Steric Effects in Di- and Tri-arylmethane Dyes. Part 13.[1] Electronic Absorption Spectra of Derivatives of Crystal Violet, Malachite Green, and Michler's Hydrol Blue exhibiting Simultaneous Central and Terminal Steric Distortion

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Spectral changes caused by the simultaneous crowding effects of *o,m*-dimethyl groups in Crystal Violet, Malachite Green, and Michler's Hydrol Blue are described and discussed in terms of molecular orbital theory. 2,3-Dimethyl derivatives of these dyes generally absorb at shorter wavelengths than their 2,5-dimethyl isomers owing to the increased spatial demands of the buttressed pair of substituents. Electronic symmetry is retained in derivatives of Crystal Violet but structurally unsymmetrical derivatives of Michler's Hydrol Blue and Malachite Green show red and blue deviations respectively. Diminished conjugation of terminal dimethylamino-groups with the central carbon atom leads to ready protonation of the crowded groups and, in certain cases, to incomplete conversion of dye base into dye in acid solution.

THE preparation of a series of 2,3-dimethyl derivatives of Crystal Violet, Malachite Green, and Michler's Hydrol Blue was originally initiated for comparison with analogues containing transversely conjugated naphthalene rings;[2] the spatial demands of the two systems are similar. It became clear, however, that excessive crowding in the 2,3-dimethyl compounds resulted in apparently inconsistent spectral changes, herein reported, and a series of 2,5-dimethyl derivatives has been synthesised in order to investigate simultaneous central and terminal hindrance without the additional complication of buttressing.

In common with previous Parts,[3] absorption spectra are described in terms of wavelengths of maximum absorption ($\lambda_{max.}$) and their molar extinction coefficients ($\varepsilon_{max.}$); the changes in these parameters with respect to the appropriate parent dyes are related to theory. The similarity in shape and narrow band width generally observed for the spectra of these closely related dyes suggests that vibrational fine structure and solvent effects are similar in each case and that one particular transition dominates. Dewar[4] has stated that singlet–triplet separation in basic dyes of this type is small.

Dewar[4] has used simple HMO wave functions to calculate absorption maxima for several basic dyes, including the parent di- and tri-arylmethane dyes considered herein, obtaining quite good agreement with experiment. Dewar was also able to minimise errors arising from the simplicity of these functions by using perturbation theory to calculate directly shifts due to small structural changes.[5] Two levels of accuracy are employed; first-order theory, in which the energy levels of the derivative are calculated using the wave functions of the parent compound, and second-order theory where perturbations of the wave functions are considered so that more accurate energy values are obtained. If the first-order approximation is adequate, substitution in one part of a molecule does not affect the remainder of the molecule and additive shifts are observed for successive substitutions at equivalent positions. Although transition energies are strictly proportional to absorption frequencies, for small shifts confined to a narrow region of the spectrum wavelength changes also approximate to linearity. Thus, additive wavelength shifts are widely observed experimentally; where departures from this electronic symmetry are observed second-order treatments are required.

First-order perturbation theory predicts[6] red shifts of the first absorption band for crowding substituents adjacent to either the central carbon atom (*ortho*-substitution) or the terminal dimethylamino-groups (*meta*-substitution) in Crystal Violet, Malachite Green, and Michler's Hydrol Blue. Additive red shifts are observed experimentally for *o*-methyl substitution,[3] but *m*-methyl groups lead to complex effects which differ for each of the three parent systems such that red shifts are observed for Crystal Violet, whereas symmetrically substituted derivatives of Michler's Hydrol Blue and Malachite Green show large and small blue shifts, respectively (Table 1).[7] Departures from electronic symmetry in unsymmetrically substituted derivatives of

TABLE 1

Absorption maxima of some *m*-methyl derivatives of Michler's Hydrol Blue, Crystal Violet, and Malachite Green[7]

Dye	λ/nm	Shift (nm)
Michler's Hydrol Blue	607.5	
(I; $R^1 = R^2 = H$, $R^3 = Me$)	602.5	−5
(I; $R^1 = H$, $R^2 = R^3 = Me$)	584	−23.5
Crystal Violet	589	
(II; $R^1 = R^2 = H$, $R^3 = Me$)	600	11
(II; $R^1 = H$, $R^2 = R^3 = Me$)	606.5	17.5
(II; $R^1 = R^2 = R^3 = Me$)	615	26
Malachite Green	621 427.5	
(I; $R^1 = Ph$, $R^2 = R^3 = Me$)	617 430	−4 2.5

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[1] Part 12, G. S. Dodd and G. Hallas, *J.C.S. Perkin II*, 1973, 2151.

[2] G. Hallas, K. N. Paskins, and D. R. Waring, *J.C.S. Perkin II*, 1972, 2281.

[3] Ref. 1 and earlier papers.

[4] M. J. S. Dewar, *J. Chem. Soc.*, 1950, 2329.

[5] M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341 *et seq.*

[6] M. J. S. Dewar, 'Steric Effects in Conjugated Systems,' ed. G. W. Gray, Butterworths, London, 1958, p. 46.

[7] C. C. Barker, G. Hallas, and A. Stamp, *J. Chem. Soc.*, 1960, 3790.

the latter two dyes are revealed by red (bathochromic) deviations.[7,8]

Dewar [9] has discussed qualitatively some of the effects of *meta*-substitution in electronically symmetrical dyes in terms of molecular orbital theory; the spectral variations can be attributed to a breakdown in the assumption, based on first-order perturbation theory, that the highest occupied molecular orbital (HOMO) in di- and tri-arylmethane dyes is a non-bonding molecular orbital (NBMO). The presence of terminal heteroatoms distorts the orbital and leads to negative terminal partial bond orders so that distortion of these bonds lowers the orbital energy. Since the energy of the first antibonding orbital is similarly lowered,[6] the ultimate direction of the spectral shift is determined by the relative magnitudes of the terminal partial bond orders in the relevant orbitals. Symmetry restrictions applicable to HMO (and many more precise) wave functions require that the highest occupied molecular orbitals of all three parent dyes have energies and partial orders of equivalent bonds identical to their counterparts in *NN*-dimethylaniline. On this basis, the comparative resultant shifts depend on the extent of lowering of the lowest unoccupied levels. Dewar's qualitative prediction [9] of a decreasing blue shift along the series Michler's Hydrol Blue, Malachite Green, and Crystal Violet is consistent with the observed blue, intermediate, and red shifts, respectively, for *m*-methyl derivatives of these dyes.

No attempt has been made to confirm quantitatively these qualitative predictions by Dewar. Application of second-order perturbation theory is beyond the scope of this work because of computational complexity. However, a quantitative estimate of the effects of deconjugation in terminal carbon–nitrogen bonds has been obtained [10] *via* simple HMO theory, using assumptions and approximations analogous to those employed in the second-order perturbation approach. The use of simple HMO wave functions is valid since the calculations are intended only to study departures from first-order perturbation theory which is itself based on these functions and neglects refinements such as establishment of a self-consistent field and configuration interaction. Thus, the distortion of molecular orbitals from alternant hydrocarbon symmetry by the electronegative heteroatom has been simulated by taking a Coulomb integral of $\alpha + \beta$ for nitrogen;[4] perturbation theory would determine this effect directly in terms of the change ($\delta\alpha$) in Coulomb integral relative to carbon. Variations in Coulomb integrals for carbon atoms adjacent to nitrogen, or for alkylated nitrogen atoms, have been neglected.[4] Steric effects have been estimated by considering variation of the terminal resonance integral. The secular equations were set up assuming all resonance integrals constant (β) except for the terminal integral ($a\beta$); a value of unity for a corresponds to a parent dye whereas $a < 1$ represents terminal hindrance. This approach is also analogous to a second-order perturbation treatment since re-solving the secular equations in each case for different values of a automatically corrects for any changes in wave function induced throughout the molecule by distortion of the terminal bond. However, average terminal partial bond orders for each orbital may be obtained from the calculated data by using the first-order perturbation theory formula [6] $p = \delta E/2\delta\beta$ (Table 2).

TABLE 2

Average terminal partial bond orders for deconjugated derivatives of Michler's Hydrol Blue, Crystal Violet, and Malachite Green

Dye	Lowest π^* orbital	Perturbed NBMO
(I; $R^1 = R^2 = H$, $R^3 = Me$)	-0.063	-0.097
(I; $R^1 = H$, $R^2 = R^3 = Me$)	-0.064	-0.101
(II; $R^1 = R^2 = H$, $R^3 = Me$)	-0.047	
(II; $R^1 = H$, $R^2 = R^3 = Me$)	-0.047	-0.101
(II; $R^1 = R^2 = R^3 = Me$)	-0.048	
(I; $R^1 = Ph$, $R^2 = R^3 = Me$)	-0.052	-0.101

The calculations confirm Dewar's prediction [9] of negative terminal partial bond orders in both the highest occupied and lowest unoccupied orbitals. The greater magnitude of the former is consistent with the blue shift observed for symmetrically deconjugated Michler's Hydrol Blue, but calculated differences in the latter do not account for the respective intermediate and red shifts observed [7] for symmetrical derivatives of Malachite Green and Crystal Violet as suggested by Dewar.

The higher symmetry of Crystal Violet requires that the highest occupied molecular orbital is doubly degenerate in many approximate methods. Some experimental evidence of splitting of these levels exists,[11] but no resolution has been obtained in visible absorption spectra measured under the conditions used herein. Given this degeneracy, one level should survive a single substitution unchanged so that the change in excitation energy depends only on the lowering of the lowest unoccupied molecular orbital; the red shift observed for the 3-methyl derivative of Crystal Violet is consistent with this behaviour.

Unsymmetrically deconjugated derivatives of Michler's Hydrol Blue and Malachite Green show red deviations from the arithmetic mean of the absorption maxima of unsubstituted and symmetrically deconjugated derivatives. These red deviations contrast with the more usual observation of blue (hypsochromic) deviations for electronically unsymmetrical species.[12] Theoretical treatments [13,14] of departure from electronic symmetry normally consider an alternation of greater and lesser resonance integrals throughout the molecule and this results in increased splitting of bonding and antibonding levels about the zero energy level, leading to increased transition energies. However, since the antibonding

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[8] R. W. Castelino and G. Hallas, *J. Chem. Soc.* (*B*), 1971, 1471.

[9] Ref. 6, p. 59.

[10] K. N. Paskins, Ph.D. Thesis, University of Leeds, 1975.

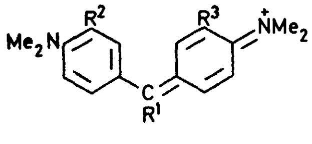
[11] P. P. Feofilov, 'Physical Basis of Polarized Emission,' Consultants Bureau, New York, 1959, p. 138.

[12] L. G. S. Brooker and R. H. Sprague, *J. Amer. Chem. Soc.*, 1945, **67**, 1869 *et seq.*

[13] M. J. S. Dewar, *J. Chem. Soc.*, 1952, 3544.

[14] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, 1959, *A*,**251**, 172.

terminal partial bond order is greater in these systems, departure from electronic symmetry is likely to raise the energy of the former relative to the latter, resulting in a red deviation. The slightly lower partial bond order calculated for the highest occupied molecular orbital in unsymmetrically deconjugated derivatives is consistent with this deviation (Table 2).



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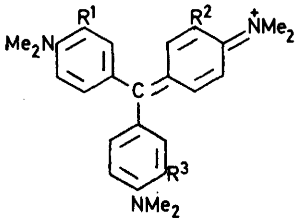

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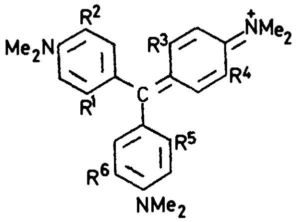

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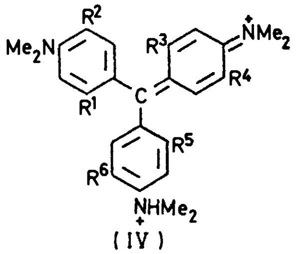

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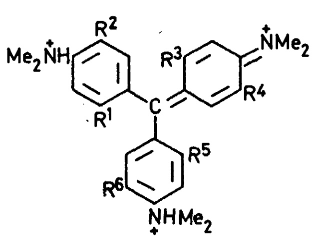

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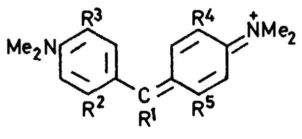

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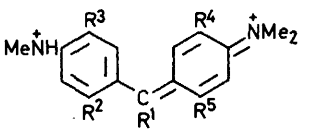

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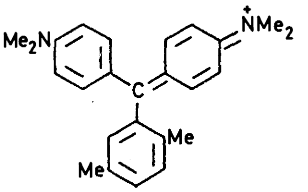

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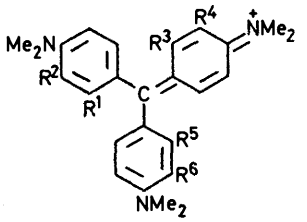

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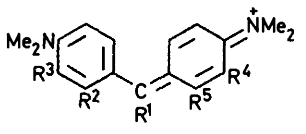

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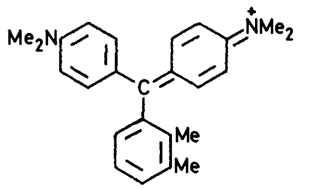

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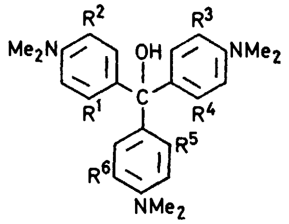

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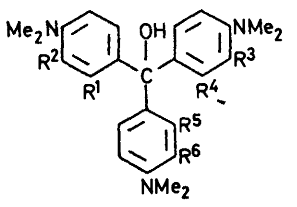

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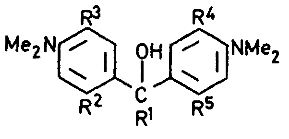

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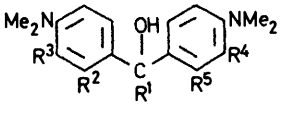

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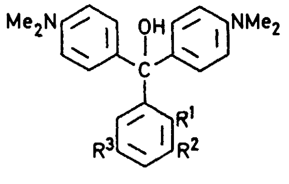


(XVI)

The study of dyes containing *meta*-crowding substituents is complicated by variations in the equilibrium between dye base and dye in acid solution; diminished conjugation of terminal dimethylamino-groups with the central carbon atom inhibits the loss of hydroxide from the dye base and also makes protonation of the nitrogen atoms more likely.[7] Absorption spectra have usually been measured in ethanol containing hydrogen chloride so as to optimise conditions for formation of univalent dye cation; in several instances even 100% acetic acid is sufficiently strong to bring about further protonation. The spectrum of the 2,5-dimethyl derivative of Crystal Violet base in ethanol containing one equivalent of hydrogen chloride is, however, typical of the univalent ion (III; R^1—R^4 = H, $R^5 = R^6$ = Me) with a single main peak in the visible region (Table 3). Little protonation occurs on the addition of further quantities of hydrogen chloride until 4 000 equivalents are exceeded whereupon the spectrum rapidly changes to that of the bivalent cation (IV; R^1—R^4 = H, $R^5 = R^6$ = Me) and the colour of the solution from violet to blue-green. The new system resembles Malachite Green so that the spectrum of the bivalent ion (IV; R^1—R^4 = H, $R^5 = R^6$ = Me) has absorption maxima similar to those of the 2,5-dimethyl derivative of Malachite Green (VIII) (Table 3). The spectrum of the 2,5-dimethyl derivative of Crystal Violet in 100% acetic acid is similar to that in ethanol containing 4 000 equivalents of hydrogen chloride and represents a mixture of univalent and bivalent cations; in 50% acetic acid the spectrum is effectively that of the bivalent ion. In the case of the 2,2′,5,5′-tetramethyl derivative of Crystal Violet (III; $R^1 = R^2$ = H, R^3—R^6 = Me), the spectrum of the dye base in ethanol containing one equivalent of hydrogen chloride exhibits a maximum at 620 nm (Table 3) but this may well be at a slightly longer wavelength than the true value for the univalent cation since low absorption *ca.* 400 nm indicates the presence of some bivalent cation (IV; $R^1 = R^2 = H$, R^3—R^6 = Me). As the acid strength of the solvent is increased the main band shifts to longer wavelength and decreases in intensity while absorption at shorter wavelength increases until in ethanol containing 5 000 equivalents of hydrogen chloride the solution is yellow and its spectrum shows a single peak at 424 nm; this absorption is due to tervalent cation (V; $R^1 = R^2 = H$, R^3—R^6 = Me) and is similar to that of the parent *NN*-dimethylfuchsoniminium ion which has $\lambda_{max.}$ 465.5 nm (ε 33 000) in acetic acid.[15] The spectrum of the dye base of the 2,2′,2″,5,5′,5″-hexamethyl derivative of Crystal Violet (III; R^1—R^6 = Me) in ethanol containing one equivalent of hydrogen chloride has a maximum at 645 nm (Table 3) but again a small band at *ca.* 400 nm suggests the presence of some bivalent cation (IV; R^1—R^6 = Me); a slightly shorter wavelength and higher intensity are therefore probably appropriate for the univalent cation. Higher concentrations of acid cause rapid fading of the colour in accord with the progressive decrease in stability of the univalent species with increase in terminal hindrance.

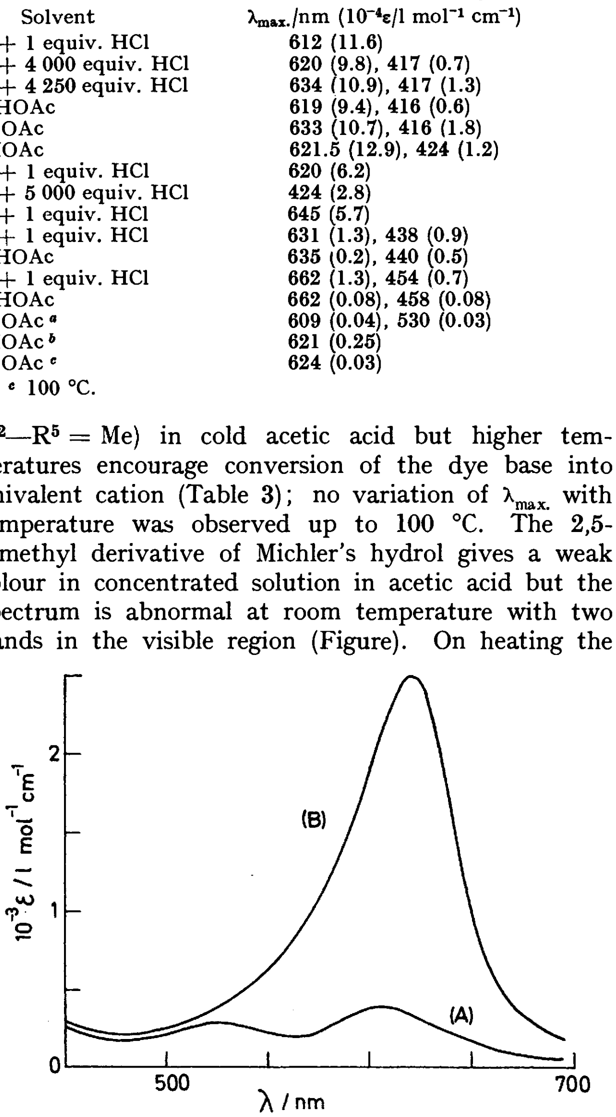
TABLE 3

Spectral data for solutions of 2,5-dimethyl derivatives of Crystal Violet, Malachite Green, and Michler's Hydrol Blue

Dye	Solvent	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1})
(III; R^1—R^4 = H, $R^5 = R^6$ = Me)	EtOH + 1 equiv. HCl	612 (11.6)
	EtOH + 4 000 equiv. HCl	620 (9.8), 417 (0.7)
	EtOH + 4 250 equiv. HCl	634 (10.9), 417 (1.3)
	100% HOAc	619 (9.4), 416 (0.6)
	50% HOAc	633 (10.7), 416 (1.8)
(VIII)	98% HOAc	621.5 (12.9), 424 (1.2)
(III; $R^1 = R^2$ = H, R^3—R^6 = Me)	EtOH + 1 equiv. HCl	620 (6.2)
	EtOH + 5 000 equiv. HCl	424 (2.8)
(III; R^1—R^6 = Me)	EtOH + 1 equiv. HCl	645 (5.7)
(VI; R^1 = Ph, $R^2 = R^3$ = H, $R^4 = R^5$ = Me)	EtOH + 1 equiv. HCl	631 (1.3), 438 (0.9)
	100% HOAc	635 (0.2), 440 (0.5)
(VI; R^1 = Ph, R^2—R^5 = Me)	EtOH + 1 equiv. HCl	662 (1.3), 454 (0.7)
	100% HOAc	662 (0.08), 458 (0.08)
(VI; R^1—R^3 = H, $R^4 = R^5$ = Me)	98% HOAc [a]	609 (0.04), 530 (0.03)
	98% HOAc [b]	621 (0.25)
(VI; R^1 = H, R^2—R^5 = Me)	98% HOAc [c]	624 (0.03)

[a] 23 °C. [b] 70 °C. [c] 100 °C.

Derivatives of Malachite Green with crowded terminal dimethylamino-groups show even more tendency to protonate than their Crystal Violet analogues and isolation of the absorption due to univalent cation is correspondingly more difficult. However, the presence of bivalent cation of the Malachite Green type (VII; R^1 = Ph) does not seriously distort the wavelength of maximum absorption of the univalent cation, unlike analogous derivatives of Crystal Violet, since the former species absorbs at much shorter wavelength and the peaks are resolved. Protonated species could not be eliminated from the absorption spectra of any of the *o,m*-dimethyl derivatives of Malachite Green; extinction coefficients are therefore meaningless and in every case the *y* band is obscured by absorption due to bivalent cation. The results for the 2′,5′-dimethyl derivative of Malachite Green (VI; R^1 = Ph, $R^2 = R^3$ = H, $R^4 = R^5$ = Me) and the 2′,2″,5′,5″-tetramethyl derivative (VI; R^1 = Ph, R^2—R^5 = Me) are given in Table 3. The 2,2′,5,5′-tetramethyl derivative of Michler's hydrol is unable to form the corresponding dye (VI; R^1 = H, R^2—R^5 = Me) in cold acetic acid but higher temperatures encourage conversion of the dye base into univalent cation (Table 3); no variation of $\lambda_{max.}$ with temperature was observed up to 100 °C. The 2,5-dimethyl derivative of Michler's hydrol gives a weak colour in concentrated solution in acetic acid but the spectrum is abnormal at room temperature with two bands in the visible region (Figure). On heating the solution the shorter wavelength absorption becomes insignificant and the major band is intensified and shifted to longer wavelength (Table 3); the minor band is probably associated with aggregation effects in the relatively concentrated solution (0.003M) required to give a detectable colour and the shortening in wavelength of the major band at low temperatures is attributed to poor resolution of the two peaks.



Absorption spectrum of 4,4′-bisdimethylamino-2,5-dimethyldiphenylmethanol in 98% acetic acid at (A) 23 °C and (B) 70 °C

The spectral shifts for the 2,5-dimethyl substituted

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[15] E. K. Branch and H. Walba, *J. Amer. Chem. Soc.*, 1951, **73**, 3341.

derivatives of Crystal Violet are in quite good agreement with the sum of the shifts for the corresponding 2-[16] and 3-methyl[7] analogues (Table 4). Thus, for this system substitution at one type of position apparently does not affect the wave function at the other; first-order perturbation theory is obeyed. This is not the case for 2,5-dimethyl derivatives of Michler's Hydrol Blue and Malachite Green for which second-order effects generally displace absorption maxima to longer wavelengths than those predicted by first-order theory.

TABLE 4

Additive and observed spectral shifts for the first bands of 2,5-dimethyl derivatives of Crystal Violet

Dye	Observed $\lambda_{max.}$/nm	Calculated $\lambda_{max.}$/nm	$\Delta\lambda$/nm
(III; R^1—R^4 = H, R^5 = R^6 = Me)	612	607.5	4.5
(III; R^1 = R^2 = H, R^3—R^6 = Me)	620	623.5	−3.5
(III; R^1—R^6 = Me)	645	640	5

The red deviation of 5.5 nm shown by the 2,5-dimethyl derivative of Michler's Hydrol Blue (VI; R^1—R^3 = H, R^4 = R^5 = Me) is similar to that observed for its 3-methyl analogue. In contrast, the 2′,5′-dimethyl derivative of Malachite Green (VI; R^1 = Ph, R^2 = R^3 = H, R^4 = R^5 = Me) exhibits a blue deviation of 10 nm; this finding is consistent with departure from electronic symmetry extending throughout the molecule beyond the anomalous terminal regions,[14] reversing the red deviation of 8.5 nm shown by the 3′-methyl derivative. This more pronounced distortion of electronic symmetry in Malachite Green compared to Michler's Hydrol Blue is commonly observed; in addition, crowding in the triarylmethane system is likely to be greater than in the diarylmethane dye.

TABLE 5

Spectral data for solutions of 2,3-dimethyl derivatives of Crystal Violet, Malachite Green, and Michler's Hydrol Blue

Dye	Solvent	$\lambda_{max.}$/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1})
(IX; R^1—R^4 = H, R^5 = R^6 = Me)	EtOH + 1 equiv. HCl	614 (9.5)
	EtOH + 1 000 equiv. HCl	626 (8.4), 417 (0.6)
	100% HOAc	619.5 (8.5), 416 (0.6)
	50% HOAc	633 (9.6), 416 (1.0)
(XI)	98% HOAc	624 (12.6), 424 (1.4)
(IX; R^1 = R^2 = H, R^3—R^6 = Me)	EtOH	593
(IX; R^1—R^6 = Me)	EtOH	618 (1.0)
	EtOH + 100 equiv. HCl	635 (0.2), 421 (0.3)
(X; R^1 = Ph, R^2 = R^3 = H, R^4 = R^5 = Me)	EtOH + 1 equiv. HCl	579 (2.15), 435 (2.0)
(X; R^1 = Ph, R^2—R^5 = Me)	EtOH + 1 equiv. HCl	625 (0.05), 442 (0.1)
(X; R^1—R^3 = H, R^4 = R^5 = Me)	98% HOAc[a]	607.5 (0.09)
	98% HOAc[b]	617.5 (0.8)
(X; R^1 = H, R^2—R^5 = Me)	98% HOAc[c]	620 (0.003)

[a] 24 °C. [b] 80 °C. [c] 100 °C.

The spectral parameters of the 2,3-dimethyl derivative of Crystal Violet (IX; R^1—R^4 = H, R^5 = R^6 = Me) are very similar (Table 5) to those of the corresponding 2,5-dimethyl isomer; protonation at the hindered dimethylamino-group takes place very readily as the acidity of the solvent is increased. The spectrum of the dye base of the 2,2′,3,3′-tetramethyl derivative of Crystal Violet (IX; R^1 = R^2 = H, R^3—R^6 = Me) in ethanol containing only one equivalent of hydrogen chloride showed typical signs of protonation; a typical Crystal Violet type curve was obtained, however, from a sample of the corresponding leuco-base which oxidised slowly in ethanol. Similarly, the dye base of the 2,2′,2″,3,3′,3″-hexamethyl derivative of Crystal Violet (IX; R^1—R^6 = Me) in ethanolic hydrogen chloride gave a series of spectra corresponding to a mixture of bivalent and tervalent cations; as the acidity of the solvent was increased, absorption due to tervalent cation at 416 nm increased while that due to bivalent cation at 635 nm fell. Fortunately, the dye perchlorate was successfully purified so that a reliable spectrum of the univalent cation could be observed in ethanol (Table 5). As in the case of the corresponding 2,5-dimethyl derivatives of Malachite Green, the dye bases of the 2′,3′-dimethyl and 2′,2″,3′,3″-tetramethyl derivatives in acid solution gave absorption spectra corresponding to mixtures of the appropriate univalent and bivalent cations (Table 5). Although the 2,3-dimethyl derivative of Michler's hydrol shows only a single broad band in acetic acid at room temperature, unlike the 2,5-dimethyl isomer, as the temperature is raised the absorption moves to longer wavelength (Table 5); in view of the similar behaviour of these two isomers, and of the correspondence of the band parameters of the symmetrically substituted tetramethyl analogues, the longer wavelength value is assumed to represent absorption by the univalent cation. The dye base of the 2,2′,3,3′-tetramethyl derivative of Michler's hydrol is even more reluctant to form the univalent cation (X; R^1 = H, R^2—R^5 = Me) in acetic acid than the 2,2′,5,5′-tetramethyl isomer (Table 5).

Steric effects in 2,3-dimethyl derivatives are expected to be greater than those in the corresponding 2,5-dimethyl compounds owing to buttressing of the two adjacent methyl groups. A comparison of effects in the two series (Table 6) shows that buttressing generally leads to absorption at shorter wavelengths. However, the 2,3-dimethyl derivative of Crystal Violet has an absorption maximum virtually identical to that of its 2,5-dimethyl isomer; this is consistent with survival unchanged of one of a degenerate pair of highest occupied molecular orbitals and suggests that changes in the lowest unoccupied orbitals are less significant than those in the highest occupied. Further support for this conclusion is given by the identical buttressing effects

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[16] C. C. Barker, M. H. Bride, and A. Stamp, *J. Chem. Soc.*, 1959, 3957.

(a blue shift of 27 nm) shown by the 2,2′,3,3′-tetramethyl and 2,2′,2″,3,3′,3″-hexamethyl derivatives of Crystal Violet relative to their unbuttressed isomers; simple HMO theory predicts identical energies for the highest occupied molecular orbitals of derivatives of Crystal Violet substituted in two or three rings.[10]

TABLE 6

Comparison of the first bands of 2,3-dimethyl and 2,5-dimethyl derivatives of Crystal Violet, Malachite Green, and Michler's Hydrol Blue

Parent dye	Number of substituted rings	$\lambda_{max.}$/nm for 2,3-dimethyl derivatives	$\lambda_{max.}$/nm for 2,5-dimethyl derivatives	$\Delta\lambda$/nm
Crystal Violet	1	614	612	2
	2	593	620	−27
	3	618	645	−27
Malachite Green	1	579	631	−52
	2	625	662	−37
Michler's Hydrol Blue	1	617.5	621	−3.5
	2	620	624	−4

TABLE 7

Derivatives of Crystal Violet base, Malachite Green base, and Michler's hydrol

Compound	Solvent	M.p. (°C)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(XII; R^1—R^4 = H, R^5 = R^6 = Me)	*a*	187—188	77.2	8.4	10.1	$C_{27}H_{35}N_3O$	77.6	8.4	10.1
(XII; R^1 = R^2 = H, R^3—R^6 = Me)	*a*	198—199	77.9	8.6	9.7	$C_{29}H_{39}N_3O$	78.2	8.8	9.4
(XII; R^1—R^6 = Me)	*a*	212—213	78.2	8.9	9.1	$C_{31}H_{43}N_3O$	78.6	9.1	8.9
(XIV; R^1 = Ph, R^2 = R^3 = H, R^4 = R^5 = Me)	*b*	108—109	80.0	8.0	7.3	$C_{25}H_{30}N_2O$	80.2	8.1	7.5
(XIV; R^1 = Ph, R^2—R^5 = Me)	*b*	132—133	80.4	8.3	6.9	$C_{27}H_{34}N_2O$	80.5	8.5	6.9
(XIV; R^1—R^3 = H, R^4 = R^5 = Me)			75.8	8.6	9.1	$C_{19}H_{26}N_2O$	76.3	8.8	9.4
(XIV; R^1 = H, R^2—R^5 = Me)			76.8	9.2	8.6	$C_{21}H_{30}N_2O$	77.2	9.3	8.6
(XIII; R^1—R^4 = H, R^5 = R^6 = Me)	*c*	139—140	77.6	8.4	10.1	$C_{27}H_{35}N_3O$	77.6	8.4	10.1
(XIII; R^1 = R^2 = H, R^3—R^6 = Me)	*c*	187—188	78.3	8.8	9.2	$C_{29}H_{39}N_3O$	78.2	8.8	9.4
(XIII; R^1—R^6 = Me)	*c*	178—179	78.4	9.2	8.7	$C_{31}H_{43}N_3O$	78.6	9.1	8.9
(XV; R^1 = Ph, R^2 = R^3 = H, R^4 = R^5 = Me)	*a*	119—120	80.2	8.0	7.1	$C_{25}H_{30}N_2O$	80.2	8.1	7.5
(XV; R^1 = Ph, R^2—R^5 = Me)			80.0	8.2	7.2	$C_{27}H_{34}N_2O$	80.5	8.5	6.9
(XV; R^1—R^3 = H, R^4 = R^5 = Me)			76.3	8.7	9.1	$C_{19}H_{26}N_2O$	76.3	8.8	9.4
(XV; R^1 = H, R^2—R^5 = Me)			77.0	9.4	8.6	$C_{21}H_{30}N_2O$	77.2	9.3	8.6
(XVI; R^2 = H, R^1 = R^3 = Me)	*a*	176—178	79.2	8.0	7.5	$C_{25}H_{30}N_2O$	80.2	8.1	7.5
(XVI; R^3 = H, R^1 = R^2 = Me)	*a*	159—160	80.1	8.3	7.6	$C_{25}H_{30}N_2O$	80.2	8.1	7.5

[a] Ethanol. [b] Ethanol–hexane (3 : 1). [c] Light petroleum (b.p. 40—60 °C).

The special effects described above for derivatives of Crystal Violet depend upon the existence of a degenerate pair of highest occupied molecular orbitals, and these in turn are a consequence of the high rotational symmetry of the parent dye. These requirements make departures from electronic symmetry unlikely in derivatives of Crystal Violet and this deduction is well supported experimentally. The occurrence of deviations is not self-evident as with lower symmetry species, but spectra can be analysed for uniform behaviour by reference to orbital degeneracy. Thus, the difference of 25 nm between Crystal Violet and its 2,3-dimethyl derivative represents the lowering in energy of the lowest unoccupied orbital per substituted ring if one of a degenerate pair of highest occupied MOs remains unchanged. Assuming that first-order perturbation theory holds for distortion of this orbital, the lowering in its energy for the 2,2′,2″,3,3′,3″-hexamethyl derivative of Crystal Violet should be equivalent to 75 nm, whereas the observed shift is 29 nm. The difference, 46 nm, represents the lowering in energy of the highest occupied orbital in both the hexamethyl and the 2,2′,3,3′-tetramethyl derivative. Consequently, a red shift of 4 nm is predicted for the latter compound and this gives excellent agreement with experiment despite the number of simplifying assumptions. A similar treatment confirms that electronic symmetry is retained for 2,5-dimethyl derivatives of Crystal Violet (Table 3), as it is for the 2- and 3-methyl series.

The 2,3-dimethyl derivative of Michler's Hydrol Blue shows a red deviation (4 nm) in similar manner to its 3-methyl and 2,5-dimethyl analogues, and the blue deviation (10 nm) observed for the 2′,5′-dimethyl derivative of Malachite Green is greatly increased (42 nm) in the 2′,3′-dimethyl isomer.

Preparations.—4-Bromo-2,5-dimethylaniline was obtained in high yield by brominating 2,5-dimethylaniline with 2,4,4,6-tetrabromocyclohexa-2,5-dienone;[17] the corresponding tertiary amine was prepared by reaction of the parent compound with methyl iodide in aqueous sodium carbonate and then converted into 4-dimethylamino-2,5-dimethylphenyl-lithium by treatment with the n-butyl-lithium–1,2-bisdimethylaminoethane complex.[18] All the dye bases containing 2,5-dimethyl substituents, except for the 2,5-dimethyl derivative of Malachite Green base, were prepared by reaction of this lithium compound with the appropriate carbonyl derivative; typical reaction conditions have been described previously.[1] The dye bases were generally purified by crystallisation but the two hydrols could only be isolated as amorphous gums; details are given in Table 7.

The dye bases containing 2,3-dimethyl substituents were generally difficult to isolate owing to relatively poor yields and high solubility of the amorphous crude products. The 2,3-dimethyl derivative of Crystal Violet base showed a marked tendency to be irreversibly

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[17] G. J. Fox, G. Hallas, J. D. Hepworth, and K. N. Paskins, *Org. Synth.*, 1976, **55**, 20.

[18] G. Hallas and D. R. Waring, *Chem. and Ind.*, 1969, 620.

converted into dye; all the derivatives of Crystal Violet yield appreciable amounts of fuchsone on treatment with base.[19] Certain unsymmetrically substituted derivatives were obtained *via* 4,4′-bisdimethylamino-2,3-dimethylbenzophenone which was prepared by the reaction of 4-dimethylamino-2,3-dimethylphenylmagnesium bromide with 4-dimethylaminobenzonitrile; a similar reaction with 4-dimethylamino-2,3-dimethylbenzonitrile afforded bis-(4-dimethylamino-3-dimethylphenyl) ketone.[20] Reduction of the ketones in ethanol using sodium amalgam gave the hydrols as gums which were purified by sublimation under reduced pressure as was the symmetrical 2′,2″,3′,3″-tetramethyl derivative of Malachite Green base. The latter compound and the corresponding unsymmetrical base were synthesised by reaction of the appropriate ketone with phenyl-lithium; the symmetrical hydrol was also obtained by the action of 4-dimethylamino-2,3-dimethylphenyl-lithium on ethyl formate. Analytical details are given in Table 7. In the case of the 2,3-dimethyl derivative of Crystal Violet, the dye base was also converted *via* the dye into the corresponding methyl ether which, unlike the parent base, did not tend to form the dye during purification. The 2,2′,3,3′-tetramethyl and the 2,2′,2″,3,3′,3″-hexamethyl derivatives of Crystal Violet base were prepared by reaction of 4-dimethylamino-2,3-dimethylphenyllithium with methyl 4-dimethylaminobenzoate and dimethyl carbonate, respectively. The perchlorate of the 2,2′,2″,3,3′,3″-hexamethyl derivative (IX; R^1—R^6 = Me) was isolated from the dye obtained on condensing *NN*,2,3-tetramethylaniline with carbon tetrachloride in the presence of aluminium chloride by treatment of the product with sodium perchlorate. The leuco-base of the 2,2′,3,3′-tetramethyl derivative was prepared by condensing the 2,2′,3,3′-tetramethyl derivative of Michler's hydrol with *NN*-dimethylaniline in dilute sulphuric acid. The 2,3-dimethyl derivative of Malachite Green base was obtained by the action of 2,3-dimethylphenyl-lithium on Michler's ketone and the corresponding 2,5-dimethyl isomer was synthesised by treatment of methyl 2,5-dimethylbenzoate with 4-dimethylaminophenyl-lithium; analytical details are given in Table 7.

EXPERIMENTAL

Absorption spectra were measured with a Unicam SP 800 recording spectrophotometer for solutions of the dye bases in ethanolic hydrogen chloride and in acetic acid. ^{1}H N.m.r. spectra were obtained with a Varian HA 100 spectrometer for solutions in deuteriochloroform at the Physicochemical Measurements Unit, Harwell; all the dye bases gave satisfactory spectra.

4,4′-*Bisdimethylamino*-2,3-*dimethylbenzophenone*.—1,2-Dibromoethane (1.2 cm^3) was added dropwise over 1 h to a gently refluxing mixture of 4-bromo-*NN*-dimethyl-2,3-xylidine [21] (3.0 g) and magnesium (0.7 g) in ether (50 cm^3). After a further 2 h the solution was decanted from unchanged magnesium and added quickly to a solution of 4-dimethylaminobenzonitrile (1.6 g) in ether (50 cm^3). The mixture was boiled for 1 h before pouring into water (100 cm^3). Concentrated hydrochloric acid (30 cm^3) was added until the ether layer became colourless. The aqueous layer was boiled for 1 h, basified with ammonia, and extracted with benzene. Column chromatography on alumina gave a solid which was twice crystallised from ethanol yielding fawn needles of the *ketone* (2.5 g), m.p. 136—137 °C (Found: C, 76.7; H, 8.1; N, 9.5. $C_{19}H_{24}N_2O$ requires C, 77.0; H, 8.2; N, 9.5%), τ 2.28 (2 H, d, J_o 9.0 Hz, 2′- and 6′-H), 2.93 (1 H, d, J_o 8.5 Hz, 6-H), 3.10 (1 H, d, J_o 8.5 Hz, 5-H), 3.38 (2 H, d, J_o 9.0 Hz, 3′- and 5′-H), 6.97 (6 H, s, 4′-NMe_2), 7.31 (6 H, s, 4-NMe_2), 7.74 (3 H, s, 2- or 3-Me), and 7.83 (3 H, s, 3- or 2-Me).

4,4′,4″-*Trisdimethylamino*-2,3-*dimethyltriphenylmethyl Methyl Ether*.—Ethereal 4-dimethylaminophenyl-lithium, from 4-bromo-*NN*-dimethylaniline (2.6 g) and the n-butyllithium–1,2-bisdimethylaminoethane complex (2.4 g), was added to a solution of 4,4′-bisdimethylamino-2,3-dimethylbenzophenone (2.7 g) in ether (40 cm^3); after 1 h under reflux the mixture was poured into water (100 cm^3). Removal of solvent from the dried organic layer gave a residue which was dissolved in acetic acid (5 cm^3). The product obtained on removal of the solvent was added to water (200 cm^3) and the filtered solution was poured into potassium perchlorate (3.8 g) in water (150 cm^3). A solution of the dried perchlorate of the dye in methanol (40 cm^3) was slowly added to methanol (20 cm^3) containing sodium methoxide (4.0 g). Crystallisation of the precipitate from benzene–methanol (1 : 4) gave colourless crystals of the *methyl ether* (1.1 g), m.p. 155—156 °C (Found: C, 78.0; H, 8.5; N, 9.6. $C_{28}H_{27}N_2O$ requires C, 77.9; H, 8.6; N, 9.7%).

4,4′,4″-*Trisdimethylamino*-2,2′,3,3′-*tetramethyltriphenylmethane*.— Bis-(4-dimethylamino-2,3-dimethylphenyl)-methanol (0.6 g) and *NN*-dimethylaniline (1.2 g) were dissolved in 2M-sulphuric acid (50 cm^3) and kept at 90 °C for 18 h. The excess of *NN*-dimethylaniline was removed after basification with ammonia and the residue was extracted with ether. Removal of solvent from the dried organic layer gave a brown oil which on crystallisation from light petroleum (b.p. 40—60 °C) yielded needles of the *leuco-base* (0.02 g), m.p. 159—160 °C (Found: M^+, 429.313 8. $C_{29}H_{39}N_3$ requires M, 429.314 4).

Perchlorate of 2,2′,2″,3,3′,3″-*Hexamethyl Derivative of Crystal Violet*.—Carbon tetrachloride (3.1 g) was added dropwise at −20 °C to a paste of powdered anhydrous aluminium chloride (11.0 g) and *NN*,2,3-tetramethylaniline (10.5 g); on removal of the cooling bath, an exothermic reaction commenced. The mixture was kept at 50 °C for 4 h and the resulting brown mass was treated with water (50 cm^3) and poured into sodium perchlorate (7.5 g) in water (250 cm^3). The resultant sticky precipitate was triturated with light petroleum (b.p. 40—60 °C) to remove unchanged amine and the crude material was dissolved in dry acetone and partly reprecipitated by pouring into dry ether. Removal of solvent from the filtered solution gave a solid which was twice subjected to the same procedure to give, after drying the product at 100 °C for 3 days, lustrous blue-black crystals of the *dye perchlorate* (Found: C, 67.4; H, 7.6; N, 7.6; Cl, 6.2. $C_{31}H_{42}ClN_3O_4$ requires C, 67.0; H, 7.6; N, 7.6; Cl, 6.4%).

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[20] K. D. Bartle, G. Hallas, and J. D. Hepworth, *Org. Magnetic Resonance*, 1975, **7**, 154.

[21] G. B. Jackman, V. Petrow, and O. Stephenson *J. Pharm. Pharmacol.*, 1960, **12**, 529.