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The Application of Some Alkyl Esters of Alkoxy Derivatives of *N*-Benzyl-*N*-phenyl-*β*-alanine in the Synthesis of 3-Amino-5-nitro[2,1]benzisothiazole-Based Dyes

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ABSTRACT

This paper is concerned with the application of alkoxy derivatives of some alkyl esters of N-benzyl-N-phenyl-β-alanine in the synthesis of heterocyclic azo dyes derived from 3-amino-5-nitro[2,1]benzisothiazole. The structure of the alkoxy intermediates was confirmed by IR and ^1H*-NMR. The dyes were evaluated on polyester-fibre fabric with respect to their basic fastness properties. IR,* ^1H*-NMR, and visible spectra of the dyes were also examined.*

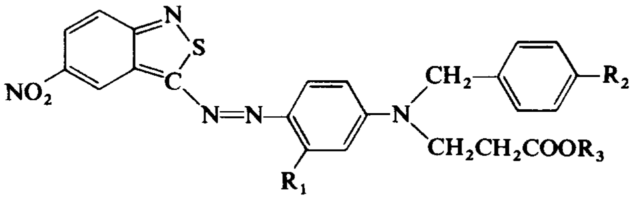
1 INTRODUCTION

During investigations of disperse azobenzene[1] and [2,1]benzisothiazole-3-azo dyes[2,3] it was found that the use as coupling components of some alkyl esters of *N*-benzyl-*N*-phenyl-*β*-alanine resulted in the formation of dyes suitable for dyeing polyester-fibre fabric.

This present paper deals with the synthesis and fastness properties of dyes of general formula **I**, prepared from 3-amino-5-nitro[2,1]benzisothiazole and new *N*-benzyl-*N*-phenyl-*β*-alanine components containing at least one alkoxy substituent in either or both of the benzyl or phenyl residues.

2 RESULTS AND DISCUSSION

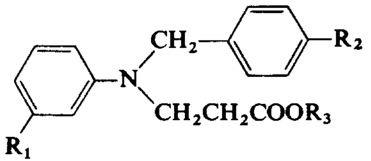
The coupling components represented by formula **II** were prepared in a two-stage reaction, via the *N*-benzylaniline derivatives **III**, as reported



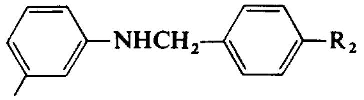
I

Dye	R_1	R_2	R_3
Ia	OC_2H_5	H	CH_3
Ib	OC_2H_5	H	C_2H_5
Ic	CH_3	OCH_3	CH_3
Id	CH_3	OCH_3	C_2H_5
Ie	OCH_3	CH_3	CH_3
If	OCH_3	CH_3	C_2H_5
Ig	OCH_3	OCH_3	CH_3
Ih	OCH_3	OCH_3	C_2H_5
Ii	OC_2H_5	OCH_3	CH_3
Ij	OC_2H_5	OCH_3	C_2H_5

previously.[4,5] The compounds **III** were synthesised by alkylation of the arylamine with benzyl chloride[6] (**IIIa**, 58% yield) or by reduction of the appropriate *N*-benzylideneanilines with sodium borohydride[7] (**IIIb–IIIe** 85–90% yield). *N*-benzylanilines **III** thus obtained were reacted with methyl or ethyl acrylate in the presence of hydroquinone and acetic acid as



II



III

Amine	*N-Benzylaniline*	R_1	R_2	R_3
IIa	**IIIa**	OC_2H_5	H	CH_3
IIb		OC_2H_5	H	C_2H_5
IIc	**IIIb**	CH_3	OCH_3	CH_3
IId		CH_3	OCH_3	C_2H_5
IIe	**IIIc**	OCH_3	CH_3	CH_3
IIf		OCH_3	CH_3	C_2H_5
IIg	**IIId**	OCH_3	OCH_3	CH_3
IIh		OCH_3	OCH_3	C_2H_5
IIi	**IIIe**	OC_2H_5	OCH_3	CH_3
IIj		OC_2H_5	OCH_3	C_2H_5

TABLE 1
Characterisation Data, Yield, and Elemental-analysis Data of Amines **II**

Amine	*Yield (%)*	*B.P. (°C/mm Hg)*	n_D^{20} *or M.P. (°C)*	*Elemental analysis (%)*					
				C		*H*		*N*	
				Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
IIa	59	188–190/1·2	1·5887	72·84	72·39	7·34	6·99	4·47	4·30
IIb	62	200/1·0	1·5629	73·39	73·02	7·64	7·48	4·28	4·15
IIc	61	217–220/2·0	48–49	72·84	72·57	7·34	7·05	4·47	4·45
IId	58	190–200/0·8	1·5738	73·39	73·42	7·64	7·70	4·28	4·35
IIe	52	230/2·5	1·5740	72·84	73·00	7·34	7·28	4·47	4·50
IIf	53	208–212/1·3	1·5652	73·39	73·35	7·64	7·50	4·28	4·20
IIg	51	230–240/1·5	1·5892	69·30	69·15	6·99	6·50	4·25	4·21
IIh	53	210–220/1·0	1·5764	69·97	69·61	7·28	7·30	4·08	4·05
IIi	52	220–225/1·4	1·5667	69·97	69·59	7·28	7·15	4·08	4·02
IIj	50	232–238/2·5	1·5717	70·58	69·98	7·56	7·09	3·92	3·81

TABLE 2
IR* and ^{1}H-NMR‡ Data of Amines **II**

Amine	*IR* (cm^{-1})	^{1}*H-NMR* [$CDCl_3$, $TMS_{int.}$, (*ppm*), *J*(*Hz*)]
IIa	3038 (ν_{CH}), 2985 ($\nu_{CH\,alk.}$), 1735 ($\nu_{C=O}$), 1190 (ν_{C-O}), 900–700 (δ_{CH})	1·26t (3H, Ph-OCH$_2\underline{\mathrm{CH}}_3$, J = 7·0), 2·55t (2H, —CH$_2\underline{\mathrm{CH}}_2$COOCH$_3$, J = 7·0), 3·46–3·63m (5H, —N$\underline{\mathrm{CH}}_2CH_2$, —COO$\underline{\mathrm{CH}}_3$), 3·90q (2H, Ph-O$\underline{\mathrm{CH}}_2CH_3$, J = 7·0), 4·48bs (2H, Ph-$\underline{\mathrm{CH}}_2$), 6·05–7·30m (9H, arom.)
IIb	3040 (ν_{CH}), 2980 ($\nu_{CH\,alk.}$), 1735 ($\nu_{C=O}$), 1185 (ν_{C-O}), 900–700 (δ_{CH})	1·20t (3H, —COOCH$_2\underline{\mathrm{CH}}_3$, J = 7·0), 1·31t (3H, Ph-OCH$_2\underline{\mathrm{CH}}_3$, J = 7·0), 2·60t (2H, —CH$_2\underline{\mathrm{CH}}_2$COOCH$_2CH_3$, J = 7·0), 3·73t (2H, —N$\underline{\mathrm{CH}}_2CH_2$, J = 7·0), 3·95q (2H, Ph-O$\underline{\mathrm{CH}}_2CH_3$, J = 7·0), 4·06q (2H, —COO$\underline{\mathrm{CH}}_2CH_3$, J = 7·0), 4·55bs (2H, Ph-$\underline{\mathrm{CH}}_2$), 6·08–7·43m (9H, arom.)
IIc	3035 (ν_{CH}), 2985 ($\nu_{CH\,alk}$.), 1730 ($\nu_{C=O}$), 1185 (ν_{C-O}), 900–700 (δ_{CH})	2·25s (3H, Ph-$\underline{\mathrm{CH}}_3$), 2·58t (2H, —CH$_2\underline{\mathrm{CH}}_2$COOCH$_3$, J = 7·0), 3·63s (3H, —COO$\underline{\mathrm{CH}}_3$), 3·70t (2H, —N—$\underline{\mathrm{CH}}_2CH_2$, partly overlapped), 3·73s (3H, Ph-O$\underline{\mathrm{CH}}_3$), 4·45bs (2H, Ph-$\underline{\mathrm{CH}}_2$), 6·40–7·50m (8H, arom.)
IId	3041 (ν_{CH}), 2980 ($\nu_{CH\,alk.}$), 1735 ($\nu_{C=O}$), 1190 (ν_{C-O}), 900–700 (δ_{CH})	1·20t (3H, —COOCH$_2\underline{\mathrm{CH}}_3$, J = 7·0), 2·26s (3H, Ph-$\underline{\mathrm{CH}}_3$), 2·58t (2H, —CH$_2\underline{\mathrm{CH}}_2$COOCH$_2CH_3$, J = 7·0), 3·60–3·85m (5H, —N$\underline{\mathrm{CH}}_2CH_2$, Ph-O$\underline{\mathrm{CH}}_3$), 4·01q (2H, —COO$\underline{\mathrm{CH}}_2CH_3$, J = 7·0), 4·45bs (2H, Ph-$\underline{\mathrm{CH}}_2$), 6·40–7·50m (8H, arom.)
IIe	3038 (ν_{CH}), 2980 ($\nu_{CH\,alk.}$), 1730 (ν_{C-O}), 1185 (ν_{C-O}), 900–700 (δ_{CH})	2·25s (3H, Ph-$\underline{\mathrm{CH}}_3$), 2·55t (2H, —CH$_2\underline{\mathrm{CH}}_2$COOCH$_3$, J = 7·0), 3·56s (3H, —COO$\underline{\mathrm{CH}}_3$), 3·58t (2H, —N$\underline{\mathrm{CH}}_2CH_2$, partly overlapped), 3·65s (3H, Ph-O$\underline{\mathrm{CH}}_3$), 4·41bs (2H, Ph-$\underline{\mathrm{CH}}_2$), 6·08–7·33m (8H, arom.)

IIf	3040 (ν_{CH}), 2990 ($\nu_{CH_{alk}}$), 1730 ($\nu_{C=O}$), 1190 (ν_{C-O}), 900–700 (δ_{CH})	1·16t (3H, $-COOCH_2\underline{CH}_3$, J = 7·0), 2·26s (3H, Ph-$\underline{CH}_3$), 2·56t (2H, $-CH_2\underline{CH}_2COOCH_2CH_3$, J = 7·0), 3·50–3·75m (5H, $-N\underline{CH}_2CH_2$, Ph-O$\underline{CH}_3$), 4·08q (2H, $-COO\underline{CH}_2CH_3$, J = 7·0), 4·46bs (2H, Ph-$\underline{CH}_2$), 6·00–7·28m (8H, arom.)
IIg	3040 (ν_{CH}), 2985 ($\nu_{CH_{alk.}}$), 1740 ($\nu_{C=O}$), 1190 (ν_{C-O}), 900–700 (δ_{CH})	2·55t (2H, $-CH_2\underline{CH}_2COOCH_3$, J = 7·0), 3·56s (3H, $-COO\underline{CH}_3$), 3·65t (2H, $-N\underline{CH}_2CH_2$, partly overlapped), 3·65s (3H, Ph-O$\underline{CH}_3$), 3·70s (3H, Ph-O$\underline{CH}_3$), 4·41bs (2H, Ph-$\underline{CH}_2$), 6·00–7·38m (8H, arom.)
IIh	3036 (ν_{CH}), 2985 ($\nu_{CH_{alk.}}$), 1735 ($\nu_{C=O}$), 1180 (ν_{C-O}), 900–700 (δ_{CH})	1·15t (3H, $-COOCH_2\underline{CH}_3$, J = 7·0), 2·53t (2H, $-COO\underline{CH}_2CH_3$, J = 7·0), 3·50–3·71m (8H, $-N\underline{CH}_2CH_2$, Ph-O$\underline{CH}_3$, Ph-O$\underline{CH}_3$), 4·03q (2H, $-COO\underline{CH}_2CH_3$, J = 7·0), 4·41bs (2H, Ph-$\underline{CH}_2$), 6·00–7·33m (8H, arom.)
IIi	3038 (ν_{CH}), 2985 ($\nu_{CH_{alk.}}$), 1740 ($\nu_{C=O}$), 1180 (ν_{C-O}), 900–700 (δ_{CH})	1·31t (3H, Ph-$OCH_2\underline{CH}_3$, J = 7·0), 2·56t (2H, $-CH_2\underline{CH}_2COO\underline{CH}_3$, J = 7·0), 3·61s (3H, $-COO\underline{CH}_3$), 3·70t (2H, $-N\underline{CH}_2CH_2$, J = 7·0), 3·71s (3H, Ph-O$\underline{CH}_3$), 3·93q (2H, Ph-$O\underline{CH}_2CH_3$, J = 7·0), 4·43bs (2H, Ph-$\underline{CH}_2$), 6·00–7·26m (8H, arom.)
IIj	3035 (ν_{CH}), 2990 ($\nu_{CH_{alk}}$), 1740 ($\nu_{C=O}$), 1180 (ν_{C-O}), 900–700 (δ_{CH})	1·21t (3H, $-COOCH_2\underline{CH}_3$, J = 7·0), 1·33t (3H, Ph-$OCH_2\underline{CH}_3$, J = 7·0), 2·58t (2H, $-CH_2\underline{CH}_2COOCH_2CH_3$, J = 7·0), 3·70t (2H, $-N\underline{CH}_2CH_2$, J = 7·0), 3·75s (3H, Ph-O$\underline{CH}_3$), 3·92q (2H, Ph-$O\underline{CH}_2CH_3$, J = 7·0), 4·09q (2H, $-COO\underline{CH}_2CH_3$, J = 7·0), 4·41bs (2H, Ph-$\underline{CH}_2$), 6·03–7·28m (8H, arom.)

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* Only the most characteristic bands are given.

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

catalyst.[8] These reactions provided (after vacuum distillation) analytically pure amines **II** in good yields (55–62%).

Characterisation data, yield, and elemental-analysis data of compounds **II** are summarised in Table 1.

The structure of compounds **II** was established by IR and ^{1}H-NMR. IR spectra showed typical aromatic absorption (ν_{CH}, δ_{CH}) and bands for the appropriate functional group ($\nu_{CHalk.}$, $\nu_{C=O}$, ν_{C-O}) (Table 2). The ^{1}H-NMR spectra also provided data in accord with the structure of the amines (Table 2).

The dyes **I** were obtained in 70–79% yield by diazotisation of 3-amino-5-nitro[2,1]benzisothiazole with nitrosylsulphuric acid in a mixture of sulphuric and orthophosphoric acid and coupling with the appropriate amine **II** in acetic acid. The crude dyes were purified by crystallisation from ethanol until a constant molar extinction coefficient and TLC purity were attained. The structure of the dyes was verified by elemental analysis (Table 3) and by spectroscopic methods.

IR spectra of the dyes showed absorption confirming their aromatic structure (ν_{C-C}: 1600–1610 cm^{-1}, δ_{CH} : 700–900 cm^{-1}), the presence of the appropriate functional group ($\nu_{C=O}$: 1730–1740 cm^{-1}, ν_{NO_2}: 1520–1525 cm^{-1}) and the presence of the hetaryl residue characterised by the absorption band at 1500–1505 cm^{-1}, due to vibrations of the C=N bond in the isothiazole ring.[9]

The structure of selected dyes was additionally confirmed by ^{1}H-NMR. These data are shown in Table 4.

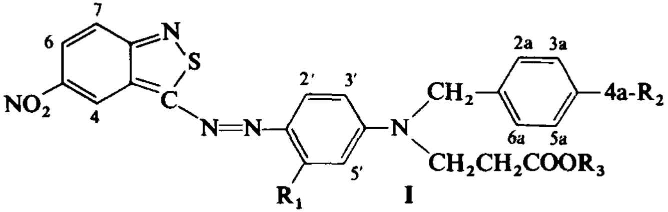
Visible spectra of the dyes **I** recorded in ethanolic solutions (Table 3) showed that the introduction of an alkoxy substituent ortho to the azo

TABLE 3

Characterisation Data, Visible Spectra, and Elemental-analysis Data of Dyes I

Dye	*Yield* (%)	*Nitrogen*		*M.P.* (°C)	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^{-4}$
		Calc.	*Found*			
Ia	72	13·48	13·38	250–252	605	3·70
Ib	70	13·13	13·09	246–248	604	3·78
Ic	76	13·48	13·30	267–269	598	3·80
Id	75	13·13	13·00	252–253	598	3·90
Ie	72	13·48	13·12	225–227	605	3·10
If	73	13·13	13·40	235–237	605	2·90
Ig	74	13·08	12·75	211–213	605	3·28
Ih	74	12·75	12·50	232–235	605	3·33
Ii	78	12·75	12·48	238–239	605	2·82
Ij	79	12·43	12·35	234–235	605	3·18

TABLE 4
^{1}H-NMR Spectral Assignments of Dyes[a]



I

Dye	^{1}*H-NMR* [$CDCl_3$, *TMS int.*, δ (*ppm*), J (*Hz*)]
Ib	1·24t (3H, $-CH_2\underline{CH_3}$, J = 7·0), 1·51t (3H, Ph-$OCH_2\underline{CH_3}$, J = 7·0), 2·75t (2H, $-CH_2\underline{CH_2}COOCH_2CH_3$, J = 7·0), 3·93t (2H, $-N\underline{CH_2}CH_2$, J = 7·0), 4·10–4·20m (4H, $-\underline{CH_2}CH_3$, Ph-$O\underline{CH_2}CH_3$), 4·76bs (2H, Ph-$\underline{CH_2}$), 6·23d (1H, $\underline{5'}$, $J_{3'5'}$ = 2·6), 6·50dd (1H, $\underline{3'}$, $J_{3'5'}$ = 2·6, $J_{2'3'}$ = 9·6), 7·15–7·40m (5H, $\underline{2a,3a,4a,5a,6a}$), 7·73d (1H, $\underline{7}$, J_{67} = 9·6), 8·06d (1H, 2′, $J_{2'3}$ = 9·6), 8·17dd (1H, $\underline{6}$, J_{67} = 9·6, J_{46} = 2·6), 9·21d (1H, $\underline{4}$, J_{46} = 2·6)
Id	1·27t (3H, $-CH_2\underline{CH_3}$, J = 7·2), 2·64s (3H, Ph-$\underline{CH_3}$), 2·72t (2H, $-CH_2\underline{CH_2}COOCH_2CH_3$, J = 7·2), 3·75–3·95m (5H, Ph-$O\underline{CH_3}$, $-N\underline{CH_2}CH_2$), 4·15q (2H, $-\underline{CH_2}CH_3$, J = 7·2), 4·69bs (2H, Ph-$\underline{CH_2}$), 6·65d (1H, 5′, $J_{3'5'}$ = 2·8), 6·70dd (1H, $\underline{3'}$, $J_{3'5'}$ = 2·8, $J_{2'3'}$ = 9·5), 6·85–7·92m (4H, $\underline{2a,3a,5a,6a}$), 7·74d (1H, 7, J_{67} = 9·5), 8·04d (1H, $\underline{2'}$, $J_{2'3'}$ = 9·5), 8·20dd (1H, 6, J_{67} = 9·5, J_{76} = 2·8), 9·15d (1H, $\underline{4}$, J_{46} = 2·8)
Ie	2·34s (3H, Ph-$\underline{CH_3}$), 2·75t (2H, $-CH_2\underline{CH_2}COOCH_3$, J = 7·0), 3·70s (3H, $-COO\underline{CH_3}$), 3·90–4·00m (5H, Ph-$O\underline{CH_3}$, $-N\underline{CH_2}CH_2$), 4·73bs (2H, Ph-$\underline{CH_2}$), 6·25d (1H, $\underline{5'}$, $J_{3'5'}$ = 2·6), 6·50dd (1H, $\underline{3'}$, $J_{3'5'}$ = 2·6, $J_{2'3'}$ = 9·5), 7·05–7·20m (4H, $\underline{2a,3a,5a,6a}$), 7·71d (1H, $\underline{7}$, J_{67} = 9·5), 8·04d (1H, $\underline{2'}$, $J_{2'3'}$ = 9·5), 8·20dd (1H, $\underline{6}$, J_{67} = 9·5, J_{46} = 2·6), 9·20d (1H, $\underline{4}$, J_{46} = 2·6)
Ih	1·27t (3H, $-CH_2\underline{CH_3}$, J = 7·0), 2·73t (2H, $-CH_2\underline{CH_2}COOCH_2CH_3$, J = 7·0), 3·80s (3H, Ph-$O\underline{CH_3}$), 3·91–3·99m (5H, Ph-$O\underline{CH_3}$, $-N\underline{CH_2}CH_2$), 4·16q (2H, $-CH_2\underline{CH_3}$, J = 7·0), 4·71bs (2H, Ph-$\underline{CH_2}$), 6·27d (1H, $\underline{5'}$, $J_{3'5'}$ = 2·4), 6·50dd (1H, $\underline{3'}$, $J_{3'5'}$ = 2·4, $J_{2'3'}$ = 9·5), 6·83–7·17m (4H, $\underline{2a,3a,5a,6a}$), 7·72d (1H, $\underline{7}$, J_{67} = 9·5), 8·04d (1H, $\underline{2'}$, $J_{2'3'}$ = 9·5), 8·20dd (1H, $\underline{6}$, J_{67} = 9·5, J_{46} = 2·4), 9·20d (1H, $\underline{4}$, J_{46} = 2·4)
Ii	1·55t (3H, Ph-$OCH_2\underline{CH_3}$, J = 7·0), 2·75t (2H, $-CH_2\underline{CH_2}COOCH_3$, J = 7·0), 3·70s (3H, $-COO\underline{CH_3}$), 3·75–3·95m (5H, $-N\underline{CH_2}CH_2$, Ph-$O\underline{CH_3}$), 4·15q (2H, Ph-$O\underline{CH_2}CH_3$, J = 7·0), 4·60bs (2H, Ph-$\underline{CH_2}$), 6·05d (1H, $\underline{5'}$, $J_{3'5'}$ = 2·6), 6·50dd (1H, $\underline{3'}$, $J_{3'5'}$ = 2·6, $J_{2'3'}$ = 9·6), 6·85–7·75m (4H, $\underline{2a,3a,5a,6a}$), 7·72d (1H, $\underline{7}$, J_{67} = 9·6), 8·03d (1H, $\underline{2'}$, $J_{2'3'}$ = 9·6), 8·20dd (1H, $\underline{6}$, J_{67} = 9·6, J_{46} = 2·6), 9·15d (1H, 4, J_{46} = 2·6)

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[a] Abbreviations: s, single; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

TABLE 5
Fastness Properties of Dyes **I**

Dye	*Fastness*[a] *to dry-heat treatment, 180°C*							*Rubbing*		*Light-fastness*[b]
	1	*2*	*3*	*4*	*5*	*6*	*7*	*Wet*	*Dry*	
Ia	4–5	5	4–5	4–5	4–5	4–5	5	5	5	5–6
Ib	4–5	5	4–5	4–5	4–5	4–5	4–5	5	5	5–6
Ic	4–5	4–5	4	4–5	5	4–5	4–5	4–5	5	4–5
Id	4	4–5	4	4–5	5	4–5	4–5	4–5	4–5	4–5
Ie	5	4–5	4–5	4–5	4–5	4	4–5	5	5	5
If	5	4–5	4–5	4–5	4	4	4–5	5	5	5
Ig	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5	5	5
Ih	4–5	4–5	4–5	4–5	4–5	4–5	4–5	5	5	5
Ii	4–5	5	5	4–5	5	4–5	5	5	5	5
Ij	4–5	5	5	4–5	4–5	4–5	5	4–5	5	5

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

[b] The dye-application level was 0·5% o.w.f. (weight of fibre).

TABLE 6
Physical Constants of *N*-Benzylanilines **III**

R_1	R_2	*B.p. °C/mm Hg*	n_D^{20}
OCH_3	CH_3	180–184/2·0–2·5	1·5979
OCH_3	OCH_3	220/2·0	1·6032
OC_2H_5	OCH_3	200–210/1·5–2·0	1·5905

group in the coupling component causes only a slight bathochromic shift in λ_{max} in comparison with ortho methyl substituted or unsubstituted dyes.[2,3] The type of the substituent in the benzyl ring does not affect the position of λ_{max} in these new dyes. The presence of an alkoxy substituent ortho to the azo group also affects the molar extinction coefficient, these dyes having values generally lower than those of their unsubstituted analogues.[2,3]

Introduction of an additional alkoxy group into the benzyl residue results in a further hypochromic effect. A similar effect is also observed for dyes containing a methyl group in the benzyl residue, but only for the dyes containing a methoxy substituent ortho to the azo linkage.[3]

Dyeings on polyester fibre of dyes **I** had excellent brightness and high intensity and showed almost complete dyebath exhaustion. Fastness properties are given in Table 5.

The over-all fastness properties of the dyes are generally satisfactory and are particularly exemplified in their fastness to rubbing in comparison with analogous unsubstituted and ortho methyl substituted dyes.[2]

It is difficult to quantify the influence of different substituents on the light-fastness of the dyes. As was previously noted[2] the highest light-fastness is shown by dyes with an ortho alkoxy substituent, in contrast to dyes with a methyl group ortho to the azo group, and this aspect is being further investigated.

3 EXPERIMENTAL

3.1 General

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

^{1}H-NMR spectra of amines were measured at 80 MHz on a Tesla BS 487 c spectrometer in $CDCl_3$ solutions, with TMS used as internal reference.

^{1}H-NMR spectra of the dyes were recorded under the same conditions on a Bruker 300-MHz spectrometer.

Visible spectra of the dyes were recorded on a Specord uv-visible spectrophotometer (Zeiss, Jena) in ethanolic solution at a concentration of $2{\cdot}5 . 10^{-5}\,\mathrm{mol\,dm^{-3}}$.

Dyeings and fastness properties were determined according to Polish Standards, which correspond with British Standards.[10]

3.2 Ethyl ester of *N*-benzyl-*N*-(*m*-ethoxyphenyl)-*β*-alanine IIb

m-Phenetidine (91·22 g, 0·665 m), water (18 m) and sodium bicarbonate (17·5 g) were heated in a steam bath to 90–95°C, and freshly distilled benzyl chloride (21·0 g, 0·165 m) was then added for 1 h. The reaction was continued for a further 3 h at 95°C. The precipitate was filtered, and the organic layer was separate from the filtrate, washed with saturated NaCl solution, dried with anhydrous magnesium sulphate, and distilled under reduced pressure at 172–190°C/0·8 mm H to give *N*-benzyl-*m*-phenetidine (**IIIa**) (17·0 g; 58·0%).

H-NMR: 1·31 t (3H, Ph-$OCH_2\underline{CH_3}$, $J = 7{\cdot}0$), 3·66–4·10 m (3H, Ph–$O\underline{CH_2}CH_3$, N$\underline{H}$), 4·25 bs (2H, $\underline{Ph–CH_2}$), 6·08–7·33 m (9H, arom.). n_D^{20} 1·5955.

N-Benzyl-*m*-phenetidine (11·35 g, 0·05 m) was heated for 25 h under reflux with freshly distilled ethyl acrylate (8·74 ml) in the presence of acetic acid (2 ml) and hydroquinone (0·1 g). Pure **IIb** was obtained, after vacuum distillation at 200°C/0·8–1·00 mm Hg (10·13 g; 62·0%).

3.3 Ethyl ester of *N*-(*p*-methoxybenzyl)-*N*-(*m*-methylphenyl)-*β*-alanine IId

A solution of *p*-methoxybenzaldehyde (13·6 g, 0·1 m) and *m*-toluidine (10·72 g, 0·1 m) in 95% aq. ethanol (40 ml) was refluxed for 20 min; water (30 ml) was then added and the separated oil was left to solidify. The precipitate was filtered and washed with ethanol, to give *N*-(*p*-methoxybenzylidene)-*m*-toluidine (20·25 g; 90%). M.p. 59°C (lit. m.p. 59°C[11]; 63°C[12,13]). A solution of *N*-(*p*-methoxybenzylidene)-*m*-toluidine (20·25 g, 0·09 m) in methanol (200 ml) was heated to 40°C, and sodium borohydride (3·47 g, 0·09 m) was added for 30 min. The solution was refluxed for 15 min and poured into water (30 ml). The organic layer was extracted with ethyl acetate, dried with anhydrous magnesium sulphate, and evaporated. The product was distilled under reduced pressure; pure **IIIb** was collected at 184–189°C/2·5 mm Hg (18·38 g; 81·0%).

^{1}H-NMR: 2·18 s (3H, Ph–$\underline{CH_3}$), 3·58 bs (4H, Ph–$\underline{OCH_3}$, N$\underline{H}$), 6·13–7·33 m (8H, arom.) $n_D^{20} = 1{\cdot}5995$.

The ethyl ester of *N*-(*p*-methoxybenzyl)-*N*-(*m*-methylphenyl)-*β*-alanine **IId** was prepared in the same way as described in Section 3.2.

3.4 Other compounds

Other compounds **II** were prepared according to the procedure described in Section 3.3, but in all cases the derivatives of *N*-benzylideneanilines were liquid. After being poured into water, they were extracted with ethyl acetate, evaporated, and directly reduced with sodium borohydride. The derivatives of *N*-benzylanilines thus obtained were also liquid and used for addition to carbonyl compounds after distillation under reduced pressure. Boiling points and n_D^{20} values are given in Table 6.

3.5 Synthesis of dyes I

The preparation of all dyes **I** was carried out by previously described procedures.[2,3]

REFERENCES

1. Sokołowska-Gajda, J. & Kraska, J., *Dyes and Pigments*, **10** (1989) 285.
2. Kraska, J. & Sokołowska-Gajda, J., *Dyes and Pigments*, **8** (1987) 345.
3. Sokołowska-Gajda, J., *Dyes and Pigments*, **15** (1991) 239.
4. Kraska, J. & Sokołowska-Gajda, J., *Dyes and Pigments*, **7** (1986) 161.
5. Sokołowska-Gajda, J., *Dyes and Pigments*, **15** (1991) 41.
6. *Organic Synthesis*, Collective Vol. 1. John Wiley & Sons, New York, 1948, p. 102.
7. Billman, J. H. & Diesing, A. C., *J. Org. Chem.*, **22** (1957) 1068.
8. Elderfield, R. C., Gensler, W. J., Bembry, T. H., Kremer, C. B., Brudy, F., Hageman, H. A. & Head, J. D., *J. Am. Chem. Soc.*, **68** (1946) 1259.
9. Geordeler, J. & Pohland, H. W., *Angew. Chem.*, **72** (1960) 77.
10. Standard methods for the determination of the colour fastness of textiles and leather. Society of Dyers and Colourists, Bradford, West Yorkshire, UK, 1978.
11. Senier, A. & Shepheard, F. G., *J. Chem. Soc.*, **95** (1909) 1943.
12. Bren, V. A., Malysheva, E. N. & Minkin, V. I., *Reakts. Sposobnost Org. Soedin., Tartu Gos. Univ.*, **4** (1967) 523.
13. Klicnar, J., Kristek, F. & Vecera, M., *Coll. Czech. Chem. Commun.*, **34** (1969) 553.