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SUBSTITUENT EFFECTS ON THE COLOUR, DYEING AND FASTNESS PROPERTIES OF 4-*N*-β-CYANOETHYL-*N*-β-HYDROXYETHYLAMINOAZOBENZENES

PART I—MONOSUBSTITUTED DERIVATIVES

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SUMMARY

Data on a series of 40 monosubstituted derivatives of 4-N-*β-hydroxyethyl*-N-*β-cyanoethylaminoazobenzene are reported. Structure–property relationships with respect to electronic spectra of the dyes, coloration and fastness properties on cellulose* secondary *acetate and polyester fibres are investigated. Reasons for the anomalous properties of the 2′-nitro derivative in exhibiting low lightfastness on synthetic polymer fibres are presented. The coloration of polyester fibres is additionally assessed in terms of data derived from tristimulus values of dyed fibres, and the effect of substituents on such data is discussed.*

1. INTRODUCTION

Some information has been reported on substituent effects in aminoazobenzene disperse dyes, particularly with respect to the influence of diazo or coupling components on the visible absorption maxima[1–4] and to general relationships between the colour, fastness properties and substituent effects in both aminoazobenzenes[5,6] and related benzothiazolylazo dyes [7,8] In some aminoazobenzenes, relationships between the Hammett σ-constants of the substituents, electronic spectra data in neutral and acidic media, and pK_a values of the dyes have been observed.[9]

Many of these investigations have been made on limited ranges of dyes and few data have been reported relating substituent effects and coloration properties. We report here some data pertinent to a series of dyes of general formula I, particularly

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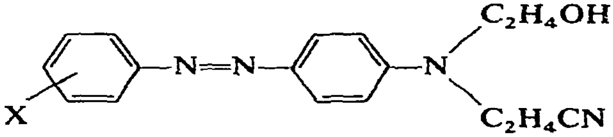


(I)

with respect to the influence of the nature and orientation of substituent X on the colour, dyeing and fastness properties of these dyes.

2 EXPERIMENTAL

All **I** were obtained by conventional diazotisation and coupling techniques,[1,5] using technical grade *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline as coupling component Gas–liquid chromatographic analysis at 220 °C on a 5 ft column packed with 20 % Silicone E301 in Embacol 100-200, injecting from a 10 % solution in chloroform, showed the presence of 18 % *N*-β-cyanoethylaniline, 1·7 % *N*,*N*-bis-β-cyanoethylaniline and 0 8 % *N*,*N*-bis-β-hydroxyethylaniline Purification of crude dyes was therefore effected by preparative layer chromatography on 2 mm-thick plates of silica gel, applying the dyes from acetone solution and developing the plates by a multiple-run technique using toluene.acetone (95·5) as eluent until the principal band had fully separated from other contaminants, extraction of this band with boiling ethanol or acetone afforded pure **I** Whilst most **I** were readily obtained analytically pure by this method, modifications were necessary with certain dyes.[10]

Electronic spectra in absolute ethanol, dyeings of **I** on cellulose *secondary* acetate and on Trevira 5051 polyester cloth (FH), lightfastness and fastness to sublimation were carried out using the procedures previously described.[1,5]

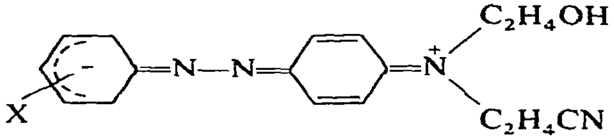
Dyeings on polyester were measured on a Kollmorgan KCS 18 Automatic Color Eye Colorimeter interfaced with a PDP 8 Digital Computer The computer was programmed to calculate, for Illuminant C, 2° observer, X, Y and Z values, together with dominant wavelength and excitation purity.

Mass spectra of selected dyes were recorded, using a direct insertion probe, on an AEI MS 902 instrument, source 250 °C, 70 eV ionising energy, 200 μA emission Spectra were normalised for measurements of relative abundance.

3. DISCUSSION

3 1 *Visible absorption maxima*

The influence of polar characteristics (usually expressed in terms of Hammett σ-constants) of substituent groups on changes in the visible absorption maxima of aminoazobenzene disperse dyes has been discussed for limited ranges of dyes.[1,3] The visible absorptive band, which has been associated with photoexcited structures involving π–π^* intramolecular charge transfer between conjugated donor and acceptor substituents in a π electron system, contains also a hidden n–π^* transition, symmetry forbidden for the *trans*-isomer, which obtains its high intensity from the neighbouring π–π^* transition.[11] In terms of valence bond resonance theory, when the conjugated system may be regarded as a resonance hybrid of two extreme canonical forms, substituent effects which tend to result in the two forms being closer in energy will bring about a bathochromic shift of the long wavelength band. In **I**, where the dyes can be regarded as a hybrid of **I** and **II**, the latter form is stabilised where X is an electron attracting group, and hence such substituents exert a bathochromic shift.



(II)

When the shifts in λ_{max} resulting from the introduction of substituent X ($\Delta\lambda$, Table 1) were plotted against Hammett σ-constants, good relationships were observed Hammett σ-constants were taken from Barlin and Perrins,[12] data being available for *meta* substituents F, Cl, Br, CF_3, SO_2CH_3, SO_2NH_2, $CONH_2$, $COOC_2H_5$, $COCH_3$, CN, NO_2, CHO and —N= (14 dyes, including X = H), and for *para* substituents F, Cl, Br, CF_3, SO_2CH_3, SO_2NH_2, $CONH_2$, $COOC_2H_5$, $COCH_3$, NO_2 and CHO (13 dyes, including R = H) Least squares analysis of the relevant data gave the relationships

$$\Delta\lambda = 39{\cdot}7505\sigma + 1{\cdot}8649\,(\text{nm}) \qquad (1)$$

for substitution at the *para* position, with a correlation coefficient $r = 0{\cdot}9869$, and

$$\Delta\lambda = 31{\cdot}5268\sigma + 0{\cdot}2028\,(\text{nm}) \qquad (2)$$

for substitution at the *meta* position, with a correlation coefficient $r = 0{\cdot}9973$. Correlations at both positions thus have an acceptably high value for predictive use

Within the range of dyes synthesised in this current work, colour shifts for substitution at the *meta* position extended over the range 9 nm ($CONH_2$ and $NHCOCH_3$) to 23 nm (NO_2), and for *para* substitution from 3 nm (F) to 54 nm (NO_2), confirming the value of *para* substitution for maximum colour shift, and, additionally, the unique value of the 4′-nitro group.[1]

The relationships in eqn 1 and eqn 2 may be valid where the substituent X is an electron acceptor, but they are not generally applicable to substituents with negative Hammett σ-constants Whilst such substituents can give the expected hypsochromic shifts in λ_{max},[1] in some cases their presence in dyes related to **I** can result in

TABLE 1
COLOUR DATA FOR DYES **I**

X	*M p* (°*C*)	λ_{max} *(ethanol)* *(nm)*	$\varepsilon_{max} \times 10^{-4}$	$\Delta\lambda$ *(nm)*
H	[a]	397	2 69	—
2'-Cl	[a]	414	2 59	16
3 -Cl	66–67	409	2 89	12
4'-Cl	154–155	408	2 95	11
2'-Br	56–57	415	2 55	18
3'-Br	81–83	410	2 87	13
4'-Br	155–156	410	2 96	13
2 -F	[a]	410	2 57	13
3'-F	56–57	408	2 61	11
4 -F	119–120	400	2 64	3
2 -CF$_3$	121–122	416	2 77	19
3 -CF$_3$	61–62	412	2 90	15
4'-CF$_3$	121–122	418	2 95	21
2 -SO$_2$CH$_3$	130–131	433	2 86	36
3'-SO$_2$CH$_3$	147–148	417	2 91	20
4'-SO$_2$CH$_3$	162–163	435	3 00	38
3 -SO$_2$NH$_2$	156–157	411	2 91	14
4 -SO$_2$NH$_2$	160–161	421	2 96	24
3 -NHCOCH$_3$	180–181	406	2 85	9
4 -NHCOCH$_3$	198–199	409	2 98	12
3'-CONH$_2$	161–162	406	2 71	9
4 -CONH$_2$	182–183	417	2 87	20
3'-CHO	93–94	409	2 72	12
4'-CHO	143–144	438	2 81	41
2'-COOC$_2$H$_5$	[a]	405	2 72	8
3'-COOC$_2$H$_5$	128–129	409	2 88	12
4 -COOC$_2$H$_5$	134–136	422	2 90	25
2'-COCH$_3$	164–166	415	2 56	18
3'-COCH$_3$	124–125	409	2 88	12
4'-COCH$_3$	184–185	429	2 91	32
2 -COC$_6$H$_5$	128–130	419	2 56	22
3'-COC$_6$H$_5$	86–87	412	2 80	15
4'-COC$_6$H$_5$	99–101	432	2 88	35
2 -CN	124–125	433	3 09	36
3'-CN	110–111	417	3 00	20
4'-CN	161–162	433	3 16	36
2 -NO$_2$	117–118	424	2 76	27
3'-NO$_2$	121–122	420	2 85	23
4'-NO$_2$	179–180	451	3 16	54
3'-aza	166–167	416	2 67	19

[a] Compound not solid at ambient temperature

bathochromic shifts.[13] In **I**, considering substitution by such groups in the *para* position, the methoxy group (Hammett σ-constant −0·27)[12] should, by substitution into eqn. 1, result in a hypsochromic shift of approximately 9 nm Synthesis of **I** (X = 4'-OCH$_3$) showed the dye to have λ_{max} at 398 nm, i e. a bathochromic shift of 1 nm. Similar deviations were observed where X was 4'-N(CH$_3$)$_2$ (σ-constant −0·83, predicted hypsochromic shift from eqn. 1 approx.

31 nm, observed λ_{max} 396 nm, a hypsochromic shift of 1 nm) and where X was 4'-OC_6H_5 (σ-constant $-0{\cdot}32$, predicted hypsochromic shift approx. 11 nm, observed λ_{max} 402 nm, a bathochromic shift of 5 nm).

Such deviations with electron donor substituents presumably arise by introduction into the dye molecule of groups containing an extra *p*-orbital and two electrons, thus raising the energy of the highest π-orbital relative to that of the lowest anti-bonding π-orbital.[14]

Where X is substituted *ortho* to the azo group, prediction of colour shifts is not possible in view of the superposition of electronic and steric factors Thus, on the basis of the inductive effect of the CF_3 group, bathochromicity should increase in the order $o > m > p$, whereas the observed shifts are $p > o > m$. Steric factors have been observed on introducing the $—CH_3$ group into azobenzenes [15,16]

A reversal of shifts in λ_{max} which may be anticipated solely on the basis of the electronic effects of the nitro and cyano groups occurs when these substituents are in the 2'-position. Thus, whereas the nitro group is the more strongly electron attracting, the dye **I** where X = 2'-NO_2 has λ_{max} 424 nm, but where X = 2'-CN, λ_{max} is 433 nm This may result from some steric inhibition of resonance in the 2'-nitro derivative, absent on introduction of the planar rod-like 2'-cyano group. The cyano group gives similar bathochromic shifts when present in the 2'- and 4'-positions; whereas the mesomeric effect for this group is in the order 4' > 2', the inductive effect is the reverse, and the two combined effects thus result in similar overall electronic effects in both positions. Similar results have been observed in dyes related to **I**, but using coupling components other than that employed in this current work [1]

Conclusions derived solely from λ_{max} values can, however, be misleading, and such data are preferably considered in conjunction with ε_{max} values. In dyes **I**, the molar extinction coefficient generally increases with substitution by X. Steric hindrance factors for substitution of the 2' position, whilst usually more apparent when two positions *ortho* to the azo linkage are substituted,[17] are indicated in some instances in Table 1.

It has been concluded[17] that the more planar substituents, such as nitro or carbonyl, when substituted *ortho* to the azo group, tend to relinquish coplanarity with the phenyl rings, thus obviating steric effects. In such cases, significant differences in λ_{max} can result when these substituents are present in the 2'- and 4'-positions. This is apparent in dyes **I** (Table 1), e.g 2'-NO_2 and 4'-NO_2, $\Delta\lambda$ 27 nm, 2'-COC_6H_5 and 4'-COC_6H_5, $\Delta\lambda$ 13 nm; 2'-$COCH_3$ and 4'-$COCH_3$, $\Delta\lambda$ 14 nm; 2'-$COOC_2H_5$ and 4'-$COOC_2H_5$, $\Delta\lambda$ 17 nm

In the case of spherical or tetrahedral substituents, there is little difference between substitution at the 2'- or 4'-positions, e.g. Cl, $\Delta\lambda$ 5 nm; Br, $\Delta\lambda$ 5 nm; $COCF_3$, $\Delta\lambda$ 2 nm; SO_2CH_3, $\Delta\lambda$ 2 nm

The steric factors operative for substitution at the 2'-position are however indicated in the lower ε_{max} values for substitution at this position. The values in Table 1 indicate a 13·85 % differential in ε_{max} values between the dyes where X = 4'-Br and

2′-Br, and an 8·5% differential for the chloro analogues (2·65% for the spatially smaller fluorine substituent). In the case of other more strongly polar substituents which show little difference in λ_{max} when substituted at the 2′- or 4′-positions, e.g methylsulphonyl, absence of significant steric effects is indicated in the much lower differential in ε_{max} values (4·7%); the rod-like shape of the cyano group results in a minimum of steric interaction, and with this substituent the ε_{max} differential is only 2·2%. Thus, with substituents X which give similar λ_{max} values when substituted at the 2′- and 4′-positions (typified by halogens, alkyl sulphone and cyano), the presence of steric factors is readily indicated by a comparison of their ε_{max} values.

3.2 *Dyeing properties*

The coloration of cellulose *secondary* acetate was excellent with all **I**, the dyes building up to intense yellow to orange shades with almost complete dyebath exhaustion at 2·5% depth of shade. Neither the nature nor orientation of substituent X had a significant effect on dyeing properties.

On Trevira 5051 polyester, differences in dyeing properties were more pronounced. Dyes in which X = SO_2NH_2, $CONH_2$, $NHCOCH_3$, SO_2CH_3 in all orientations, and in which X = 2′-$COCH_3$ and 3′-N= had poor coloration properties, these dyes not building up to deep shades. The substituents which resulted in poor dyeing properties tended to be of a type which increased aqueous solubility, and at 100°C and above, the dye liquors of the above dyes showed complete dye solubility. Some relation between aqueous solubility and dyeing properties is thus indicated, although many other dyes which showed high solubility in dyebaths used for 0·1% and 0·5% dyeings gave good coloration of polyester.

The use of data derived from tristimulus values of dyes samples before and after a fastness test can be used to assess whether the dyeing loses colour 'on-tone' or 'off-tone', i.e whether the dominant wavelength remains constant or varies.[18] In a similar manner, assessment of samples dyed at different strengths can indicate whether the dye builds up 'on-tone' or not. Few data of this nature have been previously reported for disperse dyes on polyester.

The values of the dominant wavelengths (Table 1) clearly express in more quantitative ways the visual colour of the dyeings on polyester and indicate that all dyes **I** tend to build-up to a more orange tone at heavier depths of shade. Increases in dominant wavelength between 0·1% and 2·5% dyeings vary from 18 nm for the 4′-nitro derivative to 3 nm for the 3′-sulphonamido dye. The halogen containing dyes show an orange build-up in a general area of 8 nm, differences resulting from the nature and orientation of the halogen atom being relatively insignificant. With some substituents, e.g —COMe, —COPh, —COOEt, —CHO, an enhanced orange build-up occurs with *para*-substitution, and this is especially marked with the 4′-nitro derivative. Dominant wavelengths for dyeings of this dye clearly show the intense colour value imparted by this substituent when *para* to the azo linkage; the dominant wavelength of 2·5% dyeings is 15 nm higher than that of the closest dyes, viz. the 4'-cyano and 4'-formyl derivatives, although at 0 1 % dyeings, differences are less marked.

3.3. *Lightfastness*

The lightfastness of all dyeings on cellulose *secondary* acetate (Table 2) was, with the exception of the 2'-nitro derivative, good, and generally of a higher order than on polyester.

In terms of the well documented generalisation that the introduction of electron attracting substituents decreases lightfastness on non-protein substrates,[19-21] or that lightfastness may be related to π-electron delocalisation,[22] an increase in overall electron mobility, viz introduction of electron attracting substituents X in dyes **I**, would be expected to result in a decrease in lightfastness. In certain media, fading has been related to Hammett σ-constants of substituent groups[19-21,23 24] and the significance of the basicity of the amino group in the coupling component has been indicated [25-27]

In the context of electron delocalisation, the advantage of substitution *meta* to the azo group has been indicated,[28 29] but the data in Table 2 indicate that such advantages, whilst possibly acceptable on a theoretical basis, are not visually apparent in dyes **I** The presence of electron acceptor groups in the *para* position results in a lightfastness not significantly different from that observed with similar substitution at the *meta* position.

The diminished fastness of substituents containing amino groups, e.g —$CONH_2$, —SO_2NH_2, seems most likely to be due to preferential initiation of photodegradation at the amino group. The relatively high fastness of 4'-nitro-4-*N*-β-cyanoethyl-*N*-β-hydroxyethylaminoazobenzene may be considered unusual in terms of the above conclusions pertaining to electron mobility in the dyes, since in this dye, electron mobility is most facile; it is additionally unusual in view of the known instability of other similar nitro containing dyes, e.g. 4-nitrodiphenylamine,[30,31] unless the nitro group is in a stabilised hydrogen-bonded environment. The very poor stability of the 2'-nitro isomer is anomalous, and may be compared with the low visible absorption maxima of this dye (mentioned previously)

The high fastness of the 4'-nitro isomer must arise from a strong resonance stabilisation of the photoexcited state. The low lightfastness of 2'-nitro-4-aminoazobenzenes has been associated[19] with a preferential photoreduction of the nitro group rather than the azo nitrogen atoms, but we have more recently demonstrated the relationship between the rate of photofading of some 4-aminoazobenzenes and the electronegativity of the β-nitrogen atom on the azo group[32] and also between the lightfastness of these dyes and electron-impact induced fragmentation pertinent to electron localisation on the azo nitrogen atoms [33]

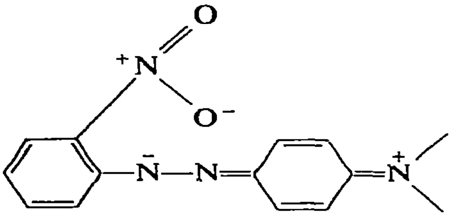
Considering possible electron delocalisation in the 2'-nitro compound, it is feasible to envisage charge repulsion in structure **III** inhibiting further electron

TABLE 2
COLOUR AND FASTNESS DATA ON DYES I

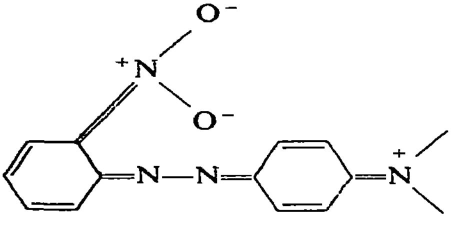
X	$\lambda_D{}^a$ on *polyester*			*Lightfastness*						*Sublimation fastness* (°C)
				Secondary *acetate*			*Polyester*			
	0.1%	*0.5%*	*2.5%*	*0.1%*	*0.5%*	*2.5%*	*0.1%*	*0.5%*	*2.5%*	
H	573	575	578	4	4–5	4–5	4	4–5	5	150
2 -Cl	574	578	583	4–5	5	5	4	5	5	160
3'-Cl	575	577	582	4	4–5	4	4	4	4	150
4'-Cl	573	578	582	5	5	5	5	5	5	160
2'-Br	575	578	583	5	5	5	4–5	5	5	160
3'-Br	574	577	581	4	5	5	4–5	5	5	150
4'-Br	574	577	582	4	5	5	4–5	5	5	150
2'-F	573	576	579	5	5	5	4	5	5	150
3'-F	574	576	581	5	5	5	4	5	5	140
4'-F	574	576	580	5	5	5	4	4–5	4–5	140
2 -CF$_3$	574	578	585	5–6	6	6	4–5	5	5	140
3'-CF$_3$	573	577	581	4–5	5–6	6	4	5	5	140
4 -CF$_3$	576	580	585	5	5	5–6	4–5	4–5	4–5	140
2 -SO$_2$CH$_3$	573	576	579	5	5–6	6	3	3–4	4–5	200
3 -SO$_2$CH$_3$	571	574	577	5	5	5	3	4	4–5	210
4 -SO$_2$CH$_3$	575	576	579	5	5	6	3	3–4	4–5	220
3 -SO$_2$NH$_2$	572	573	575	4–5	5	5	3	3	4	220
4'-SO$_2$NH$_2$	573	575	577	4	4–5	5	3	3	3–4	220
3 -NHCOCH$_3$	572	574	576	4	4–5	5	4	4	4–5	200
4 -NHCOCH$_3$	572	574	576	3–4	4–5	5	4	4	4–5	210
3 -CONH$_2$	572	573	576	4	4–5	5	2–3	4	4	220
4'-CONH$_2$	572	574	577	4	4–5	4–5	2–3	3–4	3–4	220
3 -CHO	574	576	579	5	5	5	4–5	5	5	160
4'-CHO	577	582	588	4	4–5	5	3–4	4	4	170
2'-COOC$_2$H$_5$	573	575	578	5	5–6	5–6	4	4–5	4–5	170
3'-COOC$_2$H$_5$	574	576	580	4–5	5	5–6	4–5	4–5	4–5	170
4 -COOC$_2$H$_5$	576	580	584	4–5	4–5	4	4	4–5	4–5	170
2'-COCH$_3$	574	576	579	4	4	4	4	4	4	180
3 -COCH$_3$	574	576	581	4–5	4–5	4–5	5	5	5	170
4 -COCH$_3$	575	581	585	4	4	4	4	4	4	160
2 -COC$_6$H$_5$	572	575	579	4–5	4–5	4–5	4	4	4	180
3'-COC$_6$H$_5$	572	574	576	4–5	5	5	4–5	4–5	4–5	180
4 -COC$_6$H$_5$	578	581	586	4	4	4–5	3–4	3–4	3–4	180
2'-CN	576	580	585	5	5	5	4	4–5	5	160
3 -CN	574	577	581	4–5	5	5	4	4	4	160
4'-CN	578	582	588	4–5	4–5	5	4	4–5	4–5	160
2'-NO$_2$	576	580	585	2	2–3	3–4	1–2	2	2	160
3'-NO$_2$	575	579	583	5	5	5	4	5	5	160
4'-NO$_2$	585	593	603	4–5	4–5	5	4	4–5	4–5	170
3-aza	572	574	576	4	4–5	5	4	4	5	160

[a] Dominant wavelength

delocalisation to **IV**. If this were so and the photoexcited state received a significant contribution from **III** rather than the fully delocalised **IV**, the bathochromic shift in the dye would be lower than expected, as is observed (see above), and the charge localisation on the azo nitrogen atom would also result in a higher susceptibility to photodegradation, as is also observed.



(III)



(IV)

In electron-impact induced fragmentations of aminoazobenzene disperse dyes, we have related[33] fragmentations due to charge localisation on the azo nitrogen atoms to lightfastness. In the case of dyes **I**, such fragmentation may be expressed in terms of the relative abundance of the fragment ions at *m/e* 189 and *m/e* 217 compared to that of the molecular ion (Fig 1). Ratios of such fragments were measured, and found to be, for the dye where X = 2'-NO_2, *m/e* 217(M$^+$) = 0·07 and *m/e* 189(M$^+$) = 0·44, for the dye where X = 4'-NO_2, *m/e* 217(M$^+$) = 0·02 and *m/e* 189(M$^+$) = 0·15, and for the dye where X = H, *m/e* 217(M$^+$) = 0·02 and *m/e* 189(M$^+$) = 0·23 These ratios clearly show the higher abundance of the fragments, relative to that of the molecular ion, for the dye where X = 2'-NO_2, compared to the dyes in which X = H or 4'-NO_2. Thus, the relative abundance of daughter ions resulting from fragmentation at the azo nitrogen atoms is greatest with the 2'-NO_2 compound, confirming the greater charge localisation on the azo nitrogen atoms in this dye Whilst dye degradations proceeding through a photoexcited dye molecule or an excited molecular ion occur through fundamentally different species, analogies may be made between the two modes of fragmentation.[33] Data derived from the mass spectra of the 2'-NO_2 and 4'-NO_2 isomers are however in accord with our earlier observations relating light stability and mass spectra data on aminoazobenzenes[33] and nitrodiphenylamine disperse dyes [34]

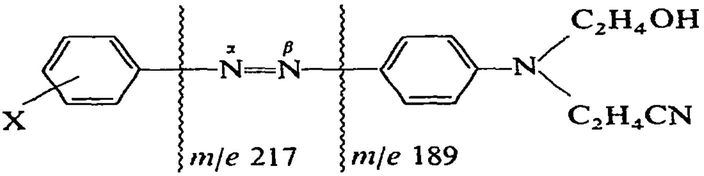


Fig 1 Fragmentation of dyes I

3.4 *Sublimation fastness*

The sublimation fastness of I was generally of a moderate order only. The apparently high fastness of dyes containing sulphonamide, carboxamide, methylsulphonyl and acetamido substituents (Table 2) must be considered in terms of their poor dyeing properties. For dyes which exhibited good coloration, the highest fastness, in the region of 180 °C initial mark-off, is of an acceptable standard The majority of dyes exhibited initial mark-off in the 160–180 °C region, although the presence of fluoro and trifluoromethyl groups was disadvantageous. Attempted correlations between molecular weight of I and mark-off temperature gave only random relationships, in general, the more polar substituents resulted in higher fastness, but correlations of Hammett σ-constants and mark-off temperature were only of a generally qualitative nature.

Both mass and polarity factors are conjointly relevant to sublimation fastness[22,35,36] and predictions of fastness based on either factor alone are not possible Thus, introduction of the bromo substituent gives no significant improvement. The benzoyl group, with a slightly higher mass and significantly larger polar effect than the bromine group, is particularly advantageous, although polar factors alone, expressed in terms of orientation effects, are not apparent, the 3′-benzoyl derivative having similar fastness to that of the 4′-benzoyl derivative Similarly, all three isomers where X = carboethoxy show fastness of a similar order, but some polar effect is apparent with the strongly electron acceptor nitro group, which gives highest fastness when substituted in the 4′-position

4 CONCLUSIONS

Whilst all monosubstituted I show excellent coloration properties on cellulose *secondary* acetate, substantivity on polyester fibres is more dependent on the nature of the substituent Comparison of the hues of dyeings resultant from introduction of different substituents into the dye molecule can be critically made on a consideration of dominant wavelengths, and the effect of substituents in imparting ‘off-tone’ build-up assessed

The lightfastness of I on polyesters is not significantly influenced by electron mobility within the range of dyes studied. The 2′-nitro derivative exhibits both poor lightfastness and a colour development less than that anticipated from the polar properties of this substituent These anomalies may be explained in terms of a preferential charge localisation on the azo nitrogen atoms This factor is confirmed by electron-impact induced fragmentation data

To extend the colour range of I from the predominantly yellow to orange of the dyes studied in this current work, and to assess the limits to which the colour may be developed without detrimental loss of coloration and/or fastness properties, an investigation of polysubstituted analogues of I is necessary. Results of such studies will be reported separately

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