Dyes and Pigments **11** (1989) 65–76

Violet to Cyan Azo Dyes Derived from 4-Amino-3-nitrobenzaldehyde as Diazo Component

Kasali A. Bello

Department of Textile Science and Technology, Ahmadu Bello University,
Zaria, Nigeria

&

John Griffiths

Department of Colour Chemistry and Dyeing, The University,
Leeds LS2 9JT, UK

(Received 27 June 1988; accepted 28 July 1988)

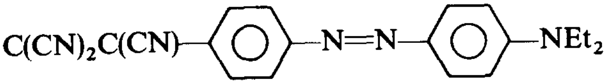
ABSTRACT

The azo dyes formed by coupling diazotised 4-amino-3-nitrobenzaldehyde to N,N-*diethylaniline and* N,N-*dimethyl-1-naphthylamine can be condensed readily with active methylene compounds to give a range of blue dyes, absorbing in the range* ca. *570–660 nm. In keeping with the highly polar character of these chromophores, the dyes show large hypsochromic shifts on protonation. The light absorption characteristics of representative examples have been examined with the aid of PPP–MO calculations.*

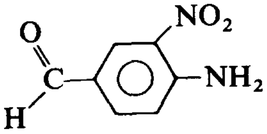
1 INTRODUCTION

Recently it has been shown that aminoazo dyes prepared from 2-amino-4-chloro-5-formylthiazole as diazo component can be reacted with active methylene compounds to give dyes which absorb in the near-infrared region.[1] If a phenyl ring system is used instead of the more polarisable and more electron-withdrawing 4-chlorothiazole residue, bathochromic shifts are less dramatic. Nevertheless, blue dyes can be prepared if the active

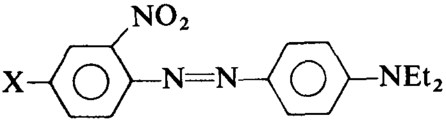
Dyes and Pigments 0143-7208/89/$03·50 © 1989 Elsevier Science Publishers Ltd, England. Printed in Great Britain



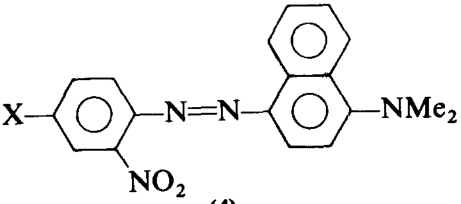
(1)



(2)



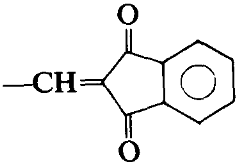
(3)



(4)

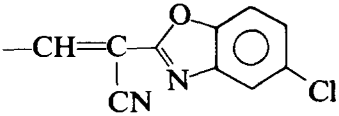
a: X = —CHO

c: X =

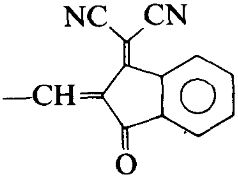


b: X = —CH=C(CN)$_2$

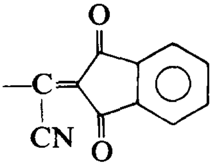
d: X =



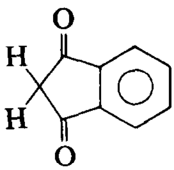
3e: X =



3g: X =



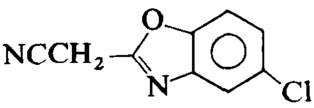
3f: X = —C(CN)=C(CN)$_2$



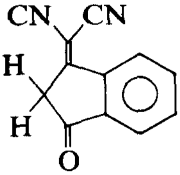
(6)

CH$_2$(CN)$_2$

(5)



(7)



(8)

methylene component is particularly electron-withdrawing, as evidenced by the tricyanovinyl dye (**1**), which absorbs at 591 nm in cyclohexane.[2] It should be possible to introduce further red shifts into systems such as **1** by incorporating additional electron-withdrawing groups into the diazo component. Perhaps the simplest and most accessible amine for demonstrating such an effect is 4-amino-3-nitrobenzaldehyde (**2**). Thus the nitro group, the most powerful of the common electron-withdrawing groups, is in the electronically most favourable position for exerting a bathochromic effect, i.e. *ortho* to the azo group in derived dyes. In addition there are no complications that might arise from steric interactions between the nitro group and the bulky active methylene-derived residue. An examination of aminoazo dyes based on this intermediate was therefore undertaken, and for this purpose two simple arylamine coupling components were used, namely *N*,*N*-diethylaniline and *N*,*N*-dimethyl-1-naphthylamine. The resultant dyes, **3a** and **4a**, were then condensed with the active methylene compounds **5**–**7** to give the dyes **3b**–**3d** and **4b**–**4d** respectively. In the case of dye series **3**, the range of structures was extended by using the active methylene compound (**8**) to give **3e**, and by cyanating **3b** and **3c** to give **3f** and **3g** respectively.

2 RESULTS AND DISCUSSION

2.1 Synthesis of intermediates and dyes

4-Amino-3-nitrobenzaldehyde (**2**) was prepared by nitrating 4-acetamidobenzaldehyde with nitric acid (*d* 1·5) in acetic anhydride at 35–50°C, using a modification of the procedure described by Hodgson & Beard.[3] The resultant 4-acetamido-3-nitrobenzylidene diacetate was hydrolysed to **2** in hot concentrated hydrochloric acid, and was fully characterised by melting point and microanalysis. As noted previously[3] the amine could be diazotised smoothly in an aqueous mixture of hydrochloric and acetic acids at 12–20°C on addition of sodium nitrite. The diazonium ion could be coupled in good yields to *N*,*N*-diethylaniline and to N,N-dimethyl-1-naphthylamine in dilute hydrochloric acid at 0–5°C, with addition of sodium acetate. Dye **3a** was obtained from *N*,*N*-diethylaniline in 95% yield, and **4a** from *N*,*N*-dimethyl-1-naphthylamine in 84% yield. The dyes showed absorption maxima in dichloromethane at 515 and 525 nm respectively, and the presence of the aldehyde group was indicated by an intense peak in the infrared spectrum at 1700 cm^{-1}. They were further characterised by microanalysis.

The two aldehyde dyes were found to react readily with the active methylene compounds **5**–**7** on heating under reflux in absolute ethanol in the presence of a catalytic amount of piperidine, and the reactions were

TABLE 1
Yields and Characterisation Data for Dyes **3** and **4**

Dye	*Yield* (%)	*M.p.*[a] (°C)	*Formula*	*Found* (%)			*Required* (%)		
				C	*H*	*N*	*C*	*H*	*N*
3a	95	126–127	$C_{17}H_{18}N_4O_3$	62·15	5·55	16·8	62·6	5·5	17·2
3b	92	196–197	$C_{20}H_{18}N_6O_2$	63·95	4·75	22·5	64·2	4·8	22·5
3c	83	241	$C_{26}H_{22}N_4O_4$	68·4	4·75	12·0	68·7	4·85	12·3
3d	70	264–266	$C_{26}H_{21}ClN_6O_3$	62·45	4·2	16·5	62·4	4·2	16·8
3e	68	202	$C_{29}H_{22}N_6O_3$	68·8	4·3	16·4	69·3	4·4	16·7
3f	84	240–245	$C_{24}H_{17}N_7O_2$	63·2	4·25	24·6	63·15	4·3	24·6
3g	87	214	$C_{27}H_{21}N_5O_4$	67·7	4·3	14·7	67·6	4·4	14·6
4a	84	152–154	$C_{19}H_{16}N_4O_3$	65·2	4·5	15·4	65·5	4·6	16·0
4b	66	213–217	$C_{22}H_{16}N_6O_2$	66·65	3·9	21·4	66·7	4·0	21·2
4c	71	235–238	$C_{28}H_{20}N_4O_4$	70·4	4·45	11·3	70·6	4·2	11·8
4d	82	243	$C_{28}H_{19}ClN_6O_3$	64·1	3·55	15·6	64·4	3.4	16·1

[a] By differential scanning calorimetry.

characterised by a rapid deepening of the colour of the solution. The products were readily isolated by filtration after cooling, and could be purified by recrystallisation from toluene. Yields were generally good, in the range 66–92%. The homogeneity of the products was indicated by TLC analysis, and the dyes were characterised by microanalysis. Yields, melting points and analytical data are summarised in Table 1.

The aldehyde dye **3a** was also condensed with the active methylene compound **8**, giving the greenish-blue dye **3e** in 70% yield. Additional bathochromic shifts in the series **3** were sought by cyanation of the dicyanovinyl and indanedione derivatives **3b** and **3c**. Thus **3b** was reacted with potassium cyanide in aqueous dimethylformamide, and the addition compound oxidised with lead(IV) acetate to give the green dye **3f**. A similar reaction with **3c** gave the blue dye **3g**.

2.2 Visible absorption spectroscopic properties

Visible absorption spectroscopic data for dyes **3** and **4** are summarised in Table 2. Absorption maxima in toluene, dichloromethane and 2-butanone are given, with molar absorption coefficients measured in dichloromethane. The parent dye, 4'-formyl-4-diethylaminoazobenzene (**9**) showed λ_{max} 472 nm in dichloromethane,[2] which may be compared with the absorption maximum for **3a** at 515 nm in the same solvent. Thus the nitro group exerts a significant bathochromic shift of *ca.* 40 nm. Comparison of dyes **3a** and **4a** also shows that the naphthalene system is slightly more bathochromic than

TABLE 2
Visible Absorption Spectroscopic Data for Dyes 3 and 4 and Their Derived Azonium Cations

Dye	$\lambda_{max}(CH_2Cl_2)$ (*nm*)	$\varepsilon_{max} \times 10^{-3}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)	λ_{max}(*toluene*) (*nm*)	λ_{max}(2-*butanone*) (*nm*)		$\Delta\lambda^b$ (*nm*)
				Neutral	*Acid*[a]	
3a	515	37·7	500	483	513	+30
3b	574	46·0	558	555	526	−29
3c	567	46·4	550	560	540	−20
3d	562	49·7	550	550	540	−10
3e	612	44·0	594	576	554	−22
3f	656	41·5	630	604	530	−74
3g	594	30·0	580	558	536	−22
4a	525	20·8	506	515	510	−5
4b	590	25·7	560	560	524	−36
4c	564	24·2	545	552	538	−14
4d	566	28·5	550	550	536	−14

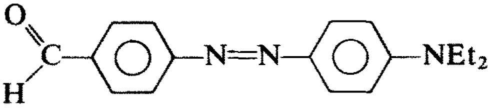
[a] Addition of the minimum of concentrated hydrochloric acid to effect complete protonation.
[b] λ_{max}(acid) − λ_{max}(neutral).

the phenyl system, although the dyes are not strictly comparable since **3a** and **4a** contain different dialkylamino groups.

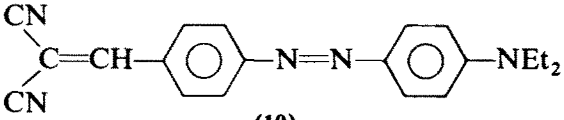
In the dye series **3** it is possible to assess the relative effectiveness of the various active methylene-derived residues in producing a bathochromic shift, and the sequence for λ_{max} values **3f** > **3e** > **3g** > **3b** > **3c** > **3d** is observed. Thus the tricyanovinyl group is most effective and the cyanobenzoxazolylvinyl group the least effective in producing a red shift. However, the latter residue does have a beneficial influence on absorption intensity, and dye **3d** has the highest molar absorption coefficient in the series (49 700 litre mol^{-1} cm^{-1} in CH_2Cl_2). Comparison of the tricyanovinyl dye **3f** with the unnitrated analogue **1** shows a bathochromic shift in cyclohexane of 29 nm due to the nitro group (λ_{max} 620 and 591 nm respectively), which compares closely with the corresponding shift in cyclohexane for the parent aldehyde dyes (35 nm). In view of the relative constancy of the shift due to the nitro group, irrespective of the nature of the 4′-substituent in the azo dye, it can be concluded that near-infrared dyes (i.e. $\lambda_{max} > 700$ nm) based on the system **3** are unlikely to be achievable.

It is interesting to compare the relative effects of introducing an α-cyano group into the dicyanovinyl and indanedione dyes **3b** and **3c**. In the former case, the resultant tricyanovinyl dye **3f** shows an exceptionally large bathochromic shift of 82 nm in dichloromethane, whereas conversion of **3c** to **3g** gives a much smaller shift (27 nm). The reduced effect of the cyano group in dye **3g** is attributable to increased steric crowding in the molecule, as shown by the marked reduction in intensity of **3g** relative to **3c** (ε_{max} 30 000 and 46 400 litre $mol^{-1} cm^{-1}$ in CH_2Cl_2 respectively). In contrast, the tricyanovinyl dye shows only a small decrease in molar absorption coefficient relative to the dicyanovinyl analogue (ε_{max} 41 500 and 46 000 litre $mol^{-1} cm^{-1}$ respectively). It is generally found in azo dyes and methine dyes that the tricyano group causes a reduction in intensity of this order compared with the dicyanovinyl group,[4] and this is due in part to the increased steric requirement of the former group.

The light absorption characteristics of system **3** were examined by carrying out PPP–MO calculations on the parent aldehyde dye **3a** and the dicyanovinyl and tricyanovinyl derivatives **3b** and **3f** respectively. To assess the electronic effect of the *ortho* nitro group in these compounds, corresponding calculations were carried for the unnitrated analogues **9**, **10** and **1**. For the calculations the standard parameters described elsewhere



(9)



(10)

were used,[5] together with the improved nitro group parameters reported by Hallas & Marsden.[6] It was found that the cyano group parameters required further refinement from those quoted earlier,[5] in order to obtain better correlation between the observed and calculated absorption maxima of polycyano compounds. In practice the adjustment needed was very small, requiring the electron affinity of the cyano nitrogen atom to be increased from 3·5 to 4·5 eV. The calculations were carried out using an assumed planar geometry and standard bond lengths and bond angles. Configuration interaction among the first nine singly excited singlet states was found to be adequate for the present purposes. Experimental λ_{max} values (in cyclohexane) are compared with the calculated values for the six dyes in Table 3.

It can be seen that wavelength trends are well predicted, and the absolute agreement between the experimental and theoretical values is good, with a maximum deviation in the case of dye **3f** of 22 nm. The exceptional bathochromic effect of the cyano group when a dicyanovinyl dye is converted to its tricyanovinyl analogue is well accounted for.

Consideration of the π-electron density changes accompanying light absorption in the visible band for the dyes in Table 3 shows the typical

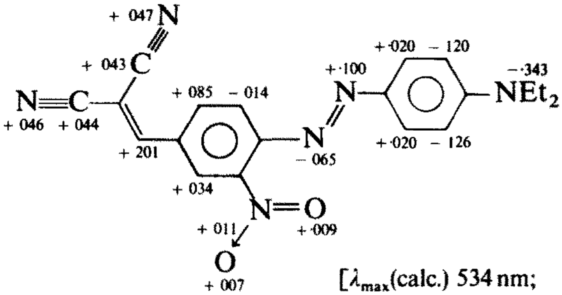
TABLE 3

Comparison of Calculated (PPP) and Experimental (Cyclohexane) λ_{max} Values for Formyl, Dicyanovinyl and Tricyanovinyl Derivatives of 4-*N*,*N*-Diethylaminoazobenzene

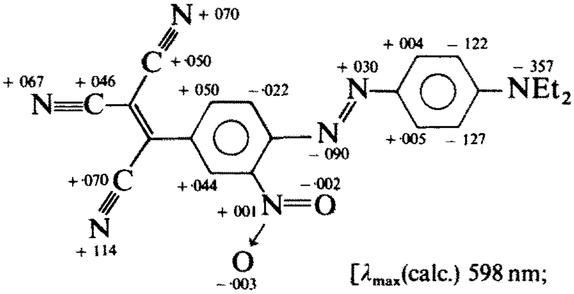
Dye	*Substituents*	$\lambda_{max}(C_6H_{12})$ *(nm)*	λ_{max}*(calc.)* *(nm)*	*f(calc.)*[a]
9	4'-CHO	443	440	1·61
3a	2'-NO_2-4'-CHO	478	491	1·18
10	4'-CH:C(CN)$_2$	515	507	1·61
3b	2'-NO_2-4'-CH:C(CN)$_2$	538	534	1·51
1	4'-C(CN):C(CN)$_2$	591	584	1·22
3f	2'-NO_2-4'-C(CN):C(CN)$_2$	620	598	1·17

[a] Oscillator strength.

donor–acceptor character of these chromophores, with excitation causing a pronounced migration of electron density from the amino group onto the electron acceptor groups of the more remote phenyl ring. The electron density changes for the dicyanovinyl and tricyanovinyl dyes **3b** and **3f** respectively are shown in Fig. 1.



(a) [λ_{max}(calc.) 534 nm; $\lambda_{max}(C_6H_{12})$ 538 nm]



(b) [λ_{max}(calc.) 598 nm; $\lambda_{max}(C_6H_{12})$ 620 nm]

Fig. 1. π-Electron density changes for the visible absorption transition for (a) dye **3b**, and (b) dye **3f**.

It is interesting to note that the 2′-nitro group in both dyes plays a relatively small role in the electron redistribution process, and the 4′-di- and tri-cyanovinyl groups have a major influence. Comparing **3b** and **3f**, it is clear that the α-cyano group in the latter is a more important electron acceptor than the two β-cyano groups, even though this is not apparent from considerations of simple resonance theory. This explains why the additional α-cyano group in the tricyanovinyl azo dyes has such a pronounced bathochromic effect.

The dyes based on *N*,*N*-dimethyl-1-naphthylamine rather unexpectedly do not show a regular bathochromic shift relative to dyes **3**, and in some instances they show a hypsochromic shift, e.g. **4c** (λ_{max} 552 nm) and **3c** (λ_{max} 560 nm), measured in 2-butanone. The shifts between comparable members of the two series of dyes are also very solvent-dependent. Clearly, the use of *N*,*N*-dimethyl-1-naphthylamine has little value in dyes of this type for producing large bathochromic shifts. Another disadvantage of this coupler is that the resultant dyes have low intensity, with molar absorption coefficients *ca.* 20–40% lower than those of corresponding *N*,*N*-diethylaniline dyes. As might be expected from simple steric considerations, the *N*,*N*-dimethyl-1-naphthylamine azo dyes are non-planar because of the presence of significant *peri*-interactions, which will be true for both the azo group and the dimethylamino group. This suggests that in dyes such as **4c** and **4d**, which have extensively conjugated electron-withdrawing groups in the *para* position of the arylazo moiety, the effectiveness of such groups in inducing bathochromic shifts depends critically on the availability of electrons from the dimethylamino group. Thus in these non-planar systems their effectiveness is greatly reduced, and the usual large red shift in naphthyl azo dyes is largely neutralised.

2.3 Halochromism effects

In common with all aminoazo dyes, the derivatives **3** and **4** show marked colour changes in solution in the presence of acids. To examine these halochromic shifts quantitatively it was necessary to find a solvent which would dissolve both the neutral and protonated dye, and which could be treated with hydrochloric acid without producing turbidity. The more commonly used alcohols are not suitable in the present case, because of the susceptibility of the tricyanovinyl group to nucleophilic attack by such solvents.[2] 2-Butanone proved to be a particularly good solvent for the series **3** and **4** and their cations, and the absorption maxima of these dyes in this solvent, before and after addition of a small amount of hydrochloric acid, are shown in Table 2. To confirm that decomposition of the dye was not occurring in acidified solution, sufficient aqueous sodium bicarbonate solution was added to neutralise the acid, when the original absorption maximum of the dye was restored.

Halochromism in the aminoazo dyes is due to protonation of the azo group, at the nitrogen atom more remote from the amino group, and is usually accompanied by a large bathochromic shift (positive halochromism). It is well known that the red shift increases as the electron-withdrawing nature of the acceptor ring decreases, and conversely the positive halochromism decreases if electron-withdrawing groups are attached to the acceptor ring.[7] When the number and strength of such groups are sufficient, the halochromism can be zero or even negative, i.e. protonation causes a hypsochromic shift.[1,2,8] Simple negatively halochromic 4-*N*,*N*-dialkylaminoazobenzenes are rare; one example is the tricyanovinyl dye (**1**), which shows a shift of the absorption maximum from 592 nm to 586 nm in benzene on adding hydrochloric acid.[2] This is the most negatively halochromic aminoazobenzene derivative yet known with a single neutral substituent in the acceptor ring.

The derivatives **3** and **4**, with two electron-withdrawing groups in the acceptor ring, show predominantly negative halochromism (Table 2). The most extreme example is the nitrotricyanovinyl derivative **3f**, which is blue–green in neutral solution and magenta in the presence of acid, corresponding to a hypsochromic shift of 74 nm in 2-butanone. The tricyanovinyl group is clearly exceptional in its influence on halochromism, and even the dicyanovinyl group has a stronger influence on negative halochromism than the other electron-withdrawing residues present in dyes **3c**–**3e** and **3g**. The *N*,*N*-dimethyl-1-naphthylamine dyes (**4**) show a somewhat greater propensity for negative halochromism than **3** (Table 2).

3 CONCLUSIONS

Diazotised 4-amino-3-nitrobenzaldehyde couples to *N*,*N*-diethylaniline and *N*,*N*-dimethyl-1-naphthylamine to give the corresponding formyl dyes, which can then be condensed with active methylene compounds to give violet to blue–green dyes. The largest bathochromic shift was observed with 2′-nitro-4′-tricyanovinyl-4-diethylaminoazobenzene (**3f**), which was bluish-green with a λ_{max} value of 656 nm in dichloromethane. Similar shifts were found for the two series of dyes **3** and **4**, but it was noted that the 4-arylazo-1-dimethylaminonaphthalene dyes were significantly less intense than their diethylaminophenyl counterparts. Both dye series show negative halochromism on protonation, the effect being greatest in the case of **3f**.

4 EXPERIMENTAL

4.1 Synthesis of 4-amino-3-nitrobenzaldehyde (2)

4-Acetylaminobenzaldehyde (60 g) was added to acetic anhydride (150 ml) and heated to 105°C with vigorous stirring until dissolved. The solution was cooled rapidly with external ice–water cooling to *ca.* 30°C to give a fine precipitate. Nitric acid (*d* 1·5, 24 ml) and acetic anhydride (60 ml) were carefully mixed, and the mixture was added dropwise to the stirred suspension of 4-acetylaminobenzaldehyde at such a rate that the temperature did not rise above 35°C. After the addition of about one-third of the acid it was noted that colourless crystals deposited, which were shown by Hodgson & Beard to be 4-acetylaminobenzylidene diacetate.[3] Further dropwise addition of the acid caused this to dissolve, and towards the end of the addition the temperature was allowed to rise to 50°C. The mixture was stirred at this temperature for a further 15 min and then poured into ice–water (800 ml). The precipitated 4-acetylamino-3-nitrobenzylidene diacetate was filtered off, washed thoroughly with ethanol and then with water, and dried. Recrystallisation from ethanol gave the diacetate as pale yellow leaflets (70 g, 61%), m.p. 113°C (lit.[3] 114°C). Found: C, 50·55; H, 4·5; N, 8·95. $C_{13}H_{14}N_2O_7$ requires: C, 50·3; N, 9·0; H, 4·5%.

The diacetate (70 g) was added to concentrated hydrochloric acid (200 ml) and heated on a water bath for 15 min. After cooling, water (300 ml) was added, and the precipitated 4-amino-3-nitrobenzaldehyde was filtered off, washed with water and dried (35 g, 93%). It was purified by recrystallisation from water, giving orange needles, m.p. 190–191°C (lit.[3] 191°C). Found: C, 50·55; N, 16·6; H, 3·55. $C_7H_6N_2O_3$ requires: C, 50·6; N, 16·9; H, 3·6%.

4.2 Diazotisation of 4-amino-3-nitrobenzaldehyde

4-Amino-3-nitrobenzaldehyde (3·2 g, 0·02 mol) was added to a mixture of acetic acid (24 ml) and water (6 ml), and cooled with stirring to 12°C. Sodium nitrite (1·5 g, 0·021 mol) dissolved in water (10 ml) was added in one portion, and then concentrated hydrochloric acid (10 ml) was added immediately. The mixture was maintained at 15–20°C for 15 min, and then excess nitrous acid was destroyed by addition of a small amount of urea. The solution was diluted with ice–water (200 ml), giving a clear solution of the diazonium salt.

4.3 General procedure for coupling diazotised 4-amino-3-nitrobenzaldehyde to *N*,*N*-dialkylarylamines

The arylamine (0·02 mol) was dissolved in a mixture of concentrated hydrochloric acid (5 ml) and ice–water (200 ml). To this was added sufficient solid sodium acetate to give a pH of *ca.* 4, and the diazonium solution was added dropwise with stirring at 0–5°C. Further sodium acetate was added as required to maintain the pH at *ca.* 4, and stirring was continued for 2 h. The resultant dye was then filtered off, washed thoroughly with water until the washings were neutral, and dried.

4′-Formyl-2′-nitro-4-diethylaminoazobenzene(***3a*** *)*
This was obtained as a deep red solid in 95% yield (m.p. 126–127°C, recrystallised from ethanol). Microanalytical data are given in Table 1.

*4-(4′-Formyl-2′-nitrophenylazo)-1-*N,N*-dimethylaminonaphthalene (* ***4a*** *)*
This was obtained as a deep red solid in 84% yield. It was recrystallised from ethanol to give an analytically pure sample (Table 1), m.p. 152–154°C.

4.4 General procedure for condensing aldehyde dyes (3a) and (4a) with active methylene compounds

The aldehyde dye (6 mmol) and the active methylene compound (6 mmol) were dissolved with warming in absolute ethanol (150 ml). One drop of piperidine was added as catalyst and the solution was heated under reflux for 15 min. On cooling the product crystallised out and was filtered off. In those instances where the product had good solubility in ethanol the solutions were concentrated under vacuum before cooling. The crude product was recrystallised from toluene and characterised by microanalysis (Table 1).

4.5 Synthesis of 2′-nitro-4′-tricyanovinyl-4-diethylaminoazobenzene (3f)

The dicyanovinyl dye **3b** (0·78 g) in dimethylformamide (18 ml) was stirred under an atmosphere of nitrogen at room temperature, and to the solution was added a solution of potassium cyanide (0·52 g) in water (2 ml). The violet colour turned brown instantly, and after 5 min the mixture was heated to 35°C and acetic acid (25 ml) added. Lead(IV) acetate (2·22 g) was then added over 2 min, and the mixture stirred under nitrogen at 35°C for 10 min. The temperature was then allowed to fall to room temperature as stirring was continued for 2 h. The dark brown suspension was poured into ice–water and the dark green precipitate filtered off, washed thoroughly with ethanol and dried. The crude product was purified by column chromatography (silica/dichloromethane) and then recrystallised from toluene. Characterisation data are summarised in Table 1.

The cyano derivative (**3g**) of the indanedione dye (**3c**) was prepared in a similar manner, by reaction of **3c** with potassium cyanide and subsequent oxidation of the anionic intermediate with lead(IV) acetate. In this case, however, the oxidation step was prolonged for 4 h, and **3g** was obtained in 87% yield (Table 2).

REFERENCES

1. Bello, K. A. & Griffiths, J., *J. Chem. Soc., Chem. Comm.*, (1986) 1639.
2. Chu, K. Y. & Griffiths, J., *Tetrahedron Lett.* (1976) 405.
3. Hodgson, H. H. & Beard, H. G., *J. Chem. Soc.* (1927) 20.
4. Chu, K. Y., Ph.D Thesis, University of Leeds (1977).
5. Griffiths, J., *Dyes and Pigments*, **3** (1982) 211.
6. Hallas, G. & Marsden, R., *Dyes and Pigments*, **6** (1985) 463.
7. Yagupol'skii, L. M. & Gandel'sman, L. Z., *J. Gen. Chem. USSR*, **35** (1965) 1259.
8. Yagupol'skii, L. M. & Gandel'sman, L. Z., *J. Gen. Chem. USSR*, **37** (1967) 1992.