Electronically asymmetric triphenylmethane dyes. Half-methoxy analogues of Malachite Green

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Abstract

A series of derivatives of 4-dimethylamino-4′-methoxytriphenylmethanol has been prepared and the electronic absorption spectra and lightfastness properties of the derived cationic dyes determined. The introduction of one terminal methoxy group results in an electronically unsymmetrical system, to which PMO treatment appears inapplicable. The effects of substitution on the values of $\lambda_{\max}(x)$ and $\lambda_{\max}(y)$ are accounted for in terms of bond rotation about essential double or single bonds in an unsymmetrical cyanine chromophoric system and by restoration of electronic symmetry. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Triphenylmethane dyes; Electronic asymmetry; Visible spectra; Cyanine-type chromogens; Brooker deviation; Lightfastness

1. Introduction

Applications of triarylmethane dyes have been limited as a result of their inherently poor lightfastness characteristics. As part of our investigations [1] into the synthesis and properties of triphenylmethane dyes with enhanced photostability, we have examined the colour and lightfastness properties of dyes based upon the 4-dimethylamino-4′-methoxytriphenylmethyl cation system (**1**) [2–5], in which one of the terminal dimethylamino groups of Malachite Green (**2**) has been replaced by a methoxy moiety. Coherent series of substituted analogues (**3**), (**4**) and (**5**) have been prepared and their electronic spectra measured to establish colour–structure relationships in this system. The lightfastness parameters of the dye cations on basic-dyeable polyacrylonitrile have also been determined.

2. Results and discussion

The dye bases (**6**), (**7**) and (**8**) were prepared by reaction of an organolithium compound with the appropriate ketone. 4-Dimethylamino-4′-methoxybenzophenone [6] was prepared from 4-methoxybenzanilide and *NN*-dimethylaniline using Vilsmeier methodology [7]. It was obtained more efficiently

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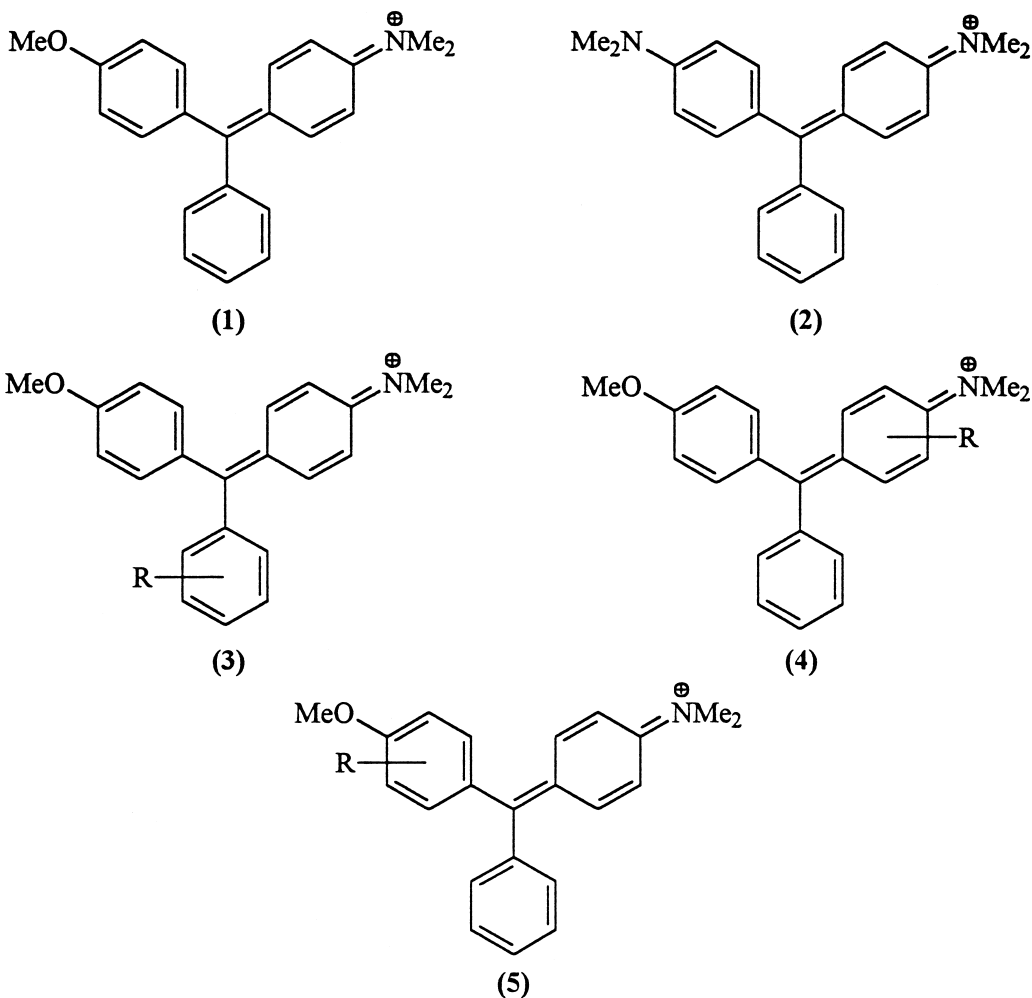
from the reaction of 4-methoxyphenyllithium with 4-dimethylaminobenzonitrile. Reaction of the benzophenone with 2-, 3- and 4-substituted phenyllithiums derived from the correspondingly substituted bromobenzenes gave the phenyl-ring-substituted dye bases (6). Dye bases (7) were obtained from the reaction of 4-methoxybenzophenone with a substituted derivative of 4-dimethylaminophenyllithium generated from the corresponding 4-bromo-*NN*-dimethylaniline and the butyllithium–TMEDA complex [8].

4-Dimethylamino-3,5-diethyl-4′-methoxytriphenylmethanol [(7) R = 3,5-di-CH$_2$CH$_3$] resulted from the interaction of 4-methoxyphenyllithium with 4-dimethylamino-3,5-diethylbenzophenone (9) obtained

from 4-dimethylamino-3,5-diethylbenzonitrile and phenyllithium. Reaction of 4-dimethylaminobenzophenone with 2- and 3- substituted derivatives of 4-methoxyphenyllithium, prepared from the corresponding 4-bromomethoxybenzene and the butyllithium–TMEDA complex at 0°C, gave the dye bases (8). 2′,4′-Dimethoxy-4-dimethylaminotriphenylmethanol [(8) R = 2′-OCH$_3$] was prepared from 4-dimethylaminophenyllithium and 2,4-dimethoxybenzophenone [9]. Preparative and analytical data for the dye bases are collated in Table 1.

For purification, dye bases [(8) R = 3′-CH$_3$, R = 3′-CH$_2$CH$_3$, R = 3′-CH(CH$_3$)$_2$] were converted into their respective cations by dissolution in ethanoic acid and isolated as the perchlorate salts.

(6)

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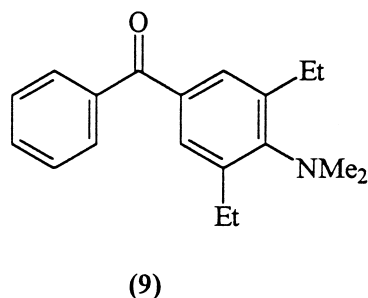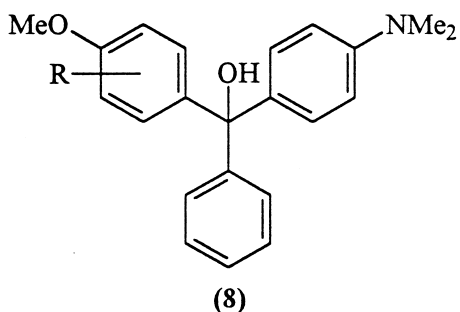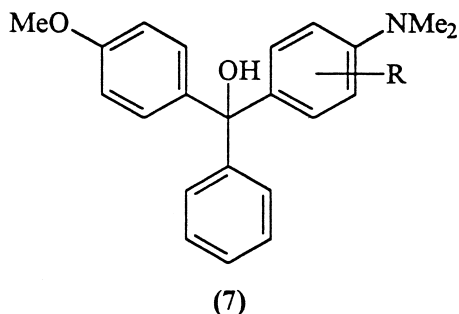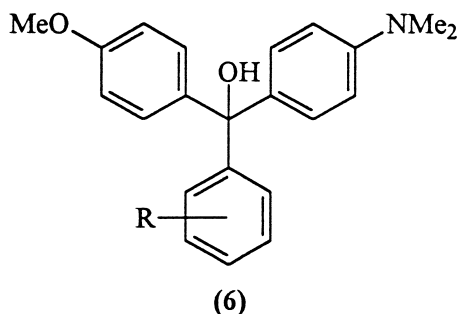
The perchlorates of cations [(**5**) R = 3′-CH$_2$CH$_3$, R = 3′-CH(CH$_3$)$_2$] were then converted into their respective methyl ethers by treatment with sodium methoxide in methanol. The data for these compounds are presented in Table 2.

The dye cations (**3**), (**4**) and (**5**) were obtained from the dye bases (**6**), (**7**) and (**8**) and the methyl ethers by dissolution in 98% ethanoic acid [10]. The spectral data for the dye cations are presented in Table 3.

The 4-dimethylamino-4′-methoxytriphenylmethyl cation [(**3**) R = H] displays an absorption spectrum typical of dyes of the Malachite Green type with two distinct bands in the visible region although the solution is red. The long-wavelength absorption, the x-band (513.5 nm), dominates the smaller y-band (382.5 nm) and both bands are broadened considerably and exhibit hypsochromic shifts compared to those of Malachite Green (621 nm and 427 nm). Furthermore, the presence of a band at 263 nm indicates the presence of unionised dye base [(**6**) R = H, λ_{max} = 269 nm] and it is clear that the replacement of one of the terminal dimethylamino groups of Malachite Green by a methoxy group leads to a displacement of the equilibrium between the dye base [(**6**) R = H] and the dye

cation [(**3**) R = H] in favour of the former species. The absolute values of molar absorptivity of the dye cations under investigation are therefore not available.

The 4-dimethylamino-4′-methoxytriphenylmethyl cation [(**3**) R = H] contains terminal groups of differing basicities and the x-band, attributed to polarisation along the x-axis, shows a large hypsochromic shift (107.5 nm) compared to Malachite Green. The value of $\lambda_{max}(x)$ does not correspond to the harmonic mean of the wavelengths of maximum absorption of the parent dyes, (**2**) and the 4,4′-dimethoxytriphenylmethyl cation [$\lambda_{max}(x)$ = 501 nm], and exhibits a 'Brooker' deviation [11–13] of 43.5 nm. The deviation is indicative of the presence of an unsymmetrical cyanine-type chromogen, rather than an electronically symmetrical system, such as Malachite Green, and implies the predominance of one canonical form (**10**) in the ground state of the molecule (Fig. 1) and bond order alternation. Castelino and Hallas [14] have used similar considerations to explain the spectroscopic properties of unsymmetrical derivatives of Malachite Green containing a hindered terminal dimethylamino group and the julolidyl moiety. This loss of electronic symmetry destroys the relationship of

Table 1
Preparative and analytical data for substituted derivatives of 4-dimethylamino-4′-methoxytriphenylmethanol

R in (6), (7) & (8)	m.p. (°C)	Yield (%)	Found (%)					Required (%)				
			C	H	N	F	Br	C	H	N	F	Br
2″-CH$_3$	120–121	65	79.2	7.30	3.91	–	–	79.5	7.25	4.03	–	–
3″-CH$_3$	92–94	83	79.6	7.25	4.05	–	–	79.5	7.25	4.03	–	–
4″-CH$_3$	121–122	85	79.3	7.25	4.05	–	–	79.5	7.25	4.03	–	–
2″-CH$_2$CH$_3$	97	43	79.7	7.55	4.1	–	–	79.7	7.53	3.87	–	–
3″-CH$_2$CH$_3$	Oil	5	79.4	7.6	3.66	–	–	79.7	7.53	3.87	–	–
4″-CH$_2$CH$_3$	115	28	79.7	7.45	4.10	–	–	79.7	7.53	3.87	–	–
2″-CH(CH$_3$)$_2$	150	72	79.6	7.80	3.5	–	–	80.0	7.78	3.73	–	–
3″-CH(CH$_3$)$_2$	97	55	79.9	7.70	3.84	–	–	80.0	7.78	3.73	–	–
4″-CH(CH$_3$)$_2$	97	45	80.0	7.82	3.62	–	–	80.0	7.78	3.73	–	–
3″-C(CH$_3$)$_3$	122	51	79.9	8.00	3.45	–	–	80.2	8.02	3.60	–	–
4″-C(CH$_3$)$_3$	112	45	80.1	7.95	3.60	–	–	80.2	8.02	3.60	–	–
3″-Br	112	92	64.1	5.40	3.30	–	19.4	64.1	5.38	3.40	–	19.4
4″-Br	125	75	64.3	5.35	3.30	–	19.4	64.1	5.38	3.40	–	19.4
3″-Si(CH$_3$)$_3$	Oil	73	74.0	7.55	3.52	–	–	74.0	7.70	3.45	–	–
4″-Si(CH$_3$)$_3$	122–123	76	73.8	7.81	3.25	–	–	74.0	7.70	3.45	–	–
2″-CF$_3$	89–90	88	69.0	5.65	3.55	13.9	–	68.8	5.52	3.49	14.2	–
3″-CF$_3$	97	36	69.1	5.62	3.60	14.2	–	68.8	5.52	3.49	14.2	–
4″-CF$_3$	118–119	58	69.0	5.57	3.45	14.0	–	68.8	5.52	3.49	14.2	–
2-CH$_3$	117	12	79.4	7.18	4.17	–	–	79.5	7.25	4.03	–	–
2-CF$_3$	124	66	68.9	5.37	3.57	14.5	–	68.8	5.52	3.49	14.2	
3-CH$_3$	Oil	43	79.4	7.31	3.92	–	–	79.5	7.25	4.03	–	
3-CH$_2$CH$_3$	Oil	49	79.5	7.58	3.71	–	–	79.7	7.53	3.87	–	–
3-CH(CH$_3$)$_2$	91	40	80.1	7.79	3.86	–	–	80.0	7.78	3.73	–	–
3,5-di-CH$_3$	71	69	79.7	7.50	3.85	–	–	79.7	7.53	3.88	–	–
3,5-di-CH$_2$CH$_3$	Oil	89	81.0	8.31	3.68	–	–	80.2	8.02	3.60	–	–
3,5-di-CH(CH$_3$)$_2$	152	44	80.4	8.45	3.48	–	–	80.5	8.44	3.35	–	–
3′-C(CH$_3$)$_3$	118	37	80.0	7.95	3.65		–	80.2	8.02	3.60	–	–
3″,5″-di-CH$_3$	161	66	79.4	7.50	3.89	–	–	79.7	7.53	3.88	–	–
3″,5″-di-CH$_2$CH$_3$	101	44	80.1	8.05	3.42	–	–	80.2	8.02	3.60	–	–
3″,5″-di-CH(CH$_3$)$_2$	131–132	5	80.4	8.41	3.28	–	–	80.5	8.44	3.35	–	–
3″,5″-di-C(CH$_3$)$_3$	146–147	45	80.8	8.90	2.98	–	–	80.9	8.82	3.14		
2′-CH$_3$	114	52	79.3	7.35	4.15	–	–	79.5	7.25	4.03	–	–
2′-OCH$_3$	121–122	80	76.2	7.11	3.97	–	–	76.0	6.93	3.85	–	–
2′,6′-di-OCH$_3$	150	51	73.3	6.85	3.45	–	–	73.2	6.92	3.56	–	–

Table 2
Preparative and analytical data for substituted derivatives of 4-dimethyamino-4′-methoxytriphenylmethyl methyl ether

R	m.p. (°C)	Yield	Found (%)				Required (%)			
			C	H	N	Cl	C	H	N	Cl
3′-CH$_3$[a]	–	53	63.8	5.77	3.38	8.25	64.3	5.63	3.26	8.25
3′-CH$_2$CH$_3$	Oil	6	79.7	7.85	3.62	–	80.0	7.78	3.73	–
3′-CH(CH$_3$)$_2$	Oil	24	79.8	8.14	3.55	–	80.2	8.02	3.60	–

[a] Isolated as perchlorate salt.

Table 3
Spectral data of derivatives of the 4-dimethylamino-4′-methoxytriphenylmethyl cation in 98% ethanoic acid

R in (3), (4) & (5)	x-Band		y-Band		
	λ_{max} (nm)	$10^{-4}\epsilon_{max}$	λ_{max} (nm)	$10^{-4}\epsilon_{max}$	$\epsilon_{max}(x):\epsilon_{max}(y)$
H	513.5	4.0	382.5	1.5	2.7
2″-CH$_3$	506	3.6	376	1.1	3.3
3″-CH$_3$	515	4.0	387.5	1.5	2.7
4″-CH$_3$	518.5	4.1	394	1.8	2.2
2″-CH$_2$CH$_3$	505	4.1	381	1.0	4.1
3″-CH$_2$CH$_3$	515	2.6	387.5	1.0	2.6
4″-CH$_2$CH$_3$	517.5	4.3	394	1.9	2.3
2″-CH(CH$_3$)$_2$	503.5	4.0	379	1.0	4.0
3″-CH(CH$_3$)$_2$	515.5	4.0	388	1.5	2.7
4″-CH(CH$_3$)$_2$	519	4.2	395	1.9	2.2
3″-C(CH$_3$)3	515.5	4.0	388	1.5	2.7
4″-C(CH$_3$)$_3$	519	4.1	395	1.9	2.2
3″-Br	512	3.7	382	1.2	3.0
4″-Br	516	3.9	389	1.7	2.3
3″-Si(CH$_3$)$_3$	515.5	3.6	384.5	1.5	2.4
4″-Si(CH$_3$)$_3$	517.5	4.0	390.5	1.8	2.2
2″-CF$_3$	500	3.8	368.5	0.8	4.8
3″-CF$_3$	510.5	3.7	376.5	1.1	3.4
4″-CF$_3$	510.5	3.7	376	1.1	3.4
2-CH$_3$	534.5	3.3	391	1.4	2.4
2-CF$_3$	592	3.2	416	1.9	1.7
3-C$_{H3}$	523	0.7	384.5	0.2	3.5
3-CH$_2$CH$_3$	522.5	0.5	383.5	0.2	2.5
3-CH(CH$_3$)$_2$	525	0.2	384	0.09	2.2
3,5-di-CH$_3$	~508	0.03	~385	0.01	3.0
3,5-di-CH$_2$CH$_3$	~512	0.04	~378	0.015	2.7
3,5-di-CH(CH$_3$)$_2$	~508	0.03	~375	0.01	3.0
3′-CH$_3$	522.5	3.4	390.5	1.1	3.0
3′-CH$_2$CH$_3$	523	3.6	391	1.2	3.0
3′-CH(CH$_3$)$_2$	524	3.9	391	1.4	2.8
3′-C(CH$_3$)$_3$	527.5	4.2	391.5	1.4	3.0
3′,5′-di-CH$_3$	493.5	3.5	373	1.0	3.5
3′,5′-di-CH$_2$CH$_3$	494.5	4.9	372	1.3	3.8
3′,5′-di-CH(CH$_3$)$_2$	495	3.5	372	1.0	3.4
3′,5′-di-C(CH$_3$)$_3$	501	3.8	378	1.1	3.4
2′-CH$_3$	504	3.3	395	1.4	2.4
2′-OCH$_3$	531	3.4	409	1.3	2.6
2′,6′-di-OCH$_3$	527	2.7	404	1.6	1.7

Malachite Green cations to odd-alternant hydrocarbon anions so that simple perturbational theory [15] cannot be applied, but the application of the Pariser–Parr–Pople approach [16] has provided an explanation of the spectrum of the parent system (1).

The spectral responses of the x-band in derivatives of Malachite Green with substituents in the 3- and 4-positions in the phenyl ring are well known [17–19]: electron-withdrawing groups produce a bathochromic shift of the x-band when compared with the parent cation, and electron-releasing groups elicit a hypsochromic response. Since the π-electrons of the phenyl ring are not involved directly in the x-band transition [20], the absorption frequency of this band varies linearly with the appropriate Hammett substituent constant. Consideration of the $\lambda_{max}(x)$ values for the
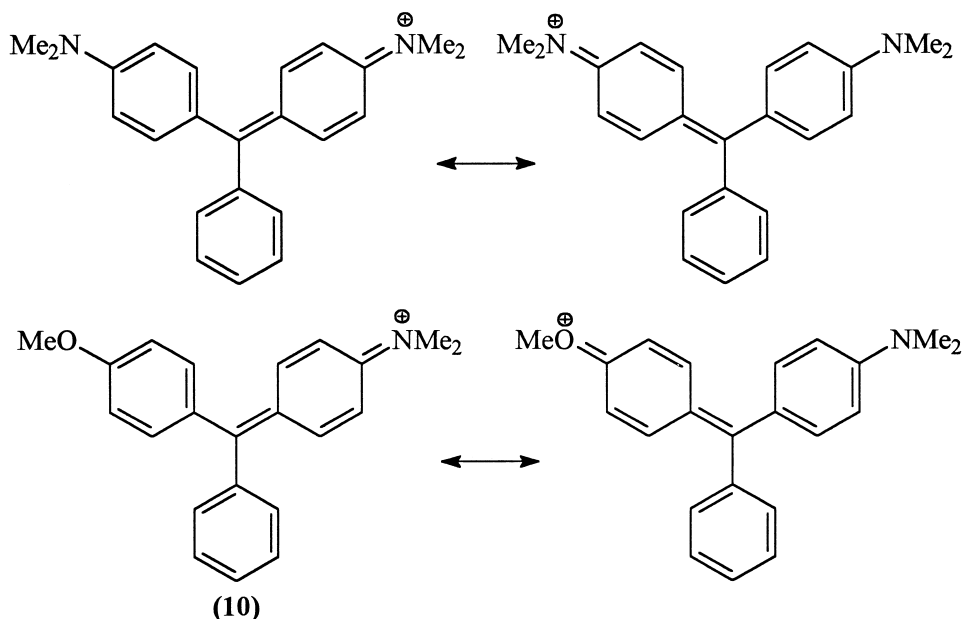
(10)

Fig. 1.

Table 4

Spectral shifts of phenyl-ring substituted derivatives of the Malachite Green and 4-dimethylamino-4′-methoxy-triphenylmethyl cations in 98% ethanoic acid relative to the parent cations

Substituent	Malachite Green cation λ (nm)		(3) λ (nm)	
	x-Band	*y*-Band	*x*-Band	*y*-Band
meta-CH₃	−2.5	+6.0	+2.0	+5.0
para-CH₃	−4.5	+10.0	+5.0	+11.5
meta-CH₂CH₃	−1.0	+4.0	+2.0	+5.0
para-CH₂CH₃	−3.5	+12.0	+4.5	+11.5
meta-CH(CH₃)₂[a]	−1.0	+3.0	+2.0	+5.5
para-CH(CH₃)₂[a]	−3.5	+12.0	+6.0	+12.5
meta-C(CH₃)₃	−2.0	+3.0	+2.0	+5.5
para-C(CH₃)₃	−5.0	+13.0	+6.0	+12.5
meta-Br	+9.0	0.00	−1.0	−0.5
para-Br	+7.0	+8.0	+3.0	+6.5
meta-CF₃	+13.0	−3.0	−3.0	−6.0
para-CF₃	+16.0	−3.0	−3.0	−6.5

[a] Unpublished results for the Malachite Green system.

3″- and 4″-substituted derivatives of the 4-dimethylamino-4′-methoxytriphenylmethyl cation (3) demonstrates contrary behaviour to the electronically-symmetrical Malachite Green system in that electron-releasing groups produce a bathochromic effect on the *x*-band and electron-withdrawing groups cause a hypsochromic effect. Furthermore, the linear relationship between $\lambda_{max}(x)$ and the Hammett σ constant is no longer valid. It is possible that the presence of an electron-releasing group in the phenyl ring of the 4-dimethylamino-4′-methoxytriphenylmethyl cation (3) to some extent restores the electronic symmetry of the system resulting in the observed small bathochromic effect. In the Malachite Green series, the *y*-band absorption arises from a $\pi \rightarrow \pi^*$ transition [20]. The energy of the π-orbital is modified by the introduction of substituents in the phenyl ring so that there is no simple relationship between $\lambda_{max}(y)$ and the substituent constant. A close correspondence exists between the spectral shifts of the *y*-bands of the 3′- and 4′-substituted derivatives of the 4-dimethylamino-4′-methoxytriphenylmethyl cation (3) and those of the correspondingly-substituted Malachite Green cations, suggesting the similar origins of the *y*-band transition (Table 4).

The spectral responses to *ortho*-substitution in the phenyl ring of the 4-dimethylamino-4′-methoxytriphenylmethyl cation (3) are hypsochromic shifts of both the *x*- and *y*-bands, irrespective of the nature

of the substituent, when compared with both the parent cation [(**3**) R = H] and the corresponding 4‴-substituted analogue. The spectral changes in 2-substituted derivatives of the Malachite Green cation have been rationalised in terms of the size of the *ortho*-substituents [17–19,21], but these steric effects are not completely understood. Rotation of the *ortho*-substituted phenyl ring results in hypsochromic and hypochromic effects on the *y*-band, but bathochromic and hyperchromic changes to the *x*-band. The hyperchromic effect can be correlated with the van der Waals' radius of the *ortho*-substituent. The steric effects of substitution in unsymmetrical cyanines exhibiting bond alternation result in bathochromic shifts of λ_{max} for rotation about a double bond and hypsochromic shifts if steric constraints cause rotation about a single bond [22,23]. Hence, in 2″-substituted derivatives of the 4-dimethylamino-4′-methoxytriphenylmethyl cation (**3**), the rotation of the methoxyphenyl ring would be expected to produce a hypsochromic shift of the *x*-band if the system possesses bond alternation along the *x*-axis, and a hypochromic effect on $\varepsilon_{max}(x)$, when compared with the 4″-isomers, which is consistent with some rotational adjustment in the *x*-axis. However, the predicted [24] bathochromic movement and hyperchromic effect on the *y*-band are not observed. Rotation of the *ortho*-substituted phenyl ring about a single bond, resulting in deconjugation from the *x*-axis [25], should induce the observed hypsochromic shifts in $\lambda_{max}(x)$ and $\lambda_{max}(y)$ and this adjustment appears to dominate the conformational changes required by the steric demands of the *ortho*-substituent.

The ^{1}H-NMR spectrum of the dye base [(**6**) R = 2″-CH(CH$_3$)$_2$] shows that the two methyl groups of the isopropyl moiety, each appearing as a doublet as result of coupling to the methine hydrogen, have measurably different chemical shifts. This feature is not apparent in the spectra of the corresponding *meta* and *para* isomers even though all three molecules are chiral. The behavior observed for the *ortho* isomer may be attributable to the closer proximity of these groups to aromatic rings of differing electronic character.

The introduction of substituents in the 2-position in the 4-dimethylamino-4′-methoxy- triphenylmethyl

cation [(**4**) R = 2-CH$_3$, R = 2-CF$_3$] has a significant effect on the visible spectra (Table 3). The bathochromic shifts of $\lambda_{max}(x)$ are consistent with rotation about an essential double bond in an electronically-unsymmetrical system [23,24] but, whereas the rotation of the substituted dimethylaminophenyl ring produces an electronically-unsymmetrical system in the Malachite Green series [21], rotation of the corresponding ring in the 2-substituted-4-dimethylamino-4′-methoxytriphenylmethyl cations indicates a significant increase in the electronic symmetry of the *x*-axis as evidenced by the diminution of the Brooker deviation (Table 5). The large bathochromic shifts of the corresponding *y*-bands for these cations implies that a significant transfer of charge from the substituted dimethylaminophenyl ring to the phenyl ring has occurred and is supported by the diminution of the $\varepsilon_{max}(x)$: $\varepsilon_{max}(y)$ ratios [24].

The introduction of substituents into positions *ortho* to the terminal dimethylamino group causes the group to twist out of conjugation with it aromatic ring resulting in a marked reduction in the stability of the univalent cation, as shown by the low values for $\varepsilon_{max}(x)$ and $\varepsilon_{max}(y)$, and an increase in electronic symmetry along the *x*-axis. The cations [(**4**) R = 3-CH$_3$, R = 3-CH$_2$CH$_3$, R = 3-CH(CH$_3$)$_2$] all exhibit bathochromic shifts of the *x*-band, while the values of $\lambda_{max}(y)$ are relatively unchanged. Restoration of electronic symmetry, albeit with weak electron-donating groups in contrast to the Malachite Greens, explains these spectral changes [26,27]. The 3,5-dialkyl derivatives of (**4**) possess terminal dimethylamino groups with severe steric crowding and the formation of the cation in 98% ethanoic acid is almost completely suppressed. Attempts to displace the equilibrium in favour of the cation [(**4**) R = 3,5-di-CH$_3$] by heating the corresponding dye base to 60°C in 98% ethanoic acid, resulted in irreversible hypsochromic shifts $\lambda_{max}(x)$ and $\lambda_{max}(y)$, with further diminution of the respective ε_{max} values. The spectral parameters for the 3,5-dialkyl derivatives should be considered unreliable.

The hypsochromic shift of $\lambda_{max}(x)$ in the spectrum of the 4-dimethylamino-4′-methoxy-2′-methyltriphenymethyl cation [(**5**) R = 2′-CH$_3$] is in accord with the rotation of the substituted methoxyphenyl

Table 5
Brooker deviations of $\lambda_{\max}(x)$ of some triphenylmethyl cations

Cation	$\lambda_{\max}(x)$ (nm)	$\Delta\lambda$ (nm) (harmonic mean)
Malachite Green	621	
4,4′-Dimethoxytriphenymethyl cation	501	
4-Dimethylamino-4′-methoxytriphenylmethyl cation	513.5	−43.5
Bis-(4-dimethylamino-2-methylphenyl)phenylmethyl cation	634	
4,4′-Dimethoxytriphenymethyl cation	501	
4-Dimethylamino-4′-methoxy-2-methyltriphenylmethyl cation	534	−25
Bis-(4-dimethylamino-2-trifluoromethylphenyl)phenylmethyl cation	678	
4,4′-Dimethoxytriphenymethyl cation	501	
4-Dimethylamino-4′-methoxy-2-trifluoromethyltriphenylmethyl cation	592	+16

ring about a single bond in an electronically unsymmetrical system and the bathochromic effect on the *y*-band could result from increased electronic symmetry along the *y*-axis, which is indicated by the decreased $\varepsilon_{\max}(x)$: $\varepsilon_{\max}(y)$ ratio. In contrast, the introduction of a 2′-methoxy group [(**5**) R = 2′-OCH$_3$], of similar effective steric demand to the methyl group, produces a bathochromic shift of both the *x*-band (17.5 nm) and *y*-band (26.5 nm) and can be attributed to a decrease in electronic asymmetry resulting from the mesomeric release by the substituent. However, the increased electronic symmetry of the *y*-axis appears to remain unchanged from consideration of the $\varepsilon_{\max}(x)$: $\varepsilon_{\max}(y)$ ratio but, since the *y*-band appears as a shoulder on the *x*-band, the intensity ratio may be affected. Further substitution by a methoxy group at the other *ortho* position [(**5**) R = 2′,6′-di-OCH$_3$] results in a small hypsochromic movement of the *x*- and *y*-bands compared to the mono-substituted compound. Hence, the steric effect of di-*ortho* substitution appears to predominate over the enhanced electron release. The spectra of *meta* alkyl substituted derivatives [(**5**) R = 3′-CH$_3$, R = 3′-CH$_2$CH$_3$, R = 3′-CH(CH$_3$)$_2$, R = 3′-C(CH$_3$)$_3$] all show bathochromic shifts of both $\lambda_{\max}(x)$ and $\lambda_{\max}(y)$ when compared with the parent ion (**1**) and, in contrast to the 3-substituted compounds (**4**), there is only a small reduction in intensity. Again these results are in accord with some restoration of electronic symmetry. Indeed, the bathochromic shifts of the *x*-band increase in keeping with the inductive electron releasing ability of the alkyl groups [28], with the 3′-*t*-butyl-4-dimethylamino-4′-methoxytri-

phenylmethyl cation [(**5**) R = 3′-C(CH$_3$)$_3$] displaying the greatest red shift and the largest incremental shift (+3.5 nm), after the initial introduction of the 3′-methyl group (+8 nm) into the parent system. Unlike the dimethylaminophenyl group, where substitution *ortho* to the amino group results in steric interaction and deconjugation, it is possible for the methoxy group to adopt a configuration where steric interactions with an *ortho* group are reduced to a minimum and conjugation maintained [29–36] or even enhanced [37]. Hence, it is possible to speculate that the introduction of the methyl group into the 3′-position reduces the rotational freedom of the terminal methoxy group and enhances the interaction ($p-\pi$) with the aromatic ring. Since the ethyl and isopropyl groups can adopt conformations such that spatial conflict can occur with a hydrogen atom, rather than with a methyl group [38], there is a minimal change in $\lambda_{\max}(x)$ (~1 nm) for the sequential substitution, methyl, ethyl, isopropyl. Introduction of the *t*-butyl group, with its greater steric demands, further constricts the methoxy group, promoting greater resonance interaction with the carbocation centre and increased electronic symmetry as evidenced by the observed bathochromic shift of the *x*-band. Di-alkylation at the 3′- and 5′-positions [(**5**) R = 3′,5′-di-CH$_3$] causes hypsochromic shifts of both the *x*- (10 nm) and *y*-bands (9 nm) compared with the parent cation (**1**). Steric deconjugation of the methoxy group [30–33] and rotation about a single bond in an electronically-unsymmetrical cyanine [23] account for the blue shift of the *x*-band. Increase in the steric demands of the substituents,

concomitant with increasing electron release [(**5**) R = 3′,5′-di-CH_2CH_3, 3′,5′-di-$CH(CH_3)_2$, 3′,5′-di-$C(CH_3)_3$], evinces slight bathochromic shifts of the *x*-band when compared to cation [(**5**) R = 3′,5′-di-CH_3], culminating in the maximum relative red shift for di-*t*-butyl-substituted cation, which could indicate some restoration of electronic symmetry along the *x*-axis. An increase in the symmetry of the *y*-axis resulting from deconjugation of the terminal methoxy group is not apparent from the increased $\varepsilon_{max}(x){:}\varepsilon_{max}(y)$ ratios (ca. 3.5) for cations [(**5**) R = 3′,5′-di-CH_3, R = 3′,5′-di-CH_2CH_3, 3′,5′-di-$CH(CH_3)_2$, 3′,5′-di-$C(CH_3)_3$] compared to that of the parent dye (**1**) (ca. 2.8).

3. Lightfastness studies

The photofading characteristics of a selection of the dye cations on Orlon 42 were determined as described previously [1] and the results are displayed in Table 6.

The photofading mechanisms in triphenylmethane dyes have been reviewed [39] and, together with the characteristics of the supporting medium, the structure of the dye cation in terms of basicity has been shown to modify the photostability of the dye cation [40]. It is interesting to note that all the simple derivatives of the 4-dimethylamino-4′-methoxytriphenylmethyl cation examined show enhanced light fastness compared with Malachite Green, with the exception of the 4-dimethylamino-4′-methoxy-3-trifluoromethyltriphenylmethyl cation; this system bears the closest similarity to Malachite Green in that it exhibits the smallest Brooker deviation and appears to approach the electronic characteristics of a symmetrical cyanine.

4. Experimental

Absorption spectra were measured with Pye-Unicam SP8-150 for solutions of the dye bases, methyl ethers or perchlorate salt in 98% ethanoic acid. The spectrometer was standardised using 4′,4″ - bisdimethylamino - 4 - cyclopropyltriphenylmethanol (10^{-5} M in 98% ethanoic acid, $\lambda_{max}(x) = 615.5$ nm). ^{1}H-NMR spectra were determined in $CDCl_3$ solution using a Jeol PMX60 spectrometer; *J* values are given in Hz.

Dye bases were converted into the perchlorate salts and methyl ethers by standard procedures [41].

4-Bromo-2,6-diethyl-*NN*-dimethylaniline was prepared from 2,6-diethylaniline by modification of existing procedures [42,43] via use 2,4,4,6-tetrabromocyclohexa-2,5-dieneone [44] and trimethyl phosphate [45].

4.1. 4-Bromo-2,6-diethyl-NN-dimethylaniline

A stirred mixture of 4-bromo-2,6-diethylaniline (17.4 g; 0.0763 mol) and trimethyl phosphate (10.68 g; 0.1 mol) was heated to 180°C (0.5 h), maintained between 170°C and 180°C (2 h) and cooled to 60°C. The mixture was stirred (2 h) at 80°C with sodium hydroxide (15 g) in water (100 cm^3), poured into cold water (500 cm^3) and extracted into ether (4×25 cm^3). Removal of the solvent from the dried (Na_2SO_4) organic phase gave an oil which was distilled to yield 4-bromo-2,6-diethyl-*NN*-dimethylaniline (14.3 g; 71%), b.p. 106–108°C/2 mm Hg. δ_H 1.20 (6H, t, *J* 7.3, CH_2CH_3), 2.67 (4H, q, *J* 7.3, CH_2CH_3), 2.79 (6 H, s, NMe_2), 7.14 (2H, s, 3-H, 5-H). (Found: C, 55.8; H, 6.7; N, 5.4. $C_{12}H_{18}BrN$ requires C, 56.0; H, 7.0; 5.40%).

Table 6
Lightfastness ratings of some 4-dimethylamino-4′-methoxytriphenylmethyl cation derivatives on Orlon 42

R	Fastness	R	Fastness
2″-CH_3	7–8	2″-CF_3	7–8
3″-CH_3	7–8	3″-CF_3	7–8
4″-CH_3	7–8	4″-CF_3	7–8
2″-CH_2CH_3	7–8	2-CH_3	7–8
4″-CH_2CH_3	7–8	2-CF_3	4
2″-$CH(CH_3)_2$	6	3-$CH(CH_3)_2$	6–7
3″-$CH(CH_3)_2$	6	3′-CH_3	7–8
4″-$CH(CH_3)_2$	7	3′-$C(CH_3)_3$	7–8
3″-$C(CH_3)_3$	7	3′,5′-di-CH_3	7–8
4″-$C(CH_3)_3$	7	3′,5′-di-$C(CH_3)_3$	8
3″-Br	7	2′-CH_3	7–8
4″-Br	8	2′-OCH_3	7
4″-$Si(CH_3)_3$	7	2′,6′-di-OCH_3	7–8

4.2. 4-Dimethylamino-3,5-diethylbenzonitrile

A mixture of 4-bromo-2,6-diethyl-*NN*-dimethyl-aniline (10.24 g; 0.04 mol) and copper (I) cyanide 4.14 g; 0.046 mol) in dimethylformamide (7.0 cm^3) was heated under reflux (4 h), cooled, transferred to a warm solution of sodium cyanide (8.0 g) in water (25 cm^3) and shaken vigorously. The lower aqueous layer was separated, extracted with ether (3×10 cm^3) and discarded. The combined organic phases were dried (MgSO$_4$), and the solvent removed to leave a brown oil which was distilled and the fraction, b.p. 160–170°C/10 mm Hg collected. The semi-solid was thrice crystallised from light petroleum (b.p. 40–60°C) to yield white crystals of 4-dimethylamino-3,5-diethylbenzonitrile (5.1 g; 63%), m.p. 42°C. δ_H 1.22 (6 H, t, *J* 7.2, CH$_2$CH$_3$), 2.67 (4 H, q, *J* 7.2, CH$_2$CH$_3$), 2.84 (6 H, s, NMe$_2$), 7.32 (2 H, s, 2-H, 6-H). $\nu_{C\equiv N}$ (nujol mull) 2240 cm^{-1}. (Found: C, 77.0; H, 9.01, N, 13.8. C$_{13}$H$_{18}$N$_2$ requires C, 77.2; H, 8.97, N, 13.9%).

4.3. 4-Dimethylamino-3,5-diethylbenzophenone (9)

A solution of 4-dimethylamino-3,5-diethylbenzonitrile (4.04 g; 0.02 mol) in dry ether (25 cm^3) was added dropwise (0.5 h) to a solution of phenyllithium (0.02 mol) in dry ether (75 cm^3), the mixture was boiled under reflux (2 h) and then quenched with water (100 cm^3). Removal of the solvent from the dried (MgSO$_4$) organic phase gave a yellow oil which was boiled under reflux (4 h) in hydrochloric acid (6 M; 100 cm^3), cooled and diluted with water (200 cm^3). Basification with sodium hydroxide (7.5 M) liberated an oil which was extracted into ether (4×50 cm^3). Removal of the solvent from the dried (MgSO$_4$) organic phase afforded a semi-solid, which, on crystallisation from light petroleum (b.p. 40–60°C) and then from ethanol, yielded pale yellow needles of 4-dimethylamino-3,5-diethylbenzophenone (1.82 g; 32.3%), m.p. 60°C. (H 1.24 (6 H, t, *J* 7.2, CH$_2$CH$_3$), 2.74 (4 H, q, *J* 7.2, CH$_2$CH$_3$), 2.91 (6 H, s, NMe$_2$), 7.92 (7 H, m, Ar-H). (Found: C, 81.2; H, 8.21; N, 5.00. C$_{19}$H$_{23}$NO requires C, 81.10; H, 8.24; N, 4.97%).

4.4. General method for preparation of dye bases

A solution of butyllithium (12.5 cm^3; 1.6 M in hexane) in dry ether (25 cm^3) was added dropwise to a solution of 2-bromoisopropylbenzene (4.0 g; 0.02 mol) in dry ether (25 cm^3) at 35°C and the mixture stirred (0.5 h). A suspension of 4-dimethyl-amino-4′-methoxybenzophenone (3.5 g; 0.014 mol) in dry ether (25 cm^3) was added, the mixture stirred under reflux (0.5 h) and quenched with water (25 cm^3). Removal of the solvent from the dried (MgSO$_4$) organic phase gave an oil, which on crystallisation from light petroleum (b.p. 60–80°C):benzene (10:1), afforded white crystals of 4-dimethylamino-2″-isopropyl-4′-methoxytriphenyl-methanol (3.7 g, 72%), m.p. 150°C. δ_H 0.88 (3H, d, *J* 6.0, CH$_3$), 0.97 (3H, d, *J* 6.0, CH$_3$), 3.36 (1H, septet, *J* 6.0, CH), 3.76 (3H, s, OCH$_3$), 3.92 (6 H, s, NMe$_2$), 6.54–7.32 (12H, m, Ar-H).

Acknowledgements

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