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Synthesis and Properties of some Disperse Dyes Derived from 3-Amino-5-nitro[2,1]benzisothiazole and Alkyl Esters of *N*-Benzyl-*N*-phenyl-*β*-alanine

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ABSTRACT

The synthesis of some disperse dyes from 3-amino-5-nitro[2,1]benzisothiazole and using as coupling components the alkyl esters of N-*benzyl*-N-*phenyl-β-alanine containing different meta or para substituents in the benzyl ring is described. IR,* ^{1}*H-NMR and visible spectra of the dyes are examined and some fastness properties of the dyes also determined.*

1 INTRODUCTION

For some time an effort has been made to replace certain anthraquinone disperse dyes by azo dyes often derived from heterocyclic diazo components.[1,2] Especially useful in this respect are dyes derived from derivatives of 2-aminobenzothiazole, 2-aminothiazole, 2-amino-1,3,4-thiadiazole, 5-aminoisothiazole and 2-aminothiophene as diazo components.

Much interest has been shown in derivatives of 3-amino-5-nitro[2,1]-benzisothiazole, which give deep colours on polyester fibres and which produce deeper dyeings than the corresponding dyes deriving from 2-amino-6-nitrobenzothiazole or 2-amino-5-nitrothiazole.[3]

In a previous paper the synthesis of azo disperse dyes derived from 3-amino-5-nitro[2,1]benzisothiazole and some alkyl esters of *N*-benzyl-*N*-phenyl-*β*-alanine with different substitutents located in the phenyl ring was reported.[4]

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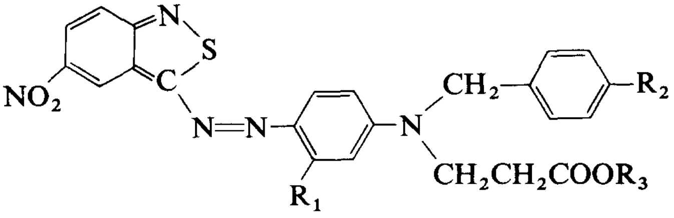
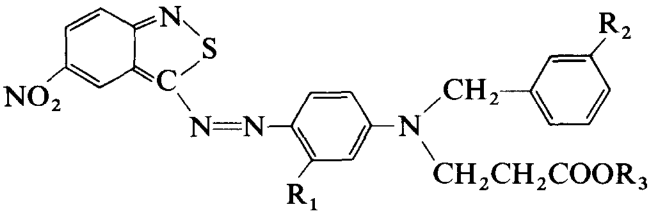
This present paper describes the synthesis and properties of some dyes of general formula **I** and **II** (see below).



I

	R_1	R_2	R_3
a	H	CH_3	CH_3
b	H	CH_3	C_2H_5
c	CH_3	CH_3	CH_3
d	CH_3	CH_3	C_2H_5
e	H	OCH_3	CH_3
f	H	OCH_3	C_2H_5



II

	R_1	R_2	R_3
a	H	NO_2	CH_3
b	H	NO_2	C_2H_5
c	CH_3	NO_2	CH_3
d	CH_3	NO_2	C_2H_5

As coupling components in these dyes, the alkyl esters of *N*-benzyl-*N*-phenyl-β-alanine containing in the benzyl ring various meta or para substituents were used. The synthesis of this type of amine has been previously described.[5]

2 EXPERIMENTAL

Dyes of general formula **I** and **II** were prepared according to procedures described in the patent literature[6,7] by coupling diazotised 3-amino-5-

nitro[2,1]benzisothiazole with some alkyl esters of *N*-benzyl-*N*-phenyl-β-alanine in acetic acid. 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.

^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal reference.

Visible spectra were recorded on a Specord UV-visible spectrophotometer (Zeiss, Jena, Germany) in ethanol solutions at concentrations of $2{\cdot}5 \times 10^{-5}$ mol dcm^{-3}.

Dyeings and fastness properties were determined according to Polish Standards which correspond with British Standards.[8] Lightfastness was measured on Xenotest (Hanau, Germany) and fastness to dry-heat treament on a Fixotest (Hanau, Germany).

2.1 Example of synthesis of the dye Ia

3-amino-5-nitro[2,1]benzisothiazole 1·95 g (0·01 mol) was dissolved at 30°C in 70% orthophosphoric acid 5 cm^3, cooled to 10°C and sulphuric acid 10 cm^3 added. Diazotisation was carried out with sodium nitrite (0·75 g) in sulphuric acid 5 cm^3 for 1·5–2 h. The resulting diazonium salt was added dropwise at 0–5°C to the methyl ester of *N*-*p*-methylbenzyl-*N*-phenyl-β-alanine 2·83 g (0·01 mol) dissolved in acetic acid 5 cm^3. This mixture was then diluted with water and ice to a volume 250 cm^3. After 30 min the reaction mixture was neutralised with sodium acetate to pH = 3–4 and the coupling continued for a further 4–5 h. The precipitate dye was filtered off, washed with water and dried; 4·03 g of the dye was obtained (82·4% yield).

Elemental analyses: calculated 14·31% N; found, 14·20% N.

3 RESULTS AND DISCUSSION

3-Amino-5-nitro[2,1]benzisothiazole was diazotised with nitrosylsulphuric acid in a mixture of sulphuric and orthophosphoric acids and coupled in acetic acid with some alkyl esters of *N*-benzyl-*N*-phenyl-β-alanine to give dyes **I** and **II** in 78–83% yields.

IR spectra of the dyes showed typical aromatic absorption ($\nu_{C=C}$:1600–1610 cm^{-1}, δ_{CH}:700–900 cm^{-1}) and bands for appropriate functional groups ($\nu_{C=O}$:1730–1740 cm^{-1}, ν_{NO_2}:1520–1525 cm^{-1}). An absorption band in the range 1500–1505 cm^{-1} corresponded to vibrations

TABLE 1
Elemental Analyses of Nitrogen in Dyes **I** and **II**

Dye	*Nitrogen (%)*	
	Calculated	*Found*
Ib	13·91	13·73
Ic	13·91	13·62
Id	13·53	13·50
Ie	13·86	13·65
If	13·48	13·33
IIa	16·15	15·95
IIb	15·73	15·68
IIc	15·73	15·62
IId	15·32	15·15

of the C=N bond in the isothiazole[9] ring (a further characteristic of the isothiazole ring band in the range 640–680 cm^{-1} was overlapped by absorption bands attributable to the aromatic ring).

The chemical shifts, multiplicity and integration of the relevant groups of protons in the ^{1}H-NMR spectra (Tables 2 and 3) also provided data in accord with the dye structures.

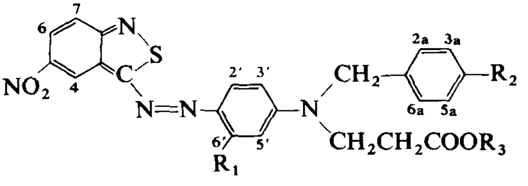
Visible spectra (Table 4) of the dyes recorded in ethanolic solutions showed that the introduction of a methyl substituent ortho to the azo group in the phenyl ring of the coupling component reacted in a bathochromic shift in λ_{max}, but that the position of the λ_{max} was similar for both para alkyl and para alkoxy substitution in the benzyl ring. A hypsochromic effect was apparent for meta-nitro substitution.

Dyeings on polyester of dyes **I** and **II** were blue and had excellent brightness and high intensity. Lightfastness and dry-heat treatment data are given in Table 4. Lightfastness of the dyes was dependent upon the structure of the coupling component and was influenced both by the substituents in the benzyl ring and by the substituents in the phenyl ring. In most cases, the best lightfastness was shown by the dyes containing a meta-nitro or para-alkoxy group in the benzyl ring (**Ie**, **f**, **IIa**, **b**). Dyes with para-alkoxy group (**Ie**, **f**) had better fastness than those with a *para*-methyl group in the benzyl ring (**Ia**, **b**, **c**, **d**). It was also apparent that introduction of a methyl group ortho to the azo linkage of the phenyl ring of the coupling component decreased the lightfastness.

The fastness to dry-heat treatment was generally good to very good, and was not dependent upon the structure of the coupling component. The presence of substituents in the benzyl ring[4] did not improve the fastness to dry-heat treatment.

TABLE 2

^{1}H-NMR Spectral Assignments of Dyes **I**

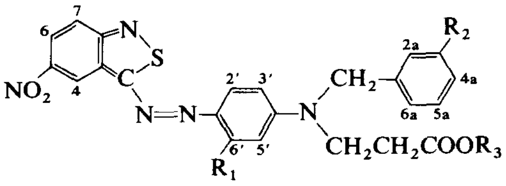


Dye	*^{1}H-NMR (CDCl$_3$, TMS int., δ (ppm), J (Hz))*
Ia	2·30s (3H, Ph—$\underline{\mathrm{CH_3}}$), 2·74t (2H, —$\mathrm{CH_2\underline{CH_2}COOCH_3}$, J = 7·0), 3·76s (3H, —$\mathrm{COO\underline{CH_3}}$), 3·91t (2H, —$\mathrm{N\underline{CH_2}CH_2}$, J = 7·0), 4·71bs (2H, Ph—$\underline{\mathrm{CH_2}}$), 6·75–6·81m (2H, $\underline{3',5'}$), 7·00–7·17m (4H, $\underline{\mathrm{2a, 3a, 5a, 6a}}$), 7·75d (1H, $\underline{7}$, $J_{6,7}$ = 9·7), 7·93–7·97m (2H, $\underline{2', 6'}$), 8·18dd (1H, $\underline{6}$, $J_{6,7}$ = 9·7, $J_{4,6}$ = 2·3), 9·15d (1H, $\underline{4}$, $J_{4,6}$ = 2·3).
Ib	1·25t (3H, —$\mathrm{CH_2\underline{CH_3}}$, J = 7·0), 2·30s (3H, Ph—$\underline{\mathrm{CH_3}}$), 2·75t (2H, —$\mathrm{CH_2\underline{CH_2}COOCH_2CH_3}$, J = 7·0), 3·90t (2H, —$\mathrm{N\underline{CH_2}CH_2}$, J = 7·0), 4·15q (2H, —$\mathrm{\underline{CH_2}CH_3}$, J = 7·0), 4·72bs (2H, Ph—$\underline{\mathrm{CH_2}}$), 6·70–6·87m (2H, $\underline{3', 5'}$), 7·00–7·18m (4H, $\underline{\mathrm{2a, 3a, 5a, 6a}}$), 7·75d (1H, $\underline{7}$, $J_{6,7}$ = 9·7), 7·92–7·98m (2H, $\underline{2', 6'}$) 8·20dd (1H, $\underline{6}$, $J_{6,7}$ = 9·7, $J_{4,6}$ = 2·3), 9·15d (1H, $\underline{4}$, $J_{4,6}$ = 2·3).
Ic	2·34s (3H, Ph—$\underline{\mathrm{CH_3}}$), 2·62s (3H, Ph—$\underline{\mathrm{CH_3}}$), 2·74t (2H, —$\mathrm{CH_2\underline{CH_2}COOCH_3}$, J = 7·0), 3·70s (3H, —$\mathrm{COO\underline{CH_3}}$), 3·89t (2H, —$\mathrm{N\underline{CH_2}CH_2}$, J = 7·0), 4·71bs (2H, Ph—$\underline{\mathrm{CH_2}}$), 6·62–6·66m (2H, $\underline{3', 5'}$), 7·06–7·17m (4H, $\underline{\mathrm{2a, 3a, 5a, 6a}}$), 7·72d (1H, $\underline{7}$, $J_{6,7}$ = 9·7), 7·98d (1H, $\underline{2'}$, $J_{2',3'}$ = 9·2), 8·16dd (1H, $\underline{6}$, $J_{6,7}$ = 9·7, $J_{4,6}$ = 2·3), 9·15d (1H, $\underline{4}$, $J_{4,6}$ = 2·2).
Id	1·25t (3H, —$\mathrm{CH_2\underline{CH_3}}$, J = 7·0), 2·35s (3H, Ph—$\underline{\mathrm{CH_3}}$), 2·70s (3H, Ph—$\underline{\mathrm{CH_3}}$), 2·75t (2H, —$\mathrm{CH_2\underline{CH_2}COOCH_2CH_3}$, J = 7·0), 3·92t (2H, —$\mathrm{N\underline{CH_2}CH_2}$, J = 7·0), 4·10q (2H, —$\mathrm{\underline{CH_2}CH_3}$, J = 7·0), 4·70bs (2H, Ph—$\underline{\mathrm{CH_2}}$), 6·60–6·70m (2H, $\underline{3', 5'}$), 7·05–7·20m (4H, $\underline{\mathrm{2a, 3a, 5a, 6a}}$), 7·70d (1H, $\underline{7}$, $J_{6,7}$ = 9·7), 8·00d (1H, $\underline{2'}$, $J_{2',3'}$ = 9·2), 8·17dd (1H, $\underline{6}$, $J_{6,7}$ = 9·7, $J_{4,6}$ = 2·2), 9·15d (1H, $\underline{4}$, $J_{4,6}$ = 2·2).
Ie	2·74t (3H, —$\mathrm{CH_2\underline{CH_2}COOCH_3}$, J = 7·0), 3·76s, (3H, —$\mathrm{COO\underline{CH_3}}$), 3·79s (3H, Ph—$\mathrm{O\underline{CH_3}}$), 3·91t (2H, —$\mathrm{N\underline{CH_2}CH_2}$, J = 7·0), 4·70s (2H, Ph—$\underline{\mathrm{CH_2}}$), 6·83–7·13m (6H, $\underline{\mathrm{3', 5', 2a, 3a, 5a, 6a}}$), 7·75d (1H, $\underline{7}$, $J_{6,7}$ = 9·3), 7·93–7·97m (2H, $\underline{2', 6'}$), 8·18dd (1H, $\underline{6}$, $J_{6,7}$ = 9·3, $J_{4,6}$ = 2·0), 9·16d (1H, $\underline{4}$, $J_{4,6}$ = 2·3).
If	1·30t (3H, —$\mathrm{CH_2\underline{CH_3}}$, J = 7·0), 2·75t (2H, —$\mathrm{CH_2\underline{CH_2}COOCH_2CH_3}$, J = 7·0), 3·80s (3H, Ph—$\mathrm{O\underline{CH_3}}$), 3·90t (2H, —$\mathrm{N\underline{CH_2}CH_2}$, J = 7·0), 4·10q (2H, —$\mathrm{CH_2\underline{CH_3}}$, J = 7·0), 4·70bs (2H, Ph—$\underline{\mathrm{CH_2}}$), 6·85–7·15m (6H, $\underline{\mathrm{3', 5', 2a, 3a, 5a, 6a}}$), 7·80d (1H, $\underline{7}$, $J_{6,7}$ = 9·3), 7·92–7·98m (2H, $\underline{2', 6'}$), 8·20dd (1H, $\underline{6}$, $J_{6,7}$ = 9·3, $J_{4,6}$ = 2·0), 9·20d (1H, $\underline{4}$, $J_{4,6}$ = 2·3).

Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

TABLE 3

^{1}H-NMR Spectral Assignments of Dyes **II**



Dye	^{1}*N-NMR (CDCl$_3$, TMS int., δ (ppm), J, (Hz)*
IIa	2·81t (2H, $-CH_2\underline{CH_2}COOCH_3$, $J = 7{\cdot}0$), 3·71s (3H, $-COO\underline{CH_3}$), 3·99t (2H, $-N\underline{CH_2}CH_2$, $J = 7{\cdot}0$), 4·89bs (2H, Ph$-\underline{CH_2}$), 6·80–6·84m (2H, $\underline{3', 5'}$), 7·54–7·56m (2H, $\underline{5a, 6a}$), 7·79d (1H, $\underline{7}$, $J_{6,7} = 9{\cdot}7$), 7·97–8·01m (2H, $\underline{2', 6'}$), 8·06bs (1H, $\underline{2a}$), 8·19–8·24m (2H, $\underline{6, 4a}$), 9·18d (1H, $\underline{4}$, $J_{4,6} = 2{\cdot}3$).
IIb	1·27t (3H, $CH_2\underline{CH_3}$, $J = 7{\cdot}0$), 2·80t (2H, $-CH_2\underline{CH_2}COOCH_2CH_3$, $J = 7{\cdot}0$), 3·98t (2H, $-N\underline{CH_2}CH_2$, $J = 7{\cdot}0$), 4·16q (2H, $-\underline{CH_2}CH_3$, $J = 7{\cdot}0$), 4·89bs (2H, Ph$-\underline{CH_2}$), 6·78–6·82m (2H, $\underline{3', 5'}$), 7·56–7·59m (2H, $\underline{5a, 6a}$), 7·74d (1H, $\underline{7}$, $J_{6,7} = 9{\cdot}7$), 7·91–7·95m (2H, $\underline{2', 6'}$), 8·07bs (1H, $\underline{2a}$), 8·12–8·19m (2H, $\underline{6, 4a}$), 9·09d (1H, $\underline{4}$, $J_{4,6} = 2{\cdot}2$).
IIc	2·33s (3H, Ph$-\underline{CH_3}$), 2·75t (2H, $-CH_2\underline{CH_2}COOCH_3$, $J = 7{\cdot}0$), 3·70s (3H, $-COO\underline{CH_3}$), 3·92d (2H, $-N\underline{CH_2}CH_2$, $J = 7{\cdot}0$), 4·73bs (2H, Ph$-\underline{CH_2}$), 6·81–6·85m (2H, $\underline{3', 5'}$), 7·46–7·50m (2H, $\underline{5a, 6a}$), 7·78d (1H, $\underline{7}$, $J_{6,7} = 9{\cdot}7$), 8·16–8·20m (4H, $\underline{2a, 4a, 6, 2}$), 9·14d (1H, $\underline{4}$, $J_{4,6} = 2{\cdot}3$).
IId	1·20t (3H, $-COOCH_2\underline{CH_3}$, $J = 7{\cdot}0$), 2·54s (3H, Ph$-\underline{CH_3}$), 2·71t (2H, $-CH_2\underline{CH_2}COOCH_2CH_3$, $J = 7{\cdot}0$), 3·87t (2H, $-N\underline{CH_2}CH_2$, $J = 7{\cdot}0$), 4·08q (2H, $-\underline{CH_2}CH_3$, $J = 7{\cdot}0$), 4·79bs (2H, Ph$-\underline{CH_2}$), 6·52–6·58m (2H, $\underline{3', 5'}$), 7·46–7·51m (2H, $\underline{5a, 6a}$), 7·68d (1H, $\underline{7}$, $J_{6,7} = 9{\cdot}7$), 7·92–8·12m (4H, $\underline{2a, 4a, 6, 2}$), 9·05d (1H, $\underline{4}$, $J_{4,6} = 2{\cdot}3$).

Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

TABLE 4

Visible Spectra and Fastness of Dyeings for Dyes **I** and **II**

Dye	λ_{max} *(in ethanol) (nm)*	$\varepsilon_{max}10^{-4}$	*Fastness[a] to dry-heat treatment, 180°C*							*Lightfastness*
			1	*2*	*3*	*4*	*5*	*6*	*7*	
Ia	585	4·18	4–5	5	4–5	4–5	4–5	4–5	5	5
Ib	584	4·22	4–5	5	4–5	4–5	4–5	4–5	5	5
Ic	598	3·79	4–5	4–5	4–5	4–5	4–5	4–5	5	4–5
Id	599	3·92	4–5	5	4–5	4–5	4–5	4–5	5	4–5
Ie	585	3·62	4–5	5	4–5	4–5	4–5	4–5	4–5	5–6
If	585	3·88	4–5	5	4–5	4–5	5	4–5	5	5–6
IIa	569	3·05	4–5	4–5	5	4–5	4–5	4–5	4–5	5–6
IIb	570	3·48	5	5	4–5	5	4–5	4–5	5	5–6
IIc	585	2·95	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5
IId	583	3·50	4–5	5	4–5	4–5	4–5	4–5	4–5	5

[a] 1, Change of shade of dyed fabric; 2, staining wool; 3, staining polyacrylonitryle; 4, staining polyester; 5, staining nylon; 6, staining cotton; 7, staining acetate.

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