Extended Conjugation in Di- and Tri-arylmethane Dyes. Part IV.[1] Electronic Absorption Spectra of Some Phenanthrene Analogues of Malachite Green

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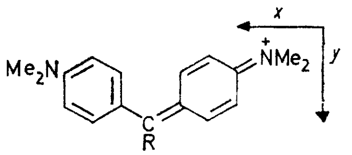
Absorption spectra of five phenanthrene analogues of Malachite Green have been determined for solutions in 98% acetic acid. The spectral changes are correlated with steric and electronic factors. For a series of α-aryl derivatives of Michler's Hydrol Blue, the position of the first band is approximately related to the ability of the aryl system to delocalise charge in the derived univalent cation.

We have previously examined the effects of extended conjugation through 9,9-dimethylfluorene[2] and naphthalene[1,3] by incorporating these ring systems severally into some basic di- and tri-phenylmethane dyes. The earlier results[1-3] suggest that this approach can usefully be extended to more complex polycyclic systems. In this paper the absorption spectra of five analogues of Malachite Green, in which the phenyl ring is replaced by phenanthryl, are discussed. In some of these dyes steric as well as electronic effects are of significance.



(I)

In Part III[1] it was pointed out that the x band † of the 1-naphthyl analogue of Malachite Green (I; R = 1-naphthyl) shows a bathochromic shift and an increase in intensity compared with that of Malachite Green itself (Table) in accord with the crowding effect of the naphthyl group;[4] a smaller shift is shown by the isomeric 2-naphthyl analogue (I; R = 2-naphthyl) from which the steric effect is absent.[3] For both dyes, the y band exhibits a pronounced bathochromic shift (Table) which can be associated with the electronic effect of the naphthyl substituent. A marked reduction in $\varepsilon_{\text{max.}\,(y)}$ is observed for the 1-naphthyl compound (I; R = 1-naphthyl) as a result of increased departure from molecular uniplanarity along the unsymmetrical y axis. Sterically, the 2- and 3-phenanthryl analogues of Malachite Green (I; R = 2- and 3-phenanthryl, respectively) are equivalent to the parent dye and its 2-naphthyl analogue (I; R = 2-naphthyl) whereas the 1- and 9-phenanthryl dyes (I; R = 1- and 9-phenanthryl, respectively) resemble the 1-naphthyl compound (I; R = 1-naphthyl); the 4-phenanthryl isomer (I; R = 4-phenanthryl) is more overcrowded. Thus, a comparison of the phenanthrene dyes with their naphthalene congeners is instructive.

Spectral data for 10^{-5}M solutions in 98% acetic acid and NBMO coefficients of some α-aryl derivatives of Michler's Hydrol Blue

		$\lambda_{\text{max.}}$/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1} in parentheses)	
α-Substituent	c_0	x Band	y Band
Phenyl	0·755	621 (10·4)	427·5 (2·0)
9,9-Dimethyl-2-fluorenyl		623 (9·7)	484 (3·9)
4-Biphenylyl	0·718	625·5 (10·2)	454 (3·1)
2-Phenanthryl	0·738	626 (10·4)	462 (3·6)
2-Naphthyl	0·728	626·5 (10·5)	458 (3·2)
3-Phenanthryl	0·715	627·5 (10·4)	474 (2·6)
1-Naphthyl	0·671	630 (12·0)	460 (1·1)
1-Phenanthryl	0·680	630·5 (12·3)	455 (1·1)
9-Phenanthryl	0·668	632·5 (12·4)	470 (1·4)
4-Phenanthryl	0·701	634 (12·7)	450 (1·0)

As anticipated, the value of $\varepsilon_{\text{max.}\,(x)}$ remains constant at 104,000 for Malachite Green and its 2-naphthyl, 2-, and 3-phenanthryl analogues (Table) and it is clear that the dye bases are completely converted into the univalent dye cations in the 98% acetic acid used as solvent.[5] On the other hand, $\varepsilon_{\text{max.}\,(x)}$ is increased to *ca.* 120,000 in the 1-naphthyl, 1-, and 9-phenanthryl dyes (Table) in agreement with the steric effect of the substituent,[4] and this is confirmed by the corresponding decrease in $\varepsilon_{\text{max.}\,(y)}$. The parameters for the latter group of dyes are very similar, but the value of $\varepsilon_{\text{max.}\,(y)}$ for the 9-phenanthryl analogue (14,000) is rather higher than that for the isosteric dyes (11,000). The highly crowded 4-phenanthryl analogue of Malachite Green (I; R = 4-phenanthryl) has the highest value of $\varepsilon_{\text{max.}\,(x)}$ and the lowest value of $\varepsilon_{\text{max.}\,(y)}$ in accord with the greatest steric effect. However, it was expected from a consideration of molecular models that the disparity between these parameters would have been even greater and it seems likely that part of the overcrowding is relieved by deformation of the phenanthrene ring system; it is relevant to recall that 4-methylphenanthrene is not planar.[6] All of the naphthalene and phenanthrene dyes show pronounced bathochromic shifts of the y band (Table) but, not unexpectedly, no obvious pattern emerges.

The values of $\lambda_{\text{max.}\,(x)}$ for the phenanthrene dyes merit special consideration and comparison with the x bands of other α-aryl derivatives of Michler's Hydrol Blue (I; R = H). The relative ability of aryl groups to

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† Dyes of the Malachite Green type (I; R = aryl) show two absorption bands in the visible region corresponding to two $\pi \longrightarrow \pi^*$ transitions which differ in direction and magnitude of transition moment.

[1] Part III, G. Hallas, K. N. Paskins, and D. R. Waring, *J.C.S. Perkin II*, 1972, 2281.

[2] G. Hallas, J. D. Hepworth, and D. R. Waring, *J. Chem. Soc.* (*B*), 1970, 975.

[3] G. Hallas and D. R. Waring, *J. Chem. Soc.* (*B*), 1970, 979.

[4] C. Aaron and C. C. Barker, *J. Chem. Soc.* (*B*), 1971, 319.

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

[6] C. Reid, *J. Mol. Spectroscopy*, 1957, **1**, 18.

stabilise carbonium ions has been determined by several workers;[7-9] good agreement is shown between experimental observations[7-9] and theoretical calculations.[7,10] It is now found that for a series of α-aryl derivatives of Michler's Hydrol Blue (Table) the bathochromic shifts shown by the first bands of these dyes approximately parallel the changes in non-bonding molecular orbital (NBMO) coefficients[7] or the probability of charge residing on the α-carbon atom,[10] apart from the overcrowded 4-phenanthryl dye (I; R = 4-phenanthryl), such that the greater the shift the less able is the aryl group to stabilise the cation. A simple relationship might well be expected since the first band originates in a transition from the NBMO to the first unoccupied MO in terms of the corresponding isoconjugate carbanion, and it is the energy of the latter orbital only which is changed by substituents.[11] This argument ignores steric effects and it is clear that a contribution towards the bathochromic shift observed in the 1-naphthyl type dyes must come from the crowding effect of the substituent. Nevertheless, the position of the first band can be approximately correlated with the ability of the aryl system to delocalise charge in the derived univalent cation, but caution is required in relating a property of a single electronic state to one based on a difference between two states.

Although phenanthrene can be formally derived from biphenyl, in practice the 2-phenanthryl system is less effective in stabilising a derived carbonium ion than is the 4-biphenylyl system and it seems more correct to compare the 2-phenanthryl with the 2-naphthyl system.[9] Our results tend to support this supposition. Thus, the parameters for the 2-naphthyl and 2-phenanthryl analogues of Malachite Green are very similar (Table), but not very different from those of the 4-biphenylyl compound (I; R = 4-biphenyl). For those dyes derived from Malachite Green in which steric effects are absent the increased intensity of the y band can be associated with extension of conjugation along the y axis, since it is well known[12] that in a conjugated system intensity is dependent on length, although the 3-phenanthryl dye (I; R = 3-phenanthryl) appears to be anomalous.

Preparations.—The various methyl phenanthroates were available by literature methods;[13] interaction of the esters with 4-dimethylaminophenyl-lithium[14] gave the required dye bases. It was not possible to purify bis-(4-dimethylaminophenyl)-4-phenanthrylmethanol owing to the ease with which the base is converted into the corresponding dye, due presumably to the reduction of strain; the dye was isolated as the perchlorate.

EXPERIMENTAL

Absorption spectra were measured with a Unicam SP 800 recording spectrophotometer for solutions of the dye bases (or perchlorate) in 98% acetic acid.

Bis-(4-dimethylaminophenyl)-1-phenanthrylmethanol.— Ethereal methyl 1-phenanthroate (1·0 g) was added to ethereal 4-dimethylaminophenyl-lithium, prepared from 4-bromo-*NN*-dimethylaniline (3·0 g) by transmetallation,[14] and the mixture was boiled for 1 h before being added to water (50 ml). The product obtained on removal of the solvent, after trituration with light petroleum (b.p. 40—60 °C), was twice crystallised from ethanol yielding crystals of the *dye base* (0·1 g), m.p. 167—168 °C (Found: C, 83·2; H, 6·7; N, 6·2. $C_{31}H_{30}N_2O$ requires C, 83·4; H, 6·8; N, 6·3%).

Bis-(4-dimethylaminophenyl)-2-phenanthrylmethanol.— By following the above procedure, methyl 2-phenanthroate (1·0 g) and 4-dimethylaminophenyl-lithium afforded a product which was eluted with benzene–acetone (99 : 1) from a column of neutral alumina; only those fractions which gave a colour with acetic acid were retained. The resultant solid was thrice crystallised from ethanol to give crystals of the *dye base* (0·1 g), m.p. 142—143 °C (Found: C, 83·1; H, 6·8; N, 6·0%).

Bis-(4-dimethylaminophenyl)-3-phenanthrylmethanol.— By following the above procedure, methyl 3-phenanthroate (1·0 g) and 4-dimethylaminophenyl-lithium yielded a product which was purified by chromatography and repeated crystallisation from ethanol to give crystals of the *dye base* (0·05 g), m.p. 145—146 °C (Found: C, 83·6; H, 6·7; N, 6·2%).

Bis-(4-dimethylaminophenyl)-9-phenanthrylmethanol.— By following the above procedure, methyl 9-phenanthroate (1·0 g) and 4-dimethylaminophenyl-lithium afforded a solid which was twice crystallised from ethanol to give crystals of the *dye base* (0·2 g), m.p. 134—135 °C (Found: C, 83·3; H, 6·8; N, 6·1%).

4-Phenanthryl Analogue of Malachite Green Perchlorate.— By following the above procedure, methyl 4-phenanthroate (1·0 g) and 4-dimethylaminophenyl-lithium yielded a product which resisted purification. The crude dye base was dissolved in ethanolic hydrogen chloride and after removal of the solvent the dye was dissolved in water and filtered into an aqueous solution of sodium perchlorate (2%; 50 ml). The resultant solid was dissolved in dry acetone and partly reprecipitated by the addition of dry ether to give crystals of the *dye perchlorate* (Found: C, 70·0; H, 5·8; Cl, 6·9; N, 5·2. $C_{31}H_{29}ClN_2O_4$ requires C, 70·2; H, 5·5; Cl, 6·7; N, 5·3%).

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