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DYES CONTAINING FLUORINE—I

ELECTRONIC ABSORPTION SPECTRUM OF 2,3,4,5,6-PENTAFLUORO MALACHITE GREEN AND THE ELECTRONIC EFFECT OF THE PENTAFLUOROPHENYL GROUP

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Abstract—The absorption spectrum of the pentafluoro derivative of malachite green supports the view that the electronic effect of the pentafluorophenyl group is less than that predicted on the basis of additivity of the fluorine substituent parameters.

POLYFLUOROAROMATIC CHEMISTRY has aroused considerable interest in recent years,[1] expecially in the study of organometallic compounds[2] and in nucleophilic replacements,[3] but the effects of fluoroaromatic groups in dyes do not appear to have been examined in any detail apart from metal perfluorophthalocyanines.[4] In view of the importance of steric as well as electronic effects in basic di- and tri-arylmethane dyes,[5] the present study was initiated.

Of particular interest is the electronic effect of the pentafluorophenyl group. Eaborn *et al.*[6] have pointed out that a number of authors suggest that the pentafluorophenyl group is rather more deactivating than expected on the basis of additivity of the fluorine substituent effects, whereas their quantitative experimental results for protodesilylation and protodestannylation show the pentafluorophenyl group to have a smaller deactivating effect than predicted. These findings have recently been confirmed by Taylor[7] who measured the rates of pyrolysis of 1-phenylethylacetate and 1-(pentafluorophenyl)ethyl acetate and found that at 625 K the latter undergoes elimination 4·60 times slower than the former in contrast to the value of 7·75 obtained on the basis of the additivity principle. In the absence of solvent effects and of steric acceleration, the difference in observed and calculated rates can be unambiguously ascribed to an electronic effect: the five fluorine atoms are less electron-withdrawing than when acting alone. Sheppard[8] has determined the substituent parameters for the pentafluorophenyl group by classical pK_a measurements and by ^{19}F NMR calibrations on the appropriate pentafluorobiphenyl derivatives. The pentafluorophenyl group inductively withdraws electrons more strongly than a phenyl group but much less than a trifluoromethyl group; the results are interpreted in terms of p–π interactions.

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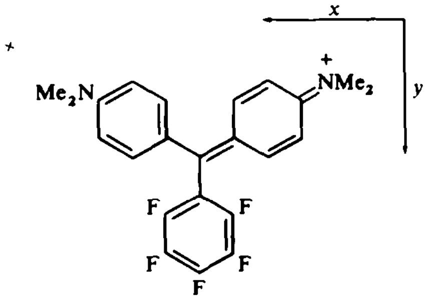
RESULTS AND DISCUSSION

The 2,3,4,5,6-pentafluoro derivative of malachite green (I) shows a strong first band (*x*-band) at 658 nm and a weak second band (*y*-band) at 423 nm in both 98% acetic acid and ethanolic hydrogen chloride (Table 1). Thus, compared with that of malachite green, the *x*-band of the pentafluoro derivative shows a bathochromic shift of 37 nm.

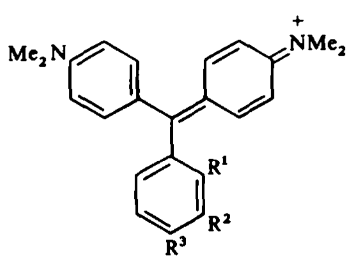
TABLE 1. SPECTRAL DATA FOR 10^{-5}M-SOLUTIONS OF DERIVATIVES OF MALACHITE GREEN

Dye	Solvent	λ_{max} (nm) (10^{-4} ε in parentheses)
Malachite green	98% HOAc	621 (10·4), 427·5 (2·0)
II (R^1 = F, R^2 = R^3 = H)	98% HOAc	635 (11·3), 424 (1·6)
II (R^2 = F, R^1 = R^3 = H)	98% HOAc	630 (10·4), 426·5 (2·2)
II (R^3 = F, R^1 = R^2 = H)	98% HOAc	620 (10·6), 430·5 (2·1)
I	98% HOAc	658 (10·2), 423 (0·95)
I	EtOH + 1 equiv HCl	658 (10·8), 423 (1·0)

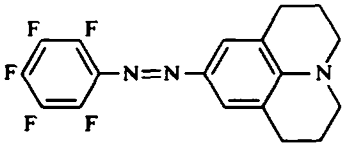
The spectral shifts brought about by substituents in the 3 or 4 position of the phenyl ring are directly proportional to the Hammett substituent constant,[9] since the first band originates in a transition from the NBMO to the first unoccupied MO and it is the energy of the latter orbital only which is changed by substituents. There is some evidence for a simple additivity relationship for substituents at positions where steric effects are unimportant: the bathochromic shift of 26 nm brought about by the introduction of two *m*-trifluoromethyl groups is exactly twice that of the 3-substituted derivative.[10] A crowding substituent in the 2 position of malachite green generally produces a bathochromic shift of the first band relative to that of the 4-substituted isomer.[9] Thus, on the basis of the known[9] effects of single fluorine atoms in the phenyl ring of malachite green (Table 1), a shift of the order of 45 nm may be anticipated for the pentafluoro compound: this estimate, however, is too low since the steric effect of the buttressed *o*-fluorine atoms must contribute to the overall bathochromic shift and must also obscure the hypsochromic mesomeric interaction of the 4-fluorine substituent. The operation of a considerable crowding effect is confirmed by molecular models and by the relative unimportance of the *y*-band of the pentafluoro derivative (Table 1): the marked reduction in intensity and the hypsochromic shift of this band, relative to that of the parent dye, is consistent with increased departure from molecular uniplanarity along the *y*-axis of the molecule mainly caused by rotation of the pentafluorophenyl group about the central bonds. It was expected that ε_{max} (x) would be somewhat higher than the observed value in accordance with the finding that progressive deconjugation of the phenyl group leads to a gradual increase in absorption intensity of the *x*-band.[11] The increase in intensity observed on passing from 98% acetic acid to ethanolic hydrogen chloride suggests that the dye base is incompletely converted into colour salt in the former solvent. In fact, the presence of a vestigial band at 265 nm in ethanolic hydrogen chloride indicates that the dye is not entirely formed even in this solvent. Although in this type of dye the dimethylamino groups bear a relatively large amount of charge delocalized from the central carbon,[12] it is noteworthy that the pentafluorophenyl carbonium ions are unstable compared with the corresponding phenylcarbonium ions;[13,14] the pK_{R^+} of tris(pentafluorophenyl)methanol[13] is *ca.* −17·5 compared with −6·63 for triphenylmethanol.[15]



I



II



III

The relatively small bathochromic shift (37 nm) of the *x*-band of the pentafluoro derivative of malachite green implies qualitatively that the electron-withdrawing effect of the pentafluorophenyl group is less than that predicted by the additivity principle. It is significant that the five fluorine atoms in 9-pentafluorophenylazojulolidine (III) produce a bathochromic shift of 33 nm of the first band, relative to that of the parent compound,[16] since this band also arises from a NBMO → π^* transition. Furthermore, whereas the long-wavelength band of the triphenylmethyl cation appears at 428 nm, the first band of the perfluoro analogue[13] is observed at only 500 nm.

EXPERIMENTAL

Absorption spectra were measured on a Unicam SP 800 recording spectrophotometer. PMR spectra were determined on a Varian HA 100 spectrometer at the Physico-Chemical Measurements Unit, Harwell.

The dye base was obtained by the action of pentafluorophenyllithium on Michler's ketone. A similar reaction using pentafluorophenylmagnesium bromide gave an impure product. The leuco base was obtained in low yield from pentafluorobenzaldehyde and N,N-dimethylaniline. Oxidation of this compound with lead dioxide[9] gave the dye, but formation of the methyl ether of the dye base using sodium methoxide was prevented by nucleophilic replacement of fluorine.

4′,4″-Bisdimethylamino-2,3,4,5,6-pentafluorotriphenylmethanol. A suspension of Michler's ketone (5·4 g, 0·02 mole) in ether (100 ml) was added rapidly to pentafluorophenyl-Li, prepared at −78° from n-BuLi (0·02 mole) in hexane and bromopentafluorobenzene (0·02 mole) in hexane (50 ml). After 1 hr, the mixture was allowed to reach room temp and was then poured into water. Removal of solvent from the dried (Na_2SO_4) organic layer gave a solid (5·5 g). Elution of this material (1·0 g) from alumina (40 g) with benzene gave a product which on crystallization from light petroleum (b.p. 60–80°) yielded the dye base (0·75 g) as colourless needles: m.p. 101–102°: NMR ($CDCl_3$) 2·90 (d, 4, $J = 9$ Hz, protons *m* to NMe_2), 3·35 (d, 4,

$J = 9$ Hz, protons *o* to NMe_2), 7·06 (s, 12, NMe_2). (Found: C, 63·3: H, 4·9: F, 21·5: N, 6·2. $C_{23}H_{21}F_5N_2O$ requires: C, 63·3: H, 4·8: F, 21·7: N, 6·4%).

4′,4″-*Bisdimethylamino*-2,3,4,5,6-*pentafluorotriphenylmethane.* A mixture of pentafluorobenzaldehyde (9·8 g, 0·05 mole), N,N-dimethylaniline (18·2 g, 0·15 mole), EtOH (40 ml), and 36% HCl (12·0 g, 0·1 mole) was boiled for 24 hr. The cooled mixture was basified with aqueous-ethanolic ammonia, and the resulting oily product yielded crystals on standing. The crude material was twice crystallized from EtOH to give the leuco base (6·0 g) as colourless needles: m.p. 123–124°: NMR ($CDCl_3$) 2·92 (d, 4, $J = 9$ Hz, protons *m* to NMe_2), 3·34 (d, 4, $J = 9$ Hz, protons *o* to NMe_2), 4·28 (s, 1, CH), 7·07 (s, 12, NMe_2). (Found: C, 65·6: H, 5·4: F, 22·5: N, 6·9. $C_{23}H_{21}F_5N_2$ requires: C, 65·7: H, 5·0: F, 22·6: N, 6·7%).

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