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Disperse dyes containing a built-in oxalanilide stabilizer

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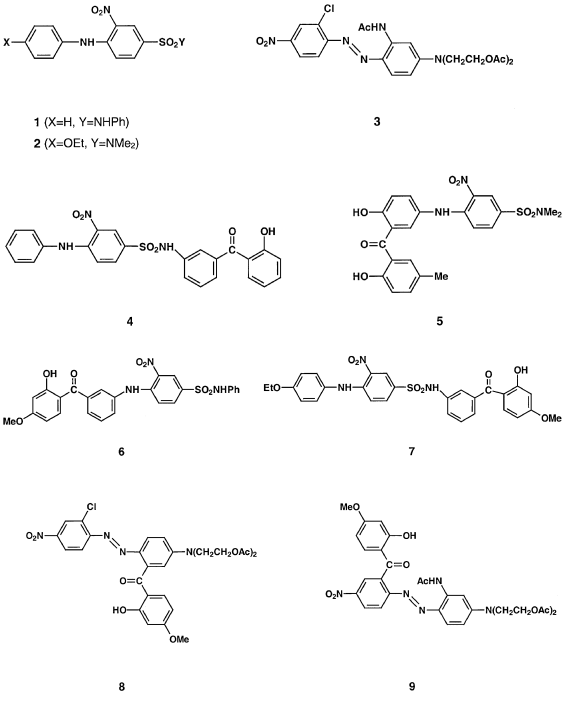
Abstract

Monoazo and nitrodiphenylamine disperse dyes containing an oxalanilide photostabilizer have been synthesized and evaluated for lightfastness as potential automotive dyes. The results showed that the lightfastness of CI Disperse Red 167 could be appreciably enhanced, depending on the substituent employed in the oxalanilide moiety. While it was also possible to improve the lightfastness of CI Disperse Yellow 86, the resulting lightfastness was not as high as that observed when a hydroxybenzophenone stabilizer was incorporated.

Keywords: Oxalanilide photostabilizer; Lightfastness; CI Disperse Yellow 86; CI Disperse Red 167; Molecular modeling

1. Introduction

In previous papers from our laboratories, we reported the synthesis and fastness properties of some automotive disperse dyes and acid dyes containing a built-in photostabilizer residue [1–3]. Those papers included analogs of CI Disperse Yellow 42 (**1**), CI Disperse Yellow 86 (**2**), and CI Disperse Red 167 (**3**), in which either an *ortho*-hydroxybenzophenone or *ortho*-hydroxybenzotriazole had been introduced. In those studies, we found that the nature and location of the stabilizer group had a significant impact on photostability. For instance, dyes such as **4** and **5** were more lightfast than the corresponding commercial (parent) dyes; but dyes **6** and **7** had lower lightfastness than the parent dyes. It was not possible to improve the lightfastness of the nitrodiphenylamine dyes by employing a built-in benzotriazole stabilizer. In addition, we were unable to enhance the lightfastness of CI Disperse Red 167 by incorporating a hydroxybenzophenone group. In the latter case, dyes such as **8** and **9** were made. Analogs of CI



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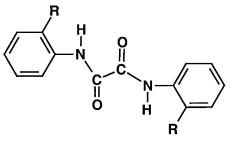
Disperse Red 167 containing a benzotriazole stabilizer were not synthesized in our prior studies.

The present paper represents an extension of the aforementioned work in which we have attempted to capitalize on the stabilizing properties of oxalanilides (**10**). We were especially interested in this system because of its potential for making CI Disperse Red 167 analogs that preserved intramolecular H-bonding present in the parent dye when the oxalanilide moiety is placed *ortho* to the azo bond. Accordingly, this paper provides a summary of the synthesis and properties of type **11–13** dyes (Schemes 1–3), where R = H, Et, and OEt.



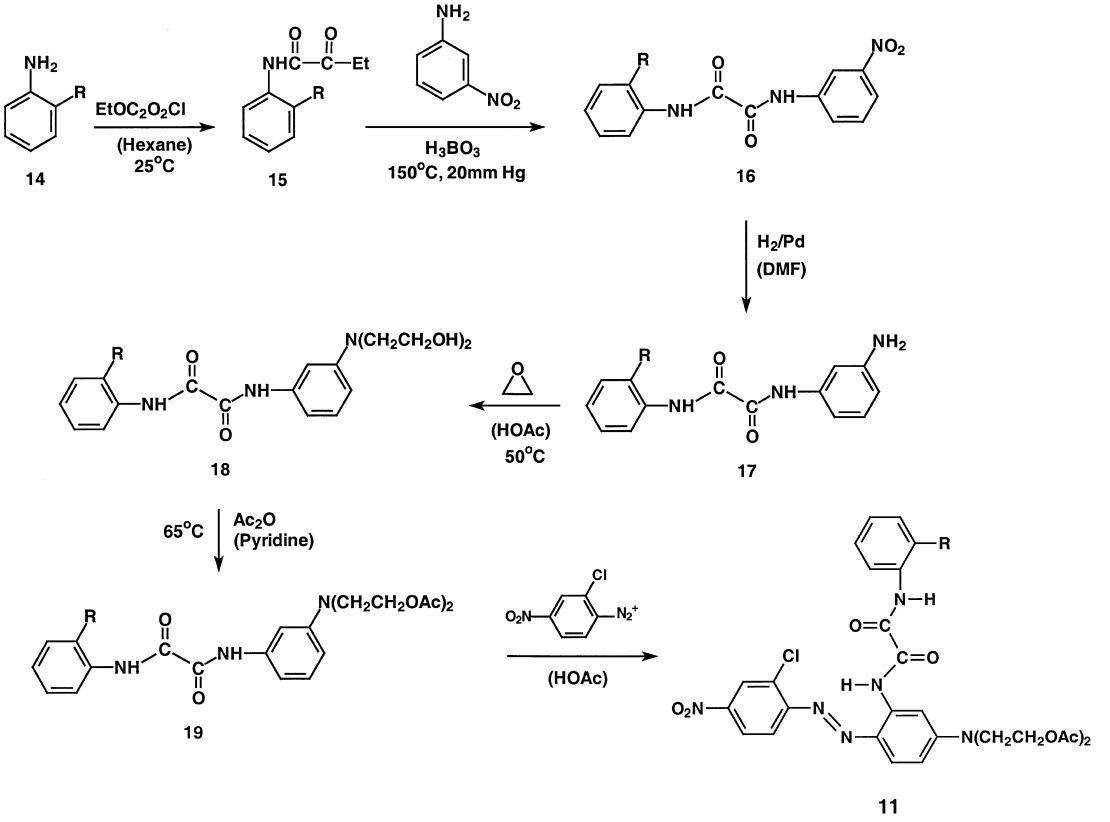
10

2. Experimental

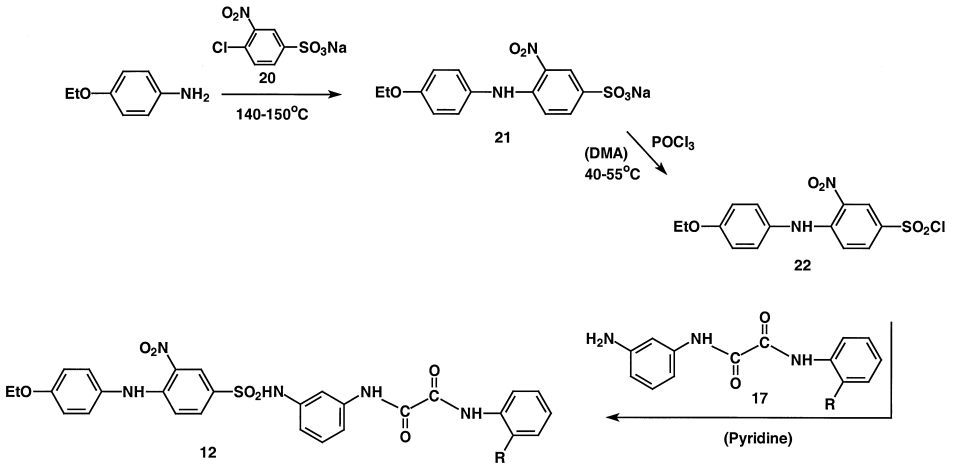
2.1. General

All starting materials were purchased from either Fisher Scientific or Aldrich Chemical Company. Whatman silica gel plates (60A, 250 μm layer, type MK6F), used for TLC (thin layer chromatography) and Davisil® 643 silica gel (type 150A, 230–425 mesh), used for flash column chromatography, were obtained from Fisher Scientific.

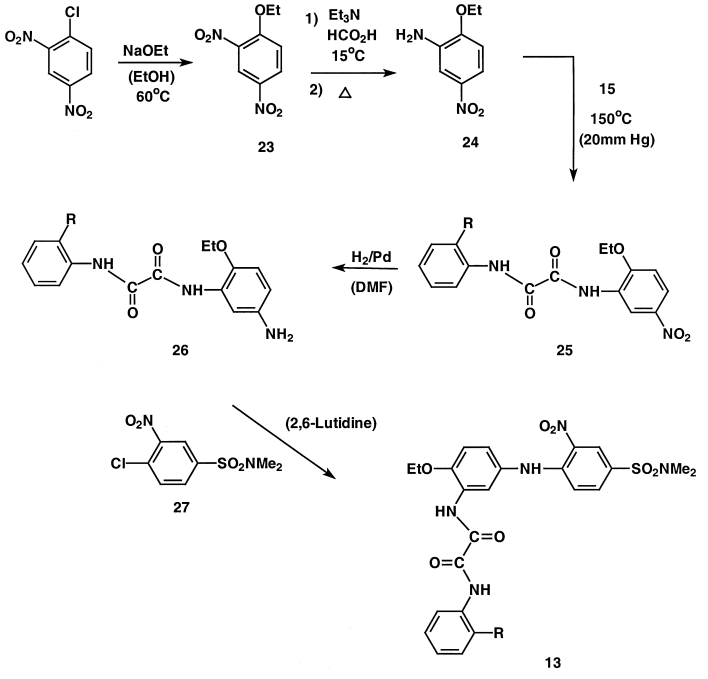
All melting points were determined using a Mel-Temp capillary apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 300 MHz Spectrometer, using solutions of the compounds in 0.5 ml of either $CDCl_3$ or DMSO-d_6 containing TMS (tetramethylsilane) as the internal standard. Mass spectral data were generated using



Scheme 1. Synthesis of type **11** dyes (R = H, Et, OEt).



Scheme 2. Synthesis of type **12** dyes (R = H, Et, OEt).



Scheme 3. Synthesis of type **13** dyes (R = H, Et, OEt).

either a JEOL (Tokyo, Japan) HX110HF double-focusing mass spectrometer, employing FAB or EI as the ionization source, or a Hewlett Packard 5985B GC/MS instrument, using CI as the ionization source. To generate FAB spectra, NBA (3-nitrobenzyl alcohol) or thioglycerol was used as the matrix. Methane or isobutane was utilized as the reagent gas for generating CI spectra. UV–visible absorption data were obtained using a Cary 3E UV/Visible spectrophotometer. Atlantic Microlabs Inc., Norcross, GA, performed elemental analyses.

Molecular modeling studies were carried out using CAChe Worksystem (Oxford Molecular [4]),

running on an Apple Macintosh Quadra 950. This system was equipped with a 40 MHz CXP RISC coprocessor, 64 MB RAM, and a 3D stereoscopic display unit. CAChe implementations of MOPAC 6.0 and an augmented MM2 mechanical forcefield were used to perform geometry optimizations.

2.2. Dyebath preparation and dyeing

Dyebath dispersions were prepared by dissolving the dye in a minimum amount of Me_2CO and adding this solution to 250 ml of distilled H_2O containing twice as much dispersing agent (Irgasol DA PDR, Ciba-Geigy Corporation) as dye. The flask containing the resulting mixture was immersed in an Ultrasound bath (50–60 Hz Branson 3200 Ultrasonic Cleaner) and heated at 60°C for 30 min to drive off Me_2CO. To half of the cooled dispersions, commercial UV absorber (Ultrafast 830) was added. The dispersions were adjusted to pH 5.5, using 1% HOAc, and diluted with distilled H_2O to give a final volume of 280 ml.

All dyes were applied to commercial Lawrence style polyester (PET) automotive body cloth, following a 20-min pre-scour in a solution of Kierlon TX-199 (BASF Corporation) at 77°C. One group of dyeings was produced at 0.5 and 1.0% owf (on weight of fiber) concentrations, using a liquor ratio of 20:1, and a second group was produced in the presence of Ultrafast 830 at the same shade depths. Dyeings were carried out in an Ahiba Polymat (type PM) dyeing machine at 130°C for 1.5 h. After the dyeing process was complete, the fabrics were rinsed in water and air-dried overnight.

2.3. Lightfastness measurements

The lightfastness of dyed fabrics was assessed by exposing the fabrics to 225.6 and 451.2 kJ of xenon arc radiation in an Atlas CI 65 xenon arc weatherometer, according to the conditions specified in SAE Automotive Test Method 1885 [5]. The conditions for the test 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)
Window glass filters: 310 nm cut-off.

The degree of fading was determined spectrophotometrically using an ACS Spectro-Sensor II (Applied Color Systems, Inc.), and expressed in terms of color co-ordinates (ΔE, ΔLab, ΔH, ΔC). The corresponding gray scale ratings for the exposed fabrics were calculated from the color co-ordinates. The results are summarised in Table 5.

2.4. Sublimation fastness measurements

Sublimation fastness of the dyes was determined according to the procedure outlined in AATCC Test Method 117-1989 [6]. A composite sample consisting of Multifiber Test Fabric No. 10A (Testfabrics Inc.), dyed fabric, and undyed PET fabric was placed in an Atlas Scorch Tester (Atlas Electric Devices Co.), and held at 177 ± 2°C for 30 and 60 sec. After storing for 4h at room temperature, each multifiber fabric was evaluated for dye transfer, using the AATCC Chromatic Transference Scale, and the dyed fabric evaluated for color change (ΔE) using the AATCC gray scale for color change. Both scales were obtained from the

Table 1
Analytical data recorded on dyes **11–13**

Dye	Yield (%)	Mp (°C)	R_f[a]	FAB MS (M^+–rel. int.)[b]	λ_{max}	ε_{max}
11a	81	198	0.64	611 (6%)	507[d]	35,600
11b	81	155–156	0.71	639 (35%)	507[d]	35,000
11c	79	192–193	0.70	655 (8%)	509[d]	35,400
Red 167	–	–	–	–	507[e]	45,500
12a	73	216–218	0.52	575 (81%)	414[e]	5200
12b	75	121–213	0.58	603 (31%)	414[e]	5900
12c	71	208–210	0.59	619 (19%)	414[e]	6100
Yellow 86	–	–	–	–	414[e]	5800
13a	79	175–176	0.52	527 (100%)[c]	411[e]	6200
13b	85	176	0.55	555 (87%)	411[e]	6200
13c	76	209–210	0.56	571 (100%)	411[e]	6200

[a]Eluent = PhMe:EtOAc (1:1).
[b]Matrix = NBA.
[c]Matrix = thioglycerol.
[d]Recorded in PhCl.
[e]Recorded in acetone.

Table 2
Synthesis and characterisation data for dye intermediates used in this study

Compound	Synthesis and characterisation of intermediates (quantities; reaction times; purification)	R_f (eluent)	% Yield	Mp (°C)	CI MS[a]
15b	**14b** (0.23 mol), $EtOC_2O_2Cl$ (0.11 mol); distill (20 mm Hg) hexane solubles	0.56 (4:1/PhMe:EtOAc)	86	44–47	222
15c	Same as **15b**, except recryst. [Me_2CO:H_2O (4:1)]	0.59 (4:1/PhMe:EtOAc)	77	78–79	238
16a	**15a** (72 mmol), H_3BO_3 (70 mmol); 2 h; recryst. [Me_2CO:H_2O (4:1)]	0.43 (9:1/PhMe:EtOAc)	71	214	286
16b	Same as **16a**	0.46 (9:1/PhMe:EtOAc)	76	186	314
16c	Same as **16a**	0.50 (9:1/PhMe:EtOAc)	61	210	330
17a	**16a** (21 mmol), Pd/C (0.6 g, 5%); 3 h; recryst. [Me_2CO:MeOH (4:1)]	0.49 (1:1/PhMe:EtOAc)	81	198	256
17b	Same as **17a**	0.56 (1:1/PhMe:EtOAc)	85	144–145	284
17c	Same as **17a**	0.56 1:1/PhMe:EtOAc)	80	147–148	300
18a	**17a** (10 mmol), NaOAc (12 mmol); 1.5 h; chromatog. (silica gel, EtOAc)	0.27 (EtOAc)	80	160–161	344
18b	Same as **18a**	0.33 (EtOAc)	83	158–161	372
18c	Same as **18a**	0.34 (EtOAc)	81	152–153	388
19a	**18a** (7.3 mmol), Ac_2O (16 mmol); 1 h; neutralize (cold HCl); recryst. (EtOH)	0.65 (1:1/PhMe:EtOAc)	83	118–120	428
19b	Same as **19a**	0.66 (1:1/PhMe:EtOAc)	78	123–124	456
19c	Same as **19a**	0.66 (1:1/PhMe:EtOAc)	73	103–104	472
21	4-Ethoxyaniline (0.33 mol), **20** (0.33 mol); 2 h; recryst. (EtOH)	0.75 (4:1/PhMe:EtOAc)	84	–	337 (M–Na)[b]
22	**21** (10 mmol), $POCl_3$; 2 h; dilute (cold H_2O); charcoal Me_2CO solution	0.55 (PhMe)	70	101–102	357
23	NaOEt (0.22 mol), 2,4-dinitrochlorobenzene (0.13 mol); 1 h; recryst. (MeOH:H_2O)	0.39 (PhMe)	80	84	213
24	(1) **23** (0.28 mol), Pd/C (6 g, 5%), Et_3N (127 g); add HCO_2H; (2) boil 10 min; chromatog. [silica gel, hexane: EtOAc (4:1)]	0.61 (4:1/PhMe:EtOAc)	33	95–97	182[b]
25a	**15a** (36 mmol), **24** (37 mmol), H_3BO_3 (11 mmol); heat 1.5 h; cool; recryst. [Me_2CO:EtOH (1:1)]	0.45 (9:1/PhMe:EtOAc)	84	209–210	330
25b	Same as **25a**	0.50 (9:1/PhMe:EtOAc)	77	188	358
25c	Same as **25a**	0.50 (9:1/PhMe:EtOAc)	63	200–202	374
26a	**25a** (12 mmol), Pd/C (0.4 g, 5%); 7.5 h; recryst. [Me_2CO:EtOH (3:1)]	0.46 (1:1/PhMe:EtOAc)	83	160–161	300
26b	Same as **26a**	0.58 1:1/PhMe:EtOAc)	86	114–115	328
26c	Same as **26a**	0.58 (1:1/PhMe:EtOAc)	84	194–195	344
27	4-Chloro-3-nitrobenzenesulfonic acid (40 mmol), Me_2NH [7.0 g, 40% (w/w)], Na_2CO_3, [10% (w/w)]; 2 h (20°C); dilute (cold H_2O), recryst. (EtOH)	0.42 (9:1/PhMe:EtOAc)	85	104	265

[a](M + H). [b](FAB/neg. ion/NBA).

American Association of Textile Chemists and Colorists, Research Triangle Park, North Carolina. The results are summarised in Table 7.

2.5. Conformational analyses

In carrying out molecular modeling studies, all structures were first optimized using MM2. Conformational analysis of the phenyl-azo-phenyl skeleton of CI Disperse Red 167 analogs was conducted by editing the MM2-optimized structure. Conformers were produced by rotating the optimized structures about the phenyl-azo bonds. Each conformer was then optimized using the PM3 [7,8] method and an Eigenvector Following converger. Convergence criterior were specified so that the structures were deemed converged when the conjugate gradient had been reduced below a value of

Table 3
Elemental analysis and proton NMR data recorded on dyes **11–13**

Dye	Elemental analysis	Proton NMR data (ppm)
11a $C_{28}H_{27}N_6O_8Cl$	Calc.: C, 55.04; H, 4.45; N, 13.75. Found: C, 55.11; H, 4.51; N, 13.68.	11.4 (s, 1 H); 11.0 (s, 1 H); 8.4 (d, 1 H); 8.28 (dd, 1 H); 8.05 (d, 1 H); 7.87 (d, 2 H); 7.78 (d, 1 H) 7.76 (d, 1 H); 7.38 (t, 2 H); 7.18 (t, 1 H); 6.85 (dd, 1 H); 4.3 (t, 4 H); 3.82 (t, 4 H); 2.0 (s, 6 H)
11b $C_{30}H_{31}N_6O_8Cl$	Calc.: C, 56.38; H, 4.89; N, 13.15. Found: C, 56.26; H, 4.84; N, 13.10.	11.6 (s, 1 H); 9.4 (s, 1 H); 8.4 (d, 1 H); 8.2 (dd, 1 H); 8.1 (d, 1 H); 8.1 (d, 1 H); 7.9 (d, 1 H); 7.85 (d, 1 H); 7.2 (m, 3 H); 6.7 (dd, 1 H); 4.4 (t, 4 H); 3.8 (t, 4 H); 2.8 (q, 2 H); 2.1 (s, 6 H); 1.3 (t, 3 H)
11c $C_{30}H_{31}N_6O_9Cl$	Calc.: C, 55.01; H, 4.77; N, 12.83. Found: C, 54.90; H, 4.76; N, 12.75.	11.5 (s, 1 H); 9.9 (s, 1 H); 8.4 (dd, 1 H); 8.3 (d, 1 H); 8.2 (dd, 1 H); 8.1 (d, 1 H); 7.9 (d, 1 H); 7.8 (d, 1 H); 7.1 (td, 1 H); 7.0 (t, 1 H); 6.9 (d, 1 H); 6.6 (dd, 1 H); 4.4 (t, 4 H); 4.1 (q, 2 H); 3.8 (t, 4 H); 2.1 (s, 6 H); 1.5 (t, 3 H)
12a $C_{28}H_{25}N_7O_7S$	Calc.: C, 58.43; H, 4.38; N, 12.17. Found: C, 58.38; H, 4.42; N, 12.22.	10.9 (s, 1 H); 10.8 (s, 1 H); 10.4 (s, 1 H); 9.8 (s, 1 H); 8.5 (d, 1 H); 7.9 (m, 3 H); 7.7 (dd, 1 H); 7.5 (d, 1 H); 7.4 (t, 2 H); 7.2 (m, 3 H); 7.1 (t, 1 H); 7.0 (d, 2 H); 6.95 (d, 1 H); 6.9 (d, 1 H); 4.0 (q, 2 H); 1.3 (t, 3 H)
12b $C_{30}H_{29}N_5O_7S$	Calc.: C, 59.69; H, 4.84; N, 11.60. Found: C, 59.57; H, 4.86; N, 11.52.	10.9 (s, 1 H); 10.4 (s, 1 H); 10.3 (s, 1 H); 9.8 (s, 1 H); 8.5 (d, 1 H); 7.9 (s, 1 H); 7.7 (dd, 1 H); 7.5 (m, 2 H); 7.3 (m, 6 H); 7.0 (d, 2 H); 6.9 (d, 1 H); 6.9 (d, 1 H); 4.0 (q, 2 H); 2.6 (q, 2 H); 1.3 (t, 3 H); 1.1 (t, 3 H)
12c $C_{30}H_{29_{N_5}}O_8S$	Calc.: C, 58.15; H, 4.72; N, 11.30. Found: C, 58.07; H, 4.70; N, 11.33.	11.0 (s, 1 H); 10.4 (s, 1 H); 9.9 (s, 1 H); 9.8 (s, 1 H); 8.5 (d, 1 H); 8.2 (d, 1 H); 7.8 (d, 1 H); 7.7 (dd, 1 H); 7.5 (d, 1 H); 7.2 (m, 5 H); 7.0 (m, 5 H); 4.2 (q, 2 H); 4.0 (q, 2 H); 1.4 (t, 3 H); 1.3 (t, 3 H).
13a $C_{24}H_{25}N_5O_7S$	Calc.: C, 54.64; H, 4.78; N, 13.27. Found: C, 54.63; H, 4.80; N, 13.20.	10.1 (s, 1 H); 9.8 (s, 1 H); 9.3 (s, 1 H); 8.7 (d, 1 H); 8.4 (d, 1 H); 7.7 (m, 3 H); 7.4 (t, 2 H); 7.1 (m, 4 H); 4.2 (q, 2 H); 2.8 (s, 6 H); 1.5 (t, 3 H)
13b $C_{26}H_{29}N_5O_7S$	Calc.: C, 56.21; H, 5.26; N, 12.60. Found: C, 56.23; H, 5.28; N, 12.55.	10.1 (s, 1 H); 9.8 (s, 1 H); 9.4 (s, 1 H); 8.6 (d, 1 H); 8.4 (d, 1 H); 8.1 (d, 1 H); 7.7 (dd, 1 H); 7.1 (m, 6 H); 4.2 (q, 2 H); 2.8 (s, 6 H); 2.7 (q, 2 H); 1.6 (t, 3 H); 1.3 (t, 3 H)
13c $C_{26}H_{29}N_5O_8S$	Calc.: C, 54.63; H, 5.11; N, 12.25. Found: C, 54.49; H, 5.15; N, 12.14.	10.1 (s, 1 H); 10.0 (s, 1 H); 9.7 (s, 1 H); 8.6 (d, 1 H); 8.5 (d, 1 H); 8.4 (dd, 1 H); 7.7 (dd, 1 H); 7.0 (m, 6 H); 4.2 (q, 2 H); 4.1 (q, 2 H); 2.8 (s, 6 H); 1.6 (t, 3 H); 1.5 (t, 3 H)

1.0 kcal $Å^{-1}$. Thus, the keywords PM3 EF HESS = 1 GNORM = 1.0 XYZ were specified in MOPAC.

2.6. Synthesis

2.6.1. Intermediates

The methods used to synthesize dye intermediates are summarised in Table 2 and Schemes 1–3.

2.6.2. Dyes

2.6.2.1. **11a–c**. The method used is illustrated in the synthesis of dye **11a**.

Nitrosyl sulfuric acid was prepared by heating a mixture of $NaNO_2$ (0.3 g, 4.1 mmol) and conc. H_2SO_4 (4 ml) at 80°C until a clear solution formed. The solution was cooled to 8°C and 2-chloro-4-nitroaniline (0.6 g, 3.5 mmol) was added at a rate such that the temperature did not exceed 15°C. The mixture was stirred at 10–15°C for 30 min, and ice (20 g) containing ammonium sulfamate (0.14 g) was added. The diazonium salt solution was added dropwise to a solution of **19a** (1.5 g, 3.5 mmol) in HOAc (34 ml), at a rate such that the temperature was kept below 10°C. Following the addition, the reaction mixture was stirred at room temperature for 1.5 h, filtered, and the red filter cake was washed with H_2O until the washings were colorless. The solid was dissolved in pyridine (30 ml) and stirred with Ac_2O (2.0 g, 20 mmol) at 60°C for 30 min, to replace acetyl groups loss during the coupling step. After cooling the reaction mixture to room temperature, crushed ice (40 g) containing conc. HCl (30 ml) was added, and the dye was extracted into EtOAc (300 ml). The EtOAc solution was washed with Na_2CO_3 (100 ml, 5%) and with

Table 4
Elemental analysis and proton NMR data recorded on dye intermediates used in this study

Compound	Elemental analysis	Proton NMR data (ppm)
15b	Calc.: C, 65.14; H, 6.83; N, 6.33.	(DMSO-d6): 10.3 (s, 1 H); 7.3 (m, 4 H); 4.3 (q, 2 H); 2.6 (q, 2 H);
$C_{12}H_{15}NO_3$	Found: C, 65.06; H, 6.81; N, 6.37	1.3 (t, 3 H); 1.1 (t, 3 H).
15c	Calc.: C, 60.75; H, 6.37; N, 5.90.	($CDCl_3$): 9.6 (s, 1 H); 8.4 (dd, 1 H); 7.1 (td, 1 H); 7.0 (td, 1 H); 6.9
$C_{12}H_{15}NO_4$	Found: C, 60.87; H, 6.37; N, 5.94.	(dd, 1 H); 4.4 (q, 2 H); 4.1 (q, 2 H); 1.5 (t, 3 H); 1.4 (t, 3 H).
16a	Calc.: C, 58.95; H, 3.89; N, 14.73.	(DMSO-d_6): 11.4 (s, 1 H); 10.9 (s, 1 H); 8.9 (d, 1 H); 8.3 (dd, 1 H);
$C_{14}H_{11}N_3O_4$	Found: C, 58.86; H, 3.91; N, 14.79.	8.0 (d, 1 H); 7.9 (d, 2 H); 7.7 (t, 1 H); 7.4 (t, 2 H); 7.2 (t, 1 H)
16b	Calc.: C, 61.34; H, 4.83; N, 13.41.	(DMSO-d_6): 11.4 (s, 1 H); 10.4 (s, 1 H); 8.9 (d, 1 H); 8.3 (dd, 1 H);
$C_{16}H_{15}N_3O_4$	Found: C, 61.45; H, 4.85; N, 13.43.	8.0 (dd, 1 H); 7.7 (t, 1 H); 7.5 (dd, 1 H); 7.3 (m, 3 H); 2.6 (q, 2 H); 1.2 (t, 3 H)
16c	Calc.: C, 58.36; H, 4.59; N, 12.76.	(DMSO-d_6): 11.5 (s, 1 H); 9.9 (s, 1 H); 8.9 (d, 1 H); 8.2 (m, 2 H);
$C_{16}H_{15}N_3O_5$	Found: C, 58.49; H, 4.57; N, 12.81.	8.0 (d, 1 H); 7.7 (dt, 1 H); 7.1 (m, 3 H); 4.2 (q, 2 H); 1.4 (t, 3 H)
17a	Calc.: C, 65.87; H, 5.13; N, 16.46.	(DMSO-d_6): 10.8 (s, 1 H); 10.4 (s, 1 H); 7.9 (m, 2 H); 7.4 (m, 2 H);
$C_{14}H_{13}N_3O_2$	Found: C, 65.94; H, 5.16; N, 16.41.	7.1 (m, 2 H); 7.0 (m, 2 H); 6.4 (dd, 1 H); 5.2 (s, 2 H)
17b	Calc.: C, 67.83; H, 6.05; N, 14.83.	(DMSO-d_6): 10.4 (s, 1 H); 10.3 (s, 1 H); 7.5 (dd, 1 H); 7.2 (m, 4 H);
$C_{16}H_{17}N_3O_2$	Found: C, 67.67; H, 6.08; N, 14.73.	7.0 (m, 2 H); 6.4 (d, 1 H); 5.1 (s, 2 H); 2.6 (q, 2 H); 1.2 (t, 3 H)
17c	Calc.: C, 64.20; H, 5.72; N, 14.04.	($CDCl_3$): 10.0 (s, 1 H); 9.3 (s, 1H); 8.4 (d, 1H); 7.1 (m, 2H); 7.0
$C_{16}H_{17}N_3O_3$	Found: C, 64.31; H, 5.77; N, 14.07.	(t, 1H); 6.9 (m, 2H); 6.5 (d, 1H); 4.2 (q, 2H); 3.8 (s, 2H); 1.5 (t, 3H).
18a	–	(DMSO-d_6): 10.8 ppm (s, 1 H); 10.6 (s, 1 H); 7.9 (d, 2 H); 7.4 (t, 2 H); 7.3 (s, 1 H); 7.1 (m, 3 H); 6.5 (d, 1 H); 4.8 (s, 2 H); 3.6 (t, 4 H); 3.4 (t, 4 H)
18b	–	(DMSO-d_6): 10.6 (s, 1 H); 10.3 (s, 1 H); 7.5 (dd, 1 H); 7.2 (m, 6 H); 6.5 (d, 1 H); 4.8 (s, 2 H); 3.6 (t, 4 H); 3.4 (t, 4 H); 2.6 (q, 2 H); 1.1 (t, 3 H)
18c	Calc.: C, 62.00; H, 6.50; N, 10.85.	(DMSO-d_6): 10.7 (s, 1 H); 9.9 (s, 1 H); 8.2 (d, 1 H); 7.1 (m, 6 H);
$C_{20}H_{25}N_3O_5$	Found: C, 61.75; H, 6.54; N, 10.74.	6.5 (d, 1 H); 4.8 (t, 2 H); 4.1 (q, 2 H); 3.6 (q, 4 H); 3.4 (t, 4 H); 1.4 (t, 3 H)
19a	Calc.: C, 61.82; H, 5.90; N, 9.83.	($CDCl_3$): 9.4 (s, 1 H); 9.3 (s, 1 H); 7.7 (d, 2 H); 7.4 (t, 2 H); 7.2
$C_{22}H_{25}N_3O_6$	Found: C, 62.09; H, 6.01; N, 9.57.	(m, 3 H); 6.9 (dd, 1 H); 6.6 (dd, 1 H); 4.3 (t, 4 H); 3.6 (t, 4 H); 2.1 (s, 6 H)
19b	Calc.: C, 63.28; H, 6.42; N, 9.22.	($CDCl_3$): 9.4 (s, 1 H); 9.3 (s, 1 H); 8.1 (d, 1 H); 7.3 (m, 5 H); 6.9
$C_{24}H_{29}N_3O_6$	Found: C, 63.05; H, 6.46; N, 9.16.	(dd, 1 H); 6.6 (dd, 1 H); 4.3 (t, 4 H); 3.6 (t, 4 H); 2.7 (q, 2 H); 2.1 (s, 6 H); 1.3 (t, 3 H).
19c	Calc.: C, 61.14; H, 6.20; N, 8.91.	($CDCl_3$): 10.0 (s, 1 H); 9.3 (s, 1 H); 8.4 (d, 1 H); 7.1 ppm (m, 6 H);
$C_{24}H_{29}N_3O_7$	Found: C, 61.22; H, 6.24; N, 8.86.	6.6 (dd, 1 H); 4.3 (t, 4 H); 4.2 (q, 2 H); 3.6 (t, 4 H); 2.1 (s, 6 H); 1.5 (t, 3 H)
21	Calc.: C, 44.45; H, 4.00; N, 7.40.	(DMSO-d_6): 9.5 (s, 1 H); 8.3 (d, 1 H); 7.6 (dd, 1 H); 7.2 (d, 2 H);
$C_{14}H_{13}N_2O_6S$ Na.H_2O	Found: C, 44.39; H, 4.02; N, 7.36.	7.0 (d, 2 H); 6.9 (d, 1 H); 4.1 (q, 2 H); 1.3 (t, 3 H)
22	Calc.: C, 47.13; H, 3.67; N, 7.85.	(DMSO-d_6): 9.4 (s, 1 H); 8.30 (d, 1 H); 7.6 (dd, 1 H); 7.2 (d, 2 H);
$C_{14}H_{13}N_2O_5SCl$	Found: C, 47.28; H, 3.70; N, 7.76.	6.7 (d, 2 H); 6.9 (d, 1 H); 4.0 (q, 2 H); 1.3 (t, 3 H).
23	Calc.: C, 45.29; H, 3.80; N, 13.20.	($CDCl_3$): 8.7 (d, 1 H); 8.4 (dd, 1 H); 7.2 (d, 1 H); 4.3 (q, 2 H);
$C_8H_8NO_5N_2$	Found: C, 45.32; H, 3.80; N, 13.19.	1.5 (t, 3 H).
24	Calc.: C, 52.74; H, 5.53; N, 15.38.	(DMSO-d_6): 7.5 (dd, 1 H); 7.4 (d, 1 H); 6.9 (d, 1 H); 5.4 (s, 2 H);
$C_8H_{10}N_2O_3$	Found: C, 52.81; H, 5.52; N, 15.40.	4.2 (q, 2 H); 1.4 (t, 3 H)
25a	Calc.: C, 58.36; H, 4.59; N, 12.76.	($CDCl_3$): 10.0 (s, 1 H); 9.34 (d, 1 H); 9.3 (s, 1 H); 8.1 (m, 1 H); 7.7
$C_{16}H_{15}N_3O_5$	Found: C, 58.38; H, 4.61; N, 12.76.	(d, 2 H); 7.4 (t, 2 H); 7.2 (m, 1 H); 7.0 (d, 1 H); 4.3 (q, 2 H); 1.6 (t, 3 H).
25b	Calc.: C, 60.50; H, 5.36; N, 11.76.	($CDCl_3$): 10.0 (s, 1 H); 9.4 (s, 1 H); 9.3 (d, 1 H); 8.1 (m, 2 H);
$C_{18}5H_{19}N_3O_5$	Found: C, 60.55; H, 5.40; N, 11.81.	7.3 (m, 3 H); 7.0 (d, 1 H); 4.3 (q, 2 H); 2.7 (q, 2 H); 1.6 (t, 3 H); 1.3 (t, 3 H).

continued

Table 4—*contd*

Compound	Elemental analysis	Proton NMR data (ppm)
25c	Calc.: C, 57.91; H, 5.13; N, 11.25.	($CDCl_3$): 10.0 (s, 1 H); 9.9 (s, 1 H); 9.4 (d, 1 H); 8.4 (dd, 1 H);
$C_{18}H_{19}N_3O_6$	Found: C, 57.74; H, 5.17; N, 11.21.	8.1 (dd, 1 H); 7.2 ppm (dt, 1 H); 7.0 (m, 3 H); 4.3 (q, 2 H); 4.2 (q, 2 H); 1.6 (t, 3 H); 1.5 (t, 3 H).
26a	Calc.: C, 64.20; H, 5.72; N, 14.04.	($CDCl_3$): 10.0 (s, 1 H); 9.5 (s, 1 H); 7.9 (d, 1 H); 7.7 (d, 2 H);
$V_{16}H_{17}N_3O_3$	Found: C, 64.13; H, 5.76; N, 13.97.	7.4 (t, 2 H); 7.2 (t, 1 H); 6.7 (d, 1 H); 6.4 (dd, 1 H); 4.1 (q, 2 H); 3.5 (s, 2 H); 1.5 (t, 3 H).
26b	Calc.: C, 66.04; H, 6.47; N, 12.83.	($CDCl_3$): 10.0 (s, 1 H); 9.5 (s, 1 H); 8.1 (d, 1 H); 7.9 (d, 1 H);
$C_{18}H_{21}NO_3N_3$	Found: C, 65.90; H, 6.51; N, 12.75.	7.2 (m, 3 H); 6.8 (d, 1 H); 6.4 (dd, 1 H); 4.1 (q, 2 H); 3.5 (s, 2 H); 2.7 (q, 2 H); 1.4 (t, 3 H); 1.3 (t, 3 H).
26c	Calc.: C, 62.96; H, 6.16; N, 12.24.	(DMSO-d_6): 10.0 (s, 1 H); 9.2 (s, 1 H); 8.3 (d, 1 H); 7.7 (d, 1 H);
$C_{18}H_{21}N_3O_4$	Found: C, 62.88; H, 6.20; N, 12.21.	7.2 (t, 1 H); 7.1 (d, 1 H); 7.0 (t, 1 H); 6.8 (d, 1 H); 6.4 (dd, 1 H); 4.7 (s, 2 H); 4.1 (q, 2 H); 4.0 (q, 2 H); 1.5 (t, 3 H); 1.4 (t, 3 H)
27	Calc.: C, 36.30; H, 3.43; N, 10.58.	($CDCl_3$): 8.3 (d, 1 H); 7.9 (dd, 1 H); 7.8 (d, 1 H); 2.8 (s, 6 H).
$C_8H9N2O4SCl$	Found: C, 36.39; H, 3.39; N, 10.48.	

Table 5
Lightfastness data for dyes **11–13** on PET

Dye	Lightfastness ratings[a] (no Ultrafast 830)				Lightfastness ratings[a] (Ultrafast 830 added)[a]			
	225.6 kJ		451.2 kJ		225.6 kJ		451.2 kJ	
	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%
11a	2–3	3	1	1–2	2–3	3	1	2
11b	2–3	2–3	1–2	2	4	4	2–3	3
11c	2	2	< 1	< 1	< 1	2	< 1	1
Red 167	2	2–3	< 1	< 1	2–3	3	< 1	1
12a	3	2	< 1	< 1	2–3	2	< 1	1
12b	2–3	1–2	1	< 1	2	2	1	1
12c	2	1–2	< 1	< 1	2	2	< 1	1
Yellow 86	2	1–2	< 1	< 1	2–3	2	< 1	< 1
13a	1–2	2	< 1	< 1	2	2	< 1	< 1
13b	2	1–2	< 1	< 1	2	2–3	< 1	1
13c	2–3	1–2	1	< 1	2	2–3	1	1

[a]Rating scale = low of 1 to high of 5.

H_2O (200 ml), and dried ($MgSO_4$). The solvent was removed and the crude dye was recrystallized from EtOH to give 1.7 g red solid.

2.6.2.2. **12a–c**. The method used is illustrated in the synthesis of dye **12a**.

A solution of **22** (1.8 g, 5 mmol) in pyridine (50 ml) was stirred as **17a** (1.4 g, 5.5 mmol) was added. The solution was heated to 70°C and held at this temperature for 1 h. After cooling to room temperature, the solution was added to conc. HCl (50 ml) containing ice (50 g). The precipitate that formed was collected by filtration and dissolved in DMSO (50 ml). Water was added very slowly to this solution until precipitation occurred. After 2 h, the solid was collected and recrystallized from Me_2CO to give 2.1 g orange needles.

2.6.2.3. ***Dyes*** **13**. The method used is illustrated in the synthesis of **13a**.

Compound **26a** (1.6 g, 5.3 mmol) and **27** (1.4 g, 5.3 mmol) were added to 2,6-lutidine (12 ml), and the mixture was stirred under reflux for 3 h. The solution was cooled to room temperature and added to aq. HCl (200 ml, 5%). The precipitate was collected by filtration and purified by flash column chromatography, using PhMe:EtOAc (4:1) as the eluent, to give 2.2 g orange dye.

Table 6
PM3 energy values for optimized dyes **11a–c**

Structure	PM3 energy (kcal mol^{-1})	Gradient (kcal Å^{-1})
11a	−139.18	0.900
11b(i)	−148.12	0.907
11b(ii)	−150.42	0.917
11c(i)	−174.15	0.585
11c(ii)	−178.68	0.904

Table 7
Sublimation fastness data for dyes **11–13** on PET

Dye	Sublimation fastness (30 s/60 s)[a]							
	Polyester[b]		Cotton[b]		Acetate[b]		ΔE[c]	
	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%
11a	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
11b	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
11c	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
Red 167	5/5	5/4	5/5	5/4	5/5	5/4	5/5	5/5
12a	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
12b	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
12c	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
Yellow 86	4/4	4/4	5/5	5/5	4/4	4/4	5/5	5/5
13a	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
13b	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5
13c	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5

[a]Rating scale = low of 1 to high of 5.
[b]Color transfer ratings.
[c]Color change ratings.

3. Results and discussion

Our target analogs of CI Disperse Red 167 required the synthesis of type **19** compounds. These novel couplers were prepared in 5 steps from anilines **14** (Scheme 1). The anilines were condensed with ethyl oxalyl chloride to form ethyl oxanilates **15**. In turn, these intermediates were condensed with *meta*-nitroaniline in the presence of boric acid to give nitrooxalanilides **16**. Catalytic hydrogenation over Pd afforded aminooxalanilides **17**. We found DMF to be the solvent of choice for the reduction step. The final two steps were alkylation with ethylene oxide and acetylation, to give couplers **19**. Reacting **19** with the diazonium salt derived from 2-chloro-4-nitroaniline gave dyes **11**.

The first of two groups of Disperse Yellow 86 analogs was synthesized according to the steps outlined in Scheme 2. In step one, *para*-phenetidine was condensed with **20** to give nitrodiphenylamine **21**. Treatment of the product with $POCl_3$ followed by reaction of sulfonyl chloride **22** with aminooxalanilides **17** gave type **12** dyes. Disperse Yellow 86 analogs **13** were synthesized using the five-step sequence shown in Scheme 3. Intermediate **27** was made from a reaction between dimethylamine and commercially available 4-chloro-3-nitrobenzenesulfonyl chloride.

Tables 1 and 2 contain reaction yields, melting points, R_f values, and absorption and mass spectral data that were generated on dyes and intermediates prepared in this study. Tables 3 and 4 contain data from elemental analysis and NMR spectroscopy. It is clear that the data support the structures of all compounds.

3.1. Absorption spectra

Absorption spectral data recorded on dyes prepared in this study are summarized in Table 1. Data shown for Disperse Red 167 were obtained from the literature [9].

We found that the incorporation of an oxalanilide moiety into the structure of Disperse Red 167 resulted in dyes having practically the same λ_{max} as the parent dye. Extinction coefficients (ε_{max}) of the new dyes were lower than the parent dye (35 000 vs 45,000), as would be expected from the significant increase in molecular weight.

The location of the stabilizer had little affect on the absorption properties of Disperse Yellow 86. Specifically, a modest hypsochromic shift in λ_{max} occurred when an oxalanilide group was incorporated into the diphenylamine group of Disperse Yellow 86, but no change resulted when the stabilizer was incorporated using the sulfonamide linkage. Similarly, small changes in ε_{max} were observed.

3.2. Lightfastness

3.2.1. Disperse Red 167 analogs

For type **11** dyes, we found that the incorporation of an oxalanilide moiety into the structure of Disperse Red 167 had a beneficial affect on light-

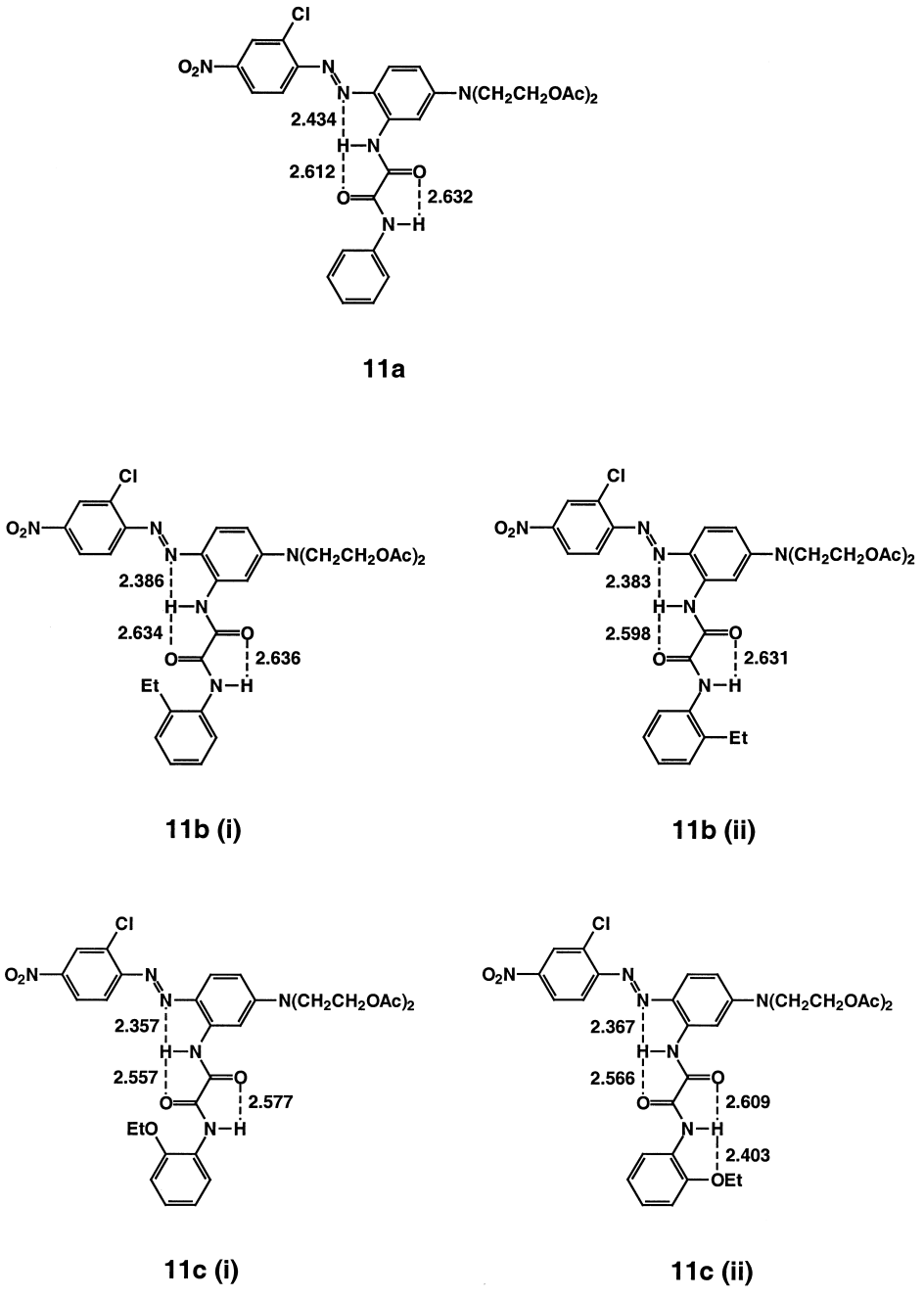


Fig. 1. Structures of dye analogs **11–13** (R = H, Et, OEt).

fastness, when R = H, Et, and that the improvement was more apparent following the 451.2 kJ exposure. In the absence of physically added photostabilizer, Disperse Red 167 itself exhibited poor lightfastness (< 1) at the 451.2 kJ exposure level, whereas two of the analogs containing an oxalanilide stabilizer (cf. **11a** and **11b**) were rated 1–2 after that exposure. Since automotive dyes are

normally applied with a commercial photostabilizer, we evaluated our analogs under such conditions. In this case, dye **11b** far outperformed the parent dye.

When R = OEt, no improvement in the lightfastness of the parent dye was observed. In this case, we believe that the OEt group undergoes intramolecular H-bonding with the hydrogen atom of the adjacent *ortho*-oxamide group, hindering the tautomerization that is responsible for the photostability of oxalanilides. This explanation is consistent with our conformational analysis results from molecular modeling studies. When conformational analysis was conducted on dyes **11b–c** (Fig. 1), PM3 predicted structure **11b(ii)** to be more stable than conformer **11b(i)**. The energy difference between these conformers was 2.30 kcal mol^{-1} (Table 6). In the case of **11c(ii)**, hydrogen bonding between the ethoxy oxygen and the adjacent oxalanilide hydrogen is possible, whereas it is not possible in conformer **11c(i)**. Conformational analysis of **11c** showed that rotamer **11c(i)** contained three hydrogen bonds, whereas rotamer **11c(ii)** contained a fourth hydrogen bond. The energy values for these structures are given in Table 6. Clearly, it is energetically favorable for **11c** to contain the additional hydrogen bond.

3.2.2. *Disperse Yellow 86 analogs*

We found that a built-in oxalanilide moiety did not give a significant improvement in the lightfastness of Disperse Yellow 86. These results parallel what we observed when a benzotriazole stabilizer was incorporated into the backbone of Disperse Yellow 86 and Disperse Yellow 42. This suggests that light in the 300—340 nm range is not responsible for the fading of Disperse Yellow 86. It is possible that the improvement in lightfastness of Disperse Yellow 86 noted previously using a built-in hydroxybenzophenone stabilizer could be attributed to the ability of such systems to quench excited states of molecules. It is not clear that oxalanilides can function as an excited state quencher.

3.2.3. *Sublimation fastness*

It is clear that the incorporation of an oxalanilide moiety into disperse dye structures enhances the sublimation fastness of both dyes. For Disperse Red 167, a reduction in color transfer was observed on PET, cotton, and acetate. A reduction in color transfer was observed on PET and acetate for Disperse Yellow 86. These results are not surprising, since the molecular weight of the parent dyes has been increased significantly.

Since there was no detectable color transfer to the nylon, wool, and acrylic bands on the multifiber fabric, Table 7 does not include data associated with those fibers.

4. Conclusion

The results of this study further demonstrate that the fading behavior of a disperse dye–PET system can vary with the type of disperse dye present. This was illustrated in the differences in the contribution of a built-in oxalanilide to the photostability of Disperse Red 167 and Disperse Yellow 86. Whereas the former dye benefited from incorporating an oxalanilide moiety, the latter did not. This contrasts previous results, which showed the reverse to be the case when a benzophenone moiety was employed.

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