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Dyes for Polyester Microfibres

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ABSTRACT

The synthesis of a series of disperse dyes obtained by diazotization of nitroanilines or heterocyclic amines and coupling with N,N-dialkylanilines is described. The compounds dye polyester microfibres in deep depths of very good fastness to washing, light and sublimation. Dyes containing cyano groups and which are also capable of intramolecular hydrogen bonding between amido groups and the azo linkage have better substantivity and higher K/S *values on polyester microfibres than other dyes.*

1 INTRODUCTION

Polyester microfibre fabrics have many distinguishing characteristics such as a soft and full handle with excellent drapeability and comfort, low weight per unit area, easy care, good dimensional stability and weather-resistant properties. The Polyester Council of America describes a polyester microfibre as being four times finer than wool, three times finer than cotton and twice as fine as high-end silk, parameters relating to the polyester microfibres having considerably more surface area.[1] Dupeuble found that the quantity of dyestuff taken up by the microfibres was inversely proportional to the square root of the filament denier count

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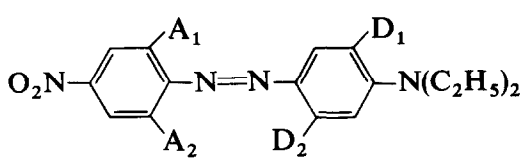
and that dyeing polyester microfilament of 0·5 denier in deep depth was very difficult.[2] Daruwalla and coworkers showed clearly that planarity in the dye molecule is essential for adequate depth of shade to be built up.[3,4] A strong 1 : 1 complex has been shown to be formed by face to face packing between planar disperse dyes and the hexacetylcellulobiose residues in cellulose triacetate, thus accounting for the fact that planar disperse dyes have much higher affinity than nonplanar dyes.[5,6]

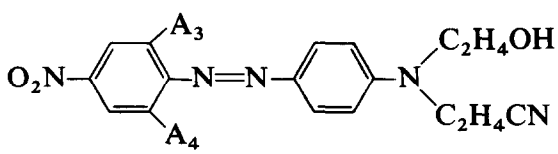
When two substituents are *ortho* to the azo group in the diazo component, bright, bathochromic and intense shades are achieved only if one of these substituents is a cyano group, because the rod-like shape of substituent permits planarity to be maintained.[7] Dyes of low molecular weight are required for dyeing polyester fibres, especially microfibres. Monoazo dyes fall into this category and nowadays cover virtually the whole of the colour spectrum. The use of heterocyclic and cyano substituted diazo components has made the production of brighter colours possible and enabled colour ranges to be extended.[8]

We report here the synthesis of a series of planar monoazo disperse dyes derived from cyanonitroanilines and *m*-dialkylamino-acetanilide (or propionanilide), and an evaluation of the substantivity and fastness properties of these dyes on polyester microfibres.



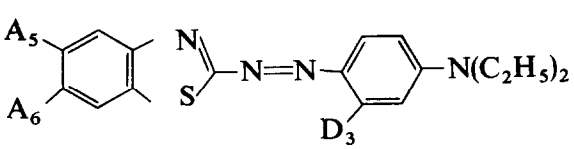
I

A_1: H, Br, CN
A_2: H, CN, NO_2
D_1: H, OCH_3
D_2: $NHCOCH_3$
$NHCOC_2H_5$,CH_3



II

A_3: Br, CN
A_4: CN, NO_2



III

A_5: H, Cl
A_6: OCH_3, Cl, NO_2
$NHCOCH_3$
$NHCOC_2H_5$

2 EXPERIMENTAL

2.1 2-(4'-Nitro)phenylazo-5-(*N,N*-diethyl)aminoacetanilide (I.1)[9]

p-Nitroaniline (0·704 g, 5·1 mmol) was dissolved in 10 ml of conc. H_2SO_4. The reaction mixture was cooled to 0°C, and HSO_4NO (formed by dissolving 0·380 g/5·1 mmol of $NaNO_2$ in 10 ml of conc. H_2SO_4 at 70°C) was added dropwise. After stirring for 2 h at 0 to 5°C, a small amount of urea was added, followed by the addition of 1·025 g (5 mmol) of 3-(*N,N*-diethyl) aminoacetanilide in 20 ml of a mixture of acetic acid and propanoic acid (5 : 1) at a rate such that the temperature did not exceed 5°C. The mixture was stirred for 2 h at 0 to 5°C, the pH then raised to 4 to 5 by adding 20% aq Na_2CO_3 and the liquor was left to stand overnight. The precipitate was filtered off and washed with acetone and then water until the washings were neutral; the product was dried in vacuum at 50°C for 8 h to give 1·283 g (yield 72·3%) of 2-(4'-nitro)phenylazo-5-(*N,N*-diethyl)aminoacetanilide (dye **I.1**) as small rubine crystals (m.p. 188–190°C).

Dyes **I.2–I.8, II.1, II.2** and **III.1—III.6** were synthesized by similar procedures, as detailed in Table 1.

2.2 2-(2',6'-dicyano-4'-nitro)phenylazo-5-(*N,N*-diethyl)aminoacetanilide (I.9)[10]

A mixture of 2·295 g (5 mmol) of dye **I.2**, 0·492 g (5·5 mmol) of CuCN and 50 ml of *N,N*-dimethylformamide (DMF) was stirred at 70 to 80°C for 2 h. The reaction mixture was poured into 200 ml of 5% HCl solution and left to stand overnight. The precipitate was filtered off and washed with water until the washings were neutral; the product was dried in vacuum at 50°C for 8 h to give 1·88 g (92·9%) of 2-(2',6'-dicyano-4'-nitro)-phenylazo-5-(*N,N*-diethyl)amino-acetanilide (dye **I.9**) m.p. 230–232°C.

Dyes **I.10–I.15, II.3** and **II.4** were synthesized by the above procedures except that dye **I.2** was replaced by dyes **I.3–I.9, II.1** and **II.2**. Relevant data on yield and mp are given in Table 2.

2.3 General

Electronic spectra were recorded (380–700 nm) on a Shimadzu UV 240 from dye solutions in DMF. Structure and purity were established by IR (Shimadzu IR 408), mass spectrometry (Hitachi M-52 GC/MS) and ^1H NMR (Varian VXR-300) (Table 3). Dyeing of polyester microfibre fabrics (0·1–0·2 denier, supplied by Union Chemical Laboratories, Industrial Technology Research Institute, Taiwan) was carried out in a liquor

TABLE 1
Synthesis and Characterization Data of Dyes (**I.2–I.8, II.1, II.2** and **III.1–III.6**)

Dye	*1° Arom. amine (5·1 mmol)*	*Coupler (5·0 mmol)*	*m.p. (0°C)*	R_f[a]	*Weight(g) (yield,%)*
I.2	2-Bromo-4-nitro-6-cyanoaniline (1·24 g)	3-(*N*,*N*-Diethyl)aminoacetanilide (1·030 g)	222–224	0·75	1·676 (73·2)
I.3	2-Bromo-4-nitro-6-cyanoaniline (1·24 g)	3-(*N*,*N*-Diethyl)aminopropionanilide (1·100 g)	184–186	0·7	1·860 (78·0)
I.4	2-Bromo-4-nitro-6-cyanoaniline (1·24 g)	3-(*N*,*N*-Diethyl)aminotoluene (1·815 g)	180–182	0·78	1·627 (80·0)
I.5	2-Bromo-4,6-dinitroaniline (1·336 g)	3-(*N*,*N*-Diethyl)aminoacetanilide (1·030 g)	186–188	0·78	1·912 (80·0)
I.6	2-Bromo-4,6-dinitroaniline (1·336 g)	3-(*N*,*N*-Diethyl)amino-4-methoxyacetanilide (1·1180 g)	196–198	0·82	1·987 (73·6)
I.7	2-Bromo-4,6-dinitroaniline (1·336 g)	3-(*N*,*N*-Diethyl)aminopropionanilide (1·100 g)	188–190	0·76	2·108 (85·7)
I.8	2-Bromo-4,6-dinitroaniline (1·336 g)	3-(*N*,*N*-Diethyl)amino-4-methoxyacetanilide (1·180 g)	176–178	0·92	1·973 (90·7)
II.1	2-Bromo-4-nitro-6-cyanoaniline (1·234 g)	*N*-2'-Cyanoethyl-*N*-2'-hydroxyethylaniline (1·950 g) at pH 3	166–168	0·78	1·898 (85·9)
II.2	2-Bromo-4,6-dinitroaniline (1·336 g)	*N*-2'-Cyanoethyl-*N*-2'-hydroxyethylaniline (0·950 g) at pH 3	168–170	0·67	1·872 (81·0)
III.1	2-Amino-6-methoxybenzothiazole (0·918 g) in H_3PO_4	3-(*N*,*N*-Diethyl)aminoacetanilide (1·030 g)	188–190	0·68	1·837 (92·5)
III.2	2-Amino-6-methoxybenzothiazole (0·918 g) in H_3PO_4	3-(*N*,*N*-Diethyl)aminopropionanilide (1·100 g)	182–184	0·69	1·778 (86·5)
III.3	2-Amino-6-methoxybenzothiazole (0·918 g) in H_3PO_4	3-(*N*,*N*-Diethyl)aminotoluene (1·815 g)	189–191	0·67	1·374 (77·6)
III.4	2-Amino-5,6-dichlorobenzothiazole (1·117 g) in H_3PO_4	3-(*N*,*N*-Diethyl)aminoacetanilide (1·030 g)	225–226	0·64	1·875 (86·0)
III.5	2-Amino-6-nitrobenzothiazole (0·995 g) in H_3PO_4	3-(*N*,*N*-Diethyl)aminopropionanilide (1·100 g)	186–188	0·67	1·594 (78·4)
III.6	2-Amino-6-nitrobenzothiazole (0·995 g) in H_3PO_4	3-(*N*,*N*-Diethyl)aminotoluene (1·815 g)	180–182	0·65	1·384 (75·0)

[a] Eluent: toluene–methanol (8 : 2).

TABLE 2
Synthesis and Characterization Data of Dyes (**I.10–I.15, II.3** and **II.4**)

Dye	*Reactant*	*CuCN (g)*	*Reaction time (h)*	*Weight (g) (yield, %)*	R_f[a]	*m.p. (°C)*
I.10	Dye **I.3** (0·470 g, 1 mmol)	0·090	2	0·389 g (93%)	0·67	220–222
I.11	Dye **I.4** (1·672 g, 4 mmol)	0·410	3	1·328 g (92%)	0·82	188–190
I.12	Dye **I.5** (0·677 g, 3·5 mmol)	0·356	3	0·324 g (89%)	0·60	180–182
I.13	Dye **I.6** (1·018 g, 2 mmol)	0·367	3	0·819 g (90%)	0·78	218–220
I.14	Dye **I.7** (1·479 g, 3 mmol)	0·430	2	1·185 g (90%)	0·69	204–206
I.15	Dye **I.8** (1·526 g, 3·5 mmol)	0·420	3	1·243 g (93%)	0·84	190–192
II.3	Dye **II.1** (0·886 g, 2 mmol)	0·200	2	0·675 g (87%)	0·72	212–214
II.4	Dye **II.2** (0·926 g, 2 mmol)	0·200	3	0·700 g (84%)	0·69	215–217

[a] Eluent: toluene–methanol (8 : 2).

ratio of 50 : 1 at 130°C at pH 5·0 to 5·5 for 1 h. The dye uptake was evaluated by extracting the dye from a known weight of dyed fabric with DMF and determining the absorbance of the solution, using the Shimadzu UV 240. Dye uptake was calculated from the calibration curve of absorbance vs. dye concentration.

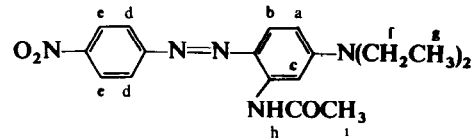
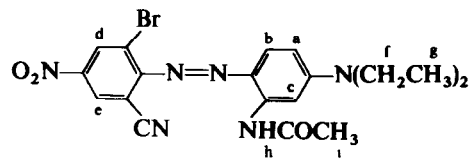
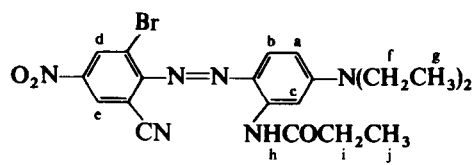
The wash fastness was tested according to CNS 1494–A2, which is similar to AATCC 61-1989-1 A, except that the test conditions used 100 ml of liquor (5 g/litre detergent and 2 g/litre anhydrous Na_2CO_3) at 50 ± 2°C for 30 min. Sublimination and light fastness assessments were carried out as for a previous investigation.[11] The *K/S* values were evaluated using an ICS Computer Match SM-6 and calculated from the Kubelka–Munk equation.

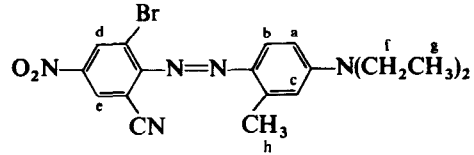
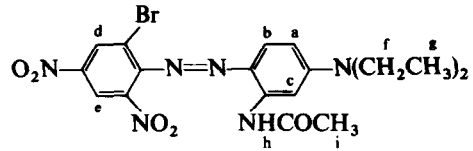
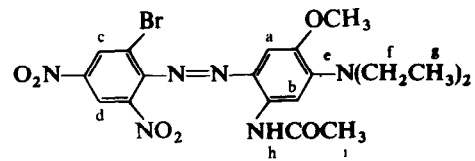
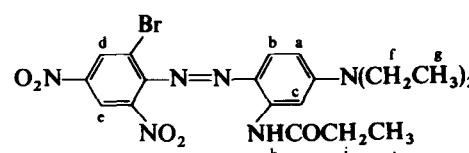
3 RESULTS AND DISCUSSION

3.1 Electronic spectra

Electronic spectra data of dyes **I–III** and four Dianix dyes are shown in Table 4. All dyes in the three series have extinction coefficients ($\varepsilon_{g\ max}$)

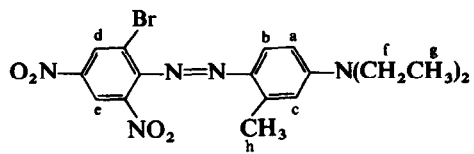
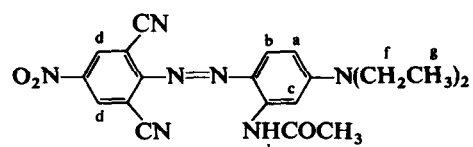
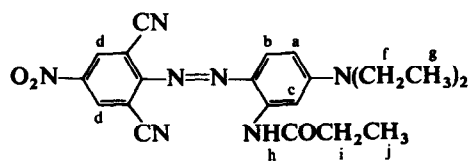
TABLE 3
Spectroscopic Data

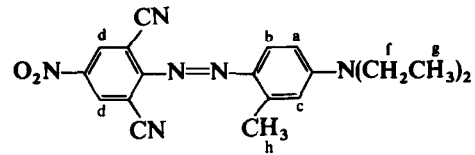
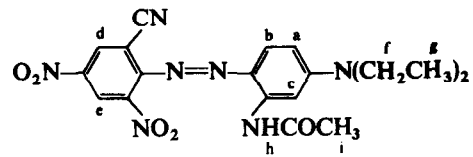
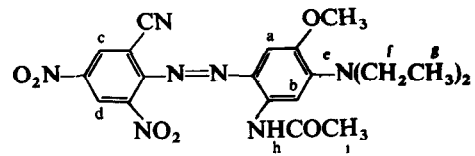
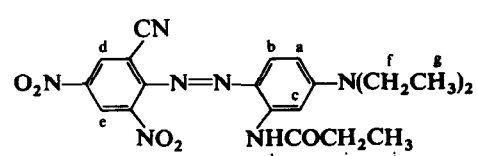
Dye	*Mass* (*m/z*)	*IR*[a] (*KBr/cm*$^{-1}$)	*NMR*[b] (*CDCl*$_3$/δ *ppm*)	*Structure*
I.1	355 $(M)^+$ 340 $(M—CH_3)^+$ 205 $(M—C_6H_4O_2N_3)^+$ 161 $(M—C_6H_4O_2N_3—C_2H_4)^+$	3300 (N—H)st 2950 (C—H)st 1660 (C=O)st 1605, 1508 (Ar ring)st 1560, 1320 (Ar—NO_2)st 956, 850, 805 (Ar—H b.o.o.p)	$1{\cdot}295_{(t)}$, 6H, g $2{\cdot}290_{(s)}$, 3H, i $3{\cdot}524_{(q)}$, 4H, f $6{\cdot}515_{(d)}$, 1H, a $7{\cdot}766_{(s)}$, 1H, c $7{\cdot}814_{(d)}$, 2H, d $8{\cdot}513_{(d)}$, 1H, b $8{\cdot}344_{(d)}$, 2H, e $9{\cdot}236_{(s)}$, 1H, h	
I.2	458/460 $(M)^+$ 443/445 $(M—CH_3)^+$ 205 $(M—C_7H_2O_2N_4Br)^+$ 161 $(M—C_7H_2O_2N_4Br—C_2H_4)^+$	3320 (N—H)st 2950 (C—H)st 2200 (C≡N)st 1700 (C=O)st 1605, 1508 (Ar ring)st 1560, 1320 (Ar—NO_2)st 954, 850, 815 (Ar—H b.o.o.p) 895 (C—Br)st	$1{\cdot}324_{(t)}$, 6H, g $2{\cdot}323_{(s)}$, 3H, i $3{\cdot}571_{(q)}$, 4H, f $6{\cdot}527_{(d)}$, 1H, a $8{\cdot}013_{(d)}$, 1H, b $8{\cdot}173_{(s)}$, 1H, c $8{\cdot}490_{(s)}$, 1H, d $8{\cdot}674_{(s)}$, 1H, e $9{\cdot}400_{(s)}$, 1H, h	
I.3	470/472 $(M)^+$ 455/457 $(M—CH_3)^+$ 416/418 $(M—COCH_3)^+$ 219 $(M—C_7H_2O_2N_4Br)^+$	3320 (N—H)st 2950 (C—H)st 2170 (C≡N)st 1690 (C=O)st 1600, 1605 (Ar ring)st 1560, 1310 (Ar—NO_2)st 958, 850, 800 (Ar—H b.o.o.p) 892 (C—Br)st	$1{\cdot}242_{(t)}$, 3H, j $1{\cdot}329_{(t)}$, 6H, g $2{\cdot}610_{(q)}$, 2H, i $3{\cdot}576_{(q)}$, 4H, f $6{\cdot}547_{(d)}$, 1H, a $8{\cdot}018_{(d)}$, 1H, b $8{\cdot}209_{(s)}$, 1H, c $8{\cdot}493_{(s)}$, 1H, d $8{\cdot}677_{(s)}$, 1H, e $9{\cdot}374_{(s)}$, 1H, h	

I.4	417/419 $(M)^+$ 402/404 $(M—CH_3)^+$ 389/391 $(M—C_2H_4)^+$ 162 $(M—C_6H_2O_4N_4Br—C_2H_4)^+$	2950 (C—H)st 2200 (C≡N)st 1592, 1508 (Ar ring)st 1550, 1312 (Ar—NO_2)st 1370 (CH_3)st 938, 830, 795 (Ar—H b.o.o.p) 895 (C—Br)st	$1{\cdot}281_{(t)}$, 6H, g $2{\cdot}763_{(t)}$, 3H, h $3{\cdot}519_{(q)}$,4H, f $6{\cdot}558_{(d)}$, 1H, a $6{\cdot}596_{(s)}$, 1H, c $7{\cdot}992_{(d)}$, 1H, b $8{\cdot}519_{(s)}$, 1H, d $8{\cdot}672_{(s)}$, 1H, e	
I.5	478/480 $(M)^+$ 463/465 $(M—CH_3)^+$ 205 $(M—C_6H_2O_4N_4Br)^+$ 161 $(M—C_8H_6O_5N_4Br)^+$	3340 (N—H)st 2960 (C—H)st 1695 (C=O)st 1614, 1546 (Ar ring)st 1575, 1310 (Ar—NO_2)st 1380 (CH_3)st 954, 850, 795 (Ar—H b.o.o.p) 900 (C—Br)st	$1{\cdot}304_{(t)}$, 6H, g $2{\cdot}312_{(s)}$, 3H, i $3{\cdot}551_{(q)}$,4H, f $6{\cdot}509_{(d)}$, 1H, a $7{\cdot}899_{(d)}$, 1H, b $8{\cdot}168_{(s)}$, 1H, c $8{\cdot}323_{(s)}$, 1H, d $8{\cdot}654_{(s)}$, 1H, e $9{\cdot}396_{(s)}$, 1H, h	
I.6	508/510 $(M)^+$ 493/495 $(M—CH_3)^+$ 477/479 $(M—OCH_3)^+$ 235 $(M—C_6H_2O_4N_4Br)^+$	3350 (N—H)st 1684 (C=O)st 1604, 1520 (Ar ring)st 1570, 1300 (NO_2)st 1365, 1385 (CH_3)st 1280 (C—O—C)st 930, 850, 790 (Ar—H b.o.o.p) 888 (C—Br)st	$1{\cdot}315_{(t)}$, 6H, g $2{\cdot}297_{(s)}$, 3H, i $3{\cdot}635_{(q)}$,4H, f $3{\cdot}863_{(s)}$, 3H, e $7{\cdot}273_{(s)}$, 1H, a $8{\cdot}150_{(s)}$, 1H, b $8{\cdot}278_{(s)}$, 1H, c $8{\cdot}638_{(s)}$, 1H, d $9{\cdot}378_{(s)}$, 1H, h	
I.7	492/494 $(M)^+$ 477/479$(M—CH_3)^+$ 445/447 $(M—OC_2H_5)^+$ 219 $(M—C_6H_2O_4N_4Br)^+$	3350 (N—H)st 3100, 2950 (C—H)st 1692 (C=O)st 1610, 1545 (Ar ring)st 1570, 1308 (Ar–NO_2)st 1360 (CH_3)st 1280 (C—O—C)st 956, 850, 790 (Ar—H b.o.o.p) 890 (C—Br)st	$1{\cdot}262_{(t)}$, 6H, j $1{\cdot}307_{(t)}$, 6H, g $2{\cdot}573_{(q)}$,2H, i $3{\cdot}554_{(q)}$,4H, f $6{\cdot}547_{(d)}$, 1H, a $8{\cdot}027_{(d)}$, 1H, b $8{\cdot}188_{(s)}$, 1H, c $8{\cdot}343_{(s)}$, 1H, d $8{\cdot}654_{(s)}$, 1H, e $9{\cdot}374_{(s)}$, 1H, h	

(continued)

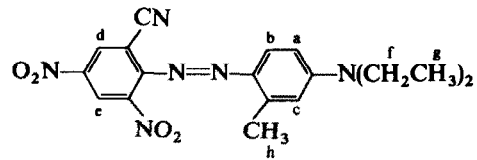
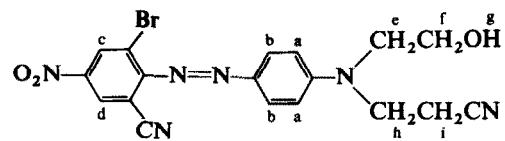
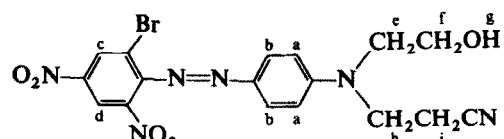
TABLE 3—*continued*

Dye	*Mass* (*m/z*)	*IR*[a] (*KBr/cm*$^{-1}$)	*NMR*[b] (*CDCl*$_3$/δ *ppm*)	*Structure*
I.8	435/437 $(M)^+$ 420/422 $(M-CH_3)^+$ 162 $(Ca_6H_4O_4N_4Br)^+$	3100 (C—H)st 1596, 1510 (Ar ring)st 1570, 1304 (Ar—NO_2)st 1360, 1400 (CH_3)st 940,850, 800 (Ar—H b.o.o.p) 900 (C—Br)st	$1{\cdot}267_{(t)}$, 6H, g $2{\cdot}478_{(s)}$, 3H, h $3{\cdot}502_{(q)}$,4H, f $6{\cdot}507_{(s)}$, 1H, c $6{\cdot}583_{(d)}$,1H, a $7{\cdot}934_{(d)}$,1H, b $8{\cdot}399_{(d)}$,1H, d $8{\cdot}654_{(d)}$,1H, e	
I.9	405 $(M)^+$ 390 $(M-CH_3)^+$ 205 $(M-C_8H_2O_2N_5)^+$	3320 (N—H)st 2950 (C—H)st 2200 (C≡N)st 1700 (C=O)st 1610, 1525 (Ar ring)st 1572, 1320 (Ar—NO_2)st 932,875, 755 (Ar—H b.o.o.p)	$1{\cdot}333_{(t)}$, 6H, g $2{\cdot}331_{(s)}$, 3H, i $3{\cdot}625_{(q)}$,4H, f $6{\cdot}586_{(d)}$,1H, a $8{\cdot}155_{(d)}$,1H, b $8{\cdot}224_{(s)}$, 1H, c $8{\cdot}655_{(s)}$, 2H, d $9{\cdot}360_{(s)}$, 1H, h	
I.10	419 $(M)^+$ 404 $(M-CH_3)^+$ 219 $(M-C_8H_2O_2N_5)^+$	3300 (N—H)st 2960 (C—H)st 2200 (C≡N)st 1696 (C=O)st 1607, 1526 (Ar ring)st 1570, 1320 (Ar—NO_2)st 932, 755 (Ar—H b.o.o.p)	$1{\cdot}234_{(t)}$, 3H, j $1{\cdot}358_{(t)}$, 6H, g $2{\cdot}622_{(q)}$,2H, i $3{\cdot}625_{(d)}$,4H, f $6{\cdot}576_{(d)}$,1H, a $8{\cdot}149_{(d)}$,1H, b $8{\cdot}248_{(s)}$, 1H, c $8{\cdot}644_{(s)}$, 2H, d $9{\cdot}321_{(s)}$, 1H, h	

I.11	362 $(M)^+$ 347 $(M—CH_3)^+$	3100, 2950 (C—H)st 2200 (C≡N)st 1592, 1514 (Ar ring)st 1590, 1315 ($Ar—NO_2$)st 1400 (CH_3)st 932, 740 (Ar—H b.o.o.p)	$1{\cdot}317_{(t)}$, 6H, g $2{\cdot}751_{(s)}$, 3H, h $3{\cdot}570_{(q)}$, 4H, f $6{\cdot}588_{(s)}$, 1H, c $6{\cdot}644_{(d)}$, 1H, a $8{\cdot}137_{(d)}$, 1H, b $8{\cdot}678_{(s)}$, 2H, d	
I.12	425 $(M)^+$ 410 $(M—CH_3)^+$ 205 $(M—C_7H_2O_4N_5)^+$	3350 (N—H)st 2900 (C—N)st 2215 (C≡N)st 1695 (C=N)st 1594, 1520 (Ar ring)st 1570, 1315 ($Ar—NO_2$)st 930, 880, 782 (Ar—H b.o.o.p)	$1{\cdot}340_{(t)}$, 6H, g $2{\cdot}328_{(s)}$, 3H, i $3{\cdot}604_{(q)}$, 4H, f $6{\cdot}536_{(d)}$, 1H, a $7{\cdot}927_{(d)}$, 1H, b $8{\cdot}169_{(s)}$, 1H, c $8{\cdot}556_{(s)}$, 2H, d $8{\cdot}636_{(s)}$, 1H, e $9{\cdot}183_{(s)}$, 1H, h	
I.13	455 $(M)^+$ 440 $(M—CH_3)^+$ 424 $(M—OCH_3)^+$	3340 (N—H)st 2200 (C≡N)st 1688 (C=O)st 1590, 1505 (Ar ring)st 1540, 1310 (NO_2)st 1285 (C—O—C)st 935, 863, 784 (Ar—H b.o.o.p)	$1{\cdot}353_{(t)}$, 6H, g $2{\cdot}345_{(s)}$, 3H, i $3{\cdot}761_{(q)}$, 4H, f $3{\cdot}863_{(s)}$, 3H, e $7{\cdot}285_{(s)}$, 1H, a $8{\cdot}252_{(s)}$, 1H, b $8{\cdot}550_{(s)}$, 2H, c $8{\cdot}606_{(s)}$, 1H, d $9{\cdot}221_{(s)}$, 1H, h	
I.14	439 $(M)^+$ 424 $(M—CH_3)^+$ 219 $(M—C_7H_2O_4N_5)^+$	3340 (N—H)st 2950 (C—H)st 2210 (C≡N)st 1690 (C=O)st 1595, 1530, 1470 (Ar ring)st 1570, 1315 (NO_2)st 930, 880, 780 (Ar—H b.o.o.p)	$0{\cdot}824_{(t)}$, 3H, j $1{\cdot}226_{(t)}$, 6H, g $2{\cdot}543_{(q)}$, 2H, i $3{\cdot}537_{(q)}$, 4H, f $6{\cdot}583_{(d)}$, 1H, a $7{\cdot}830_{(d)}$, 1H, b $8{\cdot}122_{(s)}$, 1H, c $8{\cdot}477_{(s)}$, 1H, d $8{\cdot}546_{(s)}$, 1H, e $9{\cdot}187_{(s)}$, 1H, h	

(continued)

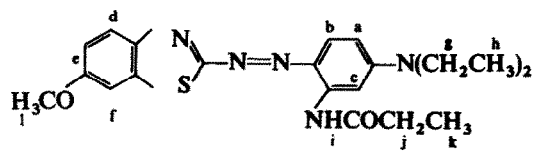
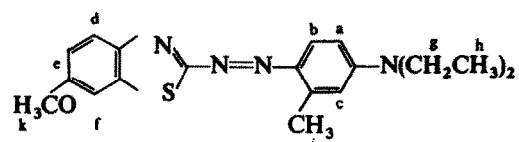
TABLE 3—*continued*

Dye	*Mass (m/z)*	*IR*[a] *(KBr/cm^{-1})*	*NMR*[b] *(CDCl$_3$/δ ppm)*	*Structure*
I.15	382 $(M)^+$ 367 $(M—CH_3)^+$ 162 $(M—C_7H_2O_4N_5)^+$	3050, 2950 (C—H)st 2200 (C≡N)st 1590, 1510 (Ar ring)st 1570, 1300 (Ar—NO_2)st 1400, 1370 (CH_3)st 930, 840, 785 (Ar—H b.o.o.p)	$1{\cdot}296_{(t)}$, 6H, g $2{\cdot}596_{(s)}$, 3H, h $3{\cdot}548_{(q)}$, 4H, f $6{\cdot}552_{(s)}$, 1H, c $6{\cdot}604_{(d)}$, 1H, a $7{\cdot}981_{(d)}$, 1H, b $8{\cdot}581_{(s)}$, 1H, d $8{\cdot}669_{(s)}$, 1H, e	
II.1	442/444 $(M)^+$ 411/413 $(M—CH_2OH)^+$	3400 (O—H)st 3100, 2900 (C—H)st 2240 (C≡N)st 1595, 1508 (Ar ring)st 1540, 1312 (Ar—NO_2)st 990, 825, 785 (Ar—H b.o.o.p) 890 (C—Br)st	$2{\cdot}802_{(t)}$, 2H, i $3{\cdot}776_{(t)}$, 2H, f $3{\cdot}826_{(t)}$, 2H, h $3{\cdot}943_{(q)}$, 2H, e $4{\cdot}062_{(broad)}$, 1H, g $6{\cdot}829_{(d)}$, 2H, a $8{\cdot}059_{(d)}$, 2H, b $8{\cdot}545_{(d)}$, 1H, c $8{\cdot}723_{(d)}$, 1H, d	
II.2	462/464 $(M)^+$ 431/433 $(M—CH_2OH)^+$ 339/401 $(M—OH—NO_2)^+$	3400 (O—H)st 3100 (C—H)st 1600, 1520 (Ar ring)st 1530, 1325 (Ar—NO_2)st 970, 825 (Ar—H b.o.o.p) 900 (C—Br)st	$2{\cdot}789_{(t)}$, 2H, i $3{\cdot}759_{(t)}$, 2H, f $3{\cdot}830_{(t)}$, 2H, h $3{\cdot}935_{(q)}$, 2H, e $4{\cdot}066_{(broad)}$, 1H, g $6{\cdot}801_{(d)}$, 2H, a $7{\cdot}913_{(d)}$, 2H, b $8{\cdot}579_{(d)}$, 1H, c $8{\cdot}716_{(d)}$, 1H, d	

II.3	389 $(M)^+$ 189 $(M—C_8H_2O_5N_5)^+$	3400 (O—H)st 3050 (C—H)st 2250 (C≡N)st 1598, 1520 (Ar ring)st 1570, 1330 (Ar—NO_2)st 930, 830, 758 (Ar—H b.o.o.p)	$2{\cdot}835_{(t)}$, 2H, i $3{\cdot}650_{(t)}$, 2H, f $3{\cdot}982_{(t)}$, 2H, e $3{\cdot}828_{(t)}$, 2H, h $4{\cdot}062_{(s)}$, 1H, g $6{\cdot}840_{(d)}$, 2H, a $8{\cdot}139_{(d)}$, 2H, b $8{\cdot}759_{(s)}$, 2H, c
II.4	409 $(M)^+$ 189 $(M—C_7H_2O_4N_5)^+$	3400 (O—H)st 3050 (C—H)st 2250 (C≡N)st 1598, 1525 (Ar ring)st 1330 (Ar—NO_2)st 930, 830, 758 (Ar—H b.o.o.p)	$2{\cdot}373_{(t)}$, 2H, i $3{\cdot}647_{(t)}$, 2H, f $3{\cdot}898_{(t)}$, 2H, h $4{\cdot}054_{(t)}$, 2H, e $4{\cdot}072_{(broad)}$, 1H, g $6{\cdot}763_{(d)}$, 2H, a $7{\cdot}263_{(d)}$, 2H, b $8{\cdot}516_{(s)}$, 1H, c $8{\cdot}581_{(s)}$, 1H, d
III.1	397 $(M)^+$ 382 $(M—CH_3)^+$ 354 $(M—COCH_3)^+$ 205 $(M—C_8H_6ON_3S)^+$	3300 (N—H)st 2950 (C—H)st 2300 (N=C—S)st 1690 (C=O)st 1590, 1485 (Ar ring)st 1400 (CH_3)st 1045 (C—O—C)st 950, 880, 820 (Ar—H b.o.o.p) 705 (C—S)st	$1{\cdot}289_{(s)}$, 6H, h $2{\cdot}331_{(t)}$, 3H, j $3{\cdot}526_{(q)}$, 4H, g $3{\cdot}893_{(s)}$, 3H, k $6{\cdot}498_{(d)}$, 1H, a $7{\cdot}050_{(d)}$, 1H, b $7{\cdot}271_{(d)}$, 1H, d $7{\cdot}283_{(d)}$, 1H, e $7{\cdot}921_{(s)}$, 1H, f $8{\cdot}100_{(d)}$, 1H, e $9{\cdot}250_{(broad)}$, 1H, i

(continued)

TABLE 3—*continued*

Dye	*Mass* (*m/z*)	*IR* (*KBr/cm*$^{-1}$)	*NMR*[b] (*CDCl*$_3$/*δ ppm*)	*Structure*
III.2	411 $(M)^+$ 396 $(M—CH_3)^+$ 382 $(M—C_2H_5)^+$ 354 $(M—COC_2H_5)^+$ 219 $(M—C_6H_6ON_3S)^+$	3300 (N—H)st 2950 (C—H)st 2300 (N=C—S)st 1690 (C=O)st 1605, 1490 (Ar ring)st 1300 (CH_3)st 1048 (C—O—C)st 960, 880, 825 (Ar—H b.o.o.p) 705 (C—S)st	$1{\cdot}294_{(t)}$, 6H, h $1{\cdot}346_{(t)}$, 3H, k $2{\cdot}594_{(q)}$, 2H, j $3{\cdot}529_{(q)}$, 4H, g $3{\cdot}894_{(s)}$, 3H, l $6{\cdot}497_{(d)}$, 1H, a $7{\cdot}043_{(d)}$, 1H, b $7{\cdot}274_{(d)}$, 1H, d $7{\cdot}280_{(d)}$, 1H, e $7{\cdot}920_{(s)}$, 1H, f $7{\cdot}926_{(s)}$, 1H, c $9{\cdot}258_{(broad)}$, 1H, i	
III.3	354 $(M)^+$ 349 $(M—CH_3)^+$ 162 $(M—C_8H_6ON_3S)^+$	2950 (C—H)st 2300 (N=C—S)st 1590, 1505 (Ar ring)st 1320 (CH_3)st 1040 (C—O—C)st 880, 740 (Ar—H b.o.o.p) 690 (C—S)st	$1{\cdot}266_{(t)}$, 6H, h $2{\cdot}683_{(s)}$, 3H, j $3{\cdot}492_{(q)}$, 4H, g $3{\cdot}900_{(s)}$, 3H, k $6{\cdot}546_{(s)}$, 3H, c $6{\cdot}593_{(d)}$, 1H, a $7{\cdot}050_{(d)}$, 1H, b $7{\cdot}280_{(s)}$, 1H, f $7{\cdot}939_{(d)}$, 1H, d $7{\cdot}992_{(d)}$, 1H, c	

III.4	433/435/437 $(M)^+$	3300 (N—H)st	$1{\cdot}319_{(t)}$, 6H, g
	364/366/368 $(M—COCH_3C_2H_2)^+$	2900 (C—H)st	$2{\cdot}324_{(s)}$, 3H, i
	205 $(M—C_6H_2N_3SCl_2)^+$	1685 (C=O)st	$3{\cdot}558_{(q)}$, 4H, f
		1605, 1520 (Ar ring)st	$6{\cdot}580_{(d)}$, 1H, a
		1320 (CH_3)st	$7{\cdot}518_{(d)}$, 1H, b
		940, 890 (Ar—H b.o.o.p)	$7{\cdot}855_{(s)}$, 1H, c
		700 (C—S)st	$8{\cdot}220_{(s)}$, 1H, d
			$8{\cdot}583_{(s)}$, 1H, e
			$9{\cdot}260_{(broad)}$, 1H, h
III.5	426 $(M)^+$	3300 (N—H)st	$1{\cdot}257_{(t)}$, 3H, k
	411 $(M—CH_3)^+$	2900 (C—H)st	$1{\cdot}343_{(t)}$, 6H, h
	219 $(M—C_7H_3N_4O_2S)^+$	2300 (N=C—S)st	$2{\cdot}634_{(q)}$, 2H, j
		1690 (C=O)st	$3{\cdot}594_{(q)}$, 4H, g
		1590, 1485 (Ar ring)st	$6{\cdot}560_{(d)}$, 1H, a
		1545, 1315 (Ar—NO_2)st	$7{\cdot}283_{(d)}$, 1H, b
		960, 880, 745 (Ar—H b.o.o.p)	$8{\cdot}037_{(s)}$, 1H, c
		696 (C—S)st	$8{\cdot}089_{(d)}$, 1H, d
			$8{\cdot}305_{(d)}$, 1H, e
			$8{\cdot}710_{(s)}$, 1H, f
III.6	369 $(M)^+$	2950 (C—H)st	$1{\cdot}296_{(t)}$, 6H, h
	354 $(M—CH_3)^+$	1590, 1490 (Ar ring)st	$2{\cdot}683_{(s)}$, 3H, i
	326 $(M—CH_3—C_2H_4)^+$	1550, 1340 (Ar—NO_2)st	$3{\cdot}537_{(q)}$, 4H, g
	162 $(M—C_7H_3N_4O_2S)^+$	1400 (CH_3)st	$6{\cdot}582_{(d)}$, 1H, a
		885, 820 (Ar—H b.o.o.p)	$6{\cdot}627_{(d)}$, 1H, b
		690 (C—S)st	$8{\cdot}032_{(s)}$, 1H, c
			$8{\cdot}065_{(s)}$, 1H, d
			$8{\cdot}306_{(d)}$, 1H, e
			$8{\cdot}706_{(d)}$, 1H, f

[a] Ar: aromatic; st; stretching; b.o.o.p.: bending out of plane.

[b] (s): Singlet; (d) doublet; (t) triplet; (q) quartet.

TABLE 4
Electronic Spectra (in DMF)

Dye	λ_{max} (*nm*)	$\Delta\lambda_{1/2}$ (*nm*)	$\varepsilon_{g\,max}$	ε_{max} (*log* ε)
I.1	525	107	138·9	49 309 (4·69)
I.2	593	116	110·4	50 563 (4·70)
I.3	588	117	111·3	52 311 (4·72)
I.4	575	139	90·6	37 599 (4·58)
I.5	567	112	108·3	51 767 (4·71)
I.6	616	111	98·5	50 038 (4·70)
I.7	566	111	116·0	57 072 (4·76)
I.8	570	128	94·1	40 933 (4·61)
I.9	617	85	186·2	75 411 (4·88)
I.10	618	87	193·7	81 160 (4·91)
I.11	609	108	149·3	54 047 (4·73)
I.12	608	110	153·4	65 195 (4·81)
I.13	639	92	127·7	58 104 (4·76)
I.14	609	102	155·2	68 133 (4·83)
I.15	604	106	108·0	41 256 (4·62)
II.1	526	140	70·0	30 940 (4·49)
II.2	522	138	71·6	33 079 (4·52)
II.3	566	124	115·9	45 085 (4·65)
II.4	549	132	88·8	36 319 (4·56)
III.1	535	96	137·4	54 548 (4·74)
III.2	534	96	147·2	60 499 (4·78)
III.3	529	97	91·5	32 391 (4·51)
III.4	540	104	95·8	41 769 (4·62)
III.5	566	94	115·3	49 118 (4·69)
III.6	561	114	77·9	28 745 (4·46)
Dianix Blue AC–E	637	105	63·1	—
	593 (s)		53·5	
Dianix Red AC–E	521	97	48·9	—
	556 (s)		43·7	
Dianix Yellow AC–E	443	67	97·3	—
Dianix Rubine GG–FS	538	131	59·1	—

s: Shoulder; $\Delta\lambda_{1/2}$: half-band width.

higher than those of the Dianix dyes. Comparing the λ_{max} values and molar extinction coefficients of dye **I.4** with **I.2** and **I.3**, dye **I.8** with **I.5** and **I.7**, dye **I.11** with **I.9** and **I.10**, dye **I.15** with **I.12** and **I.14**. dye **III.3** with **III.1** and **III.2** and dye **III.6** with **III.5**, a bathochromic (5–18 nm) and pronounced hyperchromic effect is apparent. This is probably due to the intramolecular hydrogen bond between acetamido (or propionamido) groups and the azo linkage.[12] Introducing electron-withdrawing groups into the diazo component at positions *ortho* or *para* to the azo linkage

produced a large bathochromic shift due to stabilisation of the excited state by sharing the negative charge of the β-azo nitrogen atom both by the inductive and, more importantly, the mesomeric effect.[13] For a bulky group, e.g. nitro or halogen, *ortho* to the azo group a conplanar conformation is not possible because of steric hindrance between the bulky group and the lone pair orbital on the α-nitrogen atom of the azo group. These steric interactions are minimized by the bulky group rotating out of the molecular plane, resulting in a large hypsochromic shift. In contrast, cyano groups, owing to their rod-like shape, do not have an obvious steric effect.[14] In series **I** and **II**, the increase in λ_{max} values can be correlated with the electronic and steric effect of the groups in the diazo component at the position *ortho* to the azo linkage (CN > NO_2 > Br), viz., dye **I.5** < **I.2** < **I.12** < **I.9**, dye **I.7** < **I.3** < **1.14** < **I.10**, dye **I.8** < **I.4** < **I.15** < **I.11** and dye **II.2** < **II.1** < **II.4** < **II.3**, the differences being 4 to 26 nm, 15 to 29 nm and 5 to 17 nm, respectively. Compared to the bromo group, the cyano and nitro groups increase the ε_{max} and $\varepsilon_{g\ max}$ (molar and gram extinction coefficients) viz., **I.2** < **I.9**, **I.3** < **I.10**, **I.4** < **I.11**, **I.5** < **I.12**, **I.7** < **I.14**, **I.8** < **I.15**, **II.1** < **II.3** and **II.2** < **II.4** (Br < CN); **I.2** < **I.12**, **I.3** < **I.14**, **I.4** < **I.15** and **II.1** < **II.4** (Br < NO_2). The strong electron-withdrawing nature of the nitro group in a hetero-diazo component produces a large bathchromic shift of 32 nm (**III.2** → **III.5**, **III.3** → **III.6**).

3.2 Dyeing and fastness properties

All dyes in the three series, and the four Dianix dyes, gave level colouration on polyester microfibre fabrics. The four Dianix dyes are recommended by dyeing mills in Taiwan for polyester microfibre fabrics. The dye-uptake of the four Dianix dyes is slightly lower than that of dyes **I–III**; however, the *K/S* values of the Dianix dyes are much less than those of dyes **I–III** (Table 5). This might be due to the lower extinction coefficients ($\varepsilon_{g\ max}$) of the Dianix dyes. It can be seen from Table 5 that the dye-uptake and *K/S* values of the deeper shades (3·0% o.w.f.) of dyes with an intramolecular hydrogen bond are higher than those of the other dyes, viz., **I.2** and **I.3** > **I.4**, **I.5** and **I.7** > **I.8**, **I.9** and **I.10** > **I.11**, **I.12** and **I.14** > **1.15**, **III.1** and **III.2** > **III.3** and **III.5** > **III.6**. Replacing bromo groups by nitro groups or cyano groups increases dye-uptake and *K/S* values, comparable with their higher extinction coefficients, viz., **I.9** and **I.12** > **I.2**, **I.10** and **I.14** > **I.3**, **I.11** and **I.15** > **1.4** and **II.3** and **II.4** > **II.1**. Sublimation fastnesses of dyes **I–III** are higher than those of the Dianix dyes and are of an acceptable order to meet commercial requirements, except for dyes **I.1**, **I.4**, **I.8**, **I.11** and **I.15** (Table 6).

TABLE 5
Substantivity and *K/S* Values

o.w.f. *Dye*	*Dye uptake (g/kg fibres)*				*K/S value*			
	0·5%	*1·0%*	*2·0%*	*3·0%*	*0·5%*	*1·0%*	*2·0%*	*3·0%*
I.1	3·71	7·33	14·31	18·85	5·06	8·30	12·67	13·29
I.2	3·07	6·68	14·09	19·69	2·94	6·90	11·03	14·25
I.3	3·23	6·57	14·74	20·69	3·24	8·03	13·16	15·03
I.4	3·28	7·17	14·29	19·84	2·41	5·76	10·06	13·13
I.5	3·34	6·79	13·83	22·04	3·72	6·87	13·03	17·12
I.6	3·48	7·31	14·41	19·69	2·80	6·29	10·53	14·42
I.7	3·27	7·04	15·05	22·43	4·44	8·42	12·94	17·21
I.8	3·29	7·17	14·60	19·37	2·56	6·47	11·00	13·98
I.9	3·10	8·45	17·63	21·49	5·63	10·86	15·15	16·49
I.10	3·47	8·63	17·63	22·83	5·90	11·71	14·67	16·75
I.11	2·74	6·67	13·21	18·04	2·48	5·30	10·45	13·86
I.12	2·98	6·38	14·31	21·47	5·55	11·31	13·75	16·84
I.13	3·06	7·68	12·90	19·51	2·74	6·05	10·79	15·54
I.14	3·03	7·04	15·05	22·43	4·44	8·42	12·94	16·91
I.15	3·79	7·43	15·78	22·39	3·35	6·41	11·14	13·03
II.1	2·98	7·07	12·09	16·54	2·13	5·46	8·13	12·34
II.2	2·97	6·78	12·01	17·45	2·23	5·39	9·71	12·54
II.3	3·24	6·34	15·07	19·83	3·04	6·70	11·75	16·36
II.4	2·08	6·38	14·31	21·46	5·55	11·31	13·75	16·84
III.1	2·60	5·32	11·35	18·82	3·50	6·49	11·79	15·40
III.2	4·02	7·52	14·39	19·38	6·10	8·46	12·23	16·12
III.3	3·87	6·08	13·85	19·62	4·09	6·86	11·55	14·09
III.4	2·80	6·66	13·67	19·92	4·15	7·86	12·33	15·70
III.5	3·18	6·60	13·30	19·11	4·49	8·00	12·96	15·72
III.6	4·03	8·33	14·08	18·59	2·63	5·10	10·92	14·67
Dianix Blue AC–E		7·28		21·20		2·09		9·63
Dianix Red AC–E		7·18		20·50		2·83		8·85
Dianix Yellow AC–E		5·40		17·10		9·66		13·84
Dianix Rubine GG–FS		7·77		19·10		3·60		8·90

Intramolecular hydrogen bonding between the amido groups and the azo linkage increases the light fastness of dyes on polyester microfibre fabrics, viz., **I.2** and **1.3** > **1.4**, **I.5** and **I.7** > **I.8**, **I.9** and **I.10** > **I.11**, **III.1** and **III.2** > **III.3** and **III.5** > **III.6** (Table 6). The wash fastness of all dyes in the three series are of an acceptable order to meet commercial requirements (Table 6).

It can be concluded that disperse dyes capable of intramolecular hydrogen bonding, and also containing cyano groups ortho to the azo linkage, dye polyester microfibre fabrics in deep depths with bright hues and of good fastness to washing, light and sublimation.

TABLE 6
Fastness Properties

o.w.f. Dye	*Wash fastness (cc/sp)*[a]				*Light fastness*				*Sublimation temperature (°C)*			
	0·5%	*1·0%*	*2·0%*	*3·0%*	*0·5%*	*1·0%*	*2·0%*	*3·0%*	*0·5%*	*1·0%*	*2·0%*	*3·0%*
I.1	4/4	4/4	4–5/4	5/3–4	3	3	3	3	140	130	130	130
I.2	4/5	4–5/4	4–5/4	4–5/4	4–5	4–5	4–5	5	170	16-0	160	160
I.3	4/4–5	4/4–5	4–5/4–5	4–5/4	4	4	4	5	170	160	150	150
I.4	4/4	4/4	4–5/4	4–5/4	3	3	3–4	4	160	150	140	140
I.5	4–5/5	4–5/5	4–5/4–5	5/4–5	5	5	5	6	170	170	160	150
I.6	4–5/4–5	4–5/4–5	4–5/4–5	5/4–5	4	5	5	6	190	180	170	160
I.7	4/4–5	4/4	4–5/4	4–5/4	5	5	5	5	170	160	150	140
I.8	3–4/4–5	4/4	4–5/4	5/3–4	4	4	5	5	150	150	140	140
I.9	4/5	4/4–5	4–5/4–5	4–5/4–5	5	5–6	5–6	5–6	170	160	160	150
I.10	4/4–5	4/4–5	4–5/4	4–5/4	4	4–5	5	5	180	170	160	160
I.11	4/4–5	4/4–5	4–5/4–5	4–5/4–5	4	5	5	5	160	150	150	140
I.12	4/4–5	4–5/4	4–5/4	5/4	5	6	6	6	170	170	160	150
I.13	4/5	4/4–5	4/4	4/4	4	4	4	5	190	180	180	170
I.14	4/4–5	4–5/4–5	4–5/4	4–5/4	4–5	5	5	5	190	180	170	170
I.15	4/5	4–5/4–5	5/4	5/4	5	5	5	6	160	150	140	140
II.1	4/5	4/5	4–5/4–5	4–5/4–5	4	4	4	5	190	190	180	170
II.2	3/5	3/5	3–4/5	3–4/5	3	3	3	4	190	180	160	150
II.3	3–4/4–5	4/4–5	4/4–5	4/4–5	3–4	4	4–5	4–5	200	200	190	180
II.4	3–4/4–5	3–4/4–5	4/4–5	4/4	3	3	4	4	200	200	190	180
III.1	3–4/4–5	3–4/4–5	4/4	4/4	3	3	3	4	180	170	160	150
III.2	4/4–5	4/4–5	4–5/4–5	4–5/4–5	3	3	4	4	170	160	150	150
III.3	3–4/4–5	4/4–5	4/4	4/4	3	3	3	4	170	170	160	160
III.4	4–5/4–5	4–5/4–5	5/4–5	5/4	4	4	4	4–5	170	160	150	150
III.5	3–4/4–5	3–4/4–5	4/4–5	4/4	4	4	5	5	180	170	170	160
III.6	3–4/5	3–4/5	4/4–5	4/4	3	3	4	4	170	170	160	160
Dianix Blue AC–E						5		5		160		160
Dianix Red AC–E					4	4	4	4–5	150	140	140	130
Dianix Yellow AC–E					5	5	5	6	180	160	150	150
Dianix Rubine GG–FS						4		5		160		150

[a] c.c.—change in colour; s.p.—staining of polyester.

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