Steric Effects in Di- and Tri-arylmethane Dyes. Part XII.[1] Electronic Absorption Spectra of Some Derivatives of Michler's Hydrol Blue containing α-Trifluoromethyl Groups

By **Gregory S. Dodd** and **Geoffrey Hallas,*** Department of Colour Chemistry and Dyeing, The University, Leeds LS2 9JT

Absorption spectra of some derivatives of Michler's Hydrol Blue containing α-trifluoromethyl groups have been determined for solutions in 98% acetic acid; the dye bases show very little tendency to form the corresponding univalent cations. The parent dye (I; R = CF_3) is electronically symmetrical and a pronounced bathochromic shift of the first band is observed. Unsymmetrical conformations result when further crowding substituents are introduced into the α-trifluoromethyl derivative.

ATTEMPTS to examine the effects of crowding substituents at the α-position in Michler's Hydrol Blue (I) were frustrated by the ability of simple α-alkyl derivatives to undergo dimerisation in acetic acid;[2] similar behaviour is also shown by some α-cycloalkyl derivatives.[3] The absence of a β-hydrogen atom in the α-t-butyl derivative (I; R = Bu^t) prohibits dimerisation, but this compound gives rise to a non-typical absorption spectrum which consists of two bands of low but similar intensity (Table). The large t-butyl group causes rotation of one

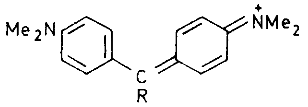
---

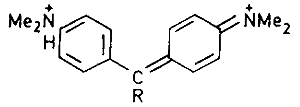
[1] Part XI, D. E. Grocock, G. Hallas, and J. D. Hepworth, *J.C.S. Perkin II*, 1973, 1792.

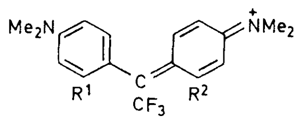
[2] C. C. Barker and G. Hallas, *J. Chem. Soc.*, 1961, 1395.

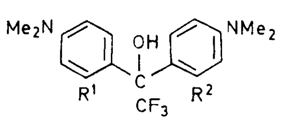
[3] G. Hallas and A. Schofield, *J. Chem. Soc.* (*B*), 1968, 933.

only of the dimethylaminophenyl groups about a central bond thereby producing an unsymmetrical conformation; incomplete conjugation of the nitrogen atom involved leads to its ready protonation, and the resulting non-degenerate bivalent ion (II; R = Bu^t) absorbs at shorter wavelength than the degenerate cation (I; R = Bu^t). The α-1-adamantyl derivative of Michler's Hydrol Blue (I; R = Ad) behaves similarly (Table).[4] It seemed likely that introduction of the trifluoromethyl group into the α-position would result in a significant steric effect without the formation of an unsymmetrical conformation and uncomplicated by the possibility of dimerisation; the CF_3 group is appreciably larger than the CH_3 group.[5] The parent compound (I; R = CF_3) and two *o*-methyl derivatives have now been examined.


(I)


(II)


(III)


(IV)

Spectral data of derivatives of Michler's Hydrol Blue in 98% acetic acid

Dye	$\lambda_{max.}$/nm (ε/l mol^{-1} cm^{-1})
(I; R = H)	607·5 (147,500)
(I; R = Bu^t)	617·5 (6400); 384 (7700)
(I; R = Ad)	623 (2700); 387 (4700)
(I; R = CF_3) [a]	690 (5); 610 (7)
(I; R = CF_3) [b]	690 (32); 610 (23)
(III; R^1 = Me, R^2 = H)	684 (10); 362 (42)
(III; R^1 = R^2 = Me)	646 (6); 354(10)

[a] 30 °C. [b] 70 °C.

The dye base (IV; $R^1 = R^2 = H$) has been reported[6] in connection with the estimation of 4-dimethylaminophenylmagnesium bromide, but the formation of a dye cation was not recorded. On dissolution in 98% acetic acid this base gives rise to a blue colour although the equilibrium between dye base and dye is almost entirely on the side of the hydrol (Table). Similar, but much less drastic, behaviour has recently been observed when trifluoromethyl groups are introduced into the *ortho*-positions of Michler's hydrol.[1] Olah has shown[7] that an α-trifluoromethyl substituent destabilises the diphenylmethyl carbonium ion, and Filler has found[8] that the cation from tris-(4-trifluoromethyltetrafluorophenyl)-methanol can only be generated in 30% oleum in contrast to that from perfluorotriphenylmethanol (93% sulphuric acid). Nevertheless, the extremely low intensity ($\varepsilon_{max.}$ 5) of the first band of the α-trifluoromethyl derivative of Michler's Hydrol Blue was rather unexpected and must in part be associated with a reduction in the resonance energy of the univalent ion (I; R = CF_3) brought about by the crowding effect of the α-substituent as well as the destabilising influence of the electron-withdrawing group. The first band shows a large bathochromic shift (82·5 nm) compared with the parent dye in accord with the overall effect of a bulky electron-withdrawing group at an inactive position[9] in an electronically symmetrical dye.[10] Although a band below 400 nm characteristic of an unsymmetrical conformation is not observed, a second band appears at 610 nm (Table) and it is suggested that this band can be associated with aggregation effects in the relatively concentrated solution (0·04M) required for the spectral measurements; the first and second bands arise from different species since an increase in temperature from 30 to 70 °C leads to a dramatic change in the ratio of the maximum absorption intensities (Table).

The introduction of *o*-methyl groups as extra crowding substituents into the α-trifluoromethyl dye leads to the production of unsymmetrical conformations in which the steric strain is alleviated by rotation of just one of the dimethylaminophenyl groups, and this is supported by an examination of molecular models. Thus, both the 2-methyl and the 2,2′-dimethyl derivatives (III; R^1 = Me, R^2 = H, and $R^1 = R^2$ = Me, respectively) show the anomalous second band associated with protonation of a partially deconjugated dimethylamino-group (Table). The univalent cations are therefore electronically unsymmetrical so that hypsochromic shifts of the first band, relative to that of the parent dye (I; R = CF_3), are to be expected[11] and are in fact observed (Table). In each case the first band arises from the univalent ion since addition of hydrochloric acid to a solution of dye base in 98% acetic acid leads to preferential reduction of this band. The absence of a band near 600 nm may be connected with the low ability to aggregate of highly twisted dyes of this type.[12]

[4] G. Hallas, *J. Chem. Soc.* (*B*), 1967, 91.

[5] R. Filler, *Adv. Fluorine Chem.*, 1970, **6**, 1.

[6] A. Mendel, *J. Organometallic Chem.*, 1966, **6**, 97.

[7] G. A. Olah and C. U. Pittman, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 3310.

[8] S. V. Kulkarni, R. Schure, and R. Filler, *J. Amer. Chem. Soc.*, 1973, **95**, 1859.

[9] M. J. S. Dewar, *J. Chem. Soc.*, 1950, 2329.

[10] M. J. S. Dewar, 'Steric Effects in Conjugated Systems,' ed. G. W. Gray, Butterworths, London, 1958, p. 46.

[11] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, and G. Van Zandt, *Chem. Rev.*, 1947, **41**, 325.

[12] C. C. Barker, M. H. Bride, and A. Stamp, *J. Chem. Soc.*, 1959, 3957.

Preparations.—The parent dye base (IV; $R^1 = R^2 =$ H) was readily obtained by interaction of 4-dimethylaminophenyl-lithium[13] with either *NN*-dimethyl-4-trifluoroacetylaniline[14] or ethyl trifluoroacetate and gave colourless needles, m.p. 162—163 °C (from ethanol) (lit.,[6] m.p. 162—163 °C). The methyl-substituted dye bases were similarly prepared from the ketone and the ester, respectively, with the appropriate aryl-lithium compound.

EXPERIMENTAL

Absorption spectra were measured with a Unicam SP 800 recording spectrophotometer for 0·04M solutions of the dye bases in 98% acetic acid. ^{1}H N.m.r. spectra were obtained with a Varian HA 100 spectrometer for solutions in deuteriochloroform at the Physico-chemical Measurements Unit, Harwell.

4,4'-*Bisdimethylamino*-2-*methyl*-α-*trifluoromethyldiphenylmethanol*.—Ethereal 4-dimethylamino-2-methylphenyl-lithium, from 2-bromo-5-dimethylaminotoluene[15] (10·0 g) and the n-butyl-lithium–1,2-bisdimethylaminoethane complex,[13] was filtered under nitrogen into *NN*-dimethyl-4-trifluoroacetylaniline (6·5 g) in ether (50 ml), and the mixture was boiled for 1 h. Addition of water and removal of solvent from the dried ($MgSO_4$) organic layer yielded a solid which, thrice crystallised from ethanol, gave colourless crystals of the *dye base* (4·3 g), m.p. 175—176 °C (Found: C, 64·6; H, 6·7; F, 15·8; N, 7·9. $C_{19}H_{23}F_3N_2O$ requires C, 64·8; H, 6·6; F, 16·2; N, 8·0%), τ 2·49 (1H, d, J_o 8·5 Hz, 6-H), 2·78 (2H, d, J_o 9·0 Hz, 2'- and 6'-H), 3·38 (2H, d, J_o 9·0 Hz, 3'- and 5'-H), 3·41—3·52 (2H, m, 3- and 5-H), 7·08 (12H, s, NMe_2), and 8·06 (3H, s, Me).

4,4'-*Bisdimethylamino*-2,2'-*dimethyl*-α-*trifluoromethyldiphenylmethanol*.—Ethereal 4-dimethylamino-2-methylphenyl-lithium, prepared as above, with ethyl trifluoroacetate (2·1 g) in ether (30 ml) yielded a solid which, twice crystallised from ethanol, gave colourless needles of the *dye base* (2·5 g), m.p. 144—145 °C (Found: C, 65·7; H, 6·9; F, 15·6; N, 7·7. $C_{20}H_{25}F_3N_2O$ requires C, 65·6; H, 6·9; F, 15·6; N, 7·7%), τ 2·58 (2H, d, J_o 8·5 Hz, 6- and 6'-H), 3·42—3·58 (4H, m, 3-, 3'-, 5-, and 5'-H), 7·09 (12H, s, NMe_2), and 8·03 (6H, s, Me).

A grant from the S.R.C. is acknowledged.

[3/1454 *Received*, 11*th June*, 1973]

---

[13] G. Hallas and D. R. Waring, *Chem. and Ind.*, 1969, 620.

[14] W. A. Sheppard, *J. Amer. Chem. Soc.*, 1965, **87**, 2410.

[15] W. S. Emerson, F. B. Dorf, and A. J. Deutschman, *J. Amer. Chem. Soc.*, 1940, **62**, 2159.