yellow dyes **1** and **2**. It is clear from

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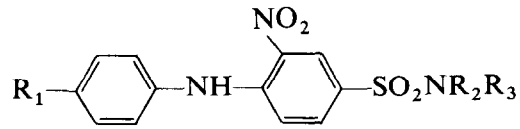


	R_1	R_2	R_3
1 (Disperse Yellow 42)	H	H	Ph
2 (Disperse Yellow 86)	EtO	Me	Me

those studies that both the lightfastness and sublimation fastness of nitrodiphenylamine disperse dyes can be improved by this approach. It is also clear from those studies, however, that both the stabilizer type employed and the site at which the stabilizer is incorporated determine the fastness properties of the final dye.

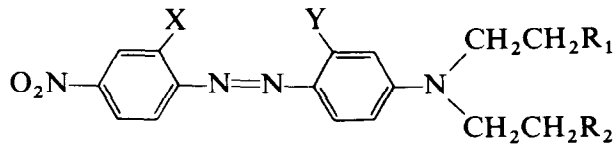
In the present paper, results from the extension of the above approach to the development of lightfast red analogs of the important monoazo dye Disperse Red 167 are described. Specifically, the synthesis and analysis of monoazo dyes **3**–**6** and disazo dye **7** are reported.

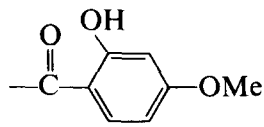
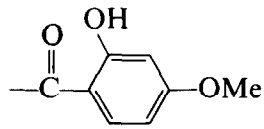
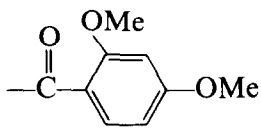
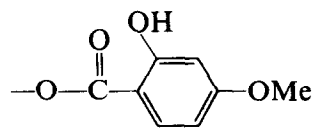
RESULTS AND DISCUSSION

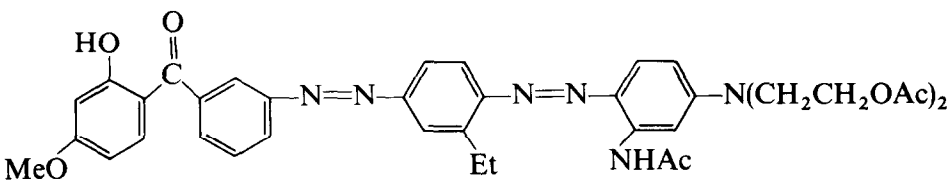
Dye **3** was synthesized by the four-step route shown in Scheme 1. The benzophenone **8** was prepared in two steps from 1,3-dimethoxybenzene and *meta*-nitrobenzoyl chloride (i.e. Friedel-Crafts acylation[4] at low temperature, followed by catalytic hydrogenation over Pd catalyst). Conversion of **8** to **9** was carried out in HOAc at 90°C. This was followed by acetylation in pyridine, demethylation with the aid of $AlCl_3$, and diazo coupling of **12** to **11**. The reaction yield in the final step was 88%.

Dyes **4** and **5** were made according to the sequence shown in Scheme 2. The process began with the amination of **13** (from the acylation of 1,3-dimethoxybenzene using 2-chloro-5-nitrobenzoyl chloride). Interestingly, treatment of **13** with potassium phthalimide gave **14** directly, along with the by-product **15** (from demethylation of the α-methoxy group of **13**, followed by cyclodehydrohalogenation). Compound **14** was either diazotized and coupled to **18** to give dye **5**, or converted to the target dye via steps **16** → **17a** → **4**.

The synthesis of dye **6** began with the preparation of azo compound **20** (cf. Scheme 3). Diazo coupler **19** was used because it permits the introduction of a single *ortho*-hydroxybenzoyl group and takes advantage of the ability of a β-cyanoethyl group to impart good lightfastness[5,6]



Dye	*X*	*Y*	R_1	R_2
3	Cl		OAc	OAc
4		NHAc	OAc	OAc
5		NHAc	OAc	OAc
6	Cl	NHAc		CN



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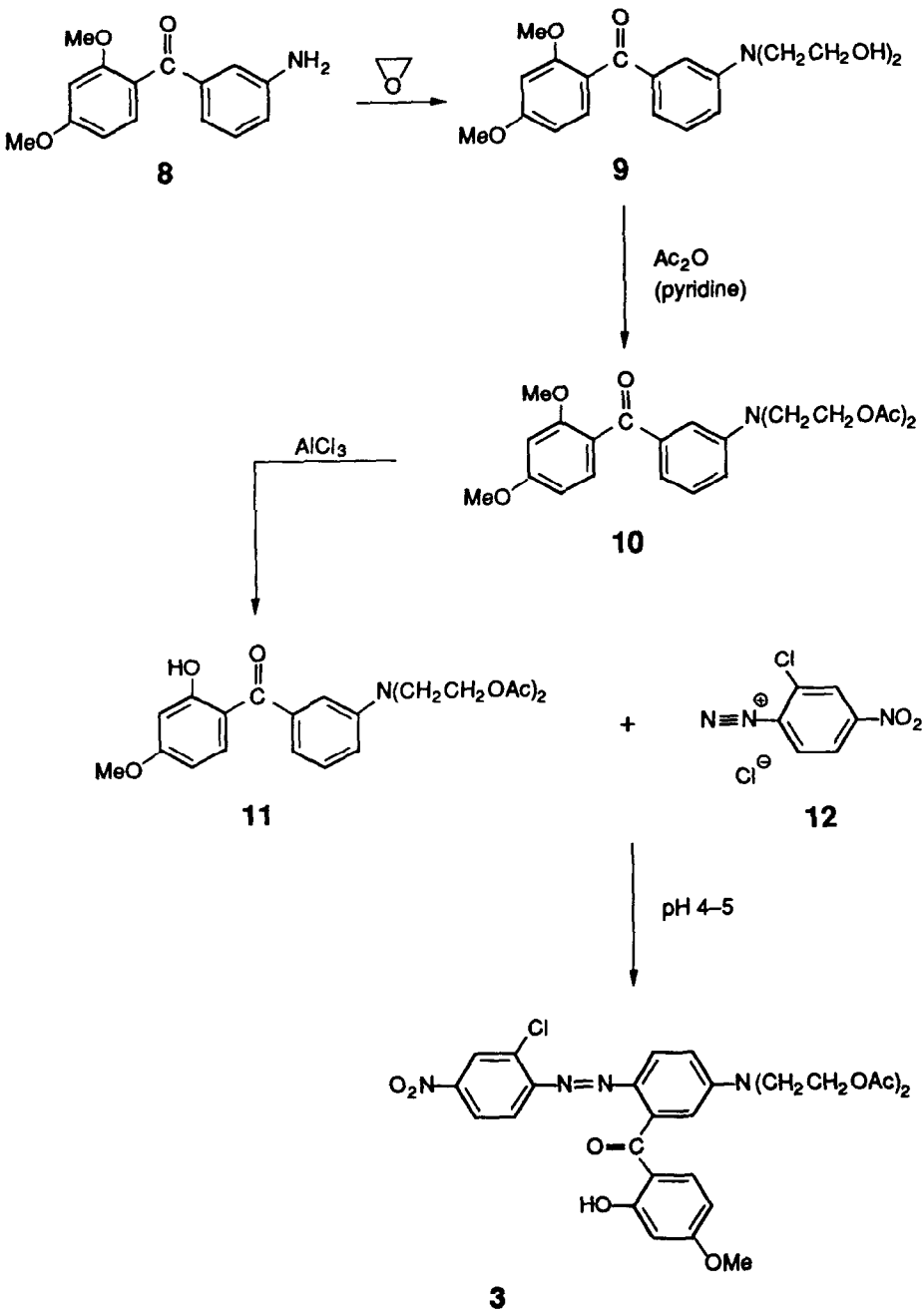
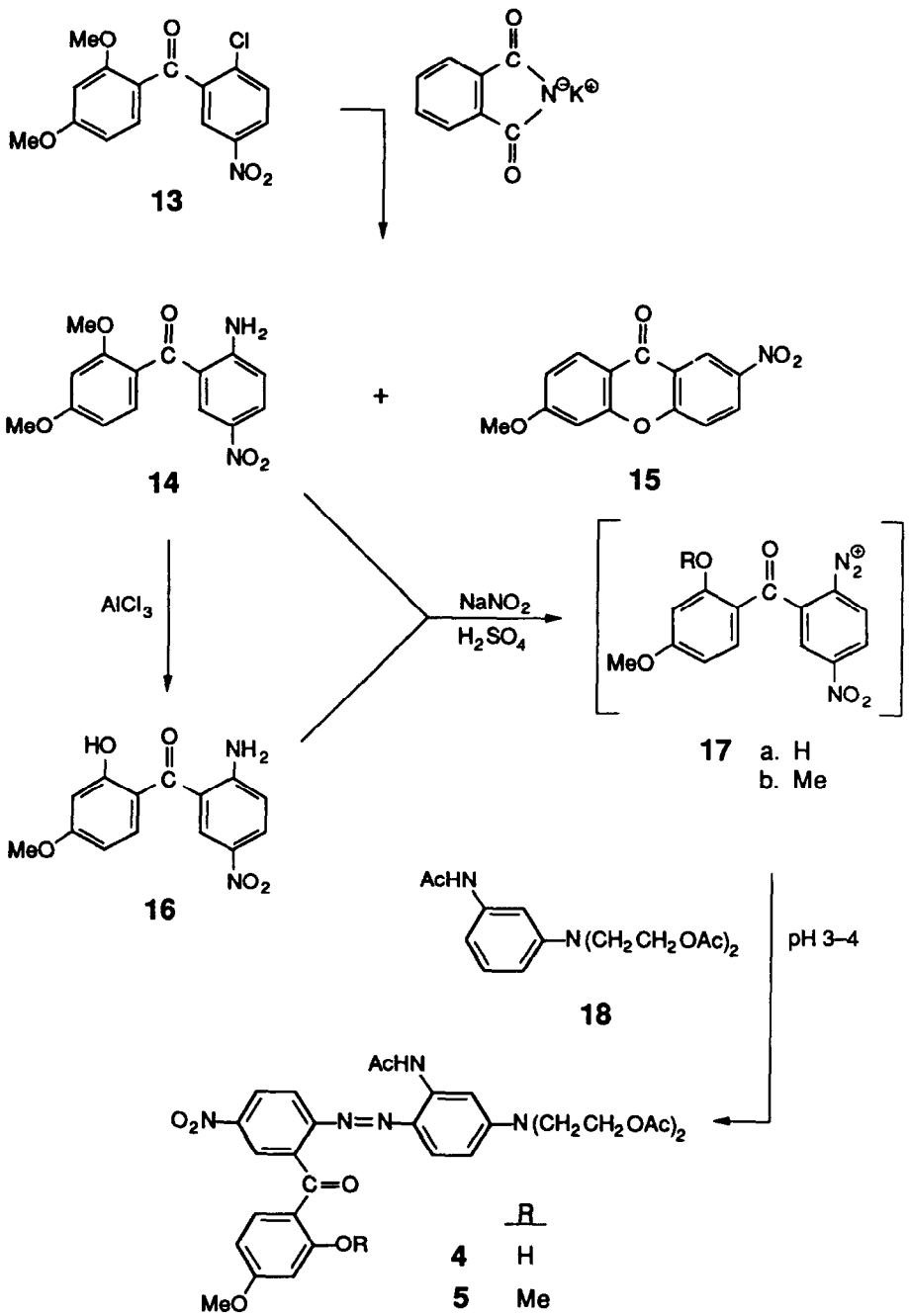
when used as the pendant side chain in a disperse dye structure. Compound **20** was then esterified using 2,4-dimethoxybenzoyl chloride to form **22**. The target dye was obtained by stirring **22** with $AlCl_3$.

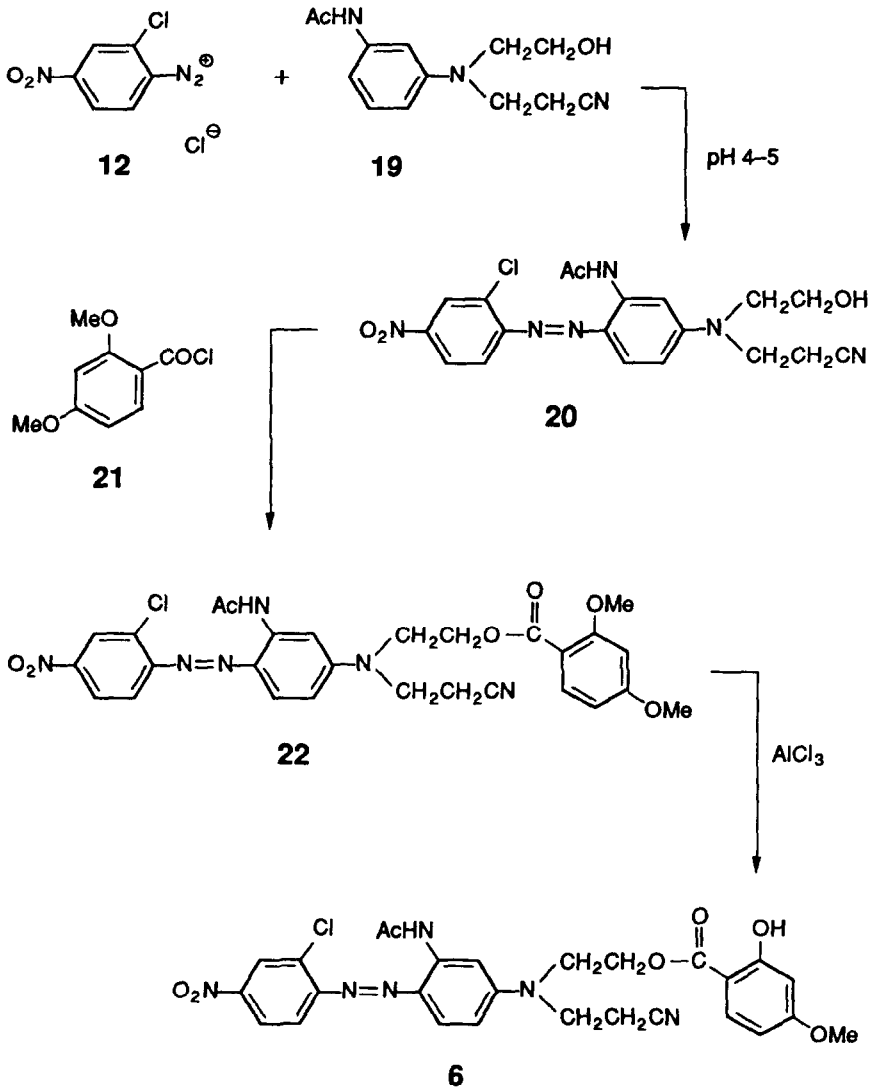
The synthesis of the disazo Disperse Red 167 analog **7** is shown in Scheme **4**. In this example, the *para*-nitro group of the parent dye is replaced by an electron-withdrawing arylazo group. This group not only possesses electronic properties similar to the nitro group, it also contains a benzophenone stabilizer. It was not possible to preserve the *ortho*-chloro substituent of the prototype dye because *ortho*-chloroaniline would not undergo the required coupling. An ethyl group was selected because of its comparable size to the chloro group and the ease with which *ortho*-ethylaniline undergoes diazo coupling.



Scheme 1. Synthesis of dye 3.

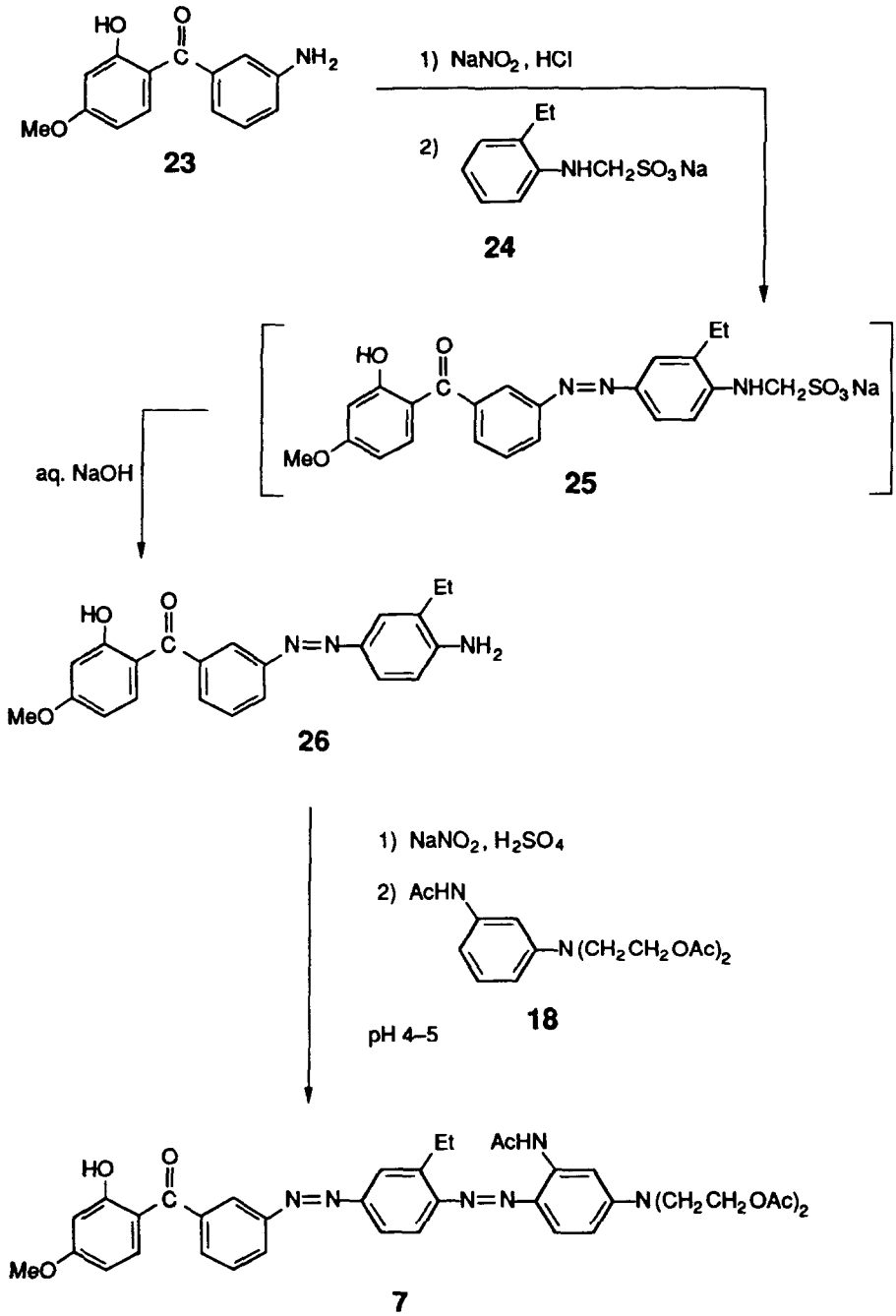


Scheme 2. Synthesis of dyes **4** and **5**.



Scheme 3. Synthesis of dye **6**.

Diazotization of the aminobenzophenone **23** was accomplished with $NaNO_2$ and HCl in the usual way.[7,8] The resulting diazonium salt was then coupled to the *N*-sulfomethyl derivative **24** (formed by condensing *ortho*-ethylaniline and $HOCH_2SO_3Na$ in EtOH[9]). The aminoazo compound **26** was obtained by heating **25** with NaOH in aqueous EtOH. Compound **26** was dizaotized using $NaNO_2$ in conc. H_2SO_4, and coupled to **18**.



Scheme 4. Synthesis of dye **7**.

TABLE 1
Lightfastness and Sublimation Fastness Data for Analogs of Disperse Red 167[a]

Lightfastness			*Dry-heat treatment*						*Δ Color*
Dye	*No UF 830 added*	*2% UF 830 added*	*Wool*	*PAN*	*PET*	*Nylon*	*Cotton*	*Acetate*	
			(expressed as results for 30s/60s)						
Red 167	2	3	5/5	4–5/4	4–5/4	5/5	4–5/4–5	5/4	5/5
3	1	3	5/5	5/5	5/5	5/5	5/5	5/5	5/5
4[b]	—	2	5/5	5/5	5/5	5/5	5/5	5/5	5/5
5	<1	—	5/5	5/5	5/5	5/5	5/5	5/5	5/5
6	1–2	3	5/5	5/5	5/5	5/5	5/5	5/5	5/5
7	1	1	5/5	5/5	5/5	5/5	5/5	5/5	5/5

[a] All samples were rated on a scale of 1–5.
[b] Dyed using thermosol procedure.

Table 1 contains the data obtained when the dyes made were evaluated. Unlike the results obtained on analogs of nitrodiphenylamine disperse dyes, the lightfastness of Disperse Red 167 was not improved by this approach. The reasons vary with dye structure. In the case of **3**, it is apparent that the loss of intramolecular H-bonding between the NHAc group and the azo bond is not compensated for by the construction of a built-in benzophenone stabilizer. In addition, it was recently shown by X-ray analysis that the *ortho*-hydroxybenzoyl group does not lie in the plane of the azobenzene skeleton (cf. Figs 1 and 2). The cell data, atomic coordinates, thermal parameters, bond lengths, and bond angles for **3** are given in Tables 2–6. This means that no *true* benzophenone group was constructed.

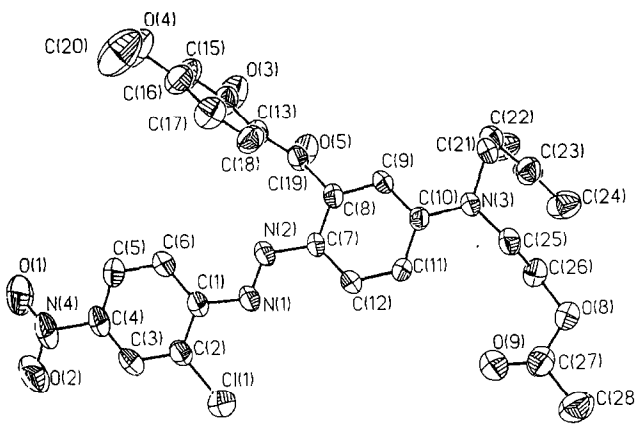


Fig. 1. Structure of **3** (viewed perpendicular to the mean plane).

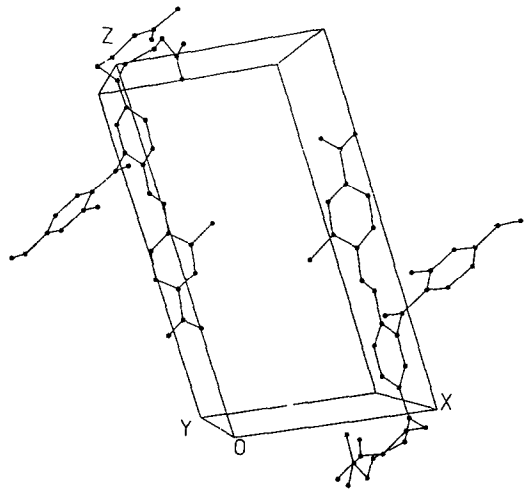


Fig. 2. Packing diagram of **3** (3-dimensional view down *Y* axis, each axis rotated 3°).

When the chloro group of the parent dye was replaced by an *ortho*-hydroxybenzoyl group, the resulting dye (**4**) underwent decomposition in the dyebath during the course of pressure dyeing. It was possible to produce a pastel shade of this dye on PET by thermosol dyeing. Since the methyl ether of **4** (cf. dye **5**) exhausted well, it would seem that the *ortho*-hydroxybenzoyl group of **4** lies in the plane of the azobenzene system, and that the OH group undergoes an adverse interaction with the azo bond. It has not been possible to produce satisfactory crystals of dye **4** for X-ray crystallographic studies, nor has it been possible to separate and characterize the myriad of products produced from the degradation of **4** in a mock dyeing experiment (fabric excluded) to confirm our hypothesis.

TABLE 2
Cell Data for Dye **3**

Composition	$C_{28}H_{27}N_4O_9Cl$
Crystal system	Triclinic
Space group	P1
a, Å	8·63 (5)
b, Å	10·88 (5)
c, Å	16·52 (7)
α	93·4 (3)
β	97·3 (4)
γ	108·5 (7)
V, Å^3	1 452·98
Z	2
Number of reflections	3 568

TABLE 3
Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å $\times 10^3$) of **3**

	x	*y*	*z*	*U*
Cl(1)	5898 (1)	−1016 (1)	4285 (1)	69 (1)*
C(1)	8763 (4)	1005 (3)	4399 (2)	42 (1)*
C(2)	7634 (4)	172 (3)	4821 (2)	45 (1)*
C(3)	7865 (4)	295 (3)	5668 (2)	51 (1)*
C(4)	9224 (4)	1261 (3)	6081 (2)	52 (1)*
C(5)	10360 (4)	2112 (3)	5691 (2)	53 (1)*
C(6)	10124 (4)	1971 (3)	4843 (2)	49 (1)*
C(7)	9042 (3)	1555 (3)	2327 (1)	40 (1)*
C(8)	9908 (3)	2617 (3)	1946 (2)	40 (1)*
C(9)	9856 (3)	2527 (2)	1108 (2)	39 (1)*
C(10)	8916 (3)	1365 (2)	611 (1)	36 (1)*
C(11)	7981 (3)	321 (2)	1006 (2)	40 (1)*
C(12)	8075 (3)	418 (3)	1840 (2)	43 (1)*
C(13)	12427 (4)	4095 (3)	2954 (2)	43 (1)*
C(14)	13276 (4)	5284 (3)	3446 (2)	54 (1)*
C(15)	14782 (4)	5450 (3)	3916 (2)	67 (1)*
C(16)	15476 (4)	4488 (3)	3903 (2)	59 (1)*
C(17)	14680 (4)	3301 (3)	3430 (2)	61 (1)*
C(18)	13168 (4)	3125 (3)	2964 (2)	53 (1)*
C(19)	10857 (4)	3907 (3)	2450 (2)	44 (1)*
C(20)	17751 (5)	3802 (4)	4433 (3)	112 (2)*
C(21)	9869 (4)	2337 (3)	−624 (2)	50 (1)*
C(22)	9162 (4)	3417 (3)	−712 (2)	59 (1)*
C(23)	6647 (4)	3698 (3)	−1258 (2)	64 (1)*
C(24)	5009 (5)	3049 (4)	−1770 (3)	84 (2)*
C(25)	8045 (3)	1 (3)	−727 (2)	42 (1)*
C(26)	6271 (4)	−171 (3)	−1043 (2)	49 (1)*
C(27)	4791 (4)	−2375 (3)	−890 (2)	57 (1)*
C(28)	3938 (4)	−3710 (3)	−1308 (2)	77 (2)*
N(1)	8484 (3)	766 (2)	3525 (1)	48 (1)*
N(2)	9211 (3)	1759 (2)	3187 (1)	44 (1)*
N(3)	8912 (3)	1247 (2)	−221 (1)	40 (1)*
N(4)	9482 (4)	1380 (3)	6988 (1)	74 (1)*
O(1)	10644 (4)	2276 (3)	7353 (1)	113 (1)*
O(2)	8528 (4)	556 (3)	7319 (1)	105 (1)*
O(3)	12625 (3)	6262 (2)	3459 (1)	82 (1)*
O(4)	16984 (3)	4786 (2)	4386 (2)	86 (1)*
O(5)	10237 (3)	4780 (2)	2408 (1)	65 (1)*
O(6)	7114 (3)	4772 (2)	−891 (2)	85 (1)*
O(7)	7582 (3)	2917 (2)	−1238 (1)	59 (1)*
O(8)	5424 (2)	−1508 (2)	−1410 (1)	54 (1)*
O(9)	4920 (3)	−2087 (2)	−168 (1)	83 (1)*

* Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

TABLE 4
Anisotropic Thermal Parameters (Å × 10^3) of **3**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	68 (1)	64 (1)	60 (1)	5 (1)	10 (1)	3 (1)
C(1)	54 (2)	45 (2)	32 (1)	7 (1)	8 (1)	20 (1)
C(2)	55 (2)	46 (2)	37 (2)	8 (1)	9 (1)	18 (1)
C(3)	65 (2)	58 (2)	41 (2)	18 (1)	24 (2)	25 (2)
C(4)	75 (2)	59 (2)	29 (1)	7 (1)	11 (2)	33 (2)
C(5)	60 (2)	61 (2)	34 (2)	−0 (1)	−0 (1)	17 (2)
C(6)	55 (2)	54 (2)	37 (2)	10 (1)	9 (1)	13 (2)
C(7)	48 (2)	45 (2)	23 (1)	4 (1)	3 (1)	11 (1)
C(8)	45 (2)	43 (2)	30 (1)	6 (1)	2 (1)	13 (1)
C(9)	46 (2)	40 (2)	30 (1)	11 (1)	6 (1)	11 (1)
C(10)	37 (2)	43 (2)	28 (1)	5 (1)	2 (1)	14 (1)
C(11)	43 (2)	38 (2)	31 (1)	−0 (1)	−1 (1)	5 (1)
C(12)	46 (2)	46 (2)	31 (1)	11 (1)	6 (1)	7 (1)
C(13)	53 (2)	42 (2)	31 (1)	2 (1)	4 (1)	11 (1)
C(14)	64 (2)	46 (2)	48 (2)	−1 (1)	−2 (2)	17 (2)
C(15)	72 (2)	47 (2)	67 (2)	−13 (2)	−11 (2)	11 (2)
C(16)	51 (2)	56 (2)	60 (2)	−0 (2)	−3 (2)	11 (2)
C(17)	64 (2)	49 (2)	69 (2)	−2 (2)	2 (2)	24 (2)
C(18)	54 (2)	44 (2)	53 (2)	−4 (1)	1 (2)	9 (2)
C(19)	61 (2)	40 (2)	30 (1)	5 (1)	8 (1)	17 (1)
C(20)	73 (3)	103 (3)	153 (4)	−10 (3)	−31 (3)	42 (3)
C(21)	58 (2)	57 (2)	29 (1)	9 (1)	8 (1)	9 (2)
C(22)	75 (2)	48 (2)	45 (2)	11 (1)	−1 (2)	10 (2)
C(23)	68 (2)	49 (2)	69 (2)	25 (2)	9 (2)	9 (2)
C(24)	66 (3)	75 (3)	102 (3)	19 (2)	−5 (2)	15 (2)
C(25)	45 (2)	52 (2)	33 (1)	2 (1)	9 (1)	19 (1)
C(26)	53 (2)	50 (2)	42 (2)	0 (1)	2 (1)	18 (1)
C(27)	53 (2)	59 (2)	54 (2)	0 (1)	5 (2)	16 (2)
C(28)	83 (3)	50 (2)	87 (3)	−6 (2)	14 (2)	7 (2)
N(1)	61 (2)	49 (1)	30 (1)	8 (1)	7 (1)	15 (1)
N(2)	53 (2)	48 (1)	31 (1)	8 (1)	7 (1)	15 (1)
N(3)	48 (1)	42 (1)	26 (1)	5 (1)	7 (1)	11 (1)
N(4)	111 (2)	87 (2)	32 (1)	10 (1)	13 (1)	44 (2)
O(1)	151 (3)	121 (2)	36 (1)	−10 (1)	−1 (2)	14 (2)
O(2)	150 (3)	114 (2)	47 (1)	26 (1)	34 (2)	28 (2)
O(3)	101 (2)	47 (1)	94 (2)	−19 (1)	−18 (1)	35 (1)
O(4)	65 (2)	73 (2)	105 (2)	−11 (1)	−26 (1)	19 (1)
O(5)	81 (2)	50 (1)	62 (1)	−2 (1)	−10 (1)	29 (1)
O(6)	79 (2)	46 (1)	121 (2)	8 (1)	10 (2)	13 (1)
O(7)	71 (1)	50 (1)	48 (1)	9 (1)	−6 (1)	14 (1)
O(8)	59 (1)	52 (1)	44 (1)	−4 (1)	2 (1)	12 (1)
O(9)	105 (2)	69 (2)	56 (1)	4 (1)	21 (1)	0 (1)

The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12})$.

TABLE 5
Bond Angles (°) of **3**

C(2)–C(1)–C(6)	119·1 (2)	C(2)–C(1)–N(1)	117·3 (2)
C(6)–C(1)–N(1)	123·6 (2)	Cl(1)–C(2)–C(1)	120·1 (2)
Cl(1)–C(2)–C(3)	119·0 (2)	C(1)–C(2)–C(3)	120·8 (2)
C(2)–C(3)–C(4)	118·1 (3)	C(3)–C(4)–C(5)	123·0 (3)
C(3)–C(4)–N(4)	118·1 (3)	C(5)–C(4)–N(4)	118·8 (2)
C(4)–C(5)–C(6)	118·2 (2)	C(1)–C(6)–C(5)	120·7 (3)
C(8)–C(7)–C(12)	118·6 (2)	C(8)–C(7)–N(2)	115·6 (2)
C(12)–C(7)–N(2)	125·7 (2)	C(7)–C(8)–C(9)	120·8 (2)
C(7)–C(8)–C(19)	120·0 (2)	C(9)–C(8)–C(19)	119·1 (2)
C(8)–C(9)–C(10)	121·0 (2)	C(9)–C(10)–C(11)	117·2 (2)
C(9)–C(10)–N(3)	121·4 (2)	C(11)–C(10)–N(3)	121·4 (2)
C(10)–C(11)–C(12)	121·0 (2)	C(7)–C(12)–C(11)	121·3 (2)
C(14)–C(13)–C(18)	117·8 (3)	C(14)–C(13)–C(19)	120·5 (3)
C(18)–C(13)–C(19)	121·7 (2)	C(13)–C(14)–C(15)	119·7 (3)
C(13)–C(14)–O(3)	120·5 (3)	C(15)–C(14)–O(3)	119·8 (2)
C(14)–C(15)–C(16)	120·9 (3)	C(15)–C(16)–C(17)	121·3 (3)
C(15)–C(16)–O(4)	115·0 (3)	C(17)–C(16)–O(4)	123·7 (3)
C(16)–C(17)–C(18)	118·1 (3)	C(13)–C(18)–C(17)	122·3 (3)
C(8)–C(19)–C(13)	120·8 (3)	C(8)–C(19)–O(5)	117·2 (2)
C(13)–C(19)–O(5)	121·9 (2)	C(22)–C(21)–N(3)	115·1 (3)
C(21)–C(11)–O(7)	108·7 (2)	C(24)–C(23)–O(6)	126·1 (4)
C(24)–C(23)–O(7)	111·2 (3)	C(6)–C(23)–O(7)	122·7 (3)
C(26)–C(25)–N(3)	113·1 (3)	C(25)–C(26)–O(8)	109·6 (3)
C(28)–C(27)–O(8)	112·8 (3)	C(28)–C(27)–O(9)	124·2 (3)
O(8)–C(27)–O(9)	123·0 (3)	C(1)–N(1)–N(2)	112·6 (2)
C(7)–N(2)–N(1)	114·8 (2)	C(10)–N(3)–C(21)	120·9 (2)
C(10)–N(3)–C(25)	121·2 (2)	C(21)–N(3)–C(25)	117·8 (2)
C(4)–N(4)–O(1)	118·0 (2)	C(4)–N(4)–O(2)	117·7 (2)
O(1)–N(4)–O(2)	124·3 (2)	C(16)–O(4)–C(20)	118·1 (3)
C(22)–O(7)–C(23)	115·8 (2)	C(26)–O(8)–C(27)	115·9 (2)

The absence of a true photostabilizer moiety in dye **6**, and the accessibility of the new azo bond of **7** to light-mediated reactions could account for inability of these dye to provide an improvement over the lightfastness of Red 167. Like the other analogs, however, these two dyes also provide an improvement in sublimation fastness on PET, as would be anticipated from a significant increase in molecular weight.

CONCLUSIONS

The lightfastness of Disperse Red 167 cannot be improved by introducing a benzophenone UV stabilizer moiety into the backbone of the parent

TABLE 6
Bond Lengths (Å) of **3**

Cl(1)–C(2)	1·730 (2)	C(1)–C(2)	1·394 (4)
C(1)–C(6)	1·387 (3)	C(1)–N(1)	1·427 (3)
C(2)–C(3)	1·381 (4)	C(3)–C(4)	1·368 (4)
C(4)–C(5)	1·375 (4)	C(4)–N(4)	1·479 (3)
C(5)–C(6)	1·383 (4)	C(7)–C(8)	1·396 (4)
C(7)–C(12)	1·388 (3)	C(7)–N(2)	1·407 (3)
C(8)–C(9)	1·377 (3)	C(8)–C(19)	1·513 (3)
C(9)–C(10)	1·409 (3)	C(10)–C(11)	1·418 (3)
C(10)–N(3)	1·372 (3)	C(11)–C(12)	1·366 (3)
C(13)–C(14)	1·411 (3)	C(13)–C(18)	1·398 (5)
C(13)–C(19)	1·445 (4)	C(14)–C(15)	1·379 (5)
C(14)–O(3)	1·353 (4)	C(15)–C(16)	1·363 (6)
C(16)–C(17)	1·388 (4)	C(16)–O(4)	1·396 (4)
C(17)–C(18)	1·378 (5)	C(19)–O(5)	1·232 (4)
C(20)–O(4)	1·428 (6)	C(21)–C(22)	1·494 (5)
C(21)–N(3)	1·464 (3)	C(22)–O(7)	1·442 (3)
C(23)–C(24)	1·484 (5)	C(23)–O(6)	1·204 (4)
C(23)–O(7)	1·345 (5)	C(25)–C(26)	1·502 (4)
C(25)–N(3)	1·469 (3)	C(26)–O(8)	1·457 (3)
C(27)–C(28)	1·483 (4)	C(27)–O(8)	1·347 (4)
C(27)–O(9)	1·198 (4)	N(1)–N(2)	1·267 (3)
N(4)–O(1)	1·214 (3)	N(4)–O(2)	1·219 (4)

dye structure in lieu of the Cl, NO_2 or NHAc group. The contrast of these results to those obtained when a photostabilizer moiety was built into the structure of nitrodiphenylamine disperse dyes suggests that the λ_{max} difference between the absorption maximum of the chromophore and stabilizer is an important consideration when employing this approach to improving disperse dye lightfastness.

EXPERIMENTAL

General

The chemicals used as starting materials in this work were obtained from either Aldrich Chemical, Fisher Scientific, or Sandoz Chemicals.

Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded using a Bruker 250 MHz spectrometer or a General Electric GN 300 MHz spectrometer. The mass spectrometric analyses employed a JEOL (Tokyo, Japan) HX 110 HF double-focusing mass spectrometer equipped with an

FAB or CI ionization source. The FAB experiments employed 3-nitrobenzyl alcohol (3-NBA) as the matrix. The intensities of the base peaks of compounds analyzed by FAB are expressed relative to the base peak of the matrix ion (M/z = 152). UV-visible spectra were recorded on a Perkin-Elmer spectrophotometer model 559A. Microanalyses were performed by Atlantic Microlab Inc., Norcross, Georgia. Infrared spectra were obtained using a Nicolet 510 P FT-IR spectrophotometer. Thin layer chromatography (TLC) was performed using Whatman 250 μm silica gel 60 AMK6F plates. Flash column chromatography was conducted using Fisher chromatographic silica gel 230–245 mesh type 150A.

The polyester fabric (a tricot-knit) used in this study was obtained from Hoechst-Celanese Corporation. The dyeings were obtained using an Ahiba Polymat (type PN) dyeing machine at 130°C for 1·5 h using a dyebath containing 2% (o.w.f.) dye and 4% (o.w.f.) dispersing agent (Irgasol DA PDR, Ciba-Geigy). For dyeings requiring UV absorber, 2% (o.w.f.) UF 830 (BASF) was also added. The dyebaths were prepared by adding a 5% acetone solution of the dye to 250 ml H_2O containing the dispersing agent. The beakers containing the resulting mixtures were then submerged in an ultrasound bath (50–60 Hz Branson 3200 ultrasonic cleaner) and heated at 60°C for 15–20 min to drive off the acetone. The dispersions were adjusted to pH = 5·5 and diluted with H_2O to give a liquor ratio of 25:1.

The thermosol application of dye **4** to PET utilized 150 mg litre^{-1} dye, 250 mg litre^{-1} Superclean 100 N (antimigrant), and 25 mg litre^{-1} Decesesol OT (wetting agent). The fabric was padded at 80% wet pick up, pre-dried at 250°F for 90 s and fixed at 410°F for 90 s. The resulting dyeing was cleared using 2% $NaOH/Na_2S_2O_4$ for 5 min at 120°F, rinsed thoroughly in hot and in cold H_2O, and dried.

Lightfastness and sublimation fastness

The lightfastness of the 2% (o.w.f.) dyeings was determined according to SAE Automotive Test Method J1885 and recorded on an Atlas Cl 65 (Xenon arc) test apparatus. The test conditions were:

3·8 h light on/1·0 h light off.
Black panel temperature: 89°C (light on)/38°C (light off).
Relative humidity: 50% (light on)/100% (light off).
Total radiation: 225·6 kJ.
Window glass filters: 310 nm cut-off.

The samples were rated with the aid of the gray scale for color

change.[10] Fastness to dry heat treatment was measured with an Atlas Scorch Tester at 177(±2)°C for 30 and 60 s according to AATCC Test Method 177–1984.[10] The change of color was evaluated using the gray scale for color change and the staining of the undyed fabrics was evaluated using the AATCC Chromatic Transference Scale.

Synthesis

Dye 3

Finely powdered $NaNO_2$ (0·42 g, 6 mmol) was added slowly with stirring to 6 ml conc. H_2SO_4. The mixture was heated to 70°C, held at this temperature for 10 min, and then cooled below 10°C. To this suspension was added slowly 2-chloro-4-nitroaniline (0·92 g, 5·33 mmol), keeping the temperature below 20°C with the aid of an ice bath. The resulting solution was stirred at 10°C for 1 h, poured over 20 g ice, and filtered. The filtrate was added dropwise to a solution of **11** (2·21 g, 5·33 mmol) in 50 ml HOAc at 10–15°C and stirred overnight, during which time the temperature reached 20°C. The liquid was decanted and the viscous precipitate extracted into 100 ml EtOAc. The EtOAc solution was dried ($MgSO_4$) and concentrated. The solid obtained was recrystallized from 1-BuOH to give 2·79 g (88%) **3** as dark red needles, m.p. 168–169°C.

Rf (5:1/PhMe:EtOAc) = 0·47.

Anal. Calcd for $C_{28}H_{27}N_4O_9Cl$: C, 56·14; H, 4·51; N, 9·36. Found: C, 56·19; H, 4·68; N, 9·21.

300 MHz [^{1}H] NMR ($CDCl_3$): 12·53 ppm (s, 1H); 8·29–8·30 ppm (d, 1H); 7·97–8·06 ppm (m, 2H); 7·32–7·36 ppm (dd, 1H); 7·07–7·11 ppm (dd, 1H); 6·98–7·02 ppm (dd, 1H); 6·78–6·79 ppm (d, 1H); 6·49–6·50 ppm (d, 1H); 6·25–6·29 ppm (dd, 1H); 4·24–4·28 ppm (t, 4H); 3·86 ppm (s, 3H); 3·79–3·84 ppm (t, 4H); 2·30 ppm (s, 6H).

Mass spectrum (pos. ion, FAB) showed m/z = 599 (71% rel. int.).

IR spectrum (KBr): OH (3440 cm^{-1}); C=O (1618 cm^{-1}); NO_2 (1510, 1352 cm^{-1}); SO_2NH (1163 cm^{-1}).

Absorption spectrum (acetone): λ_{max} = 478 nm, ϵ_{max} = 31 200.

Dye 4

Finely powdered $NaNO_2$ (0·19 g, 2·75 mmol) was slowly added with stirring to 3 ml conc. H_2SO_4. The mixture was heated to 70°C, held at this temperature for 10 min, and then cooled below 10°C. To this suspension was added very slowly finely powdered **16** (0·72 g, 2·5 mmol), keeping the temperature below 20°C with the aid of an ice bath. The resulting

solution was stirred at 10–15°C for 1 h, then ice (5 g) was added cautiously. The mixture, including the solid precipitate, was added to a solution of **18** (0·81 g, 2·5 mmol) in 25 ml glacial HOAc. After stirring for 1 h at 10–15°C and pH 4–5, the precipitate was collected by filtration, washed with 500 ml H_2O, and air-dried. The product was purified by flash column chromatography, using 4:1/PhMe:EtOAc, to give 0·84 g (54%) **4**, m.p. 52–55°C (dec.).

Rf (1:1/PhMe:EtOAc) = 0·47.

Anal. Calcd for $C_{30}H_{31}N_5O_{10}$: C, 57·97; H, 4·99; N, 11·27. Found: C, 57·63; H, 4·85; N, 10·96.

300 MHz [^{1}H] NMR (DMSO-d_6): 10·50 ppm (s, 1H); 9·83 ppm (s, 1H); 8·39–8·41 ppm (d, 1H); 8·28 ppm (s, 1H); 8·17 ppm (s, 1H); 7·94–7·97 ppm (d, 1H); 7·56–7·59 ppm (d, 1H); 6·98–7·01 ppm (d, 1H); 6·49–6·53 ppm (d, 1H); 6·44 ppm (s, 1H); 6·25–6·28 ppm (d, 1H); 4·13–4·17 ppm (t, 4H); 3·74 ppm (s, 3H); 3·66–3·73 ppm (t, 4H); 3·38 ppm (s, 3H); 2·47 ppm (s, 3H); 1·92 ppm (s, 6H).

Mass spectrum (pos. ion, FAB) showed m/z = 622 (M + H) as the base peak.

IR spectrum (KBr): OH (3436 cm^{-1}); O—C=O (1740 cm^{-1}); C=O (1615 cm^{-1}); NHC=O (1576 cm^{-1}); NO_2 (1525, 1339 cm^{-1}).

Absorption spectrum (acetone): λ_{max} = 510 nm, ϵ_{max} = 12100.

Dye 5

By the procedure described for the preparation of dye **4**, compounds **14** (0·7 g, 2·3 mmol) and **18** (0·75 g, 2·3 mmol) afforded 0·73 g of pure **5**, m.p. 82–84°C.

Rf (1:1/PhMe:EtOAc) = 0·52.

Anal. Calcd for $C_{31}H_{33}N_5O_{10}$: C, 58·58; H, 5·20; N, 11·02. Found: C, 58·77; H, 5·57; N, 10·76.

300 MHz [^{1}H] NMR (DMSO-d_6): 9·83 ppm (s, 1H); 8·34–8·37 ppm (d, 1H); 8·16 ppm (s, 1H); 8·01–8·04 ppm (d, 1H); 7·80 ppm (s, 1H); 7·63–7·66 ppm (d, 1H); 7·02–7·05 ppm (d, 1H); 6·57–6·60 ppm (d, 1H); 6·47–6·50 ppm (d, 1H); 6·40 ppm (s, 1H); 4·13–4·17 ppm (t, 4H); 3·74 ppm (s, 3H); 3·66–3·73 ppm (t, 4H); 3·38 ppm (s, 3H); 2·47 ppm (s, 3H); 1·92 ppm (s, 6H).

Mass spectrum (pos. ion, FAB) showed m/z = 636 (M + H) as the base peak.

IR spectrum (KBr): O—C=O (1735 cm^{-1}); C=O (1606 cm^{-1}); NHC=O (1575 cm^{-1}); NO_2 (1520, 1344 cm^{-1}).

Absorption spectrum (acetone): λ_{max} = 499 nm, ϵ_{max} = 13500.

Dye 6

Compound **22** (5 g, 8·4 mmol) was dissolved in 25 ml CH_2Cl_2. $AlCl_3$ (8 g) was added and the mixture stirred under reflux for 4 h. The reaction mixture was then cooled and poured cautiously into 600 g ice containing 10 ml conc. HCl. The resulting viscous precipitate was dissolved in 100 ml 10% NaOH and the pH was adjusted to 5 using 10% HCl. The crude product was collected by filtration and dried ($MgSO_4$) to give 4·09 g (84%) **6**. A portion of the dye was further purified by flash column chromatography using 2:1/PhMe:EtOAc to give a dark red solid, m.p. 222–224°C.

Rf (2:1/EtOAc:PhMe) = 0·91.

Anal. Calcd for $C_{27}H_{25}N_6O_7Cl$: C, 55·86; H, 4·31; N, 14·48. Found: C, 55·72; H, 4·40; N, 14·53.

300 MHz [^{1}H] NMR (DMF-d_7): 11·34 ppm (s, 1H); 10·83 ppm (s, 1H); 10·80 ppm (s, 1H); 8·44–8·45 ppm (d, 1H); 8·34–8·35 ppm (d, 1H); 8·25–8·29 ppm (dd, 1H); 8·02–8·05 ppm (d, 1H); 7·84–7·87 ppm (d, 1H); 7·73–7·76 ppm (d, 1H); 7·02–7·06 ppm (dd, 1H); 6·47–6·51 ppm (dd, 1H); 6·37–6·38 ppm (d, 1H); 4·67–4·70 ppm (t, 2H); 4·08–4·17 ppm (m, 4H); 3·56 ppm (s, 3H); 3·05–3·10 ppm (t, 2H); 2·31 ppm (s, 3H).

Mass spectrum (pos. ion, FAB) showed *m/z* = 580 (12% rel. int.).

IR spectrum (KBr): OH (3382 cm^{-1}); O—C=O (1665 cm^{-1}); NHC=O (1618 cm^{-1}); NO_2 (1522, 1335 cm^{-1}).

Dye 7

Using the procedure described for the synthesis of dye **4**, **26** (1·13 g, 3 mmol) and **18** (0·77 g, 3 mmol) were converted to dye **7**. The chromatographed dye (61%) was recrystallized from 2-PrOH/MeOH to give dark red needles, m.p. 134–136°C.

Rf (1:1/PhMe:EtOAc) = 0·69.

Anal. Calcd for $C_{38}H_{40}N_6O_8$: C, 64·40; H, 5·67; N, 11·86. Found: C, 64·26; H, 5·70; N, 11·79.

300 MHz [^{1}H] NMR ($CDCl_3$): 12·64 ppm (s, 1H); 10·85 ppm (s, 1H); 8·28–8·29 ppm (d, 1H); 8·20 ppm (s, 1H); 8·12–8·16 ppm (dd, 1H); 7·94–7·95 ppm (d, 1H); 7·82–7·88 ppm (m, 2H); 7·72–7·77 ppm (m, 2H); 7·64–7·69 ppm (t, 1H); 7·55–7·58 ppm (d, 1H); 6·59–6·64 ppm (dd, 1H); 6·55–6·56 ppm (d, 1H); 6·43–6·48 ppm (dd, 1H); 4·32–4·36 ppm (t, 4H); 3·88 ppm (s, 3H); 3·75–3·79 ppm (t, 4H); 3·17–3·20 ppm (m, 2H); 2·29 ppm (s, 3H); 2·08 ppm (s, 6H; 1·36–1·41 ppm (t, 3H).

Mass spectrum (pos. ion, FAB) showed *m/z* = 709 (M + H) as the base peak.

IR spectrum (KBr): OH (3441 cm^{-1}); O—C=O (1742 cm^{-1}); NHC=O (1615 cm^{-1}); C=O (1572 cm^{-1}).

Absorption spectrum (acetone): λ_{max} = 493 nm, ϵ_{max} = 43 500.

*2,4-Dimethoxy-3'-N,N-bis-(2-hydroxyethyl)-aminobenzophenone (**9**)*
2,4-Dimethoxy-3'-aminobenzophenone (**8**; 3·08 g, 0·012 mol) was dissolved in 40 ml HOAc containing 1·63 g NaOAc . $3H_2O$, and the solution was stirred at 50°C as ethylene oxide gas was added for 20 min. The addition caused a temperature rise to 90°C. The resulting solution was cooled to room temperature, poured into 250 ml H_2O, and extracted with 200 ml EtOAc. The organic layer was washed twice with 150 ml 10% $NaHCO_3$, then with 500 ml H_2O, dried ($MgSO_4$), and concentrated. The viscous oil obtained was purified by flash column chromatography[11] using 1 : 1/ PhMe:EtOAc to give 3·05 g (74%) **9**, m.p. 140–141°C.

Rf (EtOAc) = 0·57.

Anal. Calcd for $C_{19}H_{23}NO_5$: C, 66·09; H, 6·67; N, 4·06. Found: C, 65·91; H, 6·76; N, 4·00.

300 MHz [^{1}H] NMR (DMSO-d_6): 7·16–7·23 ppm (m, 2H); 7·02 ppm (s, 1H); 6·89–6·93 ppm (dd, 1H); 6·73–6·76 ppm (d, 1H); 6·64–6·65 ppm (d, 1H); 6·57–6·61 ppm (dd, 1H); 4·77–4·81 ppm (t, 4H); 3·82 ppm (s, 3H); 3·65 ppm (s, 3H); 3·49–3·54 ppm (m, 4H).

Mass spectrum (CI) showed *m/z* = 346 (M + H) as the base peak.

IR spectrum (KBr): OH (3266 cm^{-1}); C=O (1595 cm^{-1}).

*2,4-Dimethoxy-3'-N,N-bis-2-(acetoxyethyl)aminobenzophenone (**10**)*
2,4-Dimethoxy-3'-*N,N*-bis-(2-hydroxyethyl)aminobenzophenone (**9**; 2·07 g, 0·006 mol) and 1·23 g Ac_2O were dissolved in 25 ml pyridine, and the solution stirred at 60°C for 2 h. The cooled solution was poured into a solution of 25 ml conc. HCl in 500 ml H_2O, and extracted with 200 ml EtOAc. The organic layer was washed once with 100 ml 10% HCl, twice with 200 ml H_2O, dried ($MgSO_4$), and concentrated. The product was purified by flash column chromatography using 4:1/PhMe:EtOAc to give 1·76 g (68% **10** as a viscous oil).

Rf (4:1/PhMe:EtOAc) = 0·46.

Anal. Calcd for $C_{23}H_{27}NO_7$: C, 64·34; H, 6·29; N, 3·26. Found: C, 64·25; H, 6·35; N, 3·21.

300 MHz [^{1}H] NMR ($CDCl_3$): 7·34–7·37 ppm (dd, 1H); 7·21–7·27 ppm (m, 2H); 7·01–7·03 ppm (d, 1H); 6·93–6·95 ppm (d, 1H); 6·51–6·55 ppm (m, 2H); 4·22–4·26 ppm (t, 4H); 3·86 ppm (s, 3H); 3·72 ppm (s, 3H); 3·64–3·68 ppm (t, 4H); 2·04 ppm (s, 6H).

Mass spectrum (CI) showed *m/z* = 429 as the base peak.

IR spectrum (KBr): O—C=O (1740 cm^{-1}); C=O (1597 cm^{-1}).

*2-Hydroxy-4-methoxy-3'-N,N-bis-(2-acetoxyethyl)aminobenzophenone (**11**)*
2,4-Dimethoxy-3'-N,N-bis-(2-acetoxyethyl)aminobenzophenone (**10**; 6 g,

14 mmol) was dissolved in 50 ml CH_2Cl_2 and 4 g $AlCl_3$ was slowly added with vigorous stirring. The resulting mixture was stirred for 2 h at room temperature, then slowly added to 200 g ice containing 10 ml conc. HCl. The organic layer was collected and dried ($MgSO_4$). The crude product was recycled through the $AlCl_3$ treatment twice more and the product was purified by flash column chromatography using 5:1/PhMe:EtOAc to give 4·13 g (69%) **11** as a viscous oil.

Rf (5:1PhMe:EtOAc) = 0·41.

Anal. Calcd for $C_{22}H_{25}NO_7$: C, 63·61; H, 6·02; N, 3·37. Found: C, 63·66; H, 6·07; N, 3·36.

300 MHz [^{1}H] NMR ($CDCl_3$): 7·54–7·57 ppm (d, 1H); 7·31–7·34 ppm (d, 1H); 7·27–7·29 ppm (d, 1H); 6·90–6·98 ppm (m, 2H); 6·50–6·51 ppm (d, 1H); 6·38–6·42 ppm (dd, 1H); 4·23–4·27 ppm (t, 4H); 3·85 ppm (s, 3H); 3·65–3·69 ppm (t, 4H); 2·05 ppm (s, 6H).

Mass spectrum (CI) showed *m/z* = 416 (M + H) as the base peak.

IR spectrum (KBr): OH (3266 cm^{-1}); O—C=O (1742 cm^{-1}); C=O (1597 cm^{-1}).

*2,4-Dimethoxy-2'-chloro-5'-nitrobenzophenone (**13**)*

2-Chloro-5-nitrobenzoyl chloride (22 g, 0·1 mol) and 25 g $AlCl_3$ were added to 100 ml CH_2Cl_2 and cooled to −70°C. The mixture was stirred vigorously as 13·8 g (0·1 mol) 1,3-dimethoxybenzene was added at a rate such that the internal temperature remained below −70°C. The temperature of the resulting solution was allowed to increase to 15–18°C over 3·5 h. At that point, the mixture was poured over 600 g ice containing 25 ml conc. HCl, and stirred until it reached room temperature. The organic layer was dried ($MgSO_4$) and concentrated. To the resulting oil was added 100 ml 10% HCl, and the mixture was stirred under reflux for 16 h. The hot solution was cooled to room temperature and extracted with 100 ml CH_2Cl_2. The layers were filtered to remove 2-chloro-4-nitrobenzoic acid (10·5 g). The organic layer was extracted with 200 ml H_2O, then with 200 ml 10% $NaHCO_3$, dried ($MgSO_4$), and concentrated. The oil crystallized from MeOH to give 9·36 g **13** as white needles, m.p. 98–99°C.

Rf (4:1/PhMe:EtOAc) = 0·66.

Anal. Calcd for $C_{15}H_{12}NO_5Cl$: C, 56·01; H, 3·76; N, 4·35. Found: C, 55·83; H, 3·79; N, 4·31.

300 MHz [^{1}H] NMR (DMSO-d_6): 8·22–8·33 ppm (dd, 1H); 8·13 ppm (d, 1H); 7·75–7·81 ppm (d, 1H); 7·63–7·67 ppm (d, 1H); 6·55–6·72 ppm (m, 2H); 3·87 ppm (s, 3H); 3·51 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 322 (M + H) as the base peak.

IR spectrum (KBr): C=O (1603 cm^{-1}); NO_2 (1528, 1350 cm^{-1}).

*2,4-Dimethoxy-2'-amino-5'-nitrobenzophenone (**14**)*

2,4-Dimethoxy-2'-chloro-5'-nitrobenzophenone (**13**; 4·01 g, 0012 mol) was dissolved in 25 ml of anhydrous DMF and heated to 75°C. Potassium phthalimide (4·63 g, 0·025 mol) was added over 3 h and the mixture stirred under reflux for 24 h. The solution was cooled, poured into 400 ml cold 5% HCl, and stirred vigorously at room temperature for 16 h. The precipitate was collected by filtration, dried, stirred for 2 h in 100 ml PhMe, and the mixture was filtered. The filtrate was concentrated, and the solid obtained was purified by flash column chromatography using 3:1/cyclohexane:EtOAc to give 1·44 g **14** and 2·07 g **15**. Compound **14** was further purified by recrystallization from MeOH to give colorless needles, m.p. 129–130°C.

Rf (4:1/PhMe:EtOAc) = 0·36.

Anal. Calcd for $C_{15}H_{14}N_2O_5$: C, 59·60; H, 4·67; N, 9·27. Found: C, 59·52; H, 4·67; N, 9·27.

250 MHz [^{1}H] NMR (DMSO-d_6): 8·17–8·20 ppm (d, 3H[1H + NH_2]); 7·95–8·07 ppm (dd, 1H); 7·21–7·30 ppm (d, 1H); 6·85–6·95 ppm (d, 1H); 6·59–6·64 ppm (m, 2H); 3·88 ppm (s, 3H); 3·73 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 303 (M + H) as the base peak.

IR spectrum (KBr): NH_2 (3436, 3320 cm^{-1}); C=O (1744 cm^{-1}); NO_2 (1617, 1310 cm^{-1}).

*2-Hydroxy-4-methoxy-2'-amino-nitrobenzophenone (**16**)*

2,4-Dimethoxy-2'-amino-5'-nitrobenzophenone (**14**; 0·85 g, 2·8 mmol) was dissolved in 10 ml CH_2Cl_2 and stirred as 0·82 g $AlCl_3$ was slowly added. The mixture was stirred under reflux for 30 min. To the cooled reaction mixture was added 25 ml 10% HCl. The organic layer was collected and dried ($MgSO_4$). The crude product was recycled through the $AlCl_3$ treatment, and after work-up, the product was recrystallized from MeOH to give 0·70 g (86%) **16** as pale yellow crystals, m.p. 194–196°C.

Rf (4:1/PhMe:EtOAc) = 0·43.

Anal. Calcd for $C_{14}H_{12}N_2O_5$: C, 58·33; H, 4·17; N, 9·72. Found: C, 58·25; H, 4·21; N, 9·70.

250 MHz [^{1}H] NMR (DMSO-d_6): 8·10–8·12 ppm (d, 1H); 7·88–8·01 ppm (dd, 1H); 7·23–7·31 ppm (d, 1H); 6·75–6·86 ppm (d, 1H); 6·30–6·47 ppm (m, 2H); 3·79 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 289 (M + H) as the base peak.

IR spectrum (KBr): NH_2 (3490, 3380 cm^{-1}); OH (3217 cm^{-1}); C=O (1742 cm^{-1}); NO_2 (1624, 1310 cm^{-1}).

*Compound **20***

Finely powdered $NaNO_2$ (1·9 g, 0·0275 mol) was slowly added with

stirring to 25 ml conc. H_2SO_4. The mixture was heated to 70°C, held at this temperature for 10 min, and then cooled below 10°C. To this suspension was added finely powdered 2-chloro-4-nitroaniline (4·33 g, 0·025 mol), keeping the temperature below 20°C with the aid of an ice bath. The solution was stirred at 10–15°C for 1 h and ice (20 g) was added. The mixture was filtered and the filtrate added to a solution of **19** (6·18 g, 0·025 mol) in 50 ml HOAc at 10–15°C and pH 4–5. The mixture was stirred overnight, during which time the temperature reached 20°C. The precipitate was collected by filtration, rinsed with 500 ml H_2O, and dried. The crude product was purified by stirring the collected solid in MeOH to give 10·23 g (95%) **20**, m.p. 180–182°C.

Rf (EtOAc) = 0·74.

Anal. Calcd for $C_{19}H_{19}N_6O_4Cl$: C, 53·02; H, 4·42; N, 19·53. Found: C, 52·99; H, 4·40; N, 14·43.

300 MHz [^{1}H] NMR (DMSO-d_6): 11·18 ppm (s, 1H); 8·28–8·29 ppm (d, 1H); 8·11–8·15 ppm (dd, 1H); 7·97–7·98 ppm (d, 1H); 7·88–7·92 ppm (dd, 1H); 7·65–7·68 ppm (d, 1H); 6·74–6·78 ppm (dd, 1H); 4·99–5·03 ppm (t, 2H); 3·81–3·86 ppm (t, 2H); 3·60–3·66 ppm (t, 2H); 2·81–2·89 ppm (t, 2H); 2·18 ppm (s, 3H).

Mass spectrum (pos. ion, FAB) showed m/z = 431 (61% rel. int.).

IR spectrum (KBr): OH (3393 cm^{-1}); NHC=O (1618 cm^{-1}); NO_2 (1524, 1331 cm^{-1}).

Compound 22

Compound **20** (6·47 g, 0·015 mol) and 2,4-dimethoxybenzoyl chloride (3·02 g, 0·015 mol) were dissolved in 40 ml pyridine, and the solution stirred under a gentle reflux for 3 h. An additional 0·30 g of the benzoyl chloride was added, the reaction stirred hot for another 1 h, then concentrated. The product was dissolved in 100 ml EtOAc, and the solution was dried ($MgSO_4$) and concentrated to give 8·12 g (91%) **22**, m.p. 112–116°C.

Rf (EtOAc) = 0·87.

300 MHz [^{1}H] NMR ($CDCl_3$): 11·36 ppm (s, 1H); 8·43–8·44 ppm (d, 1H); 8·30–8·31 ppm (d, 1H); 8·24–8·28 ppm (dd, 1H); 8·03–8·07 ppm (d, 1H); 7·82–7·86 ppm (dd, 1H); 7·01–7·05 ppm (dd, 1H); 6·70–6·71 ppm (d, 1H); 6·59–6·65 ppm (m, 2H); 4·55–4·58 ppm (t, 2H); 3·91–4·13 ppm (m, 4H); 3·89 ppm (s, 3H); 3·87 ppm (s, 3H); 2·31 ppm (s, 3H).

Mass spectrum (pos. ion, FAB) showed m/z = 595 (M+H) as the base peak.

IR spectrum (KBr): O—C=O (1696 cm^{-1}); NHC=O (1611 cm^{-1}); NO_2 (1516, 1335 cm^{-1}).

N-Sulfomethyl-2-ethylaniline, sodium salt (24)

2- Ethylaniline (24·2 g, 0·20 mol) was added to a solution of $HOCH_2SO_3Na$

(80·4 g, 0·60 mol) in 200 ml of H_2O, and the solution was stirred at 80°C as 150 ml 95% EtOH was added. The reaction mixture was stirred at the boil for 5 min and stored in the refrigerator overnight. The solution was concentrated to 100 ml and diluted with 150 ml 95% EtOH to give a mixture that was heated until the solid redissolved. The resulting solution was refrigerated overnight. The precipitate was collected and dried to give 46·8 g **24** as light pink plates.

300 MHz [^{1}H] NMR (DMSO-d_6): 6·86–6·90 ppm (m, 2H); 6·71–6·74 ppm (d, 1H); 6·49–6·52 ppm (t, 1H); 4·12 ppm (s, 2H); 2·38–2·45 ppm (m, 2H); 1·08–1·14 ppm (t, 3H).

Mass spectrum (CI) showed *m/z* = 214 (M–Na) as the base peak.

Compound 26

2-Hydroxy-4-methoxy-3'-aminobenzophenone (**23**; 3·65 g, 0·015 mol,[3]) was dissolved in 40 ml warm 10% HCl. The solution was cooled to 0°C and 0·70 g $NaNO_2$ in 5 ml H_2O was slowly added. The mixture was stirred at this temperature for 1 h, filtered, and the filtrate was added slowly at 10–15°C to a solution of **24** (3·55 g, 0·015 mol) in 50 ml H_2O containing 6·14 g NaOAc . $3H_2O$. The resulting mixture was stirred for 3 h, then the precipitate was collected by filtration. The solid was suspended in 100 ml 1 : 1/EtOH : H_2O containing 7·2 g NaOH, and the mixture was stirred under reflux for 3 h. The solution was concentrated to remove EtOH, and diluted to 250 ml by adding ice. The pH was adjusted to 6–7 with cold 10% HCl, the resulting precipitate collected by filtration, and the product dried to give 4·46 g (79%) **26** as a dark red solid which was used without further purification.

Rf (4 : 1/PhMe : EtOAc) = 0·52.

300 MHz [^{1}H] NMR (DMSO-d_6): 11·89 ppm (s, 1H); 7·95–7·96 ppm (d, 1H); 7·57–7·65 ppm (m, 3H); 7·40–7·54 ppm (m, 2H); 7·02–7·03 ppm (d, 1H); 6·70–6·72 ppm (d, 1H); 6·54–6·57 ppm (m, 2H); 6·02 ppm (s, 1H, NH_2); 3·80 ppm (s, 3H); 2·47–2·50 ppm (m, 2H); 1·12–1·15 ppm (t, 3H).

Mass spectrum (CI) showed *m/z* = 376 (M + H, 22% rel. int.), and the base peak was *m/z* = 245.

IR spectrum (KBr): NH_2 (3387, 3480 cm^{-1}); C=O (1626 cm^{-1}).

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