# 299. *Steric Effects in Di- and Tri-arylmethanes. Part V.*[1] *Electronic Absorption Spectra of Derivatives of Malachite Green containing* ortho-*Substituents in the Dimethylaminophenyl Groups.*

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Spectral changes caused by the crowding effect of substituents in the 2′- and 2′,2″-positions of Malachite Green are described and discussed. The increase in intensity of the $x$-band which was previously reported to occur when substituents are introduced into the 2-position also occurs when substituents are already in the 2′- and 2′,2″-positions.

In Part III[2] of this series it was shown that *ortho*-substituents in the phenyl group of Malachite Green (I) produce unexpected increases in the intensity of the first absorption band ($x$-band) which also shows small bathochromic shifts. At the same time, hypsochromic shifts and reductions in intensity are produced in the second band ($y$-band). These effects are the results of conformational changes brought about by the *ortho*-substituents, but a precise interpretation cannot be put forward at present because of the large number of such changes possible in an unsymmetrical trinuclear dye of this type. The spectra of derivatives of Malachite Green containing *ortho*-substituents in the dimethylaminophenyl groups have therefore been examined.

A 2′-methyl group in Malachite Green produces a bathochromic shift and reduction in intensity of the $x$-band (Table 1), and this effect is consistent with rotation of one or both of the dimethylphenyl groups about the central bond(s), the purely electronic effect of the methyl group being hypsochromic. However, such rotation should result in increased departure from uniplanarity along the unsymmetrical $y$-axis of the molecule and thus lead to a hypsochromic shift and reduction in intensity of the $y$-band, whereas the observed shift is bathochromic and the intensity remains constant (Table 1). The introduction of a second methyl group into the 2″-position exaggerates these spectral changes

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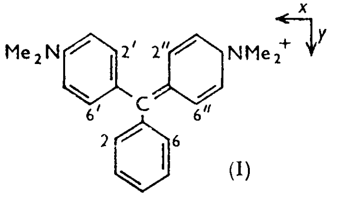
[1] Part IV, *J.*, 1961, 1395.

[2] Part III, *J.*, 1961, 1285.

and causes a slight reduction in $\varepsilon_{\max.(y)}$ from 20,000 to 18,000. Tentatively, these bathochromic shifts of the $y$-band may be attributed to the greater electronic symmetry along the $y$-axis which results from displacement of charge on to the phenyl group by rotation of the dimethylaminophenyl groups about the central bonds. These spectral shifts are thus analogous to the bathochromic shifts of the $y$-band brought about by methyl groups in the 3′,3″- and 3′,5′,3″,5″-positions in Malachite Green.[3]



(I)

$(p\text{-Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{NH})_2\text{CO}$

(II)

Substituents in the phenyl group of the hindered 2′-methyl and 2′,2″-dimethyl derivative of Malachite Green produce spectral changes which are very similar to the changes which the same substituents produce in the parent dye (Table 1). Thus the values of $\Delta\lambda_{\max.(x)}$ and $\Delta\lambda_{\max.(y)}$ agree closely, and the values of $\varepsilon_{\max.(x)}$ and $\varepsilon_{\max.(y)}$ show the same pattern. In particular, the constancy of $\varepsilon_{\max.(x)}$ (104,000—106,000) in the parent dye and its 4-methyl and 4-methoxy-derivative is repeated with the analogous 2′-methyl and 2′,2″-dimethyl derivative ($\varepsilon_{\max.(x)}$ 75,000 and 67,000—68,000, respectively), thereby confirming the previous deduction that these dyes exist wholly as the univalent, quinonoid cation in 98% acetic acid. Further, the unexpected increase in $\varepsilon_{\max.(x)}$ shown by the 2-methyl derivative is repeated in the 2,2′-dimethyl and 2,2′,2″-trimethyl derivative. The small bathochromic shift of the $x$-band shown by the first of these dyes contrasts with the small hypsochromic shifts shown by the $x$-bands of the other two, but the relevant comparison is between the corresponding 2- and 4-methyl derivatives in which case the spectral shifts are uniformly bathochromic to the extent of 6, 4, and 4 mμ, respectively.

*Preparations.*—The 2′,2″-dimethyl derivative of leuco-Malachite Green is readily prepared from *NN*-dimethyl-*m*-toluidine and benzaldehyde, but the unsymmetrical 2′-methyl derivative requires the use of Yoshino's method[4] whereby *NN*-dimethylaniline is caused to react with benzaldehyde and urea to give the substituted urea (II) which with *NN*-dimethyl-*m*-toluidine gives the required leuco-compound. The use of substituted benzaldehydes in both of these reactions is satisfactory, but the 2′,2″-dimethyl derivatives could not be oxidised to the dye with lead dioxide, chloranil, or lead tetra-acetate, despite

TABLE 1. *Spectral data for derivatives of Malachite Green in 98% acetic acid.*

| Subst. | $\lambda_{\max.(x)}$ (mμ) | $\Delta\lambda_{\max.(x)}$ (mμ) | $10^{-4}\varepsilon_x$ | $\lambda_{\max.(y)}$ (mμ) | $\Delta\lambda_{\max.(y)}$ (mμ) | $10^{-4}\varepsilon_y$ |
|---|---|---|---|---|---|---|
| None ............... | 621 | — | 10·4 | 427·5 | — | 2·0 |
| 2-Me ............... | 622·5 | 1·5 | 12·3 | 420 | −7·5 | 1·5 |
| 4-Me ............... | 616·5 | −4·5 | 10·6 | 437·5 | 10 | 2·5 |
| 4-OMe ............... | 608 | −13 | 10·6 | 465 | 37·5 | 3·4 |
| 2′-Me ............... | 635 | — | 7·5 | 437·5 | — | 2·0 |
| 2,2′-$\text{Me}_2$ ............ | 634 | −1 | 8·4 | 431 | −6·5 | 1·8 |
| 4,2′-$\text{Me}_2$ ............ | 630 | −5 | 7·5 | 447 | 9·5 | 2·5 |
| 4-OMe-2′-Me ...... | 620 | −15 | 7·5 | 475 | 37·5 | 3·3 |
| 2′,2″-$\text{Me}_2$............ | 648 | — | 6·7 | 445 | — | 1·8 |
| 2,2′,2″-$\text{Me}_3$ ......... | 647·5 | −0·5 | 7·4 | 440 | −5 | 1·6 |
| 4,2′,2″-$\text{Me}_3$ ......... | 643·5 | −4·5 | 6·8 | 475·5 | 12·5 | 2·2 |
| 4-OMe-2′,2″-$\text{Me}_2$ | 633 | −15 | 6·8 | 486 | 41 | 3·0 |

[3] Part II, *J.*, 1960, 3790.

[4] Yoshino, *Reports Govt. Chem. Ind. Res. Inst., Tokyo,* 1942, **37**, 95.

the reported oxidation of analogous compounds on a commercial scale,[5] and the 2′-methyl derivative gave a coloured salt which could not be purified. The dye bases were therefore obtained directly by interaction of the appropriate aryl-lithium compound with the 2-methyl or 2,2′-dimethyl derivative of Michler's ketone, prepared from *NN*-dimethyl-*m*-toluidine and *p*-dimethylaminobenzoyl chloride or carbonyl chloride, respectively.[6] The dye bases were converted into the dyes in the 98% acetic acid used for the spectra determinations.

## EXPERIMENTAL

4′,4′′-*Bisdimethylamino*-4,2′-*dimethyltriphenylmethane*.—A mixture of urea (3 g.), dimethylaniline (12·7 c.c.), *p*-tolualdehyde (11·8 c.c.), and 32% hydrochloric acid (10·4 c.c.) was stirred at room temperature for 20 hr. and then diluted with ethanol (200 c.c.), made alkaline with aqueous ammonia (*d* 0·88), and then refluxed until suspended material was completely crystalline, thereby yielding NN-*bis*-(4-*dimethylamino*-4′-*methyldiphenylmethyl*)*urea*, m. p. 234—235° (from pyridine) (Found: C, 78·4; H, 7·8; N, 11·2. $C_{33}H_{38}N_4O$ requires C, 78·2; H, 7·6; N, 11·1%). A mixture of this urea derivative (12·5 g.), *NN*-dimethyl-*m*-toluidine (7·2 c.c.), 32% hydrochloric acid (10·4 c.c.), and ethanol (40 c.c.) was stirred and refluxed for 24 hr. and then basified and poured into ethanol (100 c.c.), thereby yielding a solid which, twice crystallised from ethanol, gave 4′,4′′-*bisdimethylamino*-4,2′-*dimethyltriphenylmethane* (15 g.), m. p. 130—132° (Found: C, 83·5; H, 8·4; N, 7·6. $C_{25}H_{30}N_2$ requires C, 83·8; H, 8·4; N, 7·8%).

4-*Methoxy*-2′-*methyl*-4′,4′′-*bisdimethylaminotriphenylmethane*.—By replacing benzaldehyde with *p*-anisaldehyde in the previous preparation, the *urea derivative*, m. p. 242—243° (from pyridine), was obtained (Found: C, 73·3; H, 7·0; N, 10·0. $C_{33}H_{38}N_4O_3$ requires C, 73·6; H, 7·1; N, 10·4%), and with *NN*-dimethyl-*m*-toluidine gave the *triphenylmethane derivative*, m. p. 114—115° (from ethanol) (Found: C, 80·0; H, 8·0; N, 7·4. $C_{25}H_{30}N_2O$ requires C, 80·2; H, 8·1; N, 7·5%).

4,4′-*Bisdimethylamino*-2′-*methyltriphenylmethane*.—Phenyl-lithium in ether, prepared from bromobenzene (3·14 g.), was added to 4,4′-bisdimethylamino-2-methylbenzophenone (1·41 g.) in ether (10 c.c.). The mixture was stirred at room temperature for 1 hr. and then poured into water. The ether was removed from the dried ($Na_2SO_4$) organic layer, yielding a gum which became crystalline in several hours and gave colourless 4,4′-*bisdimethylamino*-2′-*methyltriphenylmethanol* (1·5 g.) (from ethanol). The other derivatives of triphenylmethanol given in Table 2 were prepared in a similar manner except that *p*-methoxyphenyl-lithium was prepared from butyl-lithium and *p*-bromoanisole by transmetallation.

TABLE 2. *Derivatives of Malachite Green base.*

| | | | Found (%) | | | Required (%) | | |
|---|---|---|---|---|---|---|---|---|
| Derivative | M. p. | Formula | C | H | N | C | H | N |
| 2′-Me ................. | 146—147° | $C_{24}H_{28}N_2O$ | 80·0 | 7·8 | 7·6 | 80·0 | 7·8 | 7·8 |
| 2,2′-Me₂ .............. | 150—151 | $C_{25}H_{30}N_2O$ | 80·2 | 8·2 | 7·3 | 80·2 | 8·1 | 7·5 |
| 4,2′-Me₂ .............. | 152—153 | ,, | 80·0 | 7·8 | 7·3 | 80·2 | 8·1 | 7·5 |
| 2′,2′′-Me₂ ........... | 142—143 | ,, | 80·4 | 8·1 | 7·3 | 80·2 | 8·1 | 7·5 |
| 2,2′,2′′-Me₃ ........... | 157—158 | $C_{26}H_{32}N_2O$ | 80·3 | 8·4 | 7·2 | 80·4 | 8·3 | 7·2 |
| 4,2′,2′′-Me₃ ........... | 164—165<br>(decomp.) | ,, | 80·6 | 8·5 | 7·0 | 80·4 | 8·3 | 7·2 |
| 4-OMe-2′-Me ......... | 152—153 | $C_{25}H_{30}N_2O_2$ | 76·6 | 7·7 | 7·0 | 76·9 | 7·8 | 7·2 |
| 4-OMe-2′,2′′-Me₂ ... | 175—176 | $C_{26}H_{32}N_2O_2$ | 77·0 | 7·9 | 6·7 | 77·2 | 8·0 | 6·9 |

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[5] Thorpe, "Dictionary of Applied Chemistry," Longman, Green and Co., London, 1954, Vol. XI, p. 705.

[6] Barker, Bride, and Stamp, *J.*, 1959, 3957.