



The Electronic Absorption Spectra of Morpholine Green and Some Derivatives¹

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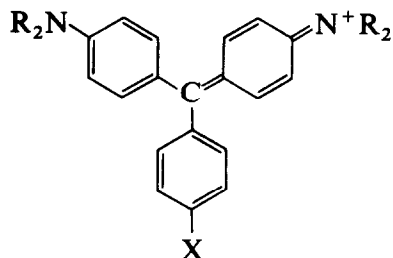
ABSTRACT

Derivatives of Morpholine Green containing methyl and trifluoromethyl groups in the phenyl ring have been prepared and their absorption spectra determined. The morpholino group is somewhat less efficient as an electron donor substituent than is the diethylamino group. Substituents in the 3- or 4-positions modify the position of the first-frequency band to an extent linearly related to the appropriate Hammett substituent constant. Substitution in the 2-position brings about a red shift and an increase in intensity of the first band, together with a blue shift and a decrease in intensity of the second band in accord with rotation about an essential single bond.

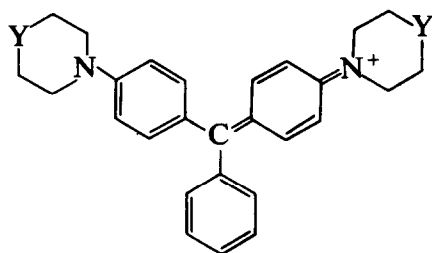
1 INTRODUCTION

We have previously examined the effects of a range of substituents on the electronic absorption spectra of Michler's Hydrol Blue, Malachite Green (1) and Crystal Violet (2). Whilst many substituents have been introduced into these dyes, two groups are particularly informative and helpful. The electronic and steric effects of a methyl substituent are usually opposed and

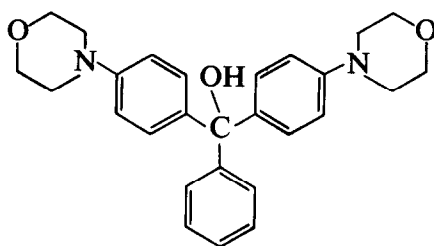
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- (1) R = Me, X = H
 (2) R = Me, X = NMe₂
 (3) R = Et, X = H



- (4) Y = O
 (5) Y = CH₂



(6)

this feature facilitates interpretation of the spectral results.² The electron withdrawing trifluoromethyl group is considerably larger than the methyl group³ and thus exhibits an enhanced steric effect which leads to significant changes in the electronic absorption spectra.⁴ Furthermore, the trifluoromethyl group often confers improved brightness and enhanced light fastness on dyes, features of no small commercial importance.⁵

The nature of the basic terminal group plays an important role in the colour and stability of triphenylmethane⁶ and azo dyes.⁷ The electronic absorption spectra of Brilliant Green (3), the diethylamino analogue of Malachite Green, and some of its derivatives have also been reported and we have noted a red shift in accord with the greater electron donating power of the terminal group.⁸ The greater stability of this series of dyes, attributable to more efficient delocalisation of the positive charge, is apparent from a study of their hydrolysis under aqueous alkaline conditions.⁹ In view of the sensitivity of di- and tri-arylmethane dyes to structural and conformational changes,¹⁰ we have studied the effects of cyclic terminal groups on both the electronic absorption spectra¹¹ and the hydrolytic stability¹² of these basic dyes. In this paper, we discuss the effects of morpholine as a terminal group

in TPM dyes and the influence of substituents on the electronic absorption spectra of Morpholine Green (4).

2 RESULTS AND DISCUSSION

4-Morpholinobromobenzene¹³ was obtained in 30% overall yield from 4-chloronitrobenzene by nucleophilic displacement of the halogen with morpholine¹⁴ followed by palladium-catalysed reduction of the nitro group by hydrazine¹⁵ and a subsequent Sandmeyer reaction.¹⁶ The required compound was more conveniently prepared by the selective para-bromination of *N*-phenylmorpholine by 2,4,4,6-tetrabromocyclohexa-2,5-dienone.¹⁷ Two routes were used to prepare 4,4'-dimorpholinobenzophenone. The conversion of aryl bromides into benzonitriles is well established¹⁸ and 4-morpholinobenzonitrile¹⁹ was so obtained from 4-morpholinobromobenzene. It is noteworthy that 4-chlorobenzonitrile did not undergo nucleophilic substitution with morpholine, even in dimethyl sulphoxide, a solvent known to promote such reactions,²⁰ although it has been reported that 4-fluorobenzonitrile reacts successfully with morpholine under these conditions.¹⁹ The optimum conversion of 4-morpholinobromobenzene into the aryl-lithium derivative was achieved by reaction with the butyl-lithium-TMEDA complex²¹ at 0–20°C; subsequent reaction with 4-morpholinobenzonitrile and hydrolysis of the imine afforded the substituted benzophenone. A more convenient route involved fluorine displacement from 4,4'-difluorobenzophenone by morpholine in boiling sulpholane,¹¹ although prolonged reaction was necessary to ensure replacement of both fluorine atoms.

The dye bases (6), details of which are given in Table 1, were prepared either by reaction of 4-morpholinophenyl-lithium with substituted methyl benzoates or from 4,4'-dimorpholinobenzophenone and an aryl-lithium. Dissolution of the dye bases in glacial acetic acid converted them into the dyes and their absorption spectra were determined for solutions in 98% acetic acid, a solvent considered to optimise conversion into the dye.²² Spectral data are collated in Table 2.

The spectrum of Morpholine Green is similar to those of Malachite Green and Brilliant Green and shows two absorption bands in the visible region. The wavelength of maximum absorption for the longer wavelength x-band, associated with polarisation along the axis containing the two morpholine units, lies between those of Malachite Green (621 nm) and Brilliant Green (629.5 nm), suggesting an electron donating ability for the morpholino terminal group intermediate between those of dimethylamino and diethylamino. However, the relative pK_a values of *N,N*-dimethyl- and *N,N*-

TABLE 1
Preparative and Microanalytical Data for Derivatives of Morpholine Green Base

Substituent in (6)	M.p. (°C)	Yield (%)	Solvent	Found (%)			Formula			Required (%)		
				C	H	N	C	H	N	C	H	N
H	181-2	50	A	75.5	7.0	6.4	C ₂₇ H ₃₀ N ₂ O ₃	75.5	7.0	6.5	7.0	6.5
2-CH ₃	200-1	55	B	75.7	7.3	6.4	C ₂₈ H ₃₂ N ₂ O ₃	75.6	7.3	6.3	7.3	6.3
3-CH ₃	101-2	50	A	75.6	7.3	6.1	C ₂₈ H ₃₂ N ₂ O ₃	75.6	7.3	6.3	7.3	6.3
4-CH ₃	171-2	35	A	75.8	7.3	6.1	C ₂₈ H ₃₂ N ₂ O ₃	75.6	7.3	6.3	7.3	6.3
2,3-(CH ₃) ₂	177-8	42	C	76.3	7.4	6.0	C ₂₉ H ₃₄ N ₂ O ₃	76.0	7.5	6.1	7.5	6.1
2,4-(CH ₃) ₂	186-8	25	C	75.9	7.7	6.4	C ₂₉ H ₃₄ N ₂ O ₃	76.0	7.5	6.1	7.5	6.1
2,5-(CH ₃) ₂	190-1	44	C	76.2	7.3	6.1	C ₂₉ H ₃₄ N ₂ O ₃	76.0	7.5	6.1	7.5	6.1
3,4-(CH ₃) ₂	180-1	62	B	76.4	7.4	6.0	C ₂₉ H ₃₄ N ₂ O ₃	76.0	7.5	6.1	7.5	6.1
3,5-(CH ₃) ₂	164.5	58	B	75.8	7.7	6.2	C ₂₉ H ₃₄ N ₂ O ₃	76.0	7.5	6.1	7.5	6.1
2-CF ₃	213-5	40	E	67.2	5.8	5.9	C ₂₈ H ₂₉ F ₃ N ₂ O ₃	67.4	5.8	5.6	5.8	11.4
3-CF ₃	161-2	40	D	67.4	5.9	5.9	C ₂₈ H ₂₉ F ₃ N ₂ O ₃	67.4	5.8	5.6	5.8	11.4
4-CF ₃	199-200	30	B	67.6	5.9	5.7	C ₂₈ H ₂₉ F ₃ N ₂ O ₃	67.4	5.8	5.6	5.8	11.4
2,4-(CF ₃) ₂	201-3	35	A	61.8	5.1	5.1	C ₂₉ H ₂₈ F ₆ N ₂ O ₃	61.5	4.9	5.0	4.9	20.1
2,5-(CF ₃) ₂	208-9	42	D	61.5	5.2	4.7	C ₂₉ H ₂₈ F ₆ N ₂ O ₃	61.5	4.9	5.0	4.9	20.1
3,5-(CF ₃) ₂	185-6	41	D	61.7	5.1	4.7	C ₂₉ H ₂₈ F ₆ N ₂ O ₃	61.5	4.9	5.0	4.9	20.1

Recrystallising solvent: A, light petroleum (b.p. 60-80°C)/toluene; B, light petroleum (b.p. 60-80°C)/ethyl acetate; C, toluene; D, light petroleum (b.p. 60-80°C); E, methanol.

TABLE 2
Spectral Data for Derivatives of Morpholine Green in 98% Acetic Acid

Substituent in (4)	<i>x</i> -Band		<i>y</i> -Band	
	λ_{\max} (nm)	$10^{-4} \epsilon_{\max}$	λ_{\max} (nm)	$10^{-4} \epsilon_{\max}$
None	625	8.8	435	1.9
2-Me	625.5	10.5	426	1.5
3-Me	623.5	8.7	438	2.0
4-Me	621	8.8	447	2.5
2,3-Me ₂	625	10.6	429	1.5
2,4-Me ₂	623	9.7	442	1.8
2,5-Me ₂	625.5	6.8	443	0.9
3,4-Me ₂	619	8.9	450	2.6
3,5-Me ₂	623	9.0	442	2.2
2-CF ₃	638.5	10.1	417	1.2
3-CF ₃	636	7.8	429	1.3
4-CF ₃	640	8.6	429	1.6
2,4-(CF ₃) ₂	648.5	9.9	418	1.1
2,5-(CF ₃) ₂	649	9.7	418	0.9
3,5-(CF ₃) ₂	649	7.8	428	1.3

diethyl aniline and *N*-phenylmorpholine of 5.07, 6.52 and 3.20, respectively²³ indicate a much greater influence of the oxygen heteroatom on the availability of the lone pair of electrons on the nitrogen atom of morpholine. The electron demand of the positive centre in Morpholine Green (4) apparently appreciably overcomes the effect of the electronegative oxygen atom. A better measure of the influence of the oxygen heteroatom in a TPM environment is provided by comparing λ_{\max} of Morpholine Green (4) (625 nm) with that of Piperidine Green (5) (634 nm),¹¹ since all other factors are identical. The intensity of the *x*-band of Morpholine Green is less than that of the corresponding band in Malachite Green and in Brilliant Green, which may be associated with incomplete conversion into the dye cation due to a shift in the equilibrium between the dye and the dye base.

Small blue shifts of the *x*-band follow the introduction of a methyl group at the 3- or 4-position of Morpholine Green, whilst the electron-withdrawing trifluoromethyl substituent causes larger red shifts. The *y*-band responds in the opposite manner for both of the substituent types. Whilst only these two different substituents have been introduced into the dye system, the linear relationship between the shift in λ_{\max} (*x*) and the appropriate Hammett substituent is considered sound because of the non-conjugative nature of the groups.²⁴

Disubstitution involving the 3-, 4- or 5-positions results in spectral

changes in accord with the additivity principle established in earlier studies for substituents free of steric constraints.²⁵

Red shifts of the x-band together with increases in intensity result following the introduction of substituents at the sterically significant 2-position. The changes are accentuated with the bulkier trifluoromethyl group and are also apparent in the 2-substituted derivatives which contain a second substituent. The hypsochromic response of the y-band together with a significant reduction in intensity is a clear indication of steric crowding, providing additional support for the proposal that the phenyl group twists further about the central bond in order to accommodate the 2-substituent; steric hindrance is most easily alleviated by rotation about an essential single bond.¹⁰

3 EXPERIMENTAL

Absorption spectra were measured with a Unicam SP800 recording spectrophotometer for solutions of the dye bases in 98% acetic acid.

3.1 General methods of preparation of dye bases

(i) A solution of 4-morpholinobromobenzene (0.015 mol) in ether (50 cm³) was added under nitrogen to an equimolar amount of an ice-cold solution of the tetramethylethylenediamine-butyl-lithium complex in ether (30 cm³). After 30 min at room temperature, a solution of the methyl benzoate (0.007 mol) in ether (10 cm³) was added dropwise and the resulting mixture was stirred for 6 h before the addition of water. The organic material was isolated with ether and subsequently recrystallised.

(ii) An ethereal solution of the aryl-lithium (0.01 mol) was added to a suspension of 4,4'-dimorpholinobenzophenone (0.01 mol) in ether (50 cm³). After 1 h, the usual work up gave the dye base.

Details of the compounds prepared by these methods are collated in Table 1.

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