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SUBSTITUENT EFFECTS ON THE COLOUR, DYEING AND FASTNESS PROPERTIES OF 4-*N*-β-CYANOETHYL-*N*-β-HYDROXYETHYLAMINOAZOBENZENES PART II—DISUBSTITUTED DERIVATIVES

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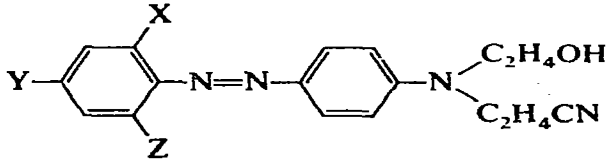
SUMMARY

*Dyeing and fastness properties on cellulose secondary acetate and polyester fibres of a series of 2'-substituted-4'-nitro, 4'-substituted-2'-nitro and 2',6'-disubstituted-4-*N-β-*cyanoethyl-*N-β-*hydroxyethylaminoazobenzenes are reported. All dyes gave good coloration, with the exception of those containing the methylsulphonyl group, which had poor substantivity for polyester. Electronic spectra data of all dyes are reported; considerable steric hindrance was apparent with certain types of 2',6' disubstitution. Data derived from tristimulus values of dyed polyester showed the degree of 'off-tone' build up is greater with red dyes, than with orange and yellow dyes. The presence of a 2'-nitro group leads to poor lightfastness.*

1. INTRODUCTION

In Part I of this investigation,[1] the effect of one substituent on the properties of dyes derived from 4-*N*-β-cyanoethyl-*N*-β-hydroxethylaminoazobenzene was described. We report here similar data pertinent to the disubstituted derivatives **I** in which either Y or Z is a hydrogen atom.



(I)

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TABLE 1

ELECTRONIC SPECTRA DATA

X	*Y*	*Z*	*m.p.* (°C)	λ_{max} (*nm*) (*ethanol*)	ε_{max} $\times 10^{-4}$	λ_{max} *Calc.* (*nm*)	$\Delta\lambda$ (*nm*)
NO_2	Cl	H	104–105	439	2·83	435	+4
NO_2	Br	H	96–97	441	2·87	437	+4
NO_2	F	H	123–124	427	2·72	427	0
NO_2	CF_3	H	104–105	451	2·84	445	+6
NO_2	CN	H	169–170	470	3·12	460	+10
NO_2	COOEt	H	107–108	452	2·77	449	+3
NO_2	SO_2CH_3	H	147–148	467	2·93	462	+5
NO_2	$COCH_3$	H	153–154	463	2·99	456	+7
Cl	NO_2	H	155–156	474	3·02	467	+7
Br	NO_2	H	166–167	476	3·00	469	+7
F	NO_2	H	169–170	470	3·16	464	+6
CF_3	NO_2	H	169–170	481	3·24	470	+9
CN	NO_2	H	161–162	505	3·81	487	+18
COOEt	NO_2	H	158–159	465	3·01	439	+6
SO_2Me	NO_2	H	188–189	500	3·47	487	+13
NO_2	NO_2	H	140–141	494	3·66	478	+16
Cl	Cl	H	105–106	425	3·24	424	+1
Cl	H	Cl	117–118	389	2·13	429	−40
NO_2	H	NO_2	147–148	449	2·51	451	−2
NO_2	H	Cl	140–141	425	2·86	440	−15
NO_2	H	Br	153–154	426	2·23	442	−16
NO_2	H	F	138–139	436	3·07	437	−1
CN	H	CN	174–175	465	3·27	469	−1
Br	H	Br	124–125	385	2·04	433	−48

TABLE 2

DYEING AND FASTNESS DATA ON DYEINGS OF **I**

X	*Y*	*Z*	λ_D *on polyester*			*Secondary acetate*			*Polyester*			*Sublimation fastness* (°C)
			0·1%	0·5%	2·5%	0·1%	0·5%	2·5%	0·1%	0·5%	2·5%	
NO_2	Cl	H	575	580	591	2	2	3	1–2	1–2	2	160
NO_2	Br	H	581	587	595	2	2	3	2	2	2	160
NO_2	F	H	573	578	587	1–2	2–3	2–3	1	1–2	2–3	140
NO_2	CF_3	H	581	589	597	2–3	3	3–4	2–3	2–3	2–3	160
NO_2	CN	H	586	593	601	2–3	3	3–4	2	2–3	3	170
NO_2	COOEt	H	583	591	597	2	2–3	2–3	2	2–3	3	180
NO_2	SO_2CH_3	H	582	587	593	2–3	3–4	4	2	2	2–3	220
NO_2	$COCH_3$	H	589	593	599	3–4	4	4	3	3	3	170
Cl	NO_2	H	595	607	615	6	6	6–7	4–5	4–5	4–5	170
Br	NO_2	H	600	609	619	6	6	6–7	5	5	5	170
F	NO_2	H	595	603	611	5	5	5–6	3–4	4	4	160
CF_3	NO_2	H	601	611	620	6–7	6–7	6	5–6	6	6	160
CN	NO_2	H	613	494*c*	492·5*c*	6–7	6–7	6–7	5–6	6	6	180
COOEt	NO_2	H	593	601	609	6–7	6–7	6–7	5–6	5–6	5–6	170
SO_2CH_3	NO_2	H	610	631	643	6–7	6–7	6–7	5–6	5–6	5–6	210
NO_2	NO_2	H	609	629	639	3	3–4	4–5	3	3–4	3–4	180
Cl	Cl	H	577	582	588	4–5	5	5	4	4	4	160
Cl	H	Cl	574	578	583	5–6	5–6	5–6	4–5	4–5	5	160
NO_2	H	NO_2	579	587	593	2	2	2–3	1–2	1–2	2	190
NO_2	H	Cl	580	584	590	2–3	3	3	2	2–3	2–3	170
NO_2	H	Br	583	586	591	2–3	3	3	2	2–3	2–3	170
NO_2	H	F	586	589	593	2	2	2–3	1–2	2	2	160
CN	H	CN	588	595	597	5–6	5–6	6	4–5	5	5	190
Br	H	Br	577	581	586	5	5–6	5–6	4–5	4–5	5	170

2. EXPERIMENTAL

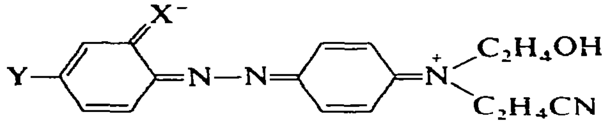
Dye synthesis, purification, electronic spectra, application to synthetic-polymer fibres and assessment of properties of the dyed materials were effected as in Part I.[1] Relevant data is given in Tables 1 and 2.

2-Nitro-6-chloro-, 2-nitro-6-bromo-, and 2-nitro-6-fluoroanilines were prepared as previously described.[2] 2',6'-Dicyano-4'-*N*-β-hydroxyethyl-*N*-β-cyanoethylaminoazobenzene was obtained by replacement of the halogen substituents in the 2',6'-dibromo derivative by standard reaction[3] with cuprous cyanide in *N*,*N*-dimethylformamide.

3. DISCUSSION

3.1. *Visible Absorption Maxima*

The red shifts in the visible absorption maxima resulting from the introduction of individual substituents into 4-*N*-β-cyanoethyl-*N*-β-hydroxyethylaminoazobenzene, i.e. dyes **I** in which Y and Z = H or X and Z = H, were reported in Part I. Introduction of a second substituent into a position conjugated with the amino nitrogen atom may, in terms of valence bond theory, be expected to result in increased resonance and the photoexcited state of the dye molecule receiving contribution from structures of type **II** and **III** (for 2',4'-disubstituted dyes; similar structures may be drawn for the 2',6'-disubstituted analogues). On this basis, it may be expected that the colour of **I** might bear some general relationship to that anticipated on a consideration of the additive effects of the substituents, X, Y and Z acting individually. Thus, the absorptive maxima of **I** in which Z = H may be related to the summation of the red shifts observed in the dyes where Y and Z = H and where X and Z = H. The calculated λ_{max} values in Table 1 are those derived from the additive effects of individual substituents as reported in Part I. Comparison with



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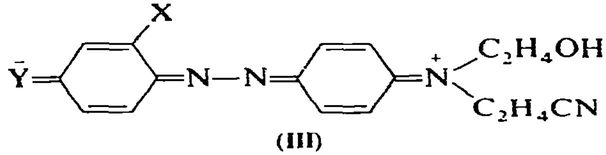


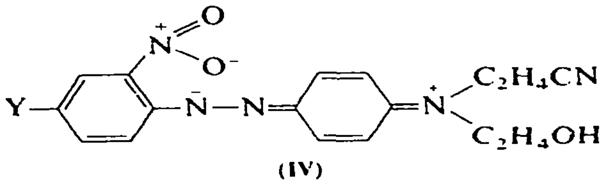
(III)

observed values clearly indicates a marked fluctuation in the relationships to calculated values of different dye structures.

In the 2'-4'-disubstituted derivatives, in which either X or Y = NO_2, the dyes all absorb at longer wavelength than the additive value calculated from individual substituents, the effect being greater in 4'-nitro derivatives than in the 2'-nitro isomers. Smallest additive shifts are observed with substitution by halogen atoms, $\Delta\lambda$ for Cl and Br being 4 nm in 2'-nitro-4'-halogeno isomers. No additive effect was apparent with the 2'-nitro-4'-fluoro compounds although in the 4'-nitro analogue, the additive effect of the fluoro compound was similar to that of the other halogens. The extent of the additive effect increased with increase in the electron acceptor properties of the substituents, the cyano group producing the largest shifts, viz. $\Delta\lambda$ 10 nm in the 2'-nitro-4'-cyano derivative and 18 nm in the 4'-nitro-2'-cyano isomer.

This marked colour development in derivatives of 4'-nitro-4-(*N*-β-cyanoethyl-*N*-β-hydroxyethyl) aminoazobenzene, e.g. the 2'-cyano and 2'-methylsulphonyl derivatives, thus renders this substitution pattern especially suitable for the synthesis of red dyes of different hues. As was observed[1] with 2'-nitro-4-(*N*-β-hydroxyethyl) aminoazobenzene, the presence of a nitro group *ortho* to the azo linkage results in inhibition of electron delocalisation. Introduction of the strongly electron accepting cyano group into the 4'-position is necessary to effect any significant enhancement of resonance, viz. for the effect of substituent Y to noticeably counterbalance the inhibited electron delocalisation resultant from structure IV. The significance of the 4'-nitro group observed in earlier studies of dyes of this type[1-4] is confirmed in the $\Delta\lambda$ value (Table 1) of the 2',4'-dinitro derivative, in which the powerful influence of the 4'-nitro group overrides to a large extent the effect of the 2'-nitro group and permits good colour development (structure V). The $\Delta\lambda$ value of the 2',4'-dinitro derivative (17 nm) is, however, lower than that of the 2'-cyano-4'-nitro derivative (18 nm), despite the stronger electron acceptor nature of the nitro group relative to cyano, and additionally confirms the inhibiting factors resultant from the presence of the 2'-nitro group.

2',6'-Disubstitution results in a considerable difference in $\Delta\lambda$ values compared to



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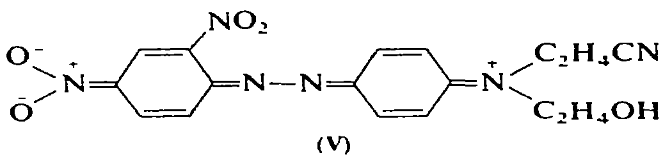
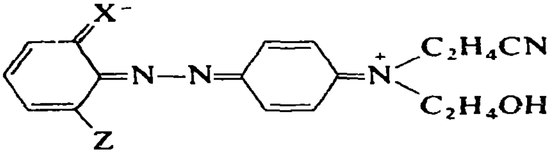


(V)

2',4'-disubstitution, and in all dyes studied in this current work, λ_{max} appeared at lower wavelength than that summated from the values of individual substituents. This is due in part, to steric crowding factors, but even with substitution by planar groups, as in the 2',6'-dicyano derivative, observed λ_{max} are lower than calculated values; the ε_{max} value of the 2',6'-dicyano derivative confirms a minimal of steric crowding. The enhancement of resonance resulting from a combination of structures **II** and **III** is thus more significant than in the analogous structures **VI** and **VII**, which will be of similar energy when the two substituents are identical. The effect is even more apparent when comparing the 2',4'-dinitro derivative ($\Delta\lambda$ + 16 nm) and the 2',6'-dinitro isomer ($\Delta\lambda$ − 2 nm); the latter dye has, in fact, absorption maxima at lower wavelength than the 4'-mono compound, with a corresponding decrease in ε_{max} value.



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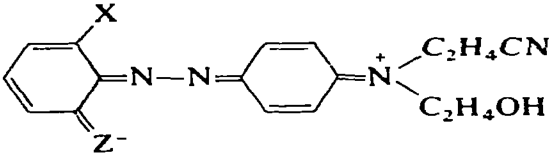

(VII)

Steric factors are apparent on consideration of the decreased ε_{max} values of the 2'-nitro-6'-chloro- and 2'-nitro-6'-bromo compounds, and in these dyes, the halogen substituent does not significantly alter the colour of the dye compared to the 2'-nitro monosubstituted derivative. The effect of the spatially smaller fluorine group is apparent from the higher ε_{max} value of the 2'-nitro-6'-fluoro compound compared with other halogen analogues. Although the 2'-fluoro derivative absorbs at lower wavelength[1] than the 2'-chloro and 2'-bromo compounds, 2'-nitro-6'-fluoro substitution, because of diminished steric crowding, results in absorption at longer wavelength than 2'-nitro-6'-chloro and 2'-nitro-6'-bromo substitution.

Steric factors resultant from the presence of two bulky substituents *ortho* to the azo link are strikingly apparent in the 2',6'-dihalogeno derivatives, which show very large decreases in ε_{max} values and remarkable blue shifts in absorption maxima. The steric crowding in these dyes is of an order which results in their absorption maxima appearing at lower wavelength than the unsubstituted parent dye (**I**, X = Y = Z = H, λ_{max} = 397 nm).

The significance of such substitution has been related[5] to the overlap of one of the substituents with the sp^2 electrons of the β-nitrogen atom of the azo group. For this to occur, it is necessary for both halogen substituents adjacent to the azo group to be in the same phenyl ring, since we have observed[6] no similar effect in 2,2′-dichloro derivatives.

3.2. *Dyeing properties*

All dyes **I** coloured cellulose secondary acetate and polyester fibres in deep shades, with the exception of dyes containing methylsulphonyl groups, which gave poor colouration of polyester.[1]

For dyeings on polyester, the shades of the dyeings are expressed in Table 2, in terms of dominant wavelength values. The 2′-nitro-4′-fluoro-, 2′,4′-dichloro, 2′,6′-dichloro and 2′,6′-dibromo derivatives gave yellow dyeings of similar hue to many monosubstituted dyes,[1] more orange shades resulting from other 2′,6′-disubstituted and 4′-substituted 2′-nitro derivatives. The value of the 4′-nitro group for colour development is shown by the close approximation of the shades and build-up of the 4′-nitro- and 4′-cyano-2′-nitro derivatives, all other 4′-substituted-2′-nitro compounds giving yellower dyeings than the 4′-nitro compound. Introduction of further substituents into the latter results in shades ranging from scarlet (e.g. 2′-fluoro-4′-nitro) to bluish-red (e.g. 2′-cyano-4′-nitro).

As was observed with monosubstituted dyes, all dyeings showed off-tone build-up, yellows and oranges building up redder, reds building up bluer. The degree of off-tone build-up varies significantly, yellow dyeings showing differences in dominant wavelength of 0·1% and 2·5% dyeings of 7–11 nm; orange dyes showed somewhat larger differences (14–16 nm), and as the dyeings increased in bathochromicity, the degree of off-tone build-up increased. Thus the red 2′-chloro-, 2′-bromo- and 2′trifluoromethyl-4′-nitro derivatives have $\Delta\lambda_D$ in the region of 20 nm, the bluish-reds showing even larger deviations, e.g. 2′,4′-dinitro, $\Delta\lambda_D$ 30 nm and 2′-methylsulphonyl-4′-nitro, $\Delta\lambda_D$ 32 nm. A general pattern of off-tone build-up in azo dyes of type **I** is thus apparent, dyeings within specific colour areas showing similar degrees of colour deviation as the strength of the dyeing increases, viz. yellow 7–11 nm, orange 14–16 nm, red 20–25 nm, bluish red +30 nm.

3.3. *Light fastness and sublimation fastness*

The use of 2-substituted 4-nitroanilines as diazo component tends to result in dyes having a lightfastness at least one point higher than the corresponding dyes without the nitro group. Data for appropriate monosubstituted dyes is given in Part I.[1] Differences are typified by comparing the 2′-cyano derivative (lightfastness 5,5,5 on secondary acetate, 4,4–5,5 on polyester) and the 4′-nitro-2′-cyano derivatives (6–7, 6–7, 6–7 on secondary acetate, 5–6, 6, 6 on polyester). In dyes containing halogen substituents in the 2′-position, the lightfastness improvement, whilst significant on secondary acetate, is not as apparent on polyester, e.g. 2′-chloro, 4–5, 5, 5, on secondary acetate, 4, 5, 5 on polyester; 2'-chloro-4'-nitro, 6,6, 6–7 on secondary acetate, 4–5, 5, 5 on polyester.

This improvement in lightfastness with introduction of a 4'-nitro group into 2'-substituted dyes is not in accordance with the accepted association of a decrease in lightfastness with increased electron mobility within the dye molecule; a similar observation was concluded in studies on monosubstituted derivatives.[1]

In contrast, dyes based on 4-substituted-2-nitroanilines cannot be considered suitable for producing dyeings of satisfactory fastness. Whilst most 4'-monosubstituted derivatives have a lightfastness[1] in the region of 5, introduction of the 2'-nitro group into such dyes results in a significant decrease in lightfastness (Table 2). Thus, the detrimental effect of the 2'-nitro group noted in monosubstituted derivatives is retained in 2'-nitro-4'-substituted derivatives; introduction of strongly electron attracting substituents is not sufficient to prevent the preferential electron localisation on the azo nitrogen atoms.

Introduction of strongly electron acceptor substituents into the 4'-position can, to some extent, override the effect the 2'-nitro group. This can be seen by comparing the fastness (Table 2) of dyes resultant from introduction of weakly polar substituents e.g. 4'-chloro-2'-nitro. The fastness improvements are, however, not of an order which can be considered acceptable in commercial dyes.

Similar effects are apparent in 2'-nitro-6'-substituted dyes, although 2',6'-derivatives, in which neither substituent is nitro, have a fastness of a similar order to that of the corresponding monosubstituted dyes.

Introduction of a second substituent results in an improvement in sublimation fastness in both 4'-nitro-2'-substituted and 2'-nitro-4'-substituted derivatives. The improvement, compared to analogous monosubstituted dyes, is in the region of 10–20 °C, although in some cases, especially 2'-nitro derivatives, no increase in fastness occurs. The effect may be considered in terms of mass and polarity factors, but, comparing the fastness of isomeric 2'-nitro and 4'-nitro derivatives, the latter tend to have higher fastness, indicating the significance of polar factors in these dyes, e.g. 4'-fluoro-2'-nitro, 140°; 2'-fluoro-4'-nitro, 160°; 4'-cyano-2'-nitro, 170°; 2'-cyano-4'-nitro, 180°; 2'-nitro, 160°; 4'-nitro, 170°; 2',4'-dinitro 180°.

4. CONCLUSIONS

Introduction of either a 2'-nitro or 4'-nitro group respectively into 4'-substituted or 2'-substituted-4-(*N*-β-hydroxyethyl-*N*-β-cyanoethyl) aminoazobenzenes results in a deepening in colour into the orange and red region. Additive effects of individual substituents on the colour of the dyes are more significant in 4'-nitro-2'-substituted dyes, which have, in addition, better fastness to light and sublimation than 2'-nitro-4'-substituted analogues. Presence of a 2'-nitro group is especially detrimental in respect of lightfastness. All dyes build-up off-tone on polyester, the degree of off-tone build-up being greater with red dyes than orange and yellow dyes. Use of 2,6-disubstituted anilines as diazo component gives dyes showing marked blue shifts in absorption maxima, especially where the substitution, as with 2',6'-dihalogeno derivatives, leads to steric crowding. In such cases, the dyes absorb at lower wavelength than the unsubstituted parent dye.

Results of current investigations into tri- and polysubstituted analogues of these dyes will be reported later.

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