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Short Communication

Synthesis of Azo Dyes from 6-Amino-2-methoxyquinoxaline and Their Use as Disperse Dyes for Polyester Fibres

SUMMARY

6-Amino-2-methoxyquinoxaline (5) was synthesised from quinoxal-2-one (1) and used as diazo component as well as coupling component in the synthesis of azo dyes which were applied on polyester fibres as disperse dyes. The spectral properties and evaluation of the dyes are discussed.

1 INTRODUCTION

We have previously reported the use of 6-amino-2-methoxyquinoxaline (**5**) in the synthesis of novel fluorescent whiteners[1] and we now report some azo dyes derived from **5** and their use as disperse dyes for polyester fibres.

Compound **5** was converted to 2-methoxyquinoxal-6-yl diazonium chloride (**6**) and coupled with 2-aminonaphthalene-1-sulphonic acid (Tobias acid) (**7a**) and *N*,*N*-dimethylaniline (**7b**) at acidic pH and with *p*-cresol (**7c**) and 3-methyl-1-*N*-phenylpyrazol-5-one (**7d**) at alkaline pH to give 6-(aryl and hetaryl)azo-2-methoxyquinoxalines **8a**–**8d**.

Additionally, *p*-toluidine (**9a**), *p*-nitroaniline (**9b**) and 4-benzamido-2-methoxy-5-methylaniline (**9c**) were diazotised and coupled with compound **5** at acidic pH to give a further range of dyes, i.e. the 6-amino-5-arylazo-2-methoxyquinoxalines **11a**–**11c**. The aminoazo dye **11a** was also acetylated to give 6-acetamido-5-(4-methylphenyl)azo-2-methoxyquinoxaline (**12**).

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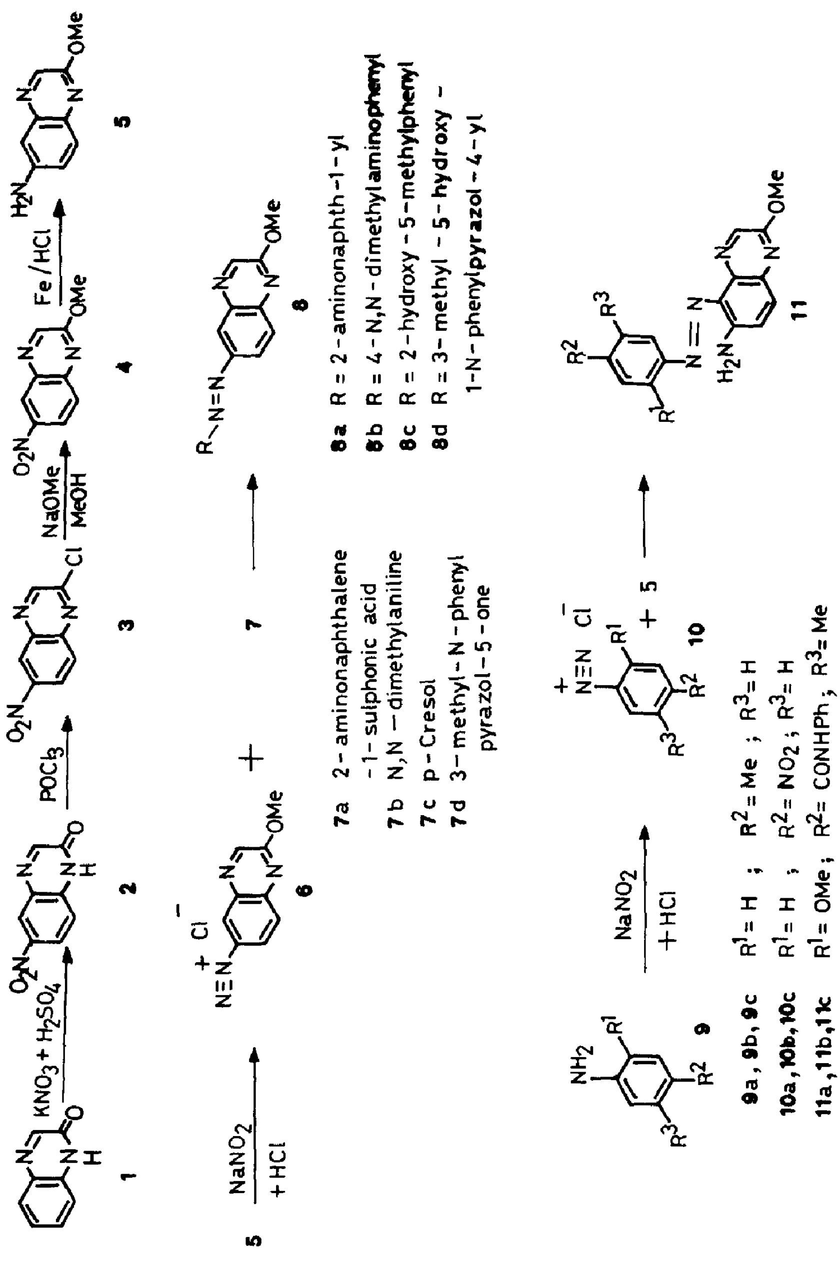
KNO3 + H2SO4
POCl3
NaOMe / MeOH
Fe / HCl
1
2
3
4
5
NaNO2 / + HCl
6
7
8
7a 2-aminonaphthalene -1-sulphonic acid
7b N,N -dimethylaniline
7c p-Cresol
7d 3-methyl-N-phenyl pyrazol-5-one
8a R = 2-aminonaphth-1-yl
8b R = 4-N,N-dimethylaminophenyl
8c R = 2-hydroxy-5-methylphenyl
8d R = 3-methyl -5-hydroxy - 1-N-phenylpyrazol-4-yl
9
10
+ 5
11
9a, 9b, 9c R1 = H ; R2 = Me ; R3 = H
10a, 10b, 10c R1 = H ; R2 = NO2 ; R3 = H
11a, 11b, 11c R1 = OMe ; R2 = CONHPh ; R3 = Me

2 RESULTS AND DISCUSSION

The 6-(aryl and hetaryl)azo-2-methoxyquinoxalines (**8**) and 6-amino-5-arylazo-2-methoxyquinoxalines (**11**) were applied to polyester fibres as disperse dyes. In general, the dyes **8a**–**8d** and **11a**–**11c** gave good colouration of polyester, building up to deep yellow to red hues, brightness of hue being particularly apparent in the dyes **8a**, **8b**, **8d**, **11a** and **11b**. The dyes **8a**–**8d**, derived from the use of compound **5** in the diazo residue, gave dyeings of excellent fastness to light, whereas dyes **11a**–**11d**, based on the use of compound **5** in the coupling residue, had only moderately good lightfastness. The fastness to sublimation of all the dyeings was very good.

Relevant absorption maxima and extinction coefficients of the dyes are given in Table 1.

TABLE 1
Absorption Spectra and Dyeing Properties of Azo Dyes from 6-Amino-2-methoxyquinoxaline

Dye	*Colour on dyed polyester fibres*	*Absorption maximum (nm)*	log ε	*Pick-up*	*Light-fastness*	*Sublimation fastness*
8a	Bright red	497	4·73	3	6	4
8b	Bright golden yellow	471	4·59	2	6	5
8c	Greenish yellow	435	4·47	2	6	5
8d	Bright lemon yellow	458	4·51	2	6	5
11a	Bright orange	483	4·62	2	4	4
11b	Bright orange red	492	4·65	3	4	4
11c	Reddish brown	518	4·15	2	4	4

3 EXPERIMENTAL

All melting points are uncorrected and are in °C. Absorption spectra in DMF solutions were recorded on a Beckman Model 25 spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer Model 397 spectrometer.

3.1 Preparation of starting materials

Commercially available 1-*N*-hydroquinoxal-2-one (**1**) was used. 6-Nitro-1-*N*-hydroquinoxal-2-one (**2**),[2] 6-nitro-2-chloroquinoxaline (**3**),[2] 6-nitro-2-methoxyquinoxaline (**4**)[1] and 6-amino-2-methoxyquinoxaline (**5**)[1] were prepared by known methods.

3.2 6-(2-Aminonaphth-1-yl)azo-2-methoxyquinoxaline (8a)

To a solution of 6-amino-2-methoxyquinoxaline (**5**) (1·75 g, 0·01 mol) in concentrated hydrochloric acid (30%, 6 ml) and water (10 ml) kept at 0–5°C was slowly added a cold solution of sodium nitrite (0·83 g, 0·012 mol) in water (5 ml). The mixture was stirred for 1 h at 0–5°C, excess nitrous acid destroyed by the addition of urea and the diazonium solution added at 0–5°C over 1 h to a solution of 2-aminonaphthalene-1-sulphonic acid (**7a**) (2·23 g, 0·01 mol) in acetic acid (5 ml). The mixture was then brought to pH 4–5 by addition of sodium carbonate and stirred for 8 h at 0–5°C. At the end of the coupling, the pH was adjusted to 7 by addition of sodium acetate and the product filtered, washed with water and dried. Recrystallisation from ethanol gave **8a** as bright red crystals (85%), m.p. 212°. Calculated for $C_{19}H_{15}N_5O$: C, 69·3; H, 4·6; N, 21·3. Found: C, 69·2; H, 4·5; N, 21·0%.

The above procedure was also used to synthesise dye **8b**.

3.3 6-(4-*N*,*N*-Dimethylaminophenyl)azo-2-methoxyquinoxaline (8b)

Crystallised from ethanol as bright golden yellow needles (78%), m.p. > 350°. Calculated for $C_{17}H_{17}N_5O$: C, 66·5; H, 5·5; N, 22·8. Found: C, 66·2; H, 5·3; N, 22·5%.

3.4 6-(2-Hydroxy-5-methylphenyl)azo-2-methoxyquinoxaline (8c)

Compound **5** (1·75 g) was diazotised as above and the diazo liquor added over 1 h to a solution of *p*-cresol (**7c**) (1·08 g, 0·01 mol) in aqueous sodium hydroxide solution (10%, 20 ml) at 0–5°C. The mixture was brought to pH 8–9 by the addition of aqueous sodium hydroxide solution as necessary and stirred for 8 h at 0–5°C. After the coupling, the pH was adjusted to 7 by the addition of dilute hydrochloric acid (5%) and the separated solid filtered, washed with water and dried. Recrystallisation from ethanol gave **8c** as greenish yellow needles (90%), m.p. 268°. Calculated for $C_{16}H_{14}N_4O_2$: C, 65·3; H, 4·8; N, 19·1. Found: C, 65·2; H, 4·2; N, 19·0%.

This procedure was also used to synthesise dye **8d**.

3.5 6-(3-Methyl-5-hydroxy-1-*N*-phenylpyrazol-4-yl)azo-2-methoxyquinoxaline (8d)

Crystallised from ethanol as bright yellow crystals (89%), m.p. 260°. Calculated for $C_{19}H_{15}N_6O_2$: C, 64·5; H, 4·2; N, 23·4. Found: C, 64·2; H, 4·0; N, 23·1%.

3.6 6-Amino-5-(4-methylphenyl)azo-2-methoxyquinoxaline (11a)

To a solution of *p*-toluidine (**9a**) (1·07 g, 0·01 mol) in conc. hydrochloric acid (30%, 6 ml) and water (10 ml) at 0–5°C was added a solution of sodium nitrite (0·83 g, 0·012 mol) in water (5 ml). The mixture was stirred for 1 h at 0–5°C, excess nitrous acid destroyed by the addition of urea and the diazonium solution added at 0–5°C over 1 h to a solution of compound **5** (1·75 g, 0·01 mol) in acetic acid. The mixture was brought to pH 4–5 by the addition of sodium carbonate and stirred for 8 h at 0–5°C. At the end of the coupling sodium acetate was added to bring the pH to 7. The product was filtered, washed with water, dried and recrystallised from ethanol to give **11a** as bright orange crystals (78%), m.p. 230°. Calculated for $C_{16}H_{15}N_5O$: C, 65·5; H, 5·1; N, 23·9. Found: C, 65·3; H, 5·0; N, 23·6%.

This procedure was also used to synthesise dyes **11b** and **11c**.

3.7 6-Amino-5-(4-nitrophenyl)azo-2-methoxyquinoxaline (11b)

Crystallised from ethanol as bright red needles (83%), m.p. 239°. Calculated for $C_{15}H_{12}N_6O_3$: C, 56·6; H, 3·7; N, 25·9. Found: C, 56·2; H, 3·4; N, 25·6%.

3.8 6-Amino-5-(4-benzamido-2-methoxy-5-methylphenyl)azo-2-methoxyquinoxaline (11c)

Crystallised from ethanol as dark brown crystals (80%), m.p. 201°. Calculated for $C_{24}H_{22}N_6O_3$: C, 65·2; H, 5·0; N, 19·0. Found: C, 65·0; H, 4·8; N, 18·9%.

3.9 6-Acetamido-5-(4-methylphenyl)azo-2-methoxyquinoxaline (12)

A mixture of dye **11a** (2·93 g, 0·01 mol) and acetic anhydride (7 ml) was refluxed for 4 h and the liquor added to ice–water (about 100 g). The solid was filtered, washed with water, dried and recrystallised from ethanol to give **12** as pale yellow crystals (65%), m.p. 159°. Calculated for $C_{18}H_{17}N_5O_2$: C, 64·5; H, 5·1; N, 20·9. Found: C, 64·3; H, 5·0; N, 20·7%.

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