Extended Conjugation in Di- and Tri-arylmethanes. Part III.[1] Electronic Absorption Spectra of Transversely Conjugated Naphthalene Analogues of Crystal Violet, Malachite Green, and Michler's Hydrol Blue

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Spectral changes caused by the effect of the additional ring in transversely conjugated naphthalene analogues of Crystal Violet, Malachite Green, and Michler's Hydrol Blue are described and discussed. Although *peri*-hindrance of the terminal dimethylamino-groups leads to incomplete conversion of dye base into dye in acid solution, and to ready protonation of the crowded groups, the univalent cations are shown to be electronically symmetrical and pronounced bathochromic shifts of the first bands are observed. The carbonyl group of bis-(4-dimethylamino-1-naphthyl) ketone is unusually resistant to reduction.

IN Part II [1] the absorption spectra of some longitudinally conjugated naphthalene analogues of Crystal Violet, Malachite Green, and Michler's Hydrol Blue, in which conjugation is extended through the 2- and 6-positions of the naphthalene ring, were discussed. The absorption spectra of a number of transversely conjugated naphthalene analogues of the same basic di- and tri-phenylmethane dyes have now been determined. In these dyes steric as well as electronic effects are of significance.

Several basic dyes of commercial importance, such as (I; R = NHEt or R = NHPh), are known to contain one naphthalene ring system in which conjugation is extended through the 1- and 4-positions of the naphthalene ring.[2] The presence of more than one naphthalene ring leads to difficulty in oxidation of the corresponding leuco-base. Friedländer and Welmans [3] were thus unable to obtain a dye from the dinaphthyl analogue of Malachite Green leuco-base (II; R = H) and Gokhle and Mason [4] could not oxidise the trinaphthyl analogue of Crystal Violet leuco-base (III; R = H). The latter workers [4] obtained a very low yield (2%) of the dinaphthyl analogue of Michler's hydrol (IV; R = H) by treatment of the corresponding analogue of methane base with chloranil, although Morgan [5] had previously failed to oxidise this base using lead dioxide. Gokhle and Mason [4] reported that the hydrol (IV; R = H) dissolves in cold acetic acid to give a faintly green solution which becomes an intense blue-violet on warming ($\lambda_{max.}$ 679 nm). The mononaphthyl hydrol (V) was obtained from the corresponding ketone and gave a blue solution in acetic acid ($\lambda_{max.}$ 651 nm).[4]

A measure of the electronic effect of the 1-naphthyl group can be obtained from the spectrum of the analogue of Malachite Green (I; R = H). The *x* band of this dye 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.[6] At the same time, the *y* band exhibits a marked bathochromic shift (32·5 nm) and a reduction in intensity compared with that of the parent dye. The decrease in $\varepsilon_{max.(y)}$ is to be expected as a result of increased departure from molecular uniplanarity along the unsymmetrical *y* axis. In simple derivatives of Malachite Green, however, such a crowding effect generally results in a hypsochromic shift of the *y* band,[7] but in this case the observed movement to longer wavelength can be associated with the electronic effect of the naphthyl substituent; the position of the *y* band ($\lambda_{max.}$ 460 nm) is virtually identical with that of the isomeric 2-naphthyl analogue (VI; R = H) from which the steric effect is absent.[1]

The introduction of a naphthalene ring conjugated through the 1- and 4-positions into a di- or tri-arylmethane dye results in a molecule which is sterically hindered both at the central carbon atom and also at the relevant dimethylamino-group. Maximum stabilisation of the univalent cation should be achieved in the mono-naphthalene analogue of Crystal Violet (I; R = NMe_2). Effective conjugation of the hindered dimethylamino-nitrogen atom with the central carbon atom in this dye would result in a spectrum with a single band in the visible region, like Crystal Violet, and this is in fact observed when the methyl ether of the dye base (VII; R^1 = Me, R^2 = NMe_2) is dissolved in ethanol containing one equiv. of hydrogen chloride (Table). The univalent ion ($\lambda_{max.}$ 623 nm) absorbs at a longer wavelength and at a slightly lower intensity (ε 98,000) than Crystal Violet ($\lambda_{max.}$ 589 nm; ε 117,000) and its 2,6-naphthalene analogue (VI; R = NMe_2) ($\lambda_{max.}$ 613·5 nm; ε 103,000).[1] The bathochromic shift (34 nm) of the first band can be attributed largely to the electronic effect of the naphthalene system, although crowding of the central carbon atom in derivatives of Crystal Violet leads to an increase in $\lambda_{max.}$ [8] as does hindrance of a dimethylamino-group;[9] thus, the 2-methyl derivative of Crystal Violet shows a bathochromic shift of 8 nm (ε 110,000) and the 3-methyl isomer a shift of 10·5 nm (ε 95,000). However, it appears that the additional ring in the naphthalene system exerts a smaller crowding effect than these methyl substituents.

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

[2] 'The Colour Index,' The Society of Dyers and Colourists, Bradford, 3rd edn., 1971, vol. 4, p. 4410.

[3] P. Friedländer and P. Welmans, *Ber.*, 1888, **21**, 3123.

[4] B. Gokhle and F. A. Mason, *J. Chem. Soc.*, 1931, 118.

[5] G. T. Morgan, *J. Chem. Soc.*, 1900, **77**, 814.

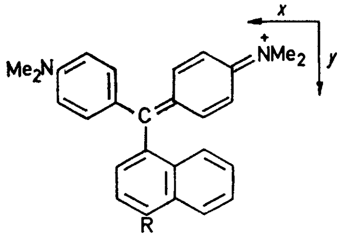
[6] C. Aaron and C. C. Barker, *J. Chem. Soc.* (*B*), 1971, 319.

[7] C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp, *J. Chem. Soc.*, 1961, 1285.

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

[9] C. C. Barker, G. Hallas, and A. Stamp, *J. Chem. Soc.*, 1960, 3790.

Thus, the intensity of the x band of the 2-methyl derivative of Malachite Green ($\varepsilon_{\text{max.}}$ 123,000) is slightly greater than that of the 1-naphthyl analogue (I; R = H) (ε 120,000); the value of $\varepsilon_{\text{max.}(x)}$ is a direct measure of the steric effect of a substituent in the 2-position.[6] Further, the absence of a second band in the visible region is indicative of the relative stability of the naphthalene dye (I; R = NMe_2) and consistent with an even distribution of charge. Similarly, in 98% acetic acid the spectrum appears to be that of the univalent ion (I; R = NMe_2), but absorption due to the bivalent cation (I; R = $^+NHMe_2$), formed by protonation of the *peri*-hindered dimethylamino-group, becomes apparent as the acidity is increased by addition of water to the solvent (Table). In 50% acetic acid a fairly close approximation to the spectrum of the bivalent ion is obtained, this being shown by the correspondence between the spectrum observed and that of the 1-naphthyl analogue of Malachite Green (I; R = H). The bathochromic and hypsochromic shifts of the first and the second band, respectively, of the bivalent ion (I; R = $^+NHMe_2$), relative to the corresponding bands of the 1-naphthyl analogue of Malachite Green (I; R = H), are consistent with the electron-withdrawing effect of a protonated dimethylamino-group. These effects are closely similar to those observed with the isomeric 2,6-naphthalene analogue of Crystal Violet (VI; R = NMe_2).[1]



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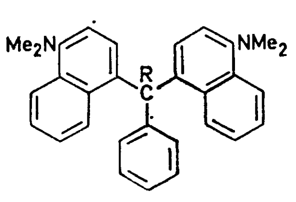

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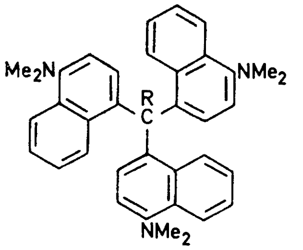

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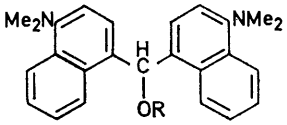

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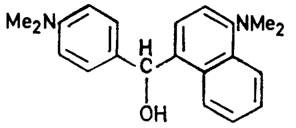

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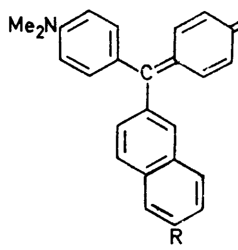

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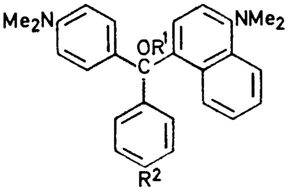

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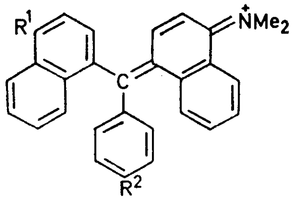

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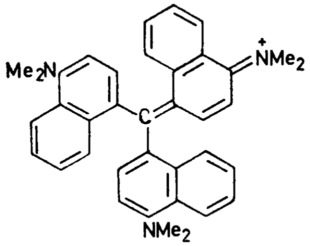

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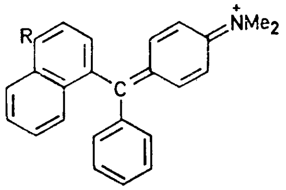
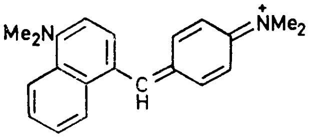


(X)



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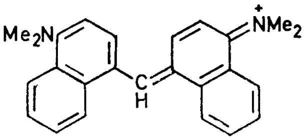

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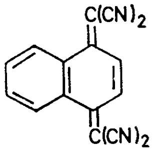


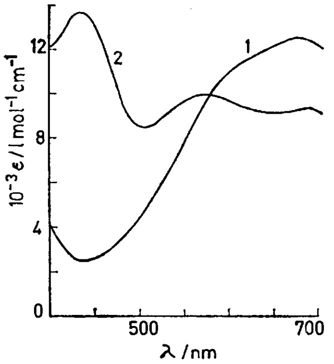
(XIII)

The analogue of Crystal Violet with two naphthalene rings (VIII; $R^1 = R^2 = NMe_2$) gives a typical spectrum in ethanolic hydrogen chloride (Table), although the intensity of the univalent ion is somewhat reduced ($\varepsilon_{\text{max.}}$ 64,000) relative to that of the mononaphthalene analogue (ε 98,000). A pronounced bathochromic shift (70 nm) is observed, compared with Crystal Violet, and again this can be largely associated with the electronic effect of the two naphthalene ring systems; the overall bathochromic shift is very similar to that given by the isomeric 2,6-naphthalene analogue (77 nm), but in the latter case the univalent ion is much less stable ($\varepsilon_{max.}$ 11,200).[1] The spectrum of the dinaphthalene analogue (VIII; $R^1 = R^2 = NMe_2$) in 98% acetic acid is closely similar to that in ethanolic hydrogen chloride (Table), but absorption due to protonated species becomes apparent on increasing the acidity of the solvent. In 30% acetic acid the first band ($\lambda_{max.}$ 677 nm) can be associated with the bivalent cation (VIII; $R^1 = {}^+NHMe_2$, $R^2 = NMe_2$). The second band ($\lambda_{max.}$ 439 nm) is relatively strong (Table) and is probably made up of the *y* band of the bivalent cation (VIII; $R^1 = {}^+NHMe_2$, $R^2 = NMe_2$) superimposed on the first band of the tervalent cation (VIII; $R^1 = R^2 = {}^+NHMe_2$); this behaviour is very similar to that shown by the 3,3′-dimethyl derivative of Crystal Violet.[9]

Spectral data for 10^{-5}M solutions of naphthalene analogues of Crystal Violet, Malachite Green, and Michler's Hydrol Blue

Dye	Solvent	Absorption maxima/nm $10^{-4}\varepsilon$/l mol^{-1} cm^{-1} (in parentheses)
Crystal Violet	98% HOAc	589 (11·7)
(I; R = NMe_2)	98% HOAc	623·5 (9·4)
(I; R = NMe_2)	50% HOAc	638·5 (10·2); 426 (0·9)
(I; R = NMe_2)	EtOH + 1 equiv. HCl	623 (9·8)
(VIII; $R^1 = R^2 = NMe_2$)	98% HOAc	660 (6·4)
(VIII; $R^1 = R^2 = NMe_2$)	30% HOAc	677 (3·4); 439 (1·0)
(VIII; $R^1 = R^2 = NMe_2$)	EtOH + 1 equiv. HCl	659 (6·4)
(IX)	98% HOAc	678 (2·5)
(IX)	12·5% HOAc	426 (1·2)
(IX)	Me_2CO + 1 equiv. HCl	664 (2·1)
Malachite Green	98% HOAc	621 (10·4); 427·5 (2·0)
(I; R = H)	98% HOAc	630 (12·0); 460 (1·1)
(X; R = NMe_2)	100% HOAc	666 (5·0); 446 (1·6)
(X; R = NMe_2)	50% HOAc	664 (1·65); 444 (2·4)
(X; R = NMe_2)	EtOH + 10 equiv. HCl	667 (4·65); 446 (1·5)
(VIII; $R^1 = NMe_2$, R^2 = H)	98% HOAc	688 (0·92); 575 (1·0); 433 (1·4)
(VIII; $R^1 = NMe_2$, R^2 = H)	EtOH + 10^4 equiv. HCl	432 (1·5)
Michler's Hydrol Blue	98% HOAc	607·5 (14·75)
(XI)	98% HOAc	651 (1·6)
(XII)	98% HOAc	692 (0·015)

A solution of the trinaphthalene analogue of Crystal Violet base (III; R = OH) in acetic acid, unlike that of the isomeric 2,6-naphthalene compound,[1] slowly develops a colour (Table), although the intensity of the first band is further reduced ($\varepsilon_{max.}$ 25,000) relative to that of the dinaphthalene compound (VIII; $R^1 = R^2 = NMe_2$). The true position and nature of the first band is a little uncertain inasmuch as a rather broad spectrum is obtained (Figure). It is clear, however, that there is a marked decrease in stability of the univalent cation relative to that of the corresponding dye base on passing from the di- to the tri-naphthalene analogue of Crystal Violet. The position of the long-wavelength band in 98% acetic acid ($\lambda_{max.}$ 678 nm), relative to that in acetone containing one equiv. of hydrogen chloride ($\lambda_{max.}$ 664 nm), suggests that species other than the univalent cation (IX) are present in the former solvent; molecular models indicate a considerable degree of steric hindrance and it is possible that in this dye the electronic symmetry of the system has been disturbed. Attempts to isolate the spectrum of the bivalent ion by using solutions of higher acidity were frustrated by the flatness of the absorption curves, but in 12·5% acetic acid a band characteristic of the tervalent ion is observed ($\lambda_{max.}$ 426 nm); a solution of the dye perchlorate in acetone containing 1000 equiv. of hydrogen chloride also shows a weak single band in the same region.



Absorption spectra of (1) tris-(4-dimethylamino-1-naphthyl)-methanol ($0{\cdot}5 \times 10^{-3}\varepsilon$ plotted) and (2) bis-(4-dimethylamino-1-naphthyl)phenylmethanol in 98% acetic acid

The naphthalene analogue of Malachite Green base (VII; $R^1 = R^2$ = H) shows much less tendency to form a univalent cation than the corresponding analogue of Crystal Violet base (VII; R^1 = H, $R^2 = NMe_2$), and the conversion of dye base into dye is incomplete; the situation is again very similar to that obtaining with the appropriate 2,6-naphthalene analogue.[1] The spectrum shows two bands in the visible region in both acetic acid and ethanolic hydrogen chloride (Table). A pronounced bathochromic shift (45 nm) of the first band is observed relative to Malachite Green and this can largely be associated with the electronic effect of the naphthalene ring, although crowding of the central carbon atom in derivatives of Malachite Green leads to an increase in $\lambda_{max.(x)}$ [10] as does hindrance of one of the dimethylamino-groups;[9] thus, the 2′-methyl derivative of Malachite Green shows a bathochromic shift of 14 nm (ε 75,000) and the 3′-methyl isomer a shift of 6·5 nm (ε 63,000). It is assumed that the second band arises mainly from the bivalent ion (X; R = $^+NHMe_2$) since increasing the acidity of the solvent leads to a reduction in the intensity of the first band and

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[10] C. C. Barker and G. Hallas, *J. Chem. Soc.*, 1961, 1529.

an increase in the second band (Table), thereby confirming the presence of two species. The position of the second band ($\lambda_{max.}$ 446 nm), which obscures the *y* band of the univalent ion (X; R = NMe$_2$), is comparable with that of the related *NN*-dimethylfuchsonimonium ion ($\lambda_{max.}$ 465·5 nm).[9]

The analogue of Malachite Green base with two naphthalene ring systems (II; R = OH) develops a colour only slowly in either acetic acid or ethanolic hydrogen chloride. A non-typical broad absorption spectrum is obtained with three bands in the visible region (Figure) so that the true position of the first band is rather uncertain, but it is clear that the introduction of a second naphthalene ring leads to a further bathochromic shift of this band. The stability of the univalent ion ($\lambda_{max.}$ 688 nm) is considerably reduced compared with that of the mononaphthalene dye (X; R = NMe$_2$) and protonated species predominate. The short-wavelength band ($\lambda_{max.}$ 433 nm) must be associated with the bivalent ion (VIII; R^1 = $^+$NHMe$_2$, R^2 = H) since this is the only peak present in concentrated ethanolic hydrogen chloride (Table). It is more difficult unambiguously to assign the band at 575 nm although it is in this region that bands due to aggregation are observed;[8] most triarylmethane basic dyes exhibit a shoulder on the short-wavelength side of the first band.[11] In this case, the shoulder presumably becomes the second band which is slightly more intense than the first band in acetic acid and considerably more intense in ethanolic hydrogen chloride (the ratio $\varepsilon_{max.(SB)} : \varepsilon_{max.(FB)}$ changes from 1·1 to 1·4) so that the second band can probably be associated with aggregation; Selwyn and Steinfeld[12] have recently shown that certain xanthen dyes are capable of dimer formation in ethanol even in dilute solutions.

The absorption spectrum of the naphthalene analogue of Michler's Hydrol Blue (XI) shows a pronounced bathochromic shift (43·5 nm) relative to the parent dye (Table) in agreement with the work of Gokhle and Mason,[4] but the conversion of dye base into dye in 98% acetic acid is only low at room temperature. Again, the movement to longer wavelength can mainly be attributed to the electronic effect of the naphthalene ring since whereas the 2-methyl derivative of Michler's Hydrol Blue shows a bathochromic shift of 7 nm (ε 130,000),[8] the 3-methyl isomer exhibits a hypsochromic shift of 5 nm (ε 600);[9] the 2,6-naphthalene analogue, in which crowding effects are not important, shows a bathochromic shift of 65·5 nm.[1] The absorption decreases as the acidity of the solvent is increased, owing to protonation of the *peri*-hindered dimethylamino-group. A solution of the hydrol (V) in ethanol containing one equiv. of hydrogen chloride gives a very weak colour which fades extremely rapidly. A decrease in stability of the univalent cation on passing from the mononaphthalene analogue of Crystal Violet (I; R = NMe$_2$) to that of Michler's Hydrol Blue (XI), *via* the corresponding analogue of Malachite Green (X; R = NMe$_2$), is to be expected since the bases of Crystal Violet and Malachite Green form univalent ions which are stable over a wider range of pH than is Michler's Hydrol Blue (pK_b 9·36, 6·90, and 5·61, respectively).[13]

Unlike the corresponding 2,6-naphthalene compound, the analogue of Michler's hydrol with two 1,4-naphthalene ring systems (IV; R = H) forms a dye cation in acetic acid, but at room temperature the conversion of dye base into dye is extremely low (Table). The bathochromic shift (84·5 nm) shown by this dye (XII) is effectively twice that given by the mononaphthalene dye (43·5 nm) and it may therefore be concluded that both dyes are electronically symmetrical.[14] The position of the first band ($\lambda_{max.}$ 692 nm) is somewhat different from that quoted by Gokhle and Mason ($\lambda_{max.}$ 679 nm);[4] again a rather broad absorption band is observed with a shoulder at *ca.* 580 nm.

The spectral results show that despite the crowding effects of the additional ring, the terminal nitrogen atoms attached to 1,4-naphthalene groups in these basic dyes have a greater tendency to conjugate with the central carbon atom than those in the corresponding 2,6-naphthalene analogues.[1] The first band of each dye shows a marked bathochromic shift compared with that of the parent, and this behaviour can largely be associated with the electronic effect of the 1,4-naphthalene groups; in this connection it is noteworthy that Suzuki and I'Haya[15] have recently demonstrated that in 1,4-bis-(dicyanomethylene)-1,4-dihydronaphthalene (XIII) the additional ring leads to a partial breakdown of the quinonoid structure.

Preparations.—4-Bromo-1-dimethylaminonaphthalene is best prepared by bromination of the tertiary amine by use of either bromine in carbon tetrachloride[3] or 2,4,4,6-tetrabromocyclohexa-2,5-dienone in dichloromethane;[16] the bromo-amine is conveniently purified *via* the picrate.

Analogues of Michler's hydrol are prepared by reduction of the corresponding ketone, and the analogues of Malachite Green and Crystal Violet are obtained by the reaction of an aryl-lithium compound or a Grignard reagent with a ketone or an ester.

Despite the earlier failure of Gokhle and Mason,[4] 1-dimethylamino-4-(4-dimethylaminobenzoyl)naphthalene is fairly readily obtained (51% yield) by the Friedel–Crafts reaction between 4-dimethylaminobenzoyl chloride and 1-dimethylaminonaphthalene by use of aluminium chloride at room temperature. The symmetrical bis-(4-dimethylamino-1-naphthyl) ketone is similarly prepared, but in low yield, by the interaction of 4-dimethylamino-1-naphthoyl chloride and 1-dimethylaminonaphthalene in the presence of zinc chloride; Gokhle and Mason[4] were unable to prepare this ketone. The unsymmetrical ketone is readily reduced to the corresponding hydrol (V)

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[11] V. I. Permogorov, L. A. Serdyukova, and M. D. Frank-Kamenetskii, *Optics and Spectroscopy*, 1968, **25**, 38.

[12] J. E. Selwyn and J. I. Steinfeld, *J. Phys. Chem.*, 1972, **76**, 762.

[13] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1949, 1724.

[14] R. W. Castelino and G. Hallas, *J. Chem. Soc.* (*B*), 1971, 1471.

[15] N. Suzuki and Y. J. I'Haya, *Tetrahedron*, 1970, **26**, 5379.

[16] V. Caló, F. Ciminale, L. Lopez, and P. E. Todesco, *J. Chem. Soc.* (*C*), 1971, 3652.

with sodium amalgam in ethanol, but the symmetrical ketone is surprisingly resistant. A poor yield of bis-(4-dimethylamino-1-naphthyl)methanol (IV; R = H) is obtained by using an excess of lithium aluminium hydride and separation from the ketone is difficult; such drastic conditions would normally result in formation of the corresponding methane base.[17] Prolonged treatment (28 h) of the ketone with lithium aluminium hydride in boiling dioxan followed by the addition of ethyl acetate gives rise to the ethyl ether of the dye base (IV; R = Et). The behaviour of the ketone must largely be attributed to the electronic effect of the naphthalene ring systems since the crowded 2,2′,3,3′-tetramethyl derivative of Michler's ketone behaves normally.[18] The reactions between the dinaphthyl ketone and either Grignard reagents or aryl-lithium compounds are so incomplete that this ketone is not a suitable intermediate for the preparation of analogues of Crystal Violet and Malachite Green.

Impure samples of (4-dimethylamino-1-naphthyl)bis-(4-dimethylaminophenyl)methanol (VII; $R^1 = H$, $R^2 = NMe_2$) are obtained by the reaction of 4-dimethylaminophenyl-lithium with 1-dimethylamino-4-(4-dimethylaminobenzoyl)naphthalene or by treatment of Michler's ketone with 4-dimethylamino-1-naphthylmagnesium bromide. Owing to the pronounced tendency of the dye base to be irreversibly converted into the corresponding colour salt, the readily purified methyl ether (VII; $R^1 = Me$, $R^2 = NMe_2$) was prepared by reaction of the perchlorate of the dye with methanolic sodium methoxide; attempts to convert the colour salt into the dye base by treatment with dilute aqueous sodium hydroxide result in appreciable amounts of red fuchsone formed by nucleophilic replacement of a dimethylamino-group.[19] The Crystal Violet base with two naphthalene groups is obtained from methyl 4-dimethylaminobenzoate and 4-dimethylamino-1-naphthyl-lithium, formed from the bromo-compound by transmetallation by use of the 1,2-bisdimethylaminoethane–butyl-lithium complex,[20] while that with three such groups is available from the lithium compound and diethyl carbonate.

The mononaphthalene analogue of Malachite Green base (VII; $R^1 = R^2 = H$) is readily obtained from the mononaphthyl ketone and phenyl-lithium, but the dinaphthyl analogue (II; R = OH) is best prepared from methyl benzoate and 4-dimethylamino-1-naphthyl-lithium. Bis-(4-dimethylaminophenyl)-(1-naphthyl)-methanol is similarly available from methyl 1-naphthoate and 4-dimethylaminophenyl-lithium.

EXPERIMENTAL

Absorption spectra were measured with a Unicam SP 800 recording spectrophotometer for solutions of the dye bases in ethanolic hydrogen chloride and in acetic acid. ^1H N.m.r. spectra were obtained with a Varian HA 100 spectrometer for solutions in deuteriochloroform at the Physico-Chemical Measurements Unit, Harwell.

1-Dimethylamino-4-(4-dimethylaminobenzoyl)naphthalene.—4-Dimethylaminobenzoyl chloride (10·3 g), prepared by Décombe's method,[21] 1-dimethylaminonaphthalene (20·0 g), and anhydrous aluminium chloride (8·0 g) were stirred at room temperature for 16 h and then at 80 °C for 2 h. The mixture was cooled to 40 °C, poured into hydrochloric acid (100 ml; 2M), stirred for 10 min, and neutralised with aqueous 5M-sodium hydroxide. The residue was purified by chromatography on alumina with benzene as eluant. Removal of the solvent and crystallisation of the solid from ethanol yielded pale yellow crystals of the ketone (5·2 g), m.p. 126—128 °C (lit.,[4] 128·5—129 °C).

(4-Dimethylamino-1-naphthyl)-4-dimethylaminophenylmethanol.—A mixture of 1-dimethylamino-4-(4-dimethylaminobenzoyl)naphthalene (1·0 g), 5% sodium amalgam (5·0 g), and ethanol (60 ml) was stirred vigorously and boiled for 3 h. The cooled solution was poured into water (100 ml) and the precipitate was chromatographed on neutral alumina with benzene as eluant; the fractions which gave a blue colour in acetic acid were retained. On removal of the solvent, the residue was sublimed at 180 °C and 1·0 mmHg and crystallised from ethanol yielding the hydrol (0·23 g), m.p. 63—64 °C (lit.,[4] *ca.* 62—63 °C).

(4-Dimethylamino-1-naphthyl)-4-dimethylaminophenyl-(phenyl)methanol.—Ethereal phenyl-lithium, from bromobenzene (1·57 g), was added under nitrogen to a stirred suspension of 1-dimethylamino-4-(4-dimethylaminobenzoyl)-naphthalene (2·0 g) in ether (40 ml); after 1 h the mixture was poured into water (100 ml). Removal of solvent from the dried organic layer gave a residue which was thrice crystallised from ethanol, yielding crystals of the *dye base* (0·30 g), m.p. 144 °C (Found: C, 81·7; H, 6·8; N, 7·1. $C_{27}H_{28}N_2O$ requires C, 81·8; H, 7·1; N, 7·1%).

(4-Dimethylamino-1-naphthyl)bis-(4-dimethylaminophenyl)methyl Methyl Ether.—Ethereal 4-dimethylamino-1-naphthylmagnesium bromide, from 4-bromo-1-dimethylaminonaphthalene (5·0 g), was added to a stirred suspension of Michler's ketone (4·0 g) in ether (40 ml); after 1 h under reflux the mixture was poured into a solution of ammonium chloride (2·5 g) in water (100 ml). Removal of solvent from the dried organic layer gave a residue which was dissolved in acetic acid (5 ml). The product obtained on removal of the solvent was added to water (250 ml) and the filtered solution was poured into potassium perchlorate (2·5 g) in water (100 ml). A solution of the dried perchlorate of the dye in methanol (20 ml) was slowly added to methanol (50 ml) containing sodium methoxide (1·2 g). Crystallisation of the precipitate from benzene–methanol (1 : 4) gave colourless crystals of the *methyl ether* (1·1 g), m.p. 152—153 °C (Found: C, 79·0; H, 7·7; N, 9·1. $C_{30}H_{35}N_3O$ requires C, 79·4; H, 7·8; N, 9·3%), τ 1·78 and 2·75 (4H, m, 5-, 6-, 7-, and 8-H), 2·49 (1H, d, $J_{2,3}$ 8·0 Hz, 2-H), 2·79 (4H, d, J_o 9·0 Hz, H *m* to NMe_2), 3·06 (1H, d, $J_{2,3}$ 8·0 Hz, 3-H), 3·39 (4H, d, J_o 9·0 Hz, H *o* to NMe_2), 6·87 (3H, s, OMe), and 7·12 (18H, s, NMe_2).

Bis-(4-dimethylamino-1-naphthyl) Ketone.—A solution of carbonyl chloride in benzene (12·5%; 60 ml) was added to 1-dimethylaminonaphthalene (85 g) during 1 h; the mixture was stirred overnight (18 h) at room temperature. After the addition of anhydrous zinc chloride (7·0 g), the mixture was kept at 20 °C for 3 h and then heated at 80 °C for 24 h. The amine liberated on basification with ammonia was

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removed in steam and the residue was extracted with ether, yielding a product which was eluted with benzene from alumina. Removal of solvent from the yellow solution gave an oil which became solid on trituration with light petroleum (b.p. 40—60 °C). The crude material was twice crystallised from ethanol giving yellow needles of the *ketone* (5·0 g), m.p. 172 °C (Found: C, 81·3; H, 6·6; N, 7·6. $C_{25}H_{24}N_2O$ requires C, 81·5; H, 6·6; N, 7·6%), τ 1·38, 1·76, and 2·50 (8H, m, 5-, 6-, 7-, and 8-H), 2·48 (2H, d, $J_{2,3}$ 8·0 Hz, 2-H), 3·12 (2H, d, $J_{2,3}$ 8·0 Hz, 3-H), and 7·05 (12H, s, NMe_2).

Bis-(4-*dimethylamino-*1-*naphthyl*)*methyl Ethyl Ether.*—A mixture of bis-(4-dimethylamino-1-naphthyl) ketone (0·5 g), lithium aluminium hydride (0·06 g), and dioxan (50 ml) was boiled for 28 h, further quantities of reducing agent (0·03 g) being added after 6 and 22 h. The cooled mixture was treated with ethyl acetate (20 ml), then with water (50 ml), and extracted with ether. The solid obtained on removal of the solvent was crystallised from ethanol to give impure ketone (0·2 g). Partial removal of solvent from the filtrate and addition of light petroleum (b.p. 60—80 °C) afforded a solid which was twice crystallised from light petroleum yielding pale yellow microcrystals of the *ethyl ether* (0·02 g), m.p. 134—135 °C (Found: C, 80·9; H, 7·3; N, 6·7. $C_{27}H_{30}N_2O$ requires C, 81·5; H, 7·3; N, 7·0%), τ 1·69, 1·97, and 2·54 (8H, m, 5-, 6-, 7-, and 8-H), 2·73 (2H, d, $J_{2,3}$ 8·0 Hz, 2-H), 3·03 (2H, d, $J_{2,3}$ 8·0 Hz, 3-H), 3·31 (1H, s, CH), 6·23 (2H, q, J 7·0 Hz, OEt), 7·13 (12H, s, NMe_2), and 8·68 (3H, t, J 7·0 Hz, OEt).

Bis-(4-*dimethylamino-*1-*naphthyl*)*phenylmethanol.*— Ethereal methyl benzoate (1·0 g; 0·009 mol) was added to ethereal 4-dimethylamino-1-naphthyl-lithium (0·018 mol), prepared from 4-bromo-1-dimethylaminonaphthalene by transmetallation,[20] the mixture was boiled for 2 h and kept at room temperature for 16 h before being added to water (100 ml). The oil obtained on removal of the solvent was triturated with light petroleum (b.p. 40—60 °C) to give a solid which was twice crystallised from methanol yielding crystals of the *dye base* (0·1 g), m.p. 213—214 °C (Found: C, 83·2; H, 6·8; N, 6·4. $C_{31}H_{30}N_2O$ requires C, 83·4; H, 6·8; N, 6·3%).

Bis-(4-*dimethylamino-*1-*naphthyl*)-4-*dimethylaminophenylmethanol.*—By following the above procedure, methyl 4-dimethylaminobenzoate (1·1 g; 0·006 mol) and 4-dimethylamino-1-naphthyl-lithium (0·012 mol) afforded an oil which was triturated with hexane. The resultant solid was thrice crystallised from ethanol to give crystals of the *dye base* (0·05 g), m.p. 190—191 °C (Found: C, 80·5; H, 7·0; N, 8·2. $C_{33}H_{35}N_3O$ requires C, 80·9; H, 7·2; N, 8·6%).

Tris-(4-*dimethylamino-*1-*naphthyl*)*methanol.*—By following the above procedure, diethyl carbonate (0·95 g; 0·008 mol) and 4-dimethylamino-1-naphthyl-lithium (0·024 mol) gave a product which was eluted with benzene from alumina. The oil obtained was triturated with ethanol and the residue was twice crystallised from methanol yielding fine needles of the *dye base* (0·05 g), m.p. 250 °C (Found: C, 82·5; H, 6·8; N, 8·0%; M^+, 539·2940. $C_{37}H_{37}N_3O$ requires C, 82·4; H, 6·9; N, 7·8%; M, 539·2937).

Bis-(4-*dimethylaminophenyl*)-(1-*naphthyl*)*methanol.*— Ethereal 4-dimethylaminophenyl-lithium, from 4-bromo-*NN*-dimethylaniline (5·45 g),[20] was filtered under nitrogen into ethereal methyl 1-naphthoate (0·95 g) obtained from 1-naphthoic acid by esterification using boron trifluoride–methanol reagent;[22] the mixture was kept for 1 h and then poured into water. The product obtained on evaporation of the solvent gave, after two crystallisations from ethanol–pyridine (9 : 1), crystals of the dye base (0·9 g), m.p. 174—175 °C (lit.,[23] 169 °C).

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