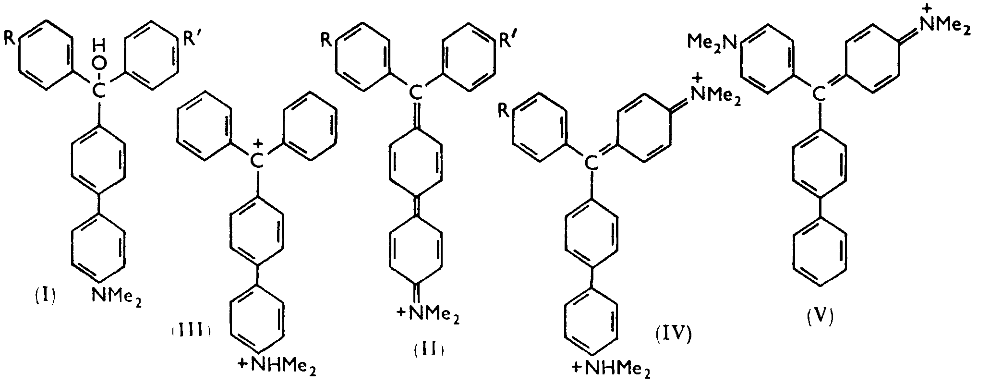
668. *Steric Effects in Di- and Tri-arylmethanes. Part VII.* Biphenyl Analogues of Crystal Violet and Malachite Green.*

By C. C. Barker and A. Stamp.

Spectral studies show 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. Conjugation is most effective in the Crystal Violet analogue (II; R = R′ = NMe_2) in which a high resonance energy counterbalances the high energy of the quinonoid biphenyl group.

In previous papers of this series the spectral changes brought about in basic di- and triphenylmethane dyes by twisting groups about central and terminal bonds have been discussed. Biphenyl analogues of these dyes appeared to provide an opportunity to study the effect of twisting the dye molecules about an intermediate bond.

One equivalent of perchloric acid with (4′-dimethylamino-4-biphenylyl)diphenylmethanol (I; R = R′ = H) in acetic acid protonates the dimethylamino-group [1] instead of forming the ion (II; R = R′ = H); more perchloric acid then gives the coloured protonated carbonium ion (III). The extended quinonoid system in (II) appears to be energetically unfavourable but this effect can be offset by resonance stabilisation in analogous di- and tri-aminotriarylmethane dyes. Thus, bis-(4′-dimethylamino-4-biphenylyl)phenylmethanol (I; R = H, R′ = *p*$Me_2N{\cdot}C_6H_4$) in hot acetic acid gives a weak green colour which fades reversibly on cooling; adding concentrated formic, perchloric, or sulphuric acid gives the red protonated carbonium ion.[2] Maximum stabilisation of the quinonoid biphenyl system should be achieved in the biphenylyl analogues of Crystal Violet, in particular, the monobiphenylyl analogue (II; R = R′ = NMe_2), the spectrum of which was therefore examined. Effective conjugation of the nitrogen atom attached to the biphenylyl group with the central carbon atom in this dye would result in a spectrum with a single band in the visible region (cf. Crystal Violet) whereas absence of conjugation, and subsequent protonation of the nitrogen atom, would result in a strong first frequency band and a weak second frequency band in the visible region (cf. Malachite Green). The closest approach to the spectrum of the univalent ion (II; R = R′ = NMe_2) is obtained from the dye base in ethanol with 1 equivalent of hydrogen chloride (Fig.) but the second frequency band ($\varepsilon_{max.}$ 8000) indicates the presence of approximately 28% of the bivalent cation (IV; R = NMe_2) and the observed value of $\lambda_{max.}$ (617·5 mμ) is therefore higher than



(I) (III) (II) (IV) (V)

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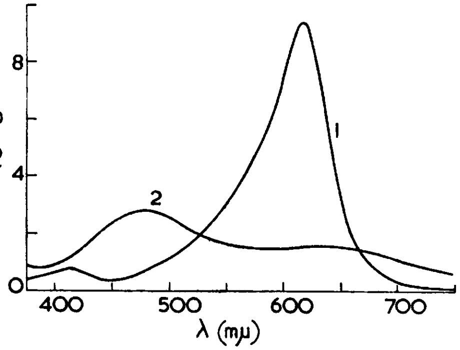
* Part VI, *J.*, 1961, 2642.

[1] Morton and Wood, *J. Amer. Chem. Soc.*, 1939, **61**, 2902.

[2] Theilacker and Schmid, *Chem. Ber.*, 1951, **84**, 204.

that of the univalent ion, but it is very probable that this ion absorbs at longer wavelength than Crystal Violet (589 mμ) and that the bathochromic shift is due to the more extended conjugation of the biphenyl system.

In 90% acetic acid or in 98% acetic acid with 12·5 equivalents of hydrogen chloride ($10^{-4} \times 1{\cdot}15$M) a close approximation to the spectrum of the bivalent ion (IV; R = NMe_2) is obtained, this being shown by the correspondence between the intensity of the second band ($\varepsilon_{max.}$ 29,000) and the intensity of the second band of the 4-phenyl derivative of Malachite Green (V; $\varepsilon_{max.}$ 30.000) (Table).



Absorption spectra of (1) *(4′-dimethylamino-4-biphenylyl)bis-(4-dimethylaminophenyl)methanol in ethanol with* 1 *equiv. of hydrochloric acid, and* (2) *(4′-dimethylamino-4-biphenylyl)-4-dimethylaminodiphenylmethanol in acetic acid.*

The biphenylyl analogue of Malachite Green base (I; R = H, R′ = NMe_2) shows much less tendency to form a univalent cation than the corresponding analogue of Crystal Violet base (I; R = R′ = NMe_2). Thus, in pure acetic acid the first band of the univalent ion (II; R = H, R′ = NMe_2) is of low intensity ($\varepsilon_{max.}$ less than 20,000 as compared with 104,000 observed with Malachite Green) and merges without a well-defined maximum into the first band of the bivalent ion (IV; R = H), $\lambda_{max.}$ 476·5 mμ, ε 28,000 (Fig.). In 90% acetic acid the intensity of the long-wavelength band is reduced below 5000, and the intensity of the second band increases to 32,000, a value comparable with that of the first band of the closely related *NN*-dimethylfuchsonimonium ion ($\lambda_{max.}$ 465·5 mμ; ε 35,000). In ethanol with one equivalent of hydrogen chloride the base gives a first band which is more intense than the second band (Table), but both of the bands fade rapidly and the absolute values of the intensities are not significant. This fading is probably due to the formation of the ethyl ether of the dye base.

Spectral data for 10^{-5}M-*solutions of biphenyl analogues of Crystal Violet and Malachite Green.*

Dye	Solvent	Absorption maxima (mμ) ($10^{-4}\varepsilon$ in parentheses)
Crystal Violet	98% HOAc	589 (11·6)
(II; R = R′ = NMe_2)	100% HOAc	621 (10·4); 448·5 (1·4)
,, ,,	98% HOAc	622·5 (10·1); 446 (2·0)
,, ,,	90% HOAc	627·5 (9·6); 444·5 (2·6)
,, ,,	98% HOAc + 12·5 equiv. HCl	626 (9·6); 445·5 (2·9)
,, ,,	EtOH + 1 equiv. HCl	617·5 (9·4); 415 (0·8)
Malachite Green	98% HOAc	621 (10·4); 427·5 (2·0)
(II; R = H, R′ = NMe_2)	100% HOAc	476·5 (2·8)
,, ,,	90% HOAc	476·5 (3·2)
,, ,,	EtOH + 1 equiv. HCl	625 (0·4); 463 (0·3) [a]
V	98% HOAc	623·5 (10·0); 453·5 (3·0)

[a] Bands faded rapidly.

Thus, it is likely that, even in the most favourable case of the monobiphenylyl analogue of Crystal Violet, twisting part of the molecule about the intermediate bond would lead to such a low concentration of ions containing the remote nitrogen atom conjugated with the central carbon atom that little useful spectroscopic information would be obtained. 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 showing effective conjugation of the terminal groups in 4-amino-4′-nitrobiphenyl[3] and in the (4′-methoxy-4-biphenylyl)diphenylmethyl ion.[4] The increased intensity of the *y*-band of the 4-phenyl derivative of Malachite Green (V) ($\varepsilon_{\text{max.}}$ 30,000) implies effective conjugation of the remote phenyl group (cf. the *y*-band of the 4-methoxy-derivative of Malachite Green, $\varepsilon_{\text{max.}}$ 34,000), 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 biphenylyl system.

Preparations.—The use of 4-bromo- and 4-iodo-4′-dimethylaminobiphenyl to prepare the dye bases is complicated by difficulty in converting these halides into lithium or Grignard compounds [2] but Rodd and Linch's method,[5] which involves condensing a diaryl ketone with aryl halide in the presence of sodium, is satisfactory. Thus, 4′-dimethylaminobiphenylyl-lithium, from 4-bromo-4′-dimethylaminobiphenyl and butyl-lithium, gives impure (4′-dimethylamino-4-biphenylyl)bis-(4-dimethylaminophenyl)methanol (I; $R = R' = NMe_2$) with Michler's ketone, but this ketone with 4-dimethylamino-4′-iodobiphenyl and sodium gives the pure base. Also, attempts to repeat the preparation of bis-(4′-dimethylamino-4-biphenylyl)phenylmethanol (I; $R = H$, $R' = p\text{-}Me_2N\cdot C_6H_4$) from 4-dimethylamino-4′-biphenylylmagnesium iodide [2] and ethyl benzoate gave impure material whereas 4-(4-dimethylaminophenyl)benzophenone with 4-dimethylamino-4′-iodobiphenyl and sodium gives the pure base. On the other hand, 4-dimethylamino-4′-iodobiphenyl with 4-dimethylaminobenzophenone and sodium gives slightly impure (4 -dimethylamino-4-biphenylyl)-4-dimethylaminodiphenylmethanol (I; $R = H$, $R' = NMe_2$) whereas 4-dimethylaminophenyl-lithium with 4-(4-dimethylaminophenyl)benzophenone gives pure base.

The 4-phenyl derivative of Malachite Green base, obtained by the interaction of 4-chlorobiphenyl, Michler's ketone and sodium, gives a first band ($\varepsilon_{\text{max.}}$ 100,000) which is a little weaker than is usual with 4-substituted derivatives of Malachite Green ($\varepsilon_{\text{max.}}$ 104,000—108,000), but purification by reduction to the leuco-compound followed by oxidation, or synthesis from 4-biphenylyl-lithium and Michler's ketone gives material showing a first band of the same intensity.

EXPERIMENTAL

4-*Bromo*-4′-*dimethylaminobiphenyl.*—A mixture of 4-amino-4′-bromobiphenyl (47·0 g.) and trimethyl phosphate (14·9 c.c.) was kept at 170—180° for 20 min. and then at 190—200° for 2 hr. The mixture was boiled for 1·5 hr. with aqueous sodium hydroxide (26·5 g. in 200 c.c.), water (300 c.c.) was then added, and the crude product was sublimed at reduced pressure and then kept at 100° for 30 min. in pyridine (160 c.c.) containing succinic anhydride (16·7 g.). The mixture was then poured into an excess of aqueous 2N-sodium hydroxide, and the precipitate was crystallised from benzene (250 c.c.) giving 4-bromo-4′-dimethylaminobiphenyl (35·5 g.), m. p. 209—210°; Banus and Medrano [6] give m. p. 209—211°.

4-(4-*Dimethylaminophenyl*)*benzophenone.*—Butyl-lithium (0·2 mole) was added to 4-bromo-4′-dimethylaminobiphenyl (5·52 g.) in benzene (200 c.c.), the mixture kept for 1 hr. and then cooled in ice, and benzonitrile (20·6 g.) added. After a further 1 hr. the mixture was poured into water, and concentrated hydrochloric acid was added until the solution was colourless. The aqueous layer was boiled for 1 hr. and then basified with ammonia (*d* 0·88). The dried precipitate, twice crystallised from 2 : 1 benzene–ethanol gave yellow leaflets of 4-(4-*dimethylaminophenyl*)*benzophenone* (3·1 g.), m. p. 184—185° (Found: C, 84·1; H, 6·5; N, 4·5. $C_{21}H_{19}NO$ requires C, 83·8; H, 6·3; N, 4·7%).

(4′-*Dimethylaminobiphenyl*)-4-*dimethylaminodiphenylmethanol.*—4-Dimethylaminophenyl-lithium in ether, from 4-bromo-*NN*-dimethylaniline (1·4 g.), was added under nitrogen to a

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[3] Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 5074.

[4] Anderson and Fisher, *J. Amer. Chem. Soc.*, 1944, **66**, 594.

[5] Rodd and Linch, *J.*, 1927, 2174.

[6] Banus and Medrano, *Anales real Soc. espan. Fis. Quim.*, 1922, **20**, 477.

suspension of 4-(4-dimethylaminophenyl)benzophenone (1·0 g.) in ether (50 c.c.). The mixture was kept for 2 hr. and then poured into water. Ether was removed from the dried (Na_2SO_4) organic layer, and the residue was twice crystallised from ethanol and then chromatographed in benzene on alumina, those eluates which gave a red colour in acetic acid being retained. The residue from these eluates, when crystallised from ethanol, gave the required *base* (0·3 g.), m. p. 119—120·5° (Found: C, 82·0; H, 7·3; N, 6·4. $C_{29}H_{30}N_2O$ requires C, 82·4; H, 7·2; N, 6·6%).

Bis-(4′-dimethylamino-4-biphenylyl)phenylmethanol.—A well-stirred mixture of 4-(4-dimethylaminophenyl)benzophenone (1·0 g.), 4-dimethylaminophenyl-4′-iodobiphenyl (1·17 g.), sodium (0·17 g.), and benzene (25 c.c.) was boiled under nitrogen for 24 hr. Water was then added and the residue from the dried (Na_2SO_4) benzene layer, after three crystallisations from toluene, gave the required base (0·9 g.), m. p. 225—226° (lit.,[2] 214—216°) (Found: C, 84·3; H, 6·9; N, 5·3. Calc. for $C_{35}H_{34}N_2O$: C, 84·3; H, 6·9; N, 5·6%).

(4′-Dimethylamino-4-biphenylyl)bis-(4-dimethylaminophenyl)methanol.—The interaction of 4-dimethylamino-4′-iodobiphenyl (2·35 g.), Michler's ketone (1·85 g.), and sodium (0·35 g.) under the conditions used in the previous preparation, and two crystallisations from ethanol, gave the required *base* (0·9 g.), m. p. 179—180° (Found: C, 79·9; H, 7·6; N, 8·9. $C_{31}H_{35}N_3O$ requires C, 79·9; H, 7·6; N, 9·0%).

αα-Bis(4-dimethylaminophenyl)-4-biphenylylmethyl Methyl Ether.—The interaction of 4-chlorobiphenyl (9·5 g.), Michler's ketone (13·4 g.), and sodium (2·3 g.) under conditions used in the previous preparation yielded, after two crystallisations from ethanol, *αα-bis-(4-dimethylaminophenyl)biphenylylmethanol* (11·3 g.), m. p. 152—153° (Found: C, 82·4; H, 7·4; N, 6·5. $C_{29}H_{30}N_2O$ requires C, 82·4; H, 7·2; N, 6·6%). To this base (2·0 g.) in dilute hydrochloric acid was added zinc dust until a drop of the solution gave no colour with sodium acetate. Basification of the solution with aqueous ammonia gave *αα-bis-(4-dimethylaminophenyl)biphenylylmethane* (1·2 g.), m. p. 189—189·5° (from 1 : 1 ethanol–benzene) (Found: C, 85·8; H, 7·4; N, 6·8. $C_{29}H_{30}N_2$ requires C, 85·7; H, 7·4; N, 6·9%). A mixture of this base (1·15 g.), chloranil (0·76 g.), and methanol (30 c.c.) was boiled for 30 min. The filtered solution was reduced to 15 c.c. and then poured into methanol (10 c.c.) containing sodium methoxide (0·4 g.), giving a precipitate of the *methyl ether* (1·0 g.), m. p. 147—148° (thrice crystallised from 2 : 1 methanol–benzene) (Found: C, 82·8; H, 7·3; N, 6·5. $C_{30}H_{32}N_2O$ requires C, 82·5; H, 7·4; N, 6·4%).

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