The Synthesis of 22 π-Electron Macrocycles. Sapphyrins and Related Compounds

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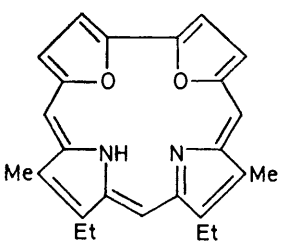
Rational syntheses are described of a number of new 22 π-electron macrocycles containing pyrrole, furan, and thiophen rings and one or two direct links. A further example of the sulphur extrusion process applied to macrocycle synthesis is provided. N.m.r. studies are used to show that all the macrocycles are aromatic, and they all contain intense Soret type bands in their visible spectra. The dioxasapphyrin does not form metal complexes and shows remarkable rate differences in the electrophilic deuteriation of the *meso*-positions.

PREVIOUS work on the synthesis of dioxacorroles (1) [1] led to the isolation of a by-product tentatively formulated as the 22 π-electron macrocycle (2).[2] This result, together with a general interest in the aromaticity of large macrocycles, prompted the study of methods for the rational synthesis of pyrrolic 22 π-electron macrocycles and related systems. The only reported example of this class of compound at the outset of our work was the all-pyrrole analogue of (2), named sapphyrin,[3] for which details of the synthesis are not available.

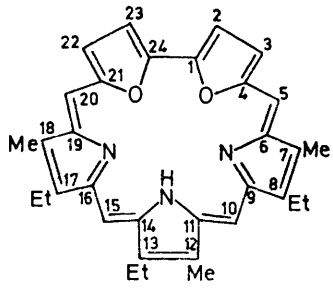
Our initial work was directed towards a synthesis of the dioxasapphyrin system, to confirm the structure of the by-product (2) isolated previously. A general method for the construction of sapphyrin-type macrocycles was developed involving the condensation of a two-ring component (3) with a bis(pyrrolylmethyl)-pyrrole diacid (4). Thus acid-catalysed condensation of compounds (3; X = O, $R^1 = R^2 = H$) and (4) followed by oxidation with either air or iodine gave the dioxasapphyrin (2), which was shown to be a single isomer by n.m.r. spectroscopy. The dioxasapphyrin (2) had an electronic spectrum identical with that of the by-product isolated previously,[1] and the n.m.r. spectra were similar. The synthesis of a representative sapphyrin [*i.e.* (5)] was also undertaken, to compare the properties of the macrocycles. Suitable two-ring precursors would be the diformylbipyrroles, and despite our earlier failure [4] to prepare the diformylalkylbipyrroles (3; X = NH, $R^1 = R^2 = Me$ and $R^1 = Me$, $R^2 = Et$) we have now succeeded in preparing these compounds in good yield (>60%) by Vilsmeier–Haack formylation of the corresponding 5,5′-unsubstituted bipyrroles with an excess of formylating reagent at 100°. The solubility of diformylalkylbipyrroles in organic solvents is low but the condensation of compounds (3; X = NH, $R^1 = Me$, $R^2 = Et$) and (4) could be successfully carried out in chloroform or chloroform–methanol to give the sapphyrin (5) (46%). A further example of this type of macrocycle, a thiasapphyrin (6), has also been prepared (19·5%), by the condensation of the bipyrrole (3; X = NH, $R^1 = Me$, $R^2 = Et$) and the dipyrrolylthiophen (7). Although the yields in these condensation reactions are not particularly high, they are perhaps remarkably better than might have been anticipated in view of the size of ring being produced. Presumably intramolecular hydrogen bonding between pyrrole rings results in conformations beneficial to the cyclisation process. Finally, our recently developed sulphur extrusion process [1] has been

[1] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J.C.S. Perkin I*, 1972, 1124.
[2] Preliminary communications, M. J. Broadhurst, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1969, 23, 1480; 1970, 807.
[3] Reported by Professor R. B. Woodward, Aromaticity Conference, Sheffield, 1966.
[4] E. Bullock, R. Grigg, A. W. Johnson, and J. W. F. Wasley, *J. Chem. Soc.*, 1963, 2326.

extended to the synthesis of the dioxasapphyrin (2). When the bis(formylfuryl) sulphide (8) was condensed with compound (4) in the presence of hydrogen bromide



(1)



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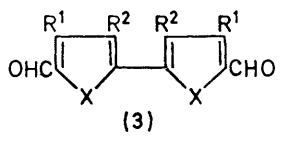
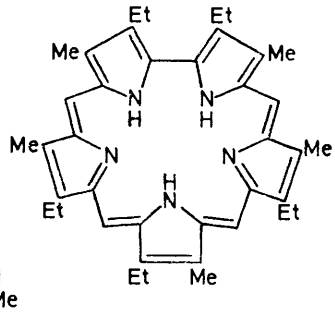


(3)



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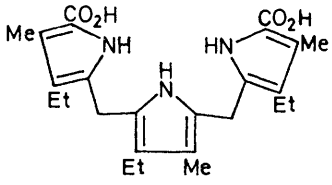

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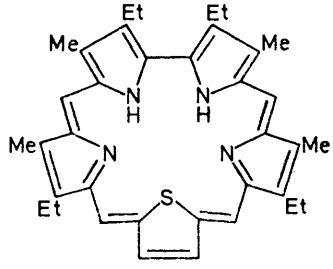

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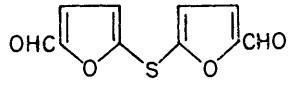
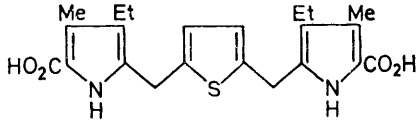


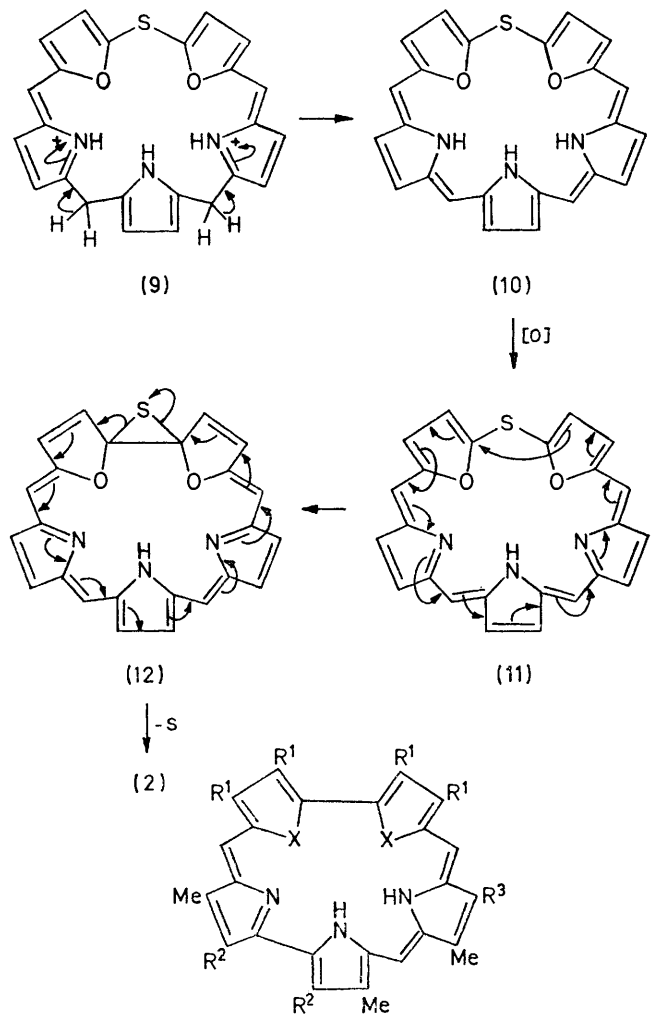
(8)



(7)

no macrocyclic product was isolated. However, addition of iodine (as oxidant) after the reaction had been allowed to proceed for 1 h was associated with the rapid development of an intense band at 435 nm in the visible spectrum of the mixture. When the oxidised mixture was worked up the previously synthesised dioxasapphyrin (2) (22%) was obtained. The motivation for the addition of iodine was the consideration that if the condensation proceeded as desired, then tautomerisation of the initial product (9) would furnish the species (10). This is a $4n$ π-electron system (excluding the sulphur atom) and this electron array is unfavourable for the disrotatory electrocyclic reaction required for generation of an intermediate thiiran which we believe [1] is the first step in the sulphur extrusion process. However oxidation of compound (10) would produce (11), a $(4n + 2)$ π-electron system (excluding the sulphur atom), which then possesses the correct complement of electrons for the disrotatory electrocyclic process [(11) ⟶ (12)] required to effect extrusion of sulphur (12; arrows).

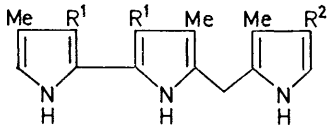
No polypyrrolic macrocycle containing two direct links has been reported,[2] but an examination of molecular models of the norsapphyrin system (13; X = NH or O) revealed that these macrocycles could exist in a relatively



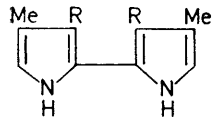
(13) a; $R^1 = R^2 = H$, $R^3 = Me$
b; $R^1 = H$, $R^2 = R^3 = Et$

planar, strain-free conformation. They are also 22 π-electron macrocycles and their syntheses were undertaken for comparison with the previously prepared sapphyrins. The route selected was the condensation of a pyrrolyldipyrromethane (14) with 5,5′-diformylbi-

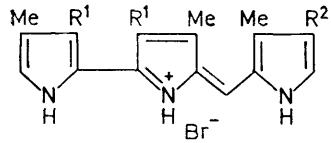
furan (3; X = O, $R^1 = R^2 = H$) or a 5,5′-diformylbipyrrole (3; X = NH). We had previously shown that the hydrogen bromide-catalysed condensation of alkylbipyrroles (15) with 2-formylpyrroles gives high yields



(14) a; R^1=H, R^2=Me
b; R^1=R^2=Et



(15) a; R = H
b; R = Et



(16) a; R^1=H, R^2=Me
b; R^1=R^2=Et

of the corresponding pyrrolyldipyrromethene salts (16),[4] and accordingly the condensation of the alkylbipyrroles (15a and b) with 3,4-dialkylpyrrole-2-carbaldehydes gave (16a and b) in 60—80% yield. The salts (16a and b) were reduced with excess of sodium borohydride to the corresponding pyrrolyldipyrromethanes (14a and b).

The unstable pyrrolyldipyrromethanes were not isolated but were condensed directly in methanolic solution with the diformylbifuran (3; X = O, $R^1 = R^2$ = H), in the presence of hydrogen bromide, to give the dioxanorsapphyrins (13a and b; X = O).

Attempts to prepare the norsapphyrins (13; X = NH) by condensation of 5,5′-diformylbipyrroles (3; X = NH, R^1 = Me, R^2 = H and R^1 = Me, R^2 = Et) with compounds (14a and b) gave reaction mixtures with the expected visible spectra ($\lambda_{max.}$ *ca.* 450 nm), but attempts to isolate the macrocycles resulted in their decomposition. However, an extensive investigation of this reaction was not undertaken; addition of suitable metal ions might allow isolation of the corresponding metal complexes.

These 22 π-electron macrocycles were of especial interest in view of the prediction that [4*n* + 2]annulenes should be aromatic up to and including [22]annulene whereas [26]annulene was predicted to be non-aromatic.[5] The macrocycles described here can be viewed as heteroatom-bridged annulenes and, in terms of their n.m.r. spectra, can be said to be strongly aromatic (Table 1).

TABLE 1

N.m.r. spectra (τ values) of sapphyrin-type macrocycles (in $CDCl_3$)

Compd.	N–H	β-H	*meso*-H
(2)	16·55	−0·04 (2H), 0·28 (2H)	−0·48, −0·45, −0·38, −0·34
(5)	13·9		−0·5 (2H), −0·32 (2H)
(6)	12·2	−0·87 (2H), −0·31 (2H)	−0·12 (2H)
(13b; X = O)	14·85	0·42 (AB, 4H)	−0·52 (1H), −0·06 (2H)

Thus the inner N–H protons are strongly shielded and the protons at the periphery, *meso*-protons and β-protons, are strongly deshielded. The ability of these macrocycles to sustain a large induced diamagnetic ring current demonstrates the presence of a delocalised aromatic π-system. A feature of the n.m.r. spectrum of the sapphyrin (5) is the upfield shift of *ca.* 0·4 p.p.m. of the signals of two of the methyl groups of the peripheral ethyl substituents, probably those at C-2 and C-23 flanking the direct link. This effect is presumably due to buckling or twisting of the macrocycle about the C(1)–C(24) direct link. The effect is less marked in 2,18-diethylcorroles.[6]

The visible spectra of these macrocycles showed interesting features. The electronic spectra of porphins

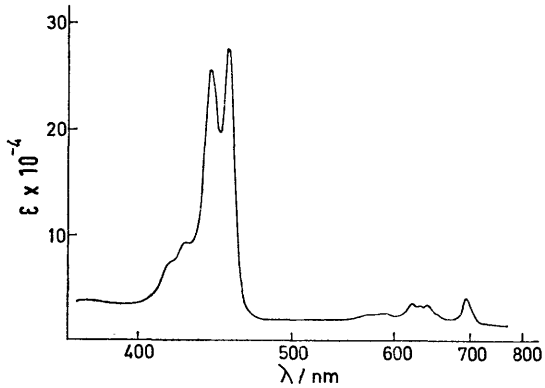
TABLE 2

Electronic spectra (Me_2CO–$HClO_4$) of sapphyrin-type macrocycles(cations)

Compound	Soret band (λ/nm)	ε
(2)	435·5	754,600
(5)	450	530,200
(6)	461	472,800
(13b; X = O) †	448 and 459	184,000 and 212,000

† In $CHCl_3$–HBr.

contain a characteristic high intensity Soret band at *ca.* 400 nm. In the 22 π-electron macrocycles the corresponding band is found at longer wavelength (435—460 nm) and the intensity is much greater (Table 2).



Electronic spectrum of the monocation of compound (13a; X = O)

The dioxasapphyrin (2) absorbs at shorter wavelength than the all-nitrogen analogue (5); a similar trend was observed with the oxaporphins.[7] Although the visible spectra of the free bases of the dioxanorsapphyrins (13a and b; X = O) resembled that of the dioxasapphyrin (2) free base, the spectra of compounds (13a and b; X = O) in acid solution differed in that the Soret-type peak split into two bands (Figure).

The mass spectra of the 22 π-electron macrocycles

[5] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1965, **87**, 685; H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, 1959, *A***251**, 172.

[6] G. Shelton, unpublished observations.

provide further examples of the occurrence of intense $M + 2$ peaks.[7] Thus, although the dioxanorsapphyrins (13a and b; X = O) showed intense molecular ion peaks with no evidence of unusually large $M + 2$ peaks, the remaining 22 π-electron macrocycles [(2), (5), and (6)] all exhibited intense $M + 2$ peaks which were larger than the molecular ion peaks in the case of sapphyrin (5) and the dioxasapphyrin (2). The dioxasapphyrin (2) showed only a very small molecular ion peak whereas in the spectrum of the thiasapphyrin (6) the parent peak was slightly more intense than the $M + 2$ peak (M, 100%; $M + 2$, 89%; ion chamber 210°; uncorrected for ^{13}C and ^{34}S isotopes). We have previously observed that the occurrence of $M + 2$ peaks in macrocycles of this type is associated with unusually high basicity of the macrocycles.[7] The dioxasapphyrin (2) illustrates this tendency since analytical data indicate it is eluted as a mixture of the mono- and di-bromides from an alumina column. Analytically pure samples of the free base could not be obtained and solutions of the free base soon revert to the mono-salt.

Studies of the chemistry of the new macrocycles are only at a preliminary stage. We have been unable to prepare metal complexes of the dioxasapphyrin (2), and although oxaporphins form charged nickel and zinc complexes, the dioxaporphins did not form metal complexes.[7] Although the dioxasapphyrin (2) has one replaceable imino hydrogen atom, as do the oxaporphins, presumably the larger ring size has a detabilising effect on metal complexation. Electrophilic deuteriation studies of a 0·25M-solution of the dioxasapphyrin (2) in trifluoroacetic [^2H]acid at 100° showed a remarkable difference between the *meso*-positions. Two of the *meso*-protons of structure (2) exchanged with $t_{\frac{1}{2}}$ 2·2 h, whereas exchange of the remaining two *meso*-protons had proceeded to only a small extent after 100 h at 100°. However, the chemical shifts of all the *meso*-protons of (2) are very similar and it has not yet proved possible to decide which protons exchange more rapidly. No exchange of the β-protons on the furan rings was observed and a similar reluctance to exchange was found in the β-protons of the furan rings in oxaporphins[7] and oxacorroles.[1]

EXPERIMENTAL

U.v. and visible spectra were determined for solutions in chloroform. N.m.r. spectra were determined for solutions in deuteriochloroform with a Perkin-Elmer R10 60 MHz or a Varian HA-100 instrument, with tetramethylsilane as internal reference. M.p.s were measured on a Kofler hot-stage apparatus. Mass spectra were obtained by direct insertion in an A.E.I. MS 902 spectrometer operating at 70 eV. Light petroleum had b.p. 60—80°, and the alumina used for chromatography was Spence type H.

Intermediates

4,4′-Dimethyl-2,2′-bipyrrole-5,5′-dicarbaldehyde (3; X = NH, R^1 = Me, R^2 = H).—4,4′-Dimethyl-2,2′-bipyrrole[4] (633 mg) was dissolved in warm, dry *NN*-dimethylformamide (30 ml) in an atmosphere of nitrogen. The solution was cooled to 20° and then phosphoryl chloride (2·0 ml) added dropwise with stirring. The bright green solution was left for 5 min and then heated at 100° (steam-bath) for 18 h, still under nitrogen. The cooled solution was poured into cold water (100 ml) and aqueous 10% sodium hydroxide solution was added with stirring until a smell of amine was apparent. The precipitate was collected on diatomite, washed with water, and dried, and the *product* was extracted from the diatomite (Soxhlet) with chloroform (50 ml); it crystallised from the hot solution as yellow needles (564 mg, 64%), m.p. >300° [Found: C, 66·75; H, 5·65; N, 13·0%; M (mass spec.), 216. $C_{12}H_{12}N_2O_2$ requires C, 66·65; H, 5·60; N, 12·95%; M, 216], $\lambda_{max.}$ 272·5, 312, and 381 nm (ε 16,630, 5050, and 35,210) $\lambda_{infl.}$ 391 nm (ε 33,680), $\nu_{max.}$ (KBr) 3267, 3176, (N–H), and 1639 (C=O) cm^{-1}, τ (CF_3·CO_2H) −1·27br (s, 2 × NH), 0·73br (s, 2 × CHO), 2·96 (s, 2 × nuclear H), and 7·51 (s, 2 × Me).

3,3′-Diethyl-4,4′-dimethyl-2,2′-bipyrrole-5,5′-dicarbaldehyde (3; X = NH, R^1 = Me, R^2 = Et).—A solution of 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole[4] (1·28 g) in dry *NN*-dimethylformamide (40 ml) was treated dropwise with phosphoryl chloride (4 ml), with stirring, in an atmosphere of nitrogen. The brown-green solution was heated at 100° (steam-bath) for 2 h, still under nitrogen, and cooled to room temperature. The product was isolated as before and crystallised from chloroform as pale yellow *needles* (977 mg, 61%), m.p. 264—266° [Found: C, 70·25; H, 7·3; N, 10·7%; M (mass spec.), 272. $C_{16}H_{20}N_2O_2$ requires C, 70·5; H, 7·4; N, 10·3%; M, 272), $\lambda_{max.}$ 284·5 and 361 nm (ε 9810 and 22,980), $\lambda_{infl.}$ 275 nm (ε 9640), $\nu_{max.}$ (KBr) 3173, 3129 (NH), and 1613 (C=O) cm^{-1}, τ (CF_3·CO_2H) −0·54br (s, 2 × NH), 0·8 (s, 2 × CHO), 7·28 (q, 2 × CH_2Me), 7·89 (s, 2 × Me), and 8·85 (t, 2 × CH_2*Me*).

3,3′4′-Trimethyl-5-(4-methylpyrrol-2-yl)dipyrromethene Hydrobromide (16a).—3,4-Dimethylpyrrole-2-carbaldehyde[8] (0·6 g) was dissolved in warm methanol (50 ml) and nitrogen was bubbled through the solution for 5 min. 4,4′-Dimethyl-2,2′-bipyrrole[4] (0·71 g) was added to the solution, which was warmed until the bipyrrole had dissolved. Hydrogen bromide (48% w/v in glacial acetic acid; 1·0 ml) was added, and the flask was stoppered and kept at room temperature for 1 h. The crystalline *product* was separated, washed with a little methanol, and dried. Recrystallisation from chloroform–methanol gave dark brown needles (1·24 g, 79%), m.p. >300° (Found: C, 59·15; H, 5·75; Br, 23·3; N, 12·2. $C_{17}H_{20}BrN_3$ requires C, 58·95; H, 5·8; Br, 23·0; N, 12·15%), $\lambda_{max.}$ 299·5, 378·5, 397, and 566 nm (ε 13,040, 5920, 6120, and 88,000), $\lambda_{infl.}$ 536·5 (ε 45,220) τ 2·8, 3·0, 3·17, 3·30, and 3·51 (all broad s, 4 × nuclear H and 1 methine H), 7·71, 7·87, 7·90, and 8·05 (all s, 4 × Me).

4,4′-Diethyl-5-(3-ethyl-4-methylpyrrol-2-yl)-3,3′-dimethyldipyrromethene Hydrobromide (16b).—3,3′-Diethyl-4,4′-dimethyl-2-2′-bipyrrole[4] (960 mg) and 4-ethyl-3-methylpyrrole-2-carbaldehyde[9] (670 mg) were dissolved in ethanol (50 ml) in an atmosphere of nitrogen. Hydrogen bromide (48% w/v solution in glacial acetic acid; 1·0 ml) was added and a deep purple colour was immediately produced but no crystals formed. Dry ether (40 ml) was then added and the solution was stored at 0° for 12 h. The *product* separated

[7] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J. Chem. Soc.* (*C*), 1971, 3681.

[8] G. M. Badger, R. L. N. Harris, and R. A. Jones. *Austral. J. Chem.*, 1964, **17**, 1022.

[9] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 22.

as golden brown needles (1·12 g, 60%), m.p. >300°, which were collected, washed with ether, and dried. The product formed oily gums on attempted recrystallisation (Found: C, 63·45; H, 6·8; Br, 19·2; N, 10·2. $C_{22}H_{30}BrN_3$ requires C, 63·45; H, 6·8; Br, 19·2; N, 10·1%), $\lambda_{max.}$ 270·5, 309, 406·5, and 585 nm (ε 6030, 6510, 10,140, and 54,100), $\lambda_{infl.}$ 389 and 562 nm (ε 8690 and 42,980), τ 2·5br (d, nuclear H), 2·9 (s, methine H), 3·03br (d, nuclear H), 7·45 (m, 2 × CH_2Me), 7·67, 7·76, and 7·95 (all s, 3 × Me), and 8·83 (3H) and 8·9 (m, 3 × CH_2Me).

Macrocycles

7,13,18-*Triethyl*-8,12,17-*trimethyldioxasapphyrin* (2).—(*a*) 2,5-Bis-(5-benzyloxycarbonyl-3-ethyl-4-methylpyrrol-2-ylmethyl)-3-ethyl-4-methylpyrrole (720 mg) [7] was dissolved in tetrahydrofuran (100 ml) and hydrogenated over 10% palladium–charcoal (200 mg) until uptake ceased. The catalyst was separated and the solution added to a solution of 2,2′-bifuran-5,5′-dicarbaldehyde (190 mg) [10] in chloroform (1500 ml), in an atmosphere of nitrogen. Nitrogen was bubbled through the solution for 10 min and then hydrogen bromide (48% w/v solution in glacial acetic acid; 2·5 ml) was added. After swirling the flask was stoppered and left for 1·5 h, and then a slow stream of air was bubbled through the solution for 12 h. The solution was washed with dilute aqueous ammonia, dried ($MgSO_4$), and evaporated, and the residue was chromatographed on alumina. Chloroform eluted a trace of aetioporphyrin (visible spectrum), followed by several dark brown fractions which had broad visible spectra and were discarded. Chloroform–methanol (1 : 2) eluted a green fraction which was purified by rechromatography. The *dihydroperchlorate* formed purple-blue prisms (282 mg, 40%), m.p. >300° (from methanol containing a few drops of perchloric acid) (Found: C, 56·35; H, 5·1; Cl, 9·95; N, 5·8. $C_{33}H_{35}Cl_2N_3O_{10}$ requires C, 56·25; H, 5·0; Cl, 10·05; N, 5·95%), $\lambda_{max.}$ (Me_2CO–0·5% $HClO_4$) 435·5, 592·5, 622·5, 648·5, and 686 nm (ε 754,600, 11,510, 13,340, 5760, and 4230), $\lambda_{infl.}$ 418·5 nm (ε 76,480), τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) −2·23 (s, 4 × *meso*-H), −1·84 (2H), −1·27 (AB, *J* 4 Hz, 4 × furan H), 5·09 (m, 3 × CH_2Me), 5·59 (3H), and 5·66 (both s, 3 × Me), 7·7 (6H), and 7·74 (m, 3 × CH_2Me), and 15·1 (1H) and 16·5 (both broad s, 3 × NH). The *free base* was obtained by dissolving the salt in acetone, adding aqueous ammonia, and extracting the aqueous layer with chloroform. The organic layer was dried ($MgSO_4$) and evaporated, and the residue crystallised from chloroform–light petroleum. The *product* formed dark blue-black prisms, m.p. >300°, τ −0·48, −0·45, −0·38, and −0·34 (all s, 4 × *meso*-H), −0·04 (2H) and 0·28 (AB, *J* 4 Hz, 4 × furan H), 5·85 (m, 3 × CH_2Me), 6·21 (3H) and 6·34 (both s, 3 × Me), 8·06 (6H) and 8·09 (m, 3 × CH_2Me), and 16·55br (s, NH).

(*b*) Bis-(5-formyl-2-furyl) sulphide (222 mg) [1] was dissolved in chloroform–methanol (*ca.* 3 : 1; 1·5 l) and then nitrogen was bubbled through the solution for 0·5 h. 2,5-Bis-(5-benzyloxycarbonyl-3-ethyl-4-methylpyrrol-2-ylmethyl)-3-ethyl-4-methylpyrrole (720 mg) [7] in tetrahydrofuran (100 ml) was hydrogenated over 10% palladium–charcoal (200 mg) until uptake ceased. The catalyst was separated and the solution added to the solution of the furyl sulphide, in an atmosphere of nitrogen. After the addition of hydrogen bromide (48% w/v solution in glacial acetic acid; 5 ml), the mixture was kept for 1 h at room temperature. Iodine (300 mg) was then added and the brown solution became green-brown, with the rapid development of an intense peak at 435·5 nm in the visible spectrum. The solution was washed with aqueous ammonia, dried ($MgSO_4$), and evaporated, and the residue was chromatographed on alumina. Elution with chloroform gave several brown bands, containing traces of aetioporphyrin, which were discarded. Chloroform–methanol (1 : 1) eluted a green fraction which was collected and rechromatographed to give the *dihydroperchlorate*, which crystallised from methanol containing a few drops of perchloric acid as purple-blue prisms (155 mg, 22%), m.p. >300°. It was identical (t.l.c.; visible and n.m.r. spectra) with a sample prepared from 2,2′-bifuran-5,5′-dicarbaldehyde in place of bis-(5-formyl-2-furyl) sulphide.

2,8,12,17,23-*Pentaethyl*-3,7,13,18,22-*pentamethylsapphyrin* (5).—2,5-Bis-(5-benzyloxycarbonyl-3-ethyl-4-methylpyrrol-2-ylmethyl)-3-ethyl-4-methylpyrrole (720 mg) in tetrahydrofuran (100 ml) was hydrogenated, until uptake ceased, over 10% palladium–charcoal (200 mg). After separation of the catalyst, the solution was added to a solution of 3,3′-diethyl-4,4′-dimethyl-2,2′-bipyrrole-5,5′-dicarbaldehyde (272 mg) in chloroform (1·5 l), in an atmosphere of nitrogen. Nitrogen was bubbled through the solution for 5 min and then hydrogen bromide (50% w/v solution in glacial acetic acid; 5 ml) was added. After 30 min, iodine (300 mg) in chloroform (50 ml) was added and the solution was left at room temperature for 10 h. (Soon after the addition of the iodine the solution became green with the rapid appearance of an intense peak at 450 nm in the visible spectrum.) The solution was washed with dilute aqueous ammonia, dried ($MgSO_4$), and evaporated. The residue was chromatographed on alumina with chloroform for elution. Several dark bands eluted first had broad, weak visible spectra and were not investigated further. Material from the green band ($\lambda_{max.}$ 450 nm) was collected and rechromatographed, and crystallised from chloroform–light petroleum as dark blue prisms (270 mg, 46%), m.p. >300°. A sample of the free base was converted into the dihydroperchlorate, which crystallised from chloroform–acetone containing a few drops of perchloric acid as blue hexagonal plates, m.p. >300° (Found: C, 59·45; H, 6·2; Cl, 8·95; N, 9·1. $C_{39}H_{49}Cl_2N_5O_8$ requires C, 59·55; H, 6·3; Cl, 9·0; N, 8·9%), $\lambda_{max.}$ (Me_2CO–0·5% $HClO_4$) 450, 579·5, 629, and 688·5 nm (ε 530,200, 3080, 13,650, and 18,190), $\lambda_{infl.}$ 393·5 and 432 nm (ε 18,670 and 74,800), τ −0·5 (s, 2 × *meso*-H), −0·32br (s, 2 × *meso*-H), 5·72 (m, 5 × CH_2Me), 6·17 (3H), 6·23 (6H), and 6·35 (all s, 5 × Me), 8·02 (m, 3 × CH_2Me), 8·41 (t, 2 × CH_2Me), and 13·9br (s, 3 × NH).

7,13,17,18-*Tetramethyldioxanorsapphyrin* (13a; X = O).—2,2′-Bifuran-5,5′-dicarbaldehyde (190 mg) [10] was dissolved in chloroform (1·5 l) by heating under reflux for *ca.* 15 min in an atmosphere of nitrogen. Meanwhile, 3,3′,4′-Trimethyl-5-(4-methylpyrrol-2-yl)dipyrromethene hydrobromide (350 mg) was dissolved in methanol (250 ml) in an atmosphere of nitrogen. Sodium borohydride (2·0 g) was added in small portions and after 30 min the solution had become almost colourless. The solution of pyrrolyldipyrromethane was decanted from excess of solid sodium borohydride and added to the chloroform solution of the bifuran, while the nitrogen atmosphere was maintained. Hydroben bromide (48% w/v solution in glacial acetic acid; 5 ml) was added, then the flask was stoppered and left overnight at room temperature. The solution was washed with dilute aqueous ammonia (1 l), dried ($MgSO_4$), and

[10] R. Grigg, J. A. Knight, and M. V. Sargeant, *J. Chem. Soc.* (*C*), 1966, 976.

evaporated. The residue was chromatographed on alumina with chloroform as eluant. The dichroic red-green fraction ($\lambda_{max.}$ 442 nm) was collected and rechromatographed. The product crystallised as dark blue-black prisms (63 mg, 15%), m.p. >300° [Found: C, 77·25; H, 5·45; N, 10·2%; *M* (mass spec.), 421. $C_{27}H_{23}N_3O_2$ requires C, 77·0; H, 5·45; N, 10·0%; *M*, 421], $\lambda_{max.}$ (pyridine) 352·5, 442, 518, 547·5, 591, 655·5, 666·5, and 730 nm (ε 20,440, 201,200, 5340, 10,160, 39,390, 4540, 3970, and 9660), $\lambda_{infl.}$ 407·5 and 432 nm (ε 55,760 and 153,100), $\lambda_{max.}$ ($CHCl_3$ + 1 drop of a 50% w/v solution of HBr in glacial acetic acid) 329, 343·5, 378·5, 427·5, 442·5, 453·5, 571, 588, 623·5, 632·5, 644, and 701 nm (ε 20,660, 20,920, 17,810, 77,750, 255,600, 282,100, 7890, 9460, 18,090, 16,340, 17,260, and 24,180), $\lambda_{infl.}$ 420 and 579 nm (ε 64,380 and 8350). The macrocycle was too insoluble for determination of its n.m.r. spectrum.

8,12,18-*Triethyl*-7,13,17-*trimethyldioxanorsapphyrin* (13b; X = O).—This macrocycle was prepared by the method just described, from 2,2′-bifuran-5,5′-dicarbaldehyde (190 mg) and 4,4′-diethyl-5-(3-ethyl-4-methylpyrrol-2-yl)-3,3′-dimethyldipyrromethene hydrobromide (420 mg). It crystallised from chloroform–petroleum as long steel-blue needles (98 mg, 20%), m.p. >300° [Found: C, 77·9; H, 6·9; N, 8·45%; *M* (mass spec.), 491. $C_{32}H_{33}N_3O_2$ requires C, 78·2; H, 6·75; N, 8·55%; *M*, 491], $\lambda_{max.}$ (pyridine) 362, 447, 527, 556, 602, 673, and 740 nm (ε 20,930, 188,400, 5660, 8750, 25,880, 4410, and 8620), $\lambda_{infl.}$ 416 nm (ε 56,000), $\lambda_{max.}$ ($CHCl_3$ + 1 drop of a 50% w/v solution of HBr in glacial acetic acid) 350, 381, 448, 459, 580, 596, 633, 647, and 707 nm (ε 24,900, 22,200, 184,000, 212,000, 7860, 8270, 16,500, 14,800, and 20,600), $\lambda_{infl.}$ 329, 424, and 434 nm (ε 20,000, 49,700, and 71,900), τ −0·56 (1H) and −0·1 (both s, 3 × *meso*-H), 0·14, 0·24, 0·59, and 0·63 (overlapping AB's, $J_{AB} = J_{A'B'}$ = 4·5 Hz, 4 × furan H), 5·6 (m, 3 × CH_2Me), 6·09 (3H) and 6·18 (both s, 3 × Me), 8·04, 8·11, and 8·15 (m, 3 × CH_2Me), and 14·85br (s, 2 × NH).

2,8,17,23-*Tetraethyl*-3,7,18,22-*tetramethylthiasapphyrin* (6).— 3,3′-Diethyl-4,4′-dimethyl-2,2′-bipyrrole-5,5′-dicarbaldehyde (55 mg) was dissolved in chloroform (1 l) in an atmosphere of nitrogen. A solution of the bispyrrolylmethylthiophen (7) (100 mg) in methanol (30 ml) was added and nitrogen was bubbled through the solution for 5 min before the addition of hydrogen bromide (50% w/v solution in acetic acid; 5 ml). The solution was then set aside for 1 h, and then a slow stream of air was bubbled through it overnight. The solution was then washed with dilute aqueous ammonia and evaporated, and the residue was chromatographed on alumina with chloroform as eluant. The bright green fraction afforded the *product* as blue prisms (22 mg, 19·5%), m.p. >300° (from chloroform–light petroleum) [Found: C, 76·7; H, 7·15; N, 9·6%; *m/e* (mass spec.), 561 (M^+) and 563 (*M* + 2). $C_{36}H_{40}N_4S$ requires C, 77·1; H, 7·2; N, 10·0%; *M*, 561], $\lambda_{max.}$ 285·5, 331·5, 468, 594, 645, and 752 nm (ε 11,200, 15,670, 209,200, 9880, 11,810, and 3550), $\lambda_{infl.}$ 384 nm (ε 15,510), τ −0·87, −0·31, and −0·12 (all s, 4 × *meso*-H and 2 × thiophen H), 5·91 (m, 4 × CH_2Me), 6·41 and 6·50 (both s, 4 × Me), 8·14 and 8·85 (both t, 4 × CH_2Me), and 12·2br (s, 2 × NH).

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