Synthesis and spectroscopic properties of novel phthalimide-derived monoazo disperse dyes containing ester groups

Coloration Technology

Society of Dyers and Colourists

Jae-hong Choi,[a,*] Oh-tak Kwon,[b] Hyun-young Lee,[b] Andrew D Towns[c] and Chun Yoon[d]

[a]Department of Textile System Engineering, Kyungpook National University, 1370 Sankyuk-dong Buk-gu, Daegu (702-701), South Korea
Email: jaehong@knu.ac.kr

[b]Department of Functional Materials Engineering, Kyungpook National University, 1370 Sankyuk-dong Buk-gu, Daegu (702-701), South Korea

[c]Vivimed Labs Europe Ltd, PO Box B3, Leeds Road, Huddersfield HD1 6BU, UK

[d]Department of Applied Chemistry, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul, South Korea

The synthesis and spectroscopic properties of monoazo dye series, whose members consist of N-alkylphthalimide diazo components combined with a coupling component containing two ester groups, are reported. Such colourants are potentially alkali-clearable as a consequence not only of the presence of diester functionality on the coupler, but also through use of the base-sensitive phthalimide system. Shortening the N-alkyl group by removing one or two methylene units from a butyl chain made little difference to absorption properties, as would be expected given the relatively minor differences in inductive character produced. Shifts in the absorption maximum of the dyes associated with dibromination of the phthalimidylazo motif and its subsequent cyanodehalogenation were in agreement with theory and literature data for related series. Diester substitution on the coupling component brought about hypsochromism and hypochromism.

Introduction

Alkali-clearable disperse dyes offer both improved performance and environmental benefits [1,2]. The first is brought about through incorporation of base-sensitive functions. These enable the destruction or solubilisation of dye that has washed off during laundering with modern detergent systems, thereby improving fastness by reducing staining. The environmental benefit arises as a consequence of these functions enhancing the clearing of surface dye under alkaline conditions following fibre coloration to the extent that the use of reducing agent may be unnecessary, thus lessening effluent loadings. One successful approach that has been utilised in commercial monoazo disperse dyes for several decades is the inclusion of two ester substituents on an aniline-based coupling component [3,4] leading to solubilisation of dye upon hydrolysis by aqueous alkali; example dyes are CI Disperse Brown 19 and CI Disperse Red 278 [5]. Another fruitful strategy has been to base chromophores on heterocyclic diazo components, for example, nitro-thiophenes [1], which are destroyed under such conditions. Other functional groups, such as fluorosulphonyl [6–13], and heterocyclic systems, for example, phthalimides [14,15] and naphthalimides [16,17], are known, which cleave to give more soluble products. Phthalimidylazo disperse dyes first appeared as the subject of patents over 30 years ago [18,19] and have also formed the basis for claims over the last few years [20–22] concerning good fastness and dyeability on polyester. While industry has exploited their chemistry

commercially [23], little has appeared in the academic literature concerning their colour and application properties and that which has been published features examples with relatively simple structures [24–27].

Recently, we have reported the synthesis and spectroscopic properties of several series of novel highly substituted phthalimidyl azo dyes [28,29], along with their dyeing performance on polyester fibres [30]. We have also explored combining the approach of diester-substituted couplers with the use of base-sensitive heterocyclic diazo components [31,32]. This paper builds on the aforementioned studies, reporting on the synthesis of dyes that incorporate two kinds of hydrolysable systems: twelve derivatives have been prepared that not only contain two ester groups on their coupling components, but also feature one of four N-alkylphthalimide ring systems in their diazo components, in the hope that such bifunctionality will further enhance clearability and fastness (Scheme 1). The synthesis and characterisation of the dyes are detailed together with a discussion of their spectroscopic properties.

Experimental

Materials

Hydrogen peroxide, hydrobromic acid, sodium nitrite and potassium carbonate were supplied by Sigma-Aldrich Chemical Co. (USA). Anhydrous tin(II) chloride and 1-bromoethane were sourced from Junsei Chemicals (Japan), while copper(I) cyanide, zinc cyanide and sodium bicarbonate were provided by DO Chemical (Korea).
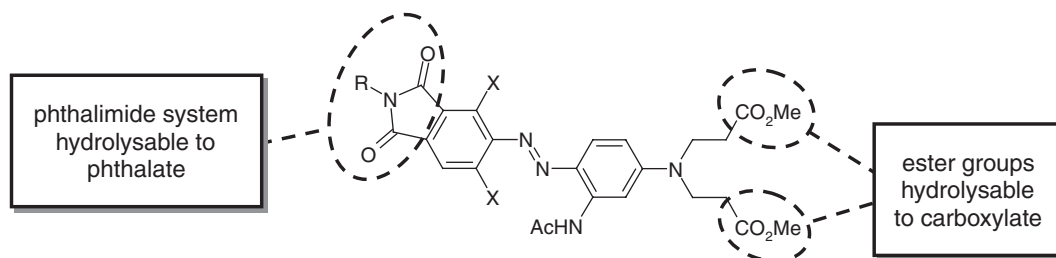
Scheme 1

N,N-Dimethylformamide (DMF), hydrochloric acid, ethanol, methanol, concentrated sulphuric acid, ethyl acetate and anhydrous magnesium sulphate were purchased from Duksan Pure Chemical (Korea). 3-Aminoacetanilide and 3-bromopropionic acid methyl ester were obtained from TCI Chemicals (Japan).

Analysis and spectroscopy

The proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained using an Avance Digital 400 spectrometer (Bruker, USA) at 400 MHz and in CDCl$_3$ solution unless stated otherwise. Elemental analyses were carried out on a Carlo Elba Model 1106 analyser (Italy) for C, H and N. Mass spectra were obtained with a QP-1000 spectrometer (Shimadzu, Japan) by electron ionisation. The absorption spectra were measured in 1-cm quartz cells on an Evolution 300 ultraviolet (UV)–visible spectrophotometer (Thermo, UK).

## Preparation of intermediates and dyes

The general pathways used in the synthesis of the diazo components and the corresponding dyes are shown in Scheme 2. Details of the preparation of these diazo components as well as the coupler employed are supplied below, together with the general procedure for dibromination of each diazo component. In addition, diazotisation and coupling conditions are given, followed by details of the cyanodehalogenation reactions for the dibromo dye derivatives.

Synthesis of phthalimide intermediates

The *N*-*n*-propyl-, *N*-iso-propyl- and *N*-*n*-butyl-derivatives of 4-aminophthalimide **3** (R = *n*-Pr, i-Pr, *n*-Bu) were prepared by previously reported procedures [28,29]. The *N*-ethyl analogue was synthesised as follows from 4-nitrophthalimide (**1**), which was obtained by nitration of phthalimide using the procedure detailed previously by Choi *et al.* [28].

N-*Ethyl-4-nitrophthalimide* **2** *(R = Et)*

4-Nitrophthalimide **1** (10.0 g, 0.052 mol) was dissolved in DMF (75 ml), then potassium carbonate (99%, 7.62 g, 0.055 mol) was added to the mixture, followed by stirring at room temperature for 6 h. 1-Bromoethane (98%, 5.78 g, 0.053 mol) was added slowly (over 30 min) and the mixture was then stirred for 8 h at 60 °C before pouring onto ice (300 g). The resultant precipitate was isolated by filtration, washed with water and dried (60–70 °C). Crude **2** (R = Et) was purified by recrystallisation from methanol, giving material in 76% yield for use in the next stage without further purification. Mass spectrometry
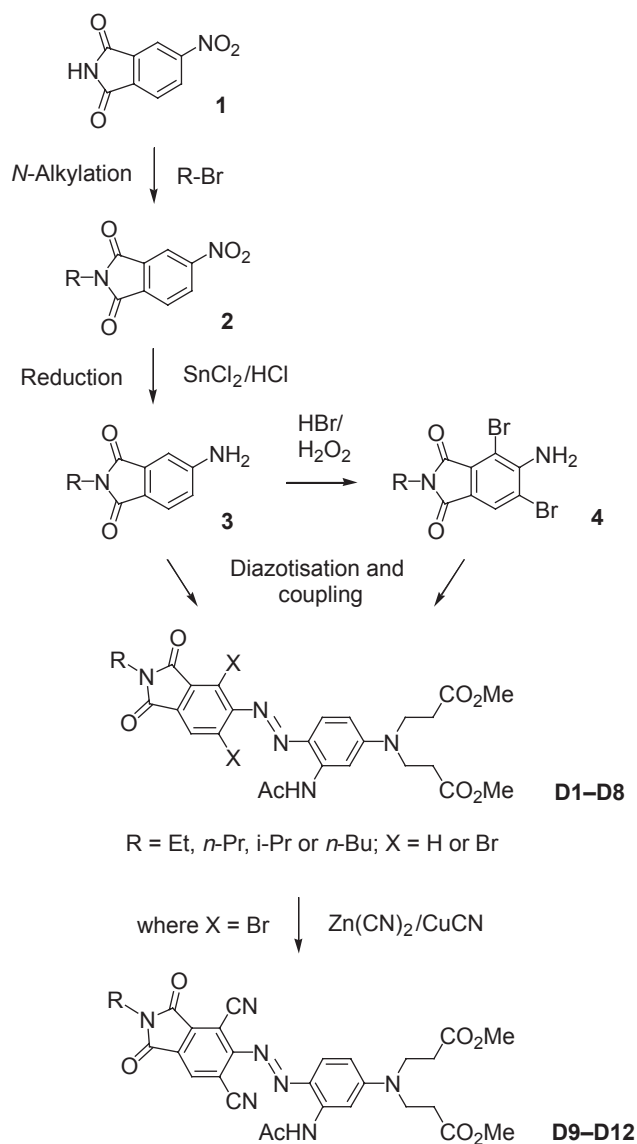
Scheme 2

(MS) (*m/z*): 220. ^{1}H-NMR (ppm): 1.3 (t, 3H, CH$_3$), 3.4 (m, 2H, CH$_2$), 8.2 (d, 1H, ArH), 8.6 (s, 1H, ArH), 8.7 (d, 1H, ArH).

N-*Ethyl-4-aminophthalimide* **3** *(R = Et)*

N-Ethyl-4-nitrophthalimide (22.0 g, 0.10 mol) was stirred into a solution of tin(II) chloride (98%, 83.4 g, 0.44 mol) in hydrochloric acid (37%, 450 ml) and water (150 ml). After 90 min, the precipitate was filtered and washed with hot water until free from residual acid, the hydrochloride thus being completely hydrolysed to give

the free base. The product was purified by recrystallisation from ethanol furnishing microanalytically pure material in 54% yield. MS (m/z): 190. ^{1}H-NMR (ppm): 1.2 (t, 3H, CH$_3$), 3.7 (d, 2H, N–CH$_2$), 5.4 (m, 2H, NH$_2$), 6.8 (s, 1H, ArH), 7.3 (d, 1H, ArH), 8.0 (d, 1H, ArH). Calculated: C 63.15%, H 5.30%, N, 14.73%; found: C 62.98%, H 5.21%, N 14.76%.

N-*Ethyl-4-amino-3,5-dibromophthalimide* **4** *(R = Et)*

Hydrogen peroxide (35%, 29.2 g, 0.3 mol) was added over 30 min to hydrobromic acid (48%, 101.1 g, 0.6 mol) below 5 °C. To this mixture was slowly added *N*-ethyl-4-aminophthalimide (19.0 g, 0.1 mol) at 15–20 °C. The reaction mass was stirred for 3 h at 15–20 °C and then poured onto ice (300 g). The resultant precipitate was isolated by filtration, washed with excess water and dried at 70–75 °C. The crude product was purified by recrystallisation from ethanol (87% yield). MS (m/z): 347. ^{1}H-NMR (ppm): 1.3 (t, 3H, CH$_3$), 3.7 (m, 2H, N–CH$_2$), 6.3 (s, 2H, NH$_2$), 8.1 (s, 1H, ArH).

Synthesis of diester coupling component

m-*[Bis(β-carbomethoxyethyl)amino]acetanilide* **5**

A solution of 3-aminoacetanilide (97%, 23.2 g, 0.15 mol) in water (100 ml) and sodium bicarbonate (99%, 31.1 g, 0.37 mol) was stirred up to 35 °C. 3-Bromopropionic acid methyl ester (99%, 68.7 g, 0.40 mol) was then added slowly, the temperature of the mixture raised to 60 °C and held at 60–65 °C for 8 h. The reaction mass was drowned to water (200 g) and ethyl acetate (300 g). The organic phase was separated off and dried over magnesium sulphate (anhydrous, 15 g). Removal of the drying agent and then the solvent under vacuo afforded a crude product of 80% yield. Microanalytical purity was attained by passage down a silica column (Silica gel 60, 70∼230 mesh) using *n*-hexane–ethyl acetate (3:1 by v/v) as eluent. MS (m/z): 322. ^{1}H-NMR (ppm): 2.1 (s, 3H, CH$_3$), 2.6 (t, 4H, 2×CH$_2$), 3.7 (s, 6H, 2×CH$_3$), 3.7 (t, 4H, 2×CH$_2$), 6.4 (d, 1H, ArH), 6.9 (d, 1H, ArH), 7.1 (s, 1H, ArH), 8.4 (t, 1H, ArH), 9.8 (s, 1H, NH). Calculated: C, 59.61; H, 6.88; N, 8.69; found: C 59.67, H 6.82, N 8.93.

Synthesis of dyes

The molecular structures of the prepared dyes **D1–D12** are given in Table 1. The general synthetic procedures employed in their synthesis follow below.

General procedure for dyes **D1–D4**

N-Alkyl-4-aminophthalimide **3** (0.04 mol) was added to a solution of concentrated hydrochloric acid (35%, 40 ml) in water (250 ml). The mixture was stirred for 2 h at room temperature. The mixture was cooled to 5 °C, sodium nitrite (97%, 0.042 mol) added to it portionwise over 20 min at 5–10 °C and then stirred for 2 h at the same temperature. The resulting solution was used immediately in the following coupling reaction. The coupling component **5** (0.036 mol) was dissolved in water (400 ml) and hydrochloric acid (35%, 40 ml) and then cooled to 0–5 °C by the addition of ice. The diazonium solution previously prepared was added dropwise over 30 min at the same temperature. The mixture was stirred for a further 5 h at 5–10 °C and then aqueous sodium

Table 1 Molecular structures of the synthesised dyes
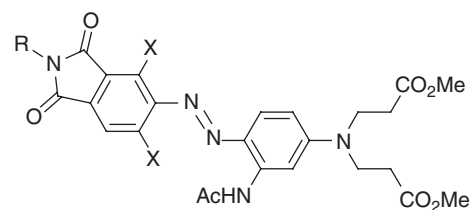
Dye	R	X
D1	CH$_2$CH$_3$	H
D2	CH$_2$CH$_2$CH$_3$	H
D3	CH(CH$_3$)$_2$	H
D4	CH$_2$CH$_2$CH$_2$CH$_3$	H
D5	CH$_2$CH$_3$	Br
D6	CH$_2$CH$_2$CH$_3$	Br
D7	CH(CH$_3$)$_2$	Br
D8	CH$_2$CH$_2$CH$_2$CH$_3$	Br
D9	CH$_2$CH$_3$	CN
D10	CH$_2$CH$_2$CH$_3$	CN
D11	CH(CH$_3$)$_2$	CN
D12	CH$_2$CH$_2$CH$_2$CH$_3$	CN

hydroxide solution (10%) was added slowly below 10 °C until the pH rose to within the range of 3–4. The precipitated product was filtered off, washed with water until the filtrate was pH 6–7 and dried at 70–75 °C. The crude dyes were purified by recrystallisation from ethanol. Yields and characterisation data are shown in Tables 2 and 3, respectively.

General procedure for dyes **D5–D8**

Sodium nitrite (97%, 0.042 mol) was added portionwise over 20 min to concentrated sulphuric acid (98%, 100 ml) at 5–10 °C and then stirred for 1 h at 60–70 °C. The mixture was cooled to below 5 °C and then the appropriate *N*-alkyl-3,5-dibromo-4-aminophthalimide **4** (0.04 mol) was added over 30 min at 5–10 °C. The resultant mixture was stirred for 1 h within the same temperature range to give a diazonium solution, which was then coupled immediately to **5** in the same manner as for dyes **D1–D4**. Isolation and purification were also carried out in the same way (see Table 2 for yields and Table 3 for characterisation data).

General procedure for cyanodehalogenation (**D9–D12**)

A mixture of dibromo-substituted dye **D5–D8** (0.02 mol), zinc cyanide (98%, 0.022 mol) and copper(I)

Table 2 Diazotisation and coupling reaction yield for the synthesised dyes **D1–D8**

Dye	Diazotisation method	Yield (%)
D1	NaNO$_2$/HCl	89
D2	NaNO$_2$/HCl	85
D3	NaNO$_2$/HCl	80
D4	NaNO$_2$/HCl	90
D5	Nitrosylsulphuric acid	79
D6	Nitrosylsulphuric acid	82
D7	Nitrosylsulphuric acid	88
D8	Nitrosylsulphuric acid	91

Table 3 Analytical data of the synthesised dyes **D1–D12**

Dye	MS[a]	^{1}H-NMR (δ, ppm, in CDCl$_3$)	Elemental analysis	mp (°C)	TLC[b]
D1	523 (0.52)	1.2 (t, 3*H*, CH$_3$), 2.0 (s, 3*H*, CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.6 (q, 2*H*, N–CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.0 (d, 1*H*, ArH), 8.4 (s, 1*H*, ArH), 8.5 (s, 1*H*, ArH), 10.0 (s, 1*H*, NHCO)	Calculated: C 59.65, H 5.58, N 13.38 Found: C 59.33, H 5.10, N 13.57	144–145	0.38 (1:2)
D2	537 (0.21)	0.9 (t, 3*H*, CH$_3$), 1.7 (m, 2*H*, CH$_2$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 4.6 (t, 2*H*, N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.0 (d, 1*H*, ArH), 8.4 (d, 1*H*, ArH), 8.5 (s, 1*H*, ArH), 10.1 (s, 1*H*, NH)	Calculated: C 60.33, H 5.81, N 13.03 Found: C 60.22, H 5.84, N 13.11	148–150	0.36 (2:1)
D3	537 (0.62)	1.4 (d, 6*H*, 2×CH$_3$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 4.4 (m, 1*H*, N–CH), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.0 (d, 1*H*, ArH), 8.4 (d, 1*H*, ArH), 8.5 (s, 1*H*, ArH), 10.1 (s, 1*H*, NH)	Calculated: C 60.33, H 5.81, N 13.03 Found: C 60.40, H 5.87, N 12.76	172–174	0.41 (2:1)
D4	551 (0.74)	1.0 (t, 3*H*, CH$_3$), 1.3 (q, 2*H*, CH$_2$), 1.6 (q, 2*H*, CH$_2$), 2.0 (s, 1*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.6 (t, 2*H*, N–CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.0 (d, 1*H*, ArH), 8.4 (d, 1*H*, ArH), 8.5 (s, 1*H*, ArH), 10.2 (s, 1*H*, NH)	Calculated: C 60.97, H 6.03, N 12.70 Found: C 61.47, H 6.43, N 13.06	135–137	0.35 (3:2)
D5	679 (0.30)	1.2 (t, 3*H*, CH$_3$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.6 (q, 2*H*, N–CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.6 (s, 1*H*, ArH), 10.2 (s, 1*H*, NH)	Calculated: C 45.83, H 3.99, N 10.28 Found: C 46.01, H 4.12, N 10.78	139–140	0.42 (1:1)
D6	693 (0.15)	0.9 (t, 3*H*, CH$_3$), 1.7 (m, 2*H*, CH$_2$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 4.6 (t, 2*H*, N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.5 (s, 1*H*, ArH), 10.1 (s, 1*H*, NH)	Calculated: C 46.64, H 4.20, N 10.07 Found: C 46.73, H 4.52, N 9.90	146–148	0.54 (1:1)
D7	693 (0.29)	1.4 (d, 6*H*, 2×CH$_3$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 4.4 (m, 1*H*, N–CH), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.5 (s, 1*H*, ArH), 10.1 (s, 1*H*, NH)	Calculated: C 46.64, H 4.20, N 10.07 Found: C 46.62, H 4.14, N 10.20	167–169	0.58 (1:1)
D8	707 (0.19)	1.0 (t, 3*H*, CH$_3$), 1.3 (m, 2*H*, CH$_2$), 1.6 (m, 2*H*, CH$_2$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.6 (t, 2*H*, N–CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 8.5 (s, 1*H*, ArH), 10.2 (s, 1*H*, NH)	Calculated: C 47.41, H 4.40, N 9.87 Found: C 47.97, H 4.74, N 9.78	174–176	0.50 (3:2)
D9	573 (0.93)	1.2 (t, 3*H*, CH$_3$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.6 (q, 2*H*, N–CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s 1*H*, ArH), 7.8 (d, 1*H*, ArH), 9.1 (s, 1*H*, ArH), 10.3 (s, 1*H*, NH)	Calculated: C 58.63, H 4.74, N 17.09 Found: C 59.21, H 4.51, N 16.91	166–168	0.36 (1:1)
D10	587 (0.27)	0.9 (t, 3*H*, CH$_3$), 1.7 (m, 2*H*, CH$_2$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 4.6 (t, 2*H*, N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 9.2 (s, 1*H*, ArH), 10.1 (s, 1*H*, NH)	Calculated: C 59.28, H 4.97, N 16.69 Found: C 59.14, H 4.89, N 16.51	178–180	0.33 (2:1)
D11	587 (0.60)	1.4 (d, 6*H*, 2×CH$_3$), 2.0 (s, 3*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 4.4 (m, 1*H*, N–CH), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 9.1 (s, 1*H*, ArH), 10.1 (s, 1*H*, NH)	Calculated: C 59.28, H 4.97, N 16.69 Found: C 58.89, H 4.81, N 16.21	199–200	0.41 (2:1)
D12	601 (0.72)	1.0 (t, 3*H*, CH$_3$), 1.3 (m, 2*H*, CH$_2$), 1.6 (m, 2*H*, CH$_2$), 2.0 (s, 1*H*, NHCO–CH$_3$), 2.6 (t, 4*H*, 2×CH$_2$), 3.6 (t, 2*H*, N–CH$_2$), 3.7 (s, 6*H*, 2×CO$_2$–CH$_3$), 3.8 (t, 4*H*, 2×N–CH$_2$), 6.7 (d, 1*H*, ArH), 7.3 (s, 1*H*, ArH), 7.8 (d, 1*H*, ArH), 9.1 (s, 1*H*, ArH), 10.2 (s, 1*H*, NH)	Calculated: C 59.89, H 5.19, N 16.30 Found: C 59.44, H 5.07, N 16.18	187–189	0.36 (2:1)

a m/z ratio (relative intensity)
b R_f value (eluent v/v ratio of *n*-hexane:ethyl acetate)

cyanide (99%, 0.01 mol) in DMF (50 ml) was stirred for 3 h at 90 °C. After cooling the reaction mixture to room temperature, methanol (100 ml) was added to precipitate the product, which was then filtered off, washed copiously with water in an attempt to remove residual inorganic matter as well as DMF and dried at 70–75 °C. Crude yields were 89%, 88%, 89% and 85%, respectively, for dyes **D9**, **D10**, **D11** and **D12**. In each case, purification was effected by recrystallisation from ethanol to give analytically pure material in 60–80% recovery (see Table 3 for characterisation data).

Results and Discussion

Synthesis of dye intermediates and dyes

4-Nitrophthalimide **1** was employed in producing four *N*-alkyl-4-nitrophthalimides **2** (R = Et, *n*-Pr, i-Pr, *n*-Bu) through reaction with the appropriate alkyl bromide (Scheme 2). These compounds were then reduced with tin chloride and hydrochloric acid to give the corresponding aminophthalimides **3** (R = Et, *n*-Pr, i-Pr, *n*-Bu). Each of the amino derivatives **3** was dibrominated in hydrobromic acid/hydrogen peroxide, as reported previously [28,29], giving compounds **4** in high yield.

It was found that the preparation of the diester coupling component employed in this study, **5**, was best accomplished using an S_N2 reaction between 3-aminoacetanilide and 3-bromopropionic acid methyl ester in the presence of aqueous sodium bicarbonate. A good yield (*ca.* 80%) was obtained, whereas attempted Michael addition of methyl acrylate to 3-aminoacetanilide gave almost no reaction.

Both the non-brominated and dibrominated derivatives **3** and **4**, respectively, were diazotised and coupled to the diester coupler **5**. The diazo components **3** were sufficiently basic to enable straightforward diazotisation by means of aqueous sodium nitrite in dilute hydrochloric acid, whereas the dibromo derivatives **4** had to be diazotised under more forceful conditions (nitrosylsulphuric acid). In both cases, controlled addition of the diazo mixtures to coupler solutions at 0–5 °C furnished azo dyes in yields of above 80% in all but one case (Table 2).

Each of the four dibromo azo dyes **D5–D8** was converted to corresponding dicyano derivatives using conventional cyanodebromination conditions [28,29] through warming with a cyanide salt in a polar aprotic solvent (DMF) and in the presence of a copper salt catalyst (Scheme 2). The dicyano-substituted dye was precipitated by addition of methanol, rather than water, to the reaction mixture to avoid co-precipitation of water-insoluble copper compounds and other impurities. As was the case with similar reactions involving analogous phthalimidylazo derivatives [28,29], crude yields were high, being in the range of 85–89%.

Spectroscopic properties

The absorption maxima and the molar absorption coefficients of synthesised dyes **D1–D12** in DMF solution are listed in Table 4. As expected, swapping between the four different *N*-alkyl groups has little influence on the absorption maximum position as they each exert similar weakly inductive electron-donating effects. Related observations have been made when examining analogous series with other *N*-alkyl functions; for example, *n*-Pr, 3-cyanopropyl and benzyl [28] as well as *n*-Bu, *sec*-Bu and i-Pr [29].

Significant hypsochromic shifts (38–50 nm) can be seen when comparing **D5–D8** with the corresponding analogues **D1–D4**. These are brought about by the presence of the two bulky bromo groups *ortho* to the azo link forcing a steric clash. The hindrance between the azo link with one of the bromo groups leads to the ring of the diazo component being twisted out of plane from the rest

Table 4 Absorption maxima and molar extinction coefficients of the synthesised dyes in DMF solution

Dye	λ_{max} (nm)	λ_{max} shift (nm)[a]	ε_{max} (dm^3 mol^{-1} cm^{-1})
D1	494		23 200
D2	496	−16	22 000
D3	494	−12	29 700
D4	497	−13	25 900
D5	444		29 300
D6	454	−15	23 200
D7	455	−10	22 400
D8	459	−9	24 600
D9	569		32 900
D10	573	−35	34 000
D11	573	−33	32 900
D12	577	−31	37 600

[a] Shifts are given relative to those of diethyl analogues (**6**; R = *n*-Pr, i-Pr, *n*-Bu) previously reported [12,13]

of the molecule's π-skeleton, causing a blue shift in the absorption maximum which swamps any bathochromism that arises as a result of inductive electron withdrawal by the bromo groups [33]. The shifts are consistent with those reported in the literature. For example, the *N,N*-diethyl analogue of **D2** (**6**; X = H, R = *n*-Pr) undergoes a hypsochromic shift of 43 nm in DMF when substituted with two bromo groups to give the *N,N*-diethyl analogue of **D6** (**6**; X = Br, R = *n*-Pr) [28].

Conversely, di-*ortho* substitution with cyano functions in the case of structures **D9–D12** produces substantial bathochromic shifts (75–80 nm) relative to the unsubstituted derivatives **D1–D4**. Steric hindrance is relatively insignificant, despite the di-*ortho* substitution pattern, as a consequence of the rod-like shape of the cyano functions, so red-shifting electron withdrawal (through resonance and induction) by these groups dominates. The differences in λ_{max} between the dibromo and dicyano derivatives are therefore pronounced: shifts of 118–125 nm are seen between corresponding pairs. The sizes of shift brought about by dicyano substitution are consistent with previously reported data: for instance, the *N,N*-diethyl derivatives (**6**; X = H, R = *n*-Pr) and (**6**; X = CN, R = *n*-Pr), analogues of **D2** and **D10**, respectively, have absorption peaks 96 nm apart in DMF solution [28].

With respect to absorption maxima, the effect of placing ester functions on the *N*-alkyl chains of the coupling component is in line with expectation. Moderate inductive electron withdrawal by the ester groups is transmitted to the terminal nitrogen atom, resulting in

6

X = H, Br or CN; R = *n*-Pr, i-Pr, *n*-Bu
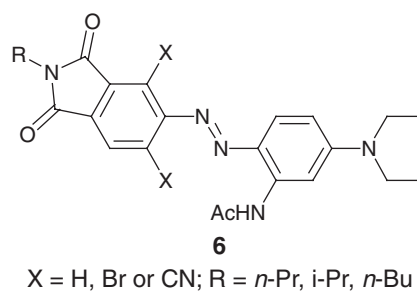
small hypsochromic shifts (9–16 nm) in the case of the parent and dibromo structures (Table 4). For example, **D4** is blue-shifted 13 nm relative to its *N,N*-diethyl analogue (**6**; X = H, R = *n*-Bu) [29]. The effect is more pronounced when the diazo component is a better electron sink: the dicyano derivatives **D10–D12** were hypsochromically shifted by 31–35 nm in comparison with their *N,N*-diethyl parent dyes; for example, **D11** was blue-shifted by 33 nm compared with **6** (X = CN, R = i-Pr).

The diester substituted dyes consistently exhibited lower extinction coefficients than their *N,N*-diethyl analogues; for example, values of 22 000 and 34 000 for dyes **D2** and **D10**, respectively, as against figures of 49 400 and 42 100 for the corresponding dyes **6**; X = H, R = *n*-Pr and **6**; X = CN, R = *n*-Pr [28].

Conclusions

Monoazo disperse dyes that contain two kinds of hydrolysable function have been synthesised through coupling *N*-alkylphthalimide diazo components to an aniline-derived diester compound. Bathochromic derivatives were also prepared by undertaking cyanodehalogenation on dibrominated dye derivatives. Intermediates and dyes were characterised by mass and proton NMR spectroscopy as well as elemental analysis. The absorption maxima of the dye series ranged from 444 to 577 nm, leading to a gamut of orange to blue colours. Variations in the *N*-alkyl function made little difference to absorption, as might be expected in view of the similarities in inductive electron-donating strength. Introduction of two bromo and cyano groups on the diazo component *ortho* to the azo bridge led to significant hypsochromism and bathochromism, respectively, in accordance with theory and findings from analogous series. The imposition of diester substitution on the *N*-alkyl chains of the coupling component led to modest hypsochromic shifts (9–16 nm) compared with the *N,N*-diethyl parent derivatives, aside from the case of the dicyano dyes where the shift was more marked (31–35 nm). While molar extinction coefficients of the dyes are typical of conventional carbocylic monoazo disperse dyes, the diester functionality resulted in hypochromism, with *N,N*-diethyl analogues showing greater extinction coefficients. However, larger values do not necessarily translate to higher tinctorial strength [34]. The coloration properties and fastness properties of the diester-substituted derivatives relative to the corresponding parent structures will be reported shortly.

References

1. P W Leadbetter and A T Leaver, *Rev. Prog. Color.*, **19** (1989) 33.
2. A T Leaver, B Glover and P W Leadbetter, *Text. Chem. Colorist*, **24** (1992) 18.
3. B Glover and J A Hansford, *J.S.D.C.*, **96** (1980) 355.
4. D Brierley and J R Provost, *J.S.D.C.*, **99** (1983) 359.
5. S I Agbo, G Hallas and A D Towns, *Dyes Pigm.*, **47** (2000) 33.
6. J S Koh and A J Greaves, *Dyes Pigm.*, **50** (2001) 117.
7. J S Koh, A J Greaves and J P Kim, *Dyes Pigm.*, **56** (2003) 69.
8. J S Koh, A J Greaves and J P Kim, *Dyes Pigm.*, **60** (2004) 155.
9. J S Koh and J P Kim, *Color. Technol.*, **120** (2004) 56.
10. J S Koh, H Y Yoo and J P Kim, *Color. Technol.*, **120** (2004) 156.
11. J S Koh and D H Cho, *Fibres Polym*. **5** (2004) 134.
12. J S Koh, *Dyes Pigm.*, **64** (2005) 17.
13. J S Koh, *Dyes Pigm.*, **69** (2006) 233.
14. J S Koh and J P Kim, *J.S.D.C.*, **114** (1998) 121.
15. J S Koh and J P Kim, *Dyes Pigm.*, **37** (1998) 265.
16. J Mokhtari, K Gharanjig, M Arami and N M Mahmoodi, *Color. Technol.*, **124** (2008) 295.
17. K Gharanjig, M Arami, H Bahrami, B Movassagh, N M Mahmoodi and S Rouhani, *Dyes Pigm.*, **76** (2008) 684.
18. M A Weaver, *US3980634* (Eastman Kodak Co.; 1976).
19. M A Weaver and J C Fleischer, *US4039522* (Eastman Kodak Co.; 1977).
20. U Lauk, A Clement, R Dreier and A Arquint, *US6555664* (Ciba Specialty Chemicals; 2003).
21. A Clement, J G Wilhelm, A Arquint and U Lauk, *US7087731* (Ciba Specialty Chemicals; 2006).
22. A Clement, J G Wilhelm, A Arquint and U Lauk, *US7012137* (Ciba Specialty Chemicals; 2006).
23. I Holme, *Int. Dyer*, **188**(9) (2003) 6.
24. J Szadowski and W Malinowski, *J.S.D.C.*, **97** (1981) 72.
25. J Szadowski, *J.S.D.C.*, **97** (1981) 358.
26. J Szadowski, K Wojciechowski and W Malinowski, *J.S.D.C.*, **101** (1985) 105.
27. K Wojciechowski, *Dyes Pigm.*, **32** (1996) 202.
28. J H Choi, J S Park, M H Kim, H Y Lee and A D Towns, *Color. Technol.*, **123** (2007) 379.
29. J H Choi, J M Jeon, M H Kim, A D Towns and C Yoon, *Color. Technol.*, **124** (2008) 92.
30. J H Choi, J Y Choi, H Y Lee, A D Towns and C Yoon, *Color. Technol.*, **124** (2008) 364.
31. J H Choi, S H Hong and A D Towns, *J.S.D.C.*, **115** (1999) 32.
32. J H Choi, S H Hong, E J Lee and A D Towns, *J.S.D.C.*, **116** (2000) 273.
33. J Griffiths, *Colour and Constitution of Organic Molecules* (London: Academic Press, 1976).
34. J-Z Hu, P Skrabal and H Zollinger, *Dyes Pigm.*, **8** (1987) 189.