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Synthesis and Properties of Monoazo Disperse Dyes Derived from the Ethyl Ester of *N*-Benzyl-*N*-phenyl-*β*-alanine

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ABSTRACT

The synthesis is described of some aminoazobenzene disperse dyes in which the ethyl ester of N-*benzyl-*N-*phenyl-β-alanine was used as coupling component.* ^{1}*H-NMR and visible spectra of the dyes are reported and the basic fastness properties of the dyes were also determined. The lightfastness of the dyes was studied in relation to mass spectra data.*

1 INTRODUCTION

During our investigations of disperse dyes derived from 3-amino-5-nitro[2,1]benzisothiazole[1,2] it was 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.

Among disperse dyes, derivatives of aminoazobenzenes are of particular industrial interest, since by substitution at various positions in the diazo component dyes ranging from yellow to violet in hue can be obtained.

We have now prepared some disperse dyes of general formulae **I** and **II** (Table 1), in the synthesis of which the ethyl ester of *N*-benzyl-*N*-phenyl-*β*-alanine was used as coupling component.

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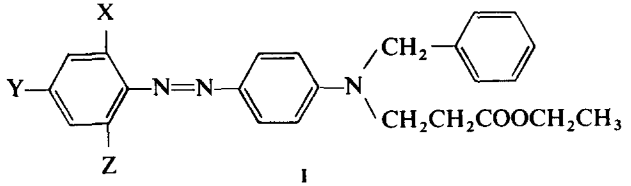
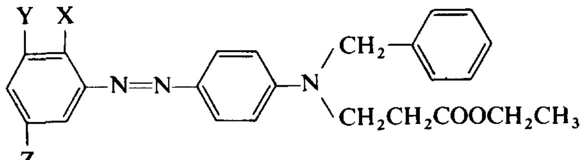
TABLE 1
Structures of the Dyes



I



II

Dye	*X*	*Y*	*Z*	*General structure*
D-I	H	NO_2	H	I
D-II	CH_3	NO_2	H	I
D-III	OCH_3	NO_2	H	I
D-IV	Cl	NO_2	H	I
D-V	NO_2	NO_2	H	I
D-VI	CN	NO_2	H	I
D-VII	Cl	NO_2	Cl	I
D-VIII	NO_2	Cl	H	I
D-IX	CN	H	H	I
D-X	H	H	NO_2	II
D-XI	CH_3	H	NO_2	II
D-XII	Cl	H	NO_2	II
D-XIII	H	$COOCH_3$	$COOCH_3$	II
D-XIV	Cl	H	CF_3	II

2 EXPERIMENTAL

All dyes **I** and **II** were generally obtained by conventional diazotisation and coupling techniques.[3] The diazotisation of 2-cyano-4-nitroaniline and of 2-cyanoaniline was carried out with glycol nitrite in a mixture of sulphuric acid and ethylene glycol.[4] The diazonium salts were coupled in acetic acid with the ethyl ester of *N*-benzyl-*N*-phenyl-*β*-alanine, the synthesis of which has been described previously.[5]

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)].

Visible spectra of the dyes were recorded on a Specord UV–visible spectrophotometer (Zeiss, Jena) in ethanol at concentration $2{\cdot}5 \times 10^{-5}$ mol litre^{-1}.

The ^{1}H-NMR spectra were measured at 80 MHz with a Tesla BS 487c spectrometer in $CDCl_3$ solutions using TMS as internal standard.

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

Dyeings and fastness properties were determined according to Polish Standards which correspond with British Standards.[6]

Lightfastness was measured with a Xenotest apparatus (Hanau) and fastness to dry-heat treatment with Fixotest apparatus (Hanau).

2.1 Synthesis of the dye D-V

Sodium nitrite (1·03 g) was slowly added with stirring to 12 ml sulphuric acid. The temperature was raised to 70°C to complete dissolution. After cooling this solution to 10°C, 2·74 g (0·015 mol) of 2,4-dinitroaniline was added.

The mixture was stirred for 1 h at room temperature, 35 g of ice was then added and impurities were filtered off. The solution of 4·24 g (0·015 mol) of the ethyl ester of *N*-benzyl-*N*-phenyl-*β*-alanine in 20 ml of acetic acid was added to the filtrate. After 30 min, the reaction mixture was neutralised with sodium acetate to pH 3–4 and the coupling reaction was continued for a further 5–6 h. The precipitated dye was filtered off, washed with water and dried; 6·6 g of the dye was obtained (92% yield).

2.2 Synthesis of the dye D-VI

To the mixture of 2·445 g (0·015 mol) of 2-cyano-4-nitroaniline in 10 ml of ethylene glycol, 72 ml of 0·625M sulphuric acid in ethylene glycol at 50°C was added. The diazotisation was carried out at 20°C with 18 ml of 10% solution of glycol nitrite for 1 h.

To the diazonium salt, a solution of 4·24 g (0·015 mol) of the ethyl ester of *N*-benzyl-*N*-phenyl-*β*-alanine in 20 ml of acetic acid was added. The remainder of the procedure was that described for Section 2.1; 5·7 g of the dye was obtained (83% yield).

The elemental analyses and melting points of dyes **D-1–D-XIV** are summarised in Table 2.

3 RESULTS AND DISCUSSION

The structure of the dyes was verified by elemental analyses (Table 2) and additionally confirmed by mass spectra and by ^{1}H-NMR spectroscopy (Tables 3 and 4).

TABLE 2
Characterisation Data, Visible Spectra and Fastness of Dyeings for Dyes **D-1–D-XIV**

Dye	*Melting point (°C)*	*Yield (%)*	*Nitrogen (%)*		λ_{max} *(nm) (in ethanol)*	$\varepsilon_{max} \times 10^{-4}$	*Fastness*[a] *to dry-heat treatment, 180°C*				*Light-fastness*
			Calc.	*Found*			*1*	2	3	*4*	
D-I	122–123	91	12·96	13·04	463	3·20	3	2–3	3	2–3	4
D-11	87–89	78	12·55	13·00	465	2·88	4	2–3	4–5	3	4
D-III	109–111	81	12·12	12·00	473	2·88	4–5	3	3–4	3–4	4
D-IV	97–98	82	12·01	11·94	485	2·85	3–4	2–3	3	2–3	4
D-V	115	92	14·67	14·51	506	2·80	3–4	3	3–4	3–4	4
D-VI	103–104	83	15·31	15·20	515	3·80	4–5	2–3	3–4	3–4	5
D-VII	89–90	81	11·17	11·21	431	2·40	4	3	3	3	4–5
D-VIII	120–121	84	12·01	11·89	450	2·88	3–4	3	3–4	3–4	2–3
D-IX	96–97	73	13·59	13·42	440	2·80	4	2–3	3–4	3–4	4
D-X	98–99	85	12·96	12·82	429	3·00	4	2–3	3–4	3–4	3–4
D-XI	92–93	88	12·55	12·31	430	2·88	4–5	3	4	3–4	4
D-XII	86–88	87	12·01	11·91	446	2·88	4	3	3–4	4	4
D-XIII	94–96	86	8·34	8·02	425	2·60	4–5	4	3–4	4–5	3
D-XIV	79–81	83	8·58	8·28	436	2·94	3	2–3	3	3	3

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

Analysis of the chemical shifts, multiplicity and integration of the relevant groups of protons in the ^{1}H-NMR spectra provided unambiguous arguments in support of the proposed structures.

Visible spectra of the dyes recorded in ethanolic solutions (Table 2) showed that the change of position of the strongly electron-attracting nitro group from *meta* (**D-X**) to *para* (**D-1**) to the azo group causes a bathochromic shift in the λ_{max} from 429 nm to 463 nm. The same effect is also observed on introduction of a substituent *ortho* to the azo group, the extent of this bathochromic shift depending on the nature of the substituent. The largest bathochromic shift is observed when a nitro or cyano group is present in the *ortho* position.

Although the nitro group is more electron-attracting than cyano group, the λ_{max} of the dye **D-V** is hypsochromic with respect to that of dye **D-VI**, this resulting from some steric inhibition of resonance in the *ortho* nitro derivative.[7]

The presence of substituents in the *ortho* position to the azo group also affects the molar extinction coefficient. In dyes possessing one substituent *ortho* to the azo group, the values of the molar extinction coefficient are generally lower than in their unsubstituted analogues. The high value of the molar extinction coefficient of dye **D-VI** is associated with the planarity of the cyano group and consequent absence of steric hindrance.[8]

When both positions *ortho* to the azo group are occupied by spatially bulky substituents the steric effect[7] is greatest. Hence dye **D-VII**, derived from 2,6-dichloro-4-nitroaniline, has λ_{max} shifted hypsochromically by 23 nm and the molar extinction coefficient is considerably lowered in comparison with the dye **D-1**, which is unsubstituted in the 2,6-positions.

Dyeings on polyester of dyes **D-I–D-XIV** were yellow to bordeaux and had excellent brightness and high intensity. Fastness properties are given in Table 2.

Lightfastness of the dyes varied from moderate and good and dyes containing a nitro group in the *para* position showed similar fastness to the *meta*-substituted analogue. Highest lightfastness was shown by dyes **D-VI** and **D-VII**, derivatives of the 2-cyano-4-nitroaniline and 2,6-dichloro-4-

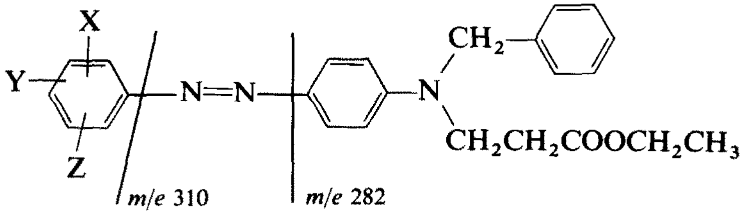
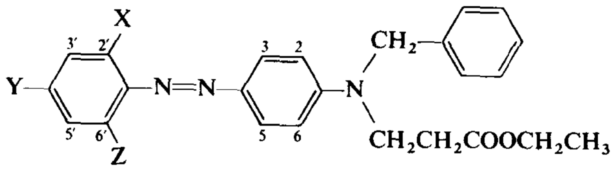


Fig. 1.

TABLE 3

^{1}H-NMR Spectral Assignments of Dyes **D-I–D-IX**[a]



Dye	*^{1}H-NMR (CDCl$_3$, TMS int., δ (ppm), J (Hz)*
D-I	1·20 t (3H, $J = 7·0$, —$OCH_2\underline{CH_3}$), 2·65 t (2H, $J = 7·0$, —$CH_2\underline{CH_2}COOCH_2CH_3$), 3·88 t (2H, $J = 7·0$, —$N\underline{CH_2}CH_2$), 4·10 q (2H, $J = 7·0$, —$\underline{CH_2}CH_3$), 4·65 bs (2H, —$Ph\underline{CH_2}$), 6·58–6·98 m (2H, 2, 6-H), 7·01–7·40 m (5H, Ph), 7·73–8·00 m (4H, 2′, 6′, 3, 5-H), 8·13–8·40 m (2H, 3′, 5′-H)
D-11	1·20 t (3H, $J = 7·0$, —$OCH_2\underline{CH_3}$), 2·63 t (2H, $J = 7·0$, —$CH_2\underline{CH_2}COOCH_2CH_3$), 2·63 s (3H, $\underline{CH_3}Ph$), 3·85 t (2H, $J = 7·0$, —$N\underline{CH_2}CH_2$), 4·10 q (2H, $J = 7·0$, —$\underline{CH_2}CH_3$), 4·65 bs (2H, —$Ph\underline{CH_2}$), 6·56–6·93 m (2H, 2, 6-H), 6·98–7·44 m (5H, Ph), 7·60d (1H, $J_{5'6'} = 9·0$, 6′-H), 7·73–7·90 m (2H, 3,5-H), 7·93–8·23 m (2H, 3′, 5′-H)
D-III	1·18 t (3H, $J = 7·0$, —$OCH_2\underline{CH_3}$), 2·65 t (2H, $J = 7·0$, —$CH_2\underline{CH_2}COOCH_2CH_3$), 3·82 t (2H, $J = 7·0$, —$N\underline{CH_2}CH_2$), 3·96 s (3H, $\underline{CH_3}OPh$), 4·10 q (2H, $J = 7·0$, —$\underline{CH_2}CH_3$), 4·63 bs (2H, —$Ph\underline{CH_2}$), 6·55–6·88 m (2H, 2, 6-H), 7·00–7·40 m (5H, Ph), 7·40–7·97 m (5H, 3′, 5′, 6′, 3, 5-H)

D-IV	1·20 t (3H, $J = 7{\cdot}0$, —$\text{OCH}_2\underline{\text{CH}_3}$), 2·66 t (2H, $J = 7{\cdot}0$, —$\text{CH}_2\underline{\text{CH}_2}\text{COOCH}_2\text{CH}_3$), 3·88 t (2H, $J = 7{\cdot}0$, —$\text{N}\underline{\text{CH}_2}\text{CH}_2$), 4·05 q (2H, $J = 7{\cdot}0$, —$\underline{\text{CH}_2}\text{CH}_3$), 4·66 bs (2H, —$\text{Ph}\underline{\text{CH}_2}$), 6·62–6·92 m (2H, 2, 6-H), 7·06–7·50 m (5H, Ph), 7·63–8·00 m (3H, 3, 5, 6′-H), 8·12 dd (1H, $J_{5'6'} = 9{\cdot}0$, $J_{3'5'} = 2{\cdot}8$, 5′-H), 8·35 d (1H, $J_{3'5'} = 2{\cdot}8$, 3′-H)
D-V	1·19 t (3H, $J = 7{\cdot}0$, —$\text{OCH}_2\underline{\text{CH}_3}$), 2·65 t 2H, $J = 7{\cdot}0$, —$\text{CH}_2\underline{\text{CH}_2}\text{COOCH}_2\text{CH}_3$), 3·88 t (2H, $J = 7{\cdot}0$, —$\text{N}\underline{\text{CH}_2}\text{CH}_2$), 4·10 q (2H, $J = 7{\cdot}0$, —$\underline{\text{CH}_2}\text{CH}_3$), 4·66 bs (—$\text{Ph}\underline{\text{CH}_2}$), 6·62–6·88 m (2H, 2, 6-H), 7·03–7·50 m (5H, Ph), 7·70–8·00 m (3H, 3, 5, 6′-H), 8·12 dd (1H, $J_{5'6'} = 9{\cdot}0$, $J_{3'5'} = 3{\cdot}0$, 5′-H), 8·49 d (1H, $J_{3'5'} = 3{\cdot}0$, 3′-H)
D-VI	1·18 t (3H, $J = 7{\cdot}0$, —$\text{OCH}_2\underline{\text{CH}_3}$), 2·67 t (2H, $J = 7{\cdot}0$, —$\text{CH}_2\underline{\text{CH}_2}\text{COOCH}_2\text{CH}_3$), 3·88 t (2H, $J = 7{\cdot}0$, —$\text{N}\underline{\text{CH}_2}\text{CH}_2$), 4·10 g (2H, $J = 7{\cdot}0$, —$\underline{\text{CH}_2}\text{CH}_3$), 4·68 bs (2H, —$\text{Ph}\underline{\text{CH}_2}$), 6·62–6·88 m (2H, 2, 6-H), 7·02–7·42 m (5H, Ph), 7·70–8·02 m (3H, 3, 5, 6′-H), 8·12 dd (1H, $J_{5'6'} = 9{\cdot}5$, $J_{3'5'} = 3{\cdot}0$, 5′-H), 8·55 d (1H, $J_{3'5'} = 3{\cdot}0$, 3′-H)
D-VII	1·22 t (3H, $J = 7{\cdot}0$, —$\text{OCH}_2\underline{\text{CH}_3}$), 2·68 t (2H, $J = 7{\cdot}0$, —$\text{CH}_2\underline{\text{CH}_2}\text{COOCH}_2\text{CH}_3$), 3·88 t (2H, $J = 7{\cdot}0$, —$\text{N}\underline{\text{CH}_2}\text{CH}_2$), 4·12 q (2H, $J = 7{\cdot}0$, —$\underline{\text{CH}_2}\text{CH}_3$), 4·72 bs (2H, —$\text{Ph}\underline{\text{CH}_2}$), 6·55–6·98 m (2H, 2, 6-H), 6·98–7·44 m (5H, Ph), 7·73–8·05 m (2H, 3, 5-H), 8·18–8·38 m (2H, 3′, 5′-H)
D-VIII	1·19 t (3H, $J = 7{\cdot}0$, —$\text{OCH}_2\underline{\text{CH}_3}$), 2·63 t (2H, $J = 7{\cdot}0$, —$\text{CH}_2\underline{\text{CH}_2}\text{COOCH}_2\text{CH}_3$), 3·84 t (3H, $J = 7{\cdot}0$, —$\text{N}\underline{\text{CH}_2}\text{CH}_2$), 4·10 q (2H, $J = 7{\cdot}0$, —$\underline{\text{CH}_2}\text{CH}_3$), 4·68 bs (2H, —$\text{Ph}\underline{\text{CH}_2}$), 6·56–6·88 m (2H, 2, 6-H), 7·00–7·43 m (5H, Ph), 7·42–7·93 m (5H, 3, 5, 3′, 5′, 6′-H)
D-IX	1·18 t (3H, $J = 7{\cdot}0$, —$\text{OCH}_2\underline{\text{CH}_3}$), 2·65 t (2H, $J = 7{\cdot}0$, —$\text{CH}_2\underline{\text{CH}_2}\text{COOCH}_2\text{CH}_3$), 3·84 t (3H, $J = 7{\cdot}0$, —$\text{N}\underline{\text{CH}_2}\text{CH}_2$), 4·10 q (2H, $J = 7{\cdot}0$, —$\underline{\text{CH}_2}\text{CH}_3$), 4·68 bs (2H, —$\text{Ph}\underline{\text{CH}_2}$), 6·56–6·93 m (2H, 2, 6-H), 7·00–7·40 m (5H, Ph), 7·40–8·08 m (6H, 3, 5, 3′, 4′, 5 , 6′-H)

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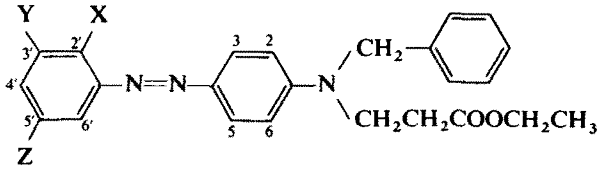
[a] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

TABLE 4
^{1}H-NMR Spectral Assignments of Dyes **D-X–D-XIV**[a]



Dye	*^{1}H-NMR ($CDCl_3$, TMS int., δ (ppm), J (Hz)*
D-X	1·14 t (3H, $J = 7{\cdot}0$, $—OCH_2\underline{CH_3}$), 2·63 t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_2CH_3$), 3·83 t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_3$), 4·10 q (2H, $J = 7{\cdot}0$, $—\underline{CH_2}CH_3$), 4·66 bs (2H, $—Ph\underline{CH_2}$), 6·60–6·88 m (2H, 2, 2, 6-H), 7·01–7·38 m (5H, Ph), 7·38–7·70 m (1H, 3′-H), 7·70–7·98 m (2H, 3, 5-H), 7·98–8·26 m (2H, 2′, 4′-H), 8·52–8·70 m (1H, 6′-H)
D-XI	1·20 t (3H, $J = 7{\cdot}0$, $—OCH_2\underline{CH_3}$), 2·67 t (2H $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_2CH_3$), 2·65 s (3H, $Ph\underline{CH_3}$), 3·83 t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_2$), 4·10 q (2H, $J = 7{\cdot}0$, $—\underline{CH_2}CH_3$), 4·66 bs (2H, $—Ph\underline{CH_2}$), 6·57–6·91 m (2H, 2, 6-H), 7·00–7·26 m (5H, Ph), 7·26–7·50 m (1H, 3′-H), 7·68–7·98 m (2H, 3, 5-H), 8· 11 dd (1H, $J_{4'6'} = 2{\cdot}8$, $J_{3'4'} = 8{\cdot}6$, 4′-H), 8·42 d (1H, $J_{4'6'} = 2{\cdot}8$, 6′-H)
D-XII	1·18 t (3H, $J = 7{\cdot}0$, $—OCH_2\underline{CH_3}$), 2·65 t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_2CH_3$), 3·83 t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_2$), 4·08 q (2H, $J = 7{\cdot}0$, $—\underline{CH_2}CH_3$), 4·66 bs (2H, $—Ph\underline{CH_2}$), 6·58–6·88 m (2H, 2, 6-H), 7·00–7·38 m (5H, Ph), 7·57 d (1H, $J_{3'4'} = 8{\cdot}9$, 3′-H), 7·85–8·01 m (2H, 3, 5-H), 8·10 dd (1H, $J_{3'4'} = 8{\cdot}9$, $J_{4'6'} = 3{\cdot}0$, 4′-H), 8·47 d (1H, $J_{4'6'} = 3{\cdot}0$, 6′-H)
D-XIII	1·19 t (3H, $J = 7{\cdot}0$, $—OCH_2\underline{CH_3}$), 2·65 t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_2CH_3$), 3·60–4·18 m (10H, $—N\underline{CH_2}CH_2$, $—\underline{CH_2}CH_3$, $—COO\underline{CH_3}$, 4·65 bs (2H, $Ph\underline{CH_2}$), 6·58–6·88 m (2H, 2, 6-H), 6·93–7·43 m (5H, Ph), 7·68–8·00 m (2H, 3, 5-H), 8·45–8·88 m (3H, 2′, 4′, 6′-H)
D-XIV	1·19 t (3H, $J = 7{\cdot}0$, $—\underline{OCH_2CH_3}$), 2·65 t (2H, $J = 7{\cdot}0$, $—CH_2\underline{CH_2}COOCH_2CH_3$), 3·83 t (2H, $J = 7{\cdot}0$, $—N\underline{CH_2}CH_2$), 4·08 q (2H, $J = 7{\cdot}0$, $—\underline{CH_2}CH_3$), 4·61 bs (2H, $—Ph\underline{CH_2}$), 6·55–6·88 m (2H, 2, 6-H), 6·95–7·35 m (5H, Ph), 7·45–7·60 m (2H, 3, 5-H), 7·70–8·05 m (3H, 3′, 4′, 6′-H)

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

TABLE 5
Relationship between Lightfastness and Mass Spectra Fragmentation

Dye	Lightfastness	m/e 310/M^+	m/e 282/M^+
D-I	4	0·007	0·195
D-VI	5	0·024	0·065
D-VIII	2–3	0·039	0·870
D-X	3–4	0·018	0·307

nitroaniline respectively, and lowest lightfastness by dye **D-VIII** derived from 2-nitro-4-chloroaniline (cf. Ref. 7).

The lightfastness of dyes **I** and **II** was investigated in relation to their electron-impact induced fragmentations, using the mass spectra of selected dyes **D-1**, **D-VI**, **D-VIII** and **D-X**. In the case of dyes **I** and **II** the fragmentation may be expressed in terms of the relative abundance of the fragment ions at m/e 282 and m/e 310 compared with that of the molecular ion (Fig. 1).

Ratios of these fragments with respect to the molecular ion were measured and the results are given in Table 5.

The results show the higher abundance of the fragments m/e 310 and m/e 282 relative to that of the molecular ion in dye **D-VIII** in comparison with the dyes **D-1**, **D-VI** and **D-X**. The order of stability of the dyes in respect of electron-impact induced fragmentation and of photochemical degradation is thus the same, in accord with previous observations on other aminoazobenzene disperse dyes.[7]

The fastness to dry-heat treatment indicated that the best fastness was shown by dye **D-XIII**, which contains two ester substituents in the diazo component. In the series of dyes derived from *m*- or *p*-nitroaniline, improvement in the dry-heat fastness resulted from the introduction of a further *ortho* substituent, with the exception of a chloro substituent, the presence of which gave no fastness improvement. The dry-heat fastness of the dyes was generally only moderate but was however better than that of analogous dyes derived from the use as coupling component of *N*-benzyl-*N*-ethylaniline.[9]

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