The Effects of Cyclic Terminal Groups on the Electronic Absorption Spectra of Di- and Tri-phenylmethane Dyes

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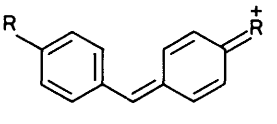
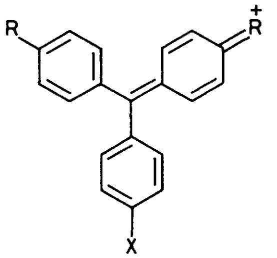
The spectral shifts of the first absorption bands brought about by cyclic terminal groups in analogues of Michler's Hydrol Blue, Malachite Green, and Crystal Violet are determined mainly by inductive effects. Dye cations containing terminal pyrrolidino substituents are significantly more stable than those possessing piperidino groups as a result of differences in basicity brought about by a change in size of the saturated heterocyclic ring.

It is well known[1] that alkylation of terminal amino groups in di- and tri-arylmethane dyes increases the electron-donating strength of the substituents and leads to bathochromic shifts of the long-wavelength absorption bands in accordance with perturbational molecular-orbital theory.[2] The influence of saturated heterocyclic terminal groups on the electronic absorption spectra of such basic dyes has not been investigated.

In view of the interesting spectral consequences of incorporating cyclic terminal groups into derivatives of 4-aminoazobenzene,[3] and bearing in mind the sensitivity of di- and tri-arylmethane dyes to structural and conformational changes,[4] various analogues of Michler's Hydrol Blue (**1**; R = NMe_2), Malachite green (**2**; R = NMe_2; X = H) and Crystal Violet (**2**; R = X = NMe_2) have now been examined.



(**1**)



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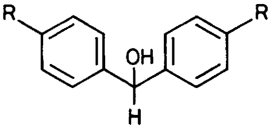

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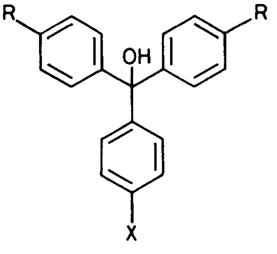

(**4**)

Experimental

Absorption spectra were measured for solutions of the dye bases in acetic acid containing varying amounts of water. Symmetrical triphenylmethanol derivatives were prepared by the reaction of an aryl-lithium with diethyl carbonate, whilst the unsymmetrical dye bases resulted from the reactions between derivatives of phenyl-lithium and appropriate ketones or esters.[5] Analogues of Michler's Hydrol Blue were obtained by borohydride reduction of the substituted benzophenones in propan-2-ol. Syntheses of the *N*-(4-bromophenyl) and *N*-(4-cyanophenyl) derivatives of pyrrolidine, piperidine, and morpholine have been described.[6] Michler's ketone was used as purchased, but commercially available 4,4′-bis(diethylamino)-benzophenone was purified by elution from alumina with chloroform and recrystallisation. Substituted benzophenones were prepared by nucleophilic substitution of 4,4′-dichloro- or 4,4′-difluoro-benzophenone[7] and, by way of confirmation of structure, from the reaction between the appropriately substituted benzonitrile and aryl-lithium.[8] 4-Dimethylamino-phenyl-lithium was prepared from the substituted bromobenzene and the butyl-lithium–TMEDA complex,[9] as were the corresponding diethylamino-,[10] pyrrolidino-, and morpholino-compounds, but 4-piperidinophenyl-lithium was derived using butyl-lithium alone. Yields, melting points, and microanalytical data for the dye bases are given in Table 1.

4,4′-Dipiperidinobenzophenone.—A mixture of 4,4′-dichlorobenzophenone (10.0 g, 0.04 mol), piperidine (15.8 cm^3, 0.16 mol) and tetramethylene sulphone (50 cm^3) was boiled under reflux for 24 h. The cooled reaction mixture was poured into ice–water (2 dm^3). The solid was collected, washed with water and ether, and recrystallised from acetone to give the ketone (52%), m.p. 140–142 °C as pale-yellow prisms (Found: C, 79.3; H, 7.8; N, 8.1. $C_{23}H_{28}N_2O$ requires C, 79.3; H, 8.1; N, 8.0%).

4,4′-Dimorpholinobenzophenone.—Cream needles from ethanol were prepared in a similar manner from 4,4′-difluorobenzophenone and morpholine (79%), m.p. 162–164 °C (Found: C, 71.5; H, 6.9; N, 7.8. $C_{21}H_{24}N_2O_3$ requires C, 71.6; H, 6.8; N, 8.0%).

Results and Discussion

The terminal nitrogen atoms in di- and tri-phenylmethane dyes are at 'active' positions[11] so that electron-donating substituents at these sites should produce bathochromic shifts. Replacement of the dimethylamino groups by diethylamino in Michler's Hydrol Blue, Malachite Green, and Crystal Violet to give the diethyl analogue (**1**; R = NEt_2),[12] brilliant green (**2**; R = NEt_2, X = H),[10] and ethyl violet (**2**; R = X = NEt_2), respectively, leads to the anticipated red shifts of λ_{max} in line with an increase in the electron-donating power of the alkyl groups; the first band also shows an increase in ε_{max} in each case (Table 2). The

Table 1. Preparative and microanalytical data for derivatives of Michler's Hydrol, Malachite Green base and Crystal Violet base.

Compound	M.p./°C	Yield/ (%)	Solvent	Found/% C	Found/% H	Found/% N	Formula	Required/% C	Required/% H	Required/% N
(**3**; R = NEt_2)	72–74	48	*d*	77.1	9.1	8.3	$C_{21}H_{30}N_2O$	77.3	9.3	8.6
(**3**; R = pyr)[a]	138	54	*e*	78.6	8.1	8.6	$C_{21}H_{26}N_2O$	78.3	8.1	8.7
(**3**; R = pip)[b]	117–118	95	*e*	79.1	8.7	8.1	$C_{23}H_{30}N_2O$	78.9	8.6	8.0
(**3**; R = morph)[c]	152–154	70	*f*	71.4	7.6	7.6	$C_{21}H_{26}N_2O_3$	71.2	7.3	7.9
(**4**; R = pyr; X = H)	160	42	*e*	81.1	7.6	6.8	$C_{27}H_{30}N_2O$	81.3	7.6	7.0
(**4**; R = pip; X = H	127	30	*d*	81.4	7.9	6.5	$C_{29}H_{34}N_2O$	81.6	8.0	6.5
(**4**; R = morph; X = H)	182–183	50	*g*	75.5	7.0	6.4	$C_{27}H_{30}N_2O_3$	75.5	7.0	6.5
(**4**; R = X = NEt_2)	135–136	68	*d*	78.6	9.1	8.6	$C_{31}H_{43}N_3O$	78.6	9.1	8.9
(**4**; R = X = pyr)	151	35	*h*	79.5	8.0	8.8	$C_{31}H_{37}N_3O$	79.6	8.0	9.0
(**4**; R = X = pip)	160	35	*d*	79.9	8.3	8.1	$C_{34}H_{43}N_3O$	80.1	8.5	8.2
(**4**; R = X = morph)	215	39	*g*	72.3	7.4	8.1	$C_{31}H_{37}N_3O_4$	72.2	7.2	8.2
(**4**; R = NMe_2; X = NEt_2)	155–156	45	*i*	77.6	8.4	10.0	$C_{27}H_{35}N_3O$	77.7	8.4	10.1
(**4**; R = NEt_2; X = NMe_2)	124–126	57	*i*	78.3	8.7	9.2	$C_{29}H_{39}N_3O$	78.2	8.8	9.4
(**4**; R = NMe_2; X = pyr)	124–126	68	*g*	78.2	8.0	10.0	$C_{27}H_{33}N_3O$	78.1	8.0	10.1
(**4**; R = NEt_2; X = pyr)	160–161	64	*j*	78.9	8.7	8.7	$C_{31}H_{41}N_3O$	79.0	8.8	8.9
(**4**; R = NMe_2; X = pip)	168	44	*d*	78.1	8.1	9.8	$C_{28}H_{35}N_3O$	78.3	8.2	9.8
(**4**; R = NEt_2; X = pip)	114–115	49	*d*	79.2	8.9	8.7	$C_{32}H_{43}N_3O$	78.9	9.0	8.5
(**4**; R = NMe_2; X = morph)	178	56	*j*	75.0	7.8	9.8	$C_{27}H_{33}N_3O_2$	75.2	7.7	9.8
(**4**; R = NEt_2; X = morph)	185–186d	58	*j*	76.1	8.5	8.5	$C_{31}H_{41}N_3O_2$	76.3	8.5	8.6
(**4**; R = pyr; X = NMe_2)	163	34	*j*	78.8	7.9	9.3	$C_{29}H_{35}N_3O$	78.9	8.0	9.5
(**4**; R = pyr; X = NEt_2)	145–147	68	*j*	79.4	8.4	8.8	$C_{31}H_{39}N_3O$	79.3	8.4	9.0
(**4**; R = pip; X = NMe_2)	156	61	*h*	79.3	8.4	8.9	$C_{31}H_{39}N_3O$	79.3	8.4	8.9
(**4**; R = pip; X = NEt_2)	132	55	*h*	79.6	8.6	8.2	$C_{33}H_{43}N_3O$	79.7	8.7	8.5
(**4**; R = morph; X = NMe_2)	185	58	*h*	73.7	7.5	9.2	$C_{29}H_{31}N_3O_3$	73.6	7.5	8.9
(**4**; R = morph; X = NEt_2)	191–192d	61	*j*	74.2	7.7	8.7	$C_{31}H_{39}N_3O_3$	74.2	7.8	8.4
(**4**; R = pyr; X = pip)	186–187	50	*k*	79.8	8.1	9.0	$C_{32}H_{39}N_3O$	79.8	8.2	8.7
(**4**; R = pyr; X = morph)	184 d.	37	*l*	77.4	6.9	9.0	$C_{31}H_{37}N_3O_2$	77.6	6.9	8.8
(**4**; R = pip; X = pyr)	123–125	38	*g*	79.9	8.1	8.4	$C_{33}H_{41}N_3O$	80.0	8.3	8.5
(**4**; R = pip; X = morph)	170	39	*m*	77.5	8.0	8.2	$C_{33}H_{41}N_3O_2$	77.5	8.1	8.2
(**4**; R = morph; X = pyr)	88–90	20	*k*	74.2	7.4	8.1	$C_{31}H_{37}N_3O_3$	74.5	7.5	8.4
(**4**; R = morph; X = pip)	107	39	*g*	74.6	7.6	8.0	$C_{32}H_{39}N_3O_3$	74.8	7.7	8.2

[a] Pyrrolidino. [b] Piperidino. [c] Morpholino. [d] Light petroleum (b.p. 60–80 °C). [e] Light petroleum (b.p. 80–100 °C). [f] Light petroleum (b.p. 100–120 °C). [g] Light petroleum (b.p. 60–80 °C)–toluene. [h] Light petroleum (b.p. 80–100 °C)–ethyl acetate. [i] Methanol. [j] Light petroleum (b.p. 60–80 °C)–dichloromethane. [k] Light petroleum (b.p. 40–60 °C). [l] Acetone. [m] Light petroleum (b.p. 40–60 °C)–dichloromethane.

Table 2. Absorption bands of some structurally symmetrical di- and triphenylmethane dyes in acetic acid (98%).

Dye	X Band λ_{max}/nm	X Band $10^{-4}\varepsilon_{max}{}^{d}$	Y Band $\lambda_{max}{}^{u}$nm	Y Band $10^{-4}\varepsilon_{max}$*
(**1**; R = NMe_2)	607.5	14.75		
(**1**; R = NEt_2)	613	17.6		
(**1**; R = pyr)[a]	613	15.7		
(**1**; R = pip)[b]	619	0.23		
(**1**; R = morph)[c]	613	3.1		
(**2**; R = NMe_2, X = H)	621	10.4	427.5	2.0
(**2**; R = NEt_2, X = H)	629.5	11.9	430	1.8
(**2**; R = pyr, X = H)	629	11.1	426	1.7
(**2**; R = pip, X = H)	634	10.4	431	1.7
(**2**; R = morph, X = H)	623	9.0	433	1.9
(**2**; R = X = NMe_2)	589	11.6		
(**2**; R = X = NEt_2)	592.5	13.0		
(**2**; R = X = pyr)	591	12.1		
(**2**; R = X = pip)	602	11.5		
(**2**; R = X = morph)	596	10.6		

[a] Pyrrolidinyl. [b] Piperidino. [c] Morpholino. [d] Apparent ε_{max} values.

λ_{max} values of the symmetrical pyrrolidino analogues of Michler's Hydrol Blue, Malachite Green, and Crystal Violet are very similar to those of the corresponding diethylamino dyes; the ε_{max} values of the pyrrolidino dyes are slightly less than those of the diethylamino compound (Table 2). The latter effect may be due to partial deconjugation of the terminal substituents arising from a clash between the α-methylene and the *ortho* protons of the benzene rings.[3] Significant bathochromic shifts of the first bands are observed in the related piperidino dyes when compared with their pyrrolidino counterparts, which can be explained on the basis of increased inductive electron donation at the terminal nitrogen atoms. Further decreases in ε_{max} are found, especially the dramatic fall observed in the case of the diphenylmethane derivative (Table 2).

This marked difference in behaviour can be accounted for in terms of the greater steric hindrance suffered by the six-membered ring system compared with the five-membered heterocycle. Thus, in the case of the piperidine ring,[13] molecular models (Dreiding) suggest that the equatorial protons of the α-methylene groups in the chair conformation of the six-membered ring interfere with the *ortho* protons of the adjacent phenyl ring to a greater extent than do the corresponding protons of the more nearly planar five-membered ring. Consequently, relief of steric strain by rotation about the terminal bonds will be greatest in the case of the piperidino dyes. Compared with the piperidino compounds, the morpholino analogues' absorbances are shifted hypsochromically in accordance with inductive electron withdrawal by the oxygen atoms (Table 2).

It is clear that the diarylmethyl cation (**1**; R = morpholino) is destabilised so that in solution the equilibrium between dye base and univalent cation is heavily in favour of the former species. The conjugation of the nitrogen lone-pair electrons is apparently insufficient to stabilise the initially formed cation. Disruption of the conjugation between terminal lone-pair

Table 3. Absorption bands of some structurally unsymmetrical triphenylmethane dyes in acetic acid.

			10% AcOH			
	100%AcOH		X Band		Y Band	
Dye (2)	λ_{max}/ nm	10^{-4}-ε_{max}[d]	λ_{max}/ nm	10^{-4}-ε_{max}[d]	λ_{max}/ nm	10^{-4}-ε_{max}[d]
R = NMe_2, X = NEt_2	591	11.8	634	5.4	424	0.7
R = NEt_2, X = NMe_2	592	12.2	637	6.3	425	1.0
R = NMe_2, X = pyr[a]	588	12.0	—	—	—	—
R = NEt_2, X = pyr	589.5	13.2	638	7.4	421	1.1
R = NMe_2, X = pip[b]	591.5	11.9	629	7.8	421	1.2
R = NEt_2, X = pip	597	12.1	642	7.8	426	1.5
R = NMe_2, X = morph[c]	592.5	10.7	—	—	—	
R = NEt_2, X = morph	597.5	10.9	—	—	422	0.6
R = pyr, X = NMe_2	594.5	9.4	—	—	—	
R = pyr, X = NEt_2	594	12.0	642	6.1	425	0.8
R = pip, X = NMe_2	597	11.9	637	7.0	423	1.4
R = pip, X = NEt_2	598.5	10.4	641	6.4	425	1.5
R = morph, X = NMe_2	594.5	10.8	—	—	—	
R = morph, X = NEt_2	597.5	10.4	—	—	—	
R = pyr, X = pip	597.5	12.7	639.5	9.5	425	1.4
R = pyr, X = morph	602.5	10.5	—	—	—	
R = pip, X = pyr	601.5	10.4	641.5	5.4	427.5	1.3
R = pip, X = morph	606.5	10.8	626	5.2	422	1.0
R = morph, X = pyr	601.5	3.1	—	—		
R = morph, X = pip	604	6.5	—	—	425	0.4

[a] Pyrrolidino. [b] Piperidino. [c] Morpholino. [d] Apparent ε_{max} values.

electrons and the aromatic system leads to an inherent decrease in ε_{max} as well as to incomplete conversion of the dye base into univalent cation.[14] Such an effect is most likely to manifest itself in the diarylmethyl system in accordance with the relative stabilities of Michler's Hydrol Blue, Malachite Green, and Crystal Violet as indicated by the pK_a values of 5.61, 6.90, and 9.36, respectively.[15]

A comparison between the effects of the different terminal groups can best be made by examining the ease of protonation of the various analogues of Crystal Violet (Table 3). Although the univalent cation of Crystal Violet itself is relatively stable, addition of hydrochloric acid to a solution of the dye in acetic acid brings about a colour change to green (divalent cation) and then to yellow (trivalent cation) due to successive protonation at the terminal dimethylamino groups linked with a progressive destruction of the charge–resonance system. A more sensitive test involves a gradual increase in acidity of the acetic acid solvent brought about by increasing the proportion of water present. Little change is apparent in the absorption spectrum of crystal violet as the solvent is changed from 100 to 10% acetic acid other than a slight bathochromic drift of λ_{max} from 589 nm to 592 nm. When one of the dimethylamino groups is replaced by diethylamino, however, an increase in the acidity leads to protonation at the more basic group and the consequent development of a Malachite Green type spectrum (Table 3) due to the presence of a significant amount of (**2**; R = NMe_2, X = $\overset{+}{N}HEt_2$). A similar result is obtained when two diethylamino groups are present (**2**; R = NEt_2, X = NMe_2) but with an increase in the quantity of divalent cation (Table 3). The amount of protonated univalent cation generated is greatest (about 60%) in the case of ethyl violet (λ_{max} 641 and 426 nm, ε_{max} 72 000 and 12 000 $dm^3\ mol^{-1}\ cm^{-1}$, respectively, in 10% aqueous acetic acid). These results demonstrate clearly the relative ease of protonation of diethylamino groups compared with dimethylamino groups.

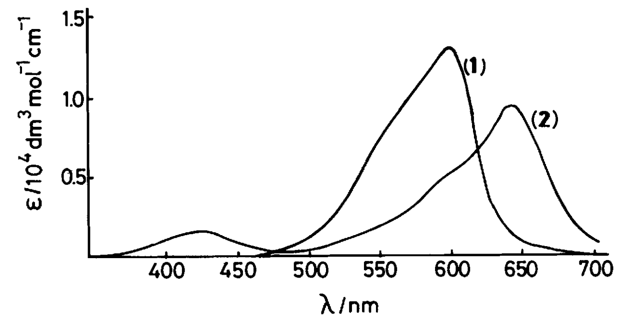

Figure. Absorption spectra of (**2**; R = pyrrolidino, X = piperidino) in acetic acid (**1**) 100% and (**2**) 10%.

The monopyrrolidino analogue of Crystal Violet (**2**; R = NMe_2, X = pyrrolidino) shows no evidence of protonation in 10% acetic acid whereas the analogous piperidino dye (**2**; R = NMe_2, X = piperidino) is extensively protonated (Table 3). Similarly, the dipyrrolidino analogue of Crystal Violet (**2**; R = pyrrolidino, X = NMe_2) is not protonated in dilute acetic acid, unlike the corresponding piperidino compound (Table 3). Not surprisingly, the tripyrrolidino dye (**2**; R = X = pyrrolidino) also resists protonation in 10% acetic acid unlike its piperidino counterpart (λ_{max} 643 and 426 nm, ε_{max} 51 000 and 16 000 $dm^3\ mol^{-1}\ cm^{-1}$, respectively). The dye system most sensitive to changes in acidity is the compound having one piperidino substituent and two pyrrolidino groups (**2**; R = pyrrolidino, X = piperidino). In this case, the conversion into divalent cation is about 85% (Figure).

This contrasting behaviour can be explained in terms of differences in electron density at the heterocyclic terminal nitrogen atoms. In this connection, it may be recalled that pK_a values increase for the series *N*-phenylpyrrolidine < *N*,*N*-dimethylaniline < *N*-phenylpiperidine < *N*,*N*-diethylaniline. The high value for *N*,*N*-diethylaniline is considered to be anomalous and has been attributed to loss of solvation as a result of the congested situation observed in the vicinity of the nitrogen atom which destabilises the base relative to the ammonium ion.[16] The present work suggests that a diethylamino substituent is less basic than a piperidino group.

It has already been pointed out, however, that crowding effects are significantly greater in the case of piperidino groups than with pyrrolidino substituents so that rotation about the terminal bond will lead to an increase in electron density at the heterocyclic nitrogen atom and to ready protonation. Conjugation between the terminal lone-pair electrons and the aromatic system is extensive, nevertheless, although pyrrolidino groups have the greater stabilising effect on the univalent dye cation; PPP molecular-orbital calculations show that there is a decrease in the π-electron density at the terminal nitrogen atoms in the first excited state.[17] These differences in behaviour can be related to earlier work in which it was suggested that an *exo* double bond will destabilise a six-membered ring but favour a five-membered ring.[18]

The data in Table 3 reveal that all dyes having piperidino substituents undergo protonation in dilute acetic acid as do most of those containing diethylamino groups. It is also clear that there is very little tendency for morpholino rings to be protonated, as might be expected in view of the decrease in basicity resulting from inductive electron withdrawal by the oxygen atoms.

It appears that the structurally unsymmetrical dyes listed in Table 3 are essentially electronically symmetrical; the relative positions of the absorption maxima in 100% acetic acid are broadly in line with those anticipated on the basis of the data given for the structurally symmetrical dyes in Table 2. By comparison with the relevant Malachite Green type parent dyes shown in Table 2, the X bands of the divalent species

Table 3 absorb bathochromically due to the electron-withdrawing effect of the quaternary *para* substituents.[19] In each case, the substituted phenyl groups are very similar so that little variation is seen in the position of the Y band.

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