The effects of cyclic terminal groups in di- and tri-arylmethane dyes. Part 3.[1] Consequences of unsymmetrical substitution in Malachite Green

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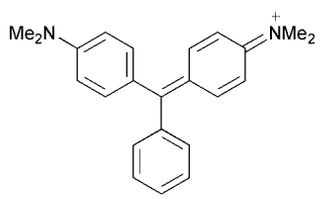
A comprehensive series of novel, unsymmetrical Malachite Green dyes containing different amino substituents has been prepared and the electronic absorption spectra have been determined. In general, the structurally unsymmetrical dyes display electronic symmetry. Hypsochromic shifts and reduced intensity of the λ_{max}(x) absorption bands were generally observed for the dyes containing the *N*-methylpiperazino group, consistent with the reduced ability of the heterocyclic moiety to stabilise the cationic system by conjugation. In solvents of increasing acidity, the dyes exhibit variable spectral responses because of the differing basicities of the terminal amino groups.

Introduction

The triphenylmethane (TPM) dye system, exemplified by Malachite Green (MG) (C.I. Basic Green 4) **1**, is sensitive to



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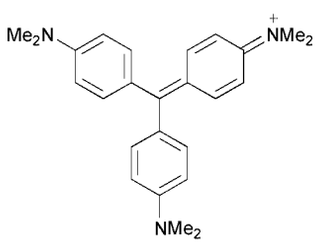
both structural modification and environmental variation and as such facilitates studies into the relationship between colour and constitution.

In TPM dyes, steric congestion arising at the *ortho*-positions prevents coplanarity of the system and the basic structure is that of a three-bladed propeller[2] with the rings twisted *ca.* 30° out of the sp^2 plane defined by the central carbon atom and its three bonds.

The steric and electronic effects of substituents in di- and tri-arylmethane dyes have been well studied[3–6] and in addition, the influence of saturated heterocyclic terminal groups on the electronic absorption spectra of the dyes has been reported.[7] The effects of such structural modifications on the main absorption bands is in accordance with perturbational molecular-orbital (PMO) theory.[8] The terminal nitrogen positions in MG are active sites and PMO theory predicts that an increase in electron density at these positions will reduce the π* energy level, thereby reducing the energy of the NBMO (non-bonding molecular orbital)→π* transition resulting in a bathochromic shift of λ_{max} of the main absorption band. The magnitude of the shift in λ_{max} is related to the extent of electron donation by the terminal amino group. It has been reported[5,9] that shifts in λ_{max}(x) arising from the inclusion of alkyl and cyclic terminal amino groups in TPM dyes arise from inductive effects. However, both ring size and shape influence the basicity of cyclic amines and consequently their ability to stabilise the dye cation, which has an impact upon the spectral parameters of the dye.

In addition, the environment in which the dye exists can have dramatic effects on the UV-visible absorption spectrum of the dye and this can be demonstrated by studying the influence of solvent pH on the dye system. The spectral responses of both symmetrical Violets, such as Crystal Violet (CV) (C.I. Basic Violet 3) **2**, and unsymmetrical Violets to an increase in acidity



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are similar.[7] For Violet systems in 98% acetic acid, the absorption band corresponds to the univalent cation. As the acidity of the medium increases, protonation may occur at another terminal amino group, which has the effect of generating a Malachite Green derivative with the consequent red shift in the main absorption band and appearance of a new low intensity band at shorter wavelength. The position, shape and intensity of the new bands are similar to the x- and y-bands of the Green dyes. The spectral responses of the x- and y-bands of the protonated Violets are in accordance with theoretical predictions for electron-withdrawing groups in the phenyl ring of the parent Green.[3,5,10]

The ease of protonation of a terminal amino group is dependent on its basicity. For the symmetrical Violets, protonation may occur at any of the identical terminal amino groups, but for unsymmetrical Violets the most basic group is expected to be protonated first. A study of a series of unsymmetrical Violets has shown that TPM dyes bearing a diethylamino or piperidino group readily undergo protonation whereas the dimethylamino, pyrrolidino and morpholino analogues are not readily protonated.[7] This contrasting behaviour was explained in terms of the differences in electron density at the terminal heterocyclic nitrogen atoms. The reluctance of morpholine to undergo protonation was attributed to the inductive electron-withdrawing ability of the oxygen.

In view of the interesting spectral consequences of incorporating cyclic terminal groups into 4-aminoazobenzenes,[11]

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Table 1 UV-visible spectral data of unsymmetrical analogues of Malachite Green in acetic acid

	Compound		98% AcOH				10% AcOH			
	NR^1_2	NR^2_2	λ_{max}(x)/nm	$10^{-4}\,\varepsilon_{max}$(x)/dm^3 mol^{-1} cm^{-1}	λ_{max}(y)/nm	$10^{-4}\,\varepsilon_{max}$(y)/dm^3 mol^{-1} cm^{-1}	λ_{max}(x)/nm	$10^{-4}\,\varepsilon_{max}$(x)/dm^3 mol^{-1} cm^{-1}	λ_{max}(y)/nm	$10^{-4}\,\varepsilon_{max}$(y)/dm^3 mol^{-1} cm^{-1}
5a	NMe_2	NEt_2	624.5	10.0	427.5	1.8	622.5	2.3	429.0	0.5
5b	Pyr[a]	NEt_2	628.5	5.2[f]	429.0	1.1[f]	626.5	3.7[f]	424.5	0.9[f]
5c	Pip[b]	NEt_2	631.0	10.6	432.0	2.1	—	—	—	—
5d	Morph[c]	NEt_2	622.5	9.3	429.0	2.2	617.5	2.1	424.0	0.5
5e	NMe_2	Pyr[a]	624.5	2.4[f]	430.0	0.6[f]	622.0	1.8[f]	424.5	0.4[f]
5f	Pip[b]	Pyr[a]	631.0	11.2	430.0	2.0	631.0	3.2	435.0	2.0
5g	Morph[c]	Pyr[a]	623.5	8.8	428.5	1.9	617.0	6.3	422.5	1.7
5h	NMe_2	Pip[b]	627.5	10.6	430.0	2.0	627.0	0.4	428.0	0.2
5i	Morph[c]	Pip[b]	626.0	9.1[f]	430.0	2.0[f]	621.5	0.7[f]	—	—[g]
5j	Morph[c]	NMe_2	621.0	9.6	429.0	2.2	615.0	6.1	424.0	1.6
5k	MPz[d]	NEt_2	610.0	7.0	421.5	2.1	594.0	2.1	414.5	0.8
5l	Mpz[d]	NMe_2	608.5	7.4	423.0	2.2	592.0	4.2	416.5	1.5
5m	Mpz[d]	Pyr[a]	607.0	5.0[f]	420.5	1.5[f]	589.0	3.8[f]	415.5	1.5[f]
5n	Mpz[d]	Pip[b]	608.5	5.5	422.0	1.5	593.0	0.5	417.0	0.2
5o	Mpz[d]	Morph[c]	613.5	8.3	430.0	2.2	602.5	4.9	426.0	1.3
5p	Tmorph[e]	NMe_2	625.0	9.4[f]	433.0	1.8[f]	620.0	5.9[f]	429.0	1.4[f]

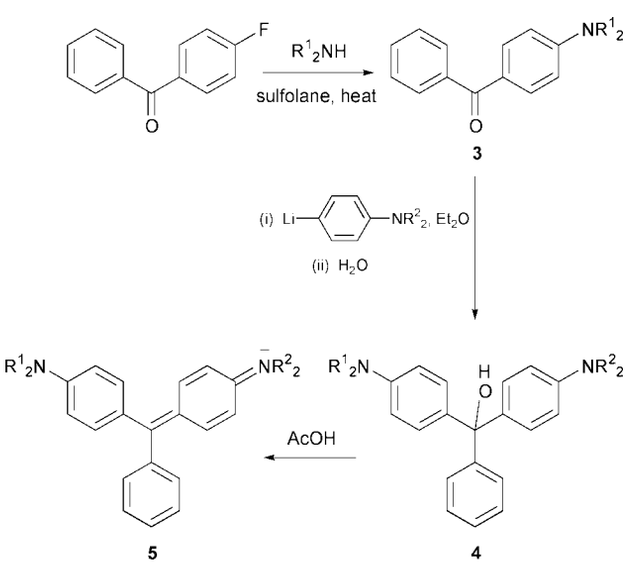
[a] Pyrrolidino. [b] Piperidino. [c] Morpholino. [d] *N*-Methylpiperazino. [e] Thiomorpholino. [f] ε_{max} possibly low due to impure sample. [g] ε values too small to be recorded.

symmetrical di- and tri-arylmethane dyes and unsymmetrical Crystal Violet type dyes,[7] various unsymmetrical analogues of Malachite Green **1** have now been examined.

Discussion

One of the major routes to TPM dyes involves prior synthesis of the dye base through reaction of an aryllithium with a derivative of Michler's ketone, 4,4′-bis(dimethylamino)benzophenone. The synthesis of the unsymmetrical analogues of MG carbinol (methanol) prepared in this study utilised the reaction between a mono-amino-substituted benzophenone and an amino-substituted aryllithium. The initially gummy product was generally purified by crystallisation, often after flash chromatography. Where this approach failed, the dye base was converted into the dye perchlorate by dissolution in glacial acetic acid and treatment with a saturated aqueous sodium perchlorate solution. The perchlorates were purified by precipitation from acetone by the addition of diethyl ether and by crystallisation.

The 4-aminobenzophenones were prepared from 4-fluorobenzophenone by nucleophilic substitution, refluxing the ketone with an excess of the cyclic amine in *S*,*S*-tetramethylene sulfone[12] (sulfolane) (Scheme 1).



Scheme 1

Table 2 Comparison of λ_{max}(x) in 98% acetic acid for Malachite Green derivatives bearing terminal dimethylamino and diethylamino groups

NR^1_2	λ_{max}(x)/nm		$\Delta\lambda_{max}$(x)/nm
	$NR^2_2 = NMe_2$	$NR^2_2 = NEt_2$	
NMe_2	621[a]	624.5	+3.5
NEt_2	624.5	629.5[a]	+5.0
Pyrrolidino	624.5	628.5	+4.0
Piperidino	627.5	631.0	+3.5
Morpholino	621.0	622.5	+1.5
N-Methylpiperazino	608.5	610.0	+1.5

[a] Ref. 7.

The 4-bromo derivatives[13] of *N*,*N*-diethylaniline, *N*-phenylpyrrolidine, *N*-phenylpiperidine and *N*-phenylmorpholine were converted into the aryllithium derivatives by reaction with the *n*-butyllithium–TMEDA complex.[14]

The terminal nitrogen atoms of the dyes are at active sites and hence any increase in the electron density at these positions should result in a bathochromic shift of the long-wavelength main absorption band, the magnitude of which will be related to the donating ability of the terminal amino group. Examination of the λ_{max}(x) values in Table 1 indicates that the most bathochromic dyes **5c** and **5f** contain a piperidino terminal group whilst *N*-methylpiperazino dyes **5k**–**5o** absorb at the shortest wavelengths.

Selected data from Table 1 are collated in Tables 2 and 3 in order to facilitate a detailed and meaningful assessment of the response of λ_{max}(x) to variation in the terminal groups. The data in Tables 2 and 3 indicate that diethylamino and pyrrolidino moieties exhibit similar electron-donating ability.

The diethylamino derivatives always absorb bathochromically of the corresponding dimethylamino bearing dyes in accord with the greater inductive electron releasing ability of an ethyl group. This increased basicity of diethylamino results in a red shift of *ca*. 4 nm, but this shift is reduced to *ca*. 2 nm when cyclic amines containing a second heteroatom are present (Table 2).

Steric considerations are important in comparisons between the five- and six-membered heterocyclic terminal amino groups, pyrrolidine and piperidine. The pyrrolidine ring exists in the envelope or half-chair conformation.[15–17] Thermodynamic studies[18,19] of the conformational interconversion in the ring indicate little or no barrier to pseudo-rotation, which ensures

Table 3 Comparison of λ_{max}(x) in 98% acetic acid for Malachite Green derivatives bearing terminal pyrrolidino and piperidino groups

	λ_{max}(x)/nm		
NR^1_2	NR^2_2 = Pyrrolidino	NR^2_2 = Piperidino	$\Delta\lambda_{max}$(x)/nm
NMe_2	624.5	627.5	+3.0
NEt_2	628.5	631.0	+2.5
Pyrrolidino	629[a]	631.0	+2.0
Piperidino	631.0	634[a]	+3.0
Morpholino	623.5	626.0	+2.5
N-Methylpiperazino	607.0	608.5	+1.5

[a] Ref. 7.

that the system exists as a puckered five-membered ring and that internal bond angle strain is averaged over all positions. Mesomeric interaction between the amine nitrogen atom and the phenyl ring in *N*-phenylpyrrolidine will increase the sp^2 character of the nitrogen and the pyrrolidine ring adopts a near planar conformation which results in a decrease in the steric clash between the *ortho* protons of the phenyl ring and the α-methylene protons of the heterocycle. This conformation will, however, cause the hydrogen atoms of the heterocyclic ring to be more eclipsed. A significant steric clash is apparent when the nitrogen has more sp^3 character.

Piperidine exists primarily in a rigid chair conformation[20,21] and thus in *N*-phenylpiperidine there is a significant steric clash between the α-methylene protons of the piperidine moiety and the *ortho* protons of the phenyl ring. Mesomeric interaction exacerbates this clash. Rotation of the piperidine moiety to overcome this conflict results in a reduction of the overlap between the nitrogen lone pair and the π-electron framework of the phenyl ring.[11] It would therefore appear that there is greater mesomeric interaction between the phenyl ring and the nitrogen heterocycle in *N*-phenylpyrrolidine than for *N*-phenylpiperidine. However, TPM and diphenylmethane (DPM) dyes containing piperidino terminal groups consistently show bathochromic shifts relative to the analogous pyrrolidino dyes[7] suggesting that in these systems piperidine exhibits the greater electron-donating ability. The data in Table 3 clearly support these findings, with the piperidine-containing dyes being *ca*. 2 nm bathochromic of the corresponding pyrrolidine derivatives.

With the introduction of a second heteroatom at the 4-position of piperidine, additional electronic interactions influence the ability of the terminal nitrogen atom to conjugate with the phenyl ring. Examination of the data in Tables 2 and 3 reveals the wavelength of the main absorption band for the morpholino derivatives is blue shifted by $\Delta\lambda$ = 6.5–8.5 nm relative to the analogous piperidino derivatives as a consequence of the inductive electron-withdrawing effect of the hetero-oxygen atom. Although limited to one example, the influence of the sulfur heteroatom in thiomorpholine is less than that of the oxygen atom in morpholine. There is a further blue shift with the introduction of the *N*-methylpiperazino moiety. The significantly reduced ability of the *N*-methylpiperazino moiety to conjugate with the π-framework of the phenyl ring is associated with the presence of the *N*-methyl group. The electron releasing ability of the methyl group coupled with the aliphatic nature of N-4 will result in preferential protonation at the methyl nitrogen atom thus enhancing its apparent electronegativity and therefore reducing still further the ability of the lone pair of electrons of the N-1 nitrogen to conjugate with the π-electron system of the phenyl ring. It thus appears that the ability of the terminal groups to stabilise the MG cation by electron donation decreases in the order piperidino > pyrrolidino ≈ NEt_2 > NMe_2 > thiomorpholino > morpholino > *N*-methylpiperazino.

A comparison of the relative donor abilities of saturated N-heterocycles and dialkylamino groups is available from the work of Azzaro *et al*. into the basicities of enaminoketones.[22] A study of a series of 3-aminocyclohex-2-enones demonstrated that the carbonyl oxygen atom is the basic site for protonation in aqueous or organic solvents and that the structural effects on the basicities can be linearly correlated using pK_{BH^+} and the nitrogen substituent constants at the 3-position of the cyclohex-2-enone ring. Following protonation at oxygen, one canonical form has the positive charge residing on the amino nitrogen. As the ability of the 3-amino substituent to accommodate this positive charge increases so the base strength of the 3-aminocyclohex-2-enone increases (Table 4). For 3-aminocyclohex-2-enones the base strength decreases in the order pyrrolidino > piperidino = NEt_2 > NMe_2 > thiomorpholino > morpholino > *N*-methylpiperazino.

Table 4 Basicity of some 3-aminocyclohex-2-enones

Amine function	pK_{BH^+}
NMe_2	3.14
NEt_2	3.28
Pyrrolidino	3.38
Piperidino	3.28
Morpholino	2.53
Thiomorpholino	2.57
N-Methylpiperazino	1.36

Apart from the fact that this study indicates that the piperidine group is only as efficient as the diethylamino group at stabilising the system, the relative order for the amino substituents is the same as that derived from the spectral data collected during this investigation, with the *N*-methylpiperazino moiety showing the lowest ability to stabilise a system by conjugation.

Further information about the behaviour of the different terminal groups can be obtained by studying the ease of protonation of the unsymmetrical MG analogues, **5**. Protonation of one of the terminal amino groups will have a dramatic effect on the absorption spectrum of the dye. Unlike the Violet dyes, where protonation of one of the terminal amino groups generates a MG system containing a strong electron-withdrawing group in one of the phenyl rings,[7] protonation of one of the terminal amino moieties in a Green type dye will considerably destabilise the cationic system by destruction of one of the basic electron-donating centres. It has been noted that in a solvent of sufficient acidity, Pyrrolidine Green (PG^+) becomes yellow as a consequence of its conversion to the protonated species, PGH^{2+}.[23]

It can be seen from the data in Table 1 that, for the majority of the dyes studied, as the acidity of the solvent is increased there is a progressive but small blue shift of both λ_{max}(x) and λ_{max}(y), presumably as a consequence of the change in polarity of the solvent. Generally, the main absorption band of TPM dyes is displaced to longer wavelengths in non-polar solvents[24,25] as a result of changes in solute–solvent interactions. For symmetrically substituted TPMs such as CV, the resolution of the main absorption band into two separate bands is quite dramatic as the polarity of the solvent is changed, a feature attributed to splitting of the doubly degenerate HOMO of CV by interaction with polar solvents or by counter-ion association in non-polar solvents.[25,26] For TPMs of the MG type the effect of polarity on the absorption spectrum is much less dramatic. These different responses to changes in solvent polarity between the two series of dyes arise since for symmetrically substituted dyes such as CV solvent induced symmetry breaking of an otherwise degenerate excited state occurs. For MG, which has no degenerate states to be separated, the visible absorption spectrum already displays two well resolved transitions in the absence of any solvent perturbations.[26]

The magnitude of the blue shift exhibited by most of the dyes on changing the solvent acidity is in the range of $\Delta\lambda$ = 2–6 nm

Table 5 Deviations in λ_{max}(x) of some structurally unsymmetrical Malachite Green derivatives

	$\Delta\lambda_{max}$(x)/nm					
	NR^2_2					
NR^1_2	NMe_2	NEt_2	Pyr[a]	Pip[b]	Morph[c]	Mpz[d]
NMe_2	—	−1.0	−0.5	0.0	−1.0	−5.0
NEt_2	−1.0	—	−1.0	−1.0	−4.0	−8.0
Pyr[a]	−0.5	−1.0	—	−0.5	−2.5	−10.5
Pip[b]	0.0	−1.0	−0.5	—	−2.5	−11.5
Morph[c]	−1.0	−4.0	−2.5	−2.5	—	−1.0
Mpz[d]	−5.0	−8.0	−10.5	−11.5	−1.0	—

[a] Pyrrolidino. [b] Piperidino. [c] Morpholino. [d] *N*-Methylpiperazino.

for λ_{max}(x) and 2–7 nm for λ_{max}(y). However, dyes containing an *N*-methylpiperazino unit show a greater shift of λ_{max}(x) of $\Delta\lambda$ = 11–18 nm, which, especially when viewed in conjunction with their consistently lower λ_{max}(x) values relative to the other Green dyes in 98% acetic acid, suggest some atypical behaviour of this heterocyclic terminal group.

The colour of all of the dyes is markedly weaker in 10% acetic acid, quantified by a general decrease in both ε_{max}(x) and ε_{max}(y), and none more so than **5c** which is completely colourless. The facile protonation of the piperidino and diethylamino groups has been noted previously,[7] although the consequences are not as dramatic in the Violets as here in the Greens. In fact, the dyes in the present study which contain a piperidino function generally exhibit the lowest values of ε_{max}(x) in 10% acetic acid. Conversely, the dyes containing the least basic terminal groups, morpholino, thiomorpholino and *N*-methylpiperazino, show the highest intensities of the x-band in 10% acetic acid. Of course, the last group is expected to protonate at N-4 decreasing the likelihood of protonation occurring at N-1 and therefore causing the smallest effect on the visible spectrum.

Protonation of a terminal group will clearly decrease the resonance stabilisation of the dye and hence reduce the stability of the carbocationic species. For instance, the parent triphenylmethyl cation, for which Rappoport[27] estimated k_{H_2O} to be 10^6–10^7 mol^{-1} s^{-1}, only exists in a non-nucleophilic environment, being readily destroyed by, for example, methanol. It thus appears that equilibrium (1) is shifted towards the colourless

$$R_3C\text{–}OH + H_3O^+ \rightleftharpoons R_3C^+ + 2H_2O \qquad (1)$$

dye base under aqueous acidic conditions when the more basic terminal groups are present in the dye.

Rather than being hypsochromically shifted in 10% acetic acid relative to 98% acetic acid, the y-bands of compounds **5a** and **5f** show red shifts of $\Delta\lambda$ = 1.5 and 5.0 nm respectively which suggests an increase in electron donation from the unsubstituted phenyl ring into the dye system. The latter dye also exhibits an unchanged intensity of the y-band in the two media.

Brooker *et al*. examined extensively the absorption spectra of unsymmetrical cyanines,[28–32] a feature of which is that the polymethine chain is no longer uniform.[33] Substitution into the dye will thus cause an uneven rotation about the chain, the consequence of which is that prediction of substitution effects is far more difficult. MO calculations using the Pariser–Parr–Pople (PPP) method show that the loss of electronic symmetry destroys the relationship to the odd alternant hydrocarbon system and perturbational theory can no longer be applied.[34] A study of substitution into the phenyl ring of **5a**, showed that the spectral shifts of the main absorption band brought about by substituents at the 3- and 4-positions were linearly related to the appropriate Hammett substituent constants.[35] Other related symmetrical Green systems[5,36,37] conform to this correlation which was explained in terms of transmission of the electronic effects to the central inactive carbon atom.[34] A structurally unsymmetrical cyanine dye having end-groups A and B can be considered to be electronically symmetrical if λ_{max}AB is approximately equal to the harmonic mean of λ_{max}AA and λ_{max}BB.[38–41] In such cases the basicities of the end-groups are similar. An electronically unsymmetrical dye gives a value of λ_{max}AB which is less than the mean of λ_{max}AA and λ_{max}BB by an amount known as the deviation,[41] the magnitude of which reflects the difference in basicity of the two end-groups. The deviations reported in Table 5 for the unsymmetrical MG dyes are obtained by comparison of the spectral data for their symmetrical analogues which have been reported previously[7] or, in the case of *N*-Methylpiperazine Green [λ_{max}(x) 606.0 nm and λ_{max}(y) 429.5 nm, ε_{max}(x) 60 000 dm^3 mol^{-1} cm^{-1} and ε_{max}(y) 15 000 dm^3 mol^{-1} cm^{-1}], which were recorded in 98% acetic acid during this study.

From the data in Table 5 it appears that the majority of the structurally unsymmetrical dyes which contain the dimethylamino, diethylamino, pyrrolidino and piperidino units are essentially electronically symmetrical, with deviations of <1 nm. However, with the introduction of the morpholino moiety, the deviations increase to 1–4 nm. The atypical behaviour of the *N*-methylpiperazino unit is again apparent from the significant increase in the magnitude of the deviation (5–11.5 nm) when this group is introduced into the dye system. The significantly reduced deviation for **5o** reflects the similar properties of the morpholino and *N*-methylpiperazino groups and further supports the idea of protonation occurring at N-4 of the *N*-methylpiperazino group in acid media thereby introducing an electron-withdrawing centre analogous to the oxygen atom of the morpholino unit. In this connection, it is noteworthy that λ_{max}(x) for *N*-Methylpiperazine Green in 98% acetic acid is shifted ~20 nm to the blue relative to Morpholine Green [λ_{max}(x) 625 nm].[9] This large hypsochromic shift suggests that under these conditions the piperazino dye is protonated at the *N*-methyl groups, a feature which could be the cause of the atypical behaviour encountered during this work.

Experimental

Visible spectra of 10^{-5} M solutions of the dye bases in 98% acetic acid were measured on a Philips PU8740 UV/Vis scanning spectrophotometer. Under these conditions, TPM dye bases are quantitatively converted to the corresponding dye cations.[42] This solvent system was chosen so as to allow direct comparison with earlier work. The use of acetic acid also allows the easy rapid generation of solutions of varying acidity by the addition of water which promotes ionisation of the acetic acid. The visible absorption spectra were measured immediately following preparation of the solutions and again after one hour and 48 hours to ensure constant ε_{max} values.

Melting points were determined in capillary tubes using a Gallenkamp melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX250MHz multinuclear magnetic resonance spectrometer

operating at 250 MHz. The ^{1}H and ^{13}C NMR spectra of the dye perchlorates were recorded in acetone-d_6 and coupling constants are given in Hz. Flash column chromatography was performed following the published procedure using Rhône-Poulenc C60 40/60 H activated silica gel.[43]

Preparation of mono-substituted benzophenones

The amine (0.2 mol) was added to a stirred solution of 4-fluorobenzophenone (0.1 mol) in sulfolane (100 cm^3) and the mixture was refluxed for several hours. The reaction mixture was then stirred into ice–water (2 dm^3) whereupon a precipitate was formed. The crude solid was collected, washed and recrystallised. The following compounds were obtained using this method.

4-Piperidinobenzophenone. From 4-fluorobenzophenone and piperidine (5 h) as yellow flakes (70%), mp 92–93 °C (lit.[44] gives 85–87 °C) after recrystallisation from aqueous acetone.

4-Pyrrolidinobenzophenone. From 4-fluorobenzophenone and pyrrolidine (6 h) as pale yellow crystals (74%), mp 149–149.5 °C (lit.[45] gives 138 °C) after recrystallisation from aqueous acetone.

4-Morpholinobenzophenone. From 4-fluorobenzophenone and morpholine (7 h) as yellow needles (68%), mp 145–146 °C (lit.[46] gives 140–142 °C) after recrystallisation from light petroleum (bp 60–80 °C).

4-(*N*-Methylpiperazino)benzophenone 3a. From 4-fluorobenzophenone and *N*-methylpiperazine (24 h) as bright yellow flakes (50%), mp 123–125 °C after recrystallisation from light petroleum (bp 60–80 °C). δ_H 2.40 (3H, s, N(CH_3)), 2.60 (4H, t, *J* 5.0, N-4-(CH_2)$_2$), 3.43 (4H, t, *J* 5.0, N-1-(CH_2)$_2$), 6.93 (2H, d, *J* 8.9, 3-H, 5-H), 7.47–7.59 (3H, m, Ar′), 7.77 (2H, d, 2′-H, 6′-H), 7.83 (2H, d, *J* 8.9, 2-H, 6-H). δ_C 46.6, 47.8, 55.2, 113.8, 127.6, 128.5, 130.0, 131.9, 133.0, 139.3, 154.4, 195.7 (Found: C, 77.2; H, 7.0; N, 10.2. $C_{18}H_{20}N_2O$ requires C, 77.1; H, 7.1; N, 10.0%).

4-(Thiomorpholino)benzophenone 3b. From 4-fluorobenzophenone and thiomorpholine (14 h) as brown crystals (55%), mp 144–144.5 °C after recrystallisation from aqueous acetone. δ_H 2.75 (4H, t, *J* 5.0, S(CH_2)$_2$), 3.84 (4H, t, *J* 5.0, N(CH_2)$_2$), 6.88 (2H, d, *J* 8.9, 3-H, 5-H), 7.47–7.62 (3H, m, Ar′), 7.77 (2H, d, 2′-H, 6′-H), 7.83 (2H, d, *J* 8.9, 2-H, 6-H). δ_C 26.3, 50.8, 114.0, 127.3, 128.6, 130.0, 131.9, 133.3, 139.2, 153.2, 195.6 (Found: C, 72.1; H, 6.2; N, 5.0. $C_{17}H_{17}NOS$ requires C, 72.1; H, 6.0; N, 4.9%).

Preparation of the unsymmetrical derivatives of Malachite Green

A solution of the appropriate bromoarylamine (11 mmol) in diethyl ether (50 cm^3) was added to the *n*-butyllithium–TMEDA complex [prepared from *n*-butyllithium in hexane (4.5 cm^3; 11 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (1.7 cm^3; 11 mmol)] in diethyl ether (50 cm^3). After 45 min at room temperature, a slurry of the 4-substituted benzophenone (10 mmol) in diethyl ether (50 cm^3) was added and the mixture was stirred at room temperature for a further 2–3 h, whereupon the mixture was poured into water (500 cm^3). The organic layer was separated, washed with water and dried (Na_2SO_4). Evaporation of the solvent gave an oil which was purified by flash chromatography and/or recrystallisation. The following compounds were obtained using this method.

4-Diethylamino-4′-dimethylaminotriphenylmethanol 4a. From 4-diethylaminophenyllithium and 4-dimethylaminobenzophenone. Elution from silica which had been basified using triethylamine with a mobile phase of hexane, ethyl acetate, and triethylamine (2 : 2 : 1) gave **4a** as a pale brown oil (66%) which would not solidify. δ_H 1.20 (6H, t, *J* 6.8, N(CH$_2$CH_3)$_2$), 2.70 (1H, s, OH), 2.99 (6H, s, N(CH_3)$_2$), 3.38 (4H, q, *J* 6.8, N(CH_2CH$_3$)$_2$), 6.64 (2H, d, *J* 8.9, 3-H, 5-H), 6.71 (2H, d, *J* 8.9, 3′-H, 5′-H), 7.11 (2H, d, *J* 8.9, 2′-H, 6′-H), 7.18 (2H, d, *J* 8.9, 2-H, 6-H), 7.30–7.37 (5H, m, Ar). δ_C 13.1, 41.1, 44.7, 82.0, 111.2, 112.2, 127.1, 128.1, 128.3, 129.3, 129.6, 134.8, 136.1, 147.2, 148.5, 149.9 (Found: C, 79.6; H, 8.6; N, 7.7. $C_{25}H_{30}N_2O$ requires C, 80.2; H, 8.0; N, 7.5%).

4-Diethylamino-4′-pyrrolidinotriphenylmethanol 4b. From 4-diethylaminophenyllithium and 4-pyrrolidinobenzophenone. Evaporation of the organic layer yielded **4b** as a green oil (65%) which would not solidify. δ_H 1.19 (6H, t, *J* 6.8, N(CH$_2$CH_3)$_2$), 2.03 (4H, m, (CH$_2$)$_2$), 3.32 (4H, m, N(CH$_2$)$_2$), 3.39 (4H, q, *J* 6.8, N(CH_2CH$_3$)$_2$), 6.57 (2H, d, *J* 8.9, 3′-H, 5′-H), 6.62 (2H, d, *J* 8.9, 3-H, 5-H), 7.11 (2H, d, *J* 8.9, 2-H, 6-H), 7.18 (2H, d, *J* 8.9, 2′-H, 6′-H), 7.28–7.39 (5H, m, Ar), no hydroxy proton signal could be detected. δ_C 13.1, 26.0, 44.8, 48.1, 82.1, 111.2, 111.3, 127.0, 128.0, 128.3, 129.4, 129.6, 133.6, 134.9, 147.2, 147.3, 148.6.

4-Diethylamino-4′-piperidinotriphenylmethanol 4c. From 4-diethylaminophenyllithium and 4-piperidinobenzophenone. Elution from silica which had been basified using triethylamine with a mobile phase of hexane gave **4c** as a pale brown oil (66%) which would not solidify. δ_H 1.21 (6H, t, *J* 7.2, N(CH$_2$CH_3)$_2$), 1.64 (2H, m, CH$_2$), 1.75 (4H, m, (CH$_2$)$_2$), 2.61 (1H, s, OH), 3.21 (4H, t, N(CH$_2$)$_2$), 3.39 (4H, q, *J* 7.2, N(CH_2CH$_3$)$_2$), 6.64 (2H, d, *J* 8.9, 3-H, 5-H), 6.91 (2H, d, *J* 8.9, 3′-H, 5′-H), 7.10 (2H, d, *J* 8.9, 2-H, 6-H), 7.20 (2H, d, *J* 8.9, 2′-H, 6′-H), 7.28–7.37 (5H, m, Ar). δ_C 13.1, 24.8, 26.3, 44.7, 50.9, 82.0, 111.2, 115.8, 127.1, 128.1, 128.3, 129.2, 129.6, 134.6, 138.5, 147.2, 148.3, 151.4 (Found: C, 81.0; H, 8.2; N, 6.6. $C_{28}H_{34}N_2O$ requires C, 81.2; H, 8.2; N, 6.6%).

4-Diethylamino-4′-morpholinotriphenylmethanol 4d. From 4-diethylaminophenyllithium and 4-morpholinobenzophenone as a yellow powder (75%), mp 131–132 °C, after recrystallisation from light petroleum (bp 60–80 °C). δ_H 1.20 (6H, t, *J* 7.0, N(CH$_2$CH_3)$_2$), 2.81 (1H, s, OH), 3.19 (4H, t, *J* 5.0, N(CH$_2$)$_2$), 3.38 (4H, q, *J* 7.0, N(CH_2CH$_3$)$_2$), 3.89 (4H, t, *J* 5.0, O(CH$_2$)$_2$), 6.63 (2H, d, *J* 8.7, 3-H, 5-H), 6.88 (2H, d, *J* 8.7, 3′-H, 5′-H), 7.08 (2H, d, *J* 8.7, 2-H, 6-H), 7.25 (2H, d, *J* 8.7, 2′-H, 6′-H), 7.28–7.39 (5H, m, Ar). δ_C 13.1, 44.7, 49.6, 67.4, 81.9, 111.2, 115.1, 127.2, 128.3, 128.6, 129.3, 129.6, 134.3, 139.5, 147.3, 148.2, 150.4 (Found: C, 78.0; H, 7.9; N, 6.6. $C_{27}H_{32}N_2O_2$ requires C, 77.9; H, 7.7; N, 6.7%).

4-Dimethylamino-4′-pyrrolidinotriphenylmethanol 4e. From 4-pyrrolidinophenyllithium and 4-dimethylaminobenzophenone as a green oil (77%) which would not solidify. δ_H 2.08 (4H, m, (CH$_2$)$_2$), 3.00 (6H, s, N(CH$_3$)$_2$), 3.14 (1H, s, OH), 3.34 (4H, m, N(CH$_2$)$_2$), 6.54 (2H, d, *J* 8.7, 3′-H, 5′-H), 6.77 (2H, d, *J* 8.7, 3-H, 5-H), 7.09–7.14 (4H, 2d, *J* 8.7, 2-H, 6-H, 2′-H, 6′-H), 7.21–7.39 (5H, m, Ar). δ_C 26.0, 41.1, 48.1, 82.1, 111.3, 112.2, 127.5, 128.1, 128.3, 129.4, 129.5, 133.3, 135.9, 147.3, 148.2, 149.9.

4-Piperidino-4′-pyrrolidinotriphenylmethanol 4f. From 4-pyrrolidinophenyllithium and 4-piperidinobenzophenone as greenish-brown flakes (63%), mp 144–145 °C, after recrystallisation from methanol to which a trace of 2 M sodium hydroxide solution had been added. δ_H 1.61 (2H, m, CH$_2$), 1.74 (4H, m, (CH$_2$)$_2$), 2.03 (4H, m, (CH$_2$)$_2$), 3.10 (1H, s, OH), 3.19 (4H, m, N(CH$_2$)$_2$), 3.33 (4H, m, N(CH$_2$)$_2$), 6.54 (2H, d, *J* 8.7, 3′-H, 5′-H), 6.89 (2H, d, *J* 8.7, 3-H, 5-H), 7.21–7.36 (7H, m, 2-H, 6-H, Ar), 7.54 (2H, d, *J* 8.7, 2′-H, 6′-H). δ_C 24.8, 26.0, 26.4, 48.0, 50.8, 87.1, 111.0, 115.6, 126.6, 128.0, 128.4, 130.1, 130.5,

130.9, 135.2, 146.6, 147.0, 151.0 (Found: C, 81.4; H, 8.1; N, 6.5. $C_{28}H_{32}N_2O$ requires C, 81.6; H, 7.8; N, 6.8%).

4-Morpholino-4′-pyrrolidinotriphenylmethanol 4g. From 4-pyrrolidinophenyllithium and 4-morpholinobenzophenone as pale greenish-yellow crystals (66%), mp 143–144 °C, after recrystallisation from hexane. δ_H 2.03 (4H, m, $(CH_2)_2$), 2.77 (1H, s, OH), 3.19 (4H, t, *J* 4.7, $N(CH_2)_2$), 3.32 (4H, m, $N(CH_2)_2$), 3.89 (4H, t, *J* 4.7, $O(CH_2)_2$), 6.53 (2H, d, *J* 8.7, 3′-H, 5′-H), 6.88 (2H, d, *J* 8.7, 3-H, 5-H), 7.12 (2H, d, *J* 8.7, 2′-H, 6′-H), 7.23 (2H, d, *J* 8.7, 2-H, 6-H), 7.27–7.37 (5H, m, Ar). δ_C 26.0, 48.0, 49.6, 67.4, 82.0, 111.2, 115.1, 127.2, 128.2, 128.3, 129.3, 129.4, 134.6, 139.6, 147.4, 148.2, 150.4 (Found: C, 78.1; H, 7.3; N, 6.7. $C_{27}H_{30}N_2O_2$ requires C, 78.3; H, 7.2; N, 6.8%).

4-Dimethylamino-4′-piperidinotriphenylmethanol 4h. From 4-piperidinophenyllithium and 4-dimethylaminobenzophenone as pale yellowish-green needles (64%), mp 124–125 °C, after recrystallisation from light petroleum (bp 60–80 °C). δ_H 1.65 (2H, m, CH_2), 1.73 (4H, m, $(CH_2)_2$), 2.71 (1H, s, OH), 2.98 (6H, s, $N(CH_3)_2$), 3.19 (4H, t, $N(CH_2)_2$), 6.69 (2H, d, *J* 8.9, 3-H, 5-H), 6.89 (2H, d, *J* 8.9, 3′-H, 5′-H), 7.13–7.18 (4H, m, 2-H, 6-H, 2′-H, 6′-H), 7.30–7.36 (5H, m, Ar). δ_C 24.8, 26.3, 41.0, 50.8, 82.0, 112.1, 115.8, 127.2, 128.1, 128.3, 129.2, 129.3, 135.9, 138.4, 148.2, 149.9, 151.4 (Found: C, 81.0; H, 7.8; N, 7.1. $C_{26}H_{30}N_2O$ requires C, 80.8; H, 7.7; N, 7.3%).

4-Morpholino-4′-piperidinotriphenylmethanol 4i. From 4-piperidinophenyllithium and 4-morpholinobenzophenone as a green oil (48%) which would not solidify. δ_H 1.49 (2H, m, CH_2), 1.63 (4H, m, $(CH_2)_2$), 2.66 (1H, s, OH), 3.07 (8H, m, $N(CH_2)_2$, $N(CH_2)_2$), 3.77 (4H, t, $O(CH_2)_2$), 6.74–6.79 (4H, m, 3-H, 5-H, 3′-H, 5′-H), 7.01 (2H, d, *J* 8.7, 2′-H, 6′-H), 7.05 (2H, d, *J* 8.7, 2-H, 6-H), 7.16–7.22 (5H, m, Ar). δ_C 24.7, 26.3, 49.5, 50.7, 67.3, 81.9, 115.1, 115.8, 127.3, 128.1, 128.2, 129.1, 129.3, 138.0, 139.2, 147.9, 150.4, 151.4.

4-Dimethylamino-4′-morpholinotriphenylmethanol 4j. From 4-dimethylaminophenyllithium and 4-morpholinobenzophenone as a pale green powder (76%), mp 163–164 °C, after recrystallisation from light petroleum (bp 100–120 °C). δ_H 2.80 (1H, s, OH), 2.99 (6H, s, $N(CH_3)_2$), 3.19 (4H, t, *J* 4.7, $N(CH_2)_2$), 3.89 (4H, t, *J* 4.7, $O(CH_2)_2$), 6.70 (2H, d, *J* 8.9, 3-H, 5-H), 6.88 (2H, d, *J* 8.9, 3′-H, 5′-H), 7.14 (2H, d, *J* 8.9, 2-H, 6-H), 7.22 (2H, d, *J* 8.9, 2′-H, 6′-H), 7.30–7.36 (5H, m, Ar). δ_C 41.0, 49.6, 67.4, 81.9, 112.1, 115.1, 127.3, 128.2, 128.3, 129.3, 129.4, 135.7, 139.4, 148.1, 150.0, 150.4 (Found: C, 77.3; H, 7.5; N, 7.1. $C_{25}H_{28}N_2O_2$ requires C, 77.3; H, 7.2; N, 7.2%).

4-Diethylamino-4′-(*N*-methylpiperazino)triphenylmethanol 4k. From 4-diethylaminophenyllithium and 4-(*N*-methylpiperazino)benzophenone as pale brown flakes (53%), mp 144–145 °C, after recrystallisation from ethyl acetate. δ_H 1.19 (6H, t, *J* 6.9, $N(CH_2CH_3)_2$), 2.38 (3H, s, NCH_3), 2.60 (4H, t, N-4-$(CH_2)_2$), 2.89 (1H, s, OH), 3.22 (4H, t, N-1-$(CH_2)_2$), 3.39 (4H, q, *J* 6.9, $N(CH_2CH_3)_2$), 6.62 (2H, d, *J* 8.7, 3-H, 5-H), 6.88 (2H, d, *J* 8.7, 3′-H, 5′-H), 7.09 (2H, d, *J* 8.7, 2-H, 6-H), 7.21 (2H, d, *J* 8.7, 2′-H, 6′-H), 7.30–7.38 (5H, m, Ar). δ_C 13.1, 44.7, 46.7, 49.3, 55.6, 81.9, 111.2, 115.4, 127.1, 128.1, 128.3, 129.3, 129.6, 134.5, 139.1, 147.2, 148.3, 150.4 (Found: C, 78.3; H, 8.4; N, 9.8. $C_{28}H_{35}N_3O$ requires C, 78.3; H, 8.2; N, 9.8%).

4-Dimethylamino-4′-(*N*-methylpiperazino)triphenylmethanol 4l. From 4-dimethylaminophenyllithium and 4-(*N*-methylpiperazino)benzophenone as an off-white powder (73%), mp 157–158 °C, after recrystallisation from light petroleum (bp 100–120 °C). δ_H 2.38 (3H, s, NCH_3), 2.60 (4H, t, *J* 4.7, N-4-$(CH_2)_2$), 2.85 (1H, s, OH), 2.98 (6H, s, $N(CH_3)_2$), 3.24 (4H, t, *J* 4.7, N-1-$(CH_2)_2$), 6.69 (2H, d, *J* 8.7, 3-H, 5-H), 6.88 (2H, d, *J* 8.7, 3′-H, 5′-H), 7.13 (2H, d, *J* 8.7, 2-H, 6-H), 7.19 (2H, d, *J* 8.7, 2′-H, 6′-H), 7.29–7.34 (5H, m, Ar). δ_C 41.0, 46.7, 49.2, 55.6, 81.9, 112.1, 115.4, 127.2, 128.1, 128.3, 129.3, 129.3, 135.8, 139.0, 148.2, 150.0, 150.4 (Found: C, 77.7; H, 7.9; N, 10.3. $C_{26}H_{31}N_3O$ requires C, 77.8; H, 7.7; N, 10.5%).

4-(*N*-Methylpiperazino)-4′-pyrrolidinotriphenylmethanol 4m. From 4-pyrrolidinophenyllithium and 4-(*N*-methylpiperazino)benzophenone. Elution from silica which had been basified using triethylamine with a mobile phase of toluene, ethyl acetate and triethylamine (2:2:1) gave **4m** as a pale brown oil (56%) which would not solidify. δ_H 2.03 (4H, t, *J* 6.5, $(CH_2)_2$), 2.38 (3H, s, NCH_3), 2.60 (4H, t, *J* 5.0, N-4-$(CH_2)_2$), 3.24 (4H, t, *J* 5.0, N-1-$(CH_2)_2$), 3.32 (4H, t, *J* 6.5, $N(CH_2)_2$), 6.53 (2H, d, *J* 8.7, 3′-H, 5′-H), 6.88 (2H, d, *J* 8.7, 3-H, 5-H), 7.12 (2H, d, *J* 8.7, 2′-H, 6′-H), 7.21 (2H, d, *J* 8.7, 2-H, 6-H), 7.27–7.38 (5H, m, Ar). δ_C 26.0, 46.6, 48.0, 49.3, 55.6, 82.0, 111.2, 115.4, 127.1, 128.1, 128.3, 129.3, 129.5, 134.7, 139.2, 147.3, 148.3, 150.4 (Found: C, 77.4; H, 7.9; N, 9.3. $C_{28}H_{33}N_3O$ requires C, 78.7; H, 7.7; N, 9.8%).

4-(*N*-Methylpiperazino)-4′-piperidinotriphenylmethanol 4n. From 4-piperidinophenyllithium and 4-(*N*-methylpiperazino)-benzophenone as pale yellow crystals (68%), mp 146–147 °C, after recrystallisation from light petroleum (bp 60–80 °C). δ_H 1.62 (2H, m, CH_2), 1.71 (4H, m, $(CH_2)_2$), 2.38 (3H, s, NCH_3), 2.60 (4H, t, *J* 4.7, N-4-$(CH_2)_2$), 2.81 (1H, s, OH), 3.17–3.26 (8H, m, $N(CH_2)_2$, N-1-$(CH_2)_2$), 6.88 (4H, 2d, *J* 8.7, 3′-H, 5′-H, 3-H, 5-H), 7.15 (4H, 2d, *J* 8.7, 2′-H, 6′-H, 2-H, 6-H), 7.27–7.34 (5H, m, Ar). δ_C 24.7, 26.3, 46.6, 49.2, 50.7, 55.6, 81.9, 115.4, 115.8, 127.3, 128.2, 128.3, 129.2, 129.3, 138.1, 138.8, 148.0, 150.5, 151.4 (Found: C, 78.7; H, 7.9; N, 9.3. $C_{29}H_{35}N_3O$ requires C, 78.9; H, 7.9; N, 9.5%).

4-(*N*-Methylpiperazino)-4′-morpholinotriphenylmethanol 4o. From 4-morpholinophenyllithium and 4-(*N*-methylpiperazino)benzophenone as a white powder (52%), mp 76–77 °C, after recrystallisation from light petroleum (bp 60–80 °C). δ_H 2.38 (3H, s, NCH_3), 2.60 (4H, t, *J* 4.7, N-4-$(CH_2)_2$), 2.89 (1H, s, OH), 3.17–3.26 (8H, m, $N(CH_2)_2$, N-1-$(CH_2)_2$), 3.89 (4H, t, *J* 4.7, $O(CH_2)_2$), 6.87 (2H, d, *J* 8.7, 3′-H, 5′-H), 6.88 (2H, d, *J* 8.7, 3-H, 5-H), 7.17 (4H, m, 2-H, 6-H, 2′-H, 6′-H), 7.30–7.33 (5H, m, Ar). δ_C 46.6, 49.2, 49.5, 55.6, 67.4, 81.9, 115.1, 115.4, 127.4, 128.2, 128.2, 129.2, 129.3, 139.1, 139.5, 147.9, 150.4, 150.5 (Found: C, 75.4; H, 7.6; N, 8.8. $C_{28}H_{33}N_3O_2$ requires C, 75.8; H, 7.4; N, 9.5%).

4-Dimethylamino-4′-thiomorpholinotriphenylmethanol 4p. From 4-dimethylaminophenyllithium and 4-thiomorpholinobenzophenone. Elution from silica which had been basified using triethylamine with a mobile phase of benzene followed by ethyl acetate gave **4p** as a pale yellow oil (46%) which would not solidify. δ_H 2.77 (4H, m, $S(CH_2)_2$), 2.98 (6H, s, $N(CH_3)_2$), 3.58 (4H, m, $N(CH_2)_2$), 6.70 (2H, d, *J* 8.7, 3-H, 5-H), 6.85 (2H, d, *J* 8.7, 3′-H, 5′-H), 7.14 (2H, d, *J* 8.7, 2-H, 6-H), 7.20 (2H, d, *J* 8.7, 2′-H, 6′-H), 7.30–7.36 (5H, m, Ar). δ_C 27.2, 41.0, 52.4, 81.9, 112.2, 116.5, 127.3, 128.2, 128.3, 129.3, 129.4, 135.7, 139.2, 148.1, 150.0, 150.4 (Found: C, 73.4; H, 7.2; N, 7.0. $C_{25}H_{28}N_2OS$ requires C, 74.3; H, 6.9; N, 6.9%).

Preparation of the perchlorate salts of the unsymmetrical derivatives of Malachite Green

A solution of the dye base in the minimum volume of glacial acetic acid was added dropwise to a saturated aqueous solution of sodium perchlorate (50 cm^3). The solid which formed was collected, washed thoroughly with water, ethanol and then with diethyl ether. The crude salt was dissolved in acetone (previously dried over a 4 Å molecular sieve), and the solution was filtered. Addition of a large excess of diethyl ether (Na-dried) to the filtrate re-precipitated the salt, which was then collected and washed with diethyl ether (Na-dried). This process was some-

times followed by recrystallisation of the salt. The following compounds were obtained using this method.

4-Diethylamino-4′-dimethylaminotriphenylmethyl perchlorate 5a. Lustrous green crystals (58%) after recrystallisation from ethyl acetate. δ_H 1.50 (6H, t, *J* 7.2, $N(CH_2CH_3)_2$), 3.55 (6H, s, $N(CH_3)_2$), 3.94 (4H, q, *J* 7.2, $N(CH_2CH_3)_2$), 7.27 (2H, d, *J* 9.4, 3-H, 5-H), 7.29 (2H, d, *J* 9.4, 3′-H, 5′-H), 7.56–7.64 (6H, m, 2-H, 6-H, 2′-H, 6′-H, 3″-H, 5″-H), 7.80 (2H, t, *J* 9.2, 2″-H, 6″-H), 7.94 (1H, t, *J* 9.2, 4″-H). δ_C 12.7, 40.7, 46.3, 114.2, 114.4, 127.5, 127.6, 129.2, 133.4, 135.0, 140.3, 141.0, 141.7, 156.2, 157.5, 177.3 (Found: C, 65.4; H, 6.4; N, 6.0. $C_{25}H_{29}ClN_2O_4$ requires C, 65.7; H, 6.4; N, 6.1%).

4-Diethylamino-4′-morpholinotriphenylmethyl perchlorate 5d. Lustrous green crystals (72%). δ_H 1.52 (6H, t, *J* 7.0, $N(CH_2CH_3)_2$), 3.94 (4H, q, *J* 7.0, $N(CH_2CH_3)_2$), 4.00 (8H, m, $N(CH_2)_2$, $O(CH_2)_2$), 7.39 (2H, d, *J* 9.0, 3-H, 5-H), 7.43 (2H, d, *J* 9.0, 3′-H, 5′-H), 7.58–7.71 (6H, m, 2-H, 6-H, 2′-H, 6′-H, 3″-H, 5″-H), 7.83 (2H, t, *J* 7.5, 2″-H, 6″-H), 7.95 (1H, t, *J* 7.5, 4″-H). δ_C 12.8, 46.7, 47.5, 66.7, 114.3, 115.2, 128.1, 128.5, 129.2, 133.6, 135.1, 140.2, 140.6, 142.3, 156.8, 157.1, 177.3 (Found: C, 64.8; H, 6.4; N, 5.6. $C_{27}H_{31}ClN_2O_5$ requires C, 65.0; H, 6.2; N, 5.6%).

4-Dimethylamino-4′-pyrrolidinotriphenylmethyl perchlorate 5e. Lustrous green crystals (70%) after recrystallisation from ethyl acetate. δ_H 2.34 (4H, m, $(CH_2)_2$), 3.55 (6H, s, $N(CH_3)_2$), 3.91 (4H, m, $N(CH_2)_2$), 7.17 (2H, d, *J* 8.7, 3′-H, 5′-H), 7.27 (2H, d, *J* 8.7, 3-H, 5-H), 7.56–7.64 (6H, m, 2-H, 6-H, 2′-H, 6′-H, 3″-H, 5″-H), 7.80 (2H, t, *J* 7.5, 2″-H, 6″-H), 7.92 (1H, t, *J* 7.5, 4″-H). δ_C 26.2, 41.3, 50.3, 114.8, 116.1, 128.1, 128.5, 129.9, 134.1, 135.7, 141.1, 141.5, 142.1, 156.0, 158.0, 178.0 (Found: C, 65.7; H, 6.1; N, 6.0. $C_{25}H_{27}ClN_2O_4$ requires C, 66.0; H, 5.9; N, 6.2%).

4-Piperidino-4′-pyrrolidinotriphenylmethyl perchlorate 5f. Lustrous green crystals (52%) after recrystallisation from ethyl acetate. δ_H 1.97 (6H, m, CH_2, $(CH_2)_2$), 2.34 (4H, m, $(CH_2)_2$), 3.93 (4H, m, $N(CH_2)_2$), 4.02 (4H, m, $N(CH_2)_2$), 7.19 (2H, d, *J* 8.4, 3′-H, 5′-H), 7.49 (2H, d, *J* 8.4, 3-H, 5-H), 7.56–7.66 (6H, m, 2-H, 6-H, 2′-H, 6′-H, 3″-H, 5″-H), 7.80 (2H, t, *J* 7.5, 2″-H, 6″-H), 7.94 (1H, t, *J* 7.5, 4″-H). δ_C 24.5, 25.4, 26.5, 49.8, 49.8, 114.8, 115.4, 127.9, 129.2, 131.7, 133.4, 134.9, 140.3, 141.3, 141.4, 155.3, 156.3, 177.8 (Found: C, 67.6; H, 6.4; N, 5.5. $C_{28}H_{31}ClN_2O_4$ requires C, 67.9; H, 6.3; N, 5.7%).

4-Dimethylamino-4′-piperidinotriphenylmethyl perchlorate 5h. Lustrous green crystals (36%) after recrystallisation from ethyl acetate. δ_H 1.97 (6H, m, CH_2, $(CH_2)_2$), 3.58 (6H, s, $N(CH_3)_2$), 4.05 (4H, m, $N(CH_2)_2$), 7.30 (2H, d, *J* 9.2, 3-H, 5-H), 7.49 (2H, d, *J* 9.2, 3′-H, 5′-H), 7.50–7.64 (6H, m, 2-H, 6-H, 2′-H, 6′-H, 3″-H, 5″-H), 7.80 (2H, t, *J* 7.2, 2″-H, 6″-H), 7.93 (1H, t, *J* 7.2, 4″-H). δ_C 24.4, 26.6, 40.8, 49.4, 114.4, 115.0, 128.4, 128.7, 129.2, 133.4, 135.0, 140.3, 141.0, 141.5, 156.7, 157.7, 176.5 (Found: C, 64.1; H, 6.4; N, 5.6. $C_{26}H_{29}ClN_2O_4$ requires C, 66.6; H, 6.2; N, 6.0%).

4-Dimethylamino-4′-morpholinotriphenylmethyl perchlorate 5j. Lustrous green crystals (58%) after recrystallisation from ethyl acetate. δ_H 3.63 (6H, s, $N(CH_3)_2$), 3.93 (4H, m, $O(CH_2)_2$), 4.01 (4H, m, $N(CH_2)_2$), 7.36 (2H, d, *J* 9.2, 3-H, 5-H), 7.43 (2H, d, *J* 9.2, 3′-H, 5′-H), 7.56–7.65 (6H, m, 2-H, 6-H, 2′-H, 6′-H, 3″-H, 5″-H), 7.81 (2H, t, *J* 7.2, 2″-H, 6″-H), 7.92 (1H, t, *J* 7.2, 4″-H). δ_C 41.1, 47.6, 66.7, 114.4, 115.2, 128.1, 128.5, 129.2, 133.6, 135.1, 140.2, 140.8, 141.9, 156.9, 158.5, 177.6 (Found: C, 63.2; H, 6.2; N, 5.4. $C_{25}H_{27}ClN_2O_5$ requires C, 63.8; H, 5.7; N, 6.0%).

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