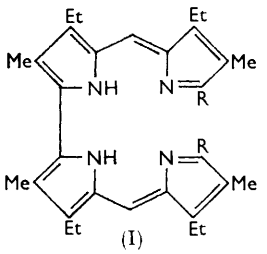
## 432. *2,2′-Bipyrrolic Macrocyclic Ring Systems.*

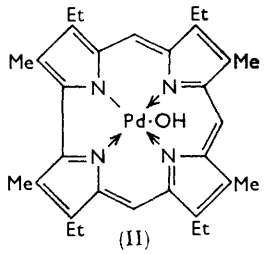
By A. W. Johnson, I. T. Kay, and R. Rodrigo.

Metallic derivatives of the 5,5″-bi(dipyrromethene) (I; R = Br) reacted with hydrochloric acid, ammonia, methylamine, and sodium sulphide to yield the corresponding metallic complexes of the macrocyclic systems (VI; X = O, NH, NMe, and S). Several reactions of the products are described including the formation of the free base (III) and certain macrocyclic ring openings.

Although much is known of the chemistry of porphyrins and azaporphyrins, few modifications of the carbon skeletons of these macrocyclic ring systems have been achieved. The elucidation of the structure of vitamin $B_{12}$ suggested that porphyrins lacking one bridging carbon atom might be capable of existence and we have examined this possibility. In an earlier paper,[1] the cyclisation of the palladium derivative of the 5,5″-bi(dipyrromethene) * [2] (I; R = Br) with formaldehyde and hydrochloric acid was described and the macrocyclic product was thought to be the palladium derivative (II). Such a reaction had been used [3] to prepare dipyrromethenes from 2-iodopyrroles. However, a re-examination [4] of our product has shown that it is the palladium derivative of the cyclic ether (III).




(I)

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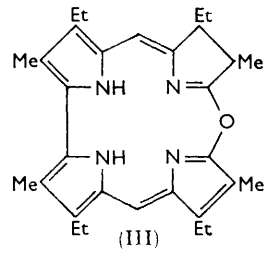


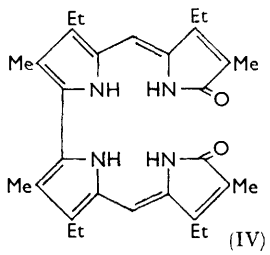

(III)

The formaldehyde thus played no part in the cyclisation of the palladium derivatives of compound (I; R = Br) to the ether (III) and when the former was heated under reflux in ethanol containing concentrated hydrochloric acid, the ether (III) was obtained in 45% yield. The cupric and cobaltous complexes of the dibromide (I; R = Br), unlike the more stable [5] palladium complex, when heated with formaldehyde and hydrochloric acid, failed to yield derivatives of the ether-macrocycle (III),[1] but instead gave a red compound formulated previously as the dialcohol (I; R = $CH_2$·OH). These reactions have now been repeated, and the red compound has also been obtained from the metal-free derivative (I; R = Br), by reaction with ethanolic hydrochloric acid without the addition of formaldehyde. In consequence, the product, which did not form metallic derivatives, has been re-formulated as the diamide (IV).[4] This reaction recalls, for example, the acid hydrolysis of 2-bromo-3-methylindoles to 3-methyloxindoles.[6] Attempts to form metallic derivatives of the macrocyclic ether (III) by treatment of the diamide (IV) with metal salts under various conditions were unsuccessful, only starting material being isolated. In addition to the diamide (IV), a second component (V) was isolated

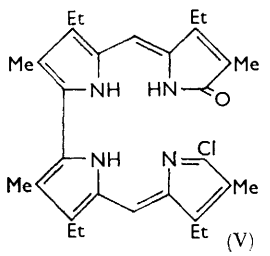
* This nomenclature is now used, in preference to bi(dipyrromethen-5-yl), so as to be consistent with that of the bipyrroles (cf., *inter alia*, the preceding paper). The numerals preceding the doubling prefix " bi " denote the points of union of the dipyrromethene units; the series 1—5, 1′—5′ of one of these units corresponds to 1″—5″, 1‴—5‴ of the other.

[1] Johnson and Price, *J.*, 1960, 1649.
[2] Fischer and Stächel, *Z. physiol. Chem.*, 1939, **258**, 121.
[3] Treibs and Kolm, *Annalen*, 1958, **614**, 176.
[4] Johnson and Kay, *Proc. Chem. Soc.*, 1961, 168.
[5] Mellor and Maley, *Nature*, 1947, **159**, 370; 1948, **161**, 436; Porter, *J.*, 1938, 368.
[6] Lawson, Patchovnik, and Witkop, *J. Amer. Chem. Soc.*, 1960, **82**, 5918.

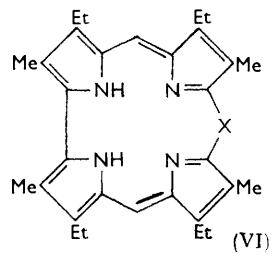
from the acid hydrolysis of the dibromide (I; R = Br). In component (V), only one of the bromine atoms has suffered hydrolysis, the other being replaced by chlorine. Halogen exchange has already been noted [2] with these compounds. Treatment of the monoamide (V) with metal salts gave the corresponding metallic complexes of the cyclic ether (III) in high yield, a reaction which is assumed to involve an initial tautomerism of the monoamide to the lactim form which then forms a metallic complex. This divergence of behaviour of the amides (IV) and (V) is paralleled in the bile-pigment series where the verdins form metal complexes whereas the rubins do not.[7] Cyclisation of derivatives of the monoamide (V) to those of the macrocyclic ether (III) finds analogy in the formation of the vitamin $B_{12}$ lactone.[8] When the copper derivative of the macrocyclic ether (III) in hot chloroform was treated with concentrated hydrochloric acid, it slowly reverted to the monoamide (V), but similar reactions with either the nickel or the palladium complex were unsuccessful, indicating that ring-opening of the macrocycle was facilitated by initial removal of the metal. The experiment also suggested that the metal might be removed from the copper derivative of the ether (III) without opening the macrocycle, and this was achieved by treating the copper compound with concentrated sulphuric acid at room temperature for 15 min., the parent macrocycle (III) being obtained as red-brown needles. Analysis of the macrocycle (III) finally proved that the oxygen was associated with the macrocycle and was not attached to the metal as in formula (II). Treatment of the parent macrocycle (III) with metallic salts in chloroform–methanol solution rapidly gave the corresponding metallic derivatives, which were detected by their characteristic absorption spectra.



(IV)



(V)



(VI)

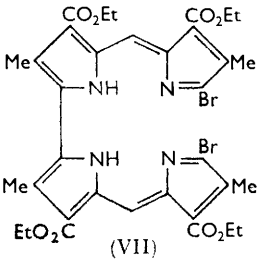
Treatment of the palladium derivative of the dibromide (I; R = Br) in pyridine with ammonia or ammonium carbonate at 160° gave the palladium derivative of the cyclic imine (VI; X = NH), and likewise reaction with methylamine or sodium sulphide gave the crystalline palladium derivatives of macrocycles containing the methylimine (cf. VI; X = NMe) and the sulphide (cf. VI; X = S) bridge, respectively. Reaction of the copper derivative of the dibromide (I; R = Br) with ammonium carbonate in pyridine gave the copper derivative of the imine (VI; X = NH), and treatment of this with concentrated sulphuric acid at room temperature for a short time gave the corresponding free base, although the last trace of copper could not be removed and a satisfactory analysis of the base was not obtained. Palladium could not be removed from its complexes with the imine (VI) by the action of strong acids. An attempt to obtain the copper derivative of the sulphur-containing macrocycle (VI; X = S) by the action of sodium sulphide on the copper derivative of the dibromide (I; R = Br) merely yielded copper sulphide and the metal-free compound (I; R = Br).

The 5,5″-bi(dipyrromethene) (VII) has been prepared through its palladium derivative from diethyl 5,5′-dibromo-4,4′-dimethyldipyrromethene-3,3′-dicarboxylate (VIII; R = Br), itself obtained by bromination of the corresponding 5,5′-unsubstituted dipyrromethane; [9] and treatment of the palladium derivative of compound (VII) with ammonium

[7] Lemberg and Legge, " Haematin Compounds and Bile Pigments," Interscience Publ., Inc., New York, 1949, p. 123.
[8] Bonnett, Cannon, Clark, Johnson, Parker, Smith, and Todd, *J.*, 1957, 1158.
[9] Fischer and Walach, *Annalen*, 1926, **450**, 127.

carbonate in pyridine as before has given the corresponding derivative (IX) of the cyclic imine. The very low solubility of this palladium derivative (IX) in the common solvents was the main cause of our failure to produce an analytically pure sample.

The visible spectra of corresponding derivatives of the new macrocycles (VI; X = O, NH, NMe, and S) were qualitatively similar to each other, but quite different from that of the parent 5,5″-bi(dipyrromethene) (I; R = Br). The size of the bromine atoms prevents the latter compound from being planar, even in the form of its metal derivatives, whereas the macrocyclic compounds are presumably essentially planar. It is significant that each of the bridging atoms involved (O, N, and S) contains at least one lone pair of electrons which contributes to the overall conjugation in the molecule. The lack of such electrons on the carbon atom is no doubt largely responsible for the difficulty we have



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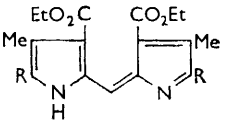
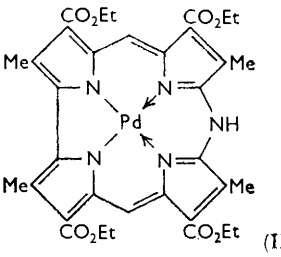
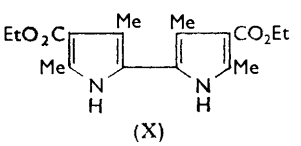


(VIII)



(IX)

experienced in replacing the terminal bromine atoms of compounds (I; R = Br or I), either alone or as their metal derivatives, by a carbon bridge. A solution of the 5,5″-bi(dipyrromethene) (VII) in dimethylformamide was hydrogenated at room temperature in the presence of Adams platinum catalyst in an attempt to replace the bromine atoms by hydrogen. A colourless solution was obtained but oxidation of this with a high-potential quinone [10] merely re-formed the starting material (VII), showing that the bromine had not been removed. The overall shape of the spectral curve of the reduced product resembled that of diethyl 3,3′,5,5′-tetramethyl-2,2′-bipyrrole-4,4′-dicarboxylate [11] (X) and suggested that the reduction product of compound (VII) was probably the 5,5″-bi(dipyrromethane) (XI).



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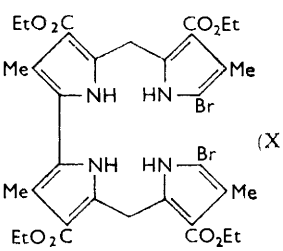

(XI)

## Experimental

M. p.s were determined on a Kofler block; ultraviolet and visible absorption spectra were determined for chloroform solutions except where otherwise stated.

*5′,5‴-Epoxy-5,5″-bi-(3,3′-diethyl-4,4′-dimethyldipyrromethene)* * (III).—(*a*) *Palladium derivative.* Palladium 5,5″-bi-(5′-bromo-3,3′-diethyl-4,4′-dimethyldipyrromethene) [2] (200 mg.) in distilled ethanol (80 c.c.) was treated with concentrated hydrochloric acid (1·6 c.c.) and heated under

* Among the numerals preceding the doubling prefix " bi," the pair 5,5′ of one dipyrromethene unit correspond to the pair 5″,5‴ of the other unit. If compounds of type (VI) become common a trivial name for the " least saturated " parent of corrin will be required, so that such compounds can be named therefrom by use of oxa, aza, etc., and hydro-prefixes, but suggestions for this purpose are deferred.

[10] Whalley, *Chem. Soc. Special Publ.*, No. 3, 1955, p. 83.
[11] Grigg, Johnson, and Wasley, *J.*, 1963, 359.

reflux for 8 hr. Water (20 c.c.) was then added and the solution kept overnight at room temperature. The solid was separated, washed with methanol, dissolved in chloroform, and chromatographed on alumina. Elution of the product was followed by means of a hand spectroscope. After removal of the solvent, the *palladium derivative* (71 mg., 45%) of (III) crystallised from chloroform–methanol as black needles, m. p. >360° (Found: C, 62·7; H, 5·55; N, 9·45. $C_{30}H_{34}N_4OPd$ requires C, 62·85; H, 5·60; N, 9·75%), $\lambda_{max.}$ 320, 385, 514, 554, 622, and 674 mμ (log ε 3·9, 3·54, 3·94, 4·14, 3·81, and 4·02, respectively).

(*b*) *Copper derivative.* 5-(5''-Chloro-3'',3'''-diethyl-4'',4'''-dimethyldipyrromethen-5'''-yl)-3,3'-diethyl-5'-hydroxy-4,4'-dimethyldipyrromethene (100 mg.) (V; see below) in chloroform (20 c.c.) and methanol (20 c.c.) containing aqueous ammonia (0·5 c.c.; *d* 0·88) was treated with cupric acetate (50 mg.). Methanol was added to the boiling solution at such a rate that the volume remained constant and when all the chloroform had been replaced by methanol the solution was cooled. The *product* was separated, washed with methanol, and crystallised from chloroform–methanol as blue needles (88 mg., 84%) (Found: C, 68·4; H, 6·55; N, 10·45. $C_{30}H_{34}CuN_4O$ requires C, 68·0; H, 6·45; N, 10·6%), $\lambda_{max.}$ 410, 436, 505, 540, 586, and 630 mμ (log ε 4·67, 4·68, 2·90, 3·03, 3·87, and 3·33, respectively).

(*c*) *Nickel derivative.* Prepared from nickel chloride (100 mg.) by a method similar to the preceding experiment, this *product* crystallised from chloroform–methanol as dark purple needles (83 mg., 80%) (Found: C, 68·7; H, 6·7; N, 10·4. $C_{30}H_{34}N_4NiO$ requires C, 68·6; H, 6·5; N, 10·65%), $\lambda_{max.}$ 311, 391, 504, 570, 640, and 691 mμ (log ε 3·8, 4·95, 4·0, 4·09, 3·72, and 3·93, respectively).

(*d*) *Free base* (III). The copper complex (330 mg.) was treated with concentrated sulphuric acid (16 c.c.) and kept at room temperature for 15 min. with occasional shaking. The solution was diluted with water (70 c.c.) and extracted with chloroform (60 c.c.), and the chloroform layer was basified with aqueous ammonia, washed with water (2 × 100 c.c.), dried ($MgSO_4$), concentrated to *ca.* 20 c.c., and chromatographed on alumina. After removal of the solvent from the main (red) fraction of the eluate the residue of *base* formed red-brown prismatic needles (116 mg., 40%), m. p. 285—286° (Found: C, 76·7; H, 7·7; N, 12·1. $C_{30}H_{36}N_4O$ requires C, 76·9; H, 7·75; N, 11·95%), $\lambda_{max.}$ 274, 314, 383, and 548 mμ (log ε 4·03, 4·08, 4·79, and 4·48, respectively).

*5,5''-Bi-(3,3'-diethyl-5'-hydroxy-4,4'-dimethyldipyrromethene)* (IV) *and 5-(5''-Chloro-3'',3'''-diethyl-4'',4'''-dimethyldipyrromethen-5'''-yl)-3,3'-diethyl-5'-hydroxy-4,4'-dimethyldipyrromethene* (V).—5,5''-Bi-(5'-bromo-3,3'-diethyl-4,4'-dimethyldipyrromethene) (1·5 g.) in ethanol (500 c.c.) was treated with concentrated hydrochloric acid (12 c.c.) and heated under reflux for 6 hr. The solution was kept overnight at room temperature, then the volume was reduced to *ca.* 100 c.c. by distillation under reduced pressure. Chloroform (250 c.c.) and water (250 c.c.) were added, the solution basified with aqueous ammonia, and the chloroform layer separated, washed with water (2 × 100 c.c.), dried ($MgSO_4$), concentrated to *ca.* 30 c.c., and chromatographed on alumina (Spence type H; 60 × 3 cm.). The two main bands which developed (red and purple) were collected separately and each rechromatographed to ensure complete separation from the other. After removal of the solvent from the first (red) fraction, the residual *diamide* (IV) formed red-brown needles (210 mg., 18%) (m. p. >360°) from chloroform–methanol (Found: C, 72·3; H, 7·6; N, 11·1. $C_{31}H_{42}N_4O_3$ requires C, 72·2; H, 7·6; N, 10·85%), and had $\lambda_{max.}$ 266, 362, and 448 mμ (log ε 4·37, 4·52, and 4·33, respectively).

After removal of the solvent from the second (purple) fraction, the residual *monochloromonoamide* (V) formed green prismatic needles (395 mg., 32%), m. p. 227—228° (decomp.), from chloroform–methanol (Found: C, 71·7; H, 7·25; Cl, 7·7. $C_{30}H_{37}ClN_4O$ requires C, 71·3; H, 7·4; Cl, 7·4%); it had $\lambda_{max.}$ 264, 309, 390, and 567 mμ (log ε 4·25, 4·06, 4·53, and 4·43, respectively).

*Ring Opening of Copper 5',5'''-Epoxy-5,5''-bi-(3,3'-diethyl-4,4'-dimethyldipyrromethene).*—The copper complex (52 mg.) in boiling chloroform (100 c.c.) was treated with concentrated hydrochloric acid (15 c.c.) and kept at room temperature for 2 hr. with occasional shaking. Water (100 c.c.) was then added, and the chloroform layer separated, basified with aqueous ammonia, washed with water (2 × 150 c.c.), dried ($MgSO_4$), concentrated to 10 c.c., and chromatographed on alumina. After removal of the solvent from the main (purple) fraction, the residue crystallised from chloroform–methanol as glittering green prisms (12 mg.), m. p. 224—227° (decomp.). The visible and ultraviolet absorption spectra were identical with those of the monochloromonoamide (V; above).

5′,5‴-*Epimino*-5,5″-*bi*-(3,3′-*diethyl*-4,4′-*dimethyldipyrromethene*) (VI; X = NH).—(*a*) *Palladium derivative.* Palladium 5,5″-bi-(5′-bromo-3,3′-diethyl-4,4′-dimethyldipyrromethene) (1 g.) in dry pyridine (30 c.c.) containing ammonium carbonate (3 g.) was heated in a sealed tube at 160° for 4 hr. After cooling, the pyridine was removed under reduced pressure and the residue washed with water, methanol, and a little cold chloroform. It was then dissolved in chloroform and chromatographed on alumina (Spence's type H). Elution of the product was followed by means of a hand spectroscope and the main diffuse apple-green band was collected. After removal of the solvent, the *product* crystallised from chloroform–methanol as short dark red rods (microscope), which appeared purple in bulk (80 mg.), m. p. >300° (Found: C, 62·8; H, 5·7; N, 12·6. $C_{30}H_{35}N_5Pd$ requires C, 63·05; H, 6·1; N, 12·25%), $\lambda_{max.}$ (in *NN*-dimethylformamide) 319, 384, 426, 552, 580, and 611 mμ (log ε 4·35, 4·54, 4·44, 3·71, 3·83, and 3·64, respectively).

(*b*) *Copper derivative.* This was prepared similarly from *copper* 5,5″-*bi*-(5′-*bromo*-3,3′-*diethyl*-4,4′-*dimethyldipyrromethene*) (1 g.) (Found: C, 53·8; H, 5·15; N, 8·3. $C_{30}H_{34}Br_2CuN_4$ requires C, 53·45; H, 5·1; N, 8·3%) and ammonium carbonate (3 g.) in dry pyridine (30 c.c.) at 160° for 4 hr. After removal of the solvent, the residue was washed and chromatographed on alumina. The *product* was eluted with pyridine as a diffuse pink band (hand spectroscope), and the solvent removed under reduced pressure. After being washed with methanol, it crystallised from chloroform–methanol as short red rods (160 mg.), m. p. >300° (Found: C, 67·8; H, 6·4; N, 12·7; residue, 15·1. $C_{30}H_{35}CuN_5$ requires C, 68·1; H, 6·65; N, 13·25; CuO, 15·1%), $\lambda_{max.}$ 377, 514, 557, and 592 mμ (log ε 4·85, 3·69, 3·91, and 4·01, respectively).

(*c*) *Free base* (VI; X = NH). The foregoing copper derivative (100 mg.) was dissolved in concentrated sulphuric acid (10 c.c.), kept for 15 min. at room temperature, and poured into ice–water, and the bluish-grey solution was extracted with chloroform; the extract was washed several times with water and then basified with aqueous ammonia (*d* 0·88). The red chloroform solution was then washed with water to remove ammonia, dried ($MgSO_4$), and chromatographed on alumina. The product formed a pale red band which was eluted off the column and then caused to crystallise by addition of methanol. It was obtained as small pink rods (20 mg.), $\lambda_{max.}$ 393, 550, and 582 mμ (log ε 4·92, 4·50, and 4·14, respectively).

5′,5‴-*Epimethylimino*-5,5″-*bi*-(3,3′-*diethyl*-4,4′-*dimethyldipyrromethene*) (VI; X = NMe): *Palladium Derivative.*—Palladium 5,5″-bi-(5′-bromo-3,3′-diethyl-4,4′-dimethyldipyrromethene) (1 g.) in dry pyridine (30 c.c.) was saturated with methylamine at 160° for 4 hr. as in the case of the corresponding imine. The pyridine was removed and the residue chromatographed as a chloroform solution on alumina. The *product* crystallised from chloroform–methanol as microscopic red needles which appeared purple in bulk (400 mg.), m. p. >300° (Found: C, 63·2; H, 6·4; N, 11·5. $C_{31}H_{37}N_5Pd$ requires C, 63·5; H, 6·35; N, 11·95%), $\lambda_{max.}$ 400, 515, 575, and 658 mμ (log ε 4·62, 3·91, 3·98, and 3·86, respectively).

5′,5‴-*Epithio*-5,5″-*bi*-(3,3′-*diethyl*-4,4′-*dimethyldipyrromethene*) (VI; X = S): *Palladium Derivative.*—Finely powdered sodium sulphide (1 g.) was added to a suspension of palladium 5,5″-bi-(5′-bromo-3,3′-diethyl-4,4′-dimethyldipyrromethene) (500 mg.) in ethanol (100 c.c.), and the mixture was heated under reflux for 2 hr. After cooling, the solid *product* was separated; it was washed with water and methanol and then crystallised from chloroform–methanol as slender dark purple needles (230 mg.), m. p. 292—293° (Found: C, 61·15; H, 5·8; N, 9·5. $C_{30}H_{34}N_4PdS$ requires C, 61·3; H, 5·8; N, 9·5%), $\lambda_{max.}$ 391, 410, 516, 533, 573, 640, and 681 mμ (log ε 4·77, 4·74, 3·92, 3·96, 3·83, 3·61, and 3·90, respectively).

*Diethyl* 4,4′-*Dimethyldipyrromethane*-3,3′-*dicarboxylate.*—Diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate was chlorinated, to give diethyl 5-chloromethyl-3-methylpyrrole-2,4-dicarboxylate [12] which on treatment with dilute acid gave tetraethyl 4,4′-dimethyldipyrromethane-3,3′,5,5′-tetracarboxylate.[13] Partial hydrolysis of this ester yielded 3,3′-diethoxycarbonyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid[14] which was decarboxylated to diethyl 4,4′-dimethyldipyrromethane-3,3′-dicarboxylate.

*Diethyl* 5,5′-*Dibromo*-4,4′-*dimethyldipyrromethene*-3,3′-*dicarboxylate.*—Diethyl 4,4′-dimethyldipyrromethane-3,3′-dicarboxylate (1 g.) was suspended in glacial acetic acid (10 c.c.) and treated with shaking with bromine (0·66 c.c.) in glacial acetic acid (5·3 c.c.). After 30 min. the crude hydrobromide (1 g.) of the product was separated, washed with acetic acid, and dried

[12] Corwin, Bailey, and Viohl, *J. Amer. Chem. Soc.*, 1942, **64**, 1267.
[13] Fischer and Halbig, *Annalen*, 1926, **447**, 132.
[14] Corwin and Buc, *J. Amer. Chem. Soc.*, 1944, **66**, 1151.

*in vacuo* over solid sodium hydroxide. The hydrobromide was dissolved in chloroform, washed with water to remove any acetic acid still remaining, and then basified with aqueous ammonia. The solution was washed thoroughly with water, then dried ($MgSO_4$) and chromatographed on alumina (Spence's type H). The free *base* was obtained as an orange band which was collected and the solvent was removed under reduced pressure. The residue crystallised from light petroleum as red needles (0·5 g.), m. p. 185° (Found: N, 5·55. $C_{17}H_{18}Br_2N_2O_4$ requires N, 5·65%), $\lambda_{max.}$ 240, 329, and 495 mμ (log ε 4·02, 3·73, and 4·73, respectively) with an inflection at 267 mμ (log ε 3·73).

The *cobalt complex* was obtained from the free base (200 mg.) in methanol (50 c.c.) by treatment with a saturated solution of cobaltous acetate in aqueous ammonia (2 c.c.). The *complex* slowly crystallised from the solution and it was separated, washed with methanol, and crystallised from chloroform–methanol as green cubes (180 mg.) (Found: C, 40·6; H, 3·5; N, 5·1; Br, 32·0. $C_{34}H_{34}Br_4CoN_4O_8$ requires C, 40·65; H, 3·4; N, 5·55; Br, 31·8%), $\lambda_{max.}$ 397, 562, and 627 mμ (log ε 4·01, 4·91, and 4·35 respectively) and an inflection at 347 mμ (log ε 3·82).

*Tetraethyl 5,5''-Bi-(5'-bromo-4,4'-dimethyldipyrromethene-3,3'-dicarboxylate)* (VII).—(*a*) *Palladium derivative.* Diethyl 5,5'-dibromo-4,4'-dimethyldipyrromethene-3,3'-dicarboxylate (6·5 g.) in ethanol (1 l.) and 3% palladous oxide–strontium carbonate (50 g.) were heated under reflux for 20 hr. The catalyst was separated and washed with chloroform, and the solvent was removed under reduced pressure from the combined filtrate and washings. The residue was chromatographed in chloroform on alumina. The product was obtained as a broad reddish-purple band which was collected. Solvent was removed from the eluate. Crystallisation of the residue from chloroform–methanol gave the *palladium complex* (1·4 g.) of the starting ester as green crystals (Found: C, 39·1; H, 3·25; N, 4·8. $C_{34}H_{34}Br_4N_4O_8Pd$ requires C, 38·8; H, 3·25; N, 5·3%), $\lambda_{max.}$ 247, 362, 415, and 562 mμ (log ε 4·36, 4·02, 4·17, and 4·81, respectively).

From the mother-liquors a second fraction was obtained, as deep red needles (1·73 g.), which was the *palladium complex* of the bi(dipyrromethene) (Found: C, 45·4; H, 3·6; N, 6·1; Br, 18·3. $C_{34}H_{32}Br_2N_4O_8Pd$ requires C, 45·8; H, 3·6; N, 6·3; Br, 17·95%), having $\lambda_{max.}$ 305, 456, 581, and 935 mμ (log ε 3·98, 4·25, 4·39, and 3·77, respectively) with an inflection at 435 mμ (log ε 4·18).

(*b*) *Free base.* A solution of the palladium complex (1·1 g.) in chloroform (200 c.c.) was shaken with 48% hydrobromic acid (10 c.c.). The solution was washed with water, aqueous ammonia, and again water and dried ($MgSO_4$). After removal of most of the chloroform, the *product* crystallised as golden-green needles (0·6 g.) (Found: C, 51·9; H, 4·65; Br, 20·8. $C_{34}H_{34}Br_2N_4O_8$ requires C, 51·9; H, 4·35; Br, 20·35%), $\lambda_{max.}$ 291, 356, and 662 mμ (log ε 4·18, 4·01, and 4·61, respectively).

*Palladium Complex* (IX) *of Tetraethyl 5',5'''-Epimino-5,5''-bi-(4,4'-dimethyldipyrromethene-3,3'-dicarboxylate*).—The palladium complex of tetraethyl 5,5''-bi-(5'-bromo-4,4'-dimethyldipyrromethene-3,3'-dicarboxylate) (100 mg.) was dissolved in dry pyridine (20 c.c.), and ammonium carbonate (2 g.) was added. The mixture was heated in a sealed tube at 160° for 4 hr. and then cooled. The solid product was separated and thoroughly washed with water, methanol, and chloroform. The residual black solid was extracted (Soxhlet) with hot pyridine, and the pyridine extract concentrated. The palladium *complex* was obtained as black prisms (200 mg.) which were sparingly soluble in the common organic solvents and had $\lambda_{max.}$ (in *NN*-dimethylformamide) 323, 416, 463, 584, and 622 mμ (log ε 4·07, 4·29, 4·53, 3·93, and 4·45, respectively), with a shoulder at 395 mμ (log ε 4·11).

*Hydrogenation and Reoxidation of Tetraethyl 5,5''-Bi-(5'-bromo-4,4'-dimethyldipyrromethene-3,3'-dicarboxylate*) (VII).—The free base (100 mg.) was dissolved in *NN*-dimethylformamide (200 c.c.) by gentle warming and hydrogenated at atmospheric pressure in the presence of 10% palladium–charcoal until hydrogen (2 mol.) had been absorbed. The catalyst was separated and the clear light brown solution poured into water and extracted several times with benzene. The combined benzene extracts were washed with dilute acid and then distilled water, dried ($MgSO_4$), and evaporated under reduced pressure. The colourless residue was dissolved in a small volume of chloroform and chromatographed on a column of alumina (Spence's type H), and the main band (blue fluorescence in ultraviolet) was collected. After removal of the solvent the residue was dissolved in ethanol. The Ehrlich test on the reduction product was negative. The reduced compound was then oxidised by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone [10] (0·5 g.) in ethanol. The resulting deep blue solution was poured into water and extracted with chloroform, and the chloroform extract was washed and dried

($MgSO_4$). The product was obtained as golden-green needles (10 mg.) by addition of methanol to the chloroform solution and it was shown to be the original bi(dipyrromethene) by its ultraviolet spectrum (Found: C, 51·8; H, 4·8. Calc. for $C_{34}H_{34}Br_2N_4O_8$: C, 51·9; H, 4·35%).

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