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Monoazo disperse dyes containing ethyleneimine moieties Part 1: Synthesis and application of some monoazo disperse dyes derived from 3-amino-4-methoxyacetanilide

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Abstract

Three aminoazobenzene disperse dyes containing a terminal ethyleneimine group derived from 3-amino-4-methoxyacetanilide were synthesised using Gabriel and Wenker's method. One aminoazobenzene disperse dye containing a terminal *N*-hydroxyethylene group as a hydrolysed form and another azo disperse dye containing a terminal *N*-dihydroxyethylene group were also synthesised. The colour properties of these five dyes in acetone were investigated. As expected, attachment of the ethyleneimine ring to the terminal *N*-atom resulted in hypsochromic shifts and decreasing ϵ_{max} values when compared with analogous compounds containing terminal *N*-hydroxyethyl and *N*,*N*-dihydroxyethyl groups. When one or two chloro substituents were attached on the diazo component of the aziridinyl azo disperse dyes, colour and fastness properties were affected. The rate of hydrolysis of three ethyleneimine dyes was investigated.

Keywords: Aminoazobenzene; Ethyleneimine; Disperse dyes; Gabriel and Wenker's method; Polyester; Nylon 6

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1. Introduction

Attention has been given to the effects of cyclic terminal groups on the spectroscopic [1–5] and dyeing properties [6,7], of monoazo dyes based on 4-aminoazobenzene. According to Hallas and Burkinshaw [6], an improvement of wash fastness on polyamide fabric was found in monoazo disperse dyes containing a terminal aziridinyl ring and this finding was explained by the possibility of self dimerisation or covalent fixation of dye on the fibre [6]. Despite this improved fastness, few papers [6,8–10], have been published concerning the synthesis and properties of such dyes.

Since the higher substantivity of a 3-amino-4-methoxyacetanilide moiety often gives high fastness properties to dyes on hydrophobic fibres as well as deep shades, 3-amino-4-methoxy-acetanilide is widely used as the basis of coupling components in many commercial dyes.

N,β-Hydroxyethylaniline derivatives can be prepared [3,9] via the hydrolysis of chloroethylcarbamates using sodium hydroxide. However, it was

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found that this method could not be employed to synthesise an aziridinyl dye derived from 3-amino-4-methoxyacetanilide since the amide bond of 3-amino-4-methoxyacetoanilide was susceptible to hydrolysis in aqueous sodium hydroxide solution.

In this paper, three aminoazobenzene disperse dyes containing an ethyleneimine residue have been derived from 3-amino-4-methoxyacetanilide using Gabriel and Wenkers' method. One aminoazobenzene disperse dye containing a terminal *N*-dihydroxyethylene group and one monoazo disperse dyes containing a terminal *N*-hydroxyethylene group derived from same compound were synthesised for comparison of fastness properties (Table 2).

This paper details the preparation of ethyleneimine dyes by cyclisation from methanesulphonylethylaniline via Gabriel and Wenker's method using sodium amide.

2. Experimental

All crude products were isolated as solids and purified by a combination of column chromatography and recrystallisation.

2.1. Preparation of intermediates

*2.1.1. Preparation of 3-(*N,β*-hydroxyethyl) amino-4-methoxy acetanilide*

A research sample of 3-amino-4-methoxy acetanilide (98%; O-Young Co. ROK) was acquired. 0.2 mol of 3-amino-4-methoxy acetanilide (36.04 g) was added to water (100 cm^3) and the temperature raised to 70°C with stirring; stirring was continued until a solution was obtained. A mixture of 2-chloroethanol (0.24 mol; 19.32 g) and water (12.9 ml) was added to the aqueous 3-amino-4-methoxy-acetanilide solution. Forty percent of aqueous sodium hydroxide solution was then dropped into the reaction mixture with stirring to adjust the pH to 9–10 at 80°C. The end point of alkylation was determined by the presence of the *N*,*N*′-dihydroxyethylaniline derivative using TLC monitoring. In this work, purification using a combination of column chromatography (ethyl acetate:n-hexane, 5:1) and recrystallisation using acetone was used.

*2.1.2. Preparation of 3-(*N,β,*-methanesulphonylethyl) amino-4-methoxy acetanilide [11]*

First, 0.03 mol (3.04cm^3; 1.5 mol equivalent) of triethylamine was added to a solution of 3-(*N*,β-hydroxyethyl)amino-4-methoxyacetanilide (4.79 g, 0.02 mol) in dichloromethane (500 cm^3) . The mixture was cooled to room temperature with stirring and then a solution of methanesulphonylchloride (0.036 mol; 2.75 cm^3) in dichloromethane (100 cm^3) was added at room temperature. The mixture was then stirred for 1 h at room temperature; any additional amount of ethanesulphonyl chloride needed was determined by frequent use of the reaction liquor. After a further 1 h, the liberated triethylamine hydrochloride salt was filtered off under vacuum and washed with dichloromethane (50 cm^3). The total reaction mixture was washed with water (300 cm^3) using a separating funnel. Removal of dichloromethane was carried out on a rotary evaporator under vacuum. The resultant crude product was used immediately in the coupling reaction. 4.98 g, 78.4% crude yield.

2.2. Preparation of dyes

2.2.1. Diazotisation

$NaNO_2/HCl$ solution was used for the diazotisation of *p*-nitroaniline and 2-chloro-4-nitroaniline. The amine was dissolved by warming in aqueous hydrochloric acid (21%, 3.6 ml per mmol amine). Sodium nitrite (5–10% excess) was added over 10 min at 0–5°C and the whole stirred at this temperature for 30–60 min.

In the case of 2,6-dichloro-4-nitroaniline, nitrosylsulphuric acid was used for the diazotisation; it was prepared by adding sodium nitrite (10% excess) to sulphuric acid (98%, 0.4 ml per mmol amine) at 20–30°C, heating to 60–65°C over 10 min with stirring and maintaining this temperature for up to 30 min to ensure complete dissolution. After allowing the solution to cool, the amine was added over 20–30 min below 5°C and the whole stirred at 0–5°C for 2–4 h. The end point of the diazotisation was determined by checking for the presence of the unreacted aniline using TLC, by sampling the diazotisation mixture after extracting with ethyl acetate. The presence of excess nitrous acid was tested using starch-iodide paper.

2.2.2. Coupling procedure

The appropriate coupling component was dissolved in acetone (20 ml per mmol amine). Addition of the diazonium liquor was made at 0–5°C over 10–20 min and the whole stirred for at least 2 h before diluting or raising the pH to 4.5 (using aqueous NaOH or sodium acetate) prior to filtering and warm water-washing.

2.2.3. Cyclisation procedure [7,10]

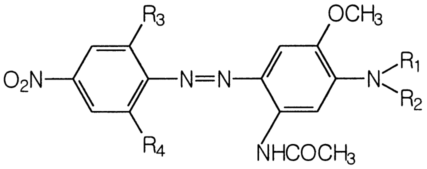
First, 0.012 mol (three molecular equivalent) of sodium amide (or sodium ethoxide) was added to acetonitrile (300 cm^3) and the mixture heated to reflux. The *N*,β-methanesulphonylethyl azo dye (0.004 mol; 1.27 g) was added and reflux continued until cyclisation was completed (the end point of reaction was easily monitored using TLC). Inorganic material was filtered off from the cooled reaction mixture and washed with acetone. The combined organic liquors were evaporated to remove solvent under vacuum. The crude products were isolated and purified using column chromatography on silica gel (Table 1).

2.3. Characterisation of dyes

2.3.1. Melting points

These were determined using a Capillary Melting Point Apparatus (Thomas Co. USA) and also using a Perkin–Elmer DSC-7 (USA). ^{1}H NMR spectra was obtained using a Varian Gemini 300 stectrometer with tetramethylsilane (TMS) as internal standard.

Table 2
Monoazo disperse dyes obtained in the work



Dye	R_1	R_2	R_3	R_4
A-1	$–CH_2CH_2OH$	$–CH_2CH_20H$	–H	–H
C-1	–H	$–CH_2CH_2OH$	–H	–H
B-1	Ethyleneimine ring		–H	–H
B-2			–Cl	–H
B-3			–Cl	–Cl

2.3.2. Determination of λ_{max} and ϵ_{max} values.

The $\lambda_{max}$and ϵ_{max} values of dyes were determined using a Hewlett-Packard 8415A UV-VIS spectrophotometer (USA).

2.4. Hydrolysis of dye dispersion

Eighty millilitres of water was heated to 97°C with stirring, 0.001 g of the appropriate aziridinyl dye (dye B-1, B-2 or B-3) dissolved in 5 ml of acetone was then added dropwise with stirring. After addition was complete, 1 ml samples of the dye liquor were taken at appropriate time intervals. Stirring was continued until reaction was

Table 1
Eluents used for column chromatography

Dye	Eluent
p-nitroaniline→3-(*N*,β-dihydroxyethyl)amino-4-methoxy acetanilide (dye A-1)	1) ethyl acetate: n-hexane 30:70 2) ethyl acetate: n-hexane 60:40
p-nitroaniline→3-(*N*,β-aziridino)amino-4-methoxyacetanilide (dye B-1)	1) toluene: ethyl acetate 90:10 2) toluene: ethyl acetate 80:20
2-chloro-*p*-nitroaniline→3-(*N*,β-aziridino)amino-4-methoxyacetanilide (dye B-2)	1) ethyl acetate: n-hexane 50:50 2) gradually changed to 70:30
2,6-dichloro-*p*-nitroanitine→3-(*N*,β-aziridino)amino-4-methoxyacetanilide (dye B-3)	1) ethyl acetate: n-hexane 40:60 2) 100% ethyl acetate
p-nitroaniline→3-(*N*,β-hydroxyethyl)amino-4-methoxyacetanilide (dye C-1)	1) ethyl acetate: n-hexane 30:70 2) 100% ethyl acetate

complete, during which time the colour of the dye liquor became much darker.

2.4.1. Examination of λ_{max} values

One millilitre of dye/water mixture, taken from dye-water mixture at appropriate time intervals, was diluted with 2.0 ml of acetone and cooled to room temperature. λ_{max} values of the dye/water/acetone mixture were then measured.

2.5. Experimental materials

2.5.1. Polyester fabrics

Commercially available, scoured, knitted conventional (167f 32, 5.2 dtexpf) fabrics were used throughout the work.

2.5.2. Nylon fabrics

Commercially available, scoured, woven conventional (78f 20, 3.9 dtexpf) fabrics were used throughout the work.

2.5.3. Chemicals and auxiliaries

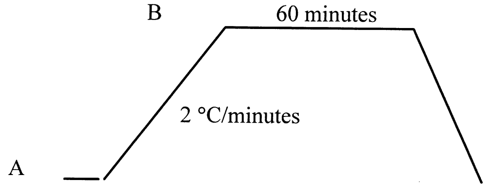
Commercial samples of Demol C (Naphthalenesulphone derivatives; Nippon Kayaku, Japan) was employed as dispersing agent in dyeing through the work. All chemicals used were laboratory grade reagents; sodium hydroxide, sodium acetate, acetic acid (99% w/w) and sulphuric acid (98% w/w) were used to control dyebath pH.

2.5.4. Preparation of dye samples

Ball-mill finishing of the aziridinyl azo disperse dyes in the presence of a dispersing agent was carried out: 1.0 g of dye, 2.0 g of dispersing agent (Demol C) and 100 cm^3 of distilled water were placed in a 250 cm^3 capacity glass jar. The jar was then filled to two thirds capacity with 1 cm diameter ceramic balls and the sealed jar rotated on a laboratory scale ball mill (US Stoneware, USA) for 10 to 24 h at room temperature. After ball mill, the stock dye solution obtained was dried in an oven. The mixture of dried dye/dispersing agent was applied to conventional decitex knitted polyester and woven nylon 6 fabrics. After ball mill finishing, appropriate amount of monazo disperse dyes/dispersing agent mixture was added to the dyebath to give the required concentration of dye.

2.6. Dyeing

Dyeing was carried out in sealed, stainless steel dyepots of 150 ml capacity housed in a laboratory scale dyeing machine (Ahiba AG, Switzerland) using a liquor ratio of 30:1. The appropriate mass of dye/dispersing agent mixture was placed in the dyepot and sufficient appropriate buffer solution and additional dispersing agent (0.5 g/1; Demol C, Nippon Kayaku; Japan) were added to make the volume up to 60 ml.



Dyeing method

A Fabric (2.0 g) added
60°C for conventional polyester fabric
40°C for conventional nylon 6 fabric
B 130°C for conventional polyester fabric
98°C for conventional nylon 6 fabric

2.7. Colour measurement

The reflectance values of the dry, dyed nylon 6 and polyester fabrics were measured using an Macbeth CE-3000 colour measurement system. The colour strength of the dyeings was determined by Kubelka-Munk (KIS) values which were calculated from the reflectance values. Each sample was folded twice to provide a total of four thickness of fabric and each sample was presented so that the measurement was carried out on the same side of the fabric using identical orientation. An average of four measurements per sample was taken.

2.8. Wash fastness assessment

Dry, rinsed and dyed nylon 6 and polyester fabrics were subjected to the ISO/105 C06/C2 wash test and the changes in shade and staining of SDC multifibre test fabric were assessed using the appropriate grey scale.

3. Results and discussion

3.1. ^1H NMR spectrum

Three aziridinyl dyes were purified using column chromatography and the existence of aziridinyl ring was conformed using ^{1}H NMR. The NMR chemical shift (δ) of aziridines was found near to δ 2.2 from TMS as a singlet peak (4 proton) in each case, as expected from Rudesil's work [8].

3.1.1. Diazo components

*3.1.1.1. 3*N-*Hydroxyethylamino-4-methoxyacetanilide*. Crude yield 19.13% (8.54 g). m.p. 109°C. Recrystallisation from acetone gave white needle. Microanalysis found C, 58.7%; H, 7.24%; N, 12.4% (M_r 239.29; $C_{12}H_{19}N_2O_3$ requires C, 58.91%; H, 7.13%; N, 12.49%). ^{1}H NMR (DMSO) δ (ppm) = 9.56 (s, 1 H,–NHCO–), 6.79–6.81 (m, 2 H, arom), 4.78 (m, I H, –N*H*CH$_2$), 3.73 (s, 1 H, –OCH$_3$), 3.59 (s, 2 H, –C*H*$_2$OH), 3.01–3.07 (m, 2 H, –NHC*H*$_2$–), 1.97 (s, 3 H, –COC*H*$_3$).

3.1.1.2. 3-N,N,*Dihydroxyethylamino-4-methoxyacetanilide*. The ^{1}H NMR spectrum of the starting material 3-dihydroxyethylamino-4-methoxyacetanilide was a useful reference for analysing the monoazo dye derived from this compound. m.p. 115°C. Light beige powder. M_r 283.34. ^{1}H NMR (DMSO) δ (ppm) = 9.66 (s, 1 H, –N*H*COCH$_3$–), 7.14–7.16 (m, 2 H, arom), 6.80 (d, 1 H, arom), 4.41 (t, 2 H, –OH), 3.71 (s, 3 H, –OCH$_3$), 3.42–3.44 (m, 4 H, –C*H*$_2$OH), 3.16 (t, 4 H, –C*H*$_2$CH$_2$), 1.97 (s, 3 H, –NHCOC*H*$_3$).

3.1.2. Dihydroxyethyene dyes

p-Nitroaniline→3-(*N*,*N*β-dihyroxyethyl)amino-4-methoxyacetanilide (dye A-1); M_r = 432.45; m.p. 202–203°C,^{1}H NMR (DMSO) δ (ppm) = 8.35 (d, J = 8.9 Hz, 2 H, arom), 8.09 (d, J = 8.9 Hz, 2 H, arom), 7.84 (s, 1 H, arom), 7.32 (s, 1 H, arom), 4.73 (s, 1 H, –OH), 3.80 (s, 3 H, –OCH$_3$), 3.55–3.61 (m, 8 H, (–CH$_2$–)$_4$), 2.20 (s, 3 H, –COCH$_3$).

3.1.3. Hydroxyethylene dyes

p-Nitroaniline→3-(*N*,β-hyroxyethyl)amino-4-methoxyacetanilide (dye C-1); ^{1}H NMR (DMSO) δ (ppm) = 10.04 (s, 1 H, –NHCO–), 8.4 (d, J = 8.8, 2 H, arom), 8.17 (d, J = 8.8, 2 H, arom), 7.84 (s, 1 H, arom), 7.32 (s, 1 H, arom), 3.86 (s, 3 H, –OCH$_3$), 2.18 (s, 7 H, aziridine, –COCH$_3$).

3.1.4. P-*Nitroaniline→3-(*N,β-*methanesulphonylethylene)amino-4-methoxyacetanilide*

M.p. 196°C, ^{1}H NMR (DMSO) δ (ppm) = 10.07 (s, 1 H, –NHCO–), 8.34 (d, J = 8.92, 2 H, arom), 8.07 (d, J = 8.92, 2 H, arom), 7.67 (s, 1 H, arom), 7.31 (s, 1 H, arom), 6.80 (m, 1 H, –N*H*CH$_2$), 4.39–4.43 (m, 2 H, –CH$_2$OSO$_2$), 3.87 (s, 3 H, –OCH$_3$), 3.55–3.87 (m, 2 H, –NHC*H*$_2$–), 3.20 (s, 3 H, –SO$_2$CH$_3$), 2.21 (s, 3 H, –COCH$_3$).

3.1.5. ^1H NMR spectrum of monoazo disperse dyes containing ethyleneimine

The presence of the aziridine moiety was conformed by the singlet peak at δ 2.18 (dye B-1, B-2), 2.22 (dye B-3), disappearance of the multiple peak for secondary amine at δ 6.80.

p-Nitroaniline→3-(*N*,β-aziridino)amino-4-methoxyacetanilide (Dye B-1) m.p. 161°C: M_r = 370.38; ^{1}H NMR (DMSO) δ (ppm) = 10.04 (s, 1 H, –NH CO–), 8.4 (d, J = 8.8, 2 H, arom), 8.17 (d, J = 8.8, 2 H, arom), 7.84 (s, 1 H, arom), 7.32 (s, 1 H, arom), 3.86 (s, 3 H, OCH$_3$), 2.18 (s, 7 H, aziridine, –COCH$_3$).

2-Chloro-*p*-nitroaniline→3-(*N*,β-aziridino)amino-4-methoxyacetanilide (Dye B-2): ^{1}H NMR (DMSO) δ (ppm) = 10.04 (s, 1 H, –NHCO–), 8.49 (s, 1 H, arom), 8.30 (d, J = 7.7, 2 H, arom), 8.10 (d, J = 8.79, 2 H, arom), 7.92 (s, 1 H, arom), 7.33 (s, 1 H, arom), 3.86 (s, 3 H, –OCH$_3$), 2.18 (s, 7 H, aziridine, –COCH$_3$).

2,6-Dichloro-*p*-nitroaniline→3-(*N*,β-aziridino)-amino-4-methoxyacetanilide (Dye B-3): M_r = 439.27; ^{1}H NMR (DMSO) δ (ppm) = 9.78 (s, 1 H, –NHCO–), 8.38 (s, 2 H, arom), 7.79 (s, 1 H, arom), 7.20 (s, 1 H, arom), 3.82 (s, 3 H, –OCH$_3$), 2.22 (s, 7 H, aziridine, –COCH$_3$).

3.2. Physical properties of the dyes

The colour strengths (ϵ_{max}) of the aziridinyl azo dyes B-1, B-2 and B-3 in acetone were 1.80, 1.82

and 0.95×10^4 lmol^{-1}cm^{-1}, respectively, while those of the dihydroxyethyl dye (dye A-1) and hydroxyethyl dye (dye C-1) in acetone were 3.65 and 2.41×10^4 lmol^{-1}cm^{-1}. It was found that the monoazo dyes containing a terminal ethyleneimine ring showed lower tinctorial strength compared with analogous compounds containing terminal hydroxyethyl and dihydroxyethyl groups (Table 3).

In the case of the dihydroxyethyl and *N*-hydroxyethylaminoazobenzene dyes, their 3- dimensional molecular structure shows reasonable planarity with the terminal *N*-dihydroxyethyl and *N*-hydroxyethyl groups. However, in the case of the aziridinyl azo dyes, the aziridinyl group is located in out of plane owing to steric hindrance between substituent (–OCH_3) in the ortho position of the terminal nitrogen atom and the lone pair electrons of the nitrogen atom. Thus, the distorted aziridinyl ring gives a decrease in tinctorial strength (ϵ_{max}).

In the case of dye B-2, the ortho-substituent in the diazo component can give an alternative conformation to relieve hindrance by rotation. Thus, much of the steric effect will not be exerted. However, dye B-3 has two ortho-chloro substituents in the same ring, and such crowding cannot be relieved by rotation and both conformations are hindered. The tinctorial strength (ϵ_{max}) of dye B-3 was 0.95×10^4 lmol^{-1}cm^{-1}, i.e., even lower than that of dyes B-1 and B-2. It produces a large hypsochromic shift and a noticeable reduction in tinctorial strength [12,13] (Fig. 1).

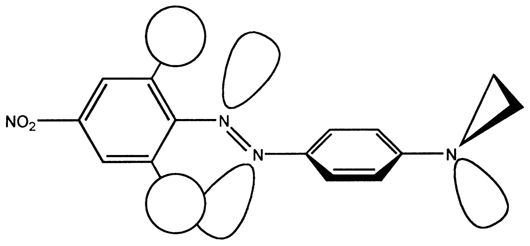
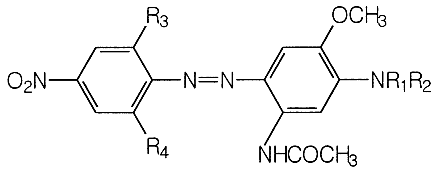


Fig. 1. Possible conformation of dye B-3.

In this work, the 4-*N*,*N*-dihydroxyethylaminoazobenzene dye A-1 (Table 3) in acetone absorbs at 536.38 nm whereas the 4-hydroxyethylaminoazobenzene dye C-1(Table 3) in acetone absorbs at 527.71 nm. These findings demonstrate the bathochromic effect resulting from alkylation of the terminal amino group. When the terminal azirdinyl group is introduced into aminoazobenzene dyes, a hypsochromic shift was observed, compared to 4-*N*,*N*-dihydroxyethyl and *N*-hydroxyethylamino azo disperse dyes derived from *p*-nitroaniline derivatives (B-1, B-2 and B-3 in Table 3) as diazo components displayed λ_{max} 480.88 nm ($R_3=R_4=H$) and 524.38 nm ($R_3=Cl$, $R_4=H$) and 503.53 nm ($R_3=R_4=Cl$). These results show that introducing an ortho chloro substituent into the dye produces a bathochromic shift. However, a second ortho chloro substituent produces a large hypsochromic shift and a great reduction of tinctorial strength.

Table 3
M_r, λ_{max} and ϵ_{max} for dyes in acetone



No.	R_1	R_2	R_3	R_4	M_r	λ_{max} (nm) in acetone	ϵ_{max} in acetone ($\times10^4$ lmom^{-1}cm^{-1})
A-1	CH_2CH_2OH	CH_2CH_2OH	H	H	432.45	536.38	3.65
C-1	H	CH_2CH_2OH	H	H	388.40	527.71	2.41
B-1	Aziridine moiety		H	H	370.38	480.88	1.80
B-2			Cl	H	404.83	524.38	1.82
B-3			Cl	Cl	439.27	503.53	0.95

3.3. The hydrolysis of azo dyes containing ethyleneimine ring

Fig. 1 shows that the variation of λ_{max} of dye B-1 in acetone during refluxing at 97°C, pH 6.0. The λ_{max} of dye B-1 in acetone/water at the beginning of reflux was 450.9 nm, but λ_{max} value increased on continued refluxing, to 524.5, which value was similar to the λ_{max} of dye C-1 (hydrolysed form of dye B-1) in acetone.

The absorbance of dye B-1 increased, giving absorbance value double while the dye was refluxing in water. The bathochromic shift of λ_{max} of dye B-1 may be explained in terms of hydrolysis of the aziridinyl ring [7,10] (Fig. 2).

Whilst the aqueous dispersion of dye B-1 was adjusted to pH 5.0, 6.0, 7.0 and the temperature kept at 97°C with stirring, 2.0 ml samples were taken at appropriate time intervals, diluted with 4.0 ml of acetone and the variation of λ_{max} evaluated.

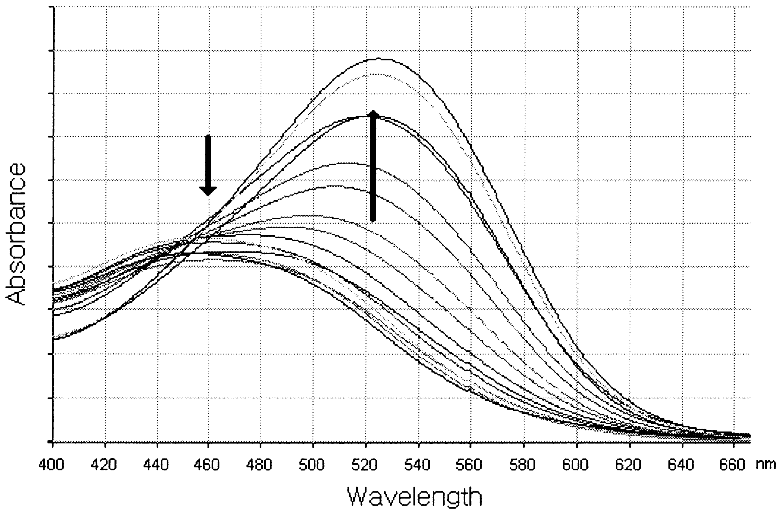


Fig. 2. λ_{max} shift of dye B-1 in acetone.

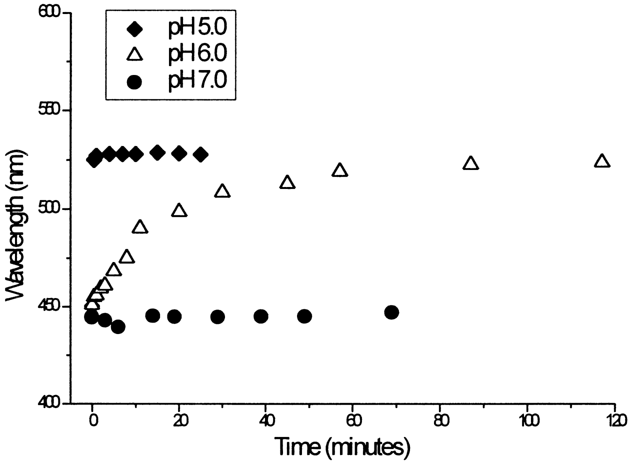


Fig. 3. λ_{max} shift of dye B-1 in water (97°C).

At pH 7.0, no change of the λ_{max} of dye B-1 was observed. However, at pH 6.0, the λ_{max} of B-1 increased gradually through 120 min of refluxing. At pH 5.0, the λ_{max} increased rapidly as soon as the dye/acetone mixture was added into boiling water.

After the aqueous dispersion of dye B-2 was adjusted to pH 5.0 or 6.0, maintaining a temperature of 97°C with stirring, 2.0 ml samples were taken and diluted with acetone.

In the case of pH 6.0, the λ_{max} of B-2 increased slowly, whilst for pH 5.0, λ_{max} increased rapidly as soon as the dye/acetone mixture was added to boiling water (Fig. 4).

In the case of dye B-3, the λ_{max} was not changed at pH 6.0, but at pH 5.0 and pH 4.0, λ_{max} increased rapidly as soon as the dye/acetone mixture was added to boiling water (Fig. 5).

3.4. Conventional decitex woven nylon 6 fabrics

3.4.1. Washfastness

The wash fastness of the washed-off nylon 6 dyeings was carried out according to the ISO/1 05

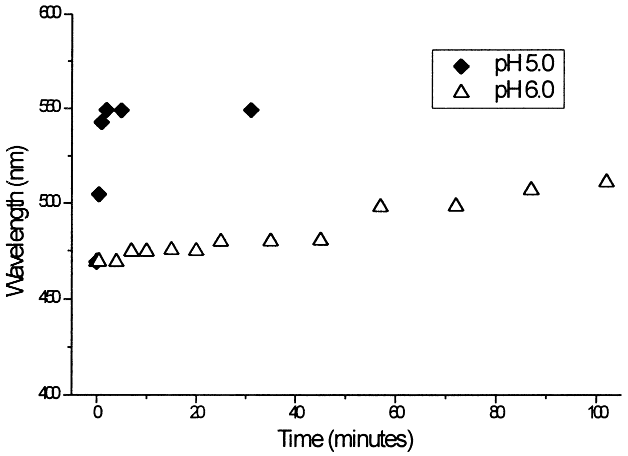


Fig. 4. λ_{max} shift of dye B-2 in water (97°C).

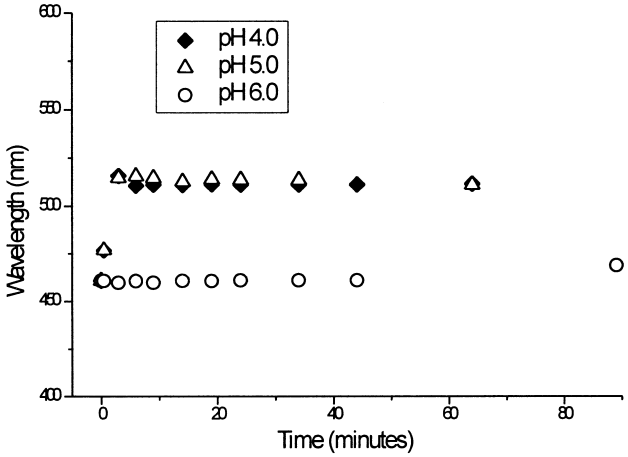


Fig. 5. λ_{max} shift of dye B-3 in water (97°C).

C06-C2 test method. Table 4 shows that the difference in wash fastness observed between the *N*,*N*-dihydroxyethyl dye A-1 and the aziridinyl dye B-1 is very marked with respect to colour change. The wash fastness of dye B-1 was slightly higher than that of the *N*-hydroxyethyl dye C-1with respect to colour change. A higher wash fastness of B-1 compared to C-1 was found in the case of staining of adjacent acetate and nylon 6 fabric.

The washing fastness of dyed nylon 6 fabrics with the aziridinyl azo dyes B-1, B-2 and B-3 is shown in Table 5. It was concluded that, considering the bulkiness and molecular size of the dyes, the wash fastness of B-3 would be higher than that of B-1 and B-2. However, colour staining of B-2 to adjacent acetate, cotton, nylon, wool fabrics was found to be higher, compared with that of B- 1 and B-3.

3.5. Conventional decitex woven polyester fabrics

3.5.1. Effect of pH

The dyeing of conventional decitex polyester fabric with dye B-1 at various pH values was carried out; Fig. 6 shows the variation in colour strength as a function of application pH for 0.05% o.m.f. of dyeings.

Table 4
Colour fastness to washing of dyed nylon 6 fabric

Dye		Dye A-1		Dye B-1		Dye C-1	
% o.m.f.		0.05	0.1	0.05	0.1	0.05	0.1
Colour change		3	3	4/5	4	4	4
Colour staining	Acetate	4	3/4	4	3/4	3	2/3
	Cotton	4/5	4/5	4/5	4/5	4/5	4
	Nylon	3/4	2/3	3/4	2/3	2/3	2
	Polyester	4/5	4/5	4/5	4/5	4/5	4/5
	Acrylic	4/5	4/5	4/5	4/5	4/5	4/5
	Wool	4/5	4	4/5	4/5	4/5	4

Table 5
Colour fastness to washing of dyed nylon 6 fabric

Dye		Dye B-1				Dye B-2				Dye B-3			
% o.m.f.		0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0
Colour change		3/4	3/4	4	4	3/4	3/4	3/4	3/4	1/2	1/2	2	2/3
Colour staining	Acetate	3/4	2/3	2	2	4	3/4	3/4	3/4	4	3/4	3	3
	Cotton	4/5	4	3/4	3	4/5	4/5	4	4	4/5	4	4	4
	Nylon	3	2	1/2	1/2	4	3	2/3	2/3	3/4	3	2	2
	Polyester	4/5	4/5	4	4	4/5	4/5	4	4	4/5	4/5	4	4
	Acrylic	4/5	4/5	4/3	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	Wool	4/5	4	3	3	4/5	4/5	4/5	4/5	4/5	4/5	4	4

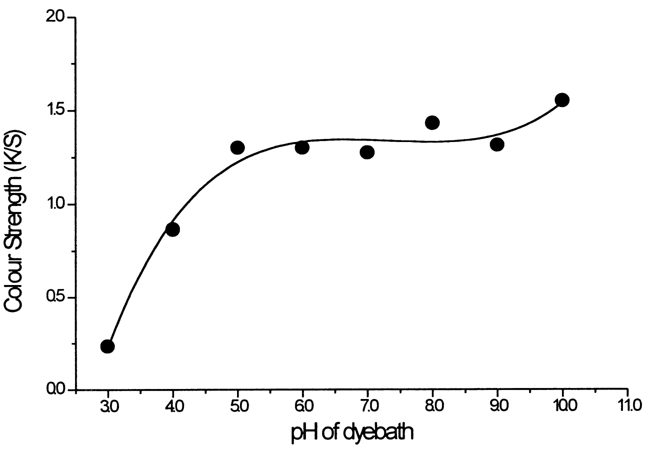


Fig. 6. Effect of pH on the colour strength of conventional decitex polyester fabric dyed with dye B-1 (0.05% omf).

The results of polyester dyeing at various pH revealed that the higher the pH of dyeing, the greater was dye build up on conventional decitex polyester fabrics. This may be due to the higher the pH of dyeing, the lower the extent of hydrolysis of aziridinyl dyes during dyeing.

3.5.2. Washfastness property

The colour yield of aziridinyl disperse dye on polyester fabrics, was increased and the wash fastness was improved with increasing pH of application [7] and similar results were obtained with dye B-1 in this work (Section 3.5.1). However, no improvement of wash fastness was found with increasing p pH of application Table 6.

Table 6
Colour fastness to washing of dyed polyester with aziridinyl azo dye (dye B-1; ISO/105 CO6-C2 method)

pH		5.0	6.0	7.0	8.0	9.0	10.0
Colour change		4/5	4/5	4/5	4/5	4/5	4/5
	Acetate	4/5	4/5	4/5	4/5	4/5	4/5
Colour staining	Cotton	4/5	4/5	4/5	4/5	4/5	4/5
	Nylon	4/5	4/5	4/5	4/5	4/5	4/5
	Polyester	4/5	4/5	4/5	4/5	4/5	4/5
	Acrylic	4/5	4/5	4/5	4/5	4/5	4/5
	Wool	4/5	4/5	4/5	4/5	4/5	4/5

The washing fastness of dyes A-1, B-1 and C-1 are shown in Table 7. No difference in the wash fastness of the *N*,*N*-dihydroxyethyl dye A-1, the aziridinyl dye (B-1) and the *N*-hydroxyethyl dye (C-1) was found with respect to colour change. The wash fastness of dye B-1 was higher than that of its hydrolysed counterpart (dye C-1), but lower than that of dye A-1 in the case of staining of adjacent fabric at higher dye concentration.

While dyeing proceeded, some aziridinyl dye will be hydrolysed and thus the polyester fabric will be dyed with the aziridinyl dye as well as with the hydrolysed dye. The hydroxyethyl type dye, i.e. hydrolysed dye, has already been shown to have much lower wash fastness. If it had been possible to completely avoid hydrolysis of the aziridinyl dye during dyeing, it could be anticipated that the

Table 7
Colour fastness to washing of dyed polyester fabrics (ISOCO6/C2)

Dye		Dye A-1				Dye B-1				Dye C-1			
% o.m.f.		0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0
Colour change		4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	Acetate	4/5	4/5	4/5	4/5	4/5	4/5	4	4	4/5	4/5	2	1/2
Colour staining	Cotton	4/5	4/5	4/5	4/5	4/5	4	4	4	4/5	4/5	3/4	3
	Nylon	4/5	4/5	4/5	4/5	4/5	4	3	3	4/5	4	1/2	1
	Polyester	4/5	4/5	4/5	4/5	4/5	4/5	4	4	4/5	4	4	3/4
	Acrylic	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4
	Wool	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	3	2/3

Table 8
Colour fastness to washing of dyed polyester fabrics with aziridinyl azo disperse dyes (pH 10.0)

		Dye B-1				Dye B-2				Dye B-3			
% o.m.f.		0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0
Colour change		4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	Acetate	4/5	4/5	4	4	4/5	4	4	4	4/5	4/5	4/5	4/5
Colour staining	Cotton	4/5	4	4	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	Nylon	4/5	4	3	3	4/5	4	4	3	4/5	4/5	4/5	4
	Polyester	4/5	4/5	4	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	Acrylic	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
	Wool	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5

fastness to washing of such dyeings would have been much higher than the results obtained in this work.

The washing fastness of the aziridinyl dyes B-1, B-2 and B-3 are shown in Table 8. Dyed polyester fabrics with dye B-3 showed excellent wash fastness, higher than those of B-1 and B-2. The wash fastness of B-2 was higher than that of B-1 in the case of staining of cotton, nylon and polyester adjacent fabrics. These results may be attributed to the difference in bulkiness and molecular size of dyes B-1, B-2 and B-3.

4. Conclusion

3-*N*-β-Hydroxyethylamino-4-methoxyacetanilide was prepared from 3-amino-4-methoxyacetanilide using chloroethanol. Although this method results in low yield of product, it was possible to avoid the hydrolysis of the acetanilide group.

Three monoazo disperse dyes containing an *N*-terminal ethyleneimine ring were synthesised *via* *N*-methanesulphonylethylene derivatives using sodium amide or sodium ethoxide. NMR spectra showed a singlet of 4 protons for the aziridine ring at δ 2.18 (dye: B-1, B-2) or, δ 2.22 (dye B-3).

The tinctorial strength of the dye containing a terminal aziridine group (dye B-1) was much lower than that of analogous dyes containing terminal *N*,*N*-dihydroxyethyl (dye A-1) and *N*-hydroxyethyl groups (dye C-1). The visible spectrum of dye B-1 in acetone showed a hypsochromic shift compared to analogous compounds containing *N*-hydroxyethylene or *N*,*N*-dihydroxyethyl groups. Compared with the unsubstituted dye B-1, dye B-3, which has two substituents, displayed a great reduction of tinctorial strength and a hypsochromic shift. However, dye B-2, which has one substituent, showed a bathochromic shift.

In the application of aziridinyl dyes to polyester, it was shown that the application to polyester of the aziridinyl dyes is favoured by high pH values. When the washing fastness of dye A-1 (*N*,*N*-dihydroxyethyl dye), B-1 (aziridinyl dye) and C-1 (*N*-hydroxyethyl dye) on nylon 6 fabrics was compared, dye B-1 showed best results: B-1 > A-1 > C-1

In the case of polyester fabrics, dye A-1 showed the best fastness to washing: A-1 > B-1 > C-1

When the wash fastness of polyester fabrics dyed with aziridinyl dyes B-1, B-2 (one chloro group in the diazo component) and B-3 (two chloro groups) were compared, B-3 showed the best results: B-3 > B-2 > B-1

Investigation of the stability against hydrolysis in aqueous conditions, showed that the stability of dye B-1 was lower than that of dyes B-2 and B-3.

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