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Water-repellent Acid Dyes: The Influence of the Perfluorobutamido Group on the Colour, Dyeing and Fastness Properties of 2-(*p*-Alkyl) Phenylazo-1-naphthol Acid Dyes

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ABSTRACT

The synthesis of a series of acid dyes obtained by diazotization of p-*alkylanilines and coupling with perfluorobutamido-1-naphthol sulphonic acid derivatives is described. The effects of alkyl groups and the perfluorobutamido group on the colour, dyeing, water-repellent and fastness properties of the dyes are discussed. The dyes coloured polyamide fibres well. It is concluded that dyes with the perfluorobutamido group have lower substantivity on polyamide fibres. It was also found that substantivity of the dyes on polyamide fibres decreased with increase in the chain length of the alkyl groups. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: water-repellent, acid dyes, perfluorobutamido, alkyl, substantivity, polyamide fibres.

1. INTRODUCTION

For comfort in wear it is necessary for the fabric to be sufficiently porous to allow moist air to circulate. Modern water-repellent finish form a water-repellent layer on the surface of the material without filling up the interstices, e.g. impregnating the fabric with an emulsion of paraffin wax or with a dispersion of aluminium soaps (or zirconium soaps), baking the fabric with stearato chromic chloride, stearamidomethyl pyridinium chloride or methylol stearamide, and curing the fabric with thermosetting silicone resins or perfluoro

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fatty compounds. The use of perfluoro fatty compounds, chromium complexes of perfluoro fatty acids or perfluoroacrylates, can confer water-repellency together with oil-repellency on the fabric [1]. Mares and Oxenrider blended the polyamide polymer melt, which was subsequently extruded into fibre, with monomeric additives containing long chain perfluoroalkyl groups, and found that the additives packed well on the surface of the fibre and orient their fluorocarbon chains away from the surface. They also found that the additives did not change the dyeing properties of the fibre [2]. We report here the preparation of perfluorobutamido derivatives of H acid, M acid and Gamma acid and the synthesis of a series of acid dyes obtained by diazotization of *p*-alkylanilines and coupling with the perfluorobutamido derivatives respectively, together with a study of the effect of a long-chain alkyl group and a perfluorobutamido group on the properties of the resulting acid dyes.

2. EXPERIMENTAL

2.1 2-(4′-Alkyl)-phenylazo-7-amino-1-naphthol-3-sulphonic acids (I)

Four monoazo dyes were synthesised by conventional methods [3]. Relevant data are given in Table 1.

2.2 2-(4′-Alkyl)-phenylazo-7-perfluorobutamido-1-naphthol-3-sulphonic acids (II)

Gamma acid (8.35 g, 0.032 mole) was dissolved at 0–5°C in 50 ml 3% aq. Na_2CO_3. 11.16 g (0.048 mole) Perfluorobutanoyl chloride was added with vigorous stirring, at such a rate that the temperature remained below 5°C. After stirring for about 3 h, complete acetylation of the amino group occurred. 6 g Na_2CO_3 was added, and the mixture was heated and stirred at 90–95°C for 1 h to hydrolyze the *O*-acetyl group [4]. The resulting solution was used directly in the coupling reaction with 0.032 mole benzenediazonium chloride to give 12.8 g (yield 70.68%) of 2-phenylazo-7-perfluorobutamido-1-naphthol-3-sulphonic acid (dye II.1) as a red solid [3].

Dyes II.2–II.4 were synthesized by the above procedure, except that aniline was replaced by the appropriate *p*-alkylaniline. Relevant data are shown in Table 1.

2.3 Other dyes (series III and IV)

The above procedures (Section 2.2) were repeated, except Gamma acid was replaced by H acid (Dyes III) and M acid (Dyes IV) (see Table 1).

2.4 General

All dyes were purified by TLC on Kieselgel 60 (Merck). Structure and purity were established by IR (Hitachi 260-50) and elemental analysis (Perkin–Elmer 240 C) (Table 2). Electronic spectra were recorded on a Shimadzu UV 240 from dye solutions in dimethylformamide (DMF) (Table 3). Dyeing of Nylon 6 was carried out in a liquor ratio of 50:1 at 100°C (pH 5.0–5.5) for 1 h; the samples were then cooled to room temperature and washed with an aqueous solution of detergent (2 g litre^{-1}) at 50°C for 20 min. The dye uptake was evaluated by extracting the dye from a known weight of dyed material with DMF and determining the absorbance of the solution using a Shimadzu

TABLE 1
Synthesis and Characterisation Data of Dyes

Dye	*1° arom. amine (3.000 g)*	*Coupler*	*Mass (yield)*	*Appearance of precipitate*
I.1	aniline (0.032 mole)	Gamma acid (8.352 g, 0.032 mole)	9.726 g (82.50%)	dark red solid
I.2	*p*-(*n*-octyl)aniline (0.015 mole)	Gamma acid (3.811 g, 0.015 mole)	5.814 g (83.48%)	dark red solid
I.3	*p*-(*n*-dodecyl)aniline (0.012 mole)	Gamma acid (3.002 g, 0.012 mole)	4.872 g (79.48%)	dark red solid
I.4.	*p*-(*n*-hexadecyl)-aniline (0.009 mole)	Gamma acid (2.469 g, 0.009 mole)	4.261 g (76.48%)	dark red solid
II.1	aniline (0.032 mole)	Gamma acid[a] (8.352 g, 0.032 mole)	12.807 g (70.68%)	red solid
II.2	*p*-(*n*-octyl)aniline (0.015 mole)	Gamma acid[a] (3.811 g, 0.015 mole)	5.906 g (60.11%)	red solid
II.3	*p*-(*n*-dodecyl)aniline (0.012 mole)	Gamma acid[a] (3.002 g, 0.012 mole)	5.215 g (62.21%)	red solid
II.4	*p*-(*n*-hexadecyl)-aniline (0.009 mole)	Gamma acid[a] (2.469 g, 0.009 mole)	4.554 g (61.32%)	red solid
III.1	aniline (0.032 mole)	H-acid[a] (11.725 g, 0.032 mole)	15.098 g (70.50%)	scarlet solid
III.2	*p*-(*n*-octyl)-aniline (0.015 mole)	H-acid[a] (5.300 g, 0.015 mole)	7.626 g (67.40%)	scarlet solid
III.3	*p*-(*n*-dodecyl)-aniline (0.012 mole)	H-acid[a] (4.175 g, 0.012 mole)	6.235 g (65.24%)	scarlet solid
III.4	*p*-(*n*-hexadecyl)-aniline (0.009 mole)	H-acid[a] (3.434 g, 0.009 mole)	5.634 g (67.14%)	scarlet solid
IV.1	aniline (0.032 mole)	M-acid[a] (8.352 g, 0.032 mole)	12.440 g (68.65%)	orange solid
IV.2	*p*-(*n*-octyl)-aniline (0.015 mole)	M-acid[a] (3.811 g, 0.015 mole)	6.463 g (65.78%)	orange solid
IV.3	*p*-(*n*-dodecyl)-aniline (0.012 mole)	M-acid[a] (3.002 g, 0.012 mole)	5.384 g (64.23%)	orange solid
IV.4	*p*-(*n*-hexadecyl)-aniline (0.009 mole)	M-acid[a] (2.469 g, 0.009 mole)	4.694 g (63.21%)	orange solid

[a] Reacted with 11.160 g perfluoro-butanoyl chloride.

TABLE 2
Spectroscopic Data

Dye	*R*	*IR*[a] *(cm^{-1}/KBr)*	*Elemental analysis (%) found (calculated)*
I.1	H	3410 (b, phenol); 1600,1500 (phenyl); 1180,1060 (SO_3^-)	C: 51.76 (52.60) H: 4.05 (3.29) N: 11.05 (11.51)
I.2	n-C_8H_{17}	3400 (b, phenol); 2930, 2860 (alkyl); 1640, 1500 (phenyl); 1220 (SO_3^-)	C: 60.30 (60.38) H: 5.96 (5.87) N: 8.78 (8.81)
I.3	n-$C_{12}H_{25}$	3440 (b, phenol); 2960, 2860 (alkyl); 1640, 1500 (phenyl); 1220 (SO_3^-)	C: 62.66 (63.04) H: 7.06 (6.75) N: 8.24 (7.88)
I.4	n-$C_{16}H_{33}$	3420 (b, phenol); 2920, 2860 (alkyl); 1630,1492 (phenyl); 1200 (SO_3^-)	C: 65.26 (65.20) H: 7.80 (7.47) N: 7.02 (7.13)
II.1	H	3400 (b, phenol); 1660 (amide); 1600, 1500 (phenyl); 1340 (CF_3), 1230 (CF_2), 1220 (SO_3^-)	C: 42.25 (42.78) H: 2.18 (1.96) N: 7.04 (7.49)
II.2	n-C_8H_{17}	3420 (b, phenol); 2940, 2870 (alkyl); 1670 (amide); 1590,1550 (phenyl); 1350 (CF_3); 1250 (CF_2); 1200 (SO_3^-)	C: 51.02 (49.92) H: 4.86 (4.01) N: 6.18 (6.24)
II.3	n-$C_{12}H_{25}$	3440 (b, phenol); 2940, 2860 (alkyl); 1650 (amide); 1580; 1500 (phenyl); 1350 (CF_3); 1235 (CF_2); 1220 (SO_3^-)	C: 52.58 (52.67) H: 5.16 (4.80) N: 5.68 (5.76)
II.4	n-$C_{16}H_{33}$	3450 (b, phenol); 2920, 2850 (alkyl); 1660 (amide); 1610, 1500 (phenyl); 1310 (CF_3); 1240 (CF_2); 1210 (SO_3^-)	C: 54.48 (55.03) H: 5.87 (5.48) N: 4.89 (5.35)
III.1	H	3450 (b, phenol); 1670 (amide); 1600, 1490 (phenyl); 1320 (CF_3); 1250 (CF_2); 1220 (SO_3^-)	C: 36.19 (36.20) H: 1.52 (1.51) N: 6.33 (6.33)
III.2	n-C_8H_{17}	3460 (b, phenol); 2925, 2850 (alkyl); 1675 (amide); 1600, 1510 (phenyl); 1350 (CF_3); 1230 (CF_2); 1200 (SO_3^-)	C: 42.24 (43.35) H: 3.95 (3.35) N: 6.16 (5.42)
III.3	n-$C_{12}H_{25}$	3440 (b, phenol); 2920, 2860 (alkyl); 1660 (amide); 1610 (phenyl); 1340 (CF_3); 1230 (CF_2); 1210 (SO_3^-)	C: 45.65 (46.21) H: 4.36 (4.09) N: 5.01 (5.05)
III.4	n-$C_{16}H_{33}$	3435 (b, phenol); 2925, 2870 (alkyl); 1650 (amide); 1600 (phenyl); 1330 (CF_3); 1225 (CF_2); 1200 (SO_3^-)	C: 49.13 (48.70) H: 3.89 (3.95) N: 4.77 (4.74)
IV.1	H	3440 (b, phenol); 1660 (amide); 1600, 1515 (phenyl); 1350 (CF_3); 1250 (CF_2); 1220 (SO_3^-)	C: 42.44 (42.78) H: 2.09 (1.96) N: 7.20 (7.49)
IV.2	n-C_8H_{17}	3440 (b, phenol); 2930; 2870 (alkyl); 1670 (amide); 1600, 1510 (phenyl); 1340 (CF_3); 1240 (CF_2); 1215 (SO_3^-)	C: 50.62 (49.93) H: 4.41 (4.01) N: 6.07 (6.24)
IV.3	n-$C_{12}H_{25}$	3430 (b, phenol); 2940, 2860 (alkyl); 1650 (amide); 1590, 1500 (phenyl); 1335 (CF_3); 1230 (CF_2); 1210 (SO_3^-)	C: 51.89 (52.67) H: 5.79 (4.80) N: 5.45 (5.76)
IV.4	n-$C_{16}H_{33}$	3460 (b, phenol); 2920,2850 (alkyl); 1660 (amide); 1600,1510 (phenyl); 1350 (CF_3); 1235 (CF_2); 1215 (SO_3^-)	C: 54.08 (55.03) H: 6.10 (5.48) N: 4.42 (5.35)

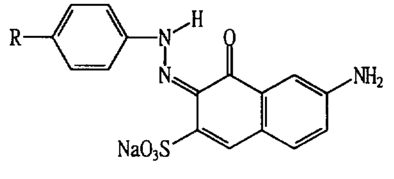
[a] b, broad.

TABLE 3
Colour and TLC Data

Dye	*Rf*[a] *(TLC)*	λ^{nm}_{max} (ε) *in DMF*
I.1	0.824	528 (12775)
I.2	0.830	531 (16814)
I.3	0.845	531 (11939)
I.4	0.858	531 (8541)
II.1	0.831	510 (5610)
II.2	0.835	510 (10600)
II.3	0.849	512 (11664)
II.4	0.862	514 (8164)
III.1	0.811	520 (4243)
III.2	0.815	520 (4960)
III.3	0.821	523 (5318)
III.4	0.825	523 (5544)
IV.1	0.829	518 (7013)
IV.2	0.837	518 (7571)
IV.3	0.854	520 (9295)
IV.4	0.864	520 (7850)

[a] Eluent: *n*-butanol/pyridine/28% aq. ammonia/water = 50/50/20/20 (by volume).

UV 240. Dye uptake was calculated from the calibration curve of absorbance vs concentration of dye. The wash fastness was tested according to CNS 1494-A3, similar to AATCC 61-1989-1A, except that the test conditions were replaced by 100 ml liquor (5 g litre^{-1} detergent and 2 g litre^{-1} anhydrous Na_2CO_3) at 60 ± 2°C for 30 min . The water-repellency was tested according to AATCC 39-1977. The light fastness assessment was carried out as for a previous investigation [5]



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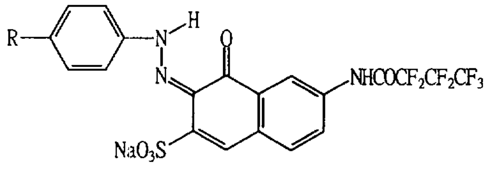

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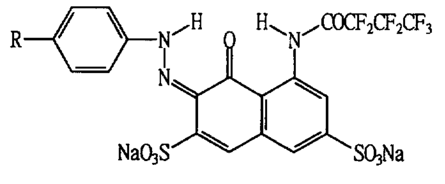

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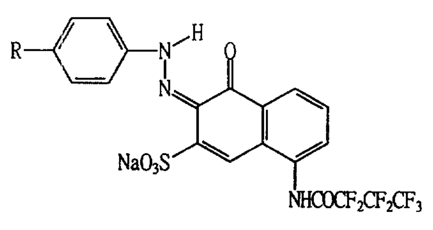
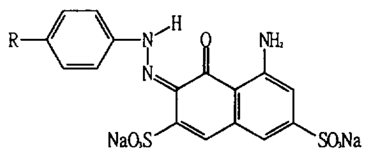


(IV)

3. RESULTS AND DISCUSSION

3.1 Electronic spectra

Two-dimensional ^{1}H, ^{13}C, and ^{15}N NMR spectra of azo dyes derived from J-, H-, and Gamma-acids were investigated by Lycka and Jirman [6]. They concluded that these aminohydroxynaphthalene-sulphonic acids undergo diazo coupling with benzenediazonium chloride ortho to the hydroxy groups under alkaline conditions. They [6] also studied the structures of monoazo dyes derived from J-acid, H-acid, and Gamma-acid by using ^{1}H, ^{13}C, ^{15}N NMR; and concluded that these dyes contained more then 80% of the hydrazone form at 300–600°K in DMSO-d_6. Thus the dyes reported in this paper are presumed to be as 2-phenylazo-1-naphthol derivatives and exist exclusively in the hydrazone form. Electronic-spectra data of the dyes are shown in Table 3. Comparison of series I with series II shows a significant hypsochromic effect of 17–21 nm (I→II), and that between III and IV with the corresponding non-perfluorobutamido analogues (series V and VI) [3] gives a similar general order (10–19 nm, V→III; 10–15 nm, VI→IV). This may be due to the electron-withdrawing effect of the perfluorobutamido group.



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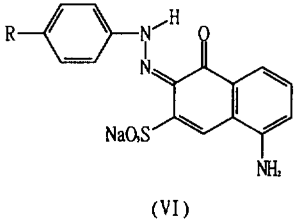

(VI)

R =	H,	C_8H_{17},	$C_{12}H_{25}$,	$C_{16}H_{33}$;	H,	C_8H_{17},	$C_{12}H_{25}$,	$C_{16}H_{33}$
λ^{nm}_{max}	530,	539,	540,	540;	528,	534,	535,	535

The smaller difference in λ_{max} values between series IV and series III (2–3 nm, IV→III) suggests that the weaker stabilizing effect of the peri-perfluorobutamido group in series III, compared with the peri-amino group in series V (3–8 nm) [3].

It can be seen from Table 3 that the λ_{max} values of α-perfluorobutamido derivatives (series IV) are higher than those of the corresponding β-isomers (series II) by 6–8 nm. Introducing long-chain alkyl groups into the diazo component causes a less-pronounced bathochromic effect (2–3 nm) in each series, irrespective of the effect of chain length. This observation is consistent with previous comparisons of analogous 2-(and 1-)phenylazo-1-(and 2-) naphthol acid dyes and possible explanations for it have been disscussed [3].

3.2 Dyeing and fastness properties

All dyes in these four series gave level colouration on polyamide-fibre fabrics. Since most dyes did not dissolve completely in the dyebath, dyeing of Nylon 6 was carried out at 100°C for 1 h and 3.5 h. On the basis of uptake results (Table 4), it can be concluded that three shades of all dyes cannot reach the equilibrium in 1 h. It can be seen from Table 4 that the exhaustion rates of all dyes at 5% o.w.f. (about 22–30%) is much lower than those of 2% (about 40–58%) and those of 1% (about 52–72%). This indicates the build-up properties of all dyes cannot meet commercial requirements. From Table 4, it is apparent that dye-uptake of the three depths of shade of dyes I–IV (1 h and 3.5 h) is in the order I > II > IV > III. The decrease in substantivity can be correlated with the solubility in the dyebath (Table 6) and the oil-repellency of the perfluorobutamido group. Comparing the up-take of 2% dyeings of dyes in series V [3] with III and VI [3] with IV, the oil-repellency of the perfluorobutamido group also decreases the substantivity of dyes by 28.5–42.6% (V→III) and 14.9–15.7% (VI→IV).

Consideration of the dye-uptake of the three shades of dyes in series II, III and IV (1 h and 3.5 h) shows that the substantivity on Nylon 6 decreases with increasing chain length of the alkyl groups, which may be due to lower solubility in the dyebath. In series I, increase in substantivity can be interpreted in terms of the chain length and solubility factors; viz. (a) 1% dyeings:

TABLE 4
Dye-uptake and Light-fastness

o.w.f.	*Dye-uptake (1 h/3.5 h)*[a] $g\,kg^{-1}$ *fibres*			*Light-fastness*		
Dye	*1%*	*2%*	*5%*	*1%*	*2%*	*5%*
I.1	6.50/7.89	11.51/13.89	14.77/16.89	4	4	4
I.2	7.01/8.37	11.62/13.92	15.09/17.12	5	5	5
I.3	7.12/8.51	11.49/13.86	14.69/16.81	6	6	6
I.4	7.11/8.47	11.42/13.65	14.58/16.72	6	6	6
II.1	6.87/7.89	10.15/12.05	12.92/15.19	4	4	4
II.2	6.55/7.53	9.98/11.96	12.79/15.01	4	4	4
II.3	6.35/7.36	9.52/11.20	12.69/14.96	4	4	4
II.4	6.20/7.18	9.12/11.15	12.45/14.56	5	5	5
III.1	5.62/6.89	8.65/10.85	11.53/14.06	4	4	4
III.2	5.57/6.52	8.51/10.59	11.20/13.85	4	4	4
III.3	5.24/6.20	8.29/10.52	11.12/13.69	4	4	4
III.4	5.17/6.15	7.91/10.01	11.05/13.56	5	5	5
IV.1	6.77/7.91	9.65/11.21	12.73/15.28	4	4	4
IV.2	6.44/7.84	9.41/11.12	12.50/14.96	4	4	4
IV.3	6.25/7.52	9.11/11.02	12.42/14.85	4	5	5
IV.4	6.10/7.14	9.01/10.95	12.07/14.23	5	5	5

[a] 1 h/3.5 h: dyeing at 100°C for 1 h and 3.5 h.

TABLE 5
Wet-fastness and Water-repellency

o.w.f. Dye	*Wet-fastness (S.N./S.W./C.C.)*[a]			*Water-repellency (1 h/3.5 h)*[b] *2% o.w.f. (s)*
	1%	*2%*	*5%*	
I.1	4/4/3–4	4/3–4/3–4	3–4/3/3–4	38/58
I.2	4/4/4	3–4/4/4	3–4/3–4/3–4	66/101
I.3	4–5/4–5/4–5	4/4/4	4/4/4	131/206
I.4	5/5/4–5	4–5/4–5/4	4–5/4–5/4	161/259
II.1	4–5/4–5/4	4–5/4/4	4–5/3–4/4	156/232
II.2	4–5/4–5/4–5	4–5/4–5/4–5	4–5/4/4–5	368/580
II.3	5/5/5	5/5/5	4–5/4–5/4–5	395/683
II.4	5/5/5	5/5/5	5/5/5	570/1065
III.1	4/4/4	4/4/3–4	3–4/3–4/3–4	132/172
III.2	5/5/5	4–5/4–5/4–5	4–5/4–5/4–5	152/205
III.3	5/5/5	5/5/5	5/5/5	176/261
III.4	5/5/5	5/5/5	5/5/5	205/334
IV.1	4–5/4–5/4	4–5/4/4	4–5/3–4/4	175/207
IV.2	5/5/5	5/5/5	4–5/4–5/4–5	248/321
IV.3	5/5/5	5/5/5	5/5/5	322/455
IV.4	5/5/5	5/5/5	5/5/5	528/752

[a] S.N., staining on nylon; S.W., staining on wool; C.C., colour change.
[b] 1 h/3.5 h, dyeing at 100°C for 1 h and 3.5 h; 19 s for undyed fabrics.

TABLE 6
Solubility[a] of Dyes in Dyebath at 100°C

Dye	*o.w.f.*		
	1%	*2%*	*5%*
I.1	1	1	1
I.2	1	1	1
I.3	1	1	1
I.4	1	2	2
II.1	1	1	1
II.2	2	2	2
II.3	3	3	3
II.4	4	4	4
III.1	1	2	2
III.2	2	3	3
III.3	3	4	4
III.4	4	5	5
IV.1	1	1	2
IV.2	2	2	3
IV.3	3	3	4
IV.4	4	4	5

[a] 1. Dissolved completely, 2. slight precipitate, 3. appreciable precipitate, 4. apparent precipitate, 5. precipitate deeply.

I.4 > I.3 > I.2 > I.1; (b) 2% dyeings: I.3 > I.2 > I.1 > I.4; (c) 5.0% dyeings: I.3 > I.2 > I.1 > I.4 (Tables 4 and 6).

It can be seen from Table 5 that the wet-fastness of dyes in every series decreases as the depth of dyeing increases, and increases with increasing chain length of the alkyl groups; this is consistent with previous results [3]. Comparison of the light-fastness of dyes I with dyes II, III and IV (Table 4) shows that the higher equilibrium dye uptake in the former results in a higher rating for the light-fastness.

On the basis of the results of water-repellency of dyes in every series at 1, 2 and 5% dyeings (Table 5), the increase in water-repellency can be correlated with the chain-length and dye-uptake factors. Comparison of the water-repellency of dyes II with I, dyes III with V [3] and dyes IV with VI [3] shows that the oil-repellenct perfluorobutamido group conferred water-repellency to the dye molecule.

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