Steric Effects in Di- and Tri-arylmethane Dyes. Part 14.[1] Electronic Absorption Spectrum of an α,*o*-Bridged Analogue of Michler's Hydrol Blue

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The absorption spectrum of 7-dimethylamino-4-(4-dimethylaminophenyl)-1,2-dihydronaphthalene (VII) has been determined in 98% acetic acid. The spectral changes observed with time are discussed in terms of molecular conformation.

In Part 4,[2] it was suggested that the effect of twisting one of the dimethylaminophenyl groups in Michler's Hydrol Blue (I; R = H) about a central bond would be to produce a bathochromic shift of the first band which, with increased rotation of the aryl group, would decrease and ultimately become hypsochromic, owing to changes in electronic symmetry. This postulate was invoked more recently [3] to account for the unexpected hypsochromic shift of the *x*-band shown by the 2-trifluoromethyl derivative of Malachite Green (II). A similar effect is found [4] in the case of the bridged analogue (III) of Malachite Green in which the unsubstituted dimethylaminophenyl group is twisted out of the molecular plane, leading to a hypsochromic movement of the long-wavelength band compared with that of the doubly-bridged dye (IV). In order to examine further the effects of variations in electronic symmetry, a suitable model compound appeared to be the α,*o*-bridged analogue of Michler's Hydrol Blue (V; R = H) in which half of the molecule is constrained by linking an *ortho*-position to the central carbon atom. Thus, introduction of crowding substituents into the dimethylaminophenyl ring will lead to rotation of this group only about the appropriate central bond.

In general, α-alkyl derivatives of dye bases readily form an alkene by loss of water in acid solution.[5] Consequently, in acetic acid an equilibrium exists between alkene (VII) and univalent dye cation (V; R = H) and there is no change in hybridisation at the central carbon atom. It is the release of compressional energy upon changing the valency distribution of the central carbon atom of Michler's hydrol from tetrahedral to trigonal which assists the formation of Michler's Hydrol Blue, so that α-alkyl derivatives give weak absorption bands in acetic acid. In the case of the α,*o*-bridged system, the dye base (VI) dehydrates to yield the corresponding alkene (VII) during work up (see Experimental section).

A freshly prepared solution of the α,*o*-bridged analogue of Michler's Hydrol Blue (V; R = H) in 98% acetic acid gives absorption bands which, apart from the relatively low intensities, are very similar to those of the parent compound (Table). The bathochromic shift (22.5 nm) of the first band can be attributed to the steric effect [6] of the α,*o*-bridge which brings about a rotation of the unsubstituted dimethylaminophenyl group. The electronic influence of the linking group is hypsochromic, since the ends of the chain are attached to inactive positions,[7] but this factor is clearly overwhelmed by the crowding effect. The bathochromic movement of the long-wavelength band is larger than that shown by the α-propyl derivative (I; R = Pr) (Table) and is also greater than that of the 2,2′-dimethyl derivative (15.5 nm).[6] It is apparent that the unsubstituted bridged dye (V; R = H) represents a sterically hindered but electronically symmetrical conjugated system. Although a reduction in $\varepsilon_{max.}$ is to be expected as a result of the crowding effect,[6] it is clear that the observed value (39 400) is somewhat lower than anticipated, owing to the presence of the related alkene (VII) in acid solution. Nevertheless, the bridged species (V; R = H) absorbs more intensely than the various α-alkyl derivatives,[2] thereby suggesting some relative stabilisation of the dye cation which may be envisaged in terms of a strong contribution from canonical structure (V; R = H) to the resonance hybrid.

$\lambda_{max.}$/nm (10^{-4} ε) of some derivatives of Michler's Hydrol Blue in 98% acetic acid

Dye	Fresh solution	Solution after *n* h	*n*
(I; R = H)	607.5 (14.75); 390 (0.45); 368.5 (0.50)		
(I; R = Pr)	620 (1.04); 402.5 (0.18); 382.5 (0.16)	638 (1.23); 347.5 (1.29)	24
(V; R = H)	629 (3.94); 406.5 (0.41); 383 (0.33)	736 (2.48); 432 (0.33)	0.5

The spectrum of the α,*o*-bridged analogue of Michler's Hydrol Blue (V; R = H) in 98% acetic acid changes with time and quickly develops a relatively strong band at 736 nm and a weaker band at 432 nm (Table); the colour of the solution rapidly changes from blue to green (Figure).[†] Increasing the acidity of the solution by addition of water leads simultaneously to a decrease in the intensity of the first band and an increase in that of the second band, a result which confirms the presence of two molecular species in solution. This behaviour is consistent with dimerisation of the alkene (VII) to give a mixture of the ions (VIII) and (IX), and is similar to that of some related α-alkyl [2] and α-cycloalkyl [5] derivatives. The extent of the bathochromic shift of the

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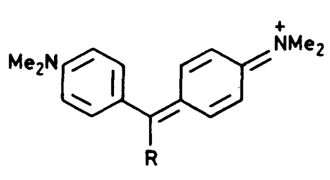
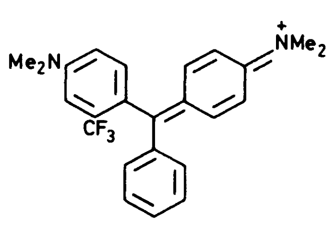
[†] The presence of an equilibrium mixture is supported by the fact that the spectral changes depicted in the Figure (10^{-5}M solution) take place much more rapidly when the concentration is increased four-fold.



(I)



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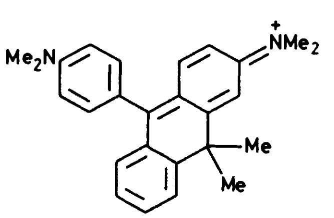

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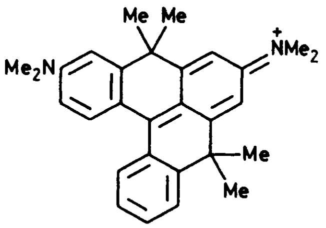
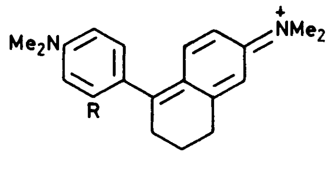
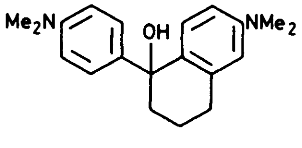


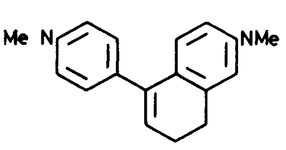
(IV)



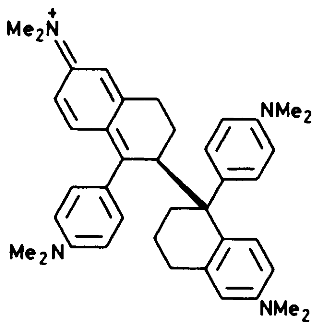
(V)



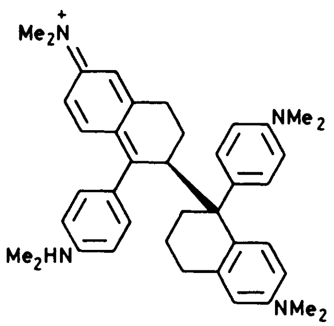
(VI)



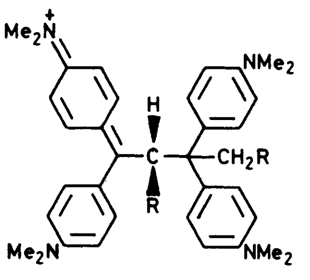
(VII)



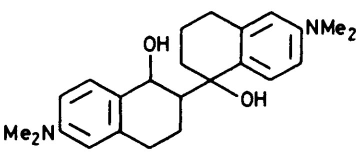
(VIII)



(IX)

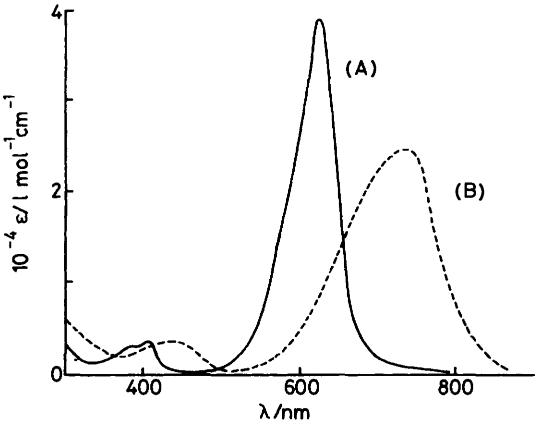


(X)



(XI)

first band (107 nm) is surprising, but is presumably a result of greatly increased crowding in the ion (VIII) compared with the ion (V; R = H). Molecular models suggest that crowding in the dimer (VIII) is much more severe than in the ions (X; R = alkyl or cycloalkyl) where it is possible to relieve steric strain by rotation of the bulky alkyl or cycloalkyl groups out of the overall plane of the ring systems; such rotation cannot take place in the bridged ion (VIII) in which the bridging group is effectively locked into the plane of the adjacent ring. The bridged dimer (VIII) has a quaternary β-carbon atom and thus resembles the α-t-butyl[2] and the α-1-adamantyl[8] derivatives of Michler's Hydrol Blue, so that steric factors enforce rotation of the free dimethylaminophenyl group thereby producing an unsymmetrical conformation leading to ready protonation of the incompletely conjugated nitrogen atom to give the bivalent ion (IX). It must be assumed, however, that, although the disposition of the dimethylaminophenyl group is sufficiently unsymmetrical to permit formation of the protonated ion (IX), the departure from electronic symmetry is still small enough for the deviation from planarity to lead to a marked bathochromic shift. The second band is considerably more bathochromic than than of the α-propyl derivative (Table), absorbing at 432 nm. The position of this band suggests that the protonated species is well represented by the canonical structure (IX).



Absorption spectrum of 7-dimethylamino-4-(4-dimethylaminophenyl)-1,2-dihydronaphthalene in 98% acetic acid: (A) fresh solution, (B) after 30 min

Attempts to prepare derivatives of the α,*o*-bridged analogue of Michler's Hydrol Blue, such as (V; R = Me), in order to examine the effects of increased steric hindrance, were frustrated by the strong tendency of the key intermediate, 6-dimethylaminotetralin-1-one, to undergo α-metallation.[9]

Preparations.—6-Dimethylaminotetralin-1-one was obtained indirectly from 6-acetyltetralin.[10] An attempt to prepare the dye base (VI) by treatment of 6-dimethylaminotetralin-1-one with 4-dimethylaminophenyllithium afforded a poor yield of the corresponding alkene (VII). Use of the Barbier reaction,[11] as a possible means of minimising α-metallation, led to the isolation of the diol (XI). This compound is formed by reaction between the ketone and the corresponding α-lithio-derivative, followed by reduction.

EXPERIMENTAL

Absorption spectra were measured with a Unicam SP 8-150 recording spectrophotometer for solutions in acetic acid. Ambient temperature ^{1}H n.m.r. spectra were recorded for solutions in deuteriochloroform on a Varian HR 220 spectrometer at the Physicochemical Measurement Unit, Harwell.

7-Dimethylamino-4-(4-dimethylaminophenyl)-1,2-dihydronaphthalene (VII).—Ethereal 4-dimethylaminophenyllithium, from 4-bromo-*NN*-dimethylaniline (1.12 g) and lithium (0.08 g), was added to a solution of 6-dimethylaminotetralin-1-one (1.0 g) in the minimum volume of dry ether; after heating overnight under reflux, the mixture was poured into water. Removal of solvent from the dried organic layer gave a brown gum which, after prolonged standing, afforded a crystalline product. Recrystallisation of the crude material from light petroleum (b.p. 40—60 °C) yielded beige crystals of the *alkene* (0.34 g), m.p. 102—103 °C (Found: C, 82.2; H, 8.1; N, 9.7. $C_{20}H_{24}N_2$ requires C, 82.1; H, 8.3; N, 9.6%), τ 2.76 (2 H, d, J_o 9.0 Hz, 2'- and 6'-H), 3.02 (1 H, d, J_o 9.0 Hz, 5-H), 3.27 (2 H, d, J_o 9.0 Hz, 3'- and 5'-H), 3.40 (1 H, d, J_m 2.5 Hz, 8-H), 3.54 (1 H, dd, J_o 9.0, J_m 2.5 Hz, 6-H), 4.20 (1 H, t, J 5.0 Hz, 3-H), 7.04 (6 H, s, 4'-NMe$_2$), 7.06 (6 H, s, 7-NMe$_2$), 7.21 (2 H, t, J 8.0 Hz, 1-H), and 7.66 (2 H, m, J 8.0 Hz, 2-H), $\nu_{max.}$ 3 020, 2 920, 2 820, 1 610, and 1 360 cm^{-1}.

6-Dimethylamino-1-hydroxy-2-(6-dimethylamino-1-hydroxy-1,2,3,4-tetrahydro-1-naphthyl)-1,2,3,4-tetrahydronaphthalene (XI).—Finely divided lithium (0.09 g) was suspended in dry ether (20 cm^3) and a solution of 6-dimethylaminotetralin-1-one (1.0 g) and 4-bromo-*NN*-dimethylaniline (1.12 g) in ether was then added. After stirring and heating under reflux for 6 h the mixture was poured into water. Removal of solvent from the dried organic layer afforded a brown oil which, after prolonged standing, yielded a crystalline product. Recrystallisation of the crude material from light petroleum (b.p. 60—80 °C) containing a little benzene gave colourless crystals of the *diol* (0.15 g), m.p. 187 °C [Found: C, 76.0; H, 8.5; N, 7.3%; $(M - 2H_2O)^+$, 344.2257. $C_{24}H_{32}N_2O_2$ requires C, 75.8; H, 8.5; N, 7.4%; $(M - 2H_2O)$, 344.2253], $\nu_{max.}$ 3 520, 2 920, 1 610, and 1 510 cm^{-1}.

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