495. *Steric Effects in Di- and Tri-arylmethanes. Part VIII.* Electronic Absorption Spectra of Planar Derivatives of Michler's Hydrol Blue.*

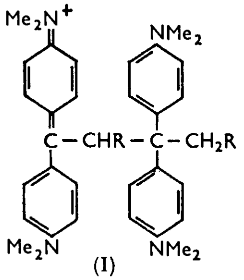
By C. Aaron and C. C. Barker.

Planarity has been enforced in Michler's Hydrol Blue and its α-alkyl derivatives by the introduction of an isopropylidene bridge at the 2,2'-positions. The α-t-butyl derivative (V; R = Bu^t) does not show an anomalous second-frequency absorption band, thus confirming the view that the anomalous band shown by the unbridged α-t-butyl derivative (II; R = Bu^t) is due to a non-degenerate, protonated cation (IV; R = Bu^t) formed because molecular crowding causes partial deconjugation of one of the dimethylaminophenyl groups. Indirectly, the view that the anomalous second-frequency bands of dimerised α-alkyl derivatives of Michler's Hydrol Blue are due to non-degenerate, protonated cations (III) is thereby supported.

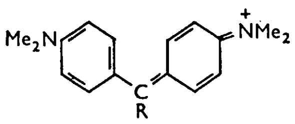
General molecular distortion in the bridged α-t-butyl derivative produces a larger bathochromic shift than is produced by extensive twisting of unbridged derivatives about the central bonds.

Molecular rigidity in the bridged Michler's Hydrol Blue results in an intense fluorescence which is greatly diminished by α-substituents.

In Part IV [1] of this series of papers the anomalous absorption spectra of dimers (I) of α-alkyl derivatives of Michler's Hydrol Blue (II), formed by keeping the latter in acetic acid, were explained in terms of steric factors which enforce rotation of one of the dimethylaminophenyl groups. Such rotation would result in ready protonation of the nitrogen atom involved, and the resulting non-degenerate cation (III) would absorb at shorter wavelength than the degenerate cation (I). The observed spectra were attributed to a mixture of these ions. The α-t-butyl derivative is exceptional in that the absence of a β-hydrogen atom prohibits dimerisation, but this compound also gives rise to an anomalous second-frequency band and it was assumed that the spatial demands of the t-butyl group are such that the monomer also has an unsymmetrical conformation and gives rise to a mixture of uni- and bi-valent cations (II and IV; R = Bu^t, respectively); it was confirmed that the first and the second bands arise from different molecular species by observing a change in the ratio of the maximum absorption intensities with change in the acidity of the solvent.



(I)



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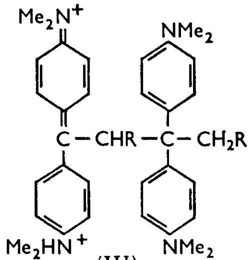

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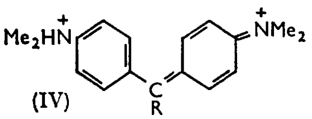

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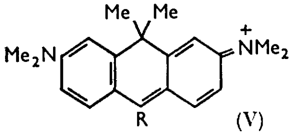

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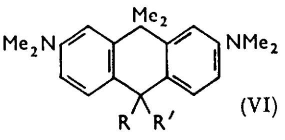

(VI)

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* Part VII, *J.*, 1961, 3445.

[1] C. C. Barker and Hallas, *J.*, 1961, 1395.

To confirm this hypothesis, a series of bridged derivatives (V) in which the aryl groups are not free to twist about the central bonds has now been prepared. Neither the bridged dimers, if formed, nor the bridged α-t-butyl derivative should give rise to absorption bands due to non-degenerate cations. In order to avoid introducing a new electronic factor, the bridge had to be incapable of conjugating with the remainder of the molecule, and the isopropylidene group was chosen; a methylene bridge is unsuitable because of the likelihood of forming an anthracene nucleus by loss of a proton.

TABLE 1.

Absorption spectra of derivatives of Michler's Hydrol Blue as 10^{-5}M-solution in 98% acetic acid.

Compound	Absorption max. (mμ) ($10^{-4}\varepsilon$ in parentheses)		
II; R = H	607·5 (14·75);	390 (0·45);	368·5 (0·50)
II; R = Et *	620 (1·90);	402·5 (0·21);	381 (0·17)
V; R = H	607 (14·75);	394 (0·27);	369·5 (0·32)
V; R = Me	603·5 (14·0);	401 (0·49);	380·5 (0·42)
V; R = Et	605 (13·7);	402 (0·46);	380·5 (0·39)
V; R = Pr^i	613 (11·9);	406 (0·64);	385·5 (0·50)
V; R = Bu^t (a)	682 (0·76);	422·5 (0·14);	402·5 (0·16)

* In 10^{-4}M-solution.

The first frequency bands of Michler's Hydrol Blue (II; R = H) and its bridged analogue (V; R = H) occur at almost the same position and have the same intensity (Table 1). Since rotation about the central bonds is impossible in the bridged compound, the similarity of the band parameters suggests that Michler's Hydrol Blue is probably a planar molecule in which the central bond angle is necessarily greater than 120°. It is a little surprising, however, that the electron-donating effect of the isopropylidene group [2] does not result in a significant hypsochromic shift, and it is possible that the bridge produces a slight distortion of the benzene rings, a type of distortion which will be shown later to result in a considerable bathochromic shift.

TABLE 2.

Values of $10^{-4}\varepsilon_{\text{max.}}$ given by Michler's Hydrol Blue and some of its bridged derivatives in acetic acid containing different amounts of water.

H_2O (%)	0	2	5	10	30	70	90
II; R = H	12·1	14·75	12·5	9·8	1·8	0·2	0·1
V; R = H	14·4	14·75	14·6	14·6	14·6	14·5	14·0
V; R = Me	13·6	14·0	13·6	13·6	13·2	12·6	11·5
V; R = Et	13·5	13·7	13·5	13·4	13·4	13·3	12·3
V; R = Pr^i	11·8	11·9	11·7	11·7	11·3	9·1	4·9

On passing from the bridged base (VI; R = H, R′ = OH), which probably has a folded structure,[3] to the quinonoid cation (V; R = H), which is probably planar, strain is released. The equilibrium between base and cation therefore favours the cation to a greater extent than it does with Michler's Hydrol Blue, and this is clearly shown by the greater range of acidity over which the bridged compound exists as a univalent cation (Table 2). The constancy of the values of $\varepsilon_{\text{max.}}$ given by the bridged dye (V; R = H) over this wide range of acidity is good evidence that under these conditions the dye base is completely converted into degenerate cation, so that 147,500 is its true molecular extinction coefficient. Since Michler's Hydrol Blue in 98% acetic acid gives the same value of $\varepsilon_{\text{max.}}$ it must be also present entirely as degenerate cation, but in this case $\varepsilon_{\text{max.}}$ decreases very rapidly as the acidity is increased by the addition of water. The bridged α-methyl, α-ethyl, and α-isopropyl derivatives (V; R = Me, Et, and Pr^i, respectively) also give maximum values of $\varepsilon_{\text{max.}}$ when in 98% acetic acid, but ions other than the degenerate

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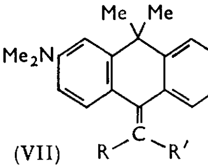
[2] Dewar, *J.*, 1950, 2329.

[3] Ferrier and Iball, *Chem. and Ind.*, 1954, 1296.

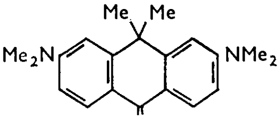
cations are probably also present. It is difficult to determine the extent to which small changes of $\varepsilon_{\text{max.}}$ are due to displacement of the dye base–dye–olefin equilibria and to loss of molecular planarity, severally, but in these bridged compounds the stability of the degenerate cation (V) tends to fall as the maximum values of $\varepsilon_{\text{max.}}$ fall (Table 2) and as the size of the R group increases. It is probable that the α-alkyl derivatives give lower absorption intensities because of incomplete formation of the degenerate cation.

The α-methyl derivative (V; R = Me) shows the hypsochromic shift expected from the electron-donating tendency of the methyl group, but $\varepsilon_{\text{max.}}$ is a little reduced (Table 1). As is the case with all α-alkyl derivatives containing a β-hydrogen atom, the α-methyl derivative can be in equilibrium, not only with the dye base (VI; R = Me, R′ = OH), but also with olefin (VII; R = R′ = H), which, like the degenerate cation, contains a central carbon atom with trigonal hybridisation; so it appears that strain in the dye base can be released by formation not only of degenerate cation but also of olefin, and with the unbridged α-alkyl derivatives (II) this leads to very low values of $\varepsilon_{\text{max.}}$ (Table 1; compound II, R = Et). However, with the bridged olefins (VII) there is unfavourable steric interaction of the 4- and the 5-hydrogen atom with the groups R and R′ attached to the β-carbon atom, so that little olefin is formed in 98% acetic acid. Thus the cation is favoured and the bridged α-alkyl derivatives give large values of $\varepsilon_{\text{max.}}$. This interaction will be at a minimum in the α-methyl derivative (VII; R = R′ = H) and, correspondingly, this is the only derivative isolated as the olefin whereas the α-ethyl and α-isopropyl derivatives were obtained as dye bases (VI; R′ = OH).

By comparison with the α-methyl group, the α-ethyl group produces a slightly greater fall in intensity and a slightly smaller hypsochromic shift. The α-isopropyl group reduces the intensity further but brings about a bathochromic shift (Table 1), thus clearly showing the presence of molecular distortion in this derivative.



(VII)



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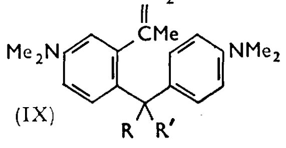
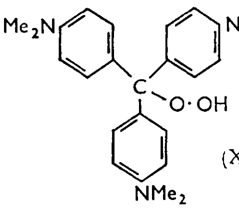


(IX)



(X)

None of these α-alkyl derivatives in 98% acetic acid develops the large second-frequency band characteristic of dimerised α-alkyl derivatives of Michler's Hydrol Blue. However, it is probable that dimers are not formed since, although extensive spectral changes occur when these solutions are kept, a bathochromic shift of the first band is not observed, and molecular distortion in the dimer should bring about such a shift. Attempts to isolate dimer failed.

The α-t-butyl group brings about a very large bathochromic shift (75 mμ). This shift occurs despite the inability of the aryl groups to rotate about the central bonds and contrasts with a shift of only 41·5 mμ produced by rotation of these groups in the 2,2′,6,6′-tetramethyl derivative of Michler's Hydrol Blue.[4] Distortion of the aryl nuclei is probably involved, and it has been pointed out by Dewar [5] that such distortion will lead to a bathochromic shift. The absorption intensity is very low and this is undoubtedly due to displacement of the dye base–dye equilibrium. The second-frequency band is small and retains the characteristic twin peaks of the second band of the degenerate cation. The absence of a band due to non-degenerate, bivalent cation strikingly confirms the hypothesis

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[4] C. C. Barker, Bride, and Stamp, *J.*, 1959, 3957.

[5] Dewar, " Steric Effects in Conjugated Systems," ed. G. W. Gray, Butterworths Scientific Publns., London, 1958, p. 51.

put forward[1] to explain the nature of the second band of the α-t-butyl derivative of Michler's Hydrol Blue and, indirectly, supports the analogous hypothesis put forward to explain the second bands of dimerised α-alkyl derivatives of Michler's Hydrol Blue.

Michler's Hydrol Blue in acetic acid is non-fluorescent but the bridged analogue (V; R = H) shows an intense red fluorescence with $\lambda_{max.}$ close to 640 mμ; on irradiation with ultraviolet light a second band close to 540 mμ is also observed, the fluorescence then becoming yellower. The introduction of a bridge into di- and tri-phenylmethane dyes frequently results in fluorescence, as in the cation from 3,6-bisdimethylamino-9-hydroxyxanthene, but in the known examples the bridge is invariably a hetero-atom which can conjugate with the rest of the molecule. In the dye now reported, conjugation of this type is impossible and the fluorescence must be due to molecular rigidity which prevents the conversion of electronic into vibrational energy.

Fluorescence of α-substituted derivatives of the dye does not follow a simple pattern. The α-methyl and the α-ethyl compound fluoresce in visible light, but the α-isopropyl, α-t-butyl, and α-phenyl derivatives only fluoresce appreciably in ultraviolet light.

Preparations.—The intermediate essential for the preparation of these dyes is the bridged analogue of Michler's ketone, 2,7-bisdimethylamino-9,9-dimethyl-10-anthrone (VIII). Initially, attempts were made to prepare this ketone from the bridged analogue of Crystal Violet (V; R = *p*-C_6H_4·NMe_2) by the procedure used by Georgevics[6] to convert Crystal Violet into Michler's ketone. *m*-Isopropenyl-*NN*-dimethylaniline condenses with Michler's hydrol to give 2-isopropenyl-4,4′,4″-tris-*p*-dimethylaminophenylmethane (IX; R = H, R′ = *p*-C_6H_4·NMe_2) which, in concentrated sulphuric acid at 20°, cyclises to 2,7-bisdimethylamino-10-*p*-dimethylaminophenyl-9,10-dihydro-9,9-dimethylanthracene (VI; R = H, R′ = *p*-C_6H_4·NMe_2). Oxidation of this leuco-compound in dilute hydrochloric acid with lead dioxide gives the bridged analogue of Crystal Violet (V; R = *p*-C_6H_4·NMe_2).

Georgevics obtained Michler's ketone by interaction of Crystal Violet and a mixture of hydrogen peroxide and aqueous ammonia or, better, aqueous sodium hydroxide. Presumably the dye is attacked by the hydroperoxide anion to give the hydroperoxide (X) which breaks down to yield the ketone and *p*-dimethylaminophenol. We find that if aqueous sodium hydroxide is added to an ethanolic solution of Crystal Violet containing 10 mol. of hydrogen peroxide, and if the reaction mixture is then decomposed with sulphuric acid, a much improved yield of Michler's ketone (80%) is obtained, but the procedure gives only a 28% yield of impure 2,7-dimethylamino-9,9-dimethyl-10-anthrone when applied to the bridged analogue of Crystal Violet. A route through 4,4′-bisdimethylamino-2-isopropenyldiphenylmethane (IX; R = R′ = H) was therefore explored.

N-4-Dimethylaminobenzylsulphanilic acid, readily obtained from sulphanilic acid, *NN*-dimethylaniline, and formaldehyde,[7] condenses with *m*-isopropenyl-*NN*-dimethylaniline in aqueous acid solution to give a mixture of bis-*p*-dimethylaminophenylmethane and its 2-isopropenyl derivative (IX; R = R′ = H) which was shown by gas–liquid chromatography to contain 92% of the latter base. 4-Dimethylaminobenzyl alcohol, readily obtained from *p*-dimethylaminobenzaldehyde and from methyl *p*-dimethylaminobenzoate by reduction with lithium aluminium hydride, can be used in place of 4-dimethylaminobenzylsulphanilic acid but gives a less pure product, partly because of the ease with which two molecules of the alcohol interact to form bis-*p*-dimethylaminophenylmethane and formaldehyde. The latter reaction is almost complete when the alcohol is kept for 4 weeks.

The impure 4,4′-bisdimethylamino-2-isopropenyldiphenylmethane does not crystallise but, without further purification, can be cyclised with concentrated sulphuric acid to the bridged leuco-base, 2,7-bisdimethylamino-9,9-dimethyl-9,10-dihydroanthracene (VI; R = R′ = H) which, after purification as the dipicrate, crystallises readily. These crystals

[6] Georgevics, *Ber.*, 1905, **38**, 886.

[7] D.R.-P. 116959/1901.

induce crystallisation of the crude base and purification through the dipicrate can then be omitted.

Oxidation of the leuco-base in ethanol with chloranil gives a good yield of 2,7-bisdimethylamino-9,10-dihydro-9,9-dimethylanthran-10-ol (VI; R = H, R′ = OH) in place of the expected anthrone. Bis-*p*-dimethylaminophenylmethane is readily oxidised to Michler's ketone under these conditions. Presumably the bridged dye base, which has already been shown to be much more strongly basic than Michler's hydrol (Table 2), exists in the reaction mixture entirely as the quinonoid cation (V; R = H) with the 2,3,5,6-tetrachloro-4-hydroxyphenoxide ion as the anion, whereas Michler's hydrol exists to an appreciable extent as free base. The dye base can be more readily obtained by oxidation of the leuco-base in aqueous nitric acid with lead dioxide; it separates as the very sparingly soluble nitrate. Crystallisation of the free base from ethanol gives its ethyl ether.

The anthrone (VIII) is obtained by oxidising the unpurified leuco-base with benzophenone in benzene in the presence of potassium t-butoxide. The dye base dismutes under a variety of conditions and by boiling its solution in benzene in the presence of charcoal the anthrone is obtained in 27% yield; it also dismutes in benzene at room temperature in the presence of alumina. The bridge appears to be essential for dismutation; Michler's hydrol does not undergo the reaction but its fluorene analogue does so in benzene in the presence of charcoal.[8] 9-Hydroxyxanthen [9] and derivatives of 9-hydroxythioxanthen [10] also dismute under a variety of conditions.

Samples of the bridged leuco-base left exposed to air gradually form the anthrone, presumably by intermediate formation of the hydroperoxide (VI; R = H, R′ = O_2H), but a satisfactory preparative procedure could not be evolved.

Alkyl derivatives of the dye base are formed by interaction of the anthrone with the appropriate alkyl-lithium or Grignard reagent.

m-Isopropenyl-*NN*-dimethylaniline, required in the initial stages of these syntheses, is readily prepared by dehydration with potassium hydrogen sulphate of 2-*m*-dimethylaminophenylpropan-2-ol, obtained from the methyl ester of the commercial *m*-dimethylaminobenzoic acid and methylmagnesium iodide. The ester can be replaced without advantage by *m*-dimethylaminoacetophenone, prepared by Rupe, Braun, and Zembruskt [11] by methylation of *m*-aminoacetophenone with methyl iodide in the presence of aqueous sodium hydroxide. These workers report that much of the methylated product separates from the reaction mixture as the hydriodide. This material is now found to be the quaternary salt, the formation of which cannot be avoided. The best procedure for preparing *m*-dimethylaminoacetophenone consists of forming the quaternary salt with an excess of methyl iodide and then decomposing the salt with boiling methanolic sodium methoxide.

EXPERIMENTAL

m-*Dimethylaminoacetophenone*.—A mixture of *m*-aminoacetophenone (48 g.), sodium hydroxide (120 g.), water (1200 c.c.), and methyl iodide (178 g.) was boiled for 2 hr. and then cooled. The sparingly soluble quaternary ammonium iodide was removed by filtration and the filtrate was extracted with ether, yielding an oil A (11·5 g.). The *iodide*, a sample of which, thrice crystallised from water, had m. p. 208—209° (Found: C, 43·6; H, 5·3; N, 4·3; I, 42·3. $C_{11}H_{16}INO$ requires C, 43·3; H, 5·3; N, 4·5; I, 41·6%), was boiled for 8 hr. with methanol (875 c.c.) containing sodium methoxide (117 g.). The mixture was then diluted with water, and the liberated amine was combined with fraction A and boiled for 2½ hr. with acetic anhydride (100 c.c.) containing a trace of concentrated sulphuric acid. The bulk of the anhydride was removed by distillation and the remainder was destroyed by addition of water. The mixture was then cooled to 0° and made acid to Congo Red with hydrochloric acid, and the non-basic

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[8] A. Barker and C. C. Barker, *J.*, 1954, 1307.

[9] Kny-Jones and Ward, *J.*, 1930, 535.

[10] Finzi, *Gazzetta*, 1932, **62**, 211; Campbell, Dick, Ferguson, and Loudon, *J.*, 1941, 747; Amstutz and Neumoyer, *J. Amer. Chem. Soc.*, 1947, **69**, 1925; Gilman and Diehl, *J. Org. Chem.*, 1961, **26**, 2132.

[11] Rupe, Braun, and Zembruskt, *Ber.*, 1901, **34**, 3522.

impurities were extracted with ether. Basification of the aqueous solution gave *m*-dimethylaminoacetophenone (25·1 g.), b. p. 162—166°/20 mm., forming yellow crystals, m. p. 41—42°. Rupe *et al.*[11] give m. p. 42—43°.

2-m-*Dimethylaminophenylpropan*-2-*ol*.—Methyl *m*-dimethylaminobenzoate (Eastman Kodak Co. Ltd.) (65·0 g.) in ether with methylmagnesium iodide, formed from magnesium (19·7 g.) and methyl iodide (115 g.), gave 2-m-*dimethylaminophenylpropan*-2-*ol* (57·2 g.) as colourless cubes, m. p. 72—73° [from light petroleum (b. p. 40—60°)] (Found: C, 73·6; H, 9·5; N, 7·9. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·5; N, 7·8%).

2-m-*Dimethylaminophenylpropene*.—2-*m*-Dimethylaminophenylpropan-2-ol (20·0 g.) to which a little catechol had been added was kept at 150° for 2 hr. with finely powdered, freshly fused potassium hydrogen sulphate. The warm mixture was then poured into water and basified with sodium hydroxide, giving 2-m-*dimethylaminophenylpropene* which, after distillation through a short column, had b. p. 76—78°/0·3 mm. (Found: C, 81·5; H, 9·6; N, 8·7. $C_{11}H_{15}N$ requires C, 81·9; H, 9·4; N, 8·7%).

2-*Isopropenyl Derivative of Leuco-Crystal Violet*.—Michler's hydrol (12·6 g.) and 2-*m*-dimethylaminophenylpropene (9·0 g.) in water (300 c.c.) containing 2N-hydrochloric acid (105 c.c.) was boiled for 12 hr. The cooled solution was poured into aqueous sodium hydroxide, and the resulting tar, twice crystallised from ethanol, gave the *leuco-base* (12·4 g.), m. p. 131—132° (Found: C, 80·8; H, 8·4; N, 10·1. $C_{28}H_{35}N_3$ requires C, 81·2; H, 8·5; N, 10·2%).

2,7-*Bisdimethylamino*-10-p-*dimethylaminophenyl*-9,10-*dihydro*-9,9-*dimethylanthracene*.—The 2-isopropenyl derivative of leuco-Crystal Violet (12·4 g.) was kept in concentrated sulphuric acid at room temperature for 24 hr. The mixture was then poured into aqueous ammonia containing ice, thus yielding a deep-blue solid which was purified by elution with benzene from an alumina column (40 × 10 mm.) followed by crystallisation (twice) from 2 : 1 ethanol–benzene, thereby giving colourless crystals of the cyclised *base* (9 g.), m. p. 167—168° (Found: C, 80·9; H, 8·4; N, 9·8. $C_{28}H_{35}N_3$ requires C, 81·2; H, 8·5; N, 10·2%).

2,7-*Bisdimethylamino*-10-p-*dimethylaminophenyl*-9,10-*dihydro*-10-*methoxy*-9,9-*dimethylanthracene*.—To a stirred solution of the aforementioned cyclised base (7·04 g.) in water (200 c.c.) containing concentrated hydrochloric acid (8·5 c.c.) and ice (45 g.), was added a lead dioxide paste prepared from lead nitrate (5·62 g.).[12] The mixture was stirred for 2 hr., sodium sulphate (8·5 g.) was added, and the lead sulphate was removed. Sodium acetate (2·9 g.), followed by sodium chloride (50 g.), was added and 12 hr. later the precipitated dye was removed and dried at 60°. A sample of the dye (0·3 g.) in dry methanol (3 c.c.) was added to dry methanol (4 c.c.) containing sodium methoxide (0·2 g.). The precipitate was dried *in vacuo* and crystallised thrice from 3 : 1 methanol–benzene containing a trace of sodium methoxide, thus giving colourless needles of 2,7-*bisdimethylamino*-10-p-*dimethylaminophenyl*-9,10-*dihydro*-10-*methoxy*-9,9-*dimethylanthracene*, m. p. 148—150° (Found: C, 78·2; H, 8·2; N, 9·3. $C_{29}H_{37}N_3O$ requires C, 78·5; H, 8·4; N, 9·5%).

2,7-*Bisdimethylamino*-9,10-*dihydro*-9,9-*dimethylanthracene*.—2-*m*-Dimethylaminophenylpropene (48·3 g.) in 2N-hydrochloric acid (150 c.c.) was added to *N*-4-dimethylaminobenzylsulphanilic acid[7] (93 g.) in water (1·5 l.) at 60° and the mixture was then kept at 60° for 12 hr. Basification of the mixture gave an oil (75·7 g.) consisting of 2-isopropenyl-4,4'-bisdimethylaminodiphenylmethane (92%) and bis-*p*-dimethylaminophenylmethane (8%). This oil (70 g.) in acetic acid (100 c.c.) was added dropwise to stirred concentrated sulphuric acid (1·5 l.), and the resulting red solution was kept at 20° for 12 hr. The mixture was then poured into aqueous ammonia containing ice, thus yielding a dark-blue oil (63 g.) which contained 2,7-bisdimethylamino-9,10-dihydro-9,9-dimethylanthracene (90%) and bis-*p*-dimethylaminophenylmethane (10%) (by gas–liquid chromatography on 1% of polypropylene sebacate at 200°). A solution of the crude anthracene derivative (5·0 g.) in benzene (10 c.c.) was added slowly to picric acid (8·3 g.) in benzene (30 c.c.), thereby giving an oil which crystallised when scratched and gave, when twice crystallised from 9 : 1 ethanol–*NN*-dimethylformamide, green crystals of 2,7-*bisdimethylamino*-9,10-*dihydro*-9,9-*dimethylanthracene dipicrate* (8·3 g.), m. p. 180—181° (decomp.) (Found: C, 51·4; H, 4·6; N, 14·9. $C_{32}H_{32}N_8O_{14}$ requires C, 51·1; H, 4·3; N, 14·9%). Decomposition of the dipicrate by warming it with aqueous-ethanolic sodium hydroxide gave an oil which crystallised when scratched. These crystals were used to seed the crude anthracene derivative which, twice crystallised from ethanol, gave colourless crystals of 2,7-*bisdimethylamino*-9,10-*dihydro*-9,9-*dimethylanthracene* (46 g.), m. p. 75—76° (Found: C, 81·4; H, 8·9; N, 9·5. $C_{20}H_{26}N_2$ requires C, 81·6; H, 8·9; N, 9·5%).

2,7-*Bisdimethylamino*-10-*ethoxy*-9,10-*dihydro*-9,9-*dimethylanthracene*.—(*a*) To a vigorously stirred solution of 2,7-bisdimethylamino-9,10-dihydro-9,9-dimethylanthracene (39·8 g.) in water (1·8 l.) containing nitric acid (70% w/w; 70·5 c.c.) was added ice (800 g.) and then, all at once, the lead dioxide paste prepared from lead nitrate (44·5 g.).[12] After the mixture had been stirred for ½ hr. the sparingly soluble nitrate was removed and basified with aqueous sodium hydroxide. The insoluble base (39·5 g.), m. p. 105—111°, was removed, washed with water, and dried *in vacuo*. A sample of the base, thrice crystallised from ethanol containing a trace of sodium hydroxide, gave 2,7-*bisdimethylamino*-10-*ethoxy*-9,10-*dihydro*-9,9-*dimethylanthracene* as pale yellow needles, m. p. 117—118° (Found: C, 77·9; H, 8·8; N, 8·3. $C_{22}H_{30}N_2O$ requires C, 78·1; H, 8·9; N, 8·3%)

(*b*) A mixture of 2,7-bisdimethylamino-9.9-dimethyl-10-anthrone (0·5 g.), 3% sodium amalgam (20 g.), and ethanol (50 c.c.) was boiled for 2 hr. The ethanolic solution was then decanted into water, and the dried precipitate was thrice crystallised from ethanol containing a trace of sodium hydroxide, yielding pale yellow needles of the ethoxy-compound (0·4 g.), m. p. 116—118°.

2,7-*Bisdimethylamino*-9,9-*dimethyl*-10-*anthrone*.—(*a*) A mixture of potassium t-butoxide, prepared from potassium (16 g.) and t-butyl alcohol,[13] benzene (2·5 l.), benzophenone (300 g.), and unpurified 2,7-bisdimethylamino-9,9-dimethyl-10-anthranol (38 g.; m. p. 105—111°) was boiled under nitrogen for 20 hr. The cooled mixture was extracted with hydrochloric acid, the extract was basified with aqueous sodium hydroxide, and the precipitated bases (34 g.), m. p. 163—189°, were crystallised twice from ethanol, yielding pale green needles of 2,7-*bisdimethylamino*-9,9-*dimethyl*-10-*anthrone* (14·2 g.), m. p. 207—208° (Found: C, 77·8; H, 7·9; N, 8·9. $C_{20}H_{24}N_2O$ requires C, 77·9; H, 7·8; N, 9·1%).

(*b*) Hydrogen peroxide (6·8 c.c.; 20-vol.) and then aqueous N-sodium hydroxide (1·4 c.c.) were added to a stirred solution of the 2,2′-isopropylidene derivative of Crystal Violet (0·50 g.) in ethanol (70 c.c.). After 30 min., concentrated sulphuric acid (10 c.c.) was added, and the mixture was then kept at 20° for a further 30 min., made alkaline with sodium hydroxide and diluted with water. The green precipitate, m. p. >360°, was chromatographed in benzene on alumina (100 × 10 mm.) and yielded 2,7-bisdimethylamino-9,9-dimethyl-10-anthrone (0·10 g.), m. p. 199—204°.

2,7-*Bisdimethylamino*-9,10-*dihydro*-9,9-*dimethyl*-10-*methyleneanthracene*.—Ethereal methyl-lithium (0·007 mole) was added to a suspension of 2,7-bisdimethylamino-9,9-dimethyl-10-anthrone (1·0 g.) in ether (50 c.c.) under nitrogen and stirred for 1 hr. The resultant solution was poured into water (100 c.c.), and the ether was removed from the dried (Na_2SO_4) ethereal layer, yielding a residue which, thrice crystallised from 4 : 1 ethanol–water, gave pale yellow needles of 2,7-*bisdimethylamino*-9,10-*dihydro*-9,9-*dimethyl*-10-*methyleneanthracene*, m. p. 144·5—146° (Found: C, 81·9; H, 8·4; N, 9·1. $C_{21}H_{26}N_2$ requires C, 82·3; H, 8·5; N, 9·2%).

2,7-*Bisdimethylamino*-10-*ethyl*-9,10-*dihydro*-9,9-*dimethyl*-10-*anthranol*.—Replacement of methyl-lithium by ethyl-lithium in the preceding experiment and recrystallisation of the product thrice from 4 : 1 ethanol–benzene containing a trace of sodium hydroxide gave almost colourless needles of 2,7-*bisdimethylamino*-10-*ethyl*-9,10-*dihydro*-9,9-*dimethyl*-10-*anthranol* (0·9 g.), m. p. 137—138° (Found: C, 78·1; H, 9·1; N, 8·5. $C_{22}H_{30}N_2O$ requires C, 78·1; H, 9·1; N, 8·7%).

2,7-*Bisdimethylamino*-9,10-*dihydro*-10-*isopropyl*-9,9-*dimethyl*-10-*anthranol*.—Isopropylmagnesium bromide, from magnesium (1·35 g.) and isopropyl bromide (6 g.) in ether (25 c.c.), was filtered into a suspension of 2,7-bisdimethylamino-9,9-dimethyl-10-anthrone (1·0 g.) in ether (50 c.c.), and the mixture was kept for 2 hr., then poured into aqueous ammonium chloride. The product from the ethereal layer, thrice crystallised from 2 : 1 ethanol–water containing a trace of sodium hydroxide, gave 2,7-*bisdimethylamino*-9,10-*dihydro*-10-*isopropyl*-9,9-*dimethyl*-10-*anthranol*, m. p. 175—176° (Found: C, 78·4; H, 9·4; N, 8·3. $C_{23}H_{32}N_2O$ requires C, 78·4; H, 9·2; N, 8·4%).

2,7-*Bisdimethylamino*-9,10-*dihydro*-9,9-*dimethyl*-10-*t*-*butyl*-10-*anthranol*.—2,7-Bisdimethylamino-9,9-dimethyl-10-anthrone was added at −70° to t-butyl-lithium,[14] prepared from lithium sand (0·5 g.) suspended in ether (20 c.c.) and t-butyl chloride (3·3 g.) at −37·5° ± 2·5°. The

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[12] Fierz-David and Blangey, "Fundamental Processes of Dye Chemistry," Interscience Publ. Ltd., London, 1949, p. 138.

[13] Woodward and Komfeld, *J. Amer. Chem. Soc.*, 1948, **70**, 2513.

[14] Bartlett and Lefferts, *J. Amer. Chem. Soc.*, 1955, **77**, 2804.

mixture was stirred for 2 hr. at that temperature. Water (50 c.c.) was then added and the product obtained from the dried (Na_2SO_4) ethereal layer was crystallised thrice from ethanol, to give crystals, m. p. 193—197°, which were then chromatographed on calcium carbonate (200 × 15 mm.) with benzene as eluant. Five fractions were collected, of which the second, third, and fourth were combined and crystallised thrice from benzene, yielding colourless cubes of 2,7-*bisdimethyamino*-9,10-*dihydro*-9,9-*dimethyl*-10-*t*-*butyl*-10-*anthranol*, m. p. 197—198° (Found: C, 79·0; H, 9·3; N, 7·55. $C_{24}H_{34}N_2O$ requires C, 78·7; H, 9·4; N, 7·6%).

The authors thank the Department of Scientific and Industrial Research for a grant (to C. A.) and Imperial Chemical Industries Limited, Dyestuffs Division, for the determination of fluorescence spectra.

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