

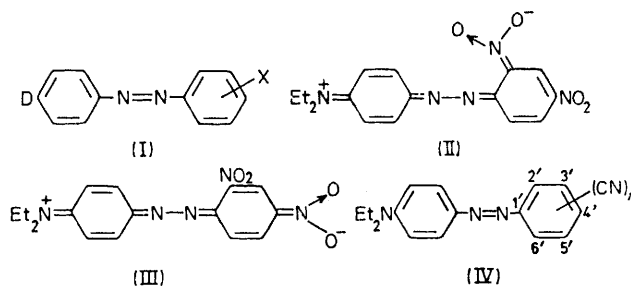
## Synthesis and Electronic Absorption Spectra of Dicyano-derivatives of 4-Diethylaminoazobenzene

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The six dicyano-derivatives of 4-diethylaminoazobenzene in which the cyano-groups and the amino-group occupy different rings have been prepared, mostly by diazotisation of the appropriate dicyanoaniline, followed by coupling to *NN*-diethylaniline. The 2',4'- and 2',6'-dicyano-compounds were prepared more conveniently by a cyanide displacement reaction with a suitable halogen-containing azo-dye precursor. The absorption spectra of the dyes were compared with those of the three monocyano-derivatives and the 2',4',6'-tricyano-compound. The intensities of the visible absorption bands confirm that steric interactions are small in the series studied, and thus spectral shifts can be attributed largely to the electronic effect of the cyano-groups. The effects of positional isomerism in the dicyano-compounds can then be assessed reliably. The 2',4'-derivative was the most bathochromic member of the dicyano-series.

DYES of the general formula (I) form a commercially important group of intensely coloured compounds. A strongly electron-donating (+*M*) group (D) (usually a substituted amino-group) is conjugated through the azo-linkage to a benzene ring bearing an electron-withdrawing group (X) (usually NO<sub>2</sub>, CN, or Ac). The visible absorption band is associated with migration of electron density from the electron donor atom into the ring containing X;<sup>1</sup> thus any factor enhancing the electron-accepting properties of this ring causes a bathochromic shift of the band. One means of achieving this is to attach more than one electron-withdrawing group to the acceptor ring. In fact, all the highly bathochromic dyes described in the technical literature that rely on this procedure have two (or three) acceptor groups in the *ortho*- and *para*-positions of the ring, relative to the azo-group. The choice of this pattern of substitution appears to be based principally on the predictions of resonance theory. Placing the substituents *ortho* and *para* to the azo-group enables low-energy resonance forms to be drawn

for the dye, *e.g.* (II) and (III), and this is presumed to lead to a low transition energy for the first absorption band. Dyes showing *ortho,meta*-, *para,meta*-, or *meta,meta*-substitution patterns have not been reported; thus



little is known about the effects of substitution pattern for dyes of type (I).

<sup>1</sup> J. Kroner and H. Bock, *Chem. Ber.*, 1968, **101**, 1922; D. Bontschev and E. Ratschin, *Monatsh.*, 1970, **101**, 1454.

Predictions of electronic absorption properties based on resonance theory are notoriously unreliable; <sup>2,3</sup> for example, in the simpler dinitrophenol series, where the first absorption is also of charge-transfer character, the most bathochromic derivative is 2,5-dinitrophenol [ $\lambda_{\text{max.}}(\text{C}_6\text{H}_6)$  365 nm], and the 2,4-dinitro-derivative is one of the most hypsochromic positional isomers [ $\lambda_{\text{max.}}(\text{C}_6\text{H}_6)$  335 nm].<sup>4</sup> It is also apparent in the dicyanoaniline series that resonance theory is inadequate. Thus in the azobenzene dyes it has yet to be established that the *ortho*-, *para*-positioning of electron-acceptor groups is the most favourable for producing bathochromic shifts.

One of the difficulties associated with the study of substituent effects in the azobenzenes is the intrusion of steric interactions. Recently Hoyer *et al.* have shown that when two substituents of roughly spherical shape occupy the same ring, and are both *ortho* to the azo-group, steric interaction between one of the substituents and the lone pair orbital of the more remote azo nitrogen atom becomes significant.<sup>5</sup> The resultant loss of planarity causes a large hypsochromic shift and decrease in intensity of the visible absorption band. Similarly, two large acceptor groups (*e.g.* NO<sub>2</sub>) *ortho* to each other would interact mutually and thus rotate out of conjugation with the ring. This would also cause a hypsochromic shift and an intensity decrease. In this respect, however, the cyano-group has ideal properties. Its rod-like shape produces minimal steric interactions of the type described,<sup>5</sup> and its strong acceptor properties provide large bathochromic shifts. We therefore undertook the preparation of various cyano-dyes of type (I) in order to examine the effect of substitution pattern on visible absorption spectra. Dicyano-derivatives of the general formula (IV;  $n = 2$ ) were chosen for this study.

## RESULTS AND DISCUSSION

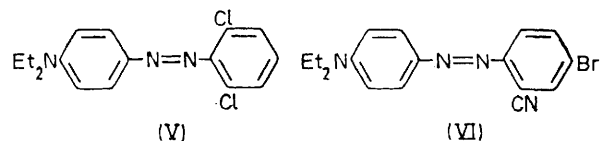
*Synthesis of Dyes.*—For comparison purposes, the three known monocyano-derivatives (IV;  $n = 1$ ) were prepared by diazotisation of *o*-, *m*-, or *p*-cyanoaniline, followed by coupling to *NN*-diethylaniline in buffered aqueous acetic acid. The azo-compounds were isolated as orange crystalline solids, in near quantitative yields.

The six dicyano-derivatives (IV;  $n = 2$ ) presented greater difficulty because of the relative inaccessibility of the dicyanoanilines, few of which have been described previously. The most general route to the latter involved conversion of the appropriate nitrobenzenedicarboxylic acid into the diamide, followed by dehydration with acetic anhydride, giving the dicyanonitrobenzene. Selective reduction of the nitro-group was then effected with iron powder and hydrochloric acid. The overall yields of dicyanoanilines from this procedure were low, principally because of the inefficiency of the dehydration step. The anilines were diazotised and coupled to *NN*-

diethylaniline in the usual way, giving the dicyano-dyes as dark red solids, in good yields.

The nitrobenzenedicarboxamides could be prepared from the acid chlorides with ammonia. However, when the two carboxy-groups were *ortho* to each other this gave mainly the monoamide; therefore a modified procedure was adopted. The nitrophthalic acid derivative was first converted into the nitrophthalimide by heating the solid monoammonium salt of the acid. The phthalimide was then treated with concentrated aqueous ammonia at 50 °C to give the diamide.

The lability of *ortho*-halogen atoms in azobenzene systems towards displacement by cyanide ion has been noted previously;<sup>6</sup> the reaction can be effected by heating the chloro- or bromo-compound with copper(I) cyanide in dimethylformamide. The application of this procedure to the synthesis of the dicyano-derivatives (IV;  $n = 2$ ) was examined. The 2',6'-dichloroazobenzene derivative (V) can be prepared readily from 2,6-dichloroaniline and *NN*-diethylaniline. When (V) was treated with copper(I) cyanide in refluxing dimethylformamide, sequential displacement of the chlorine atoms occurred (observed by t.l.c.), and the 2',6'-dicyano-compound was isolated in moderate yield. This procedure was superior to the route involving prior synthesis of the dicyanoaniline. Replacement of *para*-halogen substituents could also be achieved by this method, although the reaction was less rapid. Thus bromination of 2-cyanoaniline gave 2-cyano-4-bromoaniline, which was diazotised and coupled to *NN*-diethylaniline to give the dye (VI). Displacement by cyanide then afforded the 2',4'-dicyano-dye in 76% yield.



The synthesis of 2',4',6'-tricyano-4-diethylaminoazobenzene was also attempted by this procedure, by using the 2',6'-dibromo-4'-cyano-azo-dye as precursor. Although replacement by cyanide occurred fairly rapidly, the tricyano-dye appeared to be unstable under the conditions of the reaction, and could only be isolated in low yields.

Cyanodehalogenation is the more convenient route to cyano-azobenzene dyes, but is restricted to systems in which the halogen atom is *ortho* or *para* to the azo-group. We obtained no evidence for displacement by cyanide in dyes bearing *meta*-halogen groups. The cyano-dyes were characterised by i.r. spectroscopy and elemental analysis (Table 2).

*Visible Absorption Spectra.*—All the cyano-dyes showed a characteristic single, symmetrical absorption band in the visible region. The  $\lambda_{\text{max.}}$  values and extinction coefficients are given in Table 1.

<sup>4</sup> M. M. Davis, *J. Amer. Chem. Soc.*, 1962, **84**, 3623.

<sup>5</sup> E. Hoyer, R. Schickfluss, and W. Steckelberg, *Angew. Chem. Internat. Edn.*, 1973, **12**, 926.

<sup>6</sup> B.P. 1,208,405/1968; 1,208,406/1968.

<sup>2</sup> R. Grinter and E. Heilbronner, *Helv. Chim. Acta*, 1962, **45**, 2496.

<sup>3</sup> R. Wizinger, *Chimia (Switz.)*, 1965, **19**, 339; E. A. Steck and G. W. Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397; A. R. Osborn and K. Schofield, *J. Chem. Soc.*, 1956, 4191; J. N. Murrell, *ibid.*, 1959, 296.

The three monocyano-dyes were orange in solution, and the intensities of the absorption bands were very similar ( $\epsilon$  ca. 30 000). In ethanol, the  $\lambda_{\max}$  values followed the order 4'-CN > 2'-CN > 3'-CN, whereas in benzene the order was 2'-CN > 4'-CN > 3'-CN. The difference between the  $\lambda_{\max}$  values for the 2'- and 4'-isomers is too small to enable any significance to be attached to this solvent effect. The wavelength order conforms to the predictions of resonance theory, but contrasts with the behaviour of the nitroanilines. For example, *meta*-nitroaniline is more bathochromic than *para*-nitroaniline.<sup>2</sup>

TABLE I

Visible absorption spectral data for cyano-dyes (IV)

Position of cyano-group(s)	$\lambda_{\max}/\text{nm}$		$\epsilon_{\max}(\text{EtOH})$
	$\text{C}_6\text{H}_6$	EtOH	
2'	455	462	30 000
3'	430	446	28 100
4'	452	466	32 700
2', 3'	485	490	34 500
2', 4'	505	514	39 800
2', 5'	488	495	36 000
2', 6'	495	503	33 100
3', 4'	486	500	38 800
3', 5'	466	478	33 600
2', 4', 6'	552	562	46 600

The six isomeric dicyano-dyes are all red, and show a bathochromic displacement of about 10–40 nm relative to the monocyano-compounds. The extinction coefficients for these compounds are all similar, and are higher than those of the monocyano-dyes. This confirms the original supposition that cyano-groups should exert only a minimal steric effect when situated *ortho* to each other, or *ortho* to the azo-group. Any deviation from planarity would be indicated by a significant decrease in the extinction coefficient. It can thus be concluded that variations in the position of the visible band are due to electronic effects alone.

The  $\lambda_{\max}$  values for the dyes in ethanol follow the order 2',4' > 2',6' > 3',4' > 2',5' > 2',3' > 3',5', and in benzene this was modified slightly to 2',4' > 2',6' > 2',5' > 3',4' > 2',3' > 3',5'. Again, this is roughly the order expected from a resonance interpretation, the most bathochromic derivatives having the *ortho,para*- or *ortho,ortho*-orientation, and the most hypsochromic member having the *meta,meta*-orientation. It is curious, therefore, that resonance theory appears to hold in these relatively complex systems and yet is inapplicable to simpler donor-acceptor systems, such as the dinitrophenols or dinitroanilines. It is noteworthy perhaps that commercial dyes use the most favourable 2',4'- and 2',6'-substitution patterns for large bathochromic shifts.

As expected, the tricyano-derivative was more bathochromic than any of the dicyano-derivatives, and was violet in solution. The extinction coefficient is large, suggesting that steric interactions are relatively small.

The solvatochromism of the cyano-dyes is typical of dyes with an excited state more polar than the ground state. In the dicyano-compounds the bathochromic displacement between benzene and ethanol as solvent is

greatest for the 3',4'-derivative ( $\Delta\lambda$  14 nm). This implies that the dipole moment change on going from the ground state to the first excited state is greatest for this compound. The greater distance between the two cyano-groups and the electron donating amino-group relative to any other isomer presumably accounts for this.

The spectroscopic properties of the described dyes are currently being investigated by SCF-CI methods, and their substitution pattern relationships compared with those for the dicyanoanilines.

## EXPERIMENTAL

Visible spectra were recorded with a Unicam SP 800 spectrophotometer on analytically pure samples.

**3- and 4-Nitrophthalamides.**—The monoammonium salt of the diacid was prepared by neutralising the acid with ammonium hydroxide, followed by addition of a further equivalent amount of the diacid to the solution. Concentration gave the crystalline monoammonium salt. The solid was isolated and heated gently in an open flask until evolution of water occurred. Heating was continued until loss of water was complete, and the resultant crude nitrophthalimide was recrystallised from ethanol. 3-Nitrophthalimide (m.p. 215°) and 4-nitrophthalimide (m.p. 180–182°) were isolated in 68 and 82% yields, respectively. The nitrophthalimide ( $6.5 \times 10^{-2}$  mol) was added to ammonium hydroxide solution ( $d$  0.88; 40 ml) and the mixture was stirred at room temperature for 1 h. The temperature was raised to 50 °C for 30 min, and on cooling the solution deposited colourless crystals of the diamide (75–90%). The amides were not purified further, but were directly dehydrated.

**Dehydration of Nitrobenzenedicarboxamides to Dicyanonitrobenzenes.**—The diamide ( $2 \times 10^{-2}$  mol) was added to a mixture of acetic anhydride (25 g) and chlorobenzene (6 g) and the solution was heated under reflux for 20 h. The mixture was distilled to remove 20 ml of mixed solvent, and the residue poured into hot water (100 ml). Cooling the solution gave a crystalline deposit of the dicyanonitrobenzene. It was essential to filter off the product immediately, as starting material and other products were slowly deposited, and were difficult to remove from the cyano-compound. The yields were as follows: 1-nitro-2,3-dicyano, 26%; 1-nitro-2,5-dicyano, 43%; 1-nitro-3,4-dicyano, 13%; 1-nitro-3,5-dicyano, 15%. The products were not purified further, but were reduced to the dicyanoanilines.

**Reduction of Dicyanonitrobenzenes to Dicyanoanilines.**—The nitro-compound (4.5 mmol) was added to a mixture of methanol (16 ml) and concentrated hydrochloric acid (3.5 ml) and the suspension heated to boiling. Iron powder (0.8 g) was added in small portions over 45 min. During addition the nitro-compound gradually went into solution, and near the end of the reaction a yellow solid was deposited. The mixture was then poured into cold water and the precipitate filtered off. The dicyanoanilines were recrystallised from benzene; m.p.s and yields were as follows: 1-amino-2,3-dicyano, 195–198°, 46%; 1-amino-2,5-dicyano, 188–192°, 61%; 1-amino-3,4-dicyano, 172–174°, 78%; 1-amino-3,5-dicyano, 185–187°, 75%.

**Diazotisation of Cyanoanilines and Coupling to NN-Diethylaniline.**—The cyanoaniline (1.4 mmol) was mixed with concentrated hydrochloric acid (4 ml) and ice (10 g), and sodium nitrite (2.2 mmol) in water (5 ml) was added in

TABLE 2  
Di- and tri-cyano-derivatives (IV;  $n = 2$  or 3)

Position of cyano-groups	M.p. (°C)	Yield (%)	Found (%)			Required (%)			$\nu_{\text{CN}}/\text{cm}^{-1}$ (KBr)
			C	H	N	C	H	N	
2', 3'	159	59 <sup>a</sup>	71.0	5.75	23.1	71.3	5.61	23.1	2 230
2', 4'	175	76 <sup>b</sup>	71.0	5.85	23.1				2 220
2', 5'	152—153	75 <sup>a</sup>	71.2	6.1	23.3				2 230
2', 6'	101—103	56 <sup>b</sup>	71.3	5.65	23.1				2 220, 2 240
3', 4'	130	97 <sup>a</sup>	70.9	5.8	23.2				2 220
3', 5'	150—151	75 <sup>a</sup>	70.7	5.6	23.2				2 230
2', 4', 6'	198—200	ca. 15 <sup>b</sup>	69.0	5.1	25.3				69.8

<sup>a</sup> Diazo-coupling reaction. <sup>b</sup> Cyanodehalogenation reaction.

one portion. After 1 h at 5 °C the solution was filtered. The diazonium salt solution was added dropwise to a stirred solution of *NN*-diethylaniline (1.4 mmol) and sodium acetate (10 g) in glacial acetic acid (8 ml) and water (100 ml), ensuring that the temperature did not rise above 5 °C. The mixture was then stirred for 2—3 h, and the precipitated dye filtered off and dried. The products were purified by recrystallisation. M.p.s., yields, and elemental analysis data are summarised in Table 2 for the dyes prepared by this procedure. The i.r. cyano-stretching frequencies are also given.

**2',6'-Dicyano-4-diethylaminoazobenzene by Cyanodehalogenation.**—2',6'-Dichloro-4-diethylaminoazobenzene was prepared by diazotisation of 2,6-dichloroaniline and coupling to *NN*-diethylaniline. The dye (2.12 g, 6.5 mmol) was dissolved in dry dimethylformamide (40 ml) and copper(I) cyanide (2.7 g, 30 mmol) was added. The mixture was heated under reflux for 1.5 h, and then poured into a solution of iron(III) chloride (2.4 g) and concentrated hydrochloric acid (2 ml) in water (200 ml) (fume cupboard!). The suspension was filtered and the dye removed from the crude solid by extraction (Soxhlet) with methylene chloride. The dye was recrystallised from petroleum (b.p. 60—80°), giving red crystals (56%), m.p. 101—103°. Analytical data are in Table 2.

**2',4'-Dicyano-4-diethylaminoazobenzene.**—2'-Cyano-4'-bromo-4-diethylaminoazobenzene was prepared by diazotisation and coupling of 2-cyano-4-bromoaniline to *NN*-diethylaniline. The dye was subjected to the displacement reaction described previously, requiring 12 h for completion. The crude dicyano-dye was obtained in 76% yield, and was purified by column chromatography (silica; benzene), and crystallised from petroleum (b.p. 60—80°) as deep red crystals, m.p. 175°. Analysis figures are given in Table 2.

**2',4',6'-Tricyano-4-diethylaminoazobenzene.**—4'-Cyano-2',6'-dibromo-4-diethylaminoazobenzene was prepared by diazotisation and coupling of 2,6-dibromo-4-cyanoaniline to *NN*-diethylaniline. The dye was subjected to the displacement reaction described previously, but at lower temperatures (room temperature for 12 h, then 100 °C for 3 h; no starting material then remained). The solution was poured into water and the precipitated solid filtered off. The solid was extracted (Soxhlet) with methylene chloride, and the extracted material separated by preparative t.l.c. Two products were isolated: (i) a red solid, 2',4'-dicyano-4-diethylaminoazobenzene, presumably arising from a dehalogenation process, and (ii) a deep green solid, 2',4',6'-tricyano-4-diethylaminoazobenzene (m.p. 198—200°; elemental analysis in Table 2).

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