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Synthesis and Properties of Monoazo Disperse Dyes Derived from 3-Amino-5-nitro[2,1]benzisothiazole

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SUMMARY

Disperse dyes based on 3-amino-5-nitro[2,1]benzisothiazole have been synthesised, using as coupling components derivatives of some alkyl esters of N-*benzyl*-N-*phenyl*-β-*alanine and* N-(β-*phenylethyl*)-N-*phenyl*-β-*alanine. IR and visible spectra of the dyes were investigated and basic fastness properties were also determined. The lightfastness of the dyes was also studied in relation to mass spectral data.*

1 INTRODUCTION

During investigations of disperse dyes derived from 3-amino-5-nitro-[2,1]benzisothiazole[1,2] we found that the use as coupling components of derivatives of alkyl esters of acrylic acid gave dyes which had good fastness properties on polyester fibres.

In recent years derivatives of *N*-(*β*-cyanoethyl)-*N*-benzylaniline[3–5] and *N*-(*β*-cyanoethyl)-*N*-(*β*-phenylethyl)aniline[4,5] have been utilised in the synthesis of disperse dyes.

We have now prepared new disperse dyes **I** derived from 3-amino-5-nitro[2,1]benzisothiazole using, as coupling components, analogues of the above amines containing the acrylic acid ester group instead of the *β*-cyanoethyl group. The use of such amines was expected to give dyes which would colour polyester fibres in deep blue colours.

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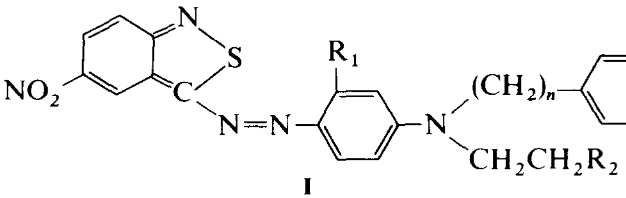


I

Dye	R_1	R_2	n
D-I	H	$COOCH_3$	1
D-II	H	$COOC_2H_5$	1
D-III	CH_3	$COOCH_3$	1
D-IV	CH_3	$COOC_2H_5$	1
D-V	OCH_3	$COOCH_3$	1
D-VI	OCH_3	$COOC_2H_5$	1
D-VII	H	$COOCH_3$	2
D-VIII	H	$COOC_2H_5$	2
D-IX	CH_3	$COOCH_3$	2
D-X	CH_3	$COOC_2H_5$	2

2 EXPERIMENTAL

Dyes of general formula **I** were prepared according to procedures described in the patent literature.[6,7] Diazotised 3-amino-5-nitro[2,1]benzisothiazole was coupled in acetic acid with some alkyl esters of derivatives of *N*-benzyl-*N*-phenyl-*β*-alanine and *N*-(*β*-phenylethyl)-*N*-phenyl-*β*-alanine.

Diazotisation of 3-amino-5-nitro[2,1]benzisothiazole was carried out with nitrosylsulphuric acid in a mixture of sulphuric and orthophosphoric acids. The crude dyes were purified by crystallisation from ethanol until a constant molar extinction coefficient and chromatographic purity were attained (TLC plates: DC–Alufolien Kieselgel 60; solvent: benzene/acetone, 5:2 v/v).

IR spectra were recorded on a Specord 71 IR spectrophotometer (Zeiss, Jena) using KBr pellets.

Visible spectra of the dyes were recorded on a Specord UV–visible spectrophotometer (Zeiss, Jena) in benzene, ethanol and 50% ethanol solutions at concentrations of 2×10^{-5} mol dcm^{-3}. Dyeings and fastness properties were determined according to Polish Standards, which correspond with British Standards.[8] Lightfastness was measured with a Xenotest apparatus (Hanau) and fastness to dry-heat treatment with a Fixotest apparatus (Hanau).

Tristimulus values, used for calculation of the chromaticity coordinates, were measured using a trichromatic colorimeter (Momcolor, Budapest).

TABLE 1
Elemental Analyses of Nitrogen in Dyes
D-II–D-X

Dye	*Nitrogen (%)*	
	Calc.	*Found*
D-II	14·31	14·08
D-III	14·31	14·20
D-IV	13·91	13·80
D-V	13·85	13·62
D-VI	13·80	13·50
D-VII	14·31	14·02
D-VIII	13·91	13·58
D-IX	13·91	13·81
D-X	13·53	13·25

Mass spectra of selected dyes were recorded on spectrometer LKB 2091, using an ionising energy of 70 eV.

2.1 Example of synthesis of the dye D-I

1·95 g (0·01 mol) of 3-amino-5-nitro[2,1]benzisothiazole were dissolved at 30°C in 5 cm^3 orthophosphoric acid (70%). After cooling this solution to 10°C, 10 cm^3 sulphuric acid were added. The diazotisation was carried out with 0·75 g sodium nitrite in 5 cm^3 sulphuric acid for a further 1·5–2 h. The resulting diazonium liquor was added dropwise at 0–5°C into 2·69 g (0·01 mol) of the methyl ester of *N*-benzyl-*N*-phenyl-β-alanine dissolved in 5 cm^3 acetic acid. This mixture was then diluted with water and ice to a volume of 250 cm^3. After 30 min the reaction mixture was neutralised with sodium acetate to pH 3–4 and the coupling reaction continued for a further 4–5 h. The precipitated dye was filtered off, washed with water and dried; 3·7 g of the dye was obtained (77·9% yield).

Elemental analyses: Calc. 14·73% N.
Found 14·52% N.

The elemental analyses of the remaining dyes are given in Table 1.

3 RESULTS AND DISCUSSION

The dyes were obtained by coupling of diazotised 3-amino-5-nitro[2,1]benzisothiazole with the appropriate amines, the synthesis of which we have described previously.[9]

TABLE 2
Infrared Spectra of Dyes **D-I–D-X**

Dye	*Wavenumber of peaks (cm^{-1})*					
D-I	1730 ($\nu_{C=O}$)	1610 ($\nu_{C=C}$)	1520 (ν_{NO_2})	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})
D-II	1740 ($\nu_{C=O}$)	1605 ($\nu_{C=C}$)	1520 (ν_{NO_2})	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})
D-III	1730 ($\nu_{C=O}$)	1605 ($\nu_{C=C}$)	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})	
D-IV	1730 ($\nu_{C=O}$)	1605 ($\nu_{C=C}$)	1530 (ν_{NO_2})	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})
D-V	1740 ($\nu_{C=O}$)	1610 ($\nu_{C=C}$)	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})	
D-VI	1740 ($\nu_{C=O}$)	1605 ($\nu_{C=C}$)	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})	
D-VII	1740 ($\nu_{C=O}$)	1600 ($\nu_{C=C}$)	1520 (ν_{NO_2})	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})
D-VIII	1740 ($\nu_{C=O}$)	1600 ($\nu_{C=C}$)	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})	
D-IX	1730 ($\nu_{C=O}$)	1605 ($\nu_{C=C}$)	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})	
D-X	1730 ($\nu_{C=O}$)	1605 ($\nu_{C=C}$)	1505 ($\nu_{C=N}$)	1340 (ν_{NO_2})	900–700 (δ_{CH})	

The structure of the dyes synthesised was verified by elemental analyses. Additionally their structure was confirmed by mass spectra of selected dyes and by IR spectroscopy (Table 2).

The IR spectra of all dyes show absorption confirming their aromatic structure and the presence of functional groups NO_2, COOR (where R is an alkyl group). All dyes showed an absorption band in the range 1500–1505 cm^{-1}, which is characteristic of stretching vibrations of the C=N bond in isothiazole.[10] Another characteristic of the isothiazole ring band in the range 640–680 cm^{-1} is overlapped by absorption bands attributable to the aromatic ring.

Visible spectra of the dyes were recorded in solvents of different dielectric constants and results are shown in Table 3.

In all solvents (benzene, ethanol, 50% ethanol) the dyes showed one visible absorption band. Using various concentrations of the dyes it was found that the value of the molar extinction coefficient was constant. This is in agreement with our earlier results,[1] in which we demonstrated that similar dyes obtained by using tertiary amines as coupling components did not show aggregation in solution.

The spectroscopic data showed also that the colour of the dyes depended considerably on the polarity of the solvents and that the change from a non-polar to a polar solvent caused a bathochromic shift in λ_{max}. The same effect was also observed on changing the solvent from ethanol to 50% ethanol. This shift is probably due to a solvatochromic effect. Alternative equilibrium states are impossible because isosbestic points are absent in the spectra of the dyes measured in various ratios of ethanol–water solutions. The

TABLE 3
Visible Spectra of Dyes **D-I–D-X**

Dye	*Solvent*					
	Ethanol		*50% Ethanol*		*Benzene*	
	λ_{max} *(nm)*	ε *(dcm³ mol⁻¹ cm⁻¹)*	λ_{max} *(nm)*	ε *(dcm³ mol⁻¹ cm⁻¹)*	λ_{max} *(nm)*	ε *(dcm³ mol⁻¹ cm⁻¹)*
D-I	591	41 200	601	41 200	570	36 000
D-II	591	40 300	600	40 300	571	36 000
D-III	595	40 400	613	40 400	581	38 800
D-IV	595	42 800	612	42 800	582	40 000
D-V	604	38 400	614	38 400	582	32 000
D-VI	606	38 400	612	38 400	582	34 000
D-VII	595	38 200	606	38 200	577	36 000
D-VIII	595	39 200	606	39 200	579	36 800
D-IX	609	36 400	618	36 400	595	33 600
D-X	609	38 400	618	38 400	595	37 600

spectroscopic data also demonstrate that the dyes **D-I–D-VI** containing the benzyl residue show a small hypsochromic effect in comparison with the dyes **D-VII–D-X** containing the β-phenylethyl moiety. The same effect is also observed in ethanolic solution in the case of the dyes **D-I–D-VI** in comparison with analogous dyes containing the methyl or ethyl group instead of the benzyl moiety.[1] This factor is associated with the small electron-attracting character of the benzyl group. When the group is

TABLE 4
Chromaticity Coordinates[a] of Dyes **D-I–D-X**

Dye	*Y*	*x*	*y*
D-I	4·21	0·2215	0·1671
D-II	4·59	0·1970	0·1494
D-III	4·65	0·1940	0·1494
D-IV	5·35	0·2511	0·1544
D-V	4·35	0·1802	0·1561
D-VI	4·42	0·1972	0·1679
D-VII	5·35	0·2215	0·2098
D-VIII	5·00	0·1769	0·1816
D-IX	3·95	0·1879	0·1484
D-X	6·52	0·1995	0·1874

[a] For these measurements the dye application level was 0·3% of weight of fibre (o.w.f.). For dyeings of **D-V**, **D-VI** and **D-IX** the dye application level was 0·4% o.w.f.

TABLE 5
Fastness[a] of Dyeings **D-I–D-X**

Dye	Water			Washing						Perspiration					
				60°C			95°C			Alkaline			Acid		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
D-I	5	5	5	5	5	5	4–5	3–4	5	5	5	5	5	4–5	5
D-II	4–5	5	5	5	5	4–5	4	4	5	4–5	4–5	5	4–5	4–5	5
D-III	5	4–5	5	4–5	5	5	4–5	3–4	4–5	4–5	5	5	5	4–5	5
D-IV	5	5	5	4–5	5	5	4–5	3–4	5	4–5	4–5	5	5	4–5	5
D-V	5	5	5	4	5	4–5	3–4	4	4–5	4–5	4–5	5	4–5	4–5	5
D-VI	4–5	5	5	4	5	5	3–4	3–4	5	4–5	5	5	4–5	5	5
D-VII	4–5	5	5	4	5	5	3–4	4	5	4–5	5	5	4–5	5	5
D-VIII	4–5	4–5	5	4–5	5	5	4	3–4	4–5	5	5	5	4–5	5	5
D-IX	5	5	5	4–5	4–5	5	4–5	3–4	4–5	4–5	5	5	4–5	5	5
D-X	5	5	5	4–5	4–5	5	4	3–4	4–5	5	5	5	5	5	5

Dye	Organic solvent			Rubbing		Fastness to heat treatment 180°C				Lightfastness
	1	2	3	Wet	Dry	1	2	3	4	
D-I	5	5	5	3–4	5	5	5	4–5	4–5	5–6
D-II	4	4–5	5	3–4	4	5	4–5	5	4–5	5–6
D-III	4–5	5	5	3–4	4–5	3–4	4–5	4–5	4–5	5
D-IV	5	5	5	3–4	4–5	4–5	4–5	5	4–5	4–5
D-V	4	4–5	5	4–5	4–5	4–5	4–5	5	4–5	5–6
D-VI	4–5	5	5	3–4	4	4–5	4–5	5	4–5	5
D-VII	4	5	5	3–4	4–5	4–5	4–5	5	4–5	5
D-VIII	5	5	5	3–4	4–5	4–5	4–5	5	4–5	4–5
D-IX	5	5	4–5	3	3–4	4–5	4–5	4–5	4–5	4–5
D-X	5	5	4–5	3–4	3–4	4–5	4–5	5	4–5	5

[a] 1, Change of shade of dyed fabric; 2, staining polyester; 3, staining cotton; 4, staining wool.

separated from the nitrogen atom by a methylene group, as in the dyes **D-VII–D-X**, λ_{max} values are similar to those of the dyes with an ethyl group.[1]

Dyeings of polyester had excellent brightness and high intensity, particularly the dyes **D-I–D-VI**. Quantitative evaluation of the colour of the dyeings was accomplished by calculating the x and y coordinates; the values of these in the CIE (1931) system are given in Table 4.

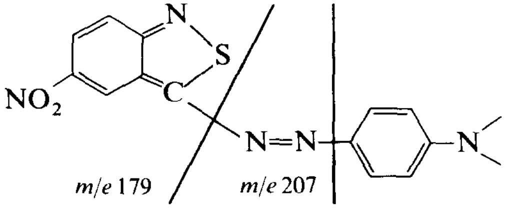
Fastness properties are given in Table 5.

These data demonstrate that the dyes synthesised have very good fastness properties. Lightfastness was particularly good in the dyes derived from the use of derivatives of *N*-benzylaniline as coupling components.

TABLE 6
The Influence of the Fragmentation on the Light Stability

Dye	*Lightfastness*	*m/e* 179 (M^+)	*m/e* 207 (M^+)
D-I	5–6	0·04	0·05
D-VIII	4–5	0·11	0·19
D-IX	4–5	0·16	0·24

According to the method described by Mehta and Peters[11,12] for derivatives of aminoazobenzenes, the lightfastness of dyes **I** was studied with respect to their electron-impact induced fragmentations, using the mass spectra of selected dyes **D-I**, **D-VIII** and **D-IX**, which have different lightfastness. Possible fragmentation of these dyes is shown in formula **II**. Ratios of these fragments with respect to the molecular ion were measured and the results are shown in Table 6.



II

These results clearly show the higher abundance of the fragments *m/e* 179 and *m/e* 207 with respect to the molecular ion in dyes **D-VIII** and **D-IX** in comparison with dye **D-I**. These results thus confirm the applicability of mass spectra fragmentation–lightfastness relationships in these dyes.

4 CONCLUSIONS

The results obtained show that dyes derived from 3-amino-5-nitro[2,1]benzisothiazole can be regarded as commercially competitive compared with more costly anthraquinone dyes. Good application properties and colour give them practical viability for the coloration of polyester fibres.

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