796. *Steric Effects in Di- and Tri-arylmethanes. Part I. Electronic Absorption Spectra of* o-*Methyl Derivatives of Michler's Hydrol Blue and Crystal Violet; Conformational Isomers of Crystal Violet.*

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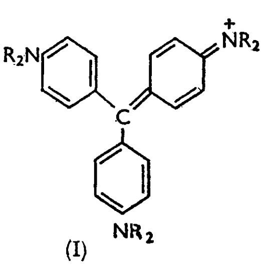
The first frequency absorption bands of *o*-methyl derivatives of Michler's Hydrol Blue and Crystal Violet show the expected reductions in frequency and intensity owing to the enforced rotation of the aryl rings.

The conformation of the 2,6-dimethyl derivative of Crystal Violet is discussed, and evidence against the existence of a conformational isomer of Crystal Violet is given.

THE introduction of an *ortho*-substituent into a triarylmethane dye invariably alters its molecular conformation and thereby alters its electronic absorption spectrum. A similar effect is produced by a *meta*-substituent when it is adjacent to a terminal dimethylamino-group, so that steric factors must exert an important influence upon the spectra of these dyes. However, the published spectra of sterically hindered charge resonance systems relate almost entirely to the heterocyclic cyanines; hindered trinuclear cyanines do not appear to have been studied, and very little attention has been given to the effect of crowding substituents upon di- and tri-arylmethane dyes. The present study was therefore initiated.

Scale drawings show that the *ortho*-hydrogen atoms in a triarylmethane dye overlap considerably, and the simplest assumption is that the shape of a structurally symmetrical dye, such as Crystal Violet (I; R = Me) or Pararosaniline (I; R = H), resembles that of a three-bladed propellor. In a diphenylmethane dye, however, the benzene rings may well be more nearly coplanar because overlap of the *ortho*-hydrogen atoms (Fig. 1) can be minimised by an increase in the phenyl–carbon–phenyl bond angle. *ortho*-Substituents modify the spectra of these dyes by increasing the departure from molecular uniplanarity and by donating or withdrawing electrons. The work of Brooker *et al.*[1] leads to the prediction that the steric response of an electronically symmetrical dye such as Michler's Hydrol Blue (II) or Crystal Violet should be a bathochromic shift and a reduction in the intensity of the first frequency absorption band, and this prediction is supported by recent theoretical treatment.[2] Also, it has been shown that the effect of an electron-donating *ortho*-substituent is hypsochromic whereas the effect of an electron-withdrawing *ortho*-substituent is predicted to be bathochromic.[3] Thus the steric and electronic effects are opposed when an *o*-methyl group is introduced, and this fact assists analysis of the resultant spectral shift and led to the frequent use of the methyl group in this study.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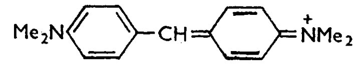
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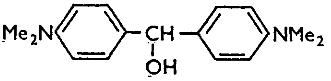
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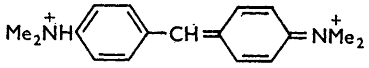
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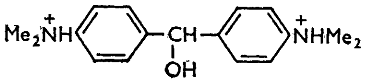
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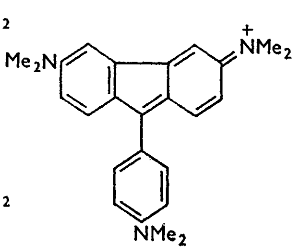
(VI)

Because of the difficulty of purifying the colour salts of these dyes, the dye bases or their methyl ethers were isolated and converted into the colour salts for the spectra determinations by using an acidic solvent. Of the common solvents, water is unsatisfactory because it tends to promote molecular aggregation of this type of dye and thus produce an abnormal spectrum, but ethanol or acetic acid gives essentially monomeric solutions, and the latter solvent is sufficiently acidic to convert the dye bases or their methyl ethers into the colour salts without the addition of mineral acid. In acid solution, Michler's Hydrol Blue could exist as the base (III) (or monoprotonated base), the univalent cation (II), and the bivalent cations (IV) and (V). In order to obtain significant values of $\varepsilon_{\max.}$ for the univalent cation, the acidity must be so adjusted that the concentrations of other forms of the dye are negligible, and it is assumed that the high and constant value of $\varepsilon_{\max.}$ (147,500) obtained with acetic acid solutions containing from 98 to 95% of water indicates that this condition is fulfilled; lower values of $\varepsilon_{\max.}$ are obtained when the water content of the acetic acid falls outside this range. Acetic acid containing 2% of water was therefore used as the standard solvent in these spectra determinations. The bases of Crystal Violet and Malachite Green form univalent cations which are stable over a wider range of pH than is Michler's Hydrol Blue, as is shown by the pK_b values (9·36, 6·90, and 5·61, respectively) obtained by Goldacre and Philips.[4]

The *ortho*-positions of Michler's Hydrol Blue are not equivalent (Fig. 1) and it is assumed that *ortho*-substituents take up less hindered " outside " positions. Molecular models suggest that an " outside " methyl group may not distort the molecule as the overlap of this group with the central hydrogen atom, shown in Fig. 1, is obviated by the overlap of the " inside " hydrogen atoms, but the 2-methyl derivative of Michler's Hydrol Blue shows a bathochromic shift and a reduction in the intensity of the first frequency absorption band, and this effect is increased in the 2,2′-dimethyl derivative (Table). These steric effects suggest that the molecule of Michler's Hydrol Blue approaches uniplanarity as a

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[1] Brooker, White, van Zandt, Dent, and Sprague, *Chem. Rev.*, 1947, **41**, 325.

[2] Dewar, " Steric Effects in Conjugated Systems," Ed. G. W. Gray, Butterworths Scientific Publications, 1958, p. 46.

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

[4] Goldacre and Phillips, *J.*, 1949, 1724.

Absorption spectra of methyl derivatives of Crystal Violet and Michler's Hydrol Blue as 10^{-5}M-solutions in 98% acetic acid.

Compound	Absorption maxima (mμ) ($10^{-4}\varepsilon$ in parentheses)	Compound	Absorption maxima (mμ) ($10^{-4}\varepsilon$ in parentheses)
Crystal Violet substituents		*Michler's Hydrol Blue substituents*	
None	589(11·7); 305(2·6)	None	607·5(14·8)
2-Methyl	597(11·0); 305·5(2·3)	2-Methyl	614·5(13·0)
2,2′-Dimethyl	605(10·3); 308(2·3)	2,2′-Dimethyl	623(12·1)
2,2′,2″-Trimethyl	614(10·0); 309(2·1)	2,2′,6,6′-Tetramethyl	649(5·5)
2,6-Dimethyl	616(11·2)		
2,6-Dimethyl *	626·5		

* In toluene containing 0·1% of 2-naphthol.

result of an increase in the phenyl–carbon–phenyl bond angle, an increase which brings the two " outside " *ortho*-carbon atoms closer together. The first frequency absorption band of the 2,2′,6,6′-tetramethyl derivative shows a much larger bathochromic shift and reduction in intensity (Table) owing to the interaction of the two " inside " methyl groups.

Fig. 1.

[Reproduced, with permission, from " Steric Effects in Conjugated Systems," Ed. Gray, Butterworths, London, 1959, p. 37.]

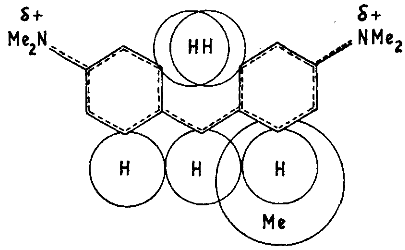


Fig. 2. *Absorption spectra of* (1) 10^{-5}M *solutions of Crystal Violet and its* (2) *2-methyl,* (3) *2,2′-dimethyl,* (4) *2,2′,2″-trimethyl derivative in* 98% *acetic acid.*

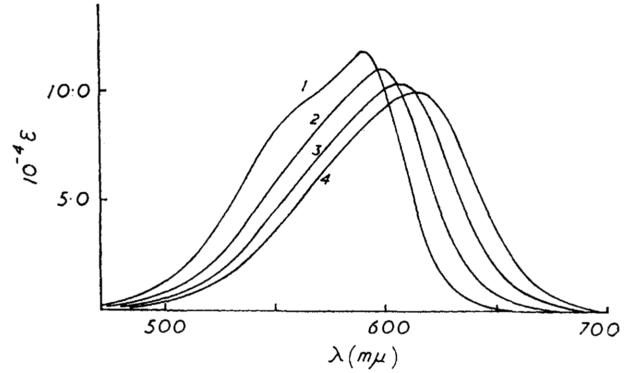
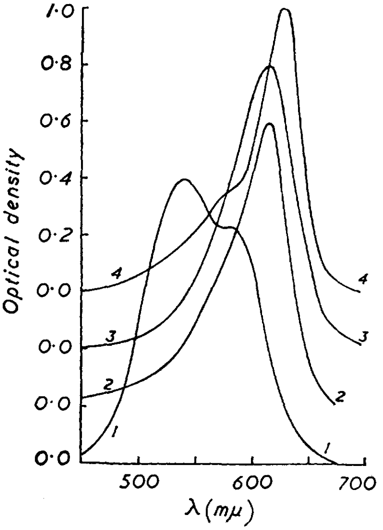


Fig. 3. *Absorption spectra of* (1) *Crystal Violet* (10^{-3}M) *in water, and its 2,6-dimethyl derivative in* (2) *water* (10^{-3}M), (3) 98% *acetic acid* (10^{-5}M), *and* (4) *toluene containing* 0·1% *of 2-naphthol* (10^{-5}M). *Maximum values of the optical density have been adjusted to* 1·0 *in each case.*



The 2-methyl, 2,2′-dimethyl, and 2,2′,2″-trimethyl derivatives of Crystal Violet show progressive bathochromic shifts and reductions in intensity of the first and second frequency absorption bands (Table), and the uniformity of the shift per methyl group of the long-wavelength band suggests that the rotational adjustment necessary to accommodate the *o*-methyl groups is shared uniformly between the aryl rings. However, the 2,6-dimethyl derivative shows a much larger bathochromic shift per methyl group and a relatively high absorption intensity (Table); these properties are consistent with the presence of a highly twisted dimethylaminoxylyl ring from which charge is concentrated onto the two dimethylaminophenyl rings. Also, the shoulder at about 540—550 mμ in the first frequency absorption band of Crystal Violet is smaller in the spectra of the 2-methyl, 2,2′-dimethyl, and 2,2′,2″-trimethyl derivatives (Fig. 2) and is completely absent from the spectrum of the 2,6-dimethyl derivative (Fig. 3).

Lewis, Magel, and Lipkin [5] attributed this shoulder given by Crystal Violet in organic solvents or in dilute aqueous solution (10^{-5}M) to the presence of a conformational isomer in which one of the dimethylaminophenyl groups is rotated in the opposite sense to that of the other two rings. However, in more concentrated aqueous solution (10^{-3}M) the molecules of Crystal Violet aggregate and give rise to a first frequency absorption band in which the normal peak at 598 mμ has become subsidiary to a peak at 540 mμ,[6] the position of the shoulder when the Crystal Violet is in organic solvents or in dilute aqueous solution (Fig. 3). Lewis *et al.* were aware of this fact but assumed that aggregation did not occur in organic solvents. The shoulder is also much exaggerated in a toluene solution of Crystal Violet, and Lewis *et al.* attributed this to an increase in the proportion of unsymmetrical conformational isomer.

Because the highly twisted dimethylaminoxylyl ring of the 2,6-dimethyl derivative of Crystal Violet would prevent face-to-face aggregation of the molecules, the absence of shoulder from the first frequency absorption band of this derivative suggests that the shoulder in that of Crystal Violet should more properly be attributed to the presence of aggregated dye molecules. This band of the 2,6-dimethyl derivative is also free from shoulder when observed in concentrated (10^{-3}M) aqueous solution, but a distinct shoulder is given by the dye in toluene (Fig. 3). Thus, it seems likely that toluene is an aggregating solvent, and this is confirmed by a study of the absorption spectrum of the fluorene analogue of Crystal Violet (VI), in which the planarity of the fluorene nucleus [7] permits the dye to aggregate readily but prohibits the existence of a conformational isomer. In 95% alcohol, the dye is monomeric and the green solution gives a single absorption band ($\lambda_{\text{max.}}$ 647 mμ) [8] in the visible region, whereas in water the dye (10^{-5}M) is largely aggregated and the blue solution shows a band ($\lambda_{\text{max.}}$ 590 mμ) in which the monomeric dye is represented only by a small shoulder. A solution of the dye in toluene is also blue and gives a band ($\lambda_{\text{max.}}$ 616 mμ) which is devoid of shoulder and which must be due to aggregated molecules because the value of $\lambda_{\text{max.}}$ is less than that of the monomeric band obtained in ethanol; toluene produces a bathochromic shift of the monomer bands of this type of dye (see Table and ref. 5).

It is likely that an unsymmetrical conformational isomer of Crystal Violet would absorb at a longer wavelength than its symmetrical isomer because the former would contain a highly rotated dimethylaminophenyl group and would thus resemble the 2,6-dimethyl derivative of Crystal Violet. On the other hand, bands arising from aggregated molecules should become more intense at lower temperatures because of increased aggregation, whereas Lewis *et al.* found the anomalous absorption of Crystal Violet to decrease as the temperature was lowered. It is now observed that the first frequency absorption band of an aqueous solution of Crystal Violet (10^{-4}M) shows a slight decrease in the intensity of the shoulder when the temperature is raised from 20° to 60°, and it seems that some other explanation must be found for the disappearance of the shoulder at low temperatures.

The derivatives of Michler's Hydrol Blue were prepared by reduction of the corresponding ketones in ethanol with sodium amalgam, and pure hydrols were readily obtained, whereas oxidation of the corresponding derivatives of diphenylmethane to hydrols was found to be impracticable when *ortho*-substituents were present. *NN*-Dimethyl-*m*-toluidine and carbonyl chloride in the presence of zinc chloride gave 4,4′-bisdimethylamino-2,2′-dimethylbenzophenone as pale-yellow crystals, m. p. 96°, without difficulty; Fierz and Koechlin [9] claim to have prepared this ketone as colourless crystals, m. p. 196°,

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[5] Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, 1942, **64**, 1774.
[6] Holmes, *Ind. Eng. Chem.*, 1924, **16**, 36.
[7] Burns and Iball, *Proc. Roy. Soc.*, 1955, *A*, **227**, 200.
[8] A. Barker and C. C. Barker, *J.*, 1954, 1307.
[9] Fierz and Koechlin, *Helv. Chim. Acta*, 1918, **1**, 223.

by the action of carbon tetrachloride on *NN*-dimethyl-*m*-toluidine in the presence of aluminium trichloride, but attempts to repeat their preparation gave only the 2,2′,2″-trimethyl derivative of Crystal Violet. Interaction of carbonyl chloride, *NN*-dimethyl-3,5-xylidine, and zinc chloride gave a mixture of 4,4′-bisdimethylamino-2,2′,6,6′-tetramethylbenzophenone and 2,4′-bisdimethylamino-2′,4,6,6′-tetramethylbenzophenone which required chromatographic separation. Reduction of the latter with sodium amalgam gave a hydrol which did not develop colour with acetic acid, showing that the original ketone contains at least one dimethylamino-group adjacent to the carbonyl group. Failure to isolate a third isomeric ketone is evidence that the initial condensation with carbonyl chloride gave only 4-dimethylamino-2,6-dimethylbenzoyl chloride, in which case the ketone which failed to form a colour salt on reduction must have the structure given. The initial formation of an isomeric acid chloride would have led, most probably, to the formation of a third ketone, *viz.*, 2,2′-bisdimethylamino-4,4′,6,6′-tetramethylbenzophenone.

The unsymmetrical 4,4′-bisdimethylamino-2-methylbenzophenone was readily prepared from *p*-dimethylaminobenzoyl chloride and *NN*-dimethyl-*m*-toluidine in the presence of zinc chloride, but attempts to condense *p*-dimethylaminobenzoyl chloride or its *o*-methyl derivative with *NN*-dimethyl-3,5-xylidine gave anomalous products which were not identified.

The 2-methyl derivative of Crystal Violet was prepared from Michler's ketone and *NN*-dimethyl-*m*-toluidine in the presence of phosphorus oxychloride, and it was isolated and purified as the dye base. The 2,6-dimethyl derivative of Crystal Violet was obtained in a similar way from *NN*-dimethyl-3,5-xylidine, but the colour salt gave a red product, believed to be essentially 4′,4″-bisdimethylamino-2′,6′-dimethylfuchsone, when treated with alkali, and the dye was isolated as the perchlorate.

The 2,2′-dimethyl derivative of Crystal Violet was obtained directly as the dye base by the action of *p*-dimethylaminophenyl-lithium on 4,4′-bisdimethylamino-2,2′-dimethylbenzophenone. The 2,2′,2″-trimethyl derivative was obtained as the colour salt from carbon tetrachloride and *NN*-dimethyl-*m*-toluidine in the presence of aluminium trichloride. Conversion of the colour salt to the dye base required treatment at room temperature with one equivalent of aqueous sodium hydroxide for 16 hours; use of an excess of sodium hydroxide gave a red product from which pure dye base could not be isolated. The formation of a red product is again associated with the presence of a highly hindered central carbon atom, but the tendency to form this type of product is less than in the case of the 2,6-dimethyl derivative of Crystal Violet.

The 2,2′,2″-trimethyl derivative of *leuco*-Crystal Violet, obtained from *NN*-dimethyl-*m*-toluidine and ethyl orthoformate, gave a blue solution when oxidised in acetic acid with lead dioxide but the dye base could not be isolated, and the condensation of *NN*-dimethyl-*m*-toluidine with 4,4′-bisdimethylamino-2,2′-dimethylbenzophenone in the presence of phosphorus oxychloride gave a small amount of the same *leuco*-compound as the only isolable product. The failure of the two latter methods must be attributed to the hindered nature of the central carbon atom in the required dye. A further anomalous reaction was encountered when attempting to repeat the preparation of the 2,2′,2″,6,6′,6″-hexamethyl derivative of *leuco*-Crystal Violet from *NN*-dimethyl-3,5-xylidine and ethyl orthoformate described by Noelting and Trautman;[10] the product was bis-(4-dimethylamino-2,6-xylyl)-methane.

EXPERIMENTAL

4,4′,4″-Trisdimethylamino-2-methyltriphenylmethanol.—Michler's ketone (1·0 g.), *NN*-dimethyl-*m*-toluidine (2·7 g.), and phosphorus oxychloride (1·0 g.) were heated in a sealed tube at 100° for 5 hr. The mixture was basified with aqueous potassium carbonate, excess of amine was removed by steam distillation, and the residue was crystallised from ethanol (70 c.c.), giving the *base* (0·75 g.), m. p. 170—173°, raised to m. p. 172—173° by recrystallisation once

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[10] Noelting and Trautman, *Ber.*, 1891, **24**, 562.

from ethanol and then twice from benzene-light petroleum (b. p. 60—80°; 2 parts) (Found: C, 77·3; H, 8·3; N, 10·2. $C_{26}H_{33}ON_3$ requires C, 77·4; H, 8·2; N, 10·4%).

4,4′,4″-*Trisdimethylamino*-2,2′-*dimethyltriphenylmethanol*.—A portion (15 c.c.) of a solution of *p*-dimethylaminophenyl-lithium, prepared from 4-bromo-*NN*-dimethylaniline (5·0 g.), lithium (0·4 g.), and ether (45 c.c.), was run into 4,4′-bisdimethylamino-2,2′-dimethylbenzophenone (1·48 g.) in benzene (50 c.c.) contained in a flask flushed with dry nitrogen. The mixture was stirred at room temperature for 15 min, and then at 50° for 30 min., then water (100 c.c.) was added. The organic layer was dried (Na_2SO_4) and the solvent removed, yielding a blue gum which gave a pale blue solid (1·6 g.), m. p. 130—155°, after trituration with light petroleum (b. p. 40—60°; 10 c.c.). Three crystallisations from benzene-light petroleum (b. p. 60—80°; 2 parts) gave the *base* as very pale blue micro-crystals, m. p. 165—166° (Found: C, 77·8; H, 8·3; N, 10·3. $C_{27}H_{35}ON_3$ requires C, 77·7; H, 8·4; N, 10·1%).

Tris-(4-*dimethylamino*-2-*tolyl*)*methanol*.—Powdered aluminium trichloride (22·0 g.) was added to cooled *NN*-dimethyl-*m*-toluidine (18·8 g.); carbon tetrachloride (6·2 g.) was added dropwise to the resultant paste and the mixture was stirred at 30° for 5 hr. The green crystals which separated were washed with a little water, stirred with water (75 c.c.) containing concentrated hydrochloric acid (0·6 c.c.) for several hr., removed, and crystallised thrice from water giving the 2,2′,2″-trimethyl derivative of Crystal Violet (2·8 g.). The dye (2·0 g.) in water (250 c.c.) was stirred with water (10 c.c.) containing sodium hydroxide (0·9 g.) for 16 hr., and the precipitated base was removed and washed with water, and then stirred with ethanol (5 c.c.) to remove coloured impurities. This product, thrice crystallised from benzene-light petroleum (b. p. 60—80°) gave the dye *base* as colourless crystals, m. p. 205—206° (decomp.) (Found: C, 77·8; H, 8·6; N, 9·7. $C_{28}H_{37}ON_3$ requires C, 78·0; H, 8·6; N, 9·7%).

2,6-*Dimethyl Derivative of Crystal Violet*.—Michler's ketone (1·0 g.), *NN*-dimethyl-3,5-xylidine (2·4 g.), and phosphorus oxychloride (1·0 g.) were heated in a sealed tube at 100° for 5 hr., and the product was purified by repeated precipitation from aqueous solution by addition of sodium chloride. The resultant dye was finally precipitated as the sparingly soluble *perchlorate* (Found: C, 64·5; H, 7·2; N, 8·4. $C_{27}H_{34}O_4N_3Cl$ requires C, 64·9; H, 6·8; N, 8·4%).

4,4′-*Bisdimethylamino*-2-*methyldiphenylmethanol*.—4-Dimethylaminobenzoyl chloride (9·65 g.), prepared by Décombé's method,[11] anhydrous zinc chloride (2·1 g.), and *NN*-dimethyl-*m*-toluidine (16·3 g.) were stirred at room temperature for 1½ hr., then at 30° for 2 hr., at 55° for 18 hr., and finally at 80° for 2 hr. The mixture was basified with aqueous sodium hydroxide, excess of *NN*-dimethyl-*m*-toluidine was removed by steam distillation, and the residue was crystallised (charcoal) from ethanol to give pale green crystals (6·9 g.), m. p. 104—108°, unchanged by recrystallisation from ethanol. This product, by elution from an alumina column (190 × 17 mm.) in benzene and crystallisation of the first 3·4 g. of eluate from ethanol, gave 4,4′-*bisdimethylamino*-2-*methylbenzophenone* as yellow crystals, m. p. 116° (Found: C, 76·4; H, 7·7; N, 9·8. $C_{18}H_{22}ON_2$ requires C, 76·6; H, 7·8; N, 9·9%). The aforementioned ketone (0·5 g.) in ethanol (30 c.c.) and water (1·5 c.c.) was stirred and refluxed with sodium amalgam (3% Na; 2·7 g.) for 2½ hr., more sodium amalgam (2·7 g.) being added after 1¼ hr. The resultant solution was poured into water (150 c.c.) and the precipitate was washed with water, dried *in vacuo*, and crystallised from benzene-light petroleum (b. p. 40—60°), thereby giving 4,4′-*bisdimethylamino*-2-*methyldiphenylmethanol* as colourless crystals, m. p. 79—80° (Found: C, 75·9; H, 8·8; N, 9·6. $C_{18}H_{24}ON_2$ requires C, 76·1; H, 8·5; N, 9·9%).

Bis-(4-*dimethylamino*-2-*tolyl*)*methanol*.—Carbonyl chloride (3·42 g.) was absorbed in cooled *NN*-dimethyl-*m*-toluidine (20·0 g.), and the mixture was stirred at room temperature for 17 hr., and then at 30° while anhydrous zinc chloride (1·38 g.) was added. The temperature was maintained at 30° for 3 hr., raised to 55° during 2 hr., then kept at 80—85° for 2 hr. The product was basified with dilute aqueous ammonia, excess of *NN*-dimethyl-*m*-toluidine was removed by steam distillation, and the residue was dissolved in benzene, and dried (Na_2SO_4), and the solution was passed through a short alumina column. Removal of the solvent and crystallisation of the residue from ethanol gave brownish-yellow crystals (2·4 g.), m. p. 92—94°. Sublimation of these crystals at 200° (bath)/10^{-4} mm., followed by recrystallisation from ethanol gave yellow crystals of 4,4′-*bisdimethylamino*-2,2′-*dimethylbenzophenone*, m. p. 96° (Found: C, 76·9; H, 8·2; N, 9·4. $C_{19}H_{24}ON_2$ requires C, 77·0; H, 8·1; N, 9·5%). The aforementioned ketone was reduced with sodium amalgam as for the reduction of the monomethyl analogue and gave *bis*-(4-*dimethylamino*-2-*tolyl*)*methanol* as colourless crystals, m. p. 114° (from light

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[11] Décombé, *Bull. Soc. chim. France*, 1951, 417.

petroleum, b. p. 60—80°) (Found: C, 75·9; H, 8·8; N, 9·3. $C_{19}H_{26}ON_2$ requires C, 76·5; H, 8·7; N, 9·4%).

Bis-(4-*dimethylamino*-2,6-*xylyl*)*methanol.*—Carbonyl chloride (3·3 g.) and *NN*-dimethyl-3,5-xylidine were allowed to react in the presence of zinc chloride as described for the preparation of 4,4′-bisdimethylamino-2,2′-dimethylbenzophenone, and the excess of *NN*-dimethyl-3,5-xylidine was removed by steam distillation. The crude product, which after one crystallisation from ethanol melted at 104—107° to a cloudy liquid which became clear at 125°, was eluted from a column of activated alumina (400 × 30 mm.) by a mixture of equal volumes of benzene and light petroleum (b. p. 60—80°) and then by benzene (4 vols.)–methanol (1 vol.) yielding the following fractions: F_1, 1·81 g., benzene–light petroleum (1945 c.c.); F_2, 0·48 g., benzene–light petroleum (1860 c.c.); F_3, 1·86 g., benzene–methanol (400 c.c.). Reduction of samples of these fractions with sodium amalgam and treatment of the products with acetic acid gave colourless, pale blue, and intense blue solutions from F_1, F_2 and F_3 respectively. Fraction F_1, twice crystallised from ethanol gave yellow crystals of 2,4′-*bisdimethylamino*-2′,4,6,6′-*tetramethylbenzophenone*, m. p. 125—125·5° (Found: C, 77·5; H, 8·5; N, 8·7. $C_{21}H_{28}ON_2$ requires C, 77·8; H, 8·6; N, 8·6%). Fraction F_3, thrice crystallised from ethanol, gave 4,4′-*bisdimethylamino*-2,2′,6,6′-*tetramethylbenzophenone* as yellow crystals, m. p. 165° (Found: C, 77·5; H, 8·7; N, 8·9%). The aforementioned ketone was reduced as for 4,4′-bisdimethylamino-2-methylbenzophenone and gave colourless crystals of *bis*-(4-*dimethylamino*-2,6-*xylyl*)-*methanol*, m. p. 165—166° (from benzene–light petroleum) (Found: C, 76·6; H, 9·3; N, 9·0. $C_{21}H_{30}ON_2$ requires C, 77·3; H, 9·2; N, 8·6%).

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