228. *The Colour of Organic Compounds. Part II. Colour Phenomena of Bis-2-(3 : 5-diphenylpyrrole)methins.*

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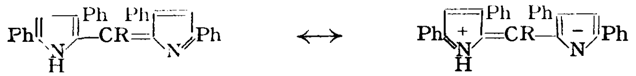
The abnormal colour changes shown on salt formation by *meso*-substituted bis-2-(3 : 5-diphenylpyrrole)methins are attributed to overcrowding and loss of nuclear planarity. The *meso*-alkyl dye bases are unstable and rapidly change into carbinol ethers in alcohol.

THE change in colour from red to green on acidification of solutions of bis-2-(3 : 5-diphenylpyrrole)*meso*phenylmethin (I; R = Ph) reported by Rogers (*J.*, **1943**, 596) is very interesting in view of the relative insensitivity of the parent dye (I; R = H) to change in pH, solutions of the latter dye in pyridine or acetic acid being red. That this sensitivity is not caused by the presence of the *meso*phenyl group *per se* has now been shown by our finding that the dihydrochloride of (I; R = Me) and the monohydrochloride of (I; R = Et) give blue solutions, changing to red on basification. Unlike the phenyl compound the *meso*alkyl bases are unstable, readily giving the carbinol ethers in alcohol. The latter regenerate the dye salts on acidification (cf. Brunings and Corwin, *J. Amer. Chem. Soc.*, **1942**, **64**, 593).

All these dye bases may be considered to have extreme structures (I*a*, *b*) of unequal energy whilst the cations of the dye salts formed by proton addition to (I) will be energetically symmetrical dyes of the cyanine type.

The bathochromic effect of the removal of non-degeneracy of a linear resonator is wel established (Brooker and Sprague, *J. Amer. Chem. Soc.*, 1941, **63**, 3203, 3214; Schwarzenbach' *Z. Elektrochem.*, 1941, **47**, 40), so that proton addition to these dye bases should be bathochromic'

(I*a*.)  (I*b*.)

The Table shows the absorption figures of the dye bases and dye salts in carbon tetrachloride and acetic acid respectively. Stable solutions of (I; R = alkyl) were obtained by adding triethylamine to a solution of the salt in anhydrous solvent.

	Dye base.		Dye salt.	
R in (I).	$\lambda_{max.}$ (mμ.).	$10^{-4}\varepsilon_{max.}$.	$\lambda_{max.}$ (mμ.).	$10^{-4}\varepsilon_{max.}$.
H	537	4·03	557	8·7
Ph	546	3·15	616	4·2
Me	550	0·74	595	3·75
Et	540	0·50	605	2·82

Figs. 1—3 are scale drawings of the dye bases or salts in which R = H, Ph, and Me, respectively. The parent base (R = H) is seen to be substantially free from crowding, and completely free if two of the phenyl residues rotate from coplanarity or bend outwards or if the bridge angle θ closes. The bathochromic shift of 20 mμ. and the doubling of the value for ε on proton addition is consistent with the loss of non-degeneracy and preservation of a planar structure in the dye salt.

FIG. 1.

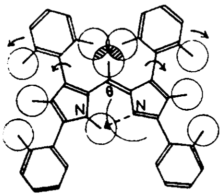


FIG. 2.

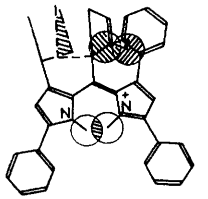


FIG. 3.

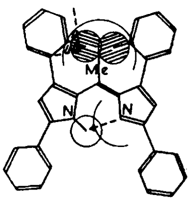


Fig. 2 shows severe overcrowding in (I; R = Ph), whether the top phenyl residues are coplanar or at right angles to the plane of the heterocyclic nuclei. The consequent distortion of the molecule can only be imagined but the decrease in $\varepsilon_{max.}$ (3·15 v. 4·03) indicates loss of nuclear (pyrrole) planarity. This must occur by the twisting of both bridge bonds. Since the base is non-degenerate the left-hand bridge bond will be of a lower order than the right hand one and as it is twisted so will its single-bond character increase. This will work hypsochromically by increasing the non-degeneracy of the system. On the other hand the twisting of the predominantly double bond will have the opposite effect (Brooker *et al.*, *Chem. Reviews*, 1948, **16**, 1124). The net result of these two factors might well explain the bathochromic shift of 9 mμ. observed on introduction of the *meso*phenyl group. Similar considerations apply for the *meso*alkyl group (Fig. 3); in this case the over-crowding is apparently even greater, as indicated by the low values for $\varepsilon_{max.}$.

The addition of a proton to these dyes with the consequent attainment of degeneracy results in the bridge bonds becoming of equal order. As Brunings and Corwin (*loc. cit.*) and Brooker *et al.* (*loc. cit.*) have shown, the twisting of adjacent bonds in a degenerate system results only in a bathochromic shift. The very large bathochromic shifts of 70, 45, and 65 mμ. in the three dyes on proton addition will thus be occasioned, first, by removal of non-degeneracy and, secondly, by twisting of both bridge bonds, there being in these cases no hypsochromic effect in action. The effect of the loss of nuclear planarity may also be seen by a comparison of $\varepsilon_{max.}$ of (I; R = H) with that of these dye salts.

EXPERIMENTAL.

(Microanalyses by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

Bis-2-(3 : 5-*diphenylpyrrole*)meso*methylmethin Dihydrochloride*.—2 : 4-Diphenylpyrrole (1 g.) and acetyl chloride (8 c.c.) were refluxed together for 10 minutes on the steam-bath. Part of the dye crystallized during this time. After chilling, the dye *salt* (0·8 g.) was collected and obtained as bronze plates, m. p. 202°, from alcoholic hydrogen chloride (Found: C, 77·0; H, 5·0; N, 4·9; Cl, 12·8. $C_{34}H_{26}N_2,2HCl$ requires C, 76·3; H, 5·25; N, 5·25; Cl, 13·3%).

Bis-2-(3 : 5-*diphenylpyrrole*)meso*ethylmethin Hydrochloride*.—2 : 4-Diphenylpyrrole (1 g.) and propionyl chloride (8 c.c.) were refluxed together for 20 minutes on the steam-bath, and the dye ***hydrochloride*** was collected after chilling. It (0·75 g.) formed bronze plates, m. p. 190°, from alcoholic hydrogen chloride (Found : N, 5·1 ; Cl, 6·55. $C_{35}H_{27}N_2$,HCl requires N, 5·45 ; Cl, 6·9%).

1 : 1-*Di*-2-(3 : 5-*diphenylpyrryl*)*ethyl Ethyl Ether*.—Bis-2-(3 : 5-diphenylpyrrole)*meso*methylmethin dihydrochloride (2 g.) was dissolved in ethanol (20 c.c.), and a slight excess of anhydrous triethylamine was added. A deep red colour developed which became paler during 72 hours. The solution was then poured into water (100 c.c.), and the resulting *ether* collected, dried, and obtained as dark brown crystals, m. p. 178°, from *n*-hexane. It gave a yellow solution in alcohol (Found : C, 84·9 ; H, 6·5 ; N, 6·05. $C_{36}H_{32}ON_2$ requires C, 85·05 ; H, 6·3 ; N, 5·5%).

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