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The Application of PPP-MO Theory to the Halochromism of 4-Aminoazobenzene Dyes

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ABSTRACT

*With simple modification of the parameters for protonated nitrogen, the visible absorption spectra of the azonium cations derived from 4-*N,N-*diethylaminoazobenzenes can be calculated satisfactorily by the PPP-MO method. In particular, the agreement between the observed spectral shift, $\Delta\lambda$, and the calculated shift of the dyes due to protonation is very good, and thus the halochromism can be predicted reliably. Using the new parameters, the PPP method has been extended to more complex bis-azonium ions with insulated chromophores, and the observed spectral changes were predicted closely.*

1 INTRODUCTION

In acidic solution the 4-aminoazobenzene dyes undergo protonation, and the accompanying colour change is commonly referred to as 'halochromism'. The phenomenon has practical significance, in that it is an undesirable feature in textile dyes but has value in pH indicators and certain colour-imaging systems. The protonation equilibria of the azobenzenes have been

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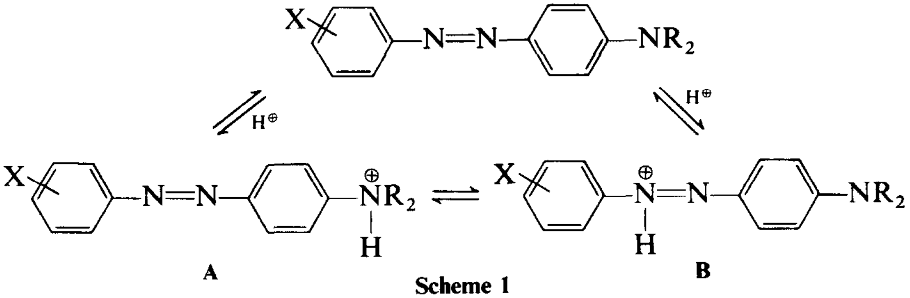
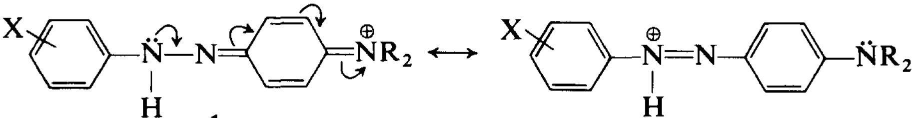


Scheme 1

the subject of many investigations,[1] and the processes known to take place are summarised in Scheme 1. The proton may add to the amino nitrogen atom to give the ammonium ion **A**, or to the β-nitrogen atom of the azo group (i.e. that more remote from the amino group) to give the azonium cation **B**.

The ammonium ion is generally very weakly coloured, absorbing at much shorter wavelengths than the parent dye, and consequently is of less interest. In most cases it is formed in relatively small proportions. In contrast, the azonium ion often absorbs at much longer wavelengths than the parent dye, and the absorption band is narrower and more intense. Such a bathochromic shift is termed 'positive halochromism', but examples are known where the azonium ion absorbs at shorter wavelengths than the neutral dye, i.e. they exhibit 'negative halochromism'.[2-6] In such cases either the amino-substituted ring carries strong electron-donating groups, or the other ring is heavily substituted with electron-withdrawing groups.

The variable nature of the halochromic effect has attracted much attention, and a simple qualitative interpretation assumes that in the neutral and protonated azo dye the electron flow accompanying light absorption is in opposite directions for the two species. Thus in the neutral dye, electronic charge migrates away from the amino group, and electron-withdrawing groups in the second ring favour a bathochromic shift of λ_{max}. In the azonium ion, however, electrons are presumed to migrate from the protonated azo nitrogen atom *towards* the amino group (drawing the azonium ion in its alternative canonical form **1**), and thus electron-withdrawing groups in the second ring now exert a hypsochromic effect. This explains the observed opposite dependence of wavelength of the two species on the electronic properties of substituents. The actual wavelength difference



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between the two species thus diminishes as the electron-withdrawing effect of substituents in the second ring increases, and may eventually become zero or even negative.

This simple interpretation has been confirmed by theoretical MO studies.[7,8] Although the colour of the neutral azo dyes can be predicted reliably by the PPP-MO method,[9,10] there does not appear to have been any attempt to extend the method to the azonium cations by developing suitable MO parameters. We now describe such parameters, which in combination with parameters used previously for the neutral azo dyes enable the calculation of the halochromism of simple aminoazobenzene dyes with reasonable accuracy. The same parameters have then permitted the complex spectra of certain bis-azonium dications to be predicted closely.

2 RESULTS AND DISCUSSION

2.1 Application of PPP theory to the halochromism of 4-*NN*-diethylaminoazobenzenes

For meaningful application of the PPP-MO method to the prediction of the spectra of azonium cations it is important to minimise the influence of the solvent when measuring the spectra. Thus, ideally, one should compare calculated λ_{max} values with values measured in a non-polar solvent such as cyclohexane. However, the general insolubility of the azonium salts in such solvents poses a major difficulty. This was overcome by adding 4-dodecylbenzenesulphonic acid to dilute solutions of the azo dye in cyclohexane until protonation was complete. The resultant salts were sufficiently soluble to permit measurement of the absorption maxima, and the acid was sufficiently strong to protonate fully even the least basic of the dyes studied. The visible absorption maxima of the neutral azo dyes **2a**–**2h** and of their azonium cations **3a**–**3h** measured in cyclohexane are summarised in Table 1. In practice it was found that the absorption maxima of the cations in cyclohexane were at some 10–20 nm shorter wavelengths than in ethanol, and there was no regular trend in the solvatochromism with the electron-withdrawing effect of ring substituents. In contrast, the bathochromic shift of the absorption band of the neutral dyes from cyclohexane to ethanol increased steadily from *ca* 5 to 40 nm as the electron-withdrawing effect of the ring substituents increased. This observation reflects the increasing ground-state dipole moment of the azo dyes, whereas the smaller variable shift found with the cations is consistent with a low dipole moment due to delocalisation of the positive charge.

TABLE 1
Experimental and Calculated Visible Absorption Spectra of Azo Dyes (**2**) and their Azonium Cations (**3**)

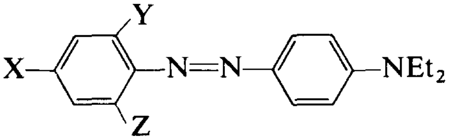
Structure **2, 3**	λ_{max} *(azo) (nm)*		λ_{max} *(azonium) (nm)*		$\Delta\lambda$ $(C_6H_{12})^b$ (nm)	$\Delta\lambda$ *(calc.)*^{b} (nm)	σ^c
	C_6H_{12}	*Calc.*	$C_6H_{12}{}^a$	*Calc.*			
a	408	411	558	563	150	152	−0·27
b	400	411	519	510	119	99	0
c	405	411	520	526	115	115	0·23
d	435	444	500	499	65	55	0·66
e	454	451	499	489	45	38	0·78
f	468	475	479	492	11	17	1·32
g	500	478	500	485	0	7	1·44
h	526	493	516	483	−10	−10	1·98

[a] Value obtained after averaging out vibrational fine structure (see Section 4).

[b] $\Delta\lambda = \lambda_{max}$(azonium) − λ_{max}(azo).

[c] Net Hammett sigma constant for substituents X, Y and Z in **3** (assuming simple additivity of *ortho* and *para* substituents).

It can be seen from Table 1 that, as is well known, the halochromism of the azo dyes, i.e. $\Delta\lambda$, decreases steadily as the Hammett sigma constant of the ring substituents increases, and in fact becomes zero in the case of dye **2g**, and negative with dye **2h**.



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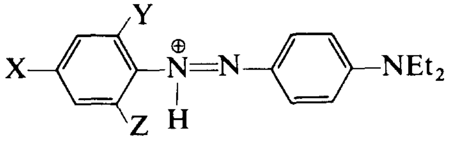

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a: X = OMe, Y = Z = H
b: X = Y = H
c: X = Cl, Y = Z = H
d: X = CN, Y = Z = H
e: X = NO_2, Y = Z = H
f: X = Y = CN, Z = H
g: X = NO_2, Y = CN, Z = H
h: X = Y = Z = CN

Application of the PPP-MO method to the neutral azo dyes is straightforward and, using the parameters described elsewhere,[6,10] the λ_{max} values shown in Table 1 were obtained. The calculated values were in good agreement with experimental values, but the discrepancy increased with the more highly substituted dyes **2f**–**2h**, and was greatest (−33 nm) in the case of the tricyano dye **2h**.

In order to calculate the absorption spectra of the azonium cations **3a**–**3h**, it was necessary to develop new parameters to take into account the positively charged β-nitrogen atom of the azo group. In the interests of simplicity and generality, such modified parameters should be kept to the absolute minimum, and ideally only the protonated nitrogen should be modified, all other atoms retaining the conventional parameters of the neutral azo dye system. Using dye **3b** as model, parameter modification was carried out systematically until good agreement between the calculated and observed absorption maxima was obtained. It was found that a satisfactory result could be obtained by using a valence state ionisation potential of 22·0 and an electron affinity of 12·5 eV for the protonated nitrogen atom. These are theoretically reasonable values, approximating to the values of a neutral nitrogen atom with lone-pair electrons, which should be the case. A minor secondary refinement was to change the resonance integral of the bond between carbon and the positively charged nitrogen from the normal C—N=N value of −2·48 eV to −2·75 eV. The core charge of the protonated nitrogen atom was of course changed from 1 to 2.

With these simple and reasonable modifications, the calculated λ_{max} values for the cations **3a**–**3h** shown in Table 1 were obtained. It can be seen that the agreement between theory and experiment is good, and is rather better than with the neutral dyes themselves. The largest discrepancy occurred with the tricyano cation **3h**, the absorption wavelength being underestimated by about 33 nm.

Comparing the predicted and observed halochromism ($\Delta\lambda$) of the dyes shows that the PPP method reproduces the dependence of $\Delta\lambda$ on substituent effects very well. This is shown in Fig. 1. Thus the trend for $\Delta\lambda$ to decrease

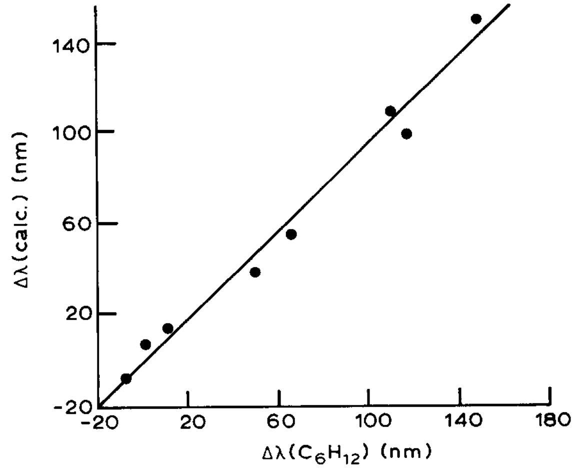
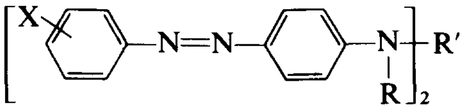


Fig. 1. Relationship between the experimental halochromism of dyes **2** [$\Delta\lambda(C_6H_{12})$] and the PPP-calculated values [$\Delta\lambda$(calc.)].

with increasing electron-withdrawing effects in the ring attached to the protonated nitrogen atom is reproduced accurately. The negative halochromism of the tricyano dye **2h** is well accounted for quantitatively. The PPP method with the suggested parameters is thus a potentially useful tool in the design of indicator dyes with specific colour-change properties.

2.2 Application of PPP-MO theory to bis-azonium dications

Dimeric azo dyes of the type **4** are of theoretical interest because of the possibility of interaction between the two aminoazobenzene chromophores, so leading to splitting of the visible absorption band. The extent and nature of the splitting will depend on the spacing between the two chromophores and their angular relationship, and such phenomena have been discussed in detail by Kiprianov.[11] Interactions are likely to be more pronounced if the dyes are doubly protonated to give the bis-azonium dications **5**, and we have examined this possibility with the two systems **6** and **7**. Dyes **6** and **7** were synthesised by coupling diazotised 4-cyanoaniline to *N*,*N*′-bis(3-methylphenyl)piperazine and to *N*,*N*′-dimethyl-*N*,*N*′-bis(3-methylphenyl)ethylenediamine respectively. In the former case the dye was prepared in two stages by first coupling one equivalent of the diazonium ion to *N*,*N*′-bis(3-methylphenyl)piperazine in a mixture of water and methanol and isolating the monoazo dye. The purified monoazo dye was then dissolved in dichloromethane and coupled with the 4-dodecylbenzenesulphonate salt of diazotised 4-cyanoaniline under anhydrous conditions. The pure disazo dye was obtained in 37% yield (based on monoazo dye). None of the double coupled product could be obtained directly by coupling excess diazonium



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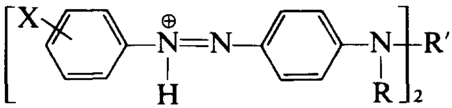

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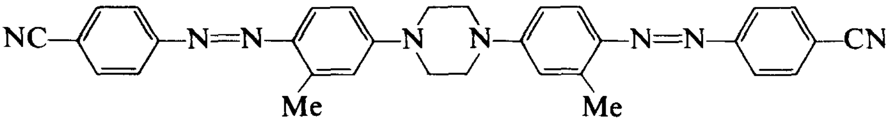

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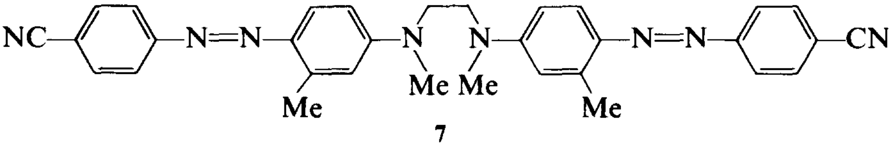

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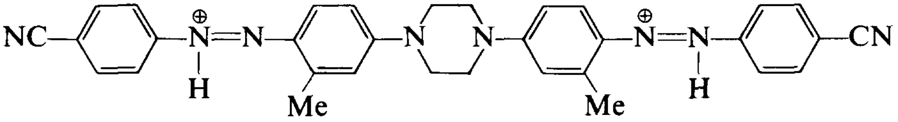
salt to *N*,*N*′-bis(3-methylphenyl)piperazine in aqueous methanol, or in other solvent mixtures containing water.

Dye **7** was obtained as a by-product in the coupling of one equivalent of 4-cyanobenzenediazonium 4-dodecylbenzenesulphonate to *N*,*N*′-dimethyl-*N*,*N*′-bis(3-methylphenyl)ethylenediamine in dichloromethane under anhydrous conditions. The main product in the reaction was the corresponding monoazo dye. Dyes **6** and **7** were characterised by elemental analysis.

The visible absorption spectra of **6** and **7** showed only limited evidence of chromophoric interactions, with slight band broadening and moderate shifts of the absorption maximum. Thus **6** showed λ_{max} 450 nm in ethanol, compared with the value of 435 nm for the corresponding monoazo dye in the same solvent. In contrast, **7** absorbed at somewhat shorter wavelengths (λ_{max} 455 nm in ethanol) than its monoazo counterpart (λ_{max} 470 nm). The bathochromic and hypsochromic shifts for **6** and **7** respectively are to be expected for the linear structure of **6** and the angular dichromophore **7**.

As anticipated, bichromophoric splitting was much more pronounced for the bis-azonium dications derived from **6** and **7**. Protonation was effected in 95% ethanol by addition of concentrated hydrochloric acid until no further spectral changes occurred (total acid concentration *ca* 10%). A large bathochromic shift of the absorption band of the neutral dye occurred in both cases, but the absorption spectra of the bis-azonium ions **8** and **9** differed dramatically (Fig. 2). Thus the effectively linear dication **8** showed essentially one intense band at 564 nm (ε_{max} 115 900 l mol^{-1} cm^{-1}), with a



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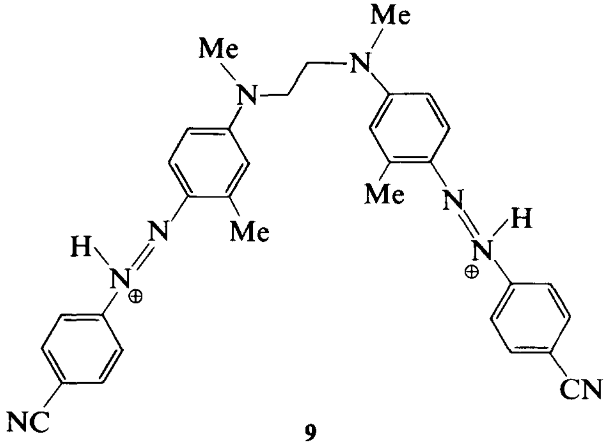

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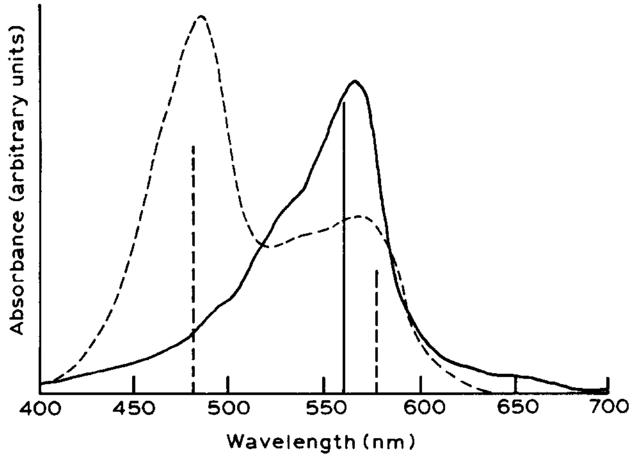

Fig. 2. Absorption spectra in ethanol of linear dication (**8**) (———) and non-linear dication (**9**) (– – – –). Vertical lines indicate PPP-MO calculated λ_{max} values for **8** (———) and **9** (– – – –); length of line is proportional to calculated oscillator strength.

shoulder at *ca* 480 nm. On the other hand, the more flexible dication **9** showed marked band splitting, with a very intense peak at 484 nm (ε_{max} 123 000 l mol^{-1} cm^{-1}) and a moderately intense peak at 570 nm (ε_{max} 59 600 l mol^{-1} cm^{-1}).

In view of the successful application of the PPP method to simple protonated azo dyes using the newly derived azonium parameters, it was of interest to see if the method could be extended to predict the complex spectral characteristics of the bis-azonium dications **8** and **9**. In principle, the PPP method is suitable for the prediction of interactive effects between insulated chromophores, and in such calculations one treats the bichromophore as a single molecule, but omits any resonance integral between the two sub-chromophores.

In the case of **8**, the two aminoazobenzene chromophores were assumed to be co-linear, with a spacing between the two amino nitrogen atoms of 2·8 Å, corresponding approximately to the C_1–C_4 distance in cyclohexane. In the case of dication **9** the greater flexibility of the molecule made the assignment of a reasonable equilibrium geometry more difficult, and therefore a method suggested by the work of Kiprianov[12] was adopted. Thus for two insulated symmetrical chromophores held at an angle θ with respect to each other, the following relationship has been derived

$$\cos\theta = \frac{r-1}{r+1}$$

where r is the ratio of the intensities of the long-wave and short-wave bands resulting from the interactive splitting. In the case of **9**, application of this equation suggests an angle of approximately 75° between the two aminoazobenzene residues. Thus for the PPP calculations this angle was assumed, together with a separation of 2·8 Å between the two amino nitrogen atoms.

The MO calculations were found to reproduce the observed spectra of **8** and **9** remarkably well. Thus, for **8**, a single intense long-wavelength band at 566 nm (experimental value 564 nm) was predicted, with a second zero-intensity band at 494 nm. Experimentally, **8** showed a weak shoulder at *ca* 480 nm. In the case of the dication **9**, an intense absorption band at 489 nm was predicted (experimental value 484 nm) with a band of approximately half the intensity at 577 nm (experimental 570 nm). The close agreement between theory and experiment can be seen from the comparisons made in Fig. 2.

Thus it would appear that the PPP method can be applied with some confidence to the interpretation of the spectra of relatively complex azonium species, and is well suited to the study of the interactions of insulated bichromophores because of its quantitative predictive value.

3 CONCLUSIONS

With a simple modification to the parameters of the protonated nitrogen atom in azonium cations, the PPP method can be used to calculate the colour of the azonium ions derived from 4-*N*,*N*-dialkylaminoazobenzenes with reasonable reliability. Using the same parameter set for the neutral and protonated forms of the azo dye, the halochromism can be calculated with even greater precision, and the well-known effect of substituents in the ring more remote from the amino group can be duplicated theoretically. The PPP method has also been applied to the spectra of bis-azonium dications, in which the two chromophores are insulated from each other but which can take part in through-space interactions. The resultant splitting of the visible absorption band, dependent on the angle between the two sub-chromophores, has been duplicated with remarkable accuracy in the case of two dye systems.

4 EXPERIMENTAL

4.1 Measurement of absorption spectra

The azo dyes **2a**–**2h** were prepared by conventional methods and were purified by a combination of column chromatography and recrystallisation until pure by TLC analysis, and melting points were in agreement with the reported values. The dyes were dissolved in cyclohexane and the absorption spectra recorded. A dilute solution of 4-dodecylbenzenesulphonic acid in cyclohexane was then added to the dye solution until no further spectral change occurred. Formation of the azonium ion was indicated by a narrowing and intensification of the absorption band, the appearance of fine structure in the band, and (in those cases with a non-zero halochromism) a shift of the absorption band. The fine structure in cyclohexane (unlike the case with ethanol as solvent) was sufficiently pronounced to reveal two closely spaced peaks within the main band envelope. Thus, for comparison of absorption wavelengths with PPP predictions, a smooth curve over the two peaks was traced, and the maximum of this taken as the true λ_{max} value.

4.2 Preparation of *N,N'*-bis[4-(4'-cyanophenylazo)-3-methylphenyl]piperazine (6)

To a solution of 4-cyanobenzenediazonium chloride (1×10^{-2} mol) in water was added a solution of *N,N'*-bis(3-methylphenyl)piperazine (1×10^{-2} mol) in methanol (200 ml) in one portion, followed by crushed ice (200 g). The mixture was stirred for 24 h, allowing the temperature to rise to room temperature, and the orange–red solid was filtered off. The solid was dried and then chromatographed over silica using toluene as eluent. The principal red fraction was evaporated to dryness and the residue recrystallised from toluene to give the mono-azo dye as a red powder (1·76 g, 44%), m.p. 193°C. (Found: C, 75·0; H, 6·7; N, 17·3. $C_{25}H_{25}N_5$ requires: C, 75·95; H, 6·33; N, 17·7%.)

The mono-azo dye (0·395 g, 1×10^{-3} mol) was dissolved in dichloromethane (100 ml) and cooled to 0°C. A solution of 4-cyanobenzenediazonium 4-dodecylbenzenesulphonate (1×10^{-3} mol) was prepared by adding powdered 4-cyanoaniline (1×10^{-3} mol) to a solution of 4-dodecylbenzenesulphonic acid (0·4 g, $1{\cdot}2 \times 10^{-3}$ mol) in dry dichloromethane (10 ml), cooling to 0°C, and then adding *n*-butyl nitrite (0·13 ml, $1{\cdot}13 \times 10^{-3}$ mol) and stirring for 30 min. The diazo solution was diluted to 50 ml with dichloromethane and then added dropwise to the solution of the monazo dye with stirring. After 2 h the precipitate was filtered off to give crude **6** as a red powder. The solid was Soxhlet-extracted with dichloromethane, and the extracts deposited the disazo dye in reasonable purity as a red powder (0·19 g, 37%), m.p. 262°C. (Found: C, 73·7; H, 5·2; N, 21·3. $C_{32}H_{28}N_8$ requires: C, 73·3; H, 5·3; N, 21·4%).

4.3 Preparation of *N,N'*-bis[4-(4'-cyanophenylazo)-3-methylphenyl]-*N,N'*-dimethylethylenediamine (7)

4-Cyanoaniline (1·18 g, 1×10^{-2} mol) was diazotised in dichloromethane (200 ml) by the action of 4-dodecylbenzenesulphonic acid (4 g, $1{\cdot}23 \times$

10^{-2} mol) and *n*-butyl nitrite (1·2 ml, $1{\cdot}1 \times 10^{-2}$ mol) as described previously. The diazo solution was cooled to 0°C and added dropwise with stirring to a solution of *N,N'*-dimethyl-*N,N'*-bis(3-methylphenyl)ethylenediamine (2·68 g, 1×10^{-2} mol) in dichloromethane (100 ml) at 0°C. The mixture was stirred at this temperature for 3 h and then pyridine (1·0 ml) was added. After stirring at room temperature for a further 24 h the red precipitate was filtered off and washed with ligroin. This was found to be the disazo dye (**7**) in a reasonable state of purity (0·30 g, 5·5%), m.p. 258°C. (Found: C, 72·3; H, 5·8; N, 21·1. $C_{32}H_{30}N_8$ requires: C, 73·0; H, 5·7; N, 21·3%).

The major product from the reaction remained in solution at the end of the coupling reaction, and was shown to be the mono-azo dye (1·38 g, 35%), m.p. 126°C.

4.4 PPP-MO calculations

These were carried out using the parameters described elsewhere,[6,10] with the modified nitro and cyano parameters recommended for the azo dyes. The calculations involved a limited configuration interaction treatment including the first nine singly excited states.

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