

**753.** *Steric Effects in Di- and Tri-arylmethanes. Part II.\* Electronic Absorption Spectra of Derivatives of Michler's Hydrol Blue, Malachite Green, and Crystal Violet containing Hindered Dimethylamino-groups.*

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Steric inhibition of the mesomerism of all or any of the dimethylamino-groups in Crystal Violet (I; all R's = H) causes bathochromic shifts of the first frequency absorption band, whereas inhibition of the mesomerism of all of these groups in Malachite Green (II; all R's = H) and Michler's Hydrol Blue (III; all R's = H) causes small and moderate hypsochromic shifts, respectively. Inhibition of the mesomerism of one only of the dimethylamino-groups in Malachite Green or Michler's Hydrol Blue causes bathochromic shifts of the first frequency band.

ALTHOUGH spectral changes brought about by introducing *ortho*-substituents into dimethylaniline have been studied extensively,<sup>1-3</sup> a comparable study of the spectra of charge-resonance dyes containing hindered dimethylamino-groups has not hitherto been made. In fact, few dyes of this type have been described, probably because many of the normal methods of preparation fail when attempts are made to utilise *ortho*-derivatives of dimethylaniline in which mesomerism is sterically inhibited. Seel and Suchanek<sup>4</sup> claim that the first frequency absorption band of the 3,5-dimethyl derivative of Crystal Violet

\* Part I, *J.*, 1959, 3957.

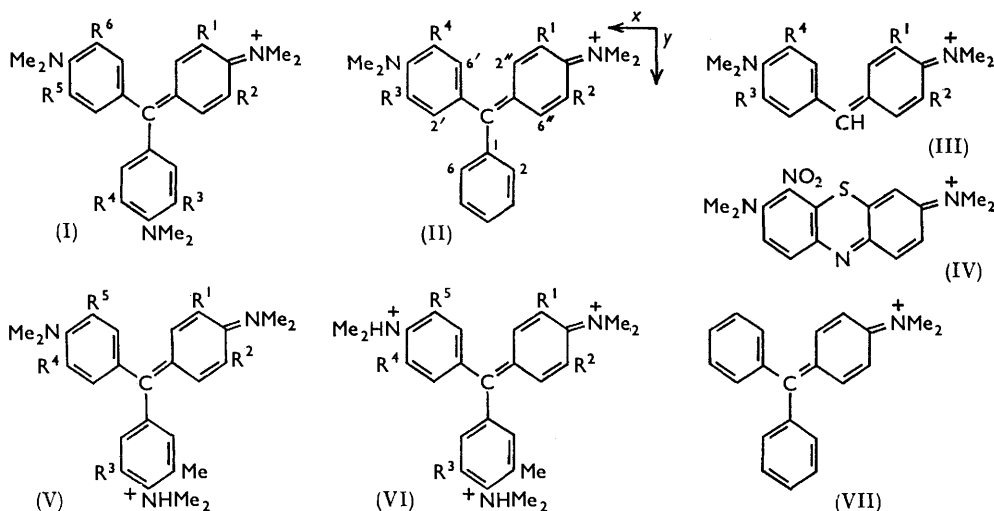
<sup>1</sup> Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838.

<sup>2</sup> Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714.

<sup>3</sup> Wepster, *Rec. Trav. chim.*, 1957, **76**, 357.

<sup>4</sup> Seel and Suchanek, *Chem. Ber.*, 1950, **83**, 438.

(I;  $R^1 = R^2 = R^3 = R^4 = H$ ,  $R^5 = R^6 = Me$ ) shows only a slight hypsochromic shift (about  $4 m\mu$  †) when compared with the first frequency band of the parent dye, although  $\epsilon_{max}$  is reduced from 111,000 to 61,000, and Kiprianov and Ushenko<sup>5</sup> claim a hypsochromic shift of approximately  $13 m\mu$  † for the first frequency band of the 3,3',3''-trimethyl



derivative (I;  $R^1 = R^3 = R^5 = Me$ ,  $R^2 = R^4 = R^6 = H$ ),  $\epsilon_{max}$  falling to 13,050 relative to a value of 70,000 quoted for Crystal Violet. Also, Chalkey<sup>6</sup> reports that the 3',3''-diacetoxymercuri-derivative of Malachite Green (II;  $R^1 = R^3 = AcOHg$ ,  $R^2 = R^4 = H$ ) absorbs more weakly than the parent dye.

Spectral changes caused by the steric effect of substituents (R) in the dyes (I, II, and III) are superimposed upon changes caused by the purely electronic effect of these substituents, and an early molecular-orbital treatment<sup>7</sup> led to the prediction that electron-withdrawing (+E) substituents in the *meta*-position should cause a bathochromic shift of the first frequency band. This prediction was supported by the increase of  $\lambda_{max}$  from 608.4 to 658  $m\mu$  observed on passing from Methylene Blue to Methylene Green (IV), but results given in the present paper make it probable that this bathochromic shift should be ascribed to enforced rotation of the hindered dimethylamino-group, and a later theoretical treatment<sup>8</sup> ascribes a hypsochromic effect to +E *meta*-substituents. The same theoretical treatments ascribe a bathochromic effect to -E *meta*-substituents and this effect is confirmed by the shift observed on passing from pararosaniline ( $\lambda_{max}$  546  $m\mu$ ) to its 3,5,3',5',3'',5''-hexamethyl derivative ( $\lambda_{max}$  558  $m\mu$ ),<sup>9</sup> and also by the shifts now observed on passing from the colour salt of *pp'*-diaminodiphenylmethanol ( $\lambda_{max}$  560.5  $m\mu$ ) to its 3,3'-dimethyl and 3,5,3',5'-tetramethyl derivative ( $\lambda_{max}$  563 and 571  $m\mu$ , respectively). These small spectral shifts cannot be confused with the shifts caused by enforced rotation of terminal dimethylamino-groups.

Hindered conjugation between terminal dimethylamino-groups and the aryl rings also reduces the stability of the univalent dye cation, which in acid solution is in equilibrium with protonated dye base or with protonated dye cations, so that in most cases the true value of the molecular extinction coefficient is unobtainable.

† Estimated from absorption curves.

<sup>5</sup> Kiprianov and Ushenko, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1950, 494.

<sup>6</sup> Chalkey, *J. Amer. Chem. Soc.*, 1941, **63**, 981.

<sup>7</sup> Dewar, *J.*, 1950, 2329.

<sup>8</sup> Dewar, "Recent Advances in the Chemistry of Colouring Matters," *Chemical Soc. Special Publ.*, No. 4, 1956, p. 79.

<sup>9</sup> Scanlan, *J. Amer. Chem. Soc.*, 1935, **57**, 889; 1936, **58**, 1427.

The 3,3'-dimethyl derivative of Michler's Hydrol in 98% acetic acid is partially converted into the dye cation (III;  $R^1 = R^3 = \text{Me}$ ,  $R^2 = R^4 = \text{H}$ ), the first frequency band of which shows a hypsochromic shift of 23.5  $m\mu$  relative to that of the parent dye (Table 1), but the corresponding 3,5,3',5'-tetramethyl derivative in 98% acetic acid or in ethanolic hydrogen chloride is colourless and in the latter solvent its ultraviolet absorption spectrum is closely similar to that of bis-(3,5-dimethyl-4-dimethylaminophenyl)methane hydrochloride in ethanol; formation of the dye cation is completely inhibited. On the other hand, the 3',5',3'',5''-tetramethyl derivative of Malachite Green (II; all R's = Me) is formed to a limited extent from the dye base in acetic acid, and the first frequency band shows a hypsochromic shift of 5  $m\mu$  (Table 1) when compared with the corresponding band of Malachite Green, a shift that is reduced to 4  $m\mu$  in the 3',3''-dimethyl derivative (II;  $R^1 = R^3 = \text{Me}$ ,  $R^2 = R^4 = \text{H}$ ). In both these derivatives of Malachite Green the second

TABLE 1. Absorption maxima of *m*-methyl derivatives of Malachite Green and Michler's Hydrol Blue in 98% acetic acid.

Substituent	Absorption maxima ( $m\mu$ ) and $10^{-4} \epsilon$ (in parentheses)		Substituent	Absorption maxima ( $m\mu$ ) and $10^{-4} \epsilon$ (in parentheses)	
<i>Malachite Green</i>			<i>Michler's Hydrol Blue</i>		
None .....	621 (10.4);	427.5 (2.0)	None .....	607.5 (14.75)	
3'-Methyl .....	627.5 (6.3);	436 (1.6)	3-Methyl .....	602.5 (0.06)	
3',5'-Dimethyl .....	630 (1.8);	452.5 (1.2)	3,3'-Dimethyl ...	584 (0.03)	
3',3''-Dimethyl .....	617 (1.1);	430 (0.4)			
3',5',3'',5''-Tetramethyl	616 (0.015);	446 (0.011)			

frequency absorption band—the *y*-band which corresponds<sup>10</sup> to polarisation along the *y*-axis of the molecule (II)—occurs at longer wavelength than the second frequency band of the parent dye. Also, the ratio  $\epsilon_{\max(\text{SFB})}/\epsilon_{\max(\text{FFB})}$  is increased relative to this ratio for Malachite Green, and these changes can be correlated with the increased electronic symmetry along the *y*-axis consequent upon displacement of charge from the terminal nitrogen atoms.

Thus, *m*-methyl groups adjacent to the dimethylamino-groups of Michler's Hydrol Blue and Malachite Green produce large and small *hypsochromic* shifts of the first frequency bands, respectively. In contrast, *m*-methyl groups in Crystal Violet produce *bathochromic* shifts of the first frequency band. The parent dye in 98% acetic acid gives rise to a single absorption band ( $\lambda_{\max}$  589  $m\mu$ ;  $\epsilon$  117,000) in the visible region,<sup>11</sup> but its 3-methyl derivative (I;  $R^1 = R^2 = R^4 = R^5 = R^6 = \text{H}$ ,  $R^3 = \text{Me}$ ) in pure acetic acid gives a first frequency band ( $\lambda_{\max}$  599.5  $m\mu$ ) which extends weakly into the region 400–450  $m\mu$  (Fig. 1), and the absorption in this region is probably caused by the bivalent cation (V; all R's = H). This absorption increases as the acidity is increased by addition of water to the acetic acid, and at the same time the first frequency band moves to a longer wavelength while its intensity moves through a minimum value (Fig. 1; Table 2). The absorption parameters obtained with the dye in 75% acetic acid are close to those of the dye in  $6 \times 10^{-5}\text{M}$ -hydrogen chloride in 98% acetic acid and probably correspond to those of the bivalent cation, the bathochromic and hypsochromic shifts of the first and the second frequency band, respectively, relative to the corresponding bands of the 3-methyl derivative of Malachite Green<sup>12</sup> ( $\lambda_{\max}$  619; 433  $m\mu$ ) being consistent with the electron-withdrawing effect of a protonated dimethylamino-group. The closest approach to the spectrum of the univalent dye cation was obtained with a  $10^{-5}\text{M}$ -solution of the dye base in  $2 \times 10^{-5}\text{M}$ -ethanolic hydrogen chloride (Fig. 2), absorption in the region 400–450  $m\mu$  then

<sup>10</sup> Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 2102.

<sup>11</sup> Barker, "Steric Effects in Conjugated Systems," ed. G. W. Gray, Butterworths, London, 1958, p. 35.

<sup>12</sup> Ref. 11, p. 39.

being a minimum. The lower absorption intensity obtained with  $10^{-5}$ M-hydrogen chloride (Table 2) indicates the presence of protonated forms of the ethyl ether of the dye base.

The spectra of the 3,5-dimethyl derivative of Crystal Violet (I;  $R^1 = R^2 = R^3 = R^4$ ,  $R^5 = R^6 = \text{Me}$ ) in aqueous acetic acid or ethanolic hydrogen chloride closely resemble the

TABLE 2. *Absorption maxima of  $10^{-5}$ M-solutions of m-methyl derivatives of Crystal Violet.*

(Crystal Violet:  $\lambda_{\text{max}}$ , 589 m $\mu$ ,  $\epsilon$  117,000.)

Solvent	Absorption max. (m $\mu$ ) and $10^{-4} \epsilon$ (in parentheses)	
	3-Methyl derivative	3,5-Dimethyl derivative
HOAc (100%)	599.5 (9.8)	608.5 (10.0)
HOAc (98%)	599.5 (9.5)	610.5 (9.6); 430 (0.8)
HOAc (95%)	601 (8.9); 430 (0.7)	—
HOAc (90%)	605 (7.5); 427.5 (1.0)	623.5 (8.5); 427 (1.3)
HOAc (80%)	632.5 (8.7); 425.5 (1.5)	633 (9.2); 426 (1.6)
HOAc (75%)	632.5 (9.1); 425.5 (1.6)	633 (9.2); 426 (1.6)
HOAc (70%)	632.5 (9.1); 425.5 (1.6)	—
$5 \times 10^{-5}$ M-HCl in HOAc (98%)	—	629 (9.1); 427 (1.6)
$6 \times 10^{-5}$ M-HCl in HOAc (98%)	629 (9.0); 426 (1.6)	—
$10^{-5}$ M-HCl in EtOH	600 (9.5)	610 (6.9)
$2 \times 10^{-5}$ M-HCl in EtOH	600 (10.3)	610 (10.2)
$3 \times 10^{-5}$ M-HCl in EtOH	600 (10.3)	—
	3,3'-Dimethyl derivative	3,5,3',5'-Tetramethyl derivative
HOAc (100%)	607.5 (7.7)	618 (5.3)
HOAc (98%)	607.5 (7.8)	618 (4.9)
HOAc (95%)	—	621 (1.4); 445 (0.6)
HOAc (90%)	616 (3.5); 435.5 (0.7)	621 (2.6); 455 (0.8)
HOAc (85%)	635 (2.4); 435 (0.7)	—
$4 \times 10^{-5}$ M-HCl in HOAc (98%)	—	621 (2.6); 450 (0.9)
$6 \times 10^{-5}$ M-HCl in HOAc (98%)	614 (4.4); 435 (0.9)	—
$7 \times 10^{-5}$ M-HCl in HOAc (98%)	635 (2.1); 435 (0.8)	—
$2 \times 10^{-5}$ M-HCl in EtOH	606.5 (8.9)	614 (4.8)
	3,3',3''-Trimethyl derivative	3,5,3',5',3'',5''-Hexamethyl derivative
HOAc (100%)	615 (1.7)	650 (0.3) <sup>a</sup>
HOAc (98%)	615 (1.3)	—
$3 \times 10^{-5}$ M-HCl in EtOH	615 (5.0)	—

<sup>a</sup>  $2 \times 10^{-4}$ M-solution.

corresponding spectra of the 3-methyl derivative, but in pure acetic acid  $\lambda_{\text{max}}$  is increased to 608.5 m $\mu$  and absorption in the region 400—450 m $\mu$  is a little more intense, and in 98% acetic acid a well-marked band ( $\lambda_{\text{max}}$  430 m $\mu$ ,  $\epsilon$  8000) is already present (Table 2), which suggests easier protonation of the more hindered dimethylamino-group of the 3,5-derivative. The spectrum of the bivalent cation (V;  $R^1 = R^2 = R^4 = R^5 = \text{H}$ ,  $R^3 = \text{Me}$ ) is almost identical with the spectrum of the bivalent ion from the 3-methyl derivative and is first obtained under slightly less acid conditions than is that of the latter ion (Table 2). Again, a close approach to the spectrum of the univalent cation is obtained with the dye in ethanolic hydrogen chloride (Fig. 2), and it is clear that the hindered dimethylamino-group participates effectively in the charge resonance and that the observed bathochromic shift is not caused by the presence of bivalent ion. This result, which was obtained by utilising the pure dye base, differs from that recorded by Seel and Suchanek<sup>4</sup> who used the dye perchlorate and, as perchlorates are not suitable for purification, it is assumed that the latter compound was impure.

The dye cations of the 3-methyl and the 3,5-dimethyl derivative of Crystal Violet are stabilised by resonance involving two unhindered dimethylamino-groups, so that conversion of the dye base into dye should be essentially complete; this is not true of the other derivatives of Crystal Violet discussed in this paper.

The 3,3'-dimethyl derivative of Crystal Violet (I;  $R^1 = R^2 = R^4 = R^6 = H$ ,  $R^3 = R^5 = Me$ ) in pure acetic acid also shows an intense first frequency band ( $\lambda_{max}$  607.5  $\mu$ ) with an incipient band in the region 400–450  $\mu$  (Fig. 3). In progressively more dilute acetic acid, this incipient band becomes more clearly defined and the first frequency band moves to a longer wavelength and becomes less intense until in 85% acetic acid (Fig. 3), or

FIG. 1. Absorption spectra of the 3-methyl derivative of Crystal Violet in acetic acid containing (1) 0%, (2) 10%, (3) 20% of water.

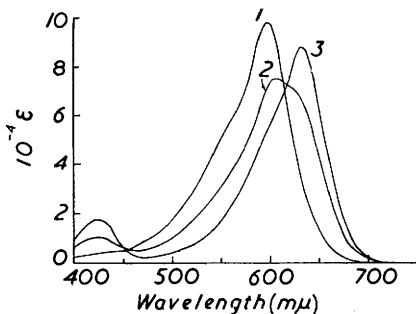


FIG. 2. Absorption spectra of the (1) 3-methyl, (2) 3,5-dimethyl, (3) 3,3'-dimethyl, (4) 3,5,3',5'-tetramethyl, (5) 3,3',3''-trimethyl derivative of Crystal Violet in ethanolic hydrogen chloride.

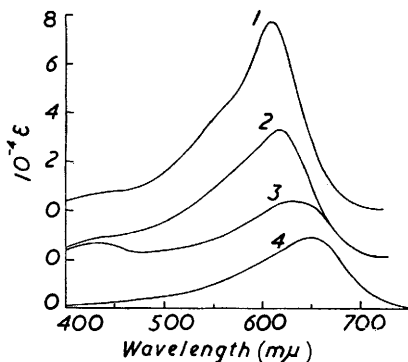
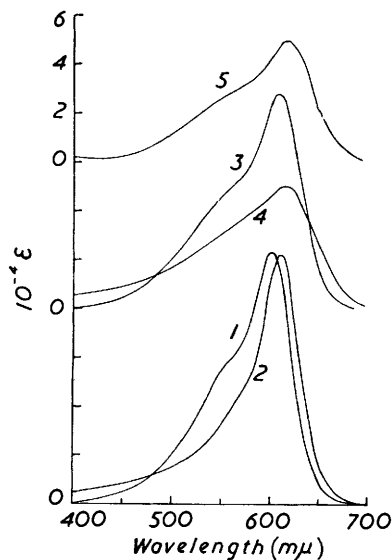


FIG. 3. Absorption spectra of (1),<sup>a</sup> (3)<sup>b</sup> the 3,3'-dimethyl, (2)<sup>a</sup> the 3,5,3',5'-tetramethyl, and (4)<sup>a,c</sup> the 3,5,3',5',3'',5''-hexamethyl derivative of Crystal Violet and (a) 100%, (b) 85% acetic acid; (c)  $10^{-2}\epsilon$  plotted.

in  $7 \times 10^{-5}M$ -hydrogen chloride in 98% acetic acid, it is probably the first frequency band of the bivalent cation (V;  $R^1 = R^2 = R^3 = R^5 = H$ ,  $R^4 = Me$ ). Under these conditions, however, the low value (3.4) of the ratio  $\epsilon_{max.(FPB)}/\epsilon_{max.(SFB)}$  suggests that the second frequency band consists of the  $\gamma$ -band of the bivalent cation superimposed on the first frequency band of the trivalent cation (VI;  $R^1 = R^2 = R^3 = R^5 = H$ ,  $R^4 = Me$ ); the first frequency band of the analogous *NN*-dimethylfuchsoniminium ion<sup>13</sup> (VII) in acetic acid has  $\lambda_{max}$  465.5  $\mu$  ( $\epsilon$  33,000). The absence of an incipient band at 400–450  $\mu$  in

<sup>13</sup> Branch and Walba, *J. Amer. Chem. Soc.*, 1951, **73**, 3341.

the first frequency band of the 3,3'-dimethyl derivative of Crystal Violet in ethanolic hydrogen chloride (Fig. 2) shows that the observed bathochromic shift is characteristic of the univalent cation.

The spectra of the 3,5,3',5'-tetramethyl derivative of Crystal Violet (I;  $R^1 = R^2 = H$ ,  $R^3 = R^4 = R^5 = R^6 = Me$ ) in solvents of different acidity are similar to those of the 3,3'-dimethyl derivative, but the highly hindered nature of two of the nitrogen atoms in the tetramethyl derivative reduces further the stability of the bivalent cation (V;  $R^1 = R^2 = H$ ,  $R^3 = R^4 = R^5 = Me$ ) relative to that of the tervalent cation (VI;  $R^1 = R^2 = H$ ,  $R^3 = R^4 = R^5 = Me$ ), and the first frequency band shows a bathochromic shift of only 3  $m\mu$  when the solvent is changed from pure acetic acid to 90% acetic acid or to  $4 \times 10^{-5}M$ -hydrogen chloride in 98% acetic acid. An unequivocal interpretation of the spectra is not possible, but it is probable that the spectrum of the dye in ethanolic hydrogen chloride (Fig. 2) is produced mainly by the univalent ion together with some tervalent ion, and that the effect of the bivalent ion on the position of the first frequency band is unimportant. Attempts to isolate the spectrum of the tervalent ion by using solutions of higher acidity were frustrated by the rapidity with which their colour faded.

The first frequency band of the 3,3',3''-trimethyl derivative of Crystal Violet (I;  $R^1 = R^3 = R^5 = H$ ,  $R^2 = R^4 = R^6 = Me$ ) in ethanolic hydrogen chloride also occurs at longer wavelength than the corresponding band of the parent dye and shows little sign of a second frequency band in the region 400—450  $m\mu$  (Fig. 2); this region remains free from a second band when the solvent is changed to 100% or 98% acetic acid, although the absorption intensity of the main band is reduced (Table 2). Presumably the absence of unhindered dimethylamino-groups reduces the stability of the bivalent cation (V;  $R^1 = R^3 = R^4 = H$ ,  $R^2 = R^5 = Me$ ) and the tervalent cation (VI;  $R^1 = R^3 = R^4 = H$ ,  $R^2 = R^5 = Me$ ) so that increased acidity favours the formation of the triprotonated cation (VIII); in concentrated sulphuric acid, Crystal Violet forms an analogous ion (IX).<sup>14</sup> The use of hydrogen chloride in 98% acetic acid, or of acetic acid containing more than 2% of water, as solvent gave solutions the colour of which faded rapidly.

The spectrum of the 3,5,3',5',3'',5''-hexamethyl derivative of Crystal Violet (I; all R's = Me) could only be observed in pure acetic acid (Fig. 3): addition of water or hydrogen chloride to the solution produced rapid fading of the colour, and fading also occurred in ethanolic hydrogen chloride. The first frequency band ( $\lambda_{max}$ , 650  $m\mu$ ) must, however, be attributed to the univalent cation, because of the absence of a second frequency band in the region 400—450  $m\mu$ .

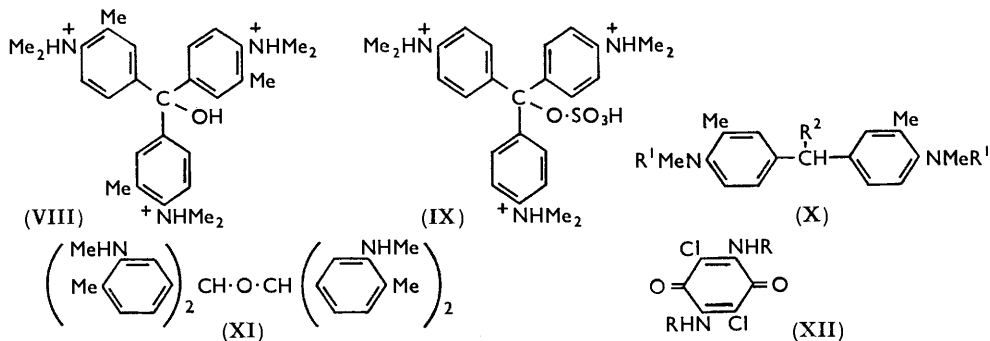
It is thus established that, whereas steric inhibition of the mesomerism of both of the dimethylamino-groups of Michler's Hydrol Blue or Malachite Green results in a hypsochromic shift of the first frequency band, inhibition of the mesomerism of any of the dimethylamino-groups of Crystal Violet produces a bathochromic shift. These different responses to crowding substituents have been discussed qualitatively in terms of molecular-orbital theory by Dewar.<sup>15</sup>

Steric hindrance of one only of the dimethylamino-groups of Michler's Hydrol Blue or Malachite Green produces a different spectral response from that produced when both of these groups are hindered. Thus, the first frequency bands of the 3'-methyl and the 3',5'-dimethyl derivative of Malachite Green (II;  $R^1 = Me$ ,  $R^2 = R^3 = R^4 = H$ ; and  $R^1 = R^2 = Me$ ,  $R^3 = R^4 = H$ , respectively) show *bathochromic* shifts of 6.5  $m\mu$  and 9  $m\mu$ , respectively, when compared with the first frequency band of the parent dye, whereas the corresponding bands of the 3',3''-dimethyl and the 3',5',3'',5''-tetramethyl derivative show *hypsochromic* shifts of 4  $m\mu$  and 5  $m\mu$ , respectively (Table 1). Electronically the last two dyes are symmetrical whereas the 3'-methyl and 3',5'-dimethyl compounds are unsymmetrical, charge tending to be localised on the unhindered dimethylamino-group, and it may

<sup>14</sup> Branch and Walba, *J. Amer. Chem. Soc.*, 1954, **76**, 1564.

<sup>15</sup> Dewar, "Steric Effects in Conjugated Systems," ed. G. W. Gray, Butterworths, London, 1958, p. 60.

be recalled that crowding substituents which cause the nuclei of heterocyclic cyanines to depart from coplanarity produce spectral shifts which vary with the degree of electronic symmetry of the cyanine. Considerable departure from electronic symmetry in a heterocyclic cyanine produces a hypsochromic deviation,<sup>16</sup> whereas these electronically unsymmetrical derivatives of Malachite Green are novel in that they show a significant bathochromic deviation. Similarly, the hypsochromic shift of 23.5  $m\mu$  produced by the two



methyl groups of the 3,3'-dimethyl derivative of Michler's Hydrol Blue is reduced to a hypsochromic shift of 5  $m\mu$  in the 3-methyl derivative which again shows a bathochromic deviation. It is probable that the bathochromic shift<sup>7</sup> caused by the nitro-group in the dye (IV) is another example of this effect.

Steric hindrance of a single dimethylamino-group in Malachite Green also causes a bathochromic shift of the second frequency band and an increase in the ratio  $\epsilon_{\max.(\text{SFB})}/\epsilon_{\max.(\text{FFB})}$ , but the second frequency band may well be composed of the  $\gamma$ -band of the univalent cation superimposed upon the first frequency band of the bivalent cation formed by protonation of the hindered dimethylamino-group.

*Preparations.*—The hindered nature of the dimethylamino-groups in these dyes usually prevents the formation of the dye from the leuco-compounds by oxidation, so that symmetrical derivatives of Michler's Hydrol were prepared by reduction of the corresponding ketones, and the derivatives of Malachite Green and Crystal Violet were prepared by the interaction of an aryl-lithium compound with a ketone or ester. Thus, 4,4'-bisdimethylamino-3,3'-dimethyldiphenylmethane (X;  $R^1 = \text{Me}$ ,  $R^2 = \text{H}$ ) is not oxidised satisfactorily to the Hydrol by lead dioxide in acid solution, neither is it oxidised to the corresponding ketone by means of chloranil in boiling ethanol. This ketone was obtained as a gum by methylation of 4,4'-diamino-3,3'-dimethylbenzophenone with trimethyl phosphate, the diacetyl derivative of the latter ketone being prepared in 79% yield by oxidation of 4,4'-diacetamido-3,3'-dimethyldiphenylmethane with chromic oxide at room temperature;<sup>17</sup> oxidation in boiling acetic acid gave none of the required product. The methylated ketone gave a crystalline picrate, m. p. 185—186°, which was identical with the picrate of the ketone obtained by slow carbonylation of 4-dimethylamino-3-methylphenyl-lithium, but regeneration of the ketone from the picrate did not give crystalline material. Reduction of the ketone with sodium amalgam gave the 3,3'-dimethyl derivative of Michler's Hydrol as a gum which did not give crystalline derivatives with perchloric acid, picric acid, or 2,4,7-trinitrofluorenone, whereas Michler's Hydrol forms a very stable complex with the last reagent. This lack of crystallinity was also encountered in all the *m*-methyl derivatives of Malachite Green and is probably to be attributed to their non-planar molecular conformations.

<sup>16</sup> Brooker and his co-workers, *J. Amer. Chem. Soc.*, 1945, **67**, 1869, 1875, 1889.

<sup>17</sup> Vongerichten and Bock, *Z. Farben- und Textilchemie*, 1903, **11**, 250.

Rassow and Reuter<sup>18</sup> claim to have obtained 4,4'-bisdimethylamino-3,3'-dimethylbenzophenone as crystals, m. p. 85°, by methylation of 4,4'-dimethylamino-3,3'-dimethylbenzophenone, m. p. 81°. However, conversion of the unhindered methylamino-group into the hindered dimethylamino-group should lower the melting point and it is likely that Rassow and Reuter were dealing with purified starting material, in which case the hydroxy-compound, m. p. 76°, which these authors obtained by reduction of their ketone should have been identical with the partially methylated hydroxy-compound (X; R<sup>1</sup> = H, R<sup>2</sup> = OH), m. p. 160°, described by Gnehm and Wright.<sup>19</sup> The last melting point is unexpectedly high (cf. Michler's Hydrol, m. p. 103°, and its 3,5,3',5'-tetramethyl derivative, m. p. 106°) and may well be that of the ether (XI).

The crystalline 3,5,3',5'-tetramethyl derivative of Michler's Hydrol was obtained by reduction of the ketone obtained by methylation of 4,4'-diamino-3,5,3',5'-tetramethylbenzophenone. The latter ketone was readily obtained by oxidising the corresponding derivative of diphenylmethane with chloranil, the normal interaction of chloranil with a primary aromatic amine to give a diarylamino-dichlorobenzoquinone (XII) being prevented by steric hindrance of the amino-groups. The crystalline 3-methyl derivative of Michler's Hydrol was obtained by reduction of the ketone obtained by the interaction of 4-dimethylamino-3-methylphenyl-lithium with *p*-dimethylaminobenzonitrile followed by hydrolysis of the product.

The 3'-methyl, 3,3''-dimethyl, and 3',5',3'',5''-tetramethyl derivatives of Malachite Green base were obtained by interaction of the corresponding derivatives of Michler's ketone with phenyl-lithium. The 3',5'-dimethyl derivative of Malachite Green base was obtained from *p*-dimethylaminobenzophenone and 4-dimethylamino-3,5-dimethylphenyl-lithium. None of these compounds crystallised, but the spectra of their colour salts showed no sign of coloured impurities.

The 3-methyl and the 3,5-dimethyl derivative of Crystal Violet base were obtained by the interaction of Michler's ketone with 4-dimethylamino-3-methyl- and 2-dimethylamino-3,5-dimethyl-phenyl-lithium, respectively. In view of the difference between the spectrum of the 3,5-dimethyl derivative of Crystal Violet obtained *via* the aryl-lithium compound and the spectrum of the perchlorate of the dye obtained by Seel and Suchanek,<sup>4</sup> the 3,5-dimethyl derivative was also prepared by Seel and Suchanek's method—4-amino-4',4''-bisdimethylamino-3,5-dimethyltriphenylmethane (from Michler's Hydrol and *vic-m*-xylidine) was methylated and the product was oxidised to the required dye with ethanolic chloranil. The dye was purified as the methyl ether of the dye base and then gave a spectrum identical with that of the dye obtained *via* the aryl-lithium compound. Methylation of the leuco-compound by means of paraformaldehyde and formic acid advantageously replaced methylation with dimethyl sulphate which gave a quaternary ammonium salt requiring decomposition with sodium ethoxide.

The 3,3'-dimethyl and the 3,3',3''-trimethyl derivative of Crystal Violet were prepared from 4-dimethylamino-3-methylphenyl-lithium with ethyl *p*-dimethylaminobenzoate and ethyl chloroformate, respectively, and the 3,5,3',5'-tetramethyl and the 3,5,3',5',3'',5''-hexamethyl derivative were prepared from 4,4'-bisdimethylamino-3,5,3',5'-tetramethylbenzophenone with *p*-dimethylaminophenyl-lithium and 4-dimethylamino-3,5-dimethylphenyl-lithium, respectively. Preparation of the trimethyl derivative from chloropicrin and *NN*-dimethyl-*o*-toluidine<sup>5</sup> could not be repeated. All the dye bases of the *m*-methyl derivatives of Crystal Violet were crystalline.

#### EXPERIMENTAL

**4,4'-Bisdimethylamino-3-methylbenzophenone.**—An ethereal solution of 4-dimethylamino-3-methylphenyl-lithium, prepared from 5-bromo-2-dimethylaminotoluene (14 g.) in an atmosphere

<sup>18</sup> Rassow and Reuter, *J. prakt. Chem.*, 1912, **85**, 503.

<sup>19</sup> Gnehm and Wright, *Ber.*, 1902, **35**, 913.



of nitrogen, was filtered into *p*-dimethylaminobenzonitrile (9.5 g.) in ether (50 c.c.), and the mixture was stirred and heated under reflux for 1 hr. The cooled solution was extracted with 5*N*-hydrochloric acid (75 c.c.), and the aqueous extract was boiled for 7 hr., cooled, basified with sodium hydroxide, and then steam-distilled. The tarry residue was eluted with benzene (300 c.c.) from a column of activated alumina (200 × 20 cm.), thereby yielding a yellow gum which, crystallised twice from ethanol, gave pale-yellow 4,4'-bisdimethylamino-3-methylbenzophenone (12.2 g.), m. p. 76—77° (Found: C, 76.9; N, 7.8; N, 9.8. C<sub>18</sub>H<sub>22</sub>ON<sub>2</sub> requires C, 76.6; H, 7.9; N, 9.9%).

4,4'-Bisdimethylamino-3-methyl-diphenylmethanol.—A mixture of 4,4'-bisdimethylamino-3-methylbenzophenone (1.4 g.), 3% sodium amalgam (8 g.), and ethanol (50 c.c.) was stirred vigorously and heated under reflux for 2 hr. The mixture was poured into water (200 c.c.), and the precipitated product was twice crystallised from light petroleum (b. p. 60—80°) to give colourless 4,4'-bisdimethylamino-3-methyl-diphenylmethanol (1.2 g.), m. p. 87—88° (Found: C, 75.8; H, 8.3; N, 10.0. C<sub>18</sub>H<sub>24</sub>ON<sub>2</sub> requires C, 76.0; H, 8.5; N, 9.9%). This method of reduction was used as a standard procedure in the preparation of similar derivatives of diphenylmethanol.

4,4'-Diamino-3,3'-dimethyl-diphenylmethanol.—4,4'-Diamino-3,3'-dimethyldiphenylmethane (45 g.) was heated with acetic acid (48 c.c.) and acetic anhydride (50 c.c.); the product was isolated by addition of water (500 c.c.) and crystallised from ethanol, giving 4,4'-diacetamido-3,3'-dimethyldiphenylmethane (48 g.), m. p. 222—223° (Vongerichten and Bock<sup>17</sup> give m. p. 202°) (Found: C, 73.3; H, 7.0; N, 9.1. Calc. for C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>N<sub>2</sub>: C, 73.5; H, 7.1; N, 9.0%). The diacetamido-compound (56.8 g.) in acetic acid (1200 c.c.) was stirred for 84 hr. at room temperature with chromic oxide (24.8 g.) in acetic acid (200 c.c.) containing a little water, and the product was isolated by pouring the mixture into water (15 l.) and crystallising the precipitate from ethanol, yielding 4,4'-diacetamido-3,3'-dimethylbenzophenone (47 g.), m. p. 263—264° (Vongerichten *et al.*<sup>17</sup> give m. p. 250—251°) (Found: C, 70.6; H, 6.0; N, 8.6. Calc. for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>N<sub>2</sub>: C, 70.6; H, 6.2; N, 8.6%). The ketone was heated under reflux with acetic acid (400 c.c.) and 35% hydrochloric acid (400 c.c.) for 1 hr.; the amine hydrochloride separated from the cooled mixture and was removed, washed with a little concentrated hydrochloric acid, basified with aqueous ammonia, and the free base crystallised from ethanol, giving pale yellow needles of 4,4'-diamino-3,3'-dimethylbenzophenone (18 g.), m. p. 215—216° (lit.,<sup>17</sup> m. p. 210°). Reduction of this ketone by the standard procedure gave 4,4'-diamino-3,3'-dimethyldiphenylmethanol as colourless crystals, m. p. 138—140° (lit.,<sup>17</sup> m. p. 135°).

4,4'-Bisdimethylamino-3,3'-dimethyl-diphenylmethanol.—A mixture of 4,4'-diamino-3,3'-dimethylbenzophenone (6.0 g.) and trimethyl phosphate (4.0 c.c.) was heated at 180° for 4 hr., then heated under reflux for 1.5 hr. with water (30 c.c.) containing sodium hydroxide (4.3 g.). The organic layer was removed and heated under reflux with acetic anhydride (12 c.c.) for 2 hr., and then the mixture was poured into water and basified. The product was removed in ether and sublimed at 10<sup>-3</sup> mm., being thus obtained as a pale-yellow glass (Rassow and Reuter<sup>18</sup> give m. p. 85.5°). The *picrate*, m. p. 185—186°, formed yellow crystals from ethanol (Found: C, 49.5; H, 4.2; N, 14.5. C<sub>31</sub>H<sub>30</sub>O<sub>15</sub>N<sub>8</sub> requires C, 49.3; H, 4.0; N, 14.8%). Reduction of this ketone by the standard procedure gave 4,4'-bisdimethylamino-3,3'-dimethyldiphenylmethanol as a colourless, viscous liquid (Rassow and Reuter give m. p. 76°).

4,4'-Diamino-3,5,3',5'-tetramethyl-diphenylmethanol.—4,4'-Diamino-3,5,3',5'-tetramethyldiphenylmethane (20.0 g.) and chloranil (40.0 g.) in ethanol (800 c.c.) were refluxed for 1 hr., then poured into 2*N*-hydrochloric acid (2 l.), and insoluble material was removed. The resultant solution was basified with ammonia; the product crystallised from ethanol giving 4,4'-diamino-3,5,3',5'-tetramethylbenzophenone, m. p. 240—242° (Found: C, 75.8; H, 7.3; N, 10.4. C<sub>17</sub>H<sub>20</sub>ON<sub>2</sub> requires C, 76.1; H, 7.5; N, 10.4%). This was reduced under standard conditions; the mixture was diluted with water and kept at 0° for 16 hr., colourless crystals of 4,4'-diamino-3,5,3',5'-tetramethyldiphenylmethanol, m. p. 163—164°, separating (Found: C, 76.0; H, 7.9; N, 10.1. C<sub>17</sub>H<sub>22</sub>ON<sub>2</sub> requires C, 75.6; H, 8.1; N, 10.4%). Recrystallisation of this compound from ethanol or benzene lowered the m. p.

4,4'-Bisdimethylamino-3,5,3',5'-tetramethyl-diphenylmethanol.—Trimethyl phosphate (3.6 g.) and 4,4'-diamino-3,5,3',5'-tetramethylbenzophenone (5.0 g.) were heated at 180° for 3.5 hr., then refluxed for 1.5 hr. with water (25 c.c.) containing sodium hydroxide (3.5 g.). The solid product was collected and heated under reflux with acetic anhydride (10 c.c.) for 2 hr., and then the mixture was stirred with water for 4 hr. The resultant solid was sublimed at 145°

(bath)/10<sup>-3</sup> mm. and the sublimate was twice crystallised from ethanol, yielding colourless 4,4'-bisdimethylamino-3,5,3',5'-tetramethylbenzophenone (1.5 g.), m. p. 151—151.5° (Found: C, 77.3; H, 8.5; N, 8.7. C<sub>21</sub>H<sub>28</sub>ON<sub>2</sub> requires C, 77.8; H, 8.6; N, 8.6%). Reduction of the ketone under standard conditions gave 4,4'-bisdimethylamino-3,5,3',5'-tetramethyltriphenylmethanol as colourless needles, m. p. 105° (from aqueous ethanol) (Found: C, 77.0; H, 9.0; N, 8.7. C<sub>21</sub>H<sub>30</sub>ON<sub>2</sub> requires C, 77.3; H, 9.2; N, 8.6%).

4,4',4''-Trisdimethylamino-3-methyltriphenylmethanol.—An ethereal solution of 4-dimethylamino-3-methylphenyl-lithium from 5-bromo-2-dimethylaminotoluene (2.15 g.) was added under nitrogen to a stirred suspension of Michler's ketone (1.34 g.) in ether (50 c.c.) and after 30 min. this mixture was poured into water. The ether was removed from the organic phase and the residual gum was caused to crystallise by trituration with light petroleum (b. p. 40—60°), yielding the dye base (0.5 g.), m. p. 141.5—142.5° after two recrystallisations from 4 : 1 light petroleum (b. p. 60—80°)—ethyl acetate (Found: C, 77.5; H, 8.0; N, 10.4. C<sub>26</sub>H<sub>33</sub>ON<sub>3</sub> requires C, 77.4; H, 8.2; N, 10.4%). Subsequent reactions involving aryl-lithium compounds were carried out in a similar manner.

4-Bromo-2,6,N,N-tetramethylaniline.—A stirred mixture of the primary bromo-amine (20 g.), paraformaldehyde (9 g.), and 90% formic acid (15.4 g.) was heated under reflux for 30 min., and the product was removed from the basified mixture in steam. Any partially methylated amine was removed as the acid-insoluble acetyl derivative, leaving the tertiary amine (16.4 g.), m. p. 32—33° (from ethanol) (Gillois and Rumpf<sup>20</sup> give b. p. 125°/14 mm.) (Found: C, 52.6; H, 6.3; N, 5.9; Br, 34.3. C<sub>10</sub>H<sub>14</sub>NBr requires C, 52.6; H, 6.2; N, 6.1; Br, 35.0%).

4,4',4''-Trisdimethylamino-3,5-dimethyltriphenylmethanol.—An ethereal solution of 2-dimethylamino-3,5-dimethylphenyl-lithium, prepared from the preceding amine (4.7 g.), with Michler's ketone (2.76 g.) gave the dye base (3.1 g.), m. p. 162.5—163.5° (from ethanol) (Found: C, 77.9; H, 8.2; N, 10.1. C<sub>27</sub>H<sub>35</sub>ON<sub>3</sub> requires C, 77.6; H, 8.4; N, 10.1%).

Methyl 4,4',4''-Trisdimethylamino-3,5-dimethyltriphenylmethyl Ether.—4-Amino-4',4''-bisdimethylamino-3,5-dimethyltriphenylmethane<sup>4</sup> (11.7 g.), 90% formic acid (160 c.c.) and 40% aqueous formaldehyde (10.6 c.c.) were heated under reflux for 2 hr. The mixture was basified with aqueous sodium hydroxide, and the crude base was removed, dried, and eluted in benzene from a column of activated alumina (20 × 3 cm.). Only those fractions which gave a coloured solution with lead dioxide in acetic acid were retained. Removal of the benzene gave a gum which was crystallised from 3 : 1 ethanol-benzene, giving 4,4',4''-trisdimethylamino-3,5-dimethyltriphenylmethane (2.6 g.), m. p. 136—137° (Seel and Suchanek<sup>4</sup> give m. p. 136.5°) (Found: C, 80.9; H, 8.8; N, 10.3. Calc. for C<sub>27</sub>H<sub>35</sub>N<sub>3</sub>: C, 80.8; H, 8.8; N, 10.5%). A mixture of this base (2.0 g.), chloranil (1.4 g.), and methanol (50 c.c.) was heated under reflux for 1 hr., then cooled, insoluble material was removed, a portion of the methanol (25 c.c.) was removed by distillation, and the solution was poured into methanol (20 c.c.) containing sodium methoxide (1.0 g.). The precipitate ether, recrystallised twice from 3 : 1 methanol-benzene, had m. p. 155—155.5° (1.4 g.) (Found: C, 77.7; H, 8.7; N, 9.9. C<sub>28</sub>H<sub>37</sub>ON<sub>3</sub> requires C, 77.9; H, 8.6; N, 9.7%).

4,4',4''-Trisdimethylamino-3,3'-dimethyltriphenylmethanol.—The gum obtained by the interaction of 4-dimethylamino-3-methylphenyl-lithium with ethyl *p*-dimethylaminobenzoate was crystallised thrice from 2 : 1 light petroleum (b. p. 40—60°)—ethyl acetate, giving the dye base (1.3 g.), m. p. 120—121° (Found: C, 77.7; H, 8.3; N, 10.0. C<sub>27</sub>H<sub>35</sub>ON<sub>3</sub> requires C, 77.6; H, 8.4; N, 10.1%).

Tris-(4-dimethylamino-3-methylphenyl)methanol.—An ethereal solution of 4-dimethylamino-3-methylphenyl-lithium, prepared from 5-bromo-2-dimethylaminotoluene (6.42 g.), was allowed to react with ethyl chloroformate (0.55 g.) for 30 min. at room temperature and the mixture was poured into water. The residue from the ether layer was steam-distilled to remove *NN*-dimethyl-*o*-toluidine and was then eluted with light petroleum (b. p. 60—80°) from a calcium carbonate column (30 × 1.5 cm.), only those fractions which gave a colour with acetic acid being retained. The eluted material crystallised from 3 : 1 light petroleum (b. p. 40—60°)—ethyl acetate, giving the dye base (0.3 g.), m. p. 98.5—99.5° (Found: C, 77.9; H, 8.6; N, 9.7. C<sub>28</sub>H<sub>37</sub>ON<sub>3</sub> requires C, 77.9; H, 8.6; N, 9.7%).

4,4',4''-Trisdimethylamino-3,5,3',5'-tetramethyltriphenylmethanol.—*p*-Dimethylaminophenyl-lithium in ether, prepared from *p*-bromo-*NN*-dimethylaniline (1.85 g.) with 4,4'-bisdimethylamino-3,5,3',5'-tetramethylbenzophenone (1.5 g.) gave the dye base (0.8 g.), m. p. 184—185°

<sup>20</sup> Gillois and Rumpf, *Bull. Soc. chim. France*, 1954, 112.

(from ethanol) (Found: C, 78.0; H, 8.6; N, 9.5.  $C_{29}H_{39}ON_3$  requires C, 78.1; H, 8.8; N, 9.4%).

*Tris-(4-dimethylamino-3,5-dimethylphenyl)methanol*.—4-Dimethylamino-3,5-dimethylphenyllithium, from the bromoamine (2.12 g.), with 4,4'-bisdimethylamino-3,5,3',5'-tetramethylbenzophenone gave the *dye base*, m. p. 179—180.5° (from ethanol) (Found: C, 78.3; H, 9.1; N, 8.9.  $C_{31}H_{43}ON_3$  requires C, 78.6; H, 9.1; N, 8.9%).

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