249. *Steric Effects in Di- and Tri-arylmethanes. Part III.* Electronic Absorption Spectra of Derivatives of Malachite Green containing Substituents in the Phenyl Ring.*

By C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp.

Absorption spectra of derivatives of Malachite Green containing substituents in the phenyl ring have been examined. With the exception of the nitro-group, substituents in the 3- or 4-position have little effect on the maximum intensity of the first frequency band but they modify the position of the band to an extent which is linearly related to the appropriate Hammett substituent constant. Substituents in the 2-position, however, markedly increase the intensity of this band, and this increase varies directly with the van der Waals radius of the substituent except in the case of the t-butyl group. Substituents in the 2-position also bring about a bathochromic shift of the first band relative to that of the 4-substituted isomer.

An equilibrium between the methyl ether of the 2-hydroxy-derivative of Malachite Green base and the zwitterion (VII) in methanol is described.

Introduction of a substituent at the central carbon atom of a diphenylmethane dye brings about spectral changes caused by the donation or withdrawal of electrons and by a change in the molecular conformation. The central carbon atom is at an " inactive " position,[1] that is, one with unit π-electron density,[2] and molecular-orbital theory predicts [3] that substituents with $-E$ (electron-donating) activity should produce hypsochromic shifts whereas $+E$ or $\pm E$ substituents should produce bathochromic shifts. The crowding effect of substituents at the central carbon atom should also result in bathochromic shifts.[4] The purely electronic effect can be demonstrated by introducing a small group with a large $-E$ effect. Thus, Michler's Hydrol Blue (I; R = H; $\lambda_{\max.}$ 607·5 mμ) absorbs at much longer wavelength than its α-amino-derivative Auramine (I; R = NH_2; $\lambda_{\max.}$ 435 mμ), but a more versatile approach is to compare the positions of the first frequency band of derivatives of Malachite Green (II) containing substituents in the 3- and 4-position. Malachite Green shows two absorption bands in the visible region (Fig. 1), the major band corresponding to polarisation along the x-axis of the molecule,[5] the minor band corresponding to polarisation along the y-axis.

Contrary to a statement by Dewar,[3] the carbon atoms of the phenyl ring in Malachite Green cannot be divided into " active " and " inactive," the π-electron density being uniform,[2] so that alternation of electronic effect round the phenyl ring is not observed and it is found [6] that the spectral shifts brought about by substituents in the 3- or 4-position are directly proportional to the appropriate Hammett substituent constant,[7] the strongly conjugated 4-hydroxy- and 4-methoxy-group being excepted (Fig. 2). The effect of the last two groups is described better by the use of the electrophilic substituent constants evaluated by Brown.[8] The simplicity of this relation depends upon the fact that the first frequency band originates in a transition from the non-bonding molecular orbital to the first unoccupied molecular orbital and it is the energy of the latter orbital only which is changed by substituents, whereas the second frequency band originates

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* Part II, *J.*, 1960, 3790.

[1] Dewar, " Recent Advances in the Chemistry of Colouring Matters," *Chem. Soc. Special Publ.*, No. 4, 1956, p. 79.

[2] Itoh, *J. Phys. Soc. Japan*, 1957, **12**, 644.

[3] Dewar, *J.*, 1950, 2329.

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

[5] Bigeleisen and Lewis, *J. Amer. Chem. Soc.*, 1943, **65**, 2102.

[6] Barker, " Steric Effects in Conjugated Systems," ed. G. W. Gray, Butterworths, London, 1958, p. 38.

[7] Jaffé, *Chem. Rev.*, 1953, **53**, 222.

[8] Brown, " Steric Effects in Conjugated Systems," ed. G. W. Gray, Butterworths, London, p. 109.

in a transition from the highest occupied bonding orbital to the first unoccupied orbital, and the energies of both of these orbitals are changed by substituents.

TABLE 1. *Absorption max.* (mμ) ($10^{-4}\varepsilon$ *in parentheses*) *for derivatives of Malachite Green in 98% acetic acid.*

Subst.			Subst.		
None	621 (10·4);	427·5 (2·0)	4-Br	628 (10·4);	435 (2·3)
2-Me	622·5 (12·3);	420 (1·5)	2-I	635 (12·8);	417·5 (1·3)
3-Me	618·5 (10·6);	433 (2·2)	3-I	630·5 (10·3);	429 (1·9)
4-Me	616·5 (10·6);	437·5 (2·5)	4-I	628 (10·3);	437·5 (2·5)
2,6-Me_2	624 (13·2);	410 (1·2)	2-MeO	625 (11·5);	442 (1·3)
2-Bu^t	623·5 (11·8);	415 (1·4)	3-MeO	622·5 (10·7);	435 (1·8)
4-Bu^t	616 (10·4);	440 (2·6)	4-MeO	608 (10·6);	465 (3·4)
2-F	635 (11·3);	424 (1·6)	4-MeO-2-Me	614 (12·4);	460 (2·2)
3-F	630 (10·4);	426·5 (2·2)	2-OH	621 (11·4);	447·5 (1·3)
4-F	620 (10·6);	430·5 (2·1)	4-OH	602·5 (10·6);	470 (3·6)
2-Cl	635 (12·1);	415·5 (1·3)	4-OH-2-Me	610 (12·1);	465 (2·4)
3-Cl	630 (10·3);	426 (1·7)	2-NO_2	637·5 (9·8);	415 (1·2)
4-Cl	627·5 (10·4);	433 (2·2)	3-NO_2	637·5 (8·7);	425 (1·4)
2-Br	636 (12·3);	415 (1·3)	4-NO_2	645 (8·3);	425 (1·7)
3-Br	630 (10·4);	427·5 (1·8)			

FIG. 1. *Absorption spectra of* (1) *methyl 4′,4″-bisdimethylamino-2-hydroxytriphenylmethyl ether in methanol* [$10^{-2}\varepsilon$ *plotted*], *and* (2) *Malachite Green in 98% acetic acid.* (*Reproduced, with permission, from "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London,* 1959, p. 37.)

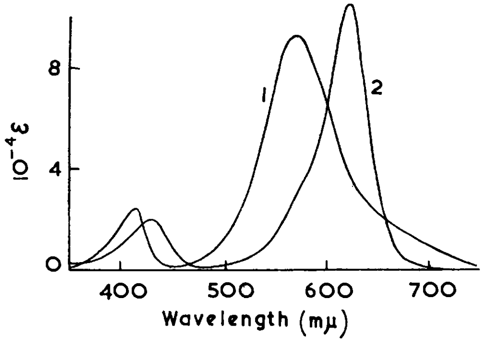
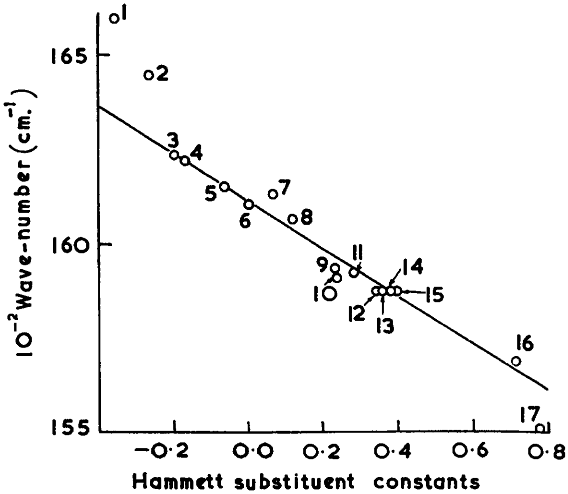
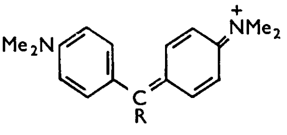


FIG. 2. *Relation between σ-constants and* $\lambda_{max.\,(x)}$ *of derivatives of Malachite Green.* 1, 4-OH; 2, 4-OMe; 3, 4-t-Bu; 4, 4-Me; 5, 3-Me; 6, unsubstituted; 7, 4-F; 8, 3-OMe; 9, 4-Cl; 10, 4-Br; 11, 4-I; 12, 3-F; 13, 3-I; 14, 3-Cl; 15, 3-Br; 16, 3-NO_2; 17, 4-NO_2. (*Reproduced, with permission, from "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London,* 1959, *p.* 38.)

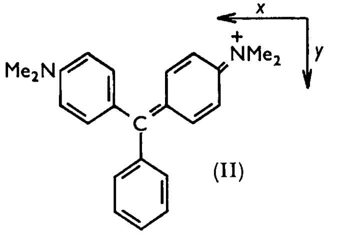


Substitution in the 2-position of Malachite Green produces a unique spectral response which is clearly illustrated by the effect of introducing the methyl group. Whereas 3- amd 4-methyl groups produce small hypsochromic shifts of the *x*-band and leave $\varepsilon_{max.\,(x)}$ essentially unchanged (106,000 compared with 104,000 for the parent dye), the 2-methyl group produces a small bathochromic shift and a marked increase in $\varepsilon_{max.\,(x)}$ (123,000; Table 1). This increase is exaggerated in the 2,6-dimethyl derivative ($\varepsilon_{max.\,(x)}$ 132,000). The 2-methyl group must produce a crowding effect and the bathochromic shift is consistent with rotation of the dimethylaminophenyl groups about the central bond, but this shift should be accompanied by a decrease in the value of $\varepsilon_{max.\,(x)}$ instead of the observed increase. The *y*-band responds to the introduction of the 2-methyl group by a hypsochromic shift and a marked reduction in intensity (Table 1), effects which are consistent with increased departure from molecular uniplanarity along the y-axis of the molecule and can be attributed to rotation of the dimethylaminophenyl or phenyl group about the central bonds. An alkyl group in the 3- or 4-position produces a bathochromic shift and increases the intensity of the y-band.

The spectra of the halogeno-derivatives of Malachite Green show the same general pattern as the spectra of the methyl derivatives (Table 1). The 3- and 4-halogeno-compounds give values of $\varepsilon_{\text{max.}\ (x)}$ in the range 103,000—106,000, whereas the 2-halogeno-derivatives give values (113,000—128,000) which vary directly with the van der Waals radii of the halogen atoms. Also, the x-bands of the 2-halogeno-derivatives occur at slightly longer wavelength than those of the 3-halogeno-isomers and these absorb at longer wavelength than the x-band of the parent dye owing to electron-withdrawal by the halogen. This bathochromic effect of the halogen is reduced in the 4-halogeno-compounds by mesomeric interaction with the central carbon atom (III; $R = H, X = Cl^+$). This mesomerism also results in increased intensity of the y-band (Table 1).



(I)



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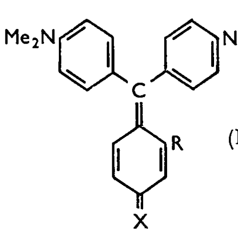
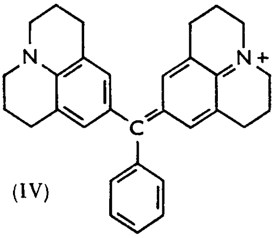
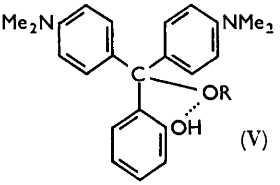


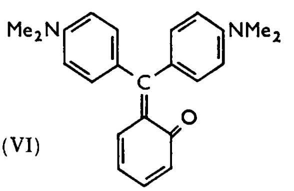
(III)



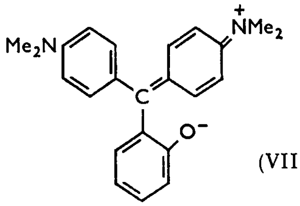
(IV)



(V)



(VI)



(VII)

The 2-methoxy- and the 2-hydroxy-derivative also show increased values of $\varepsilon_{\text{max.}\ (x)}$ (115,000 and 114,000, respectively), values which suggest that it is the radius (1·40 Å) of the oxygen atom alone which governs the absorption intensity, a view consistent with the value of 113,000 for $\varepsilon_{\text{max.}\ (x)}$ observed when the 2-fluoro-group (radius 1·35 Å) is present. The x-bands of the methoxy- and hydroxy-compound do not, however, show pronounced bathochromic shifts when compared with the x-band of the parent dye, but they do so when compared with the corresponding 4-substituted isomer in which mesomerism involving the terminal oxygen atom (III; $R = H$, $X = {}^+OH$ or ${}^+OMe$) reduces $\lambda_{\text{max.}\ (x)}$ and increases $\varepsilon_{\text{max.}\ (y)}$.

The correspondence between effective radius of a substituent in the 2-position and the value of $\varepsilon_{\text{max.}\ (x)}$ is inconsistent with the low value (118,000) observed with the 2-t-butyl derivative of Malachite Green, but it is probable that the exceptionally large t-butyl group produces exceptional conformational changes.

The 2-nitro-derivative of Malachite Green also shows an " *ortho*-effect," but the normal bathochromic shift is obscured by a reduction in the $+E$ activity of the nitro-group caused by partial rotation of this group about the bond joining it to the phenyl ring. Also, all the nitro-derivatives give x-bands of rather low intensity, a phenomenon which may be associated with the $+E$ activity of the nitro-group.

The crowding effect of *ortho*-groups in derivatives of triphenylmethanol decreases their stability relative to that of the corresponding carbonium ions. Thus, Deno *et al.*[9] obtained pK_b values of $-1{\cdot}96$ and $-2{\cdot}47$ for *o*- and *p*-tritolylmethanol, respectively, so that the increased values of $\varepsilon_{\max.\,(x)}$ observed with the 2-substituted derivatives of Malachite Green could be caused by displacement of the dye base–dye equilibrium. Interpreted in this way, the values of $\varepsilon_{\max.\,(x)}$ of 104,000 and 132,000 obtained with Malachite Green and its 2,6-dimethyl derivative, respectively, imply that in 98% acetic acid the parent dye is ionised only to the extent of 79%. If ionisation is so incomplete, the constancy of the values of $\varepsilon_{\max.\,(x)}$ obtained with the 3- and 4-substituted derivatives is surprising. The substituents would be expected to modify the position of the dye base–dye equilibrium, and the failure of the strongly conjugated 4-methoxy- and 4-hydroxy-group to do so is particularly significant. Further strong evidence for the view that these dyes are completely ionised in 98% acetic acid comes from the observation that the julolidine analogue (IV) of Malachite Green, to be described in a later paper, gives a value of $\varepsilon_{\max.\,(x)}$ of 109,000, and this dye is stabilised relative to its dye base by the release of strain which occurs when the nitrogen hybridisation changes from sp^3 to sp^2.

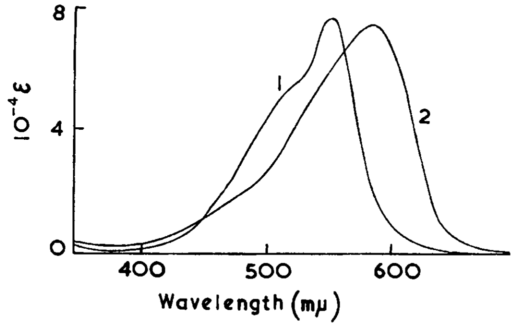


FIG. 3. *Absorption spectra of* (1) *4′,4″-bisdimethylaminofuchsone,* (2) *4′,4″-bisdimethylamino-2-methylfuchsone in methanol.*

Interpretation of the " *ortho*-effect " is made difficult by lack of knowledge of the precise conformational changes brought about by 2-substituents and of the exact rôle of the phenyl ring. The bathochromic shift of 13·5 mμ observed on passing from Michler's Hydrol Blue to Malachite Green is consistent with the predicted effect of a $\pm E$ substituent, but the crowding effect of the phenyl group should also be bathochromic, and until the relative magnitude of these spectral shifts is known it is difficult to assess the effect of rotating the phenyl ring in Malachite Green. A comparable study of bridged compounds of known conformation may shed light on the problem.

The colourless methyl ether of the 2-hydroxy-derivative of Malachite Green base (V; R = Me) is unusual in that it dissolves in methanol to give a blue solution with the spectrum shown in Fig. 1. It is probable that in methanol an equilibrium exists between the methyl ether and the merocyanine (VI) formed by elimination of methanol, but the spectrum ($\lambda_{\max.}$ 570, 415 mμ; ε 925, 240), although weak is very similar to that of Malachite Green and quite different from that (Fig. 3) of 4′,4″-bisdimethylaminofuchsone (III; R = H, X = O), observations which suggest that the highly polarised form (VII) makes the major contribution to the resonance hybrid. This high degree of polarisation is probably caused by the high energy of the *ortho*-quinonoid structure rather than by a steric effect because the hindered fuchsone (III; R = Me, X = O) gives a spectrum (Fig. 3) which is similar to that of the unhindered compound (III; R = H, X = O).

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[9] Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, 1954, **19**, 159.

It may be recalled that the 4-hydroxy-derivative of Malachite Green gives 4′,4″-bis·dimethylaminofuchsone when basified.

The ether (V; R = Me) separates from methanolic sodium methoxide as the free phenol, a fact most readily explained by intramolecular hydrogen bonding, but the OH stretching frequency, measured in a " Nujol " mull or potassium bromide pellet, is 3300 cm.$^{-1}$ which implies polymeric association, whereas dilution of a carbon tetrachloride solution from 5% to 0·1% changed the frequency only from 3320 to 3340 cm.$^{-1}$. The free dye base (V; R = H), which was not obtained analytically pure, was precipitated from an aqueous solution of the dye by means of sodium hydroxide. Methanolic solutions of the dye base and its methyl ether gave identical electronic absorption spectra.

Preparations.—The majority of the dyes was prepared by condensing the appropriate aldehyde with *NN*-dimethylaniline in acid solution and oxidising the resultant leuco-compound with lead dioxide in the presence of hydrochloric acid. The dyes were ultimately isolated as the readily purified methyl ethers of the dye bases. The preparation of the 3-nitro-derivative of Malachite Green, described in the Experimental section, represents a typical case.

The method of Rodd and Linch,[10] which uses the interaction of a mixture of Michler's ketone, sodium, and aryl halide in toluene, succeeded with 4-iodo-t-butylbenzene and 2-chloro-5-methoxytoluene but failed with 2-iodo-t-butylbenzene and 2-iodo-*m*-xylene, but by first converting these halides into the corresponding lithium compounds, interaction with Michler's ketone was achieved smoothly. Both of these processes yielded the dye base.

The 4-hydroxy- and the 4-hydroxy-2-methyl derivative of Malachite Green were isolated as the corresponding fuchsones (III; X = O, R = H and Me, respectively). These fuchsones, and the dye bases and their methyl ethers, regenerated the original dyes in the 98% acetic acid used for the spectral determinations.

EXPERIMENTAL

The following preparations are quoted as illustrations of the methods A, B, C, and D referred to in Table 3. For details see Tables 2 and 3.

Method A. Methyl 4,4′-Bisdimethylamino-3″-nitrotriphenylmethyl Ether.—*m*-Nitrobenzaldehyde (15·5 g.), ethanol (75 c.c.), *NN*-dimethylaniline (36·8 g.), and 36% hydrochloric acid (24·0 g.) were mixed and refluxed for 24 hr. The mixture was basified with aqueous ammonia, the excess of *NN*-dimethylaniline was removed by steam-distillation, and the residual base was crystallised from 1 : 1 benzene–ethanol.

This base (3·75 g.) was dissolved in water (60 c.c.) and 36% hydrochloric acid (4·0 g.). The stirred solution was cooled to 0° by addition of crushed ice, and an aqueous paste of lead dioxide, prepared [11] from lead nitrate (3·30 g.), was added in one portion. The resultant suspension was warmed to 60°, hydrated sodium sulphate (5·0 g.) was added, and the lead sulphate was removed. Hydrated sodium acetate (1·36 g.) followed by sodium chloride (15 g.) were then added, whereupon the dye separated as a tar which became crystalline overnight and was washed with aqueous sodium chloride (15%) and dried at 60°.

A solution of this dye (2·7 g.) in methanol (20 c.c.) was slowly added to methanol (40 c.c.) containing sodium methoxide (0·9 g.). The resultant *ether* separated as yellow crystals which were washed with methanol and crystallised from 3 : 1 methanol–benzene.

Method B. Methyl 4-Chloro-4′,4″-bisdimethylaminotriphenylmethyl Ether.—A warm solution of Michler's ketone (13·4 g.) in dry pyridine (70 c.c.) was added to the Grignard reagent from *p*-chloroiodobenzene (19·2 g.) and magnesium (2·4 g.) in ether (100 c.c.). After 20 min. the mixture was poured into aqueous ammonium chloride and 24 hr. later Michler's ketone was filtered off. The ether was removed, the residual dye base was dissolved in N-acetic acid, and the dye oxalate was precipitated by means of oxalic acid and ammonium oxalate. The dried oxalate was converted into the *ether* of the dye base as in method A.

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[10] Rodd and Linch, *J.*, 1927, 2174.

[11] Fierz-David and Blangey, " Fundamental Processes of Dye Chemistry," 1949, Interscience Publ. Ltd., London, p. 138.

Method C. 2,6-*Dimethyl-4′,4″-bisdimethylaminotriphenylmethanol.*—The lithium compound from 2-iodo-*m*-xylene (4·64 g.) in ether (20 c.c.) was added to a suspension of Michler's ketone (1·34 g.) in ether (50 c.c.). Water (250 c.c.) was added to the mixture after 1 hr. Removal of ether from the dried (Na_2SO_4) organic layer gave the base as a blue gum which crystallised from 75% ethanol.

TABLE 2. *Derivatives of the leuco-base of Malachite Green.*

		Found (%)					Required (%)			
Subst.	M. p.	C	H	N	Hal	Formula	C	H	N	Hal
2-F	131—131·5°	78·9	7·1	8·3		$C_{23}H_{25}FN_2$	79·3	7·2	8·0	
3-F	100·5—101	79·1	7·2	8·4		,,	79·3	7·2	8·0	
4-F	104—104·5	79·5	7·2	7·8		,,	79·3	7·2	8·0	
2-Br	150	67·7	6·5	6·9	18·9	$C_{23}H_{25}BrN_2$	67·5	6·2	6·8	19·5
3-Br	116	67·8	6·2	6·7	18·6	,,	67·5	6·2	6·8	19·5
4-Br	120—120·5[a]	67·4	6·2			,,	67·5	6·2	6·8	19·5
2-I	142·5—143	61·0	5·5	6·3	27·1	$C_{23}H_{25}IN_2$	60·5	5·5	6·1	27·8
3-I	147—147·5	60·3	5·7	6·2	28·2	,,	60·5	5·5	6·1	27·8
4-I	138·5—139	60·3	5·8	6·3	27·7	,,	60·5	5·5	6·1	27·8
4-OH-2-Me	184—185	79·7	7·8	7·8		$C_{24}H_{28}N_2O$	80·0	7·8	7·8	

[a] Dutt (*J.*, 1926, 1179) gives m. p. 128°.

TABLE 3. *Derivatives of Malachite Green* (*as base, methyl ether of the base, or fuchsone*).

			Found (%)					Required (%)			
Subst.	Method *	M. p.	C	H	N	Hal	Formula	C	H	N	Hal
Ethers											
2-F	A	156·5—157°	75·8	7·1	7·3		$C_{24}H_{27}N_2OF$	76·1	7·2	7·4	
3-F	A	149·5—150	76·4	7·3	7·1		,,	76·1	7·2	7·4	
4-F	A	136—136·5	76·2	7·3	7·1		,,	76·1	7·2	7·4	
2-Cl	A	143—143·5	73·1	6·8	7·2	9·2	$C_{24}H_{27}N_2OCl$	73·0	7·8	7·1	9·0
3-Cl	A	135—135·5	72·7	6·7	6·8	8·7	,,	73·0	6·8	7·1	9·0
4-Cl	B	135—136	73·0	6·6	7·2	8·8	,,	73·0	6·8	7·1	9·0
2-Br	A	132	65·8	6·2	6·1	17·8	$C_{24}H_{27}N_2OBr$	65·6	6·2	6·4	18·2
3-Br	A	124—124·5	65·6	6·3	6·1	18·0	,,	65·6	6·2	6·4	18·2
4-Br	A	128—129	65·8	6·3	6·1	17·8	,,	65·6	6·2	6·4	18·2
2-I	A	145·5—146	59·2	5·9	5·7	26·3	$C_{24}H_{27}N_2OI$	59·2	5·6	5·8	26·1
3-I	A	111·5—112	58·8	5·4	5·6	25·7	,,	59·2	5·6	5·8	26·1
4-I	A	135·5—136	59·0	5·7	5·9	27·2	,,	59·2	5·6	5·8	26·1
2-OH	A	138—140	76·6	7·5	7·2		$C_{24}H_{28}N_2O_2$	76·6	7·5	7·4	
2-OMe	B	104—106	76·9	7·9	7·2		$C_{25}H_{30}N_2O_2$	76·9	7·7	7·2	
3-OMe	A	92—93	76·6	7·8	7·0		,,	76·9	7·7	7·2	
4-OMe	B	104—104·5	76·7	7·6	7·1		,,	76·9	7·7	7·2	
2-NO_2	A	138—140	69·7	6·6	10·4		$C_{24}H_{27}N_3O_3$	71·1	6·7	10·4	
3-NO_2	A	122—123	71·3	6·7	10·4		,,	71·1	6·7	10·4	
4-NO_2	A	156—157	70·9	6·7	10·4		,,	71·1	6·7	10·4	
Bases											
4-OMe-2-Me	D	97—98	76·8	7·6	7·3		$C_{25}H_{30}N_2O_2$	76·9	7·8	7·2	
2-Me	A	139—140	79·4	7·8	7·7		$C_{24}H_{28}N_2O$	80·0	7·8	7·8	
3-Me	A	136—137	79·5	7·8	7·8		,,	80·0	7·8	7·8	
4-Me	A	159—160	79·8	7·8	7·9		,,	80·0	7·8	7·8	
2,6-Me_2	C	128—129	80·4	8·2	7·6		$C_{25}H_{30}N_2O$	80·2	8·1	7·5	
2-Bu^t	C	160—161	80·5	8·4	6·9		$C_{27}H_{34}N_2O$	80·6	8·5	7·0	
4-Bu^t	D	164—166	80·2	8·3	7·2		,	80·6	8·5	7·0	
Fuchsones											
4-OH	A	Decomp.	80·0	6·9	8·0		$C_2H_{24}N_2O$	80·2	7·0	8·1	
4-OH-2-Me	A	*ca.* 210	80·1	7·2	7·8		$C_{24}H_{26}N_2O$	80·4	7·3	7·8	

Method D. 4,4′-*Bisdimethylamino-4″-t-butyltriphenylmethanol.*—Sodium (4·6 g.), Michler's ketone (26·8 g.) and *p*-iodo-t-butylbenzene (18 c.c.) were refluxed in an atmosphere of nitrogen for 24 hr. Water (250 c.c.) was added to the reaction mixture and the dye base was isolated from the dried (Na_2SO_4) benzene layer and crystallised four times from ethanol containing a trace of sodium hydroxide.

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