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An Approach to the Design of Lightfast Disperse Dyes—Analogs of Disperse Yellow 42‡

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ABSTRACT

The effects of incorporating a photostabilizer moiety into the aromatic rings of Disperse Yellow 42 have been investigated. The results of this study indicate that both the ring into which the stabilizer residue is placed and the actual type of stabilizer group employed influence the lightfastness of the dyes developed. It has also been shown that the incorporation of a photostabilizer group into the backbone of Disperse Yellow 42 can lead to dyes superior in lightfastness to a physical mixture of Yellow 42 and commercial photostabilizer.

INTRODUCTION

It is well known[1–5] that the majority of the commonly used UV absorbers for protecting disperse dyes on polyester (PET) fibers are either benzophenone or benzotriazole derivatives. It is also known that certain types of hindered amines[6] are quite useful in protecting poly(propylene) against light-induced oxidative degradation. The same authors reported[6] that certain benzotriazoles protect substrates via a screening/quenching mechanism, while the hindered piperidines react with excited states of oxygen to form stable nitroxyl radicals.[7] Other papers have been published that outline

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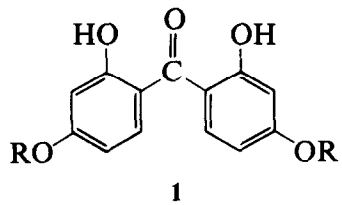
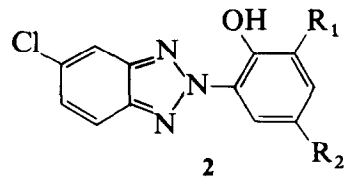


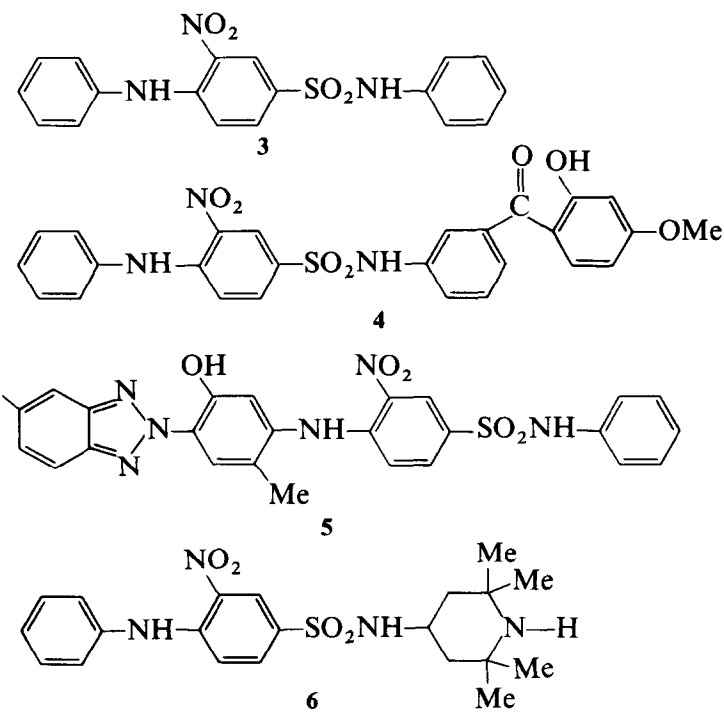
1
R = H, Me



2
R_1 = H, $C(Me)_3$, $C(Me)_2(Et)$
R_2 = Me, $C(Me)_3$, $C(Me)_2(Et)$

the mechanisms involved in the stabilization of polymers using UV absorbers,[5,8–10] and the photochemistry of benzophenones.[11] It would appear from the open literature[12–15] that benzophenones of type **1** and benzotriazoles of type **2** are among the most effective UV stabilizers for disperse dyed polyester (PET) fibers.

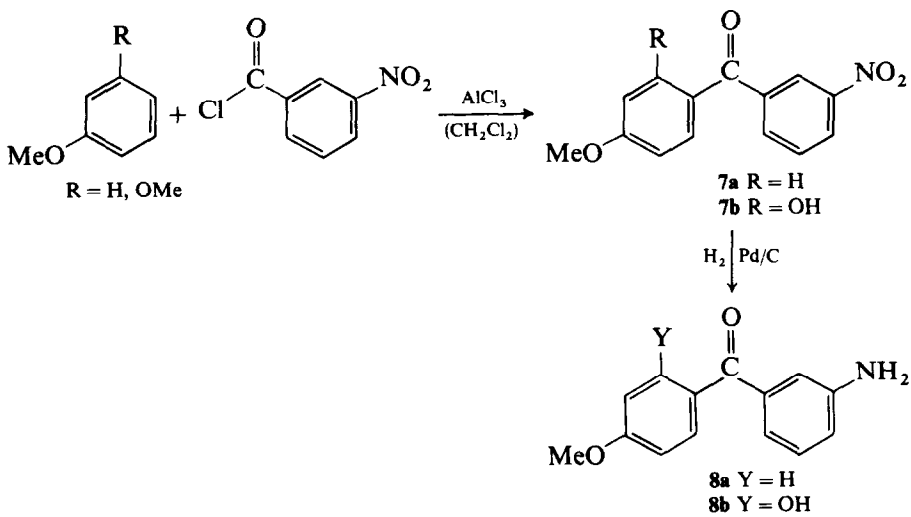
Disperse Yellow 42 (**3**), like most automotive disperse dyes, meets the specifications of automobile manufacturers only after a UV absorber is co-exhausted from the dyebath to help protect this molecule against the rigors of prolonged exposure to UV light. Relatively recent increases in the specifications for automotive dyes have led to a search for an improved



yellow (as well as red and blue) disperse dye for PET. In an attempt to develop an improved yellow dye, we prepared compounds such as **4–6** in which a photostabilizer moiety had been incorporated directly into the dye structure. It was anticipated that the increased intimacy between the Yellow 42 chromophore and the stabilizer would lead to higher light-fastness. In nearly every case, we utilized an existing ring in the parent dye structure to build in the stabilizer group, anticipating that a dye–stabilizer union via a bridging group would make dye diffusion difficult. In addition, the stabilizing moiety was placed *meta* to the NH_2 group to preserve the λ_{max} of the prototype dye.

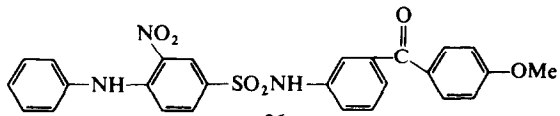
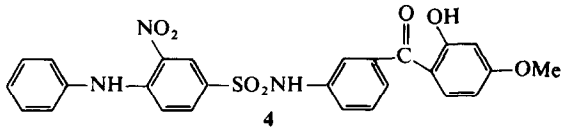
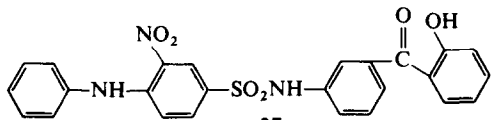
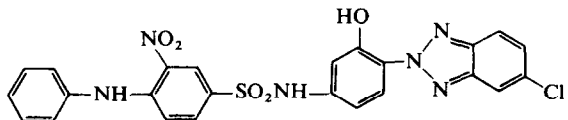
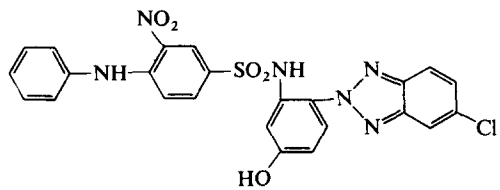
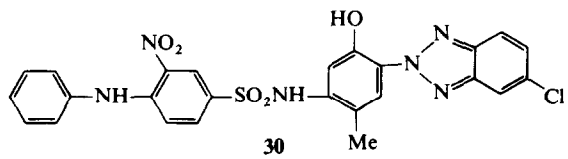
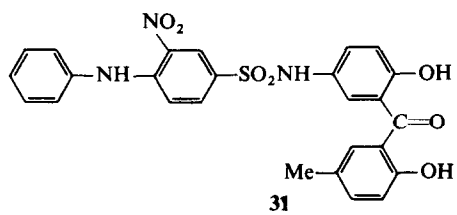
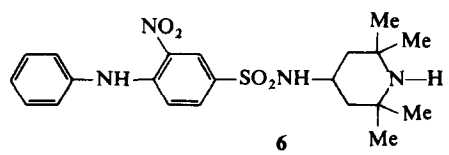
RESULTS AND DISCUSSION

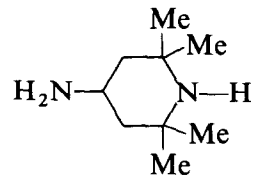
The synthesis of the target dyestuffs required the preparation of the benzophenoneamines of Schemes 1 and 2, benzotriazoleamines of Schemes 3 and 4, and the arylsulfonyl chloride of Scheme 5. The Friedel-Crafts reactions[16] of Schemes 1 and 2 typically afforded a 70% yield of the pure nitrobenzophenones **7** and **10**, and the subsequent hydrogenation gave a 90–95% yield of the required amines (**8a–c**). The aminobenzotriazoles (**17–19**, **22**) required, initially, a diazo coupling reaction between the diazo compound **11** and the appropriate phenol to give the azo compounds **12–14** and **21**. Cyclization of the azo compounds using thiourea S,S-dioxide[17] in alkali gave compounds **15–17** and **22**. Compounds **18** and **19** were then generated by acid hydrolysis of the *N*-acetyl group of the corresponding precursor, but only **18** was a useful synthetic intermediate.



Scheme 1. Preparation of compounds **8a** and **8b**.

TABLE 1
Dyes Obtained from a Reaction between Aminated Stabilizers and the Sulfonyl Chloride **25**

Amine used	*Dye obtained*
8a	 **26**
8b	 **4**
8c	 **27**
17	 **28**
18	 **29**
22	 **30**
32	 **31**
33	 **6**

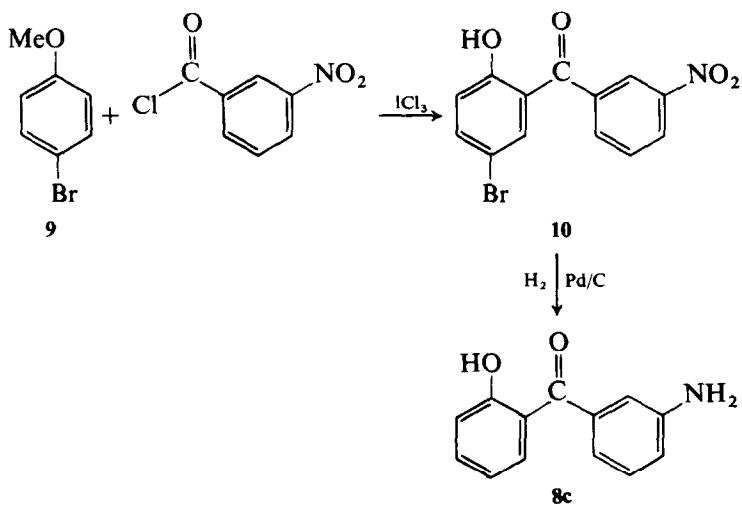


33

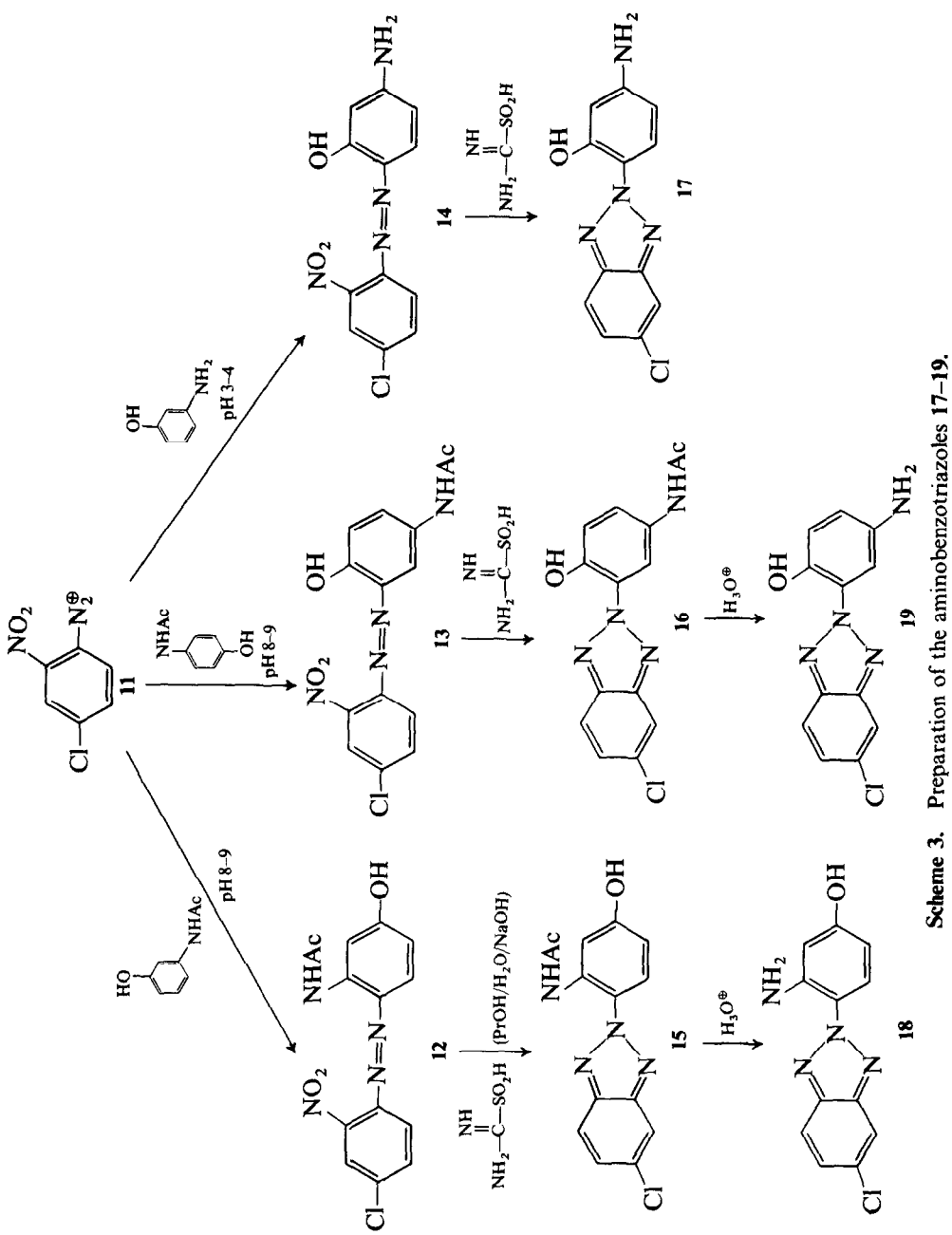
Table 1 contains the structures of the dyes prepared by reacting sulfonyl chloride **25** with amino-substituted stabilizers.

Compound **33** was purchased and **32** was prepared according to the method of Scheme 6. Instead of effecting the replacement of the chloro group of **34** by an NH_2 group, cyclodehydrohalogenation occurs to give **35**. It was then necessary to open the ring with alkali and reduce the nitro group to produce the target amine. Unlike amine **19**, compound **32** was stable enough to use in the synthesis of an analog of Yellow 42.

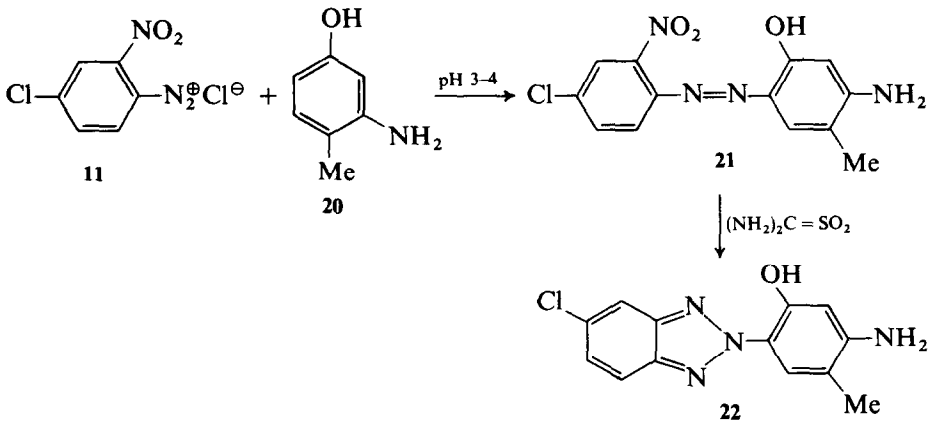
Isomers of dyes **4**, **28**, and **30** were prepared to examine the effects of building the photostabilizer moiety into the diphenylamine residue rather than connecting it via the sulfonamido group. The synthesis of these new dyestuffs is outlined in Scheme 7. It is important to use 2,6-lutidine rather than pyridine as the acid acceptor in these reactions, because the use of pyridine leads exclusively to compound **42** (cf. Scheme 8), presumably through the pyridinium salt **41**. A search of the chemical literature revealed that a similar reaction has been observed[18–22] between aniline and 2,4-dinitrochlorobenzene. In that case 2,4-dinitroaniline was obtained. Although the yield of dyes **5**, **38–39** was low, we were able to obtain



Scheme 2. Preparation of compound **8c**.



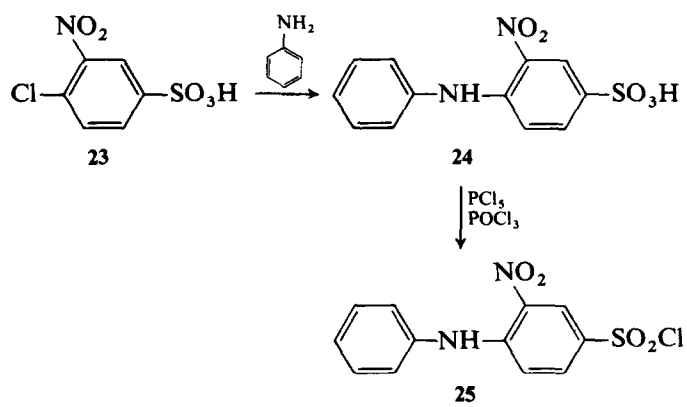
Scheme 3. Preparation of the aminobenzotriazoles **17–19.**



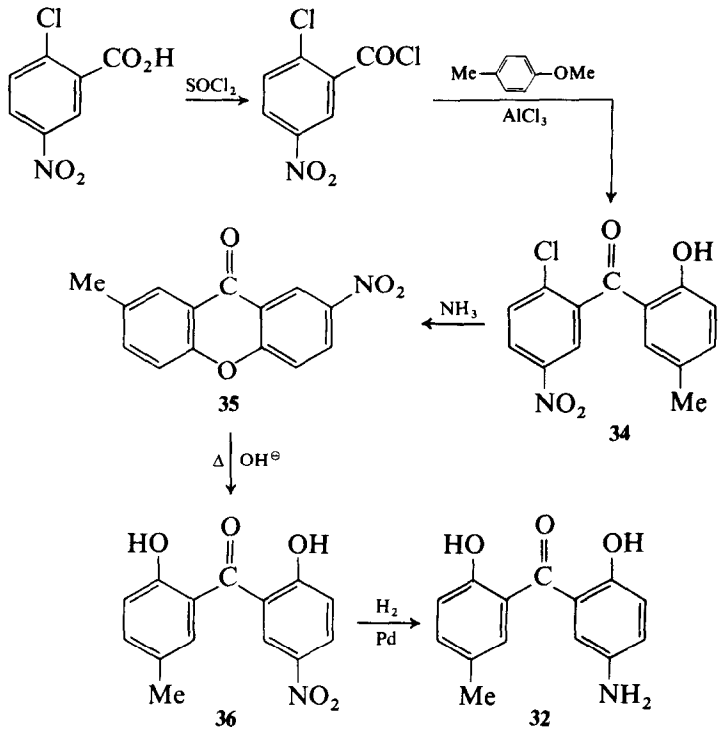
Scheme 4. Preparation of the aminohydroxybenzotriazole **22**.

sufficient amounts to conduct the necessary fastness tests, and to determine that each of these compounds possesses lower lightfastness than its isomeric counterpart (i.e. **4**, **28** and **30**).

The lightfastness of the eleven new dyes on PET was examined according to the method of Bulluck and Garrett[23] for automotive dyes. The resulting data, along with sublimation fastness and absorption spectral data, are given in Table 2. It was found that three of the new dyes are reproducibly better than a mixture of the parent dye (**3**) and physically added UV absorber. Two of the dyes (**4** and **27**) are significantly better. Interestingly, the stability of only these two dyes was increased further by the addition of 2% benzophenone or benzotriazole stabilizer to the dyebath prior to exhaustion. In the case of **4**, an increase in the rating from 3–4 to 4 was observed, whereas the rating of the isomer **38**, for instance, improved



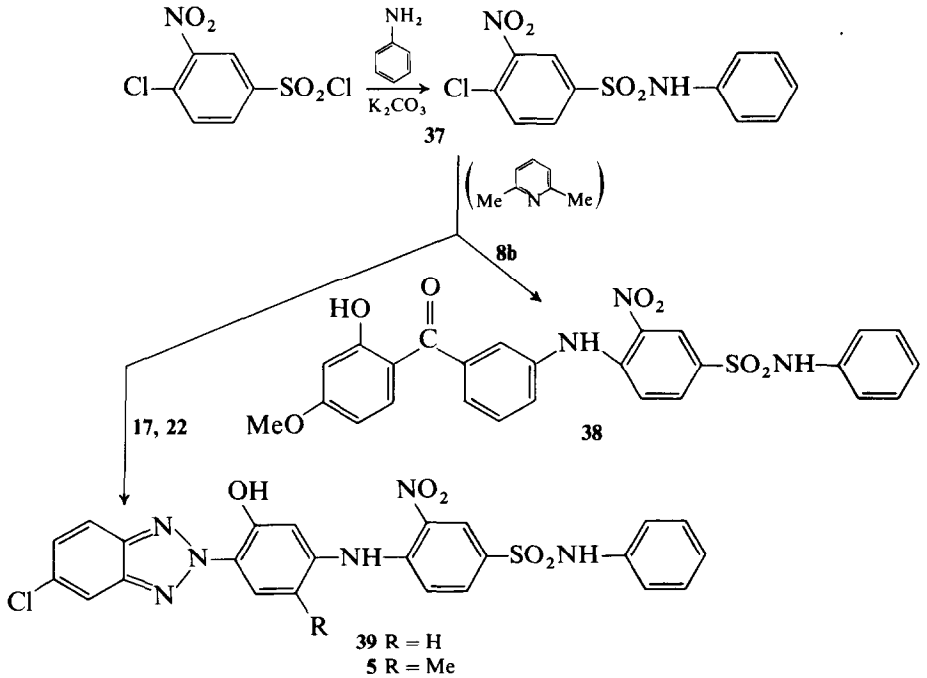
Scheme 5. Preparation of the diarylaminesulfonyl chloride **25**.



Scheme 6. Preparation of aminostabilizer **32**.

from 1–2 to 2. It was also interesting to note that the more difficult to prepare dyes **5**, **38** and **39** were inferior to the more readily synthesized isomers **4**, **28** and **30**.

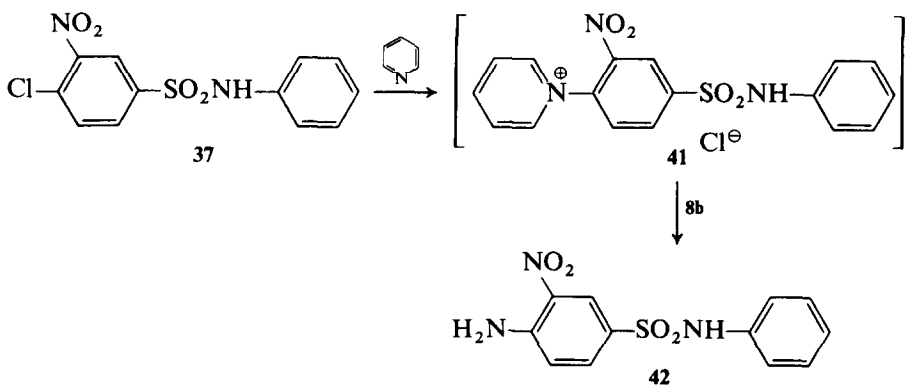
In general, the lightfastness of dyes containing a benzophenone moiety was better than that of dyes having a built-in benzotriazole or hindered amine residue. Of course dye **26**, which did not contain an *ortho*-hydroxy group in the benzophenone group, was much less photostable than Disperse Yellow 42. Dyes containing a benzotriazole group were more lightfast when the UV stabilizer was incorporated using the sulphonamide linkage. Although dyes **28** and **29** were more lightfast than Disperse Yellow 42 when the parent dye was applied without UV absorber, none of the benzotriazole-containing dyes was more lightfast than the mixture of Yellow 42 and 2% UV stabilizer. The addition of a *para*-methyl substituent to the phenolic ring slightly decreased lightfastness of **30** relative to **28**. However, when the benzotriazole moiety was incorporated into the diarylamine residue (cf. **5**), the presence of this substituent appeared to improve the lightfastness of dye **39**. The substitution of a hindered amine moiety for the anilino group of Disperse Yellow 42 led to a significant reduction in lightfastness (cf. dye **6**). This dye proved difficult to exhaust onto polyester



Scheme 7. Synthesis of dyes **5**, **38**, **39**.

due to its water solubility under normal dyeing conditions. Exhaustion could be improved by dyeing the fabric at pH 8.

Table 2 shows that an improvement in the sublimation fastness was achieved by increasing the molecular weight of the parent dye, as would be anticipated. Typical UV spectra are shown in Fig. 1. The contribution of a built-in benzophenone and benzotriazole group to the absorption properties of Yellow 42 can be seen in this figure.



Scheme 8. Amination of compound **37** in the presence of pyridine.

TABLE 2
Fastness and Spectral Data Recorded on the Dyes in This Investigation

Dye	*Lightfastness*[a,c]	*Submination fastness*[c] *(30s/60s)*	λ_{max} *(nm)*	ε_{max} $\frac{L}{cm \cdot M}$
Yellow 42	1–2	5/4–5	410	5 600
Yellow 42[b]	2–3	—	—	—
4	3–4	5/5	410	5 300
5	1–2	5/5	392	5 300
6	1–2	—	416	4 900
26	1	4–5/4–5	409	5 700
27	3–4	5/5	408	5 600
28	2–3	5/5	408	5 700
29	3	5/4–5	410	5 600
30	2	5/5	408	5 600
31	2	5/5	404	5 700
38	1–2	5/5	405	5 800
39	1	5/5	409	5 100

[a] Hunter LAB values recalculated to give a Grey Scale rating.
[b] 2% UV absorber added.
[c] Scale of 1 to 5, on PET.

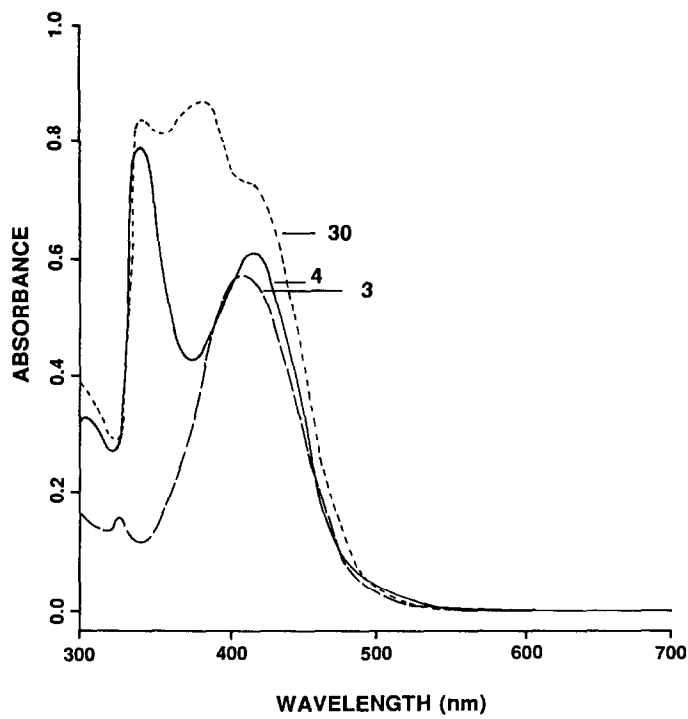


Fig. 1. Visible absorption spectra of dyes **3**, **4**, and **30**.

EXPERIMENTAL

General

The PET fabric used in this study was prepared by Celanese Fiber Operations and was a basic automotive body cloth material that did not contain TiO_2. The fabric was scoured in the usual way prior to using it, to remove knitting oils. Each of the test dyes was applied to 10-g swatches of fabric at 2% depth of shade with the aid of an Ahiba Polymat pressure dyeing machine at 130°C for 1 h in the absence of a carrier, and in the presence of Irgasol DA dispersing agent. The resulting dyeings were air-dried and irradiated in an Atlas CI 65 weatherometer according to the specifications of General Motors Corporation for automotive dyes.[23] The total level of exposure was 225·6 kJ/m^2.

The sublimation fastness testing was conducted with the aid of an Atlas Scortchtester at 177(±2)°C for 30–60 sec. The visible absorption spectra were recorded on a Perkin-Elmer model 24A spectrophotometer, the [^{1}H]NMR spectra on a Bruker 250 MHz instrument, and the mass spectra on a JEOL HX110F double-focusing mass spectrometer. The melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. The elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

Synthesis

Dye 4

2-Hydroxy-4-methoxy-3'-aminobenzophenone (**8b**; 4·86 g, 0·02 mol) and 3-nitro-4-anilinobenzenesulfonyl chloride (**25**; 6·23 g, 0·02 mol) were dissolved in 25 ml pyridine and the solution was stirred under reflux for 30 min. The mixture was cooled, then poured into 400 ml H_2O containing 25 ml conc. HCl, and extracted with 100 ml EtOAc. The organic layer was dried ($MgSO_4$), and concentrated to give 10·07 g (97%) **4**, m.p. 153–155°C.

Rf (4:1/PhMe:EtOAc) = 0·42.

Anal. Calcd for $C_{26}H_{21}N_3O_7S$: C, 60·11; H, 4·07; N, 8·09. Found: C, 60·06; H, 4·08; N, 8·00.

300 MHz [^{1}H]NMR ($CDCl_3$): 12·50 ppm (s, 1H); 9·81 ppm (s, 1H); 8·67–8·68 ppm (d, 1H); 7·63–7·67 ppm (dd, 1H); 7·27–7·47 ppm (m, 8H); 7·23–7·26 ppm (d, 2H); 7·10–7·13 ppm (d, 1H); 6·47–6·48 ppm (d, 1H); 6·35–6·39 ppm (dd, 1H); 3·84 ppm (s, 3H).

Mass spectrum (FAB, neg. ion) showed *m/z* = 518 (M − H) as the base peak.

IR spectrum (KBr): OH (3430 cm^{-1}); NH (3335 cm^{-1}); C=O (1595 cm^{-1}); NO_2 (1517, 1345 cm^{-1}); SO_2NH (1165 cm^{-1}).

Dye 5

2-(5-Chloro-2*H*-benzotriazol-2-yl)-4-methyl-5-aminophenol (**22**; 2·19 g, 8 mmol) and 4-chloro-3-nitro-*N*-phenylbenzenesulphonamide (**37**; 1·25 g, 4 mmol) were dissolved in 10 ml of 2,6-lutidine and stirred under a rapid reflux for 24 h. The cooled mixture was poured into 300 ml 10% HCl containing several grams of ice, and then extracted with 100 ml EtOAc. The organic layer was washed with 200 ml 10% HCl and dried ($MgSO_4$). The solvent was removed and the crude product was purified by flash column chromatography[24] using 2:1/PhMe:EtOAc to give 1·41 g (64%) **5**, m.p. 240–242°C.

Rf (4:1/PhMe:EtOAc) = 0·47.

Anal. Calcd for $C_{25}H_{19}N_6SO_5Cl$: C, 54·55; H, 3·45; N, 15·27. Found: C, 54·59; H, 3·49; N, 15·29.

250 MHz [^{1}H]NMR (DMSO-d_6/$CDCl_3$): 10·58 ppm (s, 1H); 10·34 ppm (s, 1H); 9·79 ppm (s, 1H); 8·50–8·51 ppm (d, 1H); 8·20 ppm (s, 1H); 8·09–8·13 ppm (d, 1H); 7·76–7·80 ppm (d, 2H); 7·53–7·57 ppm (dd, 1H); 7·25–7·31 ppm (d, 2H); 7·04–7·16 ppm (m, 4H); 6·92–6·95 ppm (dd, 1H); 2·14 ppm (s, 3H).

Mass spectrum (FAB, neg. ion) showed *m/z* = 549 (M − H, 14% rel. int.).

IR spectrum (KBr): OH (3333 cm^{-1}); NH (3268 cm^{-1}); NO_2 (1513, 1354 cm^{-1}); SO_2NH (1155 cm^{-1}).

Dye 6

3-Nitro-4-anilinobenzenesulfonyl chloride (**25**; 0·94 g, 3 mmol) was dissolved in 10 ml pyridine. To this solution was added 0·47 g 4-amino-2,2,6,6-tetramethylpiperidine (**33**; 3 mmol), and the solution was stirred under a mild reflux for 30 min. The solution was concentrated and the precipitate was stirred with 100 ml H_2O, collected by filtration, and dried to give 1·13 g (87%) **6**, m.p. 156–158°C.

Rf (5:1/EtOAc:EtOH) = 0·51.

Anal. Calcd for $C_{21}H_{28}N_4O_4S$: C, 58·33; H, 6·48; N, 12·96. Found: C, 58·07; H, 6·42; N, 13·22.

300 MHz [^{1}H]NMR (DMSO-d_6): 9·83 ppm (s, 1H); 9·48 ppm (s, 1H); 8·45 ppm (s, 1H); 8·27–8·28 ppm (d, 1H); 7·78–7·81 ppm (d, 1H); 7·37–7·47 ppm (m, 3H); 7·28–7·35 ppm (t, 2H); 7·16–7·19 ppm (d, 1H); 2·48–2·49 ppm (d, 1H); 1·65–1·69 ppm (d, 2H); 1·36–1·40 ppm (d, 2H); 1·26 ppm (s, 6H).

Mass spectrum (FAB, neg. ion) showed *m/z* = 433 (M + H) as the base peak.

IR spectrum (KBr): NH (3438 cm^{-1} and 3027 cm^{-1}); NO_2 (1509, 1356 cm^{-1}); SO_2NH (1161 cm^{-1}).

*4-Methoxy-3'-nitrobenzophenone (**7a**)*

3-Nitrobenzoyl chloride (9·28 g, 0·050 mol) and 13·3 g $AlCl_3$ were added to 50 ml CH_2Cl_2, and the mixture was cooled below 10°C. The mixture was stirred vigorously as 5·4 g (0·050 mol) anisole was added, and the resulting solution was stirred under reflux for 2·5 h. The reaction mixture was cooled and poured over 500 g ice containing 20 ml conc. HCl. The organic layer was dried ($MgSO_4$) and concentrated. The oil crystallised from MeOH to give 9·38 g (73%) **7a** as light yellow crystals, m.p. 92–93°C (lit.,[25] 93°C).

Rf (4:1/PhMe:EtOAc) = 0·76.

Anal. Calcd for $C_{14}H_{11}N_4$: C, 65·37; H, 4·28; N, 5·45. Found: C, 65·29; H, 4·30; N, 5·40.

250 MHz [^{1}H]NMR ($CDCl_3$): 8·53–8·55 ppm (d, 1H); 8·36–8·41 ppm (dd, 1H); 8·05–8·09 ppm (dd, 1H); 7·78–7·83 ppm (dd, 2H); 7·65–7·71 ppm (t, 1H); 6·96–7·01 ppm (dd, 2H); 3·89 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 258 (M + H) as the base peak.

IR spectrum (KBr): C=O (1597 cm^{-1}); NO_2 (1526, 1352 cm^{-1}).

*2-Hydroxy-4-methoxy-3'-nitrobenzophenone (**7b**)*

3-Nitrobenzoyl chloride (18·6 g, 0·10 mol) and 40 g $AlCl_3$ were added to 100 ml CH_2Cl_2 and the mixture was cooled below 10°C. The mixture was stirred vigorously as 13·8 g (0·10 mol) of 1,3-dimethoxybenzene was slowly added. The resulting solution was stirred under reflux for 2·5 h. The mixture was cooled and then poured over 500 g ice containing 50 ml conc. HCl. The organic layer was dried ($MgSO_4$) and concentrated. The oil was crystallised from MeOH/2-PrOH to give 19·3 g (71%) **7b** as pale yellow needles, m.p. 112–113°C.

Rf (4:1/PhMe:EtOAc) = 0·69.

Anal. Calcd for $C_{14}H_{11}NO_5$: C, 61·54; H, 4·03; N, 5·11. Found: C, 61·45; H, 4·10; N, 5·11.

250 MHz [^{1}H]NMR ($CDCl_3$): 12·34 ppm (s, 1H); 8·44–8·45 ppm (d, 1H); 8·36–8·40 ppm (dd, 1H); 7·92–7·96 ppm (dd, 1H); 7·65–7·71 ppm (t, 1H); 7·34–7·37 ppm (d, 1H); 6·50–6·51 ppm (d, 1H); 6·39–6·44 ppm (dd, 1H); 3·85 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 274 (M + H) as the base peak.

IR spectrum (KBr): OH (3437 cm^{-1}); C=O (1605 cm^{-1}); NO_2 (1535, 1348 cm^{-1}).

*4-Methoxy-3'-aminobenzophenone (**8a**)*

4-Methoxy-3'-nitrobenzophenone (**7a**; 6·43 g, 0·025 mol) was suspended in 200 ml of 95% EtOH and was reduced catalytically over 0·30 g 5% Pd/C. The catalyst was removed and the crude product was purified by recrystallization from H_2O to give 5·50 g (97%) white needles, m.p. 118–120°C.

Rf (4:1/PhMe:EtOAc) = 0·24.

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 74·01; H, 5·73; N, 6·17. Found: C, 73·74; H, 5·82; N, 6·14.

250 MHz [^{1}H]NMR ($CDCl_3$): 7·77–7·82 ppm (dd, 2H); 7·16–7·22 ppm (t, 1H); 7·02–7·06 ppm (dd, 2H); 6·88–6·94 ppm (dd, 2H); 6·80–6·84 ppm (dd, 1H); 3·84 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 228 (M + H) as the base peak.

IR spectrum (KBr): NH_2 (3468, 3366 cm^{-1}); C=O (1599 cm^{-1}).

*2-Hydroxy-4-methoxy-3'-aminobenzophenone (**8b**)*

2-Hydroxy-4-methoxy-3'-nitrobenzophenone (**7b**; 8·19 g, 3 mmol) was suspended in 200 ml of 95% EtOH and was reduced catalytically over 0·30 g 5% Pd/C. The catalyst and solvent were removed to give 6·99 g (96%) **8b**, m.p. 117–118°C.

Rf (4:1/PhMe:EtOAc) = 0·38.

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69·14; H, 5·35; N, 5·76. Found: C, 69·03; H, 5·40; N, 5·75.

250 MHz [^{1}H]NMR ($CDCl_3$): 7·36–7·38 ppm (d, 1H); 7·21–7·24 ppm (t, 1H); 7·10–7·16 ppm (m, 2H); 6·91–6·93 ppm (d, 1H); 6·46–6·47 ppm (d, 1H); 6·33–6·37 ppm (dd, 1H); 3·84 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 244 (M + H) as the base peak.

IR spectrum (KBr): NH_2 (3430, 3366 cm^{-1}); C=O (1595 cm^{-1}).

*2-Hydroxy-3'-aminobenzophenone (**8c**)*

2-Hydroxy-5-bromo-3'-nitrobenzophenone (**10**; 12·9 g, 0·04 mol) was suspended in 200 ml of 95% EtOH containing 12·1 g triethylamine (0·12 mol) and reduced catalytically over 0·30 g 20% $Pd(OH)_2$/C. The catalyst and volatiles were removed and the crude product was purified by recrystallization from 1-BuOH to give 8·39 g (98%) **8c** as yellow needles, m.p. 123–124°C (lit.[26] 119–120°C).

Rf (4:1/PhMe:EtOAc) = 0·58.

Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73·24; H, 5·16; N, 6·57. Found: C, 73·22; H, 5·22; N, 6·55.

250 MHz [^{1}H]NMR ($CDCl_3$): 7·36–7·66 ppm (dd, 1H); 7·46–7·53 ppm (t, 1H); 7·23–7·29 ppm (t, 1H); 6·99–7·07 ppm (m, 2H); 6·95–6·96 ppm (t, 1H); 6·83–6·90 ppm (m, 2H).

Mass spectrum (CI) showed m/z = 214 (M + H) as the base peak.
IR spectrum (KBr): NH_2 (3476, 3379 cm^{-1}); C=O (1624 cm^{-1}).

*2-Hydroxy-5-bromo-3'-nitrobenzophenone (**10**)*
3-Nitrobenzoyl chloride (9·28 g, 0·05 mol) and 13·3 g $AlCl_3$ were added to 50 ml CH_2Cl_2 and the mixture cooled to below 10°C. The mixture was stirred vigorously as 9·35 g 4-bromoanisole was added. The resulting solution was stirred under reflux for 16 h and then concentrated. Ice water (300 ml) containing 20 ml conc. HCl was slowly added. The resulting mixture was stirred for 15 min, filtered, and the solid was washed with 300 ml H_2O. The crude product was dissolved in 150 ml 10% NaOH and stirred at 75°C for 30 min. The mixture was cooled to below 10°C by adding ice, and the pH was adjusted to 3·0 using 10% HCl. The solid was collected by filtration and dried to give 13·5 g (84%) pure **10**, m.p. 121–123°C.

Rf (4:1/PhMe:EtOAc) = 0·86.

Anal. Calcd for $C_{13}H_8NO_4Br$: C, 48·45; H, 2·48; N, 4·35. Found: C, 48·18; H, 2·53; N, 4·27.

250 MHz [^{1}H]NMR ($CDCl_3$): 10·45 ppm (s, 1H); 8·44–8·47 ppm (d, 2H); 8·12–8·15 ppm (d, 1H); 7·79–7·85 ppm (t, 1H); 7·53 ppm (s, 1H); 7·59–7·62 ppm (d, 1H); 6·97–7·00 ppm (d, 1H).

Mass spectrum (CI) showed m/z = 323 (M + H) as the base peak.

IR spectrum (KBr): OH (3417 cm^{-1}); C=O (1640 cm^{-1}); NO_2 (1532, 1348 cm^{-1}).

*4-(5-Chloro-2H-benzotriazol-2-yl)-3-acetamidophenol (**15**)*
Finely powdered $NaNO_2$ (4·55 g, 0·066 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 using an ice bath. A solution of 4-chloro-2-nitroaniline (10·38 g, 0·06 mol) in 40 ml glacial HOAc was added dropwise, keeping the temperature below 20°C. Ice (50 g) was added and the solution stirred at 10–15°C for 1 h. The resulting reaction mixture was then slowly added to a solution of 3-acetamidophenol (3·78 g, 0·025 mol) in 500 ml 10% NaOH to give pH 12–13, and stirred for 1·5 h at 10–15°C. The pH was adjusted to 10 with 10% HCl and the solution stirred for an additional 16 h. The precipitate was collected by filtration and washed with 500 ml H_2O. The intermediate azo dye was dissolved in 640 ml 1:1/H_2O:2-PrOH containing 10·6 g NaOH and the mixture was heated to 70°C. Thiourea-S,S-dioxide (5·7 g, 0·075 mol) was slowly added and the solution was stirred under reflux for 3 h. The solution was then concentrated to 200 ml and cooled to room temperature. The pH was then lowered to 9 with 10%

HCl. The precipitate was collected by filtration and dried to give 5·28 g (70%) **15**.

Rf (4:1/PhMe:EtOAc) = 0·18.

250 MHz [^{1}H]NMR ($CDCl_3$): 10·10 ppm (s, 1H); 8·12–8·13 ppm (d, 1H); 8·04–8·07 ppm (d, 1H); 7·75–7·79 ppm (d, 1H); 7·67–7·68 ppm (d, 1H); 7·46–7·51 ppm (dd, 1H); 6·74–6·79 ppm (d, 1H); 2·06 ppm (s, 3H).

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

IR spectrum (KBr): OH (3432 cm^{-1}); NHC=O (1620 cm^{-1}).

2-(5-Chloro-2H-benzotriazol-2-yl)-5-aminophenol (17)

The procedure used was essentially the same as that used to make compound **15**. The diazonium salt derived from 4-chloro-2-nitroaniline was then slowly added to a solution of 3-aminophenol (6·54 g, 0·06 mol) in 100 ml 10% HCl to give pH 3–4, and stirred for 6 h at 10–15°C. The precipitate was collected by filtration, washed with 500 ml H_2O, and sucked air-dry. The intermediate azo dye was dissolved in 700 ml 1:1/H_2O:2-PrOH containing 11·4 g NaOH and the mixture was heated at 70°C. Thiourea-S,S-dioxide (14 g, 0·18 mol) was slowly added and the solution was stirred under reflux for 3 h. The solution was then concentrated to 200 ml and cooled to room temperature. The precipitate was collected by filtration and dried to give 9·05 g (58%) **17** as yellow crystals, m.p. 193–194°C.

Rf (4:1/PhMe:EtOAc) = 0·38.

Anal. Calcd for $C_{12}H_9N_4OCl$: C, 55·38; H, 3·46; N, 21·54. Found: C, 55·21; H, 3·51; N, 21·42.

250 MHz [^{1}H]NMR ($CDCl_3$): 10·25 ppm (s, 1H); 8·06–8·07 ppm (d, 1H); 7·96–8·00 ppm (dd, 1H); 7·53–7·56 ppm (d, 1H); 7·41–7·45 ppm (dd, 1H); 6·29–6·30 ppm (d, 1H); 6·23–6·27 ppm (dd, 1H); 5·68 ppm (s, 2H, NH_2).

Mass spectrum (CI) showed *m/z* = 261 (M + H) as the base peak.

IR spectrum (KBr): NH_2 (3474, 3379 cm^{-1}; overlapping a broad OH peak from 3580–3320 cm^{-1}).

4-(5-Chloro-2H-benzotriazol-2-yl)-3-aminophenol (18)

Compound **15** (2 g, 6·7 mmol) was suspended in 25 ml of 20% HCl containing 2 ml H_2SO_4 and the mixture stirred under reflux for 24 h. The solution was cooled, diluted to 800 ml with H_2O, and filtered to give 1·63 g (95%) **18**, m.p. 172–174°C.

Rf (4:1/PhMe:EtOAc) = 0·32.

Anal. Calcd for $C_{12}H_9N_4OCl$: C, 55·38; H, 3·46; N, 21·54. Found: C, 55·13; H, 3·55; N, 21·44.

250 MHz [^{1}H]NMR ($CDCl_3$): 8·12–8·13 ppm (d, 1H); 8·04–8·08 ppm

(d, 1H); 7·86–7·91 ppm (d, 1H); 7·48–7·52 ppm (dd, 1H); 6·65–6·66 ppm (d, 1H); 6·46–6·51 ppm (d, 1H).

Mass spectrum (CI) showed *m/z* = 261 (M + H) as the base peak.

IR spectrum (KBr): OH (3455 cm^{-1}); NH_2 (3386, 3301 cm^{-1}).

*2-(5-Chloro-2H-benzotriazol-2-yl)-4-methyl-aminophenol (**22**)*

The procedure used was essentially the same as described above for the synthesis of **15**. Once the diazotization of 4-chloro-2-nitroaniline was complete, the mixture was slowly added to a solution of 4-methyl-3-aminophenol (7·38 g, 0·06 mol) in 100 ml 10% HCl to give pH 3–4 and stirred for 6 hours at 10–15°C. The conditions required to complete the preparation of **15** were followed to give 9·71 g (59%) **22** as yellow crystals, m.p. 200–202°C.

Rf (4:1/PhMe:EtOAc) = 0·36.

Anal. Calcd for $C_{13}H_{11}N_4OCl$: C, 56·84; H, 4·04; N, 20·40. Found: C, 56·69; H, 4·09; N, 20·30.

300 MHz [^{1}H]NMR ($CDCl_3$/DMSO-d_6): 7·90–7·85 ppm (m, 2H); 7·79 ppm (s, 1H); 7·36–7·40 ppm (d, 1H); 6·42 ppm (s, 1H); 5·04 ppm (s, 2H, NH_2); 2·14 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 275 (M + H) as the base peak.

IR spectrum (KBr): NH_2 (3485, 3384 cm^{-1}, overlapping a broad OH peak from 3540 to 3280 cm^{-1}).

*3-Nitro-4-anilinobenzenesulfonyl chloride (**25**)*

4-Chloro-3-nitrobenzenesulfonic acid (47 g, 0·20 mol) was added to 100 ml aniline and the mixture heated under reflux for 2 h. The hot solution was poured into 500 ml H_2O at 80–85°C and stirred vigorously as 50 ml conc. H_2SO_4 was added dropwise. The resulting mixture was cooled to 75°C and filtered through a large fritted glass funnel. The collected solid was stirred with 100 ml of 10% KOH in MeOH. The solid was collected by filtration and air-dried to give 30·73 g 3-nitro-4-anilinobenzenesulfonic acid, potassium salt. This intermediate (16·6 g, 0·05 mol) and 10 g PCl_5 were added to 50 ml $POCl_3$ and the mixture was stirred under reflux for 1 h. The solution was cooled to room temperature, added cautiously to 600 g ice, and the mixture was stirred vigorously for 1 h. The viscous oil that formed was extracted into 200 ml EtOAc, and the organic layer was dried ($MgSO_4$) and concentrated. The crude product was purified by flash column chromatography, eluting with PhMe, to give 11·86 (75%) **25**, m.p. 102–103°C (lit.,[27] 104°C).

Rf (4:1/PhMe:EtOAc) = 0·88.

Anal. Calcd for $C_{12}H_9N_2SO_4Cl$: C, 46·08; H, 2·88; N, 8·96. Found: C, 46·10; H, 2·79; N, 8·88.

250 MHz [^{1}H]NMR ($CDCl_3$): 8·40–8·41 ppm (d, 1H); 7·75–7·79 ppm (dd, 1H); 7·44–7·50 ppm (m, 2H); 7·36–7·39 ppm (d, 2H); 7·20–7·29 ppm (m, 2H).

Mass spectrum (CI) showed m/z = 313 (M + H) as the base peak.

IR spectrum (KBr): NH (3331 cm^{-1}), NO_2 (1510, 1364 cm^{-1}); SO_2Cl (1177 cm^{-1}).

Dye 26

4-Methoxy-3'-aminobenzophenone (**8a**; 1·14 g, 5 mmol) and 3-nitro-4-anilinobenzenesulfonyl chloride (**25**; 1·56 g, 5 mmol) were dissolved in 20 ml pyridine, and the solution was stirred under a gentle reflux for 30 min. The mixture was cooled, poured into 300 ml H_2O containing 10 ml conc. HCl, and extracted with 100 ml EtOAc. The organic layer was collected, dried ($MgSO_4$), and concentrated. The dye was purified by recrystallization from acetone to give 2·34 g (93%) **26** as yellow crystals, m.p. 215–217°C.

Rf (4:1/PhMe:EtOAc) = 0·61.

Anal. Calcd for $C_{26}H_{21}N_3SO_6$: C, 62·03; H, 4·17; N, 8·35. Found: C, 61·94; H, 4·19; N, 8·30.

250 MHz [^{1}H]NMR (DMSO-d_6): 9·89 ppm (s, 1H); 8·48–8·49 ppm (d, 1H); 7·70–7·75 ppm (dd, 1H); 7·62–7·67 ppm (d, 2H); 7·43–7·50 ppm (m, 6H); 7·31–7·38 ppm (m, 3H); 7·14–7·18 ppm (d, 1H); 7·03–7·06 ppm (d, 2H); 3·86 ppm (s, 3H).

Mass spectrum (CI) showed m/z = 503 (51% of the base peak) and the base peak was m/z = 196.

IR spectrum (KBr): NH (3440 cm^{-1}); C=O (1595 cm^{-1}); NO_2 (1509, 1356 cm^{-1}); SO_2NH (1165 cm^{-1}).

The following five dyes (**27–31**) were synthesized using the procedure described above for the preparation of **26**.

Dye 27

2-Hydroxy-3'-aminobenzophenone (**8c**; 1·70 g, 8 mmol) and 3-nitro-4-anilinobenzenesulfonyl chloride (**25**; 2·50 g, 8 mmol) gave a crude dye that was puyrified by recrystallization from 1-BuOH to give 3·72 g (95%) **27** as orange crystals, m.p. 180–181°C.

Rf (4:1/PhMe:EtOAc) = 0·58.

Anal. Calcd for $C_{25}H_{19}N_3SO_6$: C, 61·35; H, 3·94; N, 8·63. Found: C, 61·44; H, 3·94; N, 8·63.

300 MHz [^{1}H]NMR ($CDCl_3$/DMSO-d_6): 11·68 ppm (s, 1H); 10·01 ppm (s, 1H); 9·65 ppm (s, 1H); 8·50–8·51 ppm (d, 1H); 7·49–7·53 ppm (dd, 1H); 7·38–7·42 ppm (dd, 1H); 7·24–7·34 ppm (m, 4H); 7·13–7·22 ppm

(m, 3H); 7·05–7·08 ppm (d, 3H); 6·91–6·95 ppm (dd, 1H); 6·81–6·86 ppm (dd, 1H); 6·65–6·69 ppm (dd, 1H).

Mass spectrum (CI) showed m/z = 490 (M + H) as the base peak.

IR spectrum (KBr): HH (3434 cm^{-1}); NH (3339 cm^{-1}); C=O (1618 cm^{-1}); NO_2 (1509, 1358 cm^{-1}); SO_2NH (1165 cm^{-1}).

Dye ***28***

2-(5-Chloro-2*H*-benzotriazol-2-yl)-5-aminophenol (**17**; 1·56 g, 6 mmol) and 3-nitro-4-anilinobenzenesulfonyl chloride (**25**; 1·87 g, 6 mmol) gave a precipitate that was collected by filtration and washed with 200 ml MeOH to give 2·94 g (91%) **28**, m.p. 250–251°C.

Rf (4:1/PhMe:EtOAc) = 0·49.

Anal. Calcd for $C_{24}H_{17}N_6SO_5Cl$: C, 53·73; H, 3·17; N, 15·67. Found: C, 53·75; H, 3·21; N, 15·59.

250 MHz [^{1}H]NMR ($CDCl_3$): 9·87 ppm (s, 1H); 8·58–8·59 ppm (d, 1H); 8·08–8·09 ppm (d, 1H); 7·98–8·02 ppm (d, 1H); 7·78–7·83 ppm (dd, 1H); 7·60–7·63 ppm (d, 1H); 7·40–7·46 ppm (m, 3H); 7·21–7·34 ppm (m, 3H); 7·14–7·17 ppm (d, 1H); 7·02–7·03 ppm (d, 1H); 6·79–6·83 ppm (dd, 1H).

Mass spectrum (FAB, neg. ion) showed m/z = 535 (M − H) as the base peak.

IR spectrum (KBr): OH (3337 cm^{-1}); NH (3274 cm^{-1}); NO_2 (1509, 1356 cm^{-1}); SO_2NH (1161 cm^{-1}).

Dye ***29***

4-(5-Chloro-2*H*-benzotriazol-2-yl)-3-aminophenol (**18**; 1·04 g, 4 mmol) and 3-nitro-4-anilinobenzenesulfonyl chloride (**25**; 1·25 g, 4 mmol) gave a crude dye that was purified by flash column chromatography using 2:1/cyclohexane:EtOAc to give 1·75 g (82%) **29**, m.p. 198–200°C.

Rf (4:1/PhMe:EtOAc) = 0·46.

Anal. Calcd for $C_{24}H_{17}N_6SO_5Cl$: C, 53·73; H, 3·17; N, 15·67. Found: C, 53·46; H, 3·19; N, 15·39.

300 MHz [^{1}H]NMR ($CDCl_3$/DMSO-d_6): 10·20 ppm (s, 1H); 9·77 ppm (s, 1H); 9·67 ppm (s, 1H); 8·35–8·36 ppm (d, 1H); 7·93–7·98 ppm (d, 1H); 7·84–7·85 ppm (d, 1H); 7·79–7·82 ppm (d, 1H); 7·41–7·47 ppm (t, 2H); 7·38–7·39 ppm (d, 1H); 7·33–7·36 ppm (m, 2H); 7·25–7·29 ppm (dd, 1H); 7·17–7·21 ppm (d, 2H); 6·78–6·82 ppm (dd, 1H); 6·76–6·79 ppm (d, 1H).

Mass spectrum (FAB, pos. ion) showed m/z = 537 (M + H, 87% rel. int.).

IR spectrum (KBr): OH (3426 cm^{-1}); NH (3337 cm^{-1}); NO_2 (1509, 1354 cm^{-1}); SO_2NH (1163 cm^{-1}).

Dye 30

2-(5-Chloro-2*H*-benzotriazol-2-yl)-4-methyl-5-aminophenol (**22**; 1·37 g, 5 mmol) and 3-nitro-4-anilinobenzenesulfonyl chloride (**25**; 1·56 g, 5 mmol) gave a precipitate that was collected by filtration and washed with 200 ml hot MeOH to give 2·23 g (74%) pure **30**, m.p. 245–246°C.

Rf (4:1/PhMe:EtOAc) = 0·46.

Anal. Calcd for $C_{25}H_{19}N_6SO_5Cl$: C, 54·55; H, 3·45; N, 15·27. Found: C, 54·46; H, 3·51; N, 15·23.

250 MHz [^{1}H]NMR ($CDCl_3$/DMSO-d_6): 10·43 ppm (s, 1H); 9·93 ppm (s, 1H); 8·55–8·56 ppm (d, 1H); 8·14 ppm (s, 1H); 8·04–8·07 ppm (d, 1H); 7·77–7·81 ppm (d, 1H); 7·58 ppm (s, 1H); 7·46–7·52 ppm (m, 3H); 7·32–7·40 ppm (m, 3H); 7·21–7·25 ppm (d, 1H); 6·97 ppm (s, 1H); 2·16 ppm (s, 3H).

Mass spectrum (FAB, neg. ion) showed *m/z* = 549 (M − H, 22% rel. int.).

IR spectrum (KBr): OH (3339 cm^{-1}); NH (3279 cm^{-1}); NO_2 (1509, 1356 cm^{-1}); SO_2NH (1169 cm^{-1}).

Dye 31

2,2'-Dihydroxy-5-methyl-5'-aminobenzophenone (**32**; 1·94 g, 8 mmol) and 3-nitro-4-anilinobenzenesulfonyl chloride (**25**; 2·50 g, 8 mmol) gave a crude dye that was stirred with hot MeOH and filtered to give 4·05 g (97%) pure **31**, m.p. 194–195°C

Rf (4:1/PhMe:EtOAc) = 0·45.

Anal. Calcd for $C_{26}H_{21}N_3O_7S$: C, 60·12; H, 4·05; N, 8·09. Found: C, 60·04; H, 4·12; N, 7·97.

300 MHz [^{1}H]NMR (DMSO-d_6): 10·75 ppm (s, 1H); 10·71 ppm (s, 1H); 9·97 ppm (s, 1H); 9·83 ppm (s, 1H); 8·31–8·32 ppm (d, 1H); 7·55–7·59 ppm (dd, 1H); 7·40–7·45 ppm (t, 2H); 7·22–7·29 ppm (m, 4H); 7·14–7·18 ppm (dd, 1H); 7·07–7·10 ppm (d, 1H); 6·95–6·99 ppm (t, 2H); 6·87–6·90 ppm (d, 1H); 6·82–6·85 ppm (d, 1H); 2·11 ppm (s, 3H).

Mass spectrum (FAB, pos. ion) showed *m/z* = 520 (M + H, 94% rel. int.).

IR spectrum (KBr): OH (3432 cm^{-1}); C=O (1618 cm^{-1}); NO_2 (1507, 1354 cm^{-1}); SO_2NH (1163 cm^{-1}).

2,2'-Dihydroxy-5-methyl-5'-aminobenzophenone (32)

2,2'-Dihydroxy-5-methyl-5'-nitrobenzophenone (**36**; 4·10 g, 0·015 mol) was suspended in 200 ml of 95% EtOH and was reduced catalytically over 0·30 g 5% Pd/C. The catalyst was removed and the crude product was recrystallized from cyclohexane to give 3·37 g (92%) **32** as orange crystals, m.p. 117–119°C.

Rf (4:1/PhMe:EtOAc) = 0·35.

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69·14; H, 5·35; N, 5·76. Found: C, 69·22; H, 5·43; N, 5·73.

250 MHz [^{1}H]NMR ($CDCl_3$): 10·55 ppm (s, 1H); 10·40 ppm (s, 2H); 7·20–7·24 ppm (dd, 1H); 7·10–7·11 ppm (d, 1H); 6·87–6·90 ppm (d, 1H); 6·79–6·80 ppm (d, 1H); 6·76 ppm (s, 2H); 6·58–6·59 ppm (d, 1H); 2·21 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 244 (M + H) as the base peak.

IR spectrum (KBr): OH (3441 cm^{-1}); NO_2 (3378, 3301 cm^{-1}); C=O (1609 cm^{-1}).

*2-Hydroxy-5-methyl-2'-chloro-5'-nitrobenzophenone (**34**)*

2-Chloro-5-nitrobenzoyl chloride (6·6 g, 0·03 mol) and 7·5 g $AlCl_3$ were added to 40 ml CH_2Cl_2. The mixture was stirred vigorously as 3·66 g (0·03 mol) 4-methylanisole was added. The resulting solution was stirred under reflux for 2 h. At that point, an additional 1·5 g $AlCl_3$ was added and the mixture stirred under reflux for 30 min. The solution was cooled, poured over 400 g ice containing 10 ml conc. HCl, and the mixture stirred until it reached room temperature. The organic layer was dried ($MgSO_4$), and concentrated. The oil crystallized from MeOH to give 8·24 g (94%) **34** as white needles, m.p. 134–135°C

Rf (4:1/PhMe:EtOAc) = 0·84.

Anal. Calcd for $C_{14}H_{10}NO_4Cl$: C, 57·73; H, 3·44; N, 4·79. Found: C, 57·76; H, 3·47; N, 4·79.

250 MHz [^{1}H]NMR (DMSO-d_6): 8·31–8·35 ppm (d, 2H); 7·84–7·87 ppm (d, 1H); 7·36–7·40 ppm (d, 1H); 7·26 ppm (s, 1H); 6·91–6·94 ppm (d, 1H); 2·21 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 292 (M + H) as the base peak.

IR spectrum (KBr): OH (3447 cm^{-1}); C=O (1615 cm^{-1}); NO_2 (1534, 1348 cm^{-1}).

*2-Methyl-7-nitroxanthen-9-one (**35**)*

2-Hydroxy-5-methyl-2'-chloro-5'-nitrobenzophenone (**34**; 5·85 g, 0·020 mol) was suspended in 100 ml H_2O. NaOH (5 g) was added and the mixture stirred under reflux for 15 min. To the reaction mixture was added 50 ml of 4% NaOH and it was stirred under reflux for an additional 30 min, then cooled to room temperature. The precipitate was collected by filtration and washed with 500 ml H_2O to give 5·09 g (98%) pure **35**, m.p. 220–221°C (lit.,[26] 219–221C).

Rf (4:1/PhMe:EtOAc) = 0·71.

Anal. Calcd for $C_{14}H_9NO_4$: C, 65·88; H, 3·53; N, 5·43. Found: C, 65·96; H, 3·55; N, 5·43.

250 MHz [^{1}H]NMR (D_2SO_4): 10·18 ppm (d, 1H); 9·58–9·62 ppm (dd, 1H); 9·02 ppm (s, 1H); 8·90–8·93 ppm (dd, 1H); 8·84–8·88 ppm (d, 1H); 8·66–8·70 ppm (d, 1H); 3·25 (s, 3H).

Mass spectrum (CI) showed *m/z* = 255 as the base peak.

IR spectrum (KBr): C=O (1657 cm^{-1}); NO_2 (1528, 1343 cm^{-1}).

*2-2'-Dihydroxy-5-methyl-5'-nitrobenzophenone (**36**)*

2-Methyl-7-nitroxanthen-9-one (**35**; 4·10 g, 0·016 mol) was suspended in 50 ml of 1 : 1/pyridine : H_2O. NaOH (5 g) was added and the mixture stirred under reflux for 2 h. The solution was concentrated to remove the pyridine, and the resulting hot solution was filtered through a fritted glass funnel. The filtrate was diluted to 500 ml with ice and adjusted to pH = 7 using cold 10% HCl. The crude product was collected by filtration and recrystallized from cyclohexane to give 3·64 g (83%) **36** as yellow crystals, m.p. 143–145°C.

Rf (4 : 1/PhMe : EtOAc) = 0·63.

Anal. Calcd for $C_{14}H_{11}NO_5$: C, 61·54; H, 4·03; N, 5·13. Found: C, 61·56; H, 4·07; N, 5·07.

250 MHz [^{1}H]NMR ($CDCl_3$): 11·78 ppm (s, 1H); 10·93 ppm (s, 1H); 8·27–8·31 ppm (dd, 1H); 8·22–8·23 ppm (d, 1H); 7·32–7·36 ppm (d, 1H); 7·21 ppm (s, 1H); 7·14–7·17 ppm (d, 1H); 6·90–6·93 ppm (d, 1H), 2·21 ppm (s, 3H).

Mass spectrum (CI) showed *m/z* = 273 (59% base peak); the base peak was *m/z* = 256 (M − OH).

IR spectrum (KBr): OH (3233 cm^{-1}); C=O (1597, 1574 cm^{-1}); NO_2 (1524, 1342 cm^{-1}).

*4-Chloro-3-nitro-N-phenylbenzenesulphonamide (**37**)*

4-Chloro-3-nitrobenzenesulfonyl chloride (10·24 g, 0·04 mol) was added to 40 ml anhydrous acetone containing 11·04 g dry powdered K_2CO_3. The mixture was stirred vigorously and cooled to 5–10°C. Aniline (3·72 g, 0·04 mol) was added at a rate such that the temperature did not exceed 10°C. The solution was stirred at room temperature for 3·5 h, filtered, and the filtrate concentrated. The viscous oil obtained was purified by flash column chromatography using 5 : 1/PhMe : EtOAc to give 10·88 g (87%) **37**, m.p. 80–82°C

Rf (4 : 1/PhMe : EtOAc) = 0·62.

Anal. Calcd for $C_{12}H_9N_2SO_4Cl$: C, 46·08; H, 2·91; N, 8·96. Found: C, 45·96; H, 2·92; N, 8·90.

250 MHz [^{1}H]NMR ($CDCl_3$): 8·25–8·26 ppm (d, 1H); 7·92–7·96 ppm (dd, 1H); 7·73–7·76 ppm (d, 1H); 6·93–7·00 ppm (m, 2H); 6·82–6·87 ppm (dd, 2H); 6·55–6·62 ppm (t, 1H).

Mass spectrum (CI) showed *m/z* = 313 (M + H) as the base peak.

IR spectrum (KBr): NH (3265 cm^{-1}); NO_2 (1537, 1343 cm^{-1}); SO_2NH (1397, 1167 cm^{-1}).

Dye 38

2-Hydroxy-4-methoxy-3'-aminobenzophenone (**8b**; 2·43 g, 10 mmol) and 4-chloro-3-nitro-*N*-phenylbenzenesulphonamide (**37**; 1·56 g, 5 mmol) were dissolved in 25 ml of 2,6-lutidine and heated under reflux for 24 h. The cooled mixture was poured into 500 ml of 10% HCl containing several grams of ice, and extracted with 150 ml EtOAc. The organic layer was filtered to remove an insoluble by-product and the filtrate was washed with 200 ml 10% HCl, and dried ($MgSO_4$). The solvent was removed, and the crude product was purified by flash column chromatography using 3:1/PhMe:EtOAc to give 1·51 g (58%) **38**, m.p. 156–158°C.

Rf (4:1/PhMe:EtOAc) = 0·45.

Anal. Calcd for $C_{26}H_{21}N_3O_7S$: C, 60·11; H, 4·07; N, 8·09. Found: C, 60·48; H, 4·02; N, 8·09.

300 MHz [^{1}H]NMR ($CDCl_3$): 12·49 ppm (s, 1H); 9·85 ppm (s, 1H); 8·66–8·67 ppm (d, 1H); 7·67–7·70 ppm (dd, 1H); 7·53–7·60 ppm (t, 2H); 7·45–7·47 ppm (m, 2H); 7·23–7·28 ppm (m, 2H); 7·16–7·19 ppm (d, 1H); 7·10–7·14 ppm (d, 3H); 6·52–6·56 (dd, 1H); 6·41–6·45 ppm (d, 1H); 3·85 ppm (s, 3H).

Mass spectrum (FAB, neg. ion) showed *m/z* = 518 (M − H) as the base peak.

IR spectrum (KBr): OH (3416 cm^{-1}); NH (3320 cm^{-1}); C=O (1617 cm^{-1}); NO_2 (1507, 1354 cm^{-1}); SO_2NH (1165 cm^{-1}).

Dye 39

2-(5-Chloro-2*H*-benzotriazol-2-yl)-5-aminophenol (**17**; 2·08 g, 8 mmol) and 4-chloro-3-nitro-*N*-phenylbenzenesulphonamide (**37**; 1·25 g, 4 mmol) were dissolved in 10 ml of 2,6-lutidine and stirred under reflux for 24 h. The cooled mixture was poured into 300 ml 10% HCl containing several grams of ice, and then extracted with 100 ml EtOAc. The organic layer was washed with 200 ml 10% HCl, and dried ($MgSO_3$). The solvent was removed and the crude product was purified by flash column chromatography using 2:1/PhMe:EtOAc to give 1·29 g (60%) **39**, m.p. 236–238°C.

Rf (4:1/PhMe:EtOAc) = 0·43.

Anal. Calcd for $C_{24}H_{17}N_6SO_5Cl$: C, 53·73; H, 3·17; N, 15·67. Found: C, 53·69; H, 3·23; N, 15·66.

250 MHz [^{1}H]NMR (DMSO-d_6/$CDCl_3$): 10·75 ppm (s, 1H); 10·36 ppm (s, 1H); 9·83 ppm (s, 1H); 8·46–8·47 ppm (d, 1H); 8·20 ppm (s, 1H); 8·08–8·12 ppm (d, 1H); 7·78–7·83 ppm (d, 2H); 7·52–7·56 ppm (dd, 1H);

7·42–7·45 ppm (d, 1H); 7·25–7·31 ppm (t, 2H); 7·04–7·16 ppm (m, 4H); 6·98–7·02 ppm (dd, 1H).

Mass spectrum (FAB, neg. ion) showed *m/z* = 535 (M − H, 11% rel. int.).

IR spectrum (KBr): OH (3350 cm^{-1}); NH (3284 cm^{-1}); NO_2 (1512, 1350 cm^{-1}); SO_2NH (1157 cm^{-1}).

*4-Amino-3-nitro-N-phenylbenzenesulphonamide (**42**)*

4-Chloro-3-nitro-*N*-phenylbenzenesulphonamide (**37**; 1·56 g, 5 mmol) and aniline (0·51 g, 5·5 mmol) were dissolved in 20 ml pyridine, and the solution was stirred under a gentle reflux for 2 h. The mixture was concentrated and the viscous oil obtained was extracted with 50 ml EtOAc. The organic layer was washed with 100 ml 10% HCl, dried ($MgSO_4$) and concentrated. The product crystallized from $CHCl_3$ to give 1·18 g **42** (76%) as yellow crystals, m.p. 137–138°C.

Rf (4:1/PhMe:EtOAc) = 0·48.

Anal. Calcd for $C_{12}H_{11}N_3O_4S$: C, 49·15; H, 3·75; N, 14·33. Found: C, 49·15; H, 3·75; N, 14·33.

250 MHz [^{1}H]NMR (DMSO-d_6): 10·15 ppm (s, 1H); 8·31 ppm (s, 1H); 7·98 ppm (s, 2H, NH_2); 7·57–7·60 ppm (d, 1H); 7·20–7·26 ppm (m, 2H); 7·02–7·10 ppm (m, 4H).

Mass spectrum (CI) showed *m/z* = 294 (M + H) as the base peak.

IR spectrum (KBr): NH_2 (3480, 3366 cm^{-1}); NO_2 (1514, 1350 cm^{-1}); SO_2NH (1167 cm^{-1}).

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