J. Sci. I. R. Iran

Vol. 1, No. 1
Fall 1989

SYNTHESIS AND ELECTRONIC ABSORPTION SPECTRA OF SOME METHOXY HALF-ANALOGUE OF MICHLER'S HYDROL BLUE

N. Saadatjou

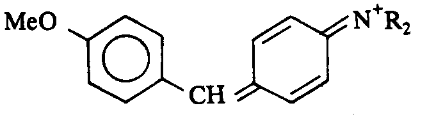
Applied Chem. Lab., Dept. of Chem., University of Tabriz, Tabriz, Iran.

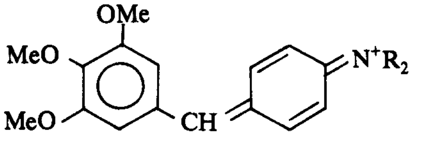
Abstract

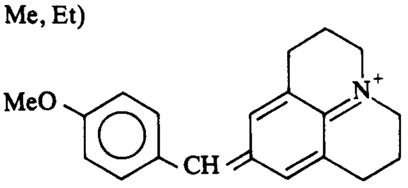
The present work comprises the synthesis of one series of diarylmethane dyes containing one or more terminal methoxy substituents together with a variable tertiary amino group. The electronic absorption spectra of the dyes have been determined. As the conjugation of the terminal nitrogen atom improves in the sequence NMe_2 > Kairoline > Julolidine, a progressive hypsochromic shift is observed.

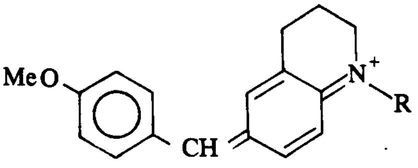
Introduction

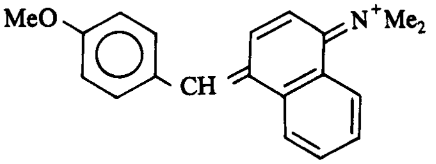
It was reported earlier[1, 2] that certain julolidine, kairoline and lilolidine, 1-methyllindoline[3] analogues of Michler's Hydrol Blue show marked bathochromic shifts relative to Michler's Hydrol Blue. The dimethoxy analogue of this compound also have been previously studied.[4] Methoxy half-analogues containing julolidine, kairoline, N-2-cyanoethyl-1, 2, 3, 4-tetrahydroquinoline and 1-dimethylnaphthylamine ring systems have now been prepared and their absorption spectra determined in order to examine the effects of inherent electronic asymmetry of the system.


(1; R = Me, Et)


(2; R = Me, Et)


(3)


(4; R = $Me_2\,C_2\,H_2CN$)


(5)

Results and Discussion

The dye (1; R=Me) shows a remarkably large hypsochromic shift of 109.5 nm when compared with Michler's Hydrol Blue (Table 1) and the absorption intensity is greatly lowered. It appears that the corresponding dye base is not fully converted into the univalent cation in 98% acetic acid. However, this behaviour can be associated with its electronically unsymmetrical structure compared with that of Michler's Hydrol Blue.

Dye	λ/nm	$10^{-4}\ \Sigma_{max}$
Michler's Hydrol Blue	607.5	14.75
(1; R = Me)	498.0	0.09
(1;R = Et)	500.0	0.06
(2;R = Me)	501.0	0.01
(2;R = Et)	495.0	0.01
(4; R =Me)	490.0	0.78
(3)	480.0	0.65
(4; R = C_2H_4CN)	504.0	0.65
(5)	474.0	0.01

Table 1. Absorption spectra of Michler's Hydrol Blue and its methoxy half-analogues in 98% acetic acid.

Michler's Hydrol Blue is a cyanine type chromogen

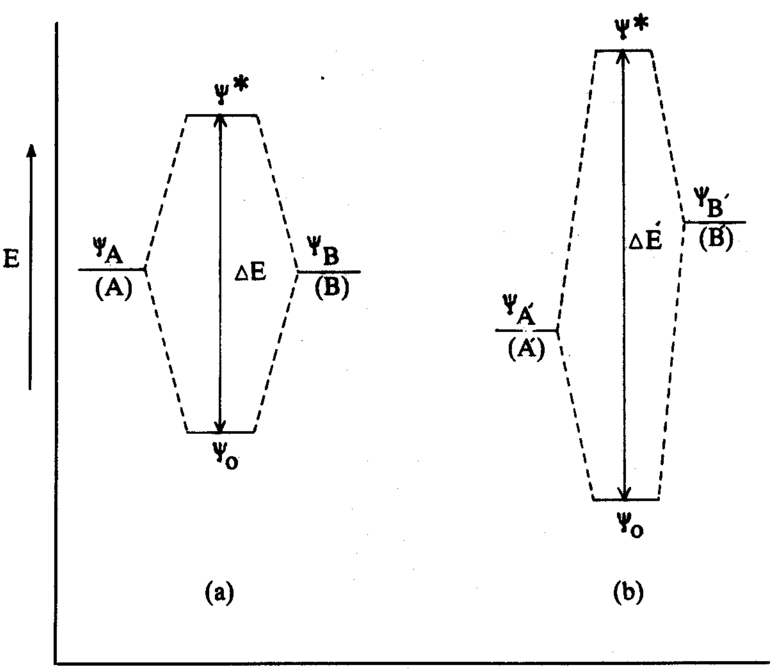
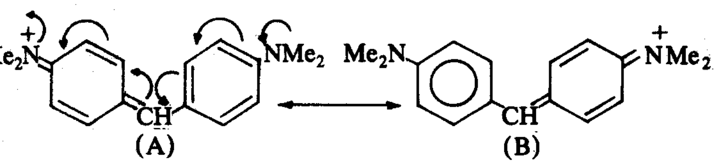


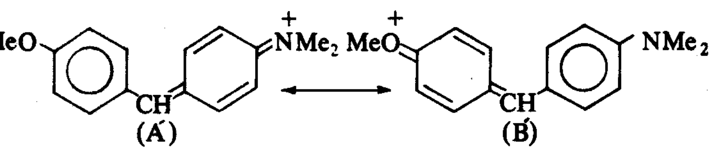
Figure. The interaction between two resonance structures when they are (a) of equal, and (b) of unequal energy.

which interms of resonance theory[5], can be represented as a hybride of two equal energy canonical structures (A,B). The molecule is electronically symmetrical and the conjugated chain in this charge-resonance system shows a high degree of bond uniformity. On the other hand, the half-methoxy analogue is no longer electronically symmetrical since contributions from the two canonicals will not be the same (A' will predominate, being of lower energy) and bond order alteration obtains along the conjugated chain as in the case of merocyanines and polyenes.

Michler's Hydrol Blue (cyanine type):



Methoxy half-analogue (polyene type):



According to the qualitative resonance approach, the wave functions of the degenerate state (A), φ_A and (B), φ_B interact to give two new molecular wave functions of different energies. The lower energy function φ_O is given by the symmetric combination of φ_A and φ_B whereas the higher energy function φ^* is given by the antisymmetric combination as follows: $\varphi_O = (\varphi_A + \varphi_B)$ and $\varphi^* = (\varphi_A - \varphi_B)$.

The lower energy wave function is equated with the ground state, and the higher energy function with the first excited state. The frequency of the first absorption band of the chromogen is then given by the separation energy (ΔE), of the two states (Figure). Unlike Michler's Hydrol Blue the methoxy half-analogue can be represented by two forms that are not equal in energy and form (A') is the more stable since nitrogen bears a positive charge more readily than oxygen. Because the two forms no longer lie at the same energy level, resonance interaction gives two states that are further a part in energy than if they had been degenerated as in the first instance. Consequently, $\Delta E' \gg \Delta E$ and the effect of this electronic asymmetry is to produce a large hypsochromic shift of the visible absorption band.

The replacement of a dimethylamino group by a methoxy group modifies the basicity of the system and it is clear that the equilibrium between dye base and dye is in favour of the former species in 98% acetic acid so that the absolute value of Σ_{max} is unobtainable.

The DPM dye (1; R=Et) exhibits a small bathochromic shift of 2nm compared with the dimethyl analogue, the absorption intensity is again very low (Σ_{max} 600). The position of the first band relative to that of Michler's Hydrol Blue, can be accounted for in terms of the electronic asymmetry of the systems, and it appears that the corresponding dye base is not fully converted into the univalent cation in 98% acetic acid. Replacement of the terminal dimethylamino group does little to change the characteristics of the system. Thus the position of the band is virtually unchanged and the tendency of the dye base to ionise in acid solution remains low.

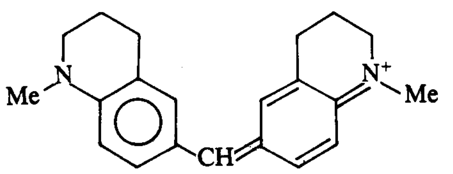
The DPM dye (2; R=Me) derived from 4-dimethylamino-3', 4', 5'-trimethoxy-benzophenone gives a very broad absorption spectrum of low intensity in acetic acid (Σ_{max} 100). This dye is comparable with dye (1;

R=Me) which contains only one methoxy group in the para-position. On passing from dye (1; R=Me) to dye (2; R=Me) a bathochromic shift of only 3nm together with a reduction in absorption intensity is observed. Thus, the additional m-methoxy groups make formation of the univalent cation more difficult by electron withdrawal so that the equilibrium between dye base and dye is very much in favour of the base.

The dye (2;R=Et) shows a hypsochromic shift of 6nm when compared with the analogues dimethylamino compound (2; R=Me). A hypsochromic shift is to be expected on the basis of an increase effective conjugation by the terminal nitrogen atom leads to increase in the electronic asymmetry of the system brought about by replacing NMe_2 with NEt_2. Similarly a hypsochromic shift of 5nm is observed when dye (2; R=Et) is compared with the monomethoxy parent dye (1; R =Et). In this case, the electronic symmetry is decreased by electron withdrawal of the two m-methoxy groups. However, these results contrast with the small bathochromic shifts observed for the corresponding dimethylamino compounds on passing from dye (1; R =Me) to (2;R=Me) and from dye (1;R=Et) to dye (2;R =Et) respectively. As in the case of the corresponding dimethylamino dye base, the equilibrium between base and dye is very much in favour of the former species.

Enhanced conjugation between the terminal nitrogen atom and the aryl rings is observed in kairoline analogues of diphenylmethane dyes in which hetero atom is lined to the meta position by trimethylene groups. Consequently, conformational changes and corresponding modifications in the electronic absorption spectra of methoxy analogues of dyes containing kairolyl groups may be expected when compared with their dialkylamino counter parts.

The kairoline analogues (4; R=Me) absorbs at 490 nm (Σ_{max}1800) in 98% acetic acid. Thus, a hypsochromic shift of 8nm is observed compared with the parent dimethylamino compound (1;R=Me) together with a very considerable increase in Σ_{max}; the kairoline analogue of Michlers' Hydrol Blue (C) shows a bathochromic shift of 15nm when compared with the parent dye. These differences can be reconciled in terms of changes in electronic symmetry. As previously mentioned, the methoxy half-analogues are electronically asymmetric so that an improvement in conjugation at the nitrogen atom should make the system even more unsymmetrical. Hence, a hypsochromic shift of the absorption band is to be anticipated. Additional electron donation by the terminal atom enables the dehydration of the protonated dye base to take place more efficiently so that a marked increase in absorption intensity is also observed.



(C)

Replacement of the methyl group in the kairoline system by a second trimethylene bridge to give the corresponding julolidine compounds should, by virtue of more effective conjugation of the terminal nitrogen atom, increase the lake of electronic symmetry and produce further hypsochromic shifts.

In the case of julolidine analogue (3) a hypsochromic shift of 10nm is observed compared with the kairoline dye and this corresponds to a shift of -18nm relative to the parent dimethylamino compound; the julolidine analogue of Michler's Hydrol Blue shows a bathochromic shift of 30nm when compared with the parent dye. A consistent pattern is therefore observed where by increasingly effective conjugation of the terminal nitrogen atom leads to a progressive increase in electronic asymmetry and to corresponding hypsochromic shifts of λ_{max}. As in the case of the kairoline derivative, a significant increase in Σ_{max} is observed.

It can be anticipated that replacement of the methyl group in the kairoline analogues by cyanoethyl will lead to a bathochromic shift by virtue of electron withdrawal of the CN group leading to a decrease in the ability of the terminal nitrogen atom to conjugate with the aromatic system.

Thus, the diphenylmethane dye (4; $R=C_2H_4CN$) absorbs at 504 nm (Σ_{max} 6500) in 98% acetic acid, thereby showing a bathochromic shift of 14nm as compared with a kairoline analogue. Although the two absorption intensities are of the same order, that of the cyanoethyl compound is unreliable owing to the presence of impurities in the dye base.

The naphthalene derivative (5) shows a marked hypsochromic shift of 24nm compared with the parent benzene derivative and this result is in agreement with an increase in electronic asymmetry owing to the electron donating effect of the naphthalene ring system. As in the case of the corresponding analogue of Michler's Hydrol Blue[6], the conversion of dye bases into dye is only low at room temperature; because the present dye base was not analytically pure.

Conclusion

Replacement of dimethylamino group in Michler's Hydrol Blue by methoxy groups produces remarkable hypsochromic shifts and decreases in intensity of the absorption band owing to the inherent electronic asymmetry. Electronically unsymmetrical derivatives of the julolidine and kairoline analogues of diarylmethane dyes shows hypsochromic shifts of the absorption bands relative to the methoxy half-analogues of Michler's Hydrol Blue in accordance with enhanced conjugation through the kirolyl and julolidyl groups leading progressively to a less electronically symmetrical system. Replacement of the terminal group in the kairoline analogue by a cyanoethyl group leads to a bathochromic shift due to the electron withdrawing effect of the CN group which decreases the

Bases of dyes	**Mehod of synthesis**	**Mol. formula**	**Solvent for cryst.**	**Wt. (g)**	**Yield (%)**	**M. P. (°C)**	**Elemental analysis found/required %**		
(1; R=Me)	A	$C_{16}H_{19}NO_2$	EtOH	1.1	70	80	C	H	N
							74.6	7.4	5.3
(1; R=Et)	A	$C_{18}H_{23}NO_2$	L.P. (80/100)*	1.2	69	41	74.7	7.4	5.4
							75.4	8.1	4.7
(2;R=Me)	B	$C_{18}H_{23}NO_4$	L.P. (40/60)	1.8	72	136	75.7	8.1	4.9
							67.7	7.1	4.2
(2;R=Et)	B	$C_{20}H_{23}NO_4$	L.P. (60/80)	2.0	71	84	68.1	7.2	4.4
							69.6	7.8	4.3
(4;R=Me)	C	$C_{18}H_{21}NO_2$	L. P. (60/80)	1.0	67	68	69.6	7.8	4.1
							76.1	7.5	4.9
(3)	A	$C_{20}H_{23}NO_2$	L. P. (60/80)	1.2	63	105	76.3	7.4	4.9
							77.6	7.5	4.5
(4;R=C_2H_4CN)	A	$C_{20}H_{22}N_2O_2$	L. P. (30/40)	0.2	20	gum	77.7	7.4	4.5
							75.1	7.2	8.0
(5)	B	$C_{20}H_{21}NO_2$	L.P. (40/60)	-	-	-	74.5	6.8	8.6
								Impure	

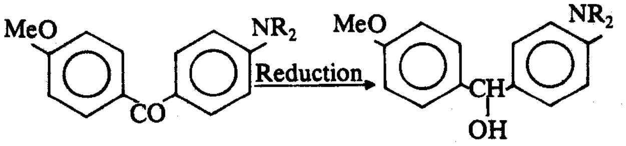
* L. P. (80/100°C): Light petroleum (B. P. 80-100°C)

Table 2. Experimental data of some DAM dye bases

ability of the terminal nitrogen atom to conjugate with the aromatic system. The effect of replacing a benzene ring in the dye by naphthalene is a marked hypsochromic shift of the band due to a decrease in electronic symmetry brought about by the electron donating effect of the naphthalene ring system. The presence of additional m-methoxy groups in the methoxy half analogue of Michler's Hydrol Blue makes the formation of the univalent cation more difficult owing to electron withdrawal so that the equilibrium between dye base and dye is very much in favour of the base. As the conjugation of the terminal nitrogen atom improves along the series NMe_2 <NEt_2 <Kairoline <Julolidine in accordance with increasing stabilisation of the ground state, a progressive hypsochromic shift is observed (with the exception of the NEt_2 derivative).

Experimental

The required diarylmethane (DAM) dye bases (or hydrols) are obtained from the corrosponding ketones[7] by reduction with soduim amalgam (Method A), sodium borohydride(MethodB)or lithium aluminium hydride (Method C).



Melting points were determined using a Gallenkamp apparatus and uncorrected. Absorption spectra were measured with Unicam SP800 recording spectrophotometer for solution in 98% acetic acid.

Method A: A mixture of ketone (0.006 M) and sodium amalgam (3%, 8.0g) in ethanol (80 ml) was stirred and heated under reflux on a magnetic stirrer hot plate. After 3 h, more sodium amalgam (4.0g) was added and the reaction was continued for a further 2 h. The solution was cooled and then poured into ice; the resulting crude solid was filtered off, dried by $MgSO_4$ and twice crystallised from an appropriate solvent to give colourless crystals of the dye base.

Method B: To a stirred solution of ketone (0. 008 M) in ethanol (75 ml), sodium borohydride (3. 5 g) was added in small portions and the reaction mixture was stirred overnight. The solvent was then removed by distillation under reduced pressure and water (200 ml) was added to the residue before the mixture was extracted with ether. The ethereal extract was washed with water and the organic layer was dried by Na_2SO_4. Removal of solvent gave crude product which was twice crystallised from light petroleum to give the dye base as colourless crystals.

Method C: A solution of ketone " 6-(4-methoxybenzoyl) kairoline" (1. 5g) in dry THF (40 ml) was added in small aliquots to a stirred suspension of lithium aluminium hydride (0.5g) in dry ether (30 ml) over a period of 30 min. The mixture was then heated under reflux for 1 h and the excess of lithium aluminium hydride was decomposed by the dropwise addition of water (10 ml). The mixture was then poured into water (300 ml). Removal of solvent from the dried ($MgSO_4$) organic layer produced a yellowish-brown gum which resisted crystallisation. Elution of an ethereal solution of the product from a neutral alumina column yielded an almost colourless solution which, on removal of the solvent, afforded a yellow solid. Colourless crystals of the dye base were obtained from light petroleum.

References

1. C. C. Barker and G. Hallas, J. C. S (B), 1065 (1969).
2. R. W. Castelino and G. Hallas, J. C. S (B), 1468 (1971).

3. R. W. Castelino, G.Hallas and D. C. Taylor, J. S. D. C, 25 (1972).
4. E. M. Arnett and R. D. Bunshick, *J. Amer. Chem. Soc.*, **86** 1564 (1964).
5. J. Griffiths, "Colour and Constitution of Organic Molecules", Academic Press, London, P. 85. (1976).
6. G. Hallas, K. N. Paskins and D. R. Waring, J. C. S, 2281. (1972).
7. N. Saadatjou, Unpublished results.