Extended Conjugation in Di- and Tri-arylmethanes. Part I. Electronic Absorption Spectra of 9,9-Dimethylfluorene Analogues of Crystal Violet and Malachite Green

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9,9-Dimethylfluorene analogues of some basic triphenylmethane dyes have been prepared and their absorption spectra have been determined. The extended quinonoid system in 9,9-dimethylfluorene is more energetically favoured than that in biphenyl, but in these dyes the mesomeric effect is not readily transmitted through the fluorenyl system.

The preparations of several 9,9-dimethylfluorene intermediates are described.

SPECTRAL studies have shown that terminal nitrogen atoms attached to biphenyl groups in analogues of Crystal Violet and Malachite Green have little tendency to conjugate with the central carbon atom.[1] The difficulty with which the mesomeric effect is transmitted through the biphenylyl system in these basic dyes is surprising in view of the spectroscopic evidence, which shows effective conjugation of the terminal groups in 4-amino-4′-nitrobiphenyl[2] and in the (4′-methoxybiphenyl-4-yl)diphenylmethyl ion.[3] However, measurements of the ionisation constants for a range of 4′-substituted biphenyl-4-carboxylic acids and 4-aminobiphenyls have shown that the electronic effects of substituents are transmitted to the 4-position, but to a lesser extent than in the case of the analogous benzene systems.[4]

The absorption spectra of some 9,9-dimethylfluorene analogues of Crystal Violet and Malachite Green have now been determined in order to examine the effect of enforced planarity on the biphenyl system. The influence of planarity upon the reactivity of the fluorene system has been described by Brown[5] and his co-workers in a series of studies on the electrophilic substitution of fluorene and of biphenyl. In all these reactions, fluorene reacted about 200 times as fast as biphenyl and it was concluded that the effect was almost certainly due to the lack of steric inhibition of resonance in fluorene, in contrast with biphenyl. Berliner and Shieh[6] have studied the rates of hydrolysis of many 1-aryl-ethyl chlorides in aqueous acetone and observed, in particular, that the fluoren-2-yl derivative reacted far more rapidly than the biphenyl-4-yl derivative. This was tentatively attributed to the planarity of the fluorene system, in which the carbonium ion formed in the rate-determining stage would be stabilised to a greater extent by resonance. From the rates of solvolysis of some α-aryl-benzyl chlorides in ethanol–acetone, Bolton[7] has similarly shown that the fluoren-2-yl system is more able to stabilise carbonium ions than is the biphenyl-4-yl system. Gray[4] has found that 2-aminofluorene is a stronger base than 4-aminobiphenyl, and that fluorene-2-carboxylic acid is a weaker acid than biphenyl-4-carboxylic acid, in accord with greater conjugative interactions resulting from the planarity of the fluorene ring system, although the results may be explained on the basis of the electronic effect of the methylene group alone. Jones[2] has compared the electronic absorption spectra of several 4,4′-disubstituted biphenyls with those of the corresponding fluorene compounds. The latter derivatives have absorption maxima at longer wavelength, and this is attributed to their molecular uniplanarity.

The 9,9-dimethylfluorene system was chosen for the present study to avoid any synthetic difficulties which may arise owing to the reactivity of the methylene bridge in fluorene.

Maximum stabilisation of the extended quinonoid system should be achieved in the mono-9,9-dimethylfluorenyl analogue of Crystal Violet (I; $R = NMe_2$). Effective conjugation of the nitrogen atom attached to the 9,9-dimethylfluorenyl group with the central carbon atom in this dye would result in a spectrum with a single band in the visible region, as for Crystal Violet, whereas absence of conjugation, and subsequent protonation of the nitrogen atom to form the bivalent cation (II; $R = NMe_2$), would result in a strong first band and a weak second band in the visible region, as for Malachite Green. The closest approach to the spectrum of the univalent ion (I; $R = NMe_2$) is obtained from the methyl ether of the dye base in ethanol in the presence of one equivalent of hydrogen chloride (Figure), but the second band ($\varepsilon_{max.}$ 5000) indicates the presence of *ca.* 16% of the bivalent ion (II; $R = NMe_2$) and the observed value of $\lambda_{max.}$ (614 nm.) is therefore higher than that of the univalent ion. It is clear, however, that this ion absorbs at longer wavelength than Crystal Violet ($\lambda_{max.}$ 589 nm.) and that the bathochromic shift is due to the more extended conjugation of the 9,9-dimethylfluorene system. In comparison with the 9,9-dimethylfluorenyl group, the biphenyl group produces a slightly larger bathochromic shift of the first band ($\lambda_{max.}$ 617·5 nm.)

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[1] C. C. Barker and A. Stamp, *J. Chem. Soc.*, 1961, 3445.

[2] R. B. Sandin, R. Melby, A. S. Hay, R. N. Jones, E. C. Miller, and J. A. Miller, *J. Amer. Chem. Soc.*, 1952, **74**, 5073.

[3] L. C. Anderson and W. A. Fisher, *J. Amer. Chem. Soc.*, 1944, **66**, 594.

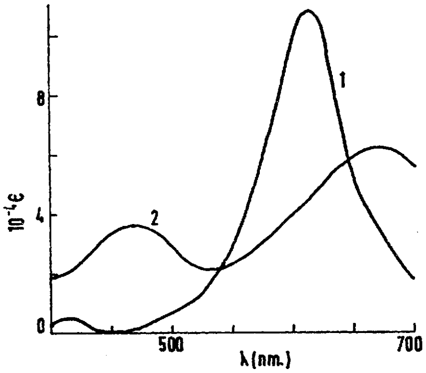
[4] D. J. Byron, G. W. Gray, and R. C. Wilson, *J. Chem. Soc.* (*C*), 1966, 831.

[5] H. C. Brown, M. Dubeck, and G. Goldman, *J. Amer. Chem. Soc.*, 1962, **84**, 1229 *et seq.*

[6] E. Berliner and N. Shieh, *J. Amer. Chem. Soc.*, 1957, **79**, 3849.

[7] R. Bolton, M. E. Jones, and S. W. Tucker, *J. Chem. Soc.*, 1964, 1464.

owing to the presence of a greater amount of the corresponding bivalent ion (IV; R = NMe_2) (28%).[1] This conclusion is supported by the increase in intensity observed on passing from the biphenyl compound (III; R = NMe_2) ($\varepsilon_{max.}$ 94,000) to its 9,9-dimethylfluorenyl analogue (I; R = NMe_2) ($\varepsilon_{max.}$ 108,000).



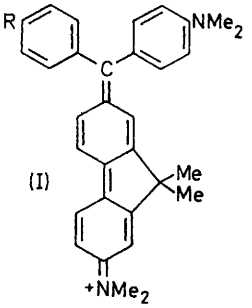
Absorption spectra of (1) (7-dimethylamino-9,9-dimethylfluoren-2-yl)bis-(4-dimethylaminophenyl)methyl methyl ether and (2) α-(7-dimethylamino-9,9-dimethylfluoren-2-yl)-α-(4-dimethylaminophenyl)benzyl alcohol [5 × $10^{-4}\varepsilon$ plotted] in ethanol with 1 equiv. of hydrochloric acid

In acetic acid the absorption due to the bivalent cation (II; R = NMe_2) increases as the acidity is increased by addition of water to the solvent (Table). In 75% acetic acid a close approximation to the spectrum of the bivalent ion is obtained, this being shown by the correspondence between the intensity of the second band ($\varepsilon_{max.}$ 30,000) and that of the second band of the 9,9-dimethylfluorene analogue of Malachite Green (V) ($\varepsilon_{max.}$ 39,000). The bathochromic and hypsochromic shifts of the first and the second band, respectively, of the bivalent ion (II; R = NMe_2), relative to the corresponding bands of the 9,9-dimethylfluorene analogue of Malachite Green (V), are consistent with the electron-withdrawing effect of a protonated dimethylamino-group. By comparison with the biphenyl group, the 9,9-dimethylfluorenyl group produces a marked bathochromic shift (30 nm.) of the second band (*y*-band), this being in accord with enhanced conjugation along the *y*-axis of the molecule (Table).

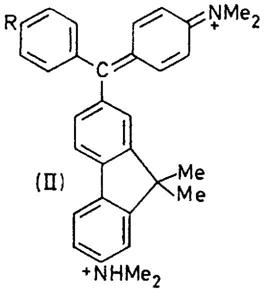
Spectral data for 10^{-5}M-solutions of 9,9-dimethylfluorene analogues of Crystal Violet and Malachite Green

Dye	Solvent	Absorption maxima (nm.) ($10^{-4}\varepsilon$ in parentheses)
Crystal Violet	98% HOAc	589 (11·6)
(I; R = NMe_2)	100% HOAc	618 (9·7), 480 (1·1)
	98% HOAc	621 (9·5), 474 (1·3)
	90% HOAc	628·5 (9·2), 464 (3·0)
	75% HOAc	629·5 (9·1), 463·5 (3·0)
	EtOH + 1 equiv. HCl	614 (10·8), 418 (0·5)
(III; R = NMe_2)	EtOH + 1 equiv. HCl	617·5 (9·4), 415 (0·8)
Malachite Green	98% HOAc	621 (10·4), 427·5 (2·0)
(I; R = H)	100% HOAc	680 (1·14), 480 (1·18)
	5% HOAc	496 (1·18)
	EtOH + 1 equiv. HCl	675 (1·25), 468 (0·72)
(III; R = H)	EtOH + 1 equiv. HCl	625 (0·4), 463 (0·3) *
(V)	98% HOAc	623 (9·7),† 484 (3·9)
(VI)	98% HOAc	625·5 (10·2), 454 (3·1)

* Bands fade rapidly. † Possibly a little low.



(I)



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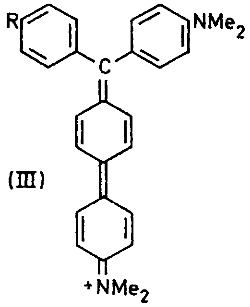

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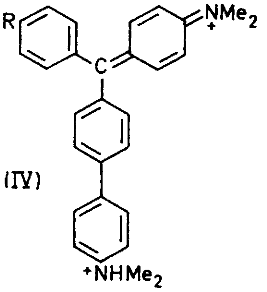

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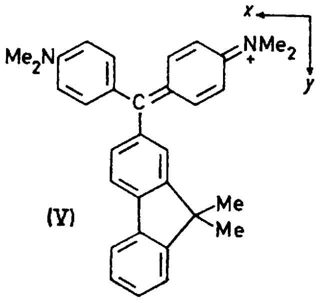
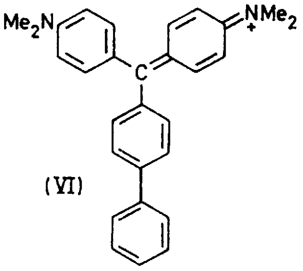
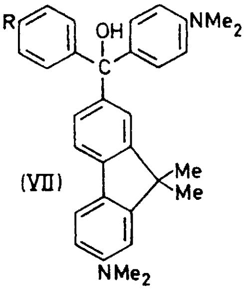


(V)



(VI)



(VII)

The small hypsochromic shift of the first band (*x*-band) is consistent with the electron-donating effect of an alkyl substituent in the 3-position of Malachite Green.[8]

The 9,9-dimethylfluorene analogue of Malachite Green base (VII; R = H) shows less tendency to form a univalent cation than the corresponding analogue of Crystal Violet base (VII; R = NMe_2). However, the absorption spectrum (Figure) is much more clearly de-

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

fined than that of the corresponding biphenyl analogue (III; R = H).[1] The closest approach to the spectrum of the univalent ion (I; R = H) is again obtained from the dye base in ethanol in the presence of one equivalent of hydrogen chloride (Table). Although the conversion of dye base into dye is incomplete, the bands do not fade, unlike those of the biphenyl analogue. A pronounced bathochromic shift (54 nm.) of the first band is observed relative to Malachite Green and this can be associated with the more extended conjugation along the x-axis. In pure acetic acid the intensity of the first band is approximately the same as that of the second band, thereby indicating the presence of a considerable amount of bivalent cation (II; R = H). Absorption due to the univalent ion (I; R = H) is completely absent only in 5% acetic acid.

Although it is established that the replacement of biphenyl by 9,9-dimethylfluorene in these dyes leads to an increase in stability of the relevant univalent ions, nevertheless, it is only with difficulty that the mesomeric effect is transmitted through the fluorenyl system. This result is surprising in view of the evidence already cited [5–7] which shows effective conjugation between the 2- and 7-positions in derivatives of fluorene. The increased intensity of the y-band of the 9,9-dimethylfluorene analogue of Malachite Green (V) ($\varepsilon_{max.}$ 39,000) implies effective conjugation along the y-axis, but in this case charge is not localised to the extent that it is when a terminal nitrogen atom is conjugated with the central carbon atom through the fluorenyl system.

Preparations.—Although 9,9-dimethylfluorene can be prepared from fluorene in one stage by methylation with, successively, methyl-lithium and methyl iodide,[9] a high yield of purer product is obtained (81% overall) by isolation of the intermediate 9-methylfluorene.

Bromination of 9,9-dimethylfluorene in chloroform at room temperature, following the procedure described by Campbell and Temple for the preparation of 2-bromofluorene,[10] gives 2-bromo-9,9-dimethylfluorene as the main product together with the 2,7-dibromo-derivative. 9,9-Dimethyl-2-nitrofluorene was obtained by the method of Campbell.[11] Bromination of the nitro-compound in acetic acid or nitration of the bromo-compound in the same solvent gives 2-bromo-9,9-dimethyl-7-nitrofluorene. Methylation of 2-amino-7-bromo-9,9-dimethylfluorene, obtained from the corresponding nitro-compound by reduction with tin(II) chloride and hydrochloric acid, in trimethyl phosphate gives 2-bromo-7-dimethylamino-9,9-dimethylfluorene.

Iodonitration of 9,9-dimethylfluorene, by the procedure used by Harley-Mason and Mann for the preparation of 4-iodo-4′-nitrobiphenyl,[12] gives mainly 2-iodo-9,9-dimethyl-7-nitrofluorene, together with 9,9-dimethyl-2,7-dinitrofluorene and a small amount of 9,9-dimethyl-2,5-dinitrofluorene. Formation of the two dinitro-compounds appears to be in accord with the partial rate factors for different positions in fluorene.[13] The iodonitro-compound is best reduced with iron and hydrochloric acid. 2-Dimethylamino-7-iodo-9,9-dimethylfluorene is obtained from the amino-compound by methylation in trimethyl phosphate.

9,9-Dimethylfluorene-2-carboxylic acid is prepared by carbonation of the Grignard reagent obtained from 2-bromo-9,9-dimethylfluorene by the entrainment technique.[14] The acid is readily esterified with boron trifluoride–methanol reagent.[15]

The use of 2-bromo-7-dimethylamino-9,9-dimethylfluorene and 2-dimethylamino-7-iodo-9,9-dimethylfluorene to prepare the dye bases is complicated by difficulty in converting these halides into lithium or Grignard compounds, as in the case of the corresponding biphenyl derivatives,[1] but Rodd and Linch's method,[16] which involves condensing a diaryl ketone with an aryl halide in the presence of sodium, is more satisfactory. Thus, Michler's ketone with 2-bromo-7-dimethylamino-9,9-dimethylfluorene and sodium gives (7-dimethylamino-9,9-dimethylfluoren-2-yl)bis-(4-dimethylaminophenyl)-methanol (VII; R = NMe_2). The dye base, which is not readily purified, is converted into the pure methyl ether by reaction of the perchlorate of the dye with methanolic sodium methoxide. Similarly, 4-dimethylaminobenzophenone with 2-bromo-7-dimethylamino-9,9-dimethylfluorene and sodium gives α-(7-dimethylamino-9,9-dimethylfluoren-2-yl)-α-(4-dimethylaminophenyl)benzyl alcohol (VII; R = H).

Bis-(4-dimethylaminophenyl)-9,9-dimethylfluoren-2-ylmethanol, prepared from 4-dimethylaminophenyllithium and methyl 9,9-dimethylfluorene-2-carboxylate, gives a first band ($\varepsilon_{max.}$ 97,000) which is little weaker than is usual with derivatives of Malachite Green containing substituents in the 3- or 4-positions. Synthesis of the dye base from 2-bromo-9,9-dimethylfluorene and Michler's ketone in the presence of sodium gives a material which shows a first band of the same intensity. In both cases persistently low microanalytical figures were obtained for carbon, but the dye base gives the expected mass spectrum.

EXPERIMENTAL

2-*Bromo*-9,9-*dimethylfluorene*.—Bromine (11·2 ml.) was added during 30 min. to a stirred solution of 9,9-dimethylfluorene [9] (40 g.) in chloroform (300 ml.) at room temperature, and the mixture was kept for 3 hr. Distillation of the crude product gave 2-*bromo*-9,9-*dimethylfluorene* (27 g.), b.p. 188—190°/2 mm., forming colourless crystals, m.p. 63—64° (Found: C, 66·2; H, 4·8; Br, 29·1. $C_{15}H_{13}Br$ requires C, 66·2; H, 4·4; Br, 29·4%). The residue was stirred with ethanol (100 ml.), filtered off, and crystallised twice from ethanol, giving 2,7-*dibromo*-9,9-*dimethylfluorene* (19 g.),

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[9] P. M. G. Bavin, *Canad. J. Chem.*, 1960, **38**, 882.

[10] N. Campbell and A. F. Temple, *J. Chem. Soc.*, 1957, 207.

[11] T. W. Campbell, R. Ginsig, and H. Schmid, *Helv. Chim. Acta*, 1953, **36**, 1489.

[12] J. Harley-Mason and F. G. Mann, *J. Chem. Soc.*, 1940, 1379.

[13] M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 1958, 3079.

[14] D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, 1959, **24**, 504.

[15] G. Hallas, *J. Chem. Soc.*, 1965, 5770.

[16] E. H. Rodd and F. W. Linch, *J. Chem. Soc.*, 1927, 2174.

m.p. 176—177° (Found: C, 51·6; H, 3·2; Br, 45·4. $C_{15}H_{12}Br_2$ requires C, 51·2; H, 3·4; Br, 45·4%).

2-*Bromo*-9,9-*dimethyl*-7-*nitrofluorene*.—(*a*) Bromine (1·4 ml.) was added to 9,9-dimethyl-2-nitrofluorene [11] (5 g.) in acetic acid (50 ml.) and the mixture was boiled for 6 hr. The precipitate obtained by pouring the cold solution into water (150 ml.) was thrice crystallised from ethanol, giving pale yellow needles of the *bromo-compound* (5·4 g.), m.p. 241—242° (Found: C, 56·4; H, 3·8; N, 4·6; Br, 25·0. $C_{15}H_{12}BrNO_2$ requires C, 56·6; H, 3·8; N, 4·4; Br, 25·1%).

(*b*) Concentrated nitric acid (35 ml.) was added to 2-bromo-9,9-dimethylfluorene (25 g.) in acetic acid (300 ml.). The mixture was heated to boiling over 30 min. and kept at this temperature for 15 min. The yellow needles which separated from the cold solution were crystallised from ethanol, yielding 2-bromo-9,9-dimethyl-7-nitrofluorene (18 g.), m.p. 241—242°.

2-*Amino*-7-*bromo*-9,9-*dimethylfluorene*.—A mixture of 2-bromo-9,9-dimethyl-7-nitrofluorene (40 g.), concentrated hydrochloric acid (120 ml.), and ethanol (900 ml.) was heated under reflux while tin(II) chloride (110 g.) was added during 1 hr. The mixture was boiled for 2 hr., cooled, and poured into sodium hydroxide (80 g.) in water (1800 ml.). The precipitate was twice crystallised from aqueous ethanol, giving needles of the *amine* (18 g.), m.p. 156—157° (Found: C, 62·0; H, 5·0; Br, 27·8; N, 5·0. $C_{15}H_{14}BrN$ requires C, 62·5; H, 4·9; Br, 27·7; N, 4·9%). Acetylation with acetic anhydride gave needles of 2-*acetylamino*-7-*bromo*-9,9-*dimethylfluorene*, m.p. 209—210° (from ethanol) (Found: C, 61·7; H, 5·0; Br, 24·5; N, 4·1%. $C_{17}H_{16}BrNO$ requires C, 61·8; H, 4·9; Br, 24·2; N, 4·2%).

2-*Bromo*-7-*dimethylamino*-9,9-*dimethylfluorene*.—A mixture of 2-amino-7-bromo-9,9-dimethylfluorene (10 g.) and trimethyl phosphate (10 ml.) was kept at 180° for 4 hr. and then boiled for 1·5 hr. with aqueous sodium hydroxide (15 g. in 100 ml.). The cooled mixture was extracted with ether, yielding a product which was boiled with acetic anhydride (10 ml.) for 15 min. The precipitate obtained by pouring the cold solution into water was stirred in 2N-hydrochloric acid (60 ml.). Basification of the filtrate gave a product which was sublimed at 180°/0·2 mm. and then crystallised from ethanol, yielding the *bromo-compound* (4·5 g.), m.p. 131—132° (Found: C, 64·2; H, 5·5; Br, 25·9; N, 4·7%. $C_{17}H_{18}BrN$ requires C, 64·6; H, 5·7; Br, 25·3; N, 4·4%).

2-*Iodo*-9,9-*dimethyl*-7-*nitrofluorene*.—Concentrated nitric acid (36 ml.) was added over 1 hr. to a powdered mixture of 9,9-dimethylfluorene (15 g.) and iodine (7·5 g.) at 100°. After the mixture had been heated for 1 hr., water (400 ml.) was quickly added to the solution and the precipitate was chromatographed on alumina (40 × 5 cm.) with benzene as eluant. A fraction corresponding to the first distinct yellow band was collected and crystallisation of the product from ethanol gave pale yellow needles of 2-*iodo*-9,9-*dimethyl*-7-*nitrofluorene* (18 g.), m.p. 241—242° (Found: C, 49·3; H, 3·6; I, 34·3; N, 3·9. $C_{15}H_{12}INO_2$ requires C, 49·2; H, 3·3; I, 34·8; N, 3·8%). A second fraction, associated with a small brighter yellow band, was collected; crystallisation of the product from ethanol gave 9,9-*dimethyl*-2,5-*dinitrofluorene* (0·1 g.), m.p. 174—175° (Found: C, 63·2; H, 4·2; N, 9·8. $C_{15}H_{12}N_2O_4$ requires C, 63·4; H, 4·3; N, 9·9%). A third yellow band was removed by boiling the alumina in benzene which contained ethanol. Removal of the solvent and crystallisation from benzene yielded yellow crystals of 9,9-*dimethyl*-2,7-*dinitrofluorene* (8 g.), m.p. 305—307° (Found: C, 63·6; H, 4·3; N, 9·7%). The 2,7-dinitro-derivative can be prepared directly by heating 9,9-dimethylfluorene with concentrated nitric acid at 100° for 1 hr.

2-*Amino*-7-*iodo*-9,9-*dimethylfluorene*.—To a stirred mixture of 2-iodo-9,9-dimethyl-7-nitrofluorene (18 g.) and iron dust (9 g.) in 1 : 1 aqueous ethanol (120 ml.) was added concentrated hydrochloric acid (2 ml.) in ethanol (5 ml.) during 10 min. The mixture was boiled for 12 hr., sodium hydroxide (2 g.) in ethanol (10 ml.) was added to the hot filtrate, and the neutralised solution was then poured into ice–water. The dried precipitate, twice crystallised from aqueous ethanol, gave crystals of 2-*amino*-7-*iodo*-9,9-*dimethylfluorene* (6 g.), m.p. 153—154° (Found: C, 53·2; H, 4·2; I, 38·4; N, 4·5. $C_{15}H_{14}IN$ requires C, 53·8; H, 4·2; I, 37·9; N, 4·2%). A sample of the amine was acetylated with acetic anhydride. Crystallisation of the crude product from ethanol gave needles of 2-*acetylamino*-7-*iodo*-9,9-*dimethylfluorene*, m.p. 216—218° (Found: C, 53·7; H, 4·2; I, 33·7; N, 3·9. $C_{17}H_{17}INO$ requires C, 54·1; H, 4·3; I, 33·7; N, 3·7%).

2-*Dimethylamino*-7-*iodo*-9,9-*dimethylfluorene*.—A mixture of 2-amino-7-iodo-9,9-dimethylfluorene (3 g.) and trimethyl phosphate (4 ml.) gave, by the method described for the preparation of the corresponding bromo-compound, a product which was sublimed at 160°/0·1 mm. This was crystallised from ethanol, yielding the *iodo-compound* crystals (1·4 g.), m.p. 94—96° (Found: C, 56·2; H, 4·9; I, 34·9; N, 4·2. $C_{17}H_{18}IN$ requires C, 56·2; H, 5·0; I, 34·9; N, 3·9%).

9,9-*Dimethylfluorene*-2-*carboxylic Acid*.—To a stirred boiling mixture of 2-bromo-9,9-dimethylfluorene (4 g.) and magnesium (0·88 g.) in ether (50 ml.) was added 1,2-dibromoethane (1·7 ml.) in ether (10 ml.) over 1 hr. The mixture was boiled for 2 hr. and poured into crushed carbon dioxide in ether; the slurry was kept for 30 min. then added to dilute hydrochloric acid (0·1%; 200 ml.). Acidification of the aqueous layer with aqueous sodium hydrogen carbonate (5%; 50 ml.) gave a precipitate which was twice crystallised from 1 : 1 aqueous ethanol, yielding plates of the *acid* (1·4 g.), m.p. 190—190·5° (Found: C, 80·4; H, 6·0. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

Methyl 9,9-*Dimethylfluorene*-2-*carboxylate*.—9,9-Dimethylfluorene-2-carboxylic acid (1 g.) was esterified with boron trifluoride–methanol reagent,[15] giving crystals of the *ester* (0·7 g.), m.p. 105·5—106° (Found: C, 81·0; H, 6·6. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

(7-*Dimethylamino*-9,9-*dimethylfluoren*-2-*yl*)*bis*-(4-*dimethylaminophenyl*)*methyl Methyl Ether*.—A well stirred mixture of 2-bromo-7-dimethylamino-9,9-dimethylfluorene (1 g.), Michler's ketone (0·92 g.), sodium (0·15 g.), and toluene (50 ml.) was boiled under nitrogen for 24 hr. Water (50 ml.) was then added and the residual dye base from the dried (Na_2SO_4) toluene layer was dissolved in acetic acid (4 ml.). The product obtained on removal of the solvent was added to water and the filtered solution was poured into potassium perchlorate (1·25 g.) in water (50 ml.). A solution of the dried perchlorate of the dye in methanol (20 ml.) was slowly added to methanol (15 ml.) containing sodium methoxide (1·3 g.) and kept for 4 hr. Crystallisation of the precipitate from benzene–methanol (1 : 4) gave colourless crystals of the *methyl ether* (0·2 g.), m.p. 163—165° (Found: C, 80·9; H, 7·8; N, 7·8. $C_{35}H_{41}N_3O$ requires C, 80·9; H, 7·9; N, 8·1%).

α-(7-*Dimethylamino*-9,9-*dimethylfluoren*-2-*yl*)-α-(4-*dimethylaminophenyl*)*benzyl Alcohol*.—The interaction of 2-bromo-7-dimethylamino-9,9-dimethylfluorene (1 g.), 4-di methylaminobenzophenone (0·82 g.), and sodium (0·15 g.) under conditions used in the previous preparation yielded, after three crystallisations from benzene–light petroleum (1 : 10), the *dye base* (0·65 g.), m.p. 64—65° (Found: C, 82·1; H, 7·1; N, 5·3%; M^+ 462·2665. $C_{32}H_{34}N_2O$ requires C, 83·1; H, 7·4; N, 6·0%; M 462·2671.).

Bis-(4-*dimethylaminophenyl*)-9,9-*dimethylfluoren*-2-*ylmethanol*.—Ethereal 4-dimethylaminophenyl-lithium, from 4-bromo-*NN*-dimethylaniline (2·5 g.), was filtered under nitrogen into ethereal methyl 9,9-dimethylfluorene-2-carboxylate (1 g.), and the mixture was kept for 1 hr. Addition of water and removal of solvent from the dried (Na_2SO_4) organic layer yielded a solid which was crystallised once from acetone–water and twice from benzene–light petroleum to give leaflets of the *dye base* (0·2 g.), m.p. 109—111° (Found: C, 81·7; H, 7·3; N, 5·8. $C_{32}H_{34}N_2O$ requires C, 83·1; H, 7·4; N, 6·0%).

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