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APPLICATION OF THE PPP-MO METHOD TO THE PREDICTION OF COLOUR IN DI- AND TRI-ARYLMETHANE DYES

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SUMMARY

The electronic absorption spectra of several examples of the di- and tri-arylmethane dyes have been computed by the PPP molecular orbital in order to test the value of the method for predicting colour properties of cationic dyes. Parameter modification was kept to the absolute minimum, using mainly values derived for unrelated dye classes, but, nevertheless, agreement between calculated and experimental spectral data was satisfactory in most cases. Discrepancies could generally be attributed to severe steric effects in the relevant molecules.

1. INTRODUCTION

The Pariser–Parr–Pople (PPP) molecular orbital (MO) method has proved an invaluable tool in the study of the colour and constitution of organic dyes, and judicious choice of parameters has permitted the reliable prediction of light absorption properties in several classes of dyes, particularly aminoazo compounds,[1,2] anthraquinones,[3] naphthoquinones,[4] and heterocyclic analogues of the anthraquinones.[5] Numerous PPP calculations of a more specific nature for other dye systems have been reviewed recently.[6a] In contrast, the di- and tri-arylmethane cationic dyes have received little attention, interest having been focused on the parent compounds Michler's Hydrol Blue (**1**), Malachite Green (**2**) and Crystal Violet (**3**).[6b] Details of the parameters used have not been published. The only general study of cationic dyes using molecular orbital methods was made by Dewar in 1950.[7] He used the Hückel method, and by suitable parameter modification was able to obtain a good correlation between theoretical and experimental absorption maxima for the dyes studied. However, this method suffers from the serious disadvantage that no account is taken of electronic repulsion effects, and consequently is not of general applicability. The dyes studied by Dewar had a high degree of electronic symmetry, and thus the shortcomings of the calculation procedure could be absorbed in the

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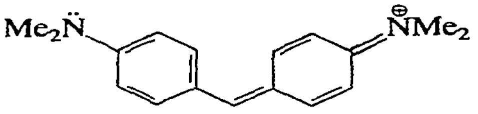

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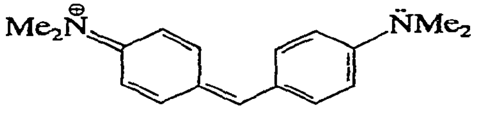

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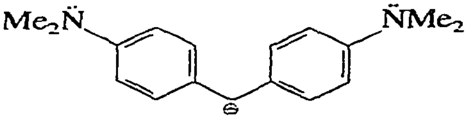

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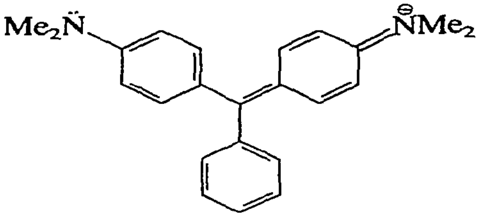

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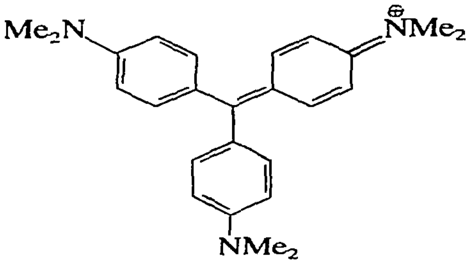


(3)

parameters used. Although the parameters employed were not disclosed, they are unlikely to be of value in totally unrelated dye systems.

It was of interest to examine the di- and tri-arylmethane dyes by the PPP method, using as far as possible parameters derived for other dye classes. In this preliminary study the simplest possible geometries were assumed for the various molecules studied, and bond orders were assumed to be uniform throughout the chromophore. In this way it was possible to determine the sensitivity of delocalised cationic dyes to parameter selection, and to assess the practical value of the PPP method for colour prediction in this general class of dye.

2. THE COMPUTATIONAL METHOD

A standard PPP molecular orbital procedure was employed,[8] within the fixed β approximation. Two-centre electron repulsion integrals were obtained by the Nishimoto–Mataga relationship.[9] Electronic excitation energies were refined by a limited configuration interaction (CI) treatment involving the nine singly excited singlet configurations obtained by promoting an electron from the three highest occupied orbitals to the three lowest unoccupied orbitals. It was found that the limited CI treatment in general influenced the wavelength of the first absorption band by less than 5%, and increasing the extent of CI had relatively little additional effect. This has been found to be the case with other dye systems.[1,4,5]

2.1. *Parameter selection*

For simplicity, a planar structure was assumed for all the molecules studied. Although this is a reasonable assumption for di-arylmethanes such as (**1**), this is not the case for the tri-aryl compounds, (**2**) and (**3**), which most probably adopt a propeller-shaped geometry.[10,11] However, in π-electron systems, moderate deviations from planarity only affect the resonance integrals, β, to any great extent, and trial calculations with (**1**)–(**3**) showed that the calculated visible absorption maxima were relatively insensitive to choice of β values. Thus in most cases specific consideration of nonplanarity was unnecessary, and the effects of a propeller-type geometry could readily be absorbed in the empirically derived parameters for the ionisation potentials and one-centre electron repulsion integrals.

The computed visible absorption maxima were also found to be quite insensitive to choice of bond lengths and bond angles, within sensible limits, and thus standard values for bond lengths (Table 1) were employed, and all bond angles were assumed to be 120°, except when five-membered rings were present. The β values, which as noted were only of secondary importance, were assumed to be $-2{\cdot}39$ eV for all carbon–carbon bonds in the main chromophore, and $-2{\cdot}75$ eV for all amino N–C bonds. Other structural units were assigned values derived for other dye classes (Table 1).

The most critical parameters in any PPP calculation are the valence state ionisation potential (VSIP) and one-centre electron repulsion integral (γ_{nn}) for each atom. If the PPP method is of genuine wide applicability, it should not be necessary to change any of these parameters from those derived for similar atoms in other dye systems. Thus the VSIP and γ_{nn} values for all atoms except the terminal amino nitrogen atoms were those used elsewhere.[1,4,5] Treating the terminal nitrogens separately is justifiable for two reasons: (a) the need to absorb nonplanarity effects into some of the parameters, and (b) the fact that the nitrogen atoms carry a high degree of positive charge, a situation that has not been encountered in previous studies.

The VSIP and γ_{nn} parameters for the dimethylamino nitrogen atoms in planar (**1**) and nonplanar (**2**) were assumed to be different. Optimum values were found empirically, and were those giving the best fit between the predicted and experimental longest wavelength absorption band for (**1**) and (**2**).

TABLE 1
PPP-MO PARAMETERS USED FOR THE CALCULATION OF ABSORPTION SPECTRA OF DI- AND TRI-ARYLMETHANE CATIONIC DYES

Bond type X—Y	r^a_{XY} (nm)	β_{XY} (eV)	$VSIP^b_Y$ (eV)	γ^c_Y (eV)	Z^d_Y
C$\cdots$C	0.140	−2·39	11·16	11·13	1
C—NMe_2	0·140	−2·75	12·7[e] 13·2[f]	6·08	2
C—NH_2[g]	0·140	−2·75	15·0	9·0	2
C—OMe	0·136	−2·60	32·9	11·43	2
C—N (julolidine)	0·140	−2·75	11·0	6·0	2
C=N	0·140	−2·40	16·0	13·5	1
C≡N	0·115	−2·67	14·18	10·7	1
N≡C	0·115	−2·67	11·19	11·09	1
N—O (nitro)	0·121	−3·05	16·3	14·5	1
C—NO_2	0·149	−2·00	24·8	12·27	2

[a] Bond length.
[b] Valence state ionisation potential of atom Y.
[c] One-centre electron repulsion integral for atom Y.
[d] Core charge of atom Y.
[e] Value for di-arylmethane systems.
[f] Value for tri-arylmethane systems.
[g] Value for Auramine (**4**).

The values for these parameters are given in Table 1, and the resultant calculated λ_{max} values are compared with experiment in Table 2. It is noteworthy that the derived parameters differ appreciably from those of a normal dimethylamino group, and in particular the VSIP values are much lower than those of the latter. This is physically reasonable, since the amino groups are directly conjugated to a positive charge, and are thus constrained to a state of sp^2 hybridisation with maximum overlap between the nitrogen lone pair orbital and the π-orbital system of the rest of the chromogen. This effectively increases the electron releasing capacity of the amino groups, which is reflected by the lower ionisation potential for the nitrogen atoms.

One problem that arises with cationic dyes of the types (**1**)–(**3**) stems from their high polarity and thus their low solubility in non-polar solvents. Because many dyes show pronounced solvatochromic properties, previous PPP studies usually refer specifically to absorption spectral data determined in non-polar solvents, in order that solvent perturbations are kept to a minimum. Thus VSIP and γ_{nn} parameters in general use give predicted λ_{max} values in relation to such solvents. In the present case it was not possible to obtain λ_{max} values other than in highly polar solvents (e.g. 98% acetic acid), and thus the dimethylamino parameters given in Table 1 were derived on the basis of absorption maxima

TABLE 2

COMPARISON OF EXPERIMENTAL AND CALCULATED VISIBLE ABSORPTION DATA FOR REPRESENTATIVE DI- AND TRI-ARYLMETHANE DYES

Compound	λ_{max}(calc.) (nm)	f(calc.)[a]	λ_{max}(exp.) (nm)	log ε (exp.)	Solvent	Reference
(1)	608	1·87	608	5·17	acetic acid	12
(2)	624	1·64	621	5·02	acetic acid	12
	409	0·71	428	4·30		
(3)	580[b]	1·29[b]	589	5·03	acetic acid	19
(4)	458	1·02	434	—	ethanol	20
(5)	686	1·87	728	—	water	21
(6)	495	1·81	498	*c*	acetic acid	22
(7)	474	1·86	480	*c*	acetic acid	22
(8)	621	1·63	623	5·03	acetic acid	12
	416	0·70	435	4·26		
(9)	613	1·59	608	5·03	acetic acid	12
	436	0·87	465	4·53		
(10)	634	1·65	637	4·95	acetic acid	13
	411	0·84	426	4·18		
(11)	634	1·69	638	4·94	acetic acid	12
	407	0·76	425	4·15		
(12)	516	1·66	515	*c*	acetic acid	22
	357	0·58	384			
(13)	526	1·60	546	*c*	acetic acid	22
	382	0·68	417			
(14)	593	1·38	623	4·99	ethanol–HCl	16
	580	1·12				
(15)	662	1·20	613	5·01	acetic acid	15
	601	1·42				
(16)	717	1·65	666	4·05	acetic acid	15
	676	0·99				
(17)	721	2·13	770	—	acetic acid	23
	687	1·07				
(18)	727	0·65	850	4·23	acetic acid	18
	640	1·77	647	4·87		
			470	3·84		
(19)	850	0·60	955,850	4·28,4·20	acetic acid	18
	463	0·96	505,470	4·32,4·30		
(20)	733	1·46	788,728	4·55,4·50	acetic acid	18
	480	0·64	570	4·0		
	396	0·33	470	3·9		

[a] Oscillator strength.

[b] Two equivalent transitions; quoted oscillator strength is for one transition only.

[c] Extinction coefficients unreliable because of incomplete salt formation.

determined in such solvents. Predicted maxima for different cationic dyes should then be compared with data obtained for polar solvents, but of course there will be a measure of uncertainty in such comparisons, since not all dyes will have the same solvatochromic properties. This uncertainty would suggest that minor refinements of the PPP method (e.g. more detailed geometry parameters or a variable β approach) are likely to be unrewarding.

It is interesting to consider briefly the relevance of canonical forms for the symmetrical dyes (**1**)–(**3**) in relation to the input data for the PPP treatment. For example, Michler's Hydrol Blue (**1**) can be represented by the forms (**1a**), (**1b**) and (**1c**), but parameter data can refer to only one of these, and thus the question arises as to which is most appropriate. Intuitively one would argue that this should not matter, since the PPP method is self consistent, and indeed, this is the case. Thus the two seemingly different dimethylamino groups in (**1a**) will have identical VSIP and core charge values, though for different reasons, and thus input data for (**1a**)–(**1c**) will be identical.

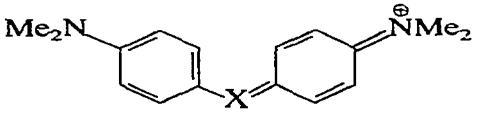
For all dimethylamino-substituted dyes, the Michler's Hydrol Blue parameters were used for di-arylmethanes, and the Malachite Green parameters used for tri-arylmethanes.

3. RESULTS AND DISCUSSION

Calculated and experimental data for various derivatives of the parent systems (**1**)–(**3**) are summarised in Table 2. Predicted absorption intensities are given as oscillator strengths, which are directly proportional to molar extinction coefficients provided half-band widths are constant for the dyes studied. Since band width variations are found with the more complex dyes, predicted intensities give only a rough guide to the expected extinction coefficient.

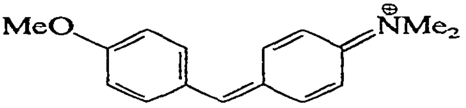
Colour and constitution effects in Michler's Hydrol Blue and Malachite Green analogues have often been interpreted in terms of perturbational theory,[7] and the qualitative success of this approach has been attributed to high electronic symmetry of these systems, and the fact that their π-electron structure approximates well to that of the corresponding iso-π-electronic odd alternant hydrocarbon. If the latter view is correct, then all 'active' (or 'starred') positions should show a decrease in π-electron density in the first excited state, and all 'inactive' (unstarred) positions should show a corresponding decrease. The PPP calculations confirm this viewpoint for (**1**), (**2**) and (**3**), and show that specific consideration of terminal heteroatoms and electron repulsion does not affect the correspondence of these systems to odd alternant hydrocarbons.

Two simple perturbations of the Michler's Hydrol Blue system that have a pronounced spectroscopic effect involve attaching an amino group to the central carbon atom, as in Auramine (**4**), or replacing the central carbon by nitrogen, as in Bindschedler's Green (**5**). The former change causes a large hypsochromic effect (λ_{max} moving from 608 nm to 434 nm), whereas the latter perturbation induces a large bathochromic shift (to 728 nm). These effects are reasonably well reproduced by the PPP method (Table 2). The amino parameters in the case of (**4**) were somewhat modified from normally accepted values (see Table 1) to render the group more electron releasing than usual. This was necessary because of the direct resonance interaction between the amino group of Auramine and the positive charge.

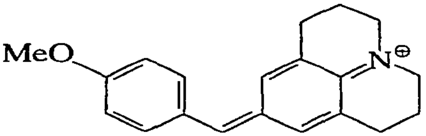


(**4**) X = C—NH$_2$
(**5**) X = N

When one of the dimethylamino groups of Michler's Hydrol Blue is replaced by a methoxy group a large hypsochromic shift results, and the dye is red. The shift in λ_{max} from 608 nm to 498 nm is predicted remarkably well (λ_{max} calc. = 495 nm) using unmodified methoxyl group parameters. The PPP calculations show that the loss of electronic symmetry in the resultant dye (**6**) destroys the simple relationship to odd alternant hydrocarbons, and thus simple perturbational theory cannot be applied to (**6**). This is well demonstrated by the corresponding julolidine dye (**7**), which in fact absorbs at shorter wavelengths than (**6**). According to perturbational theory, the stronger electron donating effect of julolidine nitrogen should cause a bathochromic shift of the visible band. PPP theory correctly predicts the hypsochromic effect, however, using appropriate nitrogen parameters (Table 1) to simulate the increase in donor strength.



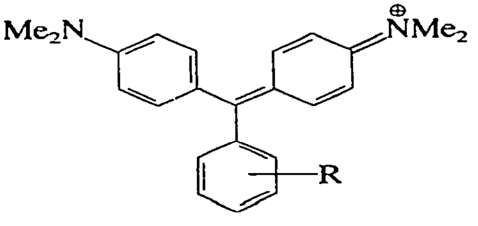
(**6**)



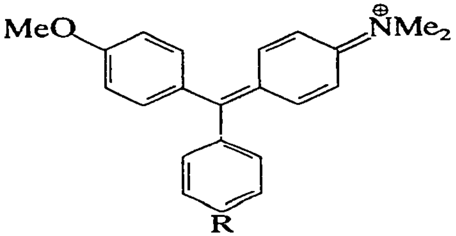
(**7**)

Malachite Green (**2**) is interesting in that it shows two visible absorption bands, the longer wavelength, more intense band (the '*x*' band) being polarised along the axis joining the two dimethylamino groups, and the weaker '*y*' band being polarised at right angles to this. The PPP calculations reproduce the two bands reasonably well, both with regard to position and intensity, although agreement is not as good for the *y* band as for the *x* band. The polarisation directions of the two bands are also confirmed. The calculated changes in π-electron densities accompanying excitation to the first excited state (i.e. absorption in the x band) show that, in agreement with predictions of perturbational theory, the unsubstituted phenyl ring of (**2**) plays little part in the x transition. Thus spectral changes due to substituents in this ring arise from transmission of their electronic effects to the central inactive carbon atom. This explains why good correlations are found between λ_{max} (x) of substituted Malachite Greens and the Hammett substituent σ constants,[12,13] a relatively rare occurrence in electronic absorption spectroscopic relationships.[14]

The general bathochromic effect of electron withdrawing groups in the phenyl ring of (**2**) and the corresponding hypsochromic effect of electron donating groups are well predicted for representative examples by the PPP method, as in the case of (**8**)–(**11**) (Table 2). The reversed effects of donors and acceptors on the position of the y band were also reproduced. In general, intensity variations between the x and y bands of the substituted derivatives (**8**)–(**11**) were not well accounted for, and this might be due to band width variations in this series. The effect of phenyl ring substituents on the position of the y band can be understood readily by consideration of electron density changes for the y transition. Thus the PPP calculations reveal a pronounced electron density migration from the phenyl ring into the rest of the chromogen in the second excited state. As in the case of Michler's Hydrol Blue, replacement of one of the dimethylamino groups of Malachite Green by a methoxy group causes a pronounced hypsochromic shift of the visible spectrum. Thus in (**12**) the x band is shifted to 515 nm, and the y band is displaced into the ultraviolet, at 384 nm. These effects are predicted satisfactorily for both (**12**) and (**13**).



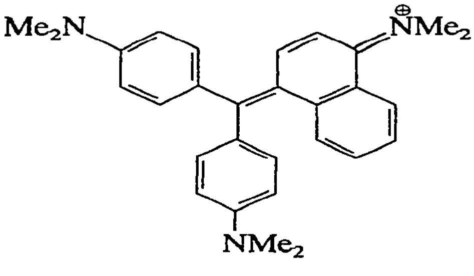
(**8**) R = *m*-MeO
(**9**) R = *p*-MeO
(**10**) R = *m*-CN
(**11**) R = *m*-NO$_2$



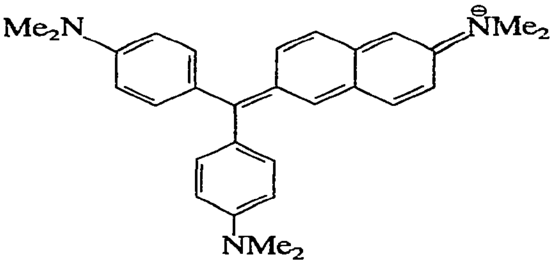
(**12**) R = H
(**13**) R = MeO

Since electron donors in the phenyl ring of (**2**) cause the x and y bands to move towards each other, it is easily understood why Crystal Violet (**3**) shows only one visible band, at shorter wavelengths than the x band of (**2**). The MO calculations show that the 589 nm band of (**3**) consists of two identical transitions polarised in the same plane, at right angles to each other. The predicted maximum, without modification of the Malachite Green parameters is in good agreement with the experimental value (λ_{max} calc. = 580 nm), but the calculated intensity (adding the oscillator strengths for the equivalent transitions) is much higher than that observed.

Increased conjugation in the di- and tri-arylmethanes may be achieved in various ways, and it was of interest to see how far the PPP method might be stretched to compute the absorption spectra of molecules much larger than (**1**)–(**3**). Naphthalene analogues of the tri-arylmethanes have long been used as textile dyes, and the spectroscopic properties of representative examples have been studied by Hallas and co-workers.[15,16] Replacement of one benzene ring in Crystal Violet by a naphthalene ring might be expected to split the degenerate x and y transitions slightly, but apparently only single visible absorption maxima are observed in the case of (**14**) and (**15**). Closely related Victoria Blue dyes, however, do show evidence of band broadening and band asymmetry,[17] suggesting x, y splitting. PPP calculations for (**14**), and a (**15**) indicate separation of the x and y bands, with a small bathochromic displacement in the case of (**14**), and a larger bathochromic shift with (**15**). The averaged predicted x and y values for (**15**) (632 nm) are in reasonable agreement with the experimental value (613 nm), whereas the calculated band position for (**14**) is appreciably shorter in wavelength than the observed value. This is most probably because of the severe steric crowding present in (**14**) but absent in (**15**). *Peri* interactions in (**14**) are most likely to cause one of the dimethylaminophenyl rings to rotate out of conjugation with the rest of the system, leaving a reasonably planar naphthalene analogue of the Michler's Hydrol Blue system. The latter should absorb at longer wavelengths than Michler's Hydrol Blue (608 nm), as observed.

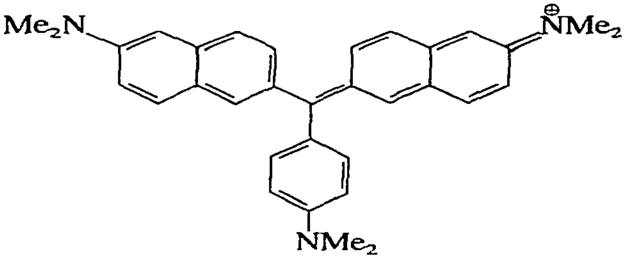


(**14**)

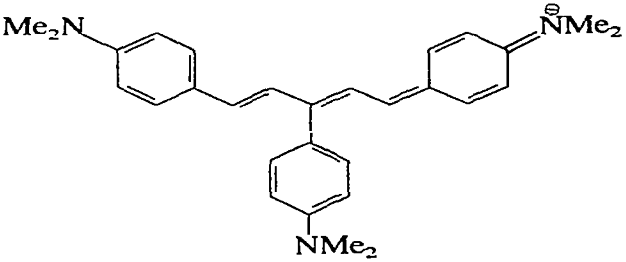


(**15**)

The Crystal Violet analogue with two naphthalene rings (**16**) absorbs at 666 nm, whereas the PPP method predicts two bands, at 717 and 676 nm. The averaged value of the latter, 696 nm, is reasonably close to the experimental value, but again steric effects are likely to be significant in (**16**). Steric effects should be small in the vinylogous Crystal Violet (**17**), and the molecule should be able to assume a planar structure. However, only a modest correspondence is found between the observed single λ_{max} value (770 nm) and the averaged value (704 nm) of the predicted *x* and *y* bands (721 and 687 nm).



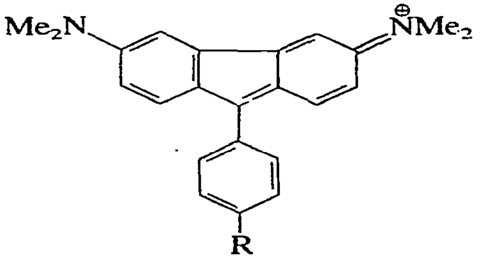
(**16**)



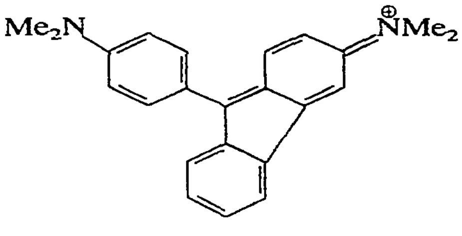
(**17**)

A much simpler type of extended conjugation exists in the fluorene analogues of Crystal Violet and Malachite Green, i.e. (**18**)–(**20**). These are formally derived from the parent triarylmethane by forming a bond between two positions *ortho* to the central carbon. Although this constitutes a relatively minor perturbation, the effect on the visible absorption spectrum of the dyes is quite dramatic,[18] and the longest wavelength bands are displaced into the near infrared (Table 2). For the purposes of the calculations, the five-membered ring in (**18**)–(**20**) was assumed to be a regular pentagon, and the fused benzene rings were retained as regular hexagons, with a resultant planar chromogen. Undoubtedly this is a gross oversimplification, but nevertheless large bathochromic shifts of the correct order were predicted by the PPP procedure. Absolute agreement was not very good however, and there did appear to be discrepancies between the number of absorption bands observed and the number predicted. However, examination of the spectra of (**18**)–(**20**) strongly suggests that the double peaks found at longest wavelengths are vibronic components of a single electronic transition, and thus averaged values should be used for comparison with theory. In this way the two bands of the x and y type are correctly predicted for the Malachite Green analogue (**19**). Three visible bands are predicted for (**20**) and are observed experimentally, but the wavelength correspondence for the second and third bands is very poor.

In the case of the Crystal Violet (**18**), the longer wavelength weak band and shorter wavelength intense band are predicted, both with regard to position and intensity. However, a third band at 470 nm is present experimentally which is not predicted. The origin of this band is unclear.



(**18**) R = NMe$_2$
(**19**) R = H



(**20**)

4. CONCLUSIONS

The most important types of structural modification in di- and tri-arylmethane cationic dyes give rise to spectroscopic effects that can be well accounted for by PPP theory, provided deviations from molecular planarity are not excessive. Reasonable agreement between theoretical and experimental absorption wavelengths and intensities is generally found, using the simplest geometrical models and the minimum of parameter modification. Whilst closer attention to optimisation of parameters and geometry should lead to better correlations in a closely related series of compounds, such sophistications are unlikely to be of value in treating arylmethane cationic dyes of wide structural diversity, because of the uncertain solvatochromic contributions to observed λ_{max} values in polar solvents. The preliminary work undertaken is encouraging, and extension to include nonplanar geometries is likely to prove helpful in explaining the more puzzling features of steric effects in di- and tri-arylmethane dyes.

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