3 : 6-*Disubstituted Fluorenes. Part III.* Fluorene Analogues of Michler's Hydrol, Malachite-green, and Crystal-violet.*

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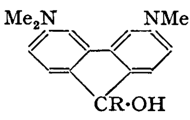
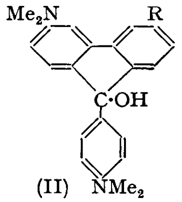
The fluorene analogues of some basic di- and tri-phenylmethane dyes have been prepared and their absorption spectra determined. The analogues of malachite-green and crystal-violet show a very large bathochromic shift when compared with the corresponding triphenylmethane dyes; the analogue of Michler's hydrol blue is colourless and possesses the structure (III).

The results of *X*-ray analysis of fluorene have been interpreted by Iball (*Z. Krist.*, 1937, **34**, 397) in favour of a non-planar molecular configuration, and it seemed that further evidence about the problem might be obtained from the absorption spectra of fluorene analogues of basic triphenylmethane dyes. Accordingly, the analogues of Michler's hydrol (I; R = H), malachite-green base (I; R = Ph), and crystal-violet base (II; R = NMe_2) were prepared from 3 : 6-bisdimethylaminofluorenone. The unsymmetrical analogue of malachite-green base (II; R = H) was prepared from the colour salt obtained from 4′ : 4″-bisdimethylaminotriphenylmethane-2-diazonium sulphate, as described by Guyot and Granderye (*Bull. Soc. chim.*, 1905, **33**, 198).

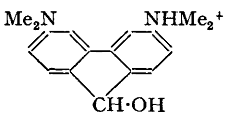
The fluorenone was obtained by methylation of 3 : 6-diaminofluorene with trimethyl phosphate followed by oxidation with chloranil. It was identical with material obtained from 4 : 4′-bisdimethylaminobenzophenone-2-diazonium sulphate (Part II *); this confirms its structure. Attempts to methylate 3 : 6-diaminofluorenone with trimethyl phosphate or with methanol and hydrogen chloride were unsuccessful. Reduction of the methylated ketone with sodium amalgam gave 3 : 6-bisdimethylaminofluoren-9-ol (I; R = H) which is more reactive than the analogously constituted Michler's hydrol—recrystallisation caused deterioration, and boiling it with benzene and charcoal gave the parent ketone. It condensed normally with *NN*-dimethylaniline giving 3 : 6-bisdimethylamino-9-*p*-dimethylaminophenylfluorene.



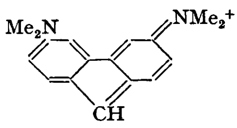
(I)



(II)



(III)



(IV)

3 : 6-Bisdimethylaminofluorenone and *p*-dimethylaminophenyl-lithium gave the analogue of crystal-violet base (II; R = NMe_2), the colour salt of which was identical with the dye obtained by Guyot and Haller (*Bull. Soc. chim.*, 1901, **25**, 750) by heating 4 : 4′ : 4″-trisdimethylaminotriphenylmethane-2-diazonium sulphate and oxidising the product. Similarly, the ketone and phenylmagnesium bromide gave the symmetrical analogue of malachite-green base (I; R = Ph). This base gave a yellow solution in acetic acid, thus disproving Dutt's claim (*J.*, 1926, 1171) to have prepared a green dye of this structure (cf. Part I, *J.*, 1953, 2034).

The Michler's hydrol analogue in glacial acetic acid showed no absorption band in the region 400—1000 mμ; instead, an ethanolic solution containing one equivalent of hydrogen chloride showed a band in the region 200—400 mμ which closely resembled that of 3 : 6-bisdimethylaminofluorene monohydrochloride (Fig. 1). The cation thus possesses the structure (III) and not the degenerate structure (IV). The absorption spectra of acetic acid solutions of the other dye bases are recorded in Fig. 2. They all show large batho-

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* Part II, *J.*, 1954, 870.

chromic shifts when compared with their triphenylmethane analogues, and these shifts were tentatively ascribed to deviation from molecular planarity. Brown and Dewar (*J.*, 1954, in the press) have shown, however, that they can be quantitatively ascribed to the formation of the additional C–C bond. But the deviation from planarity deduced by Iball (*loc. cit.*) is not great, and, while these spectra provide no evidence in favour of non-planarity, they do not demonstrate that the dyes are completely planar.

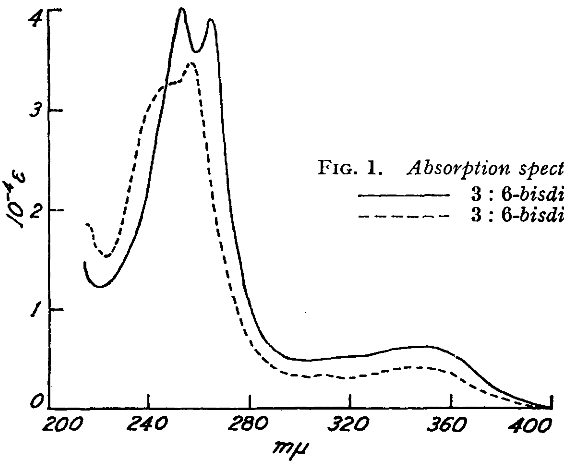

FIG. 1. *Absorption spectra of the hydrochlorides of:*
———— 3 : 6-*bisdimethylaminofluoren*-9-*ol, and*
– – – – – – 3 : 6-*bisdimethylaminofluorene in ethanol.*

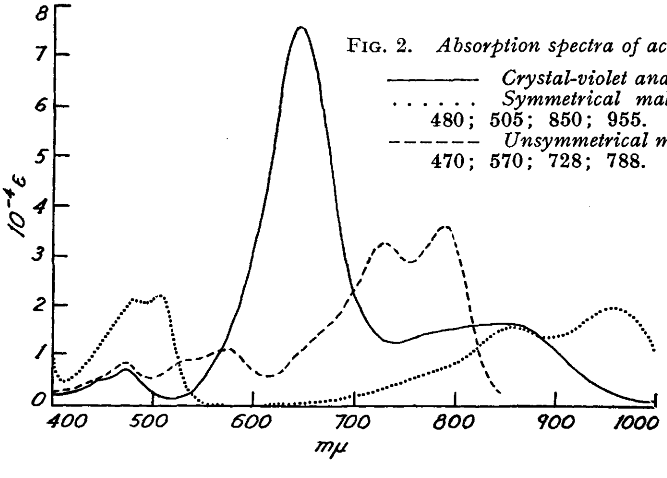

FIG. 2. *Absorption spectra of acetic acid solutions of:*
———— *Crystal-violet analogue.* $\lambda_{max.}$ (mμ) 470; 647; 850.
. . . . . . *Symmetrical malachite-green analogue.* $\lambda_{max.}$ (mμ) 480; 505; 850; 955.
– – – – – – *Unsymmetrical malachite-green analogue.* $\lambda_{max.}$ (mμ) 470; 570; 728; 788.

The blue solution of the crystal-violet analogue in acetic acid became progressively more violet upon dilution with water; Guyot and Haller (*loc. cit.*) observed a similar change when an ethanolic solution of the chloride of the dye was diluted. In water the chloride had $\lambda_{max.}$ 590 mμ; $\varepsilon_{max.}$ $4{\cdot}22 \times 10^4$. This is probably due to polymerisation of the dye in water (cf. thionine; Rabinowitch and Epstein, *J. Amer. Chem. Soc.*, 1941, **63**, 69).

EXPERIMENTAL

3 : 6-*Bisdimethylaminofluorene*.—3 : 6-Diaminofluorene (9·0 g.; cf. Part II) and trimethyl phosphate (9·0 c.c.) were mixed and stirred at 160—170° for 30 min. and at 190—200° for 30 min., cooled, and then refluxed for 1 hr. with water (130 c.c.) containing sodium hydroxide (22 g.). Water (200 c.c.) was added and the product was dried and refluxed for 30 min. with acetic anhydride (25 c.c.) which was then removed at 13 mm. The residue was sublimed at

140—150°/10^{-3} mm. and crystallised from ethanol (95 c.c.), giving 3 : 6-*bisdimethylaminofluorene* (4·7 g.), m. p. 147—149° raised by chromatography on activated alumina in benzene–alcohol to m. p. 149° (Found : C, 81·0; H, 7·9; N, 10·9. $C_{17}H_{20}N_2$ requires C, 80·9; H, 8·0; N, 11·1%).

3 : 6-*Bisdimethylaminofluorenone.*—A mixture of chloranil (2·0 g.), 3 : 6-dimethylaminofluorene (1·0 g.), and ethanol (40 c.c.) was refluxed for 75 min. and cooled, and the separated crystals were dissolved in hot dilute hydrochloric acid, and the solution was filtered and then made alkaline with sodium hydroxide. The dried precipitate was chromatographed in dry pyridine on activated alumina (1·5 × 5 cm.), and the eluate (75 c.c.) concentrated to 5 c.c. and slowly diluted with water (40 c.c.), giving orange crystals (0·70 g.), m. p. 250—252°; the m. p. of a mixture with material from 4 : 4'-bisdimethylaminobenzophenone-2-sulphate was 249—251° (Found : N, 10·2. Calc. for $C_{17}H_{18}ON_2$: N, 10·5%).

3 : 6-*Bisdimethylaminofluoren-9-ol.*—Sodium amalgam (3% of sodium; 3·5 g.), 3 : 6-bisdimethylaminofluorenone (0·50 g.), and ethanol (95%; 30 c.c.) were stirred and refluxed for 1 hr. The solution was filtered and diluted with water, and the precipitate dried in vacuum, giving 3 : 6-*bisdimethylaminofluoren*-9-*ol* (0·38 g.), m. p. 190—191° (Found : C, 76·4; H, 7·5; N, 10·5. $C_{17}H_{20}ON_2$ requires C, 76·1; H, 7·5; N, 10·4%).

3 : 6-*Bisdimethylamino-9-phenylfluoren-9-ol.*—3 : 6-Bisdimethylaminofluorenone (0·50 g.) was added to a refluxing solution of phenylmagnesium bromide, prepared from bromobenzene (1·1 c.c.) in ether (20 c.c.) and benzene (20 c.c.). A white solid separated; after being refluxed for 20 hr. the mixture was cooled and the white solid collected, stirred with aqueous ammonium chloride, and then dissolved in dilute hydrochloric acid. Basification of the filtered solution with ammonia solution and crystallisation of the product (0·24 g.) from benzene–light petroleum and then acetone, gave 3 : 6-*bisdimethylamino*-9-*phenylfluoren*-9-*ol*, m. p. 209—210° (decomp.) (Found : C, 79·6; H, 6·9; N, 7·9. $C_{23}H_{24}ON_2$ requires C, 80·2; H, 7·0; N, 8·1%). A further 0·24 g. was isolated from the reaction filtrate.

3 : 6-*Bisdimethylamino*-9-p-*dimethylaminophenylfluoren*-9-*ol.*—*p*-Dimethylaminophenyl-lithium was prepared from lithium (0·76 g.) and *p*-bromo-*NN*-dimethylaniline (10 g.) in ether (30 c.c.), and the solution filtered into a nitrogen-filled burette. A portion (2·3 c.c.) was added to a stirred mixture of benzene (50 c.c.) and 3 : 6-bisdimethylaminofluorenone (0·40 g.) in an atmosphere of nitrogen. After 30 min. water was added, the benzene layer separated and dried (Na_2SO_4), the solvent removed, and the residue (0·41 g.) crystallised from ethanol, giving 3 : 6-*bisdimethylamino*-9-p-*dimethylaminophenylfluoren*-9-*ol* as yellowish-white crystals, m. p. 196—198° (decomp.) (Found : C, 76·6; H, 7·3; N, 10·5. $C_{25}H_{29}ON_3$ requires C, 76·1; H, 7·5; N, 10·4%).

3-*Dimethylamino*-9-p-*dimethylaminophenylfluoren*-9-*ol.*—The *colour salt* corresponding to this base was prepared following Guyot and Granderye (*loc. cit.*), its warm aqueous solution basified with sodium hydroxide, the base extracted with benzene, and the solution dried (Na_2SO_4) and evaporated. The red residue solidified on trituration with light petroleum but did not crystallise (Found : N, 7·7. $C_{23}H_{24}ON_2$ requires N, 8·1%).

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