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Dyes and Pigments 44 (2000) 209–218

DYES and PIGMENTS

Carboxy-substituted monoazo dyes for wool–polyester blends

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Received 28 July 1999; accepted 24 August 1999

Abstract

The synthesis of a series of monoazo disperse dyes containing a carboxy group is described. The dyes were applied to polyester, wool and wool–polyester blend fabrics and their dyeing and fastness properties evaluated. The levelling and fastness properties of all dyed samples meet commercial requirements. The effects of the carboxy group on the colour, dyeing and fastness properties of the dyes are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carboxy-substituted monoazo dyes; Wool–polyester blends; Hydrophobicity; Fibre-selective effects

1. Introduction

Dyes with carboxy groups were seldom used as acid dyes or disperse dyes because of their moderate aqueous solubility and hydrophobicity [1]. However, large parts of the wool fibres are hydrophobic, so that it is possible for the dye molecule to reduce its potential energy by being adsorbed with its hydrophobic parts on the hydrophobic portions of the wool. Hence, the most important factor determining the affinity for wool fibres could be the hydrophobic nature of the dye molecule [2]. Early studies of the affinity of acid dyes for wool revealed that an additional sulphonic group reduced the affinity by about 1 kcal/mol, and the affinity increased by about −0.4 kcal per methylene group [2–4]. Replacement of the acetyl group of *N*-acetyl-H-acid by other *N*-acyl residues decreases the water solubility of the corresponding dyes and increases the affinity for protein fibres in the sequence acetyl > *n*-butyryl > benzoyl∼*p*-tosyl > *p*-(*t*-butyl) benzol ∼ capryl [5]. Comparing the affinity of a series of substituted azo acid dyes shows clearly that the molecular weight is an important factor in determining the affinity for wool and that the nature and position of the substituent is of minor importance, viz. higher molecular weight and higher affinity [6].

In contrast to dyes with sulphonic groups, the water-solubilizing and fibre-selective effects of dyes with carboxy groups are weak. They dye wool from slightly acid baths, the wool being unimpaired with excellent levelling and very good wet fastness properties [7]. Systematic studies of the relationship between disperse dye structure and levelling properties on the polyester fibre have shown that, in general, levelling tends to decrease as molecular size increases. Molecular size is not the only relevant factor, however, because disperse dyes with significant aqueous solubility show better migration properties than less soluble dyes of

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PII: S0143-7208(99)00081-9

similar molecular size [8]. Hence, dyes with the carboxy group could dye both wool and polyester fibres with excellent levelling and very good wet fastness properties.

Wool–polyester blend fabrics have many superior properties over pure wool fabrics for dressing. Because of the vastly different nature of wool and polyester, two classes of dyes are employed in a two-bath process, or together in a single bath containing some auxiliaries. Time- and cost-saving is the main advantage of the single bath process for dyeing wool–polyester blends. Two significant disadvantages of this process are the staining of the wool component by disperse dyes, and proportions of the two dyes varying by the ratio of the component fibres in the blends. An obvious way to eliminate the above disadvantages is to develop a single dye which exhibits equal affinity for, and high fastness properties on, both fibres of the blends [9,10].

Baumigarte found that wool rapidly adsorbed disperse dyes at low temperatures, and that these dyes were transferred to the polyester as the temperature was raised. The amount of dye remaining on the wool at equilibrium was controlled by the affinity of the dye for polyester fibre [11]. Cheetham also found that, in the case of wool and polyester, the uptake of disperse dye by the wool component reached a maximum at 90°C, but at higher temperatures was rapidly desorbed into the bath, whence it was subsequently absorbed by the polyester component [12]. Wool has a highly ordered bound-water structure, and this strongly bound water could be removed from wool by introducing large amounts of polar compounds into the fibre. Thus, the potentially high affinity of the hydrophobic sites on wool for disperse dyes can then be exploited [13]. Bell and Lewis found that the affinity of wool for disperse dyes was greatly enhanced by treating the fibre with *N*,*N*-dimethylurea, thiodiglycol, propane 1,3-diol, acetamide, glycerol or lactic acid [14]. Turner and Chanin, in a study of the distribution of disperse dye between triacetate and polyester, showed that the inclusion of a hydrophilic group in the disperse dye molecule increases the distribution ratio in favour of the polar fibre [15]. Several reports have demonstrated that disperse dyes with suitable groups could dye polyester and wool fibres, but at different depths [16,17]. Stapleton and Waters, who undertook the dyeing behaviour of reactive disperse dyes on wool–polyester blends, found that approximately equal uptake of dye by the two fibres can be achieved if the dye has part-polar and part-nonpolar characteristics [18,19]. In our previous work, we have studied the dyeing behaviour of carboxylanthraquinones and found that two of them dyed wool and polyester fibres to approximately the same depth [7].

The synthesis of a series of disperse dyes with a carboxy group is now reported, together with a study of the dyeability and fastness properties of the dyes on wool, polyester and wool–polyester blend fabrics. The levelling and fastness properties of all dyed samples meet commercial requirements. Four of them were found to dye polyester and wool fibres to approximately the same depth.

2. Experimental

2.1. Carboxylmonoazo dyes

Twenty-seven monoazo dyes were synthesized by conventional methods [20,21]. Relevant data are shown in Table 1.

2.2. General

Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in acetone or *N*,*N*-dimethylformamide (DMF) at a concentration of 5×10^{-5} g/ml. Structure and purity were confirmed by mass (Hitachi M-52), infrared (Hitachi 260-50) and elemental analysis (Perkin–Elmer 240C) (Table 2). The structures of the dyes are shown in Fig. 1.

Dyeing of wool fabrics was carried out in liquor ratio (L.R.) 50:1 at 100°C (pH 5–5.5) for 1 h; the samples were then cooled to room temperature and washed with an aqueous solution of detergent (2 g/l) at 50°C for 20 min. Dyeing of polyester fabrics was carried out with biphenyl carrier at 100°C (L.R. 50:1, pH 5–5.5) for 1 h, and the dyed samples were washed with an aq. solution of 10 ml/1 32.5% Na_2CO_3 and 5 g/l $Na_2S_2O_4$, at 70°C

Table 1
Synthesis and characterisation data of dyes

Dye 1		1° arom.amine (0.025 mol)	Coupler (0.025 mol)	m.p. (°C)
I.1	2-COOH	2-Aminobenzoic acid (3.425 g)	Diphenylamine (3.625 g)	210–213
I.2	3-COOH	3-Aminobenzoic acid (3.425 g)	Diphenylamine (3.625 g)	213–215
I.3	4-COOH	4-Aminobenzoic acid (3.425 g)	Diphenylamine (3.625 g)	216–218
II.1	2-COOH	2-Aminobenzoic acid (3.425 g)	2-Phenylphenol (3.650 g)	245–247
II.2	3-COOH	3-Aminobenzoic acid (3.425 g)	2-Phenylphenol (3.650 g)	241–242
II.3	4-COOH	4-Aminobenzoic acid (3.425 g)	2-Phenylphenol (3.650 g)	208–209
III.1	2-COOH	2-Aminobenzoic acid (3.425 g)	2-Hydroxy-3-naphthanilide (6.5 83 g)	335–336
III.2	3-COOH	3-Aminobenzoic acid (3.425 g)	2-Hydroxy-3-naphthanilide (6.5 83 g)	216–218
III.3	4-COOH	4-Aminobenzoic acid (3.425 g)	2-Hydroxy-3-naphthanilide (6.583 g)	318–320
IV.1	2-COOH	2-Aminobenzoic acid (3.425 g)	7-Methoxy-2-naphthol (4.355 g)	277–279
IV.2	3-COOH	3-Aminobenzoic acid (3.425 g)	7-Methoxy-2-naphthol (4.355 g)	247–248
IV.3	4-COOH	4-Aminobenzoic acid (3.425 g)	7-Methoxy-2-naphthol (4.355 g)	302–303
V.1	2-COOH	2-Aminobenzoic acid (3.425 g)	2,7-Dihydroxynaphthalene (4.004 g)	275–277
V.2	3-COOH	3-Aminobenzoic acid (3.425 g)	2,7-Dihydroxynaphthalene (4.004 g)	273–275
V.3	4-COOH	4-Aminobenzoic acid (3.425 g)	2,7-Dihydroxynaphthalene (4.004 g)	300–301
VI.1	2-COOH	2-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethylacetyloxy)amino-4-methoxyacetanilide (8.800 g)	231–233
VI.2	3-COOH	3-Aminobenzoic acid (3.425 g	3-(*N,N*-di-ethylacetyloxy)amino-4-methoxyacetanilide (8.800 g)	222–224
VI.3	4-COOH	4-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethylacetyloxy)amino-4-methoxyacetanilide (8.800 g)	138–140
VI.4	$4-NO_2$	4-Nitroaniline (3.450 g)	3-(*N,N*-di-ethylacetyloxy)amino-4-methoxyacetanilide (8.800 g)	150–152
VII.1	2-COOH	2-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethylacetyloxy)amino-acetanilide (8.050 g)	226–228
VII.2	3-COOH	3-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethylacetyloxy)amino-acetanilide (8.050 g)	206–208
VII.3	4-COOH	4-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethylacetyloxy)amino-acetanilide (8.050 g)	188–190
VII.4	$4-NO_2$	4-Nitroaniline (3.450 g)	3-(*N,N*-di-ethylacetyloxy)amino-acetanilide (8.050 g)	154–156
VIII.1	2-COOH	2-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethyl)amino-propionanilide (5.500 g)	242–244
VIII.2	3-COOH	3-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethyl)amino-propionanilide (5.500 g)	190–192
VIII.3	4-COOH	4-Aminobenzoic acid (3.425 g)	3-(*N,N*-di-ethyl)amino-propionanilide (5.500 g)	157–159
VIII.4	$4-NO_2$	4-Nitroaniline (3.450 g)	3-(*N,N*-di-ethyl)amino-propionanilide (5.500 g)	176–178

for 20 min. Dyeing of wool–polyester blends (45/55) was carried out at 100°C (L.R. 50:1, pH 5–5.5) for 1 h by a one bath–one stage process using biphenyl as carrier; the samples were then cooled to room temperature and washed with an aq. solution of detergent (2 g/l) at 50°C for 20 min. The dye uptake was evaluated by extracting the dye from a known weight of dyed material by DMF (polyester) and DMF/formic acid (9/1) (wool and wool–polyester) and determining the absorbance of the solution using Shimadzu UV 240. Dye uptake was calculated from calibration curve of absorbance vs concentration of dye.

The wash fastness was tested according to CNS 1494-A3, similar to AATCC 61-1989-1 A, except that test conditions were replaced by 100 ml liquor (5 g/l detergent and 2 g/l anhydrous Na_2CO_3) at 60 ± 2°C for 30 min. The sublimation and light fastness assessment was carried out as for a previous investigation [22].

3. Results and discussion

3.1. Electronic spectra

Electronic spectra data of the dyes are shown in Table 3. Based on the λ_{max} in acetone, the intramolecular hydrogen bonding of dyes with an *o*-carboxy group produces a larger bathochromic shift than the intermolcular hydrogen bonding of dyes with a *p*-carboxy group, viz. dye I.1 > I.3 > I.2, dye II.1 > II.3 > II.2, etc. However, the influence of dipole–dipole interaction between dyes with a *p*- or *m*-carboxy group and polar solvents (e.g. DMF or DMF/formic acid) on λ_{max} is higher than those of intramolecular hydrogen bonding of dyes with an *o*-carboxy group, viz. dye VI.3 > VI.2 > VI.1, dye VII.3 > VII.2 > VII.1, and dye VIII.3 > VIII.3 > VIII.1 (DMF); and dye VI.2 and VI.3 > VI.1, dye VII.2 and VII.3 > VII.1, and dye VIII.2 and VIII.3 > VIII.1 (DMF/formic acid).

Table 2
Spectroscopic data

Dye	Mass (m/z)	IR^a(cm^{-1}, KBr)	NMR (δ ppm, DMSO$-d_6$)	Element analysis % found (calculated)
I.1	317.1 (M$^+$), 272.1 (M-COOH)$^+$	3390 (b,NH), 1720, 1615, 1559 (C=O), 1550, 1508 (Ar-ring), 126O (C–O)	13.05 (s, 1H, COOH), 8.955 (s, 1H, NH), 7.790–7.151 (m, 13H, aromatic)	C: 71.75 (71.84), H: 4.50 (4.72) N: 13.53 (13.23)
I.2	317.1 (M$^+$), 196.1 (M-C$_6$H$_4$COOH)$^+$	3400 (b,NH), 1720, 1615, 1600 (C=O), 1550, 1510 (Ar-ring), 1260 (C–O)	13.12 (s, 1H, COOH), 8.938 (s, 1H, NH), 8.303–6.997 (m, 13H, aromatic)	C: 72.38 (71.84), H: 5.03 (4.72) N: 13.30 (13.23)
I.3	317.1 (M$^+$), 196.1 (M-C$_6$H$_4$COOH)$^+$	3480 (b, NH), 1710, 1610, (C=O), 1530, 1510 (Ar-ring), 1230 (C–O)	13.04 (s, 1H, COOH), 8.997 (s, 1H, NH), 8.111–7.004 (m, 13H, aromatic)	C: 72.71 (71.84), H: 5.17(4.72) N: 14.70 (13.23)
II.1	318.I (M$^+$), 197.1 (M-C$_6$H$_4$COOH)$^+$	3100 (b, Ar-OH), 1710, 1600 (C=O), 1500 (Ar-ring), 1270 (C–O)	12.944 (b, 1H, COOH), 10.732 (b, 1H, OH), 7.801–7.125 (m, 12H, aromatic)	C: 69.58 (71.92), H: 4.04 (4.10) N: 9.25 (8.83)
II.2	318.1 (M)$^+$, 197.1 (M-C$_6$H$_4$COOH)$^+$	3200 (b, Ar-OH), 1710, 1600, (C=O), 1500 (Ar-ring); 1435, 1270 (C–O)	12.823 (b, 1H, COOH), 10.632 (b, 1H, OH), 7.792–7.129 (m, 12H, aromatic)	C: 72.14 (71.92), H: 4.04 (4.10) N: 8.92 (8.83)
II.3	318.1 (M)$^+$, 197.1 (M-C$_6$H$_4$COOH)$^+$	3100 (b, Ar-OH), 1690, 1610 (C=O), 1515, 1495 (Ar-ring); 1438, 1260 (C–O)	13.082 (b, 1H, COOH), 10.622 (b, 1H, OH), 8.127–7.136 (m, 12H, aromatic)	C: 71.57 (71.92), H: 4,52 (4.10) N: 10.31 (8.83)
III.1	411.2 (M$^+$) 319.1 (M-C$_6$H$_5$N)$^+$	3300, 3100 (b, Ar-OH), 1690, 1605 (C=O), 1500 (Ar-ring), 1250 (C–O) 1660, 1560 (amide)	17.322 (b, 0.75H, OH), 13.034 (b, 1H, COOH), 12.20 (s, 1H, NH), 10.943 (b, 0.25H, OH), 8.752–7.095 (m, 14H, aromatic)	C: 69.0 (70.00), H: 3.75 (4.13) N: 9.04 (10.21)
III.2	411.2 (M$^+$), 29.1 (M-C$_6$H$_5$CONH)$^+$	3300, 3100 (b, Ar-OH), 1700, 1630, 1605 (C=O), 1505 (Ar-ring), 1255, (C–O) 1645, 1560 (amide)	12.934 (b, 1H, COOH), 11.251 (s, 1H, NH), 10.601 (s, 1H, OH), 8.741–7.096 (m, 14H, aromatic)	C: 73.54 (70.00), H: 4.95 (4.13) N: 8.43 (10.21)
III.3	411.2 (M$^+$), 319.1 (M-C$_6$H$_5$N)$^+$	3300, 3100 (b,Ar-OH), 1730, 1620, 1610 (C=O), 1500 (Ar-ring), 1270 (C–O), 1680, 1560 (amide)	16.030 (s, 1H, OH), 13.104 (b, 1H, COOH), 11.162 (d, 1H, NH), 10.579 (s, 1H, OH), 8.775–7.098 (m, 14H, aromatic)	C: 69.51 (70.00), H: 4.01 (4.13) N: 9.65 (10.21)
IV.1	322.1 (M$^+$), 289.1 (M-CH$_3$-H$_2$O)$^+$	3100 (b, Ar-OH), 2580 (OCH$_3$), 1700, 1620 (C = O), 1500 (Ar-ring), 1260 (C–O)	16.384 (s, 1H, OH), 13.405 (b, 1H, COOH), 8.294–6.431 (m, 9H, aromatic), 3.909 (s, 3H, OCH$_3$)	C: 66.34 (67.01) H: 4.21 (4.34) N: 8.62 (8.68)
IV.2	322.1 (M$^+$), 291.1 (M-OCH$_3$)$^+$	3100 (b, Ar-OH), 2580 (OCH$_3$), 1700, 1620 (C=O), 1620, 1520 (Ar-ring), 1260 (C–O)	15.610 (s, 1H, OH), 13.085 (b, 1H, COOH), 8.263–6.671 (m, 9H, aromatic), 3.906 (s, 3H, OCH$_3$)	C: 67.39 (67.01), H: 4.27 (4.34) N: 8.73 (8.68)
IV.3	322.1 (M$^+$), 291 (M-OCH$_3$)$^+$	3050 (b, Ar-OH), 2800 (OCH$_3$), 1705, 1630, 1610 (C=O), 1520 (Ar-ring), 1260 (C–O)	15.942 (s, 1H, OH), 12.782 (b, 1H, COOH), 8.068–6.578 (m, 9H, aromatic), 3.928 (s, 3H, OCH3)	C: 67.05 (67.01), H: 4.20 (4.34) N: 8.70 (8.68)
V.1	308.1 (M$^+$), 290.1 (M-OH)$^+$	3100 (b, Ar-OH), 1710, 1660, 1620 (C=O), 1500 (Ar-ring), 1250 (C–O)	16.251 (s, 1H, OH), 13.252 (b, 1H, COOH), 10.082 (b, 1H, OH), 8.252–6.598 (m, 9H, aromatic)	C: 65.35 (66.17),H:3.78(3.89) N: 8.84 (9.08)
V.2	308.1 (M$^+$), 187.1 (M-C$_6$H$_4$COOH)$^+$	3200 (b, Ar-OH), 1705, 1620, (C=O), 1510 (Ar-ring), 1260 (C–O)	15.7751 (s, 1H, OH), 13.202 (b, 1H, COOH), 10.185 (s, 1H, OH), 8.294–6.598 (m, 9H, aromatic)	C: 64.38 (66.17), H: 3.69 (3.89) N: 8.40 (9.08)
V.3	308.1 (M$^+$), 263.1 (M-COOH)$^+$	3250 (b, Ar-OH), 1730, 1615, (C=O), 1500 (Ar-ring), 1260 (C–O)	15.933 (s, 1H, OH), 12.973 (b, 1H, COOH), 10.123 (b, 1H, OH), 8.058–6.510 (m, 9H, aromatic)	C: 66.83 (66.17), H: 3.89 (3.89) N: 9.22 (9.08)
VI.1	500.3 (M$^+$), 485.2 (M-CH$_3$)$^+$	3415 (b, Ar-NH), 3288 (b, Ar-OH), 1736, 1662, 1595 (C=O), 1514 (Ar-ring), 1353 (Car-N), 1252, 1200 (Car-OH)	9.832 (s, 1H, i); 7.839 (s, 1H, b); 7.661 (d, 1H, a); 7.536 (d, 1H, d); 7.467 (t, 1H, c); 7.345 (t, 1H, g); 7.130 (s, 1H, f) 4.011 (t, 4H, k); 3.631 (s, 3H, h); 3.443 (t, 4H, l); 2.004 (s, 3H, j); 1.778 (s, 6H, m)	C: 57.5 (57.6), H: 2.37 (5.6), N: 12.21 (11.2), O: 27.93 (25.6)
VI.2	500.3 (M$^+$) 469.2 (M-OCH$_3$)$^+$	3449 (b, Ar-NH), 1736, 1689, 1610 (C=O), 1560, 1533 (Ar-ring), 1385 (Car-N), 1223 (Car-OH)	10.36 (s, 1H, i); 8.106 (d, 2H, a, e); 7.992 (d, 2H, b, c); 7.885 (s, lH, g); 7.178 (s, 1H, f); 4.048 (t, 4H, k); 3.665 (s, 3H, h); 3.498 (t, 4H, 1); 2.04 (s, 3H, j); 1.785 (s, 6H, m)	C: 58.02 (57.6), H: 5.48 (5.6), N: 10.47 (11.2), O: 26.03 (25.6)
VI.3	500.3 (M$^+$), 469.2 (M-OCH$_3$)$^+$	3462 (b, Ar-NH), 1743, 1635 (C=O), 1561, 1474 (Ar-ring), 1380 (Car-N), 1246 (Car-OH)	10.44 (s, 1H, i); 8.401 (d, 2H, a, e); 7.985 (d, 2H, b, c); 7.875 (s, 1H, g); 7.187 (s, 1H); 4.046 (t,4H,k); 3.664 (s, 3H, h); 3.503 (t, 4H, I); 2.035 (s, 3H, j); 1.785 (s, 6H, m)	C: 57.82 (57.6), H: 5.55 (5.60), N: 12.25 (11.2), O: 24.38 (25.6)
VI.4	501.3 (M$^+$), 486.2 (M-CH$_3$)$^+$	3449 (b, Ar-NH), 3355 (b, Ar-OH), 1790, 1622, 1600 (C=O), 1508, 1333 (Ar-NO$_2$ring), 1353 (Car-N), 1180 (Car-OH)	9.86 (s, 1H, i); 8.203 (d, 2H, a, e); 7.960 (d, 2H, b, d); 7.680 (s, IH, g); 7.167 (s, 1H, f); 4.028 (t, 4H, k); 3.647 (s, 3H, h); 3.483 (t, 4H, l); 2.02 (s, 3H, j); 1.777 (s, 6H, m)	C: 55.82 (55.08), H: 4.31 (5.38), N: 13.55 (13.97), O: 26.32 (25.54)
VII.1	470.2 (M$^+$) 455.2 (M-CH$_3$)$^+$	3442 (b, Ar-NH), 3375 (b, Ar-OH), 1736, 1608 (C=O), 1561, 1474 (Ar-ring), 1373 (Car-N), 1226 (Car-OH)	9.187 (s, 1H, i); 8.359 (d, 2H, h); 8.176 (s, 1H, g); 7.790 (d, 1H, a), 7.62 (m, 2H, c, d); 7.514 (t, 1H, b); 6.604 (d, 1H, f); 4.319 (t, 4H, k); 3.789 (t, 4H, 1); 2.303 (s, 3H, f); 2.05 (s, 6H, m);	C: 57.76 (58.72), H: 5.64 (5.53), N: 12.40 (11.91), O: 24.21 (23.82)
VII.2	470.2 (M$^+$), 455.2 (M-CH$_3$)$^+$	3442 (b, Ar-NH), 1736, 1689, 1615 (C=O), 1565, 1535 (Ar-ring), 1380, 1293 (Car-N), 1226 (Car-OH)	9.787 (s, 1H, i); 8.345 (d, 2H, h); 8.175 (s, 1H, g); 7.784 (d, 2H, a); 6.614 (d, 1H-f); 4.422 (t, 4H, k); 3.789 (t, 4H, 1); 2.301 (s, 3H, j); 2.07 (s, 6H, m);	C: 57.98 (58.72), H: 5.38 (5.53), N: 12.04 (11.91), O: 25.60 (23.82)

(Table continued overpage)

Table 2 (*continued*)

Dye	Mass (*m*/*z*)	IR[a] (cm^{-1}, KBr)	NMR (δ ppm, DMSO−d_6)	Element analysis % found (calculated)
VII.3	470.2 (M^+), 455.2 ($M\text{-}CH_3)^+$	3449 (b, Ar-NH), 3280 (b, Ar-OH), 1703, 1608 (C=O), 1514, 1465 (Ar-ring), 1230, 1200 (Car-OH)	10.24, (s, 1H, i); 7.88 (d, 2H, g, e); 7.75 (d, 2H, b, d); 7.705 (s, 1H, g); 7.55 (d, 1H, h); 6.545 (d, 1H, f); 4.06 (t, 4H, k); 3.555 (t, 4H, l); 2.04 (s, 3H, j); 1.82 (s, 6H, m);	C: 58.45 (58.72), H4.57 (5.53), N: 12.14 (11.91), O: 24.84 (23.82)
VII.4	471.2 (M^+), 456.2 ($M\text{-}CH_3)^+$	3442 (b, Ar-NH), 1615 (C=O), 1535 (Ar-ring), 1510, 1326 (Ar-NO_2), 1380, 1259 (Car-N),	10.23 (s, 1H, i); 8.18 (d, 2H, g, e); 7.90 (d, 2H, b, d); 7.715 (s, 1H, g); 7.58 (d, 1H, h); 6.573 (d, 1H, f); 4.07 (t, 4H, k); 3.57 (t, 4H, l); 2.05 (s, 3H, j); 1.82 (s, 6H, m);	C: 54.91 (52.69), H: 4.22 (4.99) N: 16.94 (13.97), O: 23.93 (22.53)
VII.1	368.2 (M^+), 453.2 ($M\text{-}CH_3)^+$	3462 (b, Ar-NH), 3355 (b, Ar-OH), 1709, 1676,1622, 1600 (C=O), 1561, 1474 (Ar-ring), 1353 (Car-N), 1179 (Car-OH)	8.304 (d, 1H, h) 8.076 (s, 1H, g); 7.783 (d, 1H, a); 7.609 (d, 1H, d); 7.575 (t, 1H, c); 7.419 (t, 1H, b); 6.501 (d, 1H, f); 3.529 (q, 4H, l); 2.563 (q, 2H, j); 1.29 (m, 9H, m, k);	C: 64.94 (65.21), H: 6.60 (6.52), N: 15.22 (15.21), O: 13.24 (13.04)
VIII.2	368.2 (M^+), 323.1 ($M\text{-}OC_2H_5)^+$	3489, 3449 (b, Ar-NH), 1725, 1642, 1605 (C=O), 1548, 1516 (Ar-ring), 1380 (Car-N), 1239 (Car-OH)	8.441 (s, 1H, e); 8.157 (s, 1H, g); 8.703 (d, 1H, h); 7.89 (d, 1H, a); 7.78 (d, 1H, c); 7.56 (t, 1H, b); 6.484 (d, 1H, f); 3.489 (q, 4H, 1); 2.533 (q, 2H, j); 1.321 (t, 3H, k); 1.252 (t, 6H, m);	C: 64.94 (65.21), H: 6.45 (6.52), N: 15.15 (15.21), O: 13.46 (13.04)
VIII.3	368.2 (M^+), 323.1 ($M\text{-}OC_2H_5)^+$	3449 (b, Ar-NH), 1696, 1608 (C=O), 1561, 1528, 1461 (Ar-ring), 1367 (Car-N), 1179 (Car-OH)	10.52 (s, 1H, h); 7.89 (d, 2H, a, e); 7.75 (m, 3H, b, d, g); 7.57 (d, 1H, h); 6.435 (d, 1H, f); 3.505 (q, 4H, l); 2.365 (q, 2H, j); 1.005 (m, 9H, m, k);	C: 64.78 (65.21), H: 5.95 (6.52), N: 15.45 (15.21), O: 13.82 (13.04)
VIII.4	369.2 (M^+), 324.1 ($M\text{-}OC_2H_5)^+$	3449 (b, Ar-NH), 1743, 1689, 1622 (C=O), 1582 (Ar-ring), 1508, 1326 (Ar-NO_2), 1310, 1232 (Car-N)	10.42 (s, 1H, i); 8.161 (d, 2H, a, e); 7.827 (d, 2H, b, d); 7.749 (s, 1H, g); 7.579 (d, 1H, h); 6.4565 (d, 1H, f); 3.314 (q, 4H, 1); 2.361 (q, 2H, j); 1.003 (t, 6H, m); 0.967 (t, 3H, k);	C: 59.11 (61.78), H: 5.24 (6.23), N: 17.9 (18.97), O: 19.75 (13.00)

[a] Ar and ar, aromatic; b, broad.

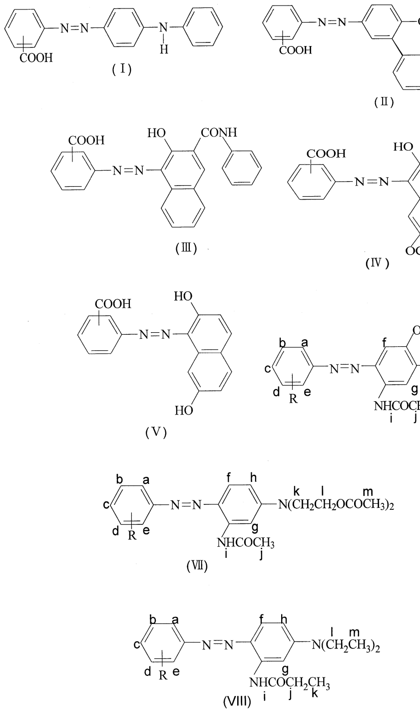

Fig. 1. Structure of dyes.

Table 3
Electronic spectra and aqueous solubility

Dye	λ_{max} (nm) (ε) in acetone	λ_{max} (nm) (ε) in DMF	λ_{max} (nm) (ε) in DMF/formic acid (9/1)	Aqueous solubility (g/l) at 70°C
I.1	485 (31634)			0.254
I.2	428 (26834)			0.275
I.3	432 (33534)			0.273
II.1	433 (2724)			1.000
II.2	420 (6573)			1.080
II.3	426 (2141)			1.050
III. 1	523 (15737)			0.314
III.2	495 (11275)			0.352
III.3	518 (21270)			0.322
IV.1	462 (18469)			0.810
IV.2	448 (16210)			1.030
IV.3	456 (21698)			0.930
V.1	492 (18469)			0.510
V.2	458 (15529)			1.000
V.3	470 (22914)			0.700
VI.1	504	440 (33009)	470 (29705)	0.102
VI.2	439	460 (47415)	485 (51986)	0.110
VI.3	463	481 (54318)	483 (45478)	0.128
VI.4	520	520 (72101)	528 (62786)	0.007
VII.1	491	425 (51110)	439 (32985)	0.123
VII.2	425	460 (69807)	483 (45488)	0.128
VII.3	440	480 (52815)	484 (53369)	0.135
VII.4	512	520 (81207)	530 (60670)	0.009
VIII.1	516	452 (51138)	471 (31706)	0.126
VIII.2	455	462 (57008)	485 (42203)	0.131
VIII.3	472	481 (68311)	484 (45502)	0.143
VIII.4	518	524 (78418)	518 (63069)	0.011

When the $\Delta\lambda$ values (λ_{max}/DMF-λ_{max}/acetone) are studied, it is found that there is a large hypsochromic shift (64–66 nm) in dyes with an *o*-carboxy group and a pronounced bathochromic shift (6–40 nm) in the other dyes. This could be due to the intramolecular hydrogen bonding of dyes with an *o*-carboxy group overriding the stabilisation of the excited states of the dyes by DMF.

Protonation of a 4-aminoazobenzene derivative can occur either at the terminal amino group to give the ammonium tautomer, or at the β-nitrogen atom of the azo group to give the azonium tautomer. Increasing the acidity of the medium increases the proportion of azonium tautomer. Electron-donating groups *meta* to the terminal amino group generally stabilise the azonium tautomer, and the increase in stability is exceptional when the substituent also forms an intramolecular hydrogen-bond with the proton on the azo group. Thus dyes VI–VIII in DMF/formic acid (9/1) exist exclusively in the azonium. form. The azonium tautomer contains a delocalised positive charge and absorbs in the longer wavelength region than the neutral dye [23]. Hence, from Table 3, it is apparent that the λ_{max} values of dyes VI–VIII in DMF/formic acid are higher than those in DMF.

Comparison of λ_{max} values of dyes I–V shows the dyes to be bathochromic in the order III > V > IV > I > II. Whilst 1-phenylazo-2-naphthol derivatives (dyes III, IV and V) exist exclusively in the hydrazone form, 4-aminoazobenzene derivatives (dye I) and 4-hydroxyazobenzene derivatives (dye II) exist exclusively in the azo form. Usually, the hydrazone form is bathochromic compared to the azo form [24]. Comparison of series V with series III shows a pronounced bathochromic shift of 31–48 rim (V→III), and comparison of II with I gives a similar general order (6–52 mn, II→I). This may be due to the better coplanarity of dyes V and II. Comparing λ_{max} values of dye IV with

Table 4
Dyeing properties

o.m.f.	Dye uptake (g/kg polyester fabrics)				Dye uptake (g/kg wool fabrics)				Dye uptake (g/kg wool–polyester blends)			
Dye	0.1%	0.5%	1.0%	1.5%	0.1%	0.5%	1.0%	1.5%	0.1%	0.5%	1.0%	1.5%
I.1	0.52	2.53	5.01	7.33	0.39	1.90	3.72	5.41	0.45	2.24	4.38	6.50
I.2	0.64	3.18	6.32	9.47	0.46	2.15	4.10	6.03	0.53	2.55	5.01	7.48
I.3	0.60	2.92	5.72	8.46	0.41	2.02	3.89	5.76	0.49	2.39	4.65	6.88
II.1	0.72	3.54	7.03	10.35	0.56	2.74	5.38	7.95	0.62	3.07	6.06	9.01
II.2	0.79	3.95	7.81	11.42	0.85	4.25	8.14	11.85	0.83	4.15	8.08	11.70
II.3	0.73	3.63	7.23	10.84	0.75	3.69	6.95	10.23	0.74	3.67	7.14	10.63
III.1	0.70	3.51	6.82	10.12	0.45	2.12	4.20	6.27	0.54	2.65	5.15	7.68
III.2	0.77	3.75	7.32	10.83	0.61	2.85	5.42	7.91	0.67	3.25	6.35	9.30
III.3	0.72	3.56	7.06	10.49	0.48	2.41	4.60	6.72	0.58	2.81	5.56	8.17
IV.1	0.75	3.69	7.32	10.87	0.50	2.43	4.67	6.89	0.60	2.90	5.69	8.49
IV.2	0.89	4.39	8.23	12.35	0.80	3.87	7.43	10.98	0.84	4.19	8.19	12.17
IV.3	0.80	3.82	7.58	11.30	0.76	3.55	6.71	9.93	0.77	3.70	7.18	10.62
V.1	0.28	1.36	2.41	3.52	0.46	2.14	4.36	6.47	0.39	1.93	3.78	5.59
V.2	0.43	1.98	3.73	5.49	0.67	3.11	6.09	8.69	0.58	2.79	5.38	7.96
V.3	0.36	1.76	3.36	4.98	0.60	2.75	5.41	7.98	0.51	2.45	4.72	6.92
VI.1	0.50	2.42	4.86	7.21	0.51	2.05	3.68	5.20	0.51	2.40	4.58	6.63
VI.2	0.60	2.85	5.64	8.46	0.53	2.12	3.84	5.25	0.54	2.58	5.01	7.31
VI.3	0.56	2.75	5.46	8.16	0.59	2.48	4.04	5.30	0.58	2.60	5.05	7.47
VI.4	0.82	3.90	7.66	11.23	0.32	1.50	2.45	3.56	0.53	2.56	4.95	7.23
VII.1	0.70	3.42	6.78	10.06	0.53	2.12	3.84	5.25	0.59	2.93	5.31	7.58
VII.2	0.77	3.75	7.36	11.04	0.62	2.46	4.20	5.36	0.68	3.07	5.73	7.98
VII.3	0.73	3.58	7.05	10.48	0.66	2.53	4.42	5.64	0.69	3.13	5.78	8.04
VII.4	0.89	4.40	8.66	12.92	0.34	1.57	2.47	3.59	0.61	3.04	5.49	7.81
VIII.1	0.81	3.91	7.83	11.52	0.56	2.31	4.12	5.32	0.67	3.15	5.97	8.26
VIII.2	0.90	4.21	8.13	11.92	0.64	2.52	4.35	5.51	0.74	3.62	6.24	8.67
VIII.3	0.85	4.05	8.61	11.78	0.67	2.55	4.50	5.85	0.75	3.64	6.55	8.72
VIII.4	0.91	4.45	8.82	13.10	0.31	1.48	2.31	3.30	0.61	2.87	5.56	8.05

V indicates that strong reinforcement of electron density from the electron-donating hydroxy group to the coupling-component ring gives a pronounced bathochromic shift (IV→V, 10–30 nm).

3.2. Dyeing and fastness properties

All dyes in the eight series gave level coloration on polyester, wool and wool–polyester blend fabrics. Dyes with an *o*-carboxy group, e.g. dyes I.1, II.1, etc., have lower dye-uptake on polyester fabrics than dyes with a *m*- or *p*- carboxy group, viz. dye I.2 > I.3 > I.1, dye II.2 > II.3 > II.1, etc. (Table 4). This might be due to the interaction of the carboxy group with the azo linkage of dyes, hindering the formation of an intermolecular hydrogen-bond between the carboxy group and the azo linkage of dyes and the ester groups of fibres. It can be seen from Table 4 that the dye-uptake of the four shades of dyes I–V on polyester is in the order IV > II > III > I > V. The increase in dye-uptake indicates that dyes with higher hydrophobicity with respect to fibres have higher substantivity than those of other dyes [6]. Comparison of the dye-uptake of dyes VI, VII and VIII on polyester fabrics, viz. VIII > VII > VI, shows that the substantivity decreases with increasing molecular weight, which may be due to easy penetration into the fibre.

The main types of acid dyes used for wool are monosulphonated levelling acid dyes with relative molcular mass values in the 300–500 region, and disulphonated milling acid dyes with relative molcular mass of 600–900. Monosulphonated dyes of relative molcular mass 500–600, that are somewhat more hydrohobic than levelling acid dyes, also

Table 5
Fastness on polyester fabrics

o.m.f.	Sublimation fastness (S.P./C.C)[a]				Wet fastness (S.P/C.C)[a]				Light fastness			
Dye	0.1%	0.5%	1.0%	1.5%	0.1%	0.5%	1.0%	1.5%	0.1%	0.5%	1.0%	1.5%
I.1	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
I.2	5/5	5/4–5	4–5/4–5	4/4–5	5/4–5	5/4–5	4/4–5	4–5/4–5	6	5–6	5–6	5–6
I.3	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
II.1	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	6	6	6	6
II.2	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
II.3	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
III.1	5/5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
III.2	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	6	6	6	6
III.3	5/5	5/4–5	5/4–5	5/4–5	5/5	5/4–5	5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
IV.1	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	6	6	6	6
IV.2	5/5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
IV.3	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
V.1	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	6	6	6	6
V.2	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
V.3	5/5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	6	6	6	6
VI.1	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VI.2	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VI.3	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VI.4	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VII.1	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VII.2	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VII.3	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VII.4	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VIII.1	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VIII.2	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VIII.3	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5
VIII.4	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5/5	5	5	5	5

[a] S.P., staining on polyester; C.C., colour change.

migrate and cover well, but they are a little inferior to milling dyes in wet fastness, and thus are sometimes described as half-milling dyes [25]. The dyes reported here have a weak acidic carboxy group and molcular weights of 300~500, and might therefore be regarded as half-milling dyes. Hence, they dye wool fabrics from an almost neutral dyebath at pH 5.5, which is higher than the pH of the isoelectric point for wool (pH 4.9).

From Table 4, it is apparent that dyes with an *o*-carboxy group, e.g. dye I.1, etc., have lower dye-uptake on wool fabrics than dyes with *m*- and *p*-carboxy groups, viz. I.2 and I.3 > I.1, II.2 and II.3 > II.1, etc. This might be due to the intramolecular hydrogen-bond of the *o*-carboxy group with the azo linkage of dyes weakening the interaction of dyes with the bound water in wool and disrupting less the highly ordered bound-water structure of wool. It can also be seen from Table 4 that the dye-uptake of the four shades of dyes on wool is in the order II > IV > V > III > I > VIII > VII > VI, and that dyes with a nitro group, e.g. dyes VI.4, VII.4 and VIII.4, have lower dye-uptake on wool than dyes with a carboxy group. These observations are consistent with comparisons of the aqueous solubility of the dyes (Table 3). A possible explanation for this could be the same as that mentioned above.

The uptake of all dyes on wool–polyester blend fabrics were found to be between those on wool fabrics and those on polyester fabrics (Table 4). Tables 5 and 6 show that the sublimation, wet and light fastness of all the dyes on polyester and wool fabrics are of an acceptable order to meet commercial requirements. It can be concluded that dyes II.2, II.3, IV.2 and IV.3 colour polyester and wool fabrics to approximately the same depth with good build-up and fastness properties.

Table 6
Fastness on wool fabrics

o.m.f.	Sublimation fastness (S.W./C.C)[a]				Wet fastness (S.W./C.C.)				Light fastness			
Dye	0.1%	0.5%	1.0%	1.5%	0.1%	0.5%	1.0%	1.5%	0.1%	0.5%	1.0%	1.5%
I.1	5/4–5	5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4/4	4/4	4/4	5–6	5–6	5–6	5–6
I.2	5/4–5	5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4/4	4/4	4/4	6	6	6	6
I.3	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
II.1	5/5	5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4/4	4/4	4/4	6	6	6	6
II.2	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
II.3	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
III.1	5/5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
III.2	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	6	6	6	6
III.3	5/5	5/4–5	5/4–5	5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
IV.1	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	6	6	6	6
IV.2	5/5	5/4–5	4–5/4–5	4–5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
IV.3	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5/5	5/4–5	4–5/4–5	4–5/4–5	5–6	5–6	5–6	5–6
V.1	5/4–5	5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4/4	4/4	4/4	5–6	5–6	5–6	5–6
V.2	5/4–5	5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4/4	4/4	4/4	5–6	5–6	5–6	5–6
V.3	5/5	5/4–5	4–5/4–5	4–5/4–5	4–5/4–5	4/4	4/4	4/4	5–6	5–6	5–6	5–6
VI.1	4–5/4–5	4/4–5	4/4–5	4/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	4–5	4–5	4–5	4–5
VI.2	5/4–5	5/4–5	5/4–5	5/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5	5	5	5
VI.3	5/4–5	4–5/4–5	4/4–5	4/4	5/5	5/4–5	4–5/4–5	4/4	4–5	4–5	4–5	4–5
VI.4	4–5/4–5	4/4–5	4/4–5	4/4–5	5/4–5	5/4–5	4–5/4–5	4–5/4–5	5	5	5	5
VII.1	4–5/4–5	4–5/4–5	4–5/4–5	4/4	5/4–5	4–5/4–5	4–5/4–5	4/4	5	5	5	5
VII.2	5/4–5	5/4–5	4–5/4–5	4/4	5/4–5	5/4–5	4–5/4–5	4/4	4–5	4–5	4–5	4–5
VII.3	5/4–5	5/4–5	4–5/4–5	4/4	5/4–5	5/4–5	4–5/4–5	4/4	5	5	5	5
VII.4	4–5/4–5	4–5/4–5	4/4	4/4	5/4–5	5/4–5	4–5/4–5	4–4	4–5	4–5	4–5	4–5
VIII.1	4–5/4–5	4–5/4–5	4/4	4/4	5/5	5/4–5	4–5/4–5	4–5/4–5	4–5	4–5	4–5	4–5
VIII.2	4–5/4–5	4–5/4–5	4/4–5	4/4	5/4–5	5/4–5	4–5/4–5	4/4	4–5	4–5	4–5	4–5
VIII.3	4–5/4–5	4/4–5	4/4	4/4	5/5	5/4–5	4–5/4–5	4/4	4–5	4–5	4–5	4–5
VIII.4	5/5	5/4–5	4–5/4–5	4/4–5	5/5	5/4–5	4–5/4	4/4	4–5	4–5	4–5	4–5

[a] S.W., staining on wool; C.C., colour change.

Acknowledgements

The financial support of this project by National Science Council of Taiwan, ROC is gratefully acknowledged.

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