Sulphur Extrusion Reactions Applied to the Synthesis of Corroles and Related Systems

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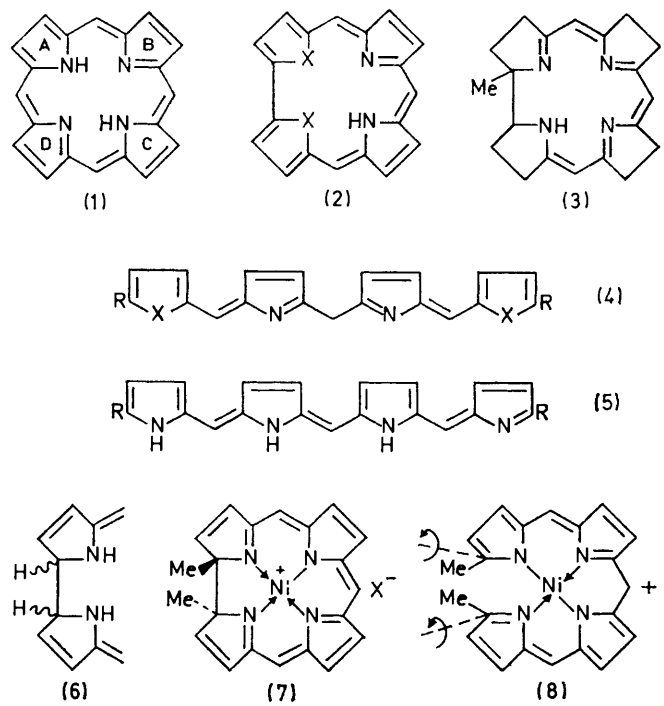
The preparation of 21,24-dioxacorroles by condensation of dipyrromethane-5.5'-dicarboxylic acids with 5,5'-diformyl-2,2'-bifuryl or bis-(5-formyl-2-furyl) sulphide is described. It is suggested that the latter reaction involves a non-aromatic *meso*-thia-macrocyclic intermediate which loses sulphur by a disrotatory cyclisation to a thiiran intermediate followed by cheletropic loss of sulphur. Some evidence for this proposal is provided by the preparation of *meso*-thiaphlorins and a study of their thermolyses to give corroles. Further examples of sulphur extrusion from a *meso*-dithiaphlorin, to give a *meso*-thiacorrole, are given and rate enhancements, in the sulphur extrusion process. which are observed in metal complexes are discussed. Some electrophilic deuteriation studies on the 21,24-dioxacorroles are reported.

A NUMBER of methods have been developed in our laboratories for the preparation of aromatic polypyrrolic macrocycles such as the porphins (1) [1] and the corroles (2; X = NH)[2]. Our particular interest in macrocycles with direct links, such as (2; X = NH), developed from early work on vitamin B_{12}, which contains a 1-methylcorrin (3) chromophore. Corroles (2; X = NH) can be prepared in high yield by the oxidative cyclisation of linear tetrapyrroles (4; R = H, X = NH) and the cyclisation has been shown to involve initial deprotonation at C-10 to give a bilatriene (5).[3] Although it has not proved possible to detect the presumed cyclic dihydro-intermediate (6; partial formula) a related cyclisation of (4; R = Me, X = NH) to the corresponding nickel 1,19-dimethyltetradehydrocorrin salt (7) has been shown to give a *trans* arrangement of the 1- and 19-methyl groups.[4] Evidence has also been obtained which suggests that the salt (7) results from the orbital symmetry-allowed conrotatory cyclisation of the cationic species (8).[4]

The ease of cyclisation of linear tetrapyrroles (4; R = H, X = NH) to corroles led us to examine the possibility of incorporating furan and thiophen rings into macrocycles of the corrole type in order to ascertain the effect of different heteroatoms on the chemistry of these systems.[5] Previous results with porphin analogues containing furan and thiophen rings indicated they were aromatic, as judged by their ability to support an induced diamagnetic ring current, and that the analogues containing two furan rings showed unexpectedly high basicity.[6] This enhanced basicity is apparently not displayed by some related aromatic polyfuran and furan–thiophen [7] macrocycles, such as the [18]annulene trioxide (9), and thus the pyrrole rings are implicated in this effect.

Attempts to prepare the precursors (4; X = O or S, R = H), required for oxidative cyclisation to (2; X = O or S), by an acid-catalysed condensation of (10; X = O or S) with the dipyrromethane-5,5'-dicarboxylic acids (11a—c) were unsuccessful. However a synthesis

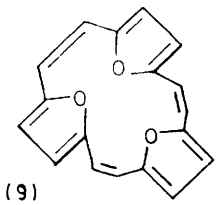


patterned on the MacDonald porphin synthesis [8] and involving the acid-catalysed condensation of the bifuryl dialdehyde (12; X = O) with acids (11a and b) gave the required products (13a and b; X = O) in low yield (*ca.* 7%), together with a macrocyclic by-product containing three pyrrole and two furan rings (5—10%).[5] The formation of the by-products evidently resulted from the long reaction time and/or heating at *ca.* 60°; conditions known to facilitate cleavage–recombination reactions of the labile dipyrromethane system (*e.g.* ref. 9). The macrocyclic by-products were tentatively formulated as

[1] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *Quart. Rev.*, 1966, **20**, 211.
[2] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.
[3] D. Dolphin, A. W. Johnson, J. Leng, and P. van den Broek, *J. Chem. Soc.* (*C*), 1966, 880.
[4] R. Grigg, A. P. Johnson, A. W. Johnson, and M. Smith, *J. Chem. Soc.* (*C*), 1971, 2457.
[5] Preliminary communications, M. J. Broadhurst, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1969, 23; 1970, 807.
[6] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J. Chem. Soc.* (*C*), 1971, 3681.
[7] J. A. Elix, *Chem. Comm.*, 1968, 343; G. M. Badger, J. A. Elix, and G. E. Lewis, *Austral. J. Chem.*, 1966, **19**, 1221; G. M. Badger, G. E. Lewis, and U. P. Singh, *ibid.*, p. 1461.
[8] G. B. Arsenault, E. Bullock, and F. S. MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 4384.
[9] A. Treibs and G. Fritz, *Annalen*, 1958, **611**, 162; D. Mauzerall, *J. Amer. Chem. Soc.*, 1960, **82**, 2601 and 2605.

(14; R = Me or Et) * and this assignment was confirmed by a rational synthesis.[5]

The low yield of the dioxacorroles (13a and b; X = O) and the failure of a similar condensation using (12; X = S) to give the dithiacorrole (13; X = S) prompted a search for a more efficient synthesis. The thermal cyclisation of linear conjugated polyolefins can occur in a conrotatory or disrotatory manner depending on whether the olefin contains $4n$ or $(4n + 2)$ π-electrons,[10] and a process of this type is thought to be involved in the formation of corroles.[2] Although our attempts to apply this process directly to the synthesis of the macrocycles (13; X = O or S) had not been successful, a possible way of circumventing the difficulties, while still utilising an electrocyclic process, would be to incorporate into the molecule an extrudable atom or fragment, the removal of which at a later stage would generate the direct link. Sulphur and its oxides have long been known as fragments readily extrudable from organic molecules;[11] accordingly sulphur-containing reactants were investigated. Perusal of the literature aided by the rules of



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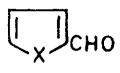

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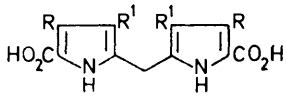
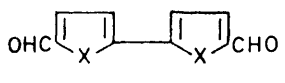


(11) a; R = R¹ = Me
b; R = Me, R¹ = Et
c; R = R¹ = Et



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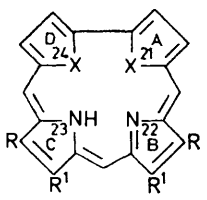
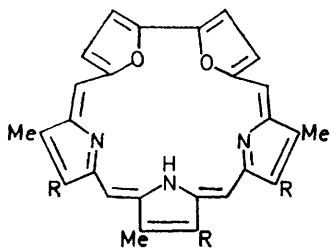
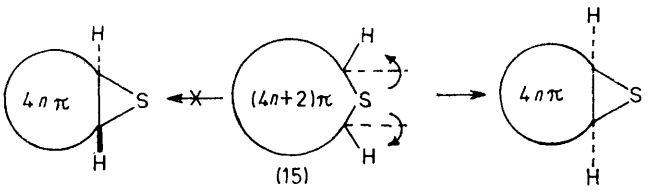


(13) a; R = R¹ = Me
b; R = Me, R¹ = Et
c; R = R¹ = Et



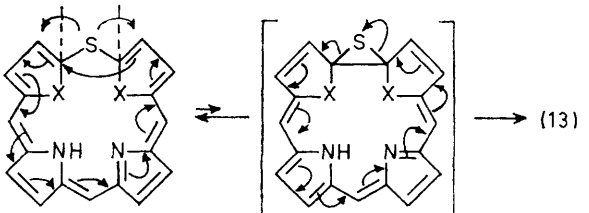
(14)

Woodward and Hoffmann [10] revealed numerous examples of extrusion of sulphur and its oxides probably occurring by a combined disrotatory $(4n + 2)$ π-electron electrocyclic process followed by cheletropic loss of the sulphur fragment.[12] This combination of pericyclic processes has been little investigated but offers numerous advantages in the synthesis of macrocycles. Only if the electrocyclic process occurs in a disrotatory manner (in all-*cis* olefins) is the energetically favoured *cis*-fused thiiran intermediate (15) generated. The corresponding compounds required for the macrocycle syntheses are the *meso*-thiamacrocycles (16) in which a disrotatory cyclisation (16; arrows) of the 18 π-electron system would lead to the thiiran intermediate (17), which could then lose sulphur by a cheletropic process (17; arrows) giving the macrocycle (13) containing a direct link between rings A and D.

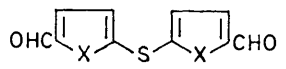


(15)

The synthesis of *meso*-thiamacrocycles containing furan rings was investigated in the first instance. When bis-(5-formylfuryl) sulphide (18; X = O) was treated with the dipyrromethane diacids (11a—c), in the presence of hydrogen bromide, condensation occurred to give macrocycles which did not contain sulphur and which



(16) (17) (13)



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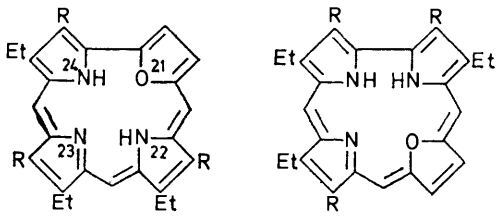


(19) (20)

were shown to be identical with compounds (13a and b; X = O) prepared previously from the diformylbifuryl (12) and the acids (11a and b). Although this represented an improved synthesis (27—30%), attempts to detect the formation of an intermediate [*e.g.* (16)] by

* Professor R. B. Woodward (Aromaticity Conference, Sheffield, 1966) reported the syntheses of the all-pyrrole analogue of (14), which he named sapphryin.

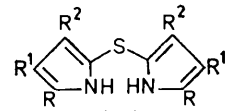
[10] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[11] B. P. Stark and A. J. Duke, 'Extrusion Reactions,' Pergamon, Oxford, 1967.

[12] R. Grigg, R. Hayes, and J. L. Jackson, *Chem. Comm.*, 1969, 1167.

monitoring the reaction spectroscopically or by t.l.c. were unsuccessful. Small amounts of by-products (1—2%) were isolated from the reaction, and microanalysis and spectral data demonstrated the presence of three pyrrole rings and one furan ring in these products. The n.m.r. spectrum showed the presence of only three *meso*-protons, suggesting corrole-type macrocycles, and their formulation as (19; R = Me or Et) accounts for these observations [the n.m.r. spectrum of (19; R = Me) showed it to be a mixture of isomers]. The data supporting structure (19) are also accommodated by the isomeric structure (20), but this alternative is considered less likely on the grounds of the presumed mode of formation.

It was not clear from these results whether sulphur extrusion [(16) ⟶ (17) ⟶ (13)] was occurring as envisaged, and we therefore explored related reactions in an effort to provide more evidence on the mechanism of this process. Once again efforts to incorporate thiophen rings into the synthesis were unsuccessful and condensations involving (18; X = S) and (11a—c) did not lead to macrocyclic products. The oxidation level of the intermediate (16) in the postulated sulphur extrusion process is that of a dihydroporphin (phlorin), and since such species have been isolated [13] and shown to be reasonably stable, we extended our investigations to the all-pyrrole macrocycle (16; X = NH). Two related approaches to the synthesis of (16; X = NH) were considered: the first involves the condensation of a biscarboxypyrrolyl sulphide (21; R = CO_2H) with a 5,5′-diformyldipyrromethane (22; R = CHO) and the second of a bisformylpyrrolyl sulphide (21; R = CHO) with a diacid (22; R = CO_2H). Although the diacid (21; R = CO_2H, R^1 = Me, R^2 = Et) was prepared in almost quantitative yield by the reaction of ethyl 4-ethyl-3-methylpyrrole-2-carboxylate with freshly distilled sulphur dichloride, followed by alkaline hydrolysis, the condensation of the diacid (21; R = CO_2H, R^1 = Me, R^2 = Et) with the dialdehyde (22; R = CHO, R^1 = Me) failed to yield any identifiable product other than a trace of octa-alkylporphin. The alternative approach involved preparation of the dialdehyde (21; R = CHO, R^1 = R^2 = Me), which was only obtained in poor yield (12%) by the action of sulphur dichloride on 2-formyl-3,4-dimethylpyrrole. The majority of the formylpyrrole reacted to give a mixture of highly coloured dipyrromethene-like compounds, from which a crystalline product was isolated in low yield (8%). Microanalysis of the latter product demonstrated the presence of sulphur, and the n.m.r. spectrum was consistent with the thiolactam structure (23). When the dialdehyde (21; R = CHO, R^1 = R^2 = Me) was treated with the diacid (22; R = CO_2H, R^1 = Me or Et) at −10° in the presence of hydrogen chloride, chromatography gave a purple-red product (10—20%) together with traces of an unstable green compound. Although such green compounds could not be isolated, they did form stable, charged, zinc complexes (10—15%) which are formulated as the zinc *meso*-thiaporphins (24; R = Me or Et). Microanalyses and spectral characteristics supported this assignment; in particular the *meso*-protons of (24; R = Et) resonated at τ 0·11 (1H) and 0·37 (2H) in the n.m.r. spectrum, supporting the presence of an aromatic system involving π-electron delocalisation through the sulphur atom. Although part of the deshielding of the *meso*-protons may arise from the charge on the system, the influence of the cyclic delocalisation in (24) is emphasised by comparison with the charged, but blocked, π-system present in the nickel 1,19-dimethyltetradehydrocorrin salts (7), in which the *meso*-protons resonate at τ 2·30—2·60.[14] While our work was in progress, Harris [15] reported a



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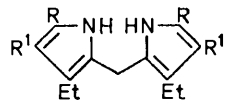

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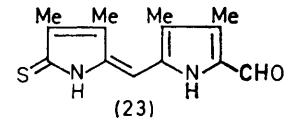
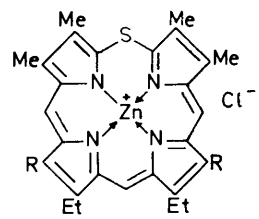


(23)

similar synthesis of the *meso*-thiaporphin salt (25), and again the corresponding free base was extremely unstable. Although the n.m.r. spectrum of compound (25) could not be determined owing to its insolubility, the electronic spectra of (24) and (25) are very similar.



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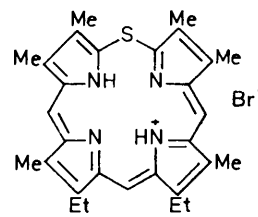

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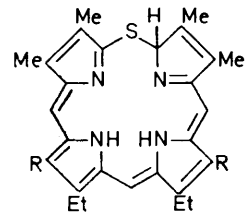


(26)

The structure of the purple-red products obtained by condensation of the dialdehyde (21; R = CHO, R^1 = R^2 = Me) and the diacid (22; R = CO_2H, R^1 = Me or Et) is still uncertain, but the n.m.r. spectrum of these products (*e.g.* Figure 1) clearly indicates a non-aromatic, non-symmetrical structure. The broad signal at τ −0·55 is assigned to an imino-proton and this was supported by exchange studies with deuterium oxide, but the proton resonating at τ 0·68 did not exchange on

[13] R. B. Woodward, *Ind. chem. belge*, 1962, 1293.
[14] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), 1966, 30.
[15] R. L. N. Harris, *Tetrahedron Letters*, 1969, 3689.

addition of deuterium oxide. A structure consistent with these features is (26), which contains an angular proton, and it is of interest to note that the two methyl groups (τ 7·84 and 8·24) show long-range coupling (*J* *ca.* 0·5 Hz), as do the two methyl groups in the angularly blocked system (27) (*J* 1 Hz).[16] We were unable to locate another N–H proton signal in the n.m.r. spectrum as required by structure (26), but this is not unusual in polypyrrolic macrocycles. The mass spectra of the

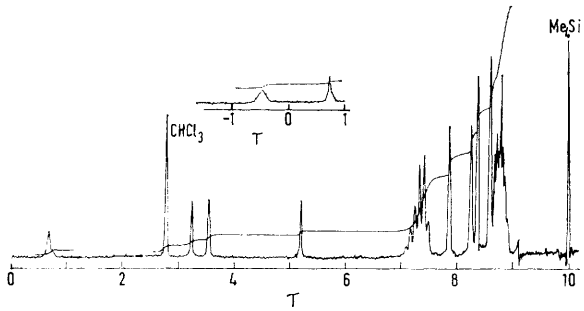
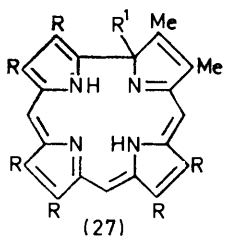
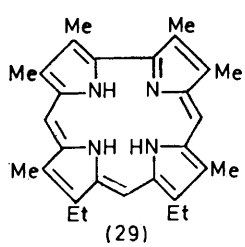
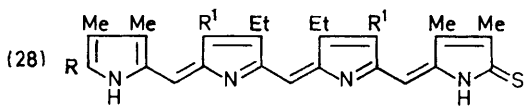


FIGURE 1 N.m.r. spectrum ($CDCl_3$) of purple-red product tentatively formulated as (26; R = Et)

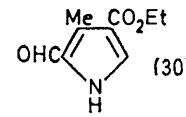
purple-red products did not contain parent peaks but the base peak was at *M* − 32 (*i.e.* *M* − S). An alternative linear tetrapyrrole structure such as (28; R = H, R^1 = Et or Me) is considered unlikely, as the visible spectrum differed considerably from that reported for (28; R = OMe, R^1 = Me),[15] and since treatment of solutions of the purple-red compounds with zinc acetate slowly gave zinc thiaporphin complexes (24; R = Me or Et) (10—30%). When the complex (26; R = Me) was heated with an excess of triphenylphosphine in boiling dichlorobenzene it gave the corresponding corrole (29) (15%). These reactions are readily understandable in terms of angularly protonated structures such as (26), which are tautomeric forms of the thiaphlorin (16; X = NH), and lead us tentatively to formulate the purple-red products as (26; R = Me or Et).

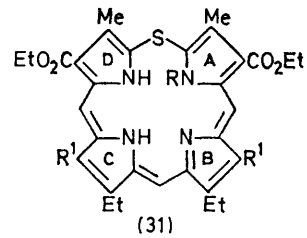


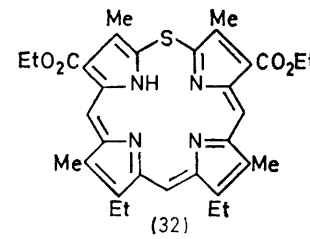




Efforts were next directed towards the synthesis of *meso*-thiaphlorins containing electron-withdrawing substituents in rings adjacent to the sulphur bridge in the hope that these would influence favourably the formation and stability of the *meso*-thiaphlorin. A study of the reaction of sulphur dichloride with pyrroles substituted with electronegative substituents showed that compounds (21; R = R^2 = CO_2Et, R^1 = Me) and (21; R = CHO, R^1 = CO_2Et, R^2 = Me) could be prepared from the corresponding α-unsubstituted pyrroles, whereas the aldehyde (30) did not react under the same conditions. The preparation of the dialdehyde (21; R = CHO, R^1 = CO_2Et, R^2 = Me) was achieved in much higher yield (51%) than of (21; R = CHO, R^1 = R^2 = Me) (12%), presumably owing to the electronegative ester substituent inhibiting self-condensation of the pyrrole. When the bis(formylpyrrolyl) sulphide (21; R = CHO, R^1 = CO_2Et, R^2 = Me) was condensed with the dipyrromethane (22; R = CO_2H, R^1 = Me) in chloroform at 0°, using dry hydrogen chloride as catalyst, a blue, air-stable, crystalline product (52%) was obtained which is formulated as the *meso*-thiaphlorin (31; R = H, R^1 = Me) on the basis of spectral and chemical evidence.







The electronic spectrum of the new macrocycle closely resembled that of a phlorin (Figure 2) and the n.m.r. spectrum supported a non-aromatic structure with *meso*-

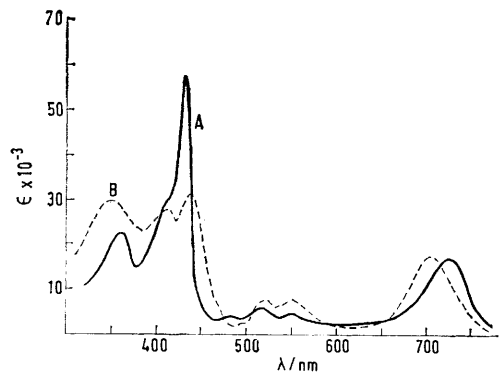
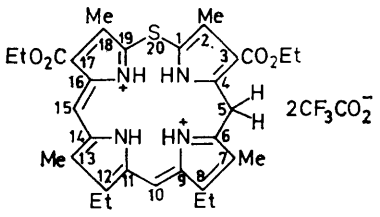


FIGURE 2 U.v. spectra of (A) a phlorin monocation and (B) a *meso*-thiaphlorin monocation

proton resonances at τ 2·43 (2H) and 3·70 (1H) and imino-proton signals at 5·44. Confirmation of the absence of an induced diamagnetic ring current was obtained by examination of the n.m.r. spectrum of the

[16] D. A. Clarke, R. Grigg, R. L. N. Harris, A. W. Johnson, I. T. Kay, and K. W. Shelton, *J. Chem. Soc.* (*C*), 1967, 1648.

N-methyl derivative (31; R = Me), in which the *N*-methyl signal occurred at τ 7·08. Although compounds (31; R = H or Me) exhibited parent ions at *m/e* 586 and 600 in accord with their formulation as *meso*-thiaphlorins, this was not regarded as unequivocal evidence for structure (31; R = H or Me, R^1 = Me) rather than the corresponding *meso*-thiaporphin structures (mol. wt. 2 units lower) because of the tendency of some polypyrrolic macrocycles to give intense $M + 2$ peaks.[17] However, oxidation of the blue product with 1 mol. equiv. of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in the cold caused an immediate colour change from blue to green, forming the unstable *meso*-thiaporphin (32), which could be isolated as its stable zinc complex in high yield. The same zinc complex could be prepared from the *meso*-thiaphlorin and zinc acetate in the presence of air. In the absence of air a stable orange-brown solution was obtained which rapidly was converted into the zinc *meso*-thiaporphin when air was admitted. Rapid exchange of all the *meso*-protons of (31; R = H) occurs in deuteriotrifluoracetic acid in less than 10 min, and the n.m.r. spectrum of (31; R = H) in trifluoroacetic acid (TFA) clearly shows that protonation of the macrocycle has occurred at the *meso*-position adjacent to the sulphur bridge (33) [τ 1·70 and 2·42 (C-10 and C-15 protons), and 4·95 (C-5 protons)], in contrast to phlorins, which are reported[13] to give (34). Modification of the macrocycle synthesis gave the corresponding tetraethyl *meso*-thiaphlorins (31; R = H or Me, R^1 = Et).



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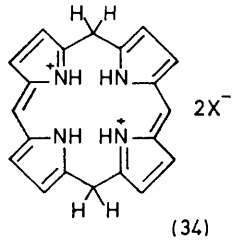
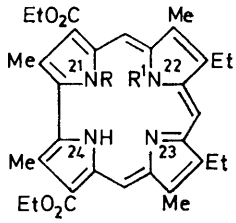


(34)

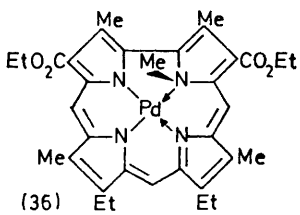


(35)

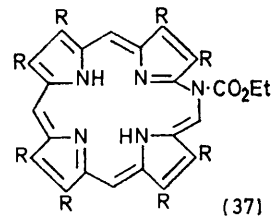
With the structures of the *meso*-thiaphlorins firmly established, extrusion of sulphur was attempted by heating (31; R = H, R^1 = Me) in boiling *o*-dichlorobenzene for 2 h. The anticipated loss of sulphur occurred to give the corrole (35; R = R^1 = H) (35—40%), but when the reaction was carried out in the presence of triphenylphosphine the yield of corrole was increased to 60%. The possibility of the sulphur extrusion occurring by a radical-cleavage mechanism was considered, but repeating the reaction in the presence of a large excess of either hydroquinone or 4-t-butylcatechol caused no significant difference in yield (36 and 40%, respectively). The *N*-methylthiaphlorin (31; R = R^1 = Me), prepared (75%) by methylation of the parent thiaphlorin with methyl iodide in the presence of di-isopropylethylamine, was also investigated. The *N*-methyl substituent was assigned to the ring adjacent to the sulphur bridge on the basis of an examination of its n.m.r. spectrum which showed an upfield shift of the resonances of one β-methyl group and an ester ethyl group. Shifts of this nature are characteristic for *N*-alkyl macrocycles.[2,17] The specificity of the alkylation is intriguing and is clearly related to the presence of the highly polarisable sulphur atom *ortho* to the ring A nitrogen atom. It is interesting that in the *N*-methylation of the corresponding corrole (35; R = R^1 = H) the deactivating influence of the ester substituents results in a predominance of the *N*(22)-methylcorrole (35; R = H, R^1 = Me) (46%) over the *N*(21)-methylcorrole (35; R = Me, R^1 = H) (26%), in contrast to the results obtained with octa-alkylcorroles where the *N*(21)-isomer predominates.[2,18] The *N*-methylthiaphlorin proved more resistant to extrusion of sulphur, and after heating for 12 h at 180° a considerable amount of starting material could be recovered, which is good evidence for the stability of the sulphide link to radical cleavage, and reflects the steric influence of the *N*-methyl group. When the *N*-methylthiaphlorin (31; R = R^1 = Me) was heated in trichlorobenzene (b.p. 213°) in the presence of triphenylphosphine, extrusion of sulphur occurred, generating the *N*-methylcorrole (35; R = Me, R^1 = H) (85%). The n.m.r. spectrum of the *N*-methylcorrole, in which the *N*-methyl group resonated at τ 11·03, clearly demonstrated the formation of the aromatic corrole chromophore. A remarkable increase in the rate of the extrusion reaction was observed when (31; R = R^1 = Me) was heated in boiling acetic acid in the presence of palladium acetate. After 2 min the corresponding palladium *N*(21)-methylcorrole (36) (27%) could be isolated. A similar remarkably easy expulsion of a nitrogen atom from a *meso*-homoazaporphin (37) in the presence of metal ions (Cu^{II}, Zn^{II}) has been observed.[19] These rate enhancements may result from the effort of the complexed metal ion to form four equivalent bonds to the ligand nitrogen atoms. Assuming the C–S–C bond angle in the *meso*-thiaphlorins is *ca.* 90—100°, as found in H_2S, thiophen, and dithiins,[20] models show that the efforts of the metal ion to form four equi-length bonds result in a twisting of the *p*-orbitals on the carbon atoms flanking the sulphur bridge in a manner (38) beneficial to a disrotatory cyclisation [(16) ⟶ (17)], which we consider is the first step in the sulphur extrusion process. Some evidence for the prior formation of a

[17] M. J. Broadhurst, R. Grigg, G. Shelton, and A. W. Johnson, *Chem. Comm.*, 1970, 231.
[18] R. Grigg, A. W. Johnson, and G. Shelton, *Annalen*, 1971, **746**, 32.
[19] R. Grigg, *J. Chem. Soc.* (*C*), 1971, 3664.
[20] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1961, **7**, 58; S. C. Abrahams, *Quart. Rev.*, 1956, 407; P. A. Howell, R. M. Curtis, and W. N. Lipscomb, *Acta Cryst.*, 1954, **7**, 498.

palladium *N*-methyl-*meso*-thiaphlorin complex was obtained by warming an acetic acid solution of (31; R = R^1 = Me) with palladium acetate; a green solution with a visible spectrum different from those of the monocation



(36)



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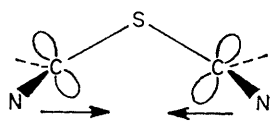


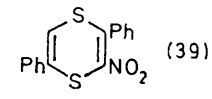
(38)

of (31; R = R^1 = Me) and the palladium *N*-methylcorrole (36) was obtained. The same palladium complex (36) can also be prepared directly from palladium acetate with the *N*-methylcorrole (35; R = Me, R^1 = H) obtained either by sulphur extrustion from (31; R = R^1 = Me), or by methylation of (35; R = R^1 = H).

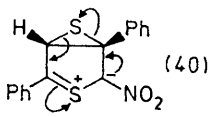
In the thermal extrusion of sulphur from the nitro-*p*-dithiin (39) the stabilising influence of the nitro-group on the intermediate zwitterion (40) results in the specific elimination of only one of the two available sulphur atoms, giving the corresponding 2-nitrothiophen (40; arrows).[21] We have investigated a similar case, using the dithia-macrocycle prepared (44%) by the condensation of the dialdehyde (21; R = CHO, R^1 = CO_2Et, R^2 = Me) and the diacid (21; R = CO_2H, R^1 = Me, R^2 = Et). The *meso*-dithia-macrocycle (41) exhibited a *meso*-proton signal in its n.m.r. spectrum at τ 2·23 (s, 2H) and formed neutral palladium and zinc complexes (42; M = Pd^{II} or Zn^{II}). It was hoped that the asymmetry in the substitution pattern would influence the zwitterion formation and would be reflected in an uneven pattern of sulphur extrusion from the two possible sites. The extrusion of sulphur was much slower than in the corresponding *meso*-thiaphlorin case and required heating, in the presence of triphenylphosphine, at 213° for 10 h. The product (42%) was examined by n.m.r. spectroscopy; it was an approximately 50 : 50 mixture of the two possible *meso*-thiacorrole isomers (43) and (44). Once again incorporation of a metal ion into the macrocycle favourably influenced the sulphur extrusion process. However, although the thermolysis of the zinc complex (42; M = Zn^{II}) was complete in a shorter time (4·5 h) and gave a higher yield (66%) of the zinc *meso*-thiacorroles, the isomer distribution was unaffected (*ca.* 50 : 50).

The extrusion of sulphur from structure (41) to give the *meso*-thiacorroles represents the first direct synthesis of this uncomplexed macrocycle; a previous synthesis of the palladium complex was achieved by cyclisation of the complex (45) with sodium sulphide.[22]

Preliminary work indicates that the presence of furan rings in corrole-type macrocycles has a deactivating effect on the reactivity of the macrocycle towards electrophilic attack. Thus whereas exchange of all the *meso*-protons of compound (35; R = R^1 = H) was complete in less than 15 min at 35° in deuteriotrifluoroacetic acid, no detectable exchange of the *meso*-protons of the 21,24-dioxacorrole (13c) occurred after several hours



(39)



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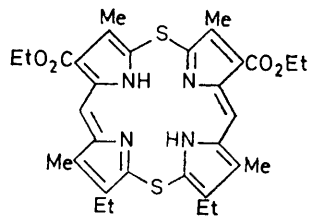
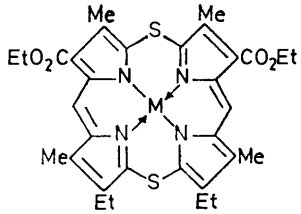
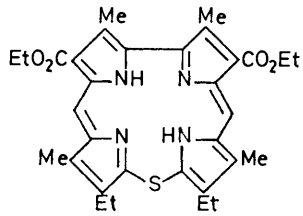


(41)



(42)



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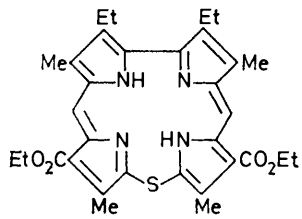
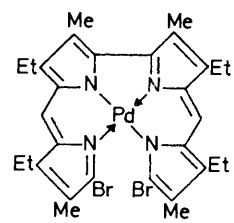


(44)



(45)

under the same conditions. However, at 100° virtually complete exchange of the *meso*-protons of (13c) had occurred after 1 h, but no detectable exchange (n.m.r.) of the β-protons on the furan rings was observed after 100 h at 100°, indicating a remarkable difference in reactivity between the two sites. In related experiments on porphins and their furan and thiophen analogues no exchange of β- or *meso*-protons occurred under these conditions.[6]

The 21-oxacorroles (19) readily form stable, neutral, transition metal complexes (Ni^{II}, Co^{II}, Cu^{II}) when treated with the appropriate metal acetates in acetic acid solution, as do the corroles.[2] However since only very small quantities of the 21-oxacorroles (19) were available these complexes were not investigated further. All attempts

[21] W. E. Parham and V. J. Traynelis, *J. Amer. Chem. Soc.* 1955, **77**, 68; D. S. Breslow and H. Skolnik, 'Multi-Sulphur and Sulphur and Oxygen Five- and Six-Membered Heterocycles,' Interscience, New York, 1966, part 2, ch. 12.

[22] A. W. Johnson, I. T. Kay, and R. Rodrigo, *J. Chem. Soc.*, 1963, 2336.

to prepare metal complexes (Co, Ni, Cu, Zn) of the 21,24-dioxacorroles (13a—c) failed, and these results parallel similar observations with porphins containing two furan rings.[6]

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 Varian HA-100 instrument, with tetramethylsilane as internal reference. M.p.s were measured with a Kofler hot-stage apparatus. Mass spectra were obtained by direct insertion in an A.E.I. MS902 spectrometer. Light petroleum had b.p. 60—80°, and the alumina used for chromatography was Spence type H.

Intermediates

Bis-(5-formyl-2-furyl) Sulphide (18; X = O).—5-Bromo-2-formylfuran [23] (17·5 g) was suspended in water (750 ml) containing sodium sulphide (3·9 g). The mixture was heated at 100° for 2 h with stirring and was then filtered hot to remove a little polymeric material. On cooling, the product separated as pale orange crystals which were collected and washed with water. The combined aqueous filtrates were extracted with ether and the ether layer was dried and evaporated to give more of the product. Recrystallisation from aqueous acetone gave pale yellow plates (8·2 g, 74%), m.p. 129—132° (lit.,[23] 132°).

Bis-(5-ethoxycarbonyl-3-ethyl-4-methylpyrrol-2-yl) Sulphide (21; R = CO_2Et, R^1 = Me, R^2 = Et).—Ethyl 4-ethyl-3-methylpyrrole-2-carboxylate (9·0 g) was dissolved in dry ether (20 ml). The solution was cooled to 0° and freshly distilled sulphur dichloride [24] (2·6 g; b.p. 56—60°) in dry ether (20 ml) was added rapidly with stirring. After a vigorous evolution of hydrogen chloride the product separated and was collected, washed with petroleum, and dried; yield 9·5 g (97·5%). Crystallisation from chloroform–light petroleum gave needles, m.p. 152—153° [Found: C, 61·5; H, 7·35; N, 7·25; S, 7·9%; *M* (mass spec.), 392. $C_{20}H_{28}N_2O_4S$ requires C, 61·2; H, 7·25; N, 7·15; S, 8·15%; *M*, 392]; $\lambda_{max.}$ (EtOH) 208·5, 271, and 293·5 nm (ε 17,680, 20,870, and 25,300); $\nu_{max.}$ (KBr) 3351 (N–H) and 1653 (C=O) cm^{-1}; τ 0·07br (s, 2 × NH), 5·64 (4H, q, ester $CH_2{\cdot}CH_3$), 7·37 (4H, q, nuclear $CH_2{\cdot}CH_3$), 7·72 (6H, s, 2 × CH_3), and 8·75 (12H, m, nuclear and ester $CH_2{\cdot}CH_3$).

Bis-(5-carboxy-3-ethyl-4-methylpyrrol-2-yl) Sulphide (21; R = CO_2H, R^1 = Me, R^2 = Et).—The foregoing diester (6·0 g) was dissolved in ethanol (40 ml), sodium hydroxide (0·8 g) in water (3·0 ml) was added, and the solution was heated under reflux for 3 h. The ethanol was then distilled with gradual addition of water to maintain the volume at *ca.* 40 ml. The hot aqueous solution was cooled and filtered, and sulphur dioxide was bubbled through until precipitation of the diacid was complete. The *product* was collected, washed thoroughly with cold water, and dried, to give a powder (5·1 g, 99%). Crystallisation from chloroform–light petroleum gave needles, m.p. 185—195° (decomp.), which slowly became pink (Found: C, 57·4; H, 6·15; N, 8·5. $C_{16}H_{20}N_4O_4S$ requires C, 57·15; H, 6·0; N, 8·35%); $\lambda_{max.}$ (EtOH) 208, 269, and 292 nm (ε 18,230, 19,580, and 23,850); $\nu_{max.}$ (KBr) 1676 cm^{-1} (C=O).

Bis-(3,5-bisethoxycarbonyl-4-methylpyrrol-2-yl) Sulphide (21; R = R^2 = CO_2Et, R^1 = Me).—2,4-Bisethoxycarbonyl-3-methylpyrrole [25] (1·12 g) and sulphur dichloride (0·25 g) in dry 1,2-dichloroethane (30 ml) were heated under reflux for 1 h. The solvent was evaporated off under reduced pressure and the dark residue was triturated with ether, and crystallised from chloroform–light petroleum to give *prisms* (350 mg, 29·5%), m.p. 208—209·5° (Found: C, 55·1; H, 5·85; N, 5·8; S, 6·5. $C_{22}H_{28}N_2O_8S$ requires C, 55·0; H, 5·85; N, 5·85; S, 6·7%); $\lambda_{max.}$ 275·5 nm (ε 23,090); $\nu_{max.}$ (KBr) 3204 (N–H), 1710, and 1674 (C=O) cm^{-1}; τ 5·67 and 5·90 (8H, ester $CH_2{\cdot}CH_3$, both q), 8·51 (6H, s, 2 × CH_3), 8·63 and 8·71(12H, m, ester and nuclear $CH_2{\cdot}CH_3$).

Bis-(4-ethoxycarbonyl-5-formyl-3-methylpyrrol-2-yl) Sulphide (21; R = CHO, R^1 = CO_2Et, R^2 = Me).—3-Ethoxycarbonyl-2-formyl-4-methylpyrrole [26] (3·64 g) and sulphur dichloride (1·1 g) were dissolved in dry 1,2-dichloroethane (35 ml) and the solution was heated on a steam-bath for 20 min. More sulphur dichloride (0·25 g) was then added and the solution was heated for a further 5 min. On cooling the deep purple solution the product separated and was collected and washed with ether until it was almost colourless (yield 2·0 g, 51%). It crystallised from chloroform–light petroleum as needles, m.p. 266—267° (Found: C, 55·0; H, 5·1; N, 7·1. $C_{18}H_{20}N_2O_6S$ requires C, 55·1; H, 5·15; N, 7·15%); $\lambda_{max.}$ 272·5, 315·5, and 328·5sh nm (ε 9560, 18,960, and 17,300); $\nu_{max.}$ (KBr) 3314 (N–H), 1711, and 1665 (C=O) cm^{-1}; τ ($CDCl_3$–TFA) −1·04br (2 × NH, s), −0·09 (2 × CHO, s), 5·59 (4H, q, ester $CH_2{\cdot}CH_3$), 7·55 (6H, s, 2 × CH_3), and 8·59 (6H, t, ester $CH_2{\cdot}CH_3$).

Bis-(5-formyl-3,4-dimethylpyrrol-2-yl) Sulphide (21; R = CHO, R^1 = R^2 = Me).—2-Formyl-3,4-dimethylpyrrole [27] (2·46 g) was dissolved in dry dichloromethane (25 ml) and the solution cooled to 15°. Sulphur dichloride (1·0 g) in ether (70 ml) was then added rapidly with stirring and the mixture kept at 0° for 1·5 h. The precipitated solid was filtered off and washed with ethanol to give crystals (350 mg, 12%). Recrystallisation from chloroform–light petroleum gave *needles*, m.p. 272—274° (decomp.) [Found: C, 60·55; H, 5·4; N, 10·15; S, 11·05%; *M* (mass spec.), 272. $C_{14}H_{16}N_2O_2S$ requires C, 60·85; H, 5·85; N, 10·15; S, 11·6%; *M*, 272]; $\lambda_{max.}$ 279sh, 299·5, and 330 nm (ε 16,240, 19,390, and 21,940); $\nu_{max.}$ (KBr) 3291, 3242 (N–H), and 1651 (C=O) cm^{-1}; τ ($CDCl_3$–TFA) 0·78 (2 × CHO, s), and 7·76 (6H) and 7·97 (6H) (4 × CH_3, both s). The filtrate was neutralised by the addition of excess of triethylamine and set aside for 2 days, during which a red-brown microcrystalline solid (250 mg) was deposited. This was collected, washed with a little chloroform, then ethanol, and recrystallised from chloroform (20 ml; micro-Soxhlet); it formed bright red needles (210 mg, 8%), m.p. >300° [Found: C, 64·45; H, 6·3; N, 10·5%; *M* (mass spec.), 260. Calc. for $C_{14}H_{16}N_2OS$: C, 64·5; H, 6·2; N, 10·75%; *M*, 260]; $\lambda_{max.}$ 307·5, 461, and 488·5 nm (ε 17,570, 32,630, and 32,250); $\nu_{max.}$ (KBr) 3318 (NH), 1602 (C=O), and 1262 (C=S) cm^{-1}; τ (TFA) −0·4br (NH, s), 0·35 (CHO, s), 2·7 (methine H, s), and 7·58 (6H), 7·8, and 7·91 (total 12H, 4 × CH_3, all s).

[23] Z. N. Nazarova, *Zhur. obshchei Khim.*, 1954, **24**, 575; Z. N. Nazarova and G. F. Potemkin, *ibid.*, 1964, **34**, 157.
[24] 'Gmelins Handbuch der Anorganischem Chemie; Schwefel,' Teil B, Lieferung, 3 p. 1781.
[25] R. Grigg, A. W. Johnson, and J. W. F. Wasley, *J. Chem. Soc.*, 1963, 359.
[26] A. H. Corwin and G. G. Kleinspehn, *J. Amer. Chem. Soc.*, 1953, **75**, 2089.
[27] G. M. Badger, R. L. N. Harris, and R. A. Jones, *Austral. J. Chem.*, 1964, **17**, 1022.

21,24-Dioxacorroles

8,12-*Diethyl*-7,13-*dimethyl*-21,24-*dioxacorrole* (13b; X = O).—(*a*) 5,5′-Diformyl-2,2′-bifuryl[28] (192 mg) was finely powdered and dissolved in chloroform (500 ml) by heating under reflux for 15 min. A solution of 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid[29] (318 mg) in methanol (50 ml) was added with stirring, followed by hydrobromic acid (48% w/v solution in glacial acetic acid; 5 ml). The solution was heated under reflux for 24 h, cooled to room temperature, washed with dilute aqueous ammonia (200 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was taken up in the minimum volume of chloroform and the solution chromatographed on alumina. Chloroform eluted a red-brown band containing traces of aetioporphyrin (visible spectrum). A second brown band was eluted which was shown (see later) to contain very impure 8,12-diethyl-7,13-dimethyl-21,24-dioxacorrole (t.l.c. and visible spectrum). Chloroform–methanol (1 : 1) eluted a brown-green band which, after rechromatography, gave a bright green fraction. This fraction was collected, the solvent was evaporated off, and the residue crystallised from methanol–acetone containing a few drops of hydrobromic acid. It formed dark blue microprisms (30 mg), m.p. >300°. The n.m.r. spectrum ($CDCl_3$–TFA) showed that the product was a mixture of isomers of triethyl-trimethyl-26,30-dioxasapphyrin and contained signals at τ −2·11 (2H), −2·08 (4 × *meso*-H; two overlapping singlets with broadening due to the presence of several isomers), −1·19 (2H), −0·92 (4 × nuclear furan H; essentially two doublets of an AB system with broadening and shoulders due to the presence of several isomers), 5·07 (m, 6H, CH_2·CH_3), 5·58 5·71, and 5·73 (all, s, 9H, 3 × Me), 7·68 and 7·71 (9H, overlapping triplets, CH_2·CH_3), 15·0 (1H), and 16·25 (3 × NH, broad s). The electronic spectrum ($\lambda_{max.}$ 418·5sh, 435·5, 592·5, 622·5, 648·5, and 686 nm) was similar to that of a pure sample of 7,13,18-triethyl-8,12,17-trimethyl-26,30-dioxasapphyrin.

(*b*) Bis-(5-formyl-2-furyl) sulphide (166 mg) and 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid[29] (239 mg) were dissolved in methanol (60 ml). The solution was warmed to 50° and aqueous hydrogen bromide (48%; 1·0 ml) was added; then, after swirling to mix, the solution was left for 40 h at room temperature. The solvent was evaporated off under reduced pressure and the residue dissolved in chloroform (150 ml). The chloroform solution was washed with dilute aqueous ammonia, dried ($MgSO_4$), concentrated to *ca.* 15 ml, and chromatographed on alumina. Chloroform–benzene (1 : 1) eluted a small amount of a by-product as a pink-red band. Crystallisation from chloroform–methanol gave dark red needles (5 mg), m.p. 184—187°. The n.m.r. spectrum indicated that it was a mixture of isomers of triethyl-trimethyl-21-oxacorrole [Found: C, 79·1; H, 7·25; N, 9·8%; *M* (mass spec.), 425. Calc. for $C_{28}H_{31}N_3O$: C, 79·1; H, 7·3; N, 9·9%; *M*, 425]; $\lambda_{max.}$ (pyridine) 389, 488, 519·5, 545·5, and 592·5 nm (ε 225,600, 10,250, 28,210, 13,700, and 33,030); τ 0·6, 0·75, and 1·12 (3 × *meso*-H, all s broadened due to the presence of more than one isomer), 1·23 and 1·43 (2 × nuclear furan H, AB system, J_{AB} 4·5 Hz), 6·2 (6H, m, CH_2·CH_3), 6·64, 6·78, and 6·84 (9H, 3 × CH_3, all s), 8·25 (9H, m, CH_2·CH_3), and 14·0 (2 × N–H, broad s).

Chloroform eluted the major product as a red-brown band which was rechromatographed; the bright red fraction was collected. A few drops of hydrobromic acid were added to convert the free base into the salt, then the solvent was evaporated off and the residue crystallised from methanol with the addition of acetone at the boil. 8,12-*Diethyl*-7,13-*dimethyl*-21,24-*dioxacorrole hydrobromide* formed purple-red prisms (75 mg, 21%), m.p. >300° (Found: C, 64·55; H, 5·45; N, 6·05. $C_{25}H_{25}BrN_2O_2$ requires C, 64·5; H, 5·4; N, 6·0%); $\lambda_{max.}$ (EtOH) 221·5, 277·5, 321·5sh, 367·5sh, 383sh, 386·5, 486·5, 499, 522·5, 536, 540sh, and 580·5 nm (ε 13,580, 18,000, 14,130, 93,500, 189,000, 204,000, 9450, 8690, 16,360, 17,500, 15,790, and 18,220); τ (TFA) 0·01 (2 × nuclear furan H, AB system, J_{AB} 4 Hz), 0·17 (2 × *meso*-H, s), 0·23 (2 × nuclear furan H, AB system, J_{AB} 4 Hz), 0·48 (1 *meso*-H, s), 5·81 (4H, q, CH_2·CH_3), 6·26 (6H, 2 × CH_3, s), and 7·96 (6H, t, CH_2·CH_3).

The free base was obtained by dissolving the hydrobromide (150 mg) in warm methanol (30 ml) and then adding a solution of ammonia (*d* 0·88; 5 ml) in water (10 ml). After 2 h at room temperature the crystalline free base (115 mg, 92·5%) was collected. Recrystallisation from chloroform–methanol gave dark red *needles*, m.p. 230—232° [Found: C, 77·95; H, 6·05; N, 7·15%; *M* (mass spec.), 384. $C_{25}H_{24}N_2O_2$ requires C, 78·0; H, 6·25; N, 7·3%; *M*, 384]; $\lambda_{max.}$ (pyridine) 375, 478·5, 506·5, 551, and 601·5 nm (ε 147,900, 10,300, 23,560, 8660, and 17,320); τ ($CDCl_3$) 0·82 (2H), 0·96 (3 × *meso*-H, both s), 1·8, 1·36 (4 × nuclear furan H, AB system, J_{AB} 4·5 Hz), 6·29 (4H, q, CH_2·CH_3), 6·83 (6H, s, 2 × CH_3), and 8·36 (6H, t, CH_2·CH_3).

Several dark brown fractions which were eluted from the column had broad, weak electronic spectra and were discarded.

7,8,12,13-*Tetramethyl*-21,24-*dioxacorrole* (13a; X = O).—(*a*) 5,5′-Diformyl-2,2′-bifuryl (96 mg) was finely powdered and dissolved in chloroform (250 ml) by heating under reflux for 10 min. A suspension of 3,3′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid[29] (290 mg, 2 mol. equiv.) in methanol (50 ml) was added and the mixture was swirled during the addition of hydrogen bromide (48% w/v solution in glacial acetic acid; 3 ml). The mixture was heated under reflux for 10 min and then left for 1 week at room temperature. The solution was washed with dilute aqueous ammonia (100 ml), dried ($MgSO_4$), concentrated to *ca.* 15 ml, and chromatographed on alumina. Chloroform eluted a red-brown band which was rechromatographed, and the red band was collected. The solution was evaporated and the residue was crystallised from acetone containing a few drops of hydrobromic acid to give 7,8,12,13-*tetramethyl*-21,24-*dioxacorrole hydrobromide* (15 mg, 7%), m.p. >300°, identical (t.l.c. and visible spectrum) with a sample prepared from bis-(5-formyl-2-furyl) sulphide in place of 5,5′-diformyl-2,2′-bifuryl (see later). Chloroform–methanol (1 : 1) eluted a small amount of a green fraction which was identified as 7,8,12,13,17,18-*hexamethyl*-26,30-*dioxasapphyrin* by its characteristic electronic spectrum.

(*b*) Hydrobromic acid (aqueous 48%; 5 ml) was added to a suspension of 3,3′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid (1·16 g; finely ground) in warm methanol (500 ml) containing bis-(5-formyl-2-furyl) sulphide (0·88 g). The mixture was stirred until all the suspended dipyrromethane diacid had dissolved. The solution was kept at room temperature for 48 h, then evaporated under reduced pressure to *ca.* 20 ml. Dilute aqueous ammonia

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

[29] R. J. Abraham, A. H. Jackson, G. W. Kenner, and D. H. Warburton, *J. Chem. Soc.*, 1963, 853.

(300 ml) was added and the solution was extracted with chloroform. The extracts were dried ($MgSO_4$), concentrated to *ca.* 30 ml, and chromatographed on alumina. Chloroform eluted the product as a bright red band. A few drops of hydrobromic acid in methanol were added, the solvent was evaporated off, and the residue was crystallised from methanol–acetone to give the *product* as its hydrobromide salt, red needles (475 mg, 27%), m.p. >300° (Found: C, 62·8; H, 5·3; N, 6·5. $C_{23}H_{21}BrN_2O_2$ requires C, 63·2; H, 4·85; N, 6·4%); $\lambda_{max.}$ (EtOH) 278·5, 325·5sh, 368·5sh, 383·5sh, 387, 486·5, 500, 522·5, 537·5, and 582 nm ($\varepsilon_{max.}$ 15,490, 14,080, 87,400, 164,000, 188,900, 8170, 8110, 13,970, 14,420, and 15,180); τ ($CDCl_3$–TFA) 0·15 (2 × nuclear furan H, AB system, J_{AB} 4·5 Hz), 0·25 (2 × *meso*-H, s), 0·43 (2 × nuclear furan-H, AB system, J_{AB} 4·5 Hz), 0·73 (1 *meso*-H, s), and 6·51 (12H, s, 4 × CH_3).

The free base was obtained by dissolving the salt (110 mg) in methanol (30 ml) and then adding aqueous ammonia (20 ml). It crystallised from chloroform–methanol as dark red prisms (70 mg, 78%), m.p. >300° [Found: C, 76·95, 78·05; H, 5·8, 5·65; N, 8·15, 7·75%; *M* (mass spec.), 356. $C_{23}H_{20}N_2O_2$ requires C, 77·55; H, 5·65; N, 7·85%; *M*, 356]; $\lambda_{max.}$ (pyridine) 375, 476, 506, 551, and 601·5 nm ($\varepsilon_{max.}$ 121,200, 8420, 19,580, 7080, and 14,020).

7,8,12,13-*Tetraethyl*-21,24-*dioxacorrole* (13c; X = O).—Bis-(5-formyl-2-furyl) sulphide (0·888 g) and 3,3′,4,4′-tetraethyldipyrromethane-5,5′-dicarboxylic acid [30] (1·4 g) were dissolved in warm methanol (500 ml) and hydrogen bromide (48% aqueous; 10 ml) was added. The solution was heated under reflux for 1 h and then kept at room temperature for a further 48 h. It was evaporated under reduced pressure to *ca.* 30 ml, poured into dilute aqueous ammonia (300 ml), and extracted with chloroform. The extract was dried ($MgSO_4$), concentrated to *ca.* 20 ml, and chromatographed on alumina. Chloroform–benzene (1 : 1) eluted a small quantity of a by-product, which crystallised from chloroform–methanol as dark red needles (20 mg), m.p. 197·5—199·5°, formulated as 7,8,12,13,17,18-*hexaethyl*-21-*oxacorrole* [Found: N, 9·05%; *M* (mass spec.), 467. $C_{31}H_{37}N_3O$ requires N, 9·0%; *M*, 467]; $\lambda_{max.}$ (pyridine) 391, 488·5, 520, 546·5, and 593·5 nm (ε 186,800, 8030, 22,410, 10,670, and 27,420); τ ($CDCl_3$) 0·38, 0·54, and 0·58 (3 × *meso*-H, all s), 0·66 and 0·86 (2 × nuclear furan H, AB system, J_{AB} 4 Hz), 6·03 (12H, m, $CH_2{\cdot}CH_3$), 8·05, 8·11, and 8·13 (18H, m, $CH_2{\cdot}CH_3$), and 13·6 (2 × N–H, vbr, s).

The major product was eluted, with chloroform, as a bright red band. Addition of a few drops of hydrobromic acid in methanol and removal of the solvent gave 7,8,12,13-*tetraethyl*-21,24-*dioxacorrole hydrobromide*, which crystallised from methanol–acetone as dark red prisms (596 mg, 30%), m.p. >300° (Found: N, 5·55. $C_{27}H_{29}BrN_2O_2$ requires N, 5·7%); $\lambda_{max.}$ (EtOH) 216·5, 278, 322sh, 368sh, 383sh, 387, 486·5, 496, 522, 536·5, 541sh, and 580 nm (ε 15,540, 20,200, 15,740, 109,900, 233,600, 257,500, 10,850, 10,060, 17,490, 19,480, 17,490, and 20,120).

The free base was obtained by dissolving the salt (100 mg) in methanol (20 ml) and then adding a solution of ammonia (*d* 0·88; 5 ml) in water (10 ml). It slowly crystallised and was collected after 2 h. Recrystallisation from chloroform–methanol gave dark red prisms (65 mg, 78%), m.p. 167—169° [Found: C, 78·85; H, 7·2; N, 6·85%; *M* (mass spec.), 412. $C_{27}H_{28}N_2O_2$ requires C, 78·6; H, 6·85; N, 6·8%; *M*, 412]; $\lambda_{max.}$ (pyridine) 376, 384sh, 461·5sh, 476·5, 506, 550, 573·5sh, and 602 nm (ε 131,000, 123,300, 7400, 9610, 21,800, 7920, 2570, and 15,900); τ ($CDCl_3$–CCl_4) 0·76 (2H) and 0·85 (3 × *meso*-H, both s), 1·16 and 1·4 (4 × nuclear furan H, AB system, J_{AB} 4 Hz), 6·3 (8H, m, $CH_2{\cdot}CH_3$), and 8·26 (6H) and 8·31 (12H, m, $CH_2{\cdot}CH_3$).

meso-*Thiamacrocycles.*—*Condensation of Bis-*(5-*formyl*-3,4-*dimethylpyrrol*-2-*yl*) *Sulphide* (21; R = CHO, R^1 = R^2 = Me) *with Dipyrromethane Diacids* (11b *and* c).—(a) *With* 3,3′,4,4′-*tetraethyldipyrromethane*-5,5′-*dicarboxylic acid.* (i) Bis-(5-formyl-3,4-dimethylpyrrol-2-yl) sulphide (295 mg) was dissolved in chloroform (1·7 l) and a solution of 3,3′,4,4′-tetraethyldipyrromethane-5,5′-dicarboxylic acid (346 mg) in methanol (200 ml) was added. The mixture was cooled to −20°, dry hydrogen chloride was slowly bubbled through for 10 min, and the mixture was then left for 10 h at 0°. It was washed with aqueous sodium acetate, dried ($MgSO_4$), concentrated to *ca.* 30 ml, and chromatographed on alumina. Benzene–chloroform (1 : 2) eluted a purple-red fraction which, on evaporation and crystallisation from chloroform–methanol gave dark brown *needles* (60 mg, 12%), m.p. >300°, tentatively assigned structure (26; R = Et) (Found: C, 74·9; H, 7·85; N, 11·05; S, 6·2. $C_{31}H_{38}N_4S$ requires, C, 74·65; H, 7·7; N, 11·25; S, 6·45%); $\lambda_{max.}$ 346, 543, and 592 nm (ε 41,400, 18,500, and 13,310); τ ($CDCl_3$) −0·54 (NH, br, s) 0·7 (1H, angular C-1 proton, s), 3·22, 3·53, and 5·18 (3 × *meso*-H, all s), 7·16 (8H, m, $CH_2{\cdot}CH_3$), 7·84, 8·24, 8·36, and 8·6 (12H, 4 × CH_3, all s), and 8·8 (12H, m, $CH_2{\cdot}CH_3$).

Chloroform eluted a number of green and green-brown fractions which were combined and treated with a solution of zinc acetate (1·0 g) in methanol (100 ml). The solution was evaporated, the residue chromatographed on alumina, and the column was eluted with chloroform until the eluate was almost colourless. The chloroform fractions were discarded. Chloroform–methanol (1 : 1) eluted a green fraction which was rechromatographed, and the bright green band [eluted with chloroform–methanol (2 : 1)] was collected. The solvent was evaporated off, the residue was dissolved in chloroform, and the solution was washed with aqueous sodium chloride and then water. Evaporation left *zinc* 7,8,12,13-*tetraethyl*-2,3,17,18-*tetramethyl*-20-*thiaporphin chloride* (24; R = Et), which crystallised as purple needles (22 mg, 3·5%), m.p. >300° (from chloroform–acetone) [Found: C, 61·8; H, 5·9; Cl, 6·1; N, 9·15; S, 5·0%; *m/e* (mass spec.), 559. $C_{31}H_{35}ClN_4SZn$ requires C, 62·4; H, 5·9; Cl, 5·95; N, 9·4; S, 5·05%; *M* − Cl, 559]; $\lambda_{max.}$ (EtOH) 299sh, 309·5, 355, 401·5, 534, 569, 625sh, and 665 nm (ε 17,760, 34,760, 32,730, 73,400, 4660, 5700, 8720, and 41,370); τ ($CDCl_3$) 0·12 (1H), 0·38 (3 × *meso*-H, both s), 6·2 (8H, m, $CH_2{\cdot}CH_3$), 6·83 (6H) and 6·94 (12H, 4 × CH_3, both s), and 8·18 (6H) and 8·22 (12H, m, $CH_2{\cdot}CH_3$).

(ii) The reaction (i) was repeated as described except that the chloroform solution of the condensation products was shaken with saturated aqueous sodium acetate (1 l) containing zinc acetate (10 g). Chromatography and subsequent crystallisation of the products gave compound (26; R = Et) as brown needles (18 mg, 4%), m.p. >300°, and (24; R = Et) as purple needles (80 mg, 13·5%), m.p. >300°. Both products were identical (t.l.c. and visible spectrum) with those obtained from preparation (i).

(b) *With* 3,3′-*diethyl*-4,4′-*dimethyldipyrromethane*-5,5′-*dicarboxylic acid.* A reaction similar to (a) (i) with 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (318 mg) gave *compound* (26; R = Me) as dark brown prisms (52 mg, 11%), m.p. >300° (Found: C, 74·0; H, 7·05; N,

[30] H. Fischer and H. Orth, ' Die Chemie des Pyrroles,' vol. I, Leipzig.

11·9; S, 6·45. $C_{29}H_{34}N_4S$ requires C, 74·05; H, 7·3; N, 11·9; S, 6·75%); $\lambda_{max.}$ 330·5sh, 343·5, 535·5, and 584·5 nm (ε 28,610, 42,270, 18,260, and 12,600). The compound was too insoluble for determination of its n.m.r. spectrum in $CDCl_3$ and decomposed in the presence of TFA.

The green fractions eluted from the column, after treatment with zinc acetate and crystallisation, gave *zinc* 8,12-*diethyl*-2,3,7,13,17,18-*hexamethyl*-20-*thiaporphin chloride* (24; R = Me) as purple prisms (25 mg, 4·5%), m.p. >300° (Found: C, 60·9; H, 5·55; N, 9·65; S, 5·8. $C_{29}H_{31}ClN_4SZn$ requires C, 61·3; H, 5·5; N, 9·85; S, 5·65%); $\lambda_{max.}$ (EtOH) 276·5sh, 299sh, 309, 355, 401·5, 533, 569·5, 624·5sh, and 664·5 nm (ε 7160, 17,540, 34·490, 32,330, 75,570, 4880, 5590, 8910, and 39,390); τ ($CDCl_3$–TFA) −0·32 (1H) and −0·16 (3 × *meso*-H, both s), 6·1 (4H, q, $CH_2{\cdot}CH_3$), 6·6 (12H) and 6·62 (18H, 6 × CH_3, both s), and 8·31 (6H, t, $CH_2{\cdot}CH_3$).

When a solution of compound (26; R = Me) (50 mg) in chloroform was treated with a solution of zinc acetate (100 mg) in methanol (25 ml) containing one drop of glacial acetic acid and kept overnight, the zinc thiaporphin (24; R = Me) was isolated in increased yield (15 mg, 25%).

3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18-*tetramethyl*-20-*thiaphlorin* (31; R = H, R^1 = Me).—Bis-(4-ethoxycarbonyl-5-formyl-3-methylpyrrol-2-yl) sulphide (400 mg) was dissolved in chloroform (1·9 l) and a solution of 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid (318 mg) in methanol (30 ml) was added. After swirling to mix, the solution was cooled to 0° and then a slow stream of dry hydrogen chloride was bubbled through for 10 min. The solution was kept at −5° for 18 h, washed thoroughly with saturated aqueous sodium acetate, and evaporated, and the residue was chromatographed on alumina. Chloroform eluted a bright blue band, material from which was crystallised from chloroform–methanol. The *product* formed long purple-brown hairs (308 mg, 52%), m.p. >300° [Found: C, 67·45; H, 6·4; N, 9·55; S, 5·3; *M* (mass spec), 586. $C_{33}H_{38}N_4O_4S$ requires C, 67·55; H, 6·55; N, 9·55; S, 5·45%; *M*, 586]; $\lambda_{max.}$ 249, 315, 396, and 639 nm (ε 24,400, 19,700, 46,700, and 15,400); τ ($CDCl_3$) 2·43 (2 × *meso*-H, s), 3·71 (1 *meso*-H, s), 5·44 (3 × N–H, br, s), 5·7 (4H, q, ester $CH_2{\cdot}CH_3$), 7·37 (6H, 2- and 18-CH_3, s), 7·69 (6H, 7- and 13-CH_3, s), 8·62 (6H, t, ester $CH_2{\cdot}CH_3$), and 8·72 (6H, t, nuclear $CH_2{\cdot}CH_3$); $\lambda_{max.}$ (TFA) 255, 316, 382·5, 408·5sh, 668·5sh, and 712·5 nm (ε 17,900, 15,900, 40,500, 23,000, 17,100 and 21,700); τ (TFA) 1·7 and 2·42 (2 × *meso*-H, both s), 4·95 (2H, C-10 bridge CH_2, br, s), 5·5 (4H, m, ester $CH_2{\cdot}CH_3$), 7·25 (4H, q, nuclear $CH_2{\cdot}CH_3$), 7·4, 7·57, 7·66, and 7·7 (12H, 4 × CH_3, all s), and 8·6 (12H, m, nuclear and ester $CH_2{\cdot}CH_3$).

The *hydrobromide* was prepared by dissolving the free base (100 mg) in chloroform and washing the solution with dilute hydrobromic acid. After evaporation the salt crystallised from chloroform–acetone as dark blue hairs (104 mg, 92%), m.p. >300° (Found: C, 59·2; H, 5·5; N, 8·4; S, 4·5. $C_{33}H_{39}BrN_4O_4S$ requires C, 59·35; H, 5·9; N, 8·4; S, 4·8%); $\lambda_{max.}$ 247, 266sh, 384, 412, 438·5, 519, 550, and 702·5 nm (ε 22,680, 16,050, 30,140, 27,750, 30,910, 7560, 7620, and 17,600); τ ($CDCl_3$) 0·35 (2 × NH, br, s), 1·61 (2 × *meso*-H, s), 3·15 (2 × N–H, br, s), 3·31 (1 *meso*-H, s), 5·7 (4H, q, ester $CH_2{\cdot}CH_3$), 7·11 (4H, q, nuclear $CH_2{\cdot}CH_3$), 7·33 (6H, s, 2- and 18-CH_3), 7·48 (6H, s, 13- and 7-CH_3), and 8·65 (12H, m, nuclear and ester $CH_2{\cdot}CH_3$).

3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18,21-*pentamethyl*-20-*thiaphlorin* (31; R = R^1 = Me).—3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18-tetramethyl-20-thiaphlorin (150 mg) (31; R = H, R^1 = Me) was dissolved in acetone (150 ml) and a mixture of methyl iodide (10 ml) and di-isopropylethylamine (3 ml) was added. The solution was heated under reflux in nitrogen for 2·5 h, cooled, and filtered from the precipitated amine salt. The solvent was removed and the residue was dissolved in chloroform and chromatographed on alumina. Chloroform eluted a bright blue band. The *product* crystallised from chloroform–light petroleum as brown prisms (116 mg, 75·5%), m.p. 220—222° (decomp.) [Found: C, 68·25; H, 6·6; N, 9·1; S, 4·95%; *M* (mass spec.), 600. $C_{34}H_{40}N_4O_4S$ requires C, 67·95; H, 6·7; N, 9·3; S, 5·35%; *M*, 600]; $\lambda_{max.}$ 248·5, 353·5sh, 390, and 617 nm (ε 24,040, 22,510, 28,250, and 16,590); $\lambda_{max.}$ ($CHCl_3$ +0·5% HBr in glacial acetic acid) 344·5, 401·5, 439sh, 521, 557·5, and 689 nm (ε 27,150, 22,580, 16,480, 6320, 7510, and 18,050); τ ($CDCl_3$) 2·17, 3·16, and 3·94 (3 × *meso*-H, all s), 5·65 and 5·83 (4H, both q, ester $CH_2{\cdot}CH_3$), 7·08 (3H, s, NMe), 7·36 (4H, m, nuclear $CH_2{\cdot}CH_3$), 7·38, 7·62, 7·7, and 7·75 (12H, all s, 4 × CH_3), and 8·73 (12H, m, nuclear and ester $CH_2{\cdot}CH_3$).

3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18-*tetramethyl*-20-*thiaporphin* (32).—3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18-tetramethyl-20-thiaphlorin (50 mg) (31; R = H, R^1 = Me) was dissolved in dichloromethane (20 ml) and alumina (2 g; Spence type H) was added. The mixture was stirred vigorously and a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (20 mg) in dichloromethane (10 ml) was added dropwise. The colour of the solution changed rapidly from blue to green. The alumina was separated, petroleum (30 ml) was added, and the solution was evaporated under reduced pressure at 20°. The *product* was washed with ether, collected, and dried. It formed dark blue microneedles (25 mg, 50%), m.p. >300°, was extremely unstable in solution, and decomposed on attempted recrystallisation (Found: C, 67·7; H, 6·0; N, 9·5. $C_{33}H_{36}N_4O_4S$ requires C, 67·8; H, 6·2; N, 9·6%). Light absorption data were measured with a Unicam SP 800 spectrometer, using the fast-scan setting in order to minimise effects due to decomposition: $\lambda_{max.}$ ($CHCl_3$ +1% diisopropylethylamine) 320·5, 420·5, 549·5sh, 610·5, 627, and 677 nm (ε 19,400, 39,800, 4770, 7410, 10,650, and 27,250). The product was too unstable for determination of its n.m.r. spectrum.

Zinc Complex.—3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18-tetramethyl-20-thiaphlorin (31; R = H, R^1 = Me) (100 mg) was dissolved in chloroform (100 ml) and a solution of zinc acetate (300 mg) in methanol (100 ml) was added. The solution was warmed (steam-bath) for 30 min and evaporated under reduced pressure, and the residue was dissolved in chloroform (50 ml), and washed with dilute sodium chloride solution (3 × 50 ml) and then water (50 ml). The zinc complex crystallised as the *chloride* from chloroform–acetone as long, dark blue needles (94 mg, 80·5%), m.p. >300° [Found: C, 57·65; H, 4·85; N, 8·4; S, 4·95%; *m/e* (mass spec.), 647. $C_{33}H_{35}ClN_4O_4SZn$ requires C, 58·0; H, 5·15; N, 8·2; S, 4·7%; *M* − Cl, 647]; $\lambda_{max.}$ (EtOH) 232, 309sh 322·5, 350sh, 362·5, 424, 545, 580, 649·5sh, and 703 nm (ε 16,600, 17,100, 28,600, 10,800, 21,500, 70,200, 6730, 3660, 6910, and 32,400); τ −0·47(2H), 0·36 (3 *meso*-H, both s), 5·14 (4H, q, ester $CH_2{\cdot}CH_3$), 6·2 (4H, q, nuclear $CH_2{\cdot}CH_3$), 6·68 (6H, s, 2- and 18-CH_3, s), 6·83 (6H, s, 7- and 13-CH_3, s), and 8·22 (12H, t, ester and nuclear $CH_2{\cdot}CH_3$).

The zinc complex could also be obtained in yields of *ca.*

70—80% by treating a freshly prepared chloroform solution of the thiaporphin with zinc acetate in methanol.

3,17-*Bisethoxycarbonyl*-7,8,12,13-*tetraethyl*-2,18-*dimethyl*-20-*thiaphlorin* (31; R = H, R^1 = Et).—Prepared by the method already described from bis-(4-ethoxycarbonyl-5-formyl-3-methylpyrrol-2-yl) sulphide (400 mg) and 3,3′,4,4′-tetraethyldipyrromethane-5,5′-dicarboxylic acid (346 mg), the *product* crystallised from chloroform–light petroleum as purple-blue prisms (310 mg, 50·5%), softening at *ca.* 215° (decomp.) [Found: C, 68·45; H, 7·0; N, 8·95; S, 4·75%; *M* (mass spec.), 614. $C_{35}H_{42}N_4O_4S$ requires C, 68·35; H, 6·9; N, 9·1; S, 5·2%; *M*, 614]; $\lambda_{max.}$ 315, 394·5, and 634·5 nm (ε 22,520, 53,420 and 17,650); τ 2·48 (2 × *meso*-H, s), 3·35 (3 × NH, br, s), 3·73 (1 × *meso*-H, s), 5·75 (4H, q, ester CH_2·CH_3), 7·3 (8H, q, nuclear CH_2·CH_3), 7·42 (6H, s, 2 × CH_3), and 8·7 (18H, m, nuclear and ester CH_2·CH_3).

3,17-*Bisethoxycarbonyl*-7,8,12,13-*tetraethyl*-2,18,21-*trimethyl*-20-*thiaphlorin* (31; R = Me, R^1 = Et).—Prepared from the foregoing 20-thiaphlorin (150 mg) with methyl iodide and di-isopropylethylamine as already described, the *product* (105 mg, 68·5%) crystallised from chloroform–light petroleum as dark blue hairs (Found: C, 68·7; H, 6·9; N, 8·6; S, 4·5. $C_{36}H_{44}N_4O_4S$ requires C, 68·75; H, 7·05; N, 8·9; S, 5·1%); $\lambda_{max.}$ 248·5, 346·5sh, 392, and 617 nm (ε 24,110, 22,900, 27,990, and 16,740); τ 2·09 and 3·10 (2 × *meso*-H, both s), 3·12 (2 × NH, br, s), 3·86 (*meso*-H, s), 5·58 (2H), 5·75 (4H, m, ester CH_2·CH_3), 7·07 (NMe, s), 7·33 and 7·60 (2- and 18-Me, both s), 7·3 (8H, m, nuclear CH_2·CH_3), and 8·68 (18H, m, nuclear and ester CH_2·CH_3).

3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18-*tetramethyl*-10,20-*dithiaphlorin* (41).—Bis-(4-ethoxycarbonyl-5-formyl-3-methylpyrrol-2-yl) sulphide (400 mg) was dissolved in chloroform (1·9 l) and a solution of bis-(5-carboxy-3-ethyl-4-methylpyrrol-2-yl) sulphide (336 mg) in ether (30 ml) was added. The solution was cooled to 15° and a slow stream of dry hydrogen chloride was bubbled through until saturation (30 min). The solution was stored at 0° overnight, washed with aqueous sodium acetate, and evaporated to dryness, and the residue was chromatographed on alumina with chloroform as eluant. The first yellow-brown band contained the *product*, which crystallised from chloroform–light petroleum as long brown hairs (266 mg, 44%), softening at *ca.* 240° (decomp.) [Found: C, 63·25; H, 6·1; N, 9·25; S, 10·4%; *M* (mass spec.), 604. $C_{32}H_{36}N_4O_4S_2$ requires C, 63·55; H, 6·0; N, 9·25; S, 10·6%; *M*, 604]; $\lambda_{max.}$ 340, 444, 508·5sh, and 592·5 nm (ε 10,460, 56,040, 9170, and 5340); τ 2·23 (2 × *meso*-H, s), 5·68 (4H, q, ester CH_2·CH_3), 7·5 (4H, q, nuclear CH_2·CH_3), 7·6 (6H, s, 2 × CH_3), 7·85 (6H, s, 2 × CH_3), and 8·4—9·0 (12H, m, ester and nuclear CH_2·CH_3).

Palladium Complex (42; M = Pd^{II}).—The 10,20-dithiaphlorin (150 mg) was dissolved in pyridine (30 ml) and chloroform (15 ml), palladium acetate (60 mg) in pyridine (15 ml) was added, and the solution was heated at 100° (steam-bath) for 2 h. It was then evaporated to dryness and the residue was chromatographed on alumina. The *product* (148 mg, 84%) crystallised from chloroform–light petroleum as dark brown needles, m.p. 271·5—272·5° (decomp.) (Found: C, 54·3; H, 5·1; N, 7·7; S, 8·8; ash-(PdO), 15·6. $C_{32}H_{34}N_4O_4PdS_2$ requires C, 54·2; H, 4·8; N, 7·9; S, 9·05; ash, 15·0%); $\lambda_{max.}$ 290·5, 369·5, 400, 495, and 581 nm (ε 11,100, 14,700, 13,300, 63,600, and 22,900). The n.m.r. spectrum showed partial 'paramagnetic' broadening, no *meso*-H signals were observed, and β-methyl and β-methylene signals were very broad; τ 5·74 (4H, q, ester CH_2·CH_3), 8·04 (br, s, methyls), 8·65 (6H, t, ester CH_2·CH_3), and 8·98 (6H, t, nuclear CH_2·CH_3).

Zinc Complex (42; M = Zn^{II}).—Prepared in the usual way, the *product* (330 mg, 99·5%) crystallised from chloroform–light petroleum as brown hairs, m.p. >300° (Found: C, 57·65; H, 5·0; N, 8·15. $C_{32}H_{34}N_4O_4S_2Zn$ requires C, 57·55; H, 5·15; N, 8·4%); $\lambda_{max.}$ 290, 354, 413sh, 479·5, and 550·5 nm (ε 13,650, 13,920, 9960, 96,920, and 15,340). The complex was too insoluble for determination of its n.m.r. spectrum.

3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18-*tetramethyl*-10-*thiacorrole* (43) *and* 7,13-*Bisethoxycarbonyl*-2,18-*diethyl*-3,8,12,17-*tetramethyl*-10-*thiacorrole* (44).—(*a*) A solution of the foregoing zinc complex (300 mg) in 1,2,4-trichlorobenzene (300 ml) containing triphenylphosphine (1·5 g) was boiled under reflux (nitrogen atmosphere) for 4·5 h; the solvent was evaporated off and the residue chromatographed on alumina. Chloroform eluted a bright green fraction; evaporation and crystallisation of the residue from chloroform–light petroleum gave a mixture (186 mg, 66%) of the zinc complexes (*ca.* 50 : 50) of compounds (43) and (44) as dark blue needles (Found: C, 60·6; H, 5·45; N, 8·5. Calc. for $C_{32}H_{34}N_4O_4SZn$: C, 60·4; H, 5·4; N, 8·8%).

The mixture of zinc complexes (220 mg) was dissolved in trifluoroacetic acid (1 ml), kept for 5 min, then poured into water (50 ml); the mixture was neutralised with aqueous ammonia and extracted with chloroform. The extract was evaporated to dryness and the residue chromatographed on alumina. Benzene eluted a green fraction which afforded the *product*, tentatively formulated as (43) (101 mg, 51%), m.p. 280—282° (decomp.), as dark blue hairs (from chloroform–light petroleum) (Found: C, 67·05; H, 6·1; N, 9·65. $C_{32}H_{36}N_4O_4S$ requires C, 67·15; H, 6·35; N, 9·8%); $\lambda_{max.}$ 250sh, 311sh, 355sh, 443, 546, 579, and 641 nm (ε 17,770, 8200, 13,380, 115,800, 8020, 11,740, and 16,960); τ ($CDCl_3$–TFA) −0·32 (2 × *meso*-H, s), 5·33 (4H, q, ester CH_2·CH_3), 6·48 (4H, q, nuclear CH_2·CH_3), 6·81 (6H, s, 2 × CH_3), 6·95 (6H, s, 2 × CH_3), and 8·5 (12H, m, ester and nuclear CH_2·CH_3).

The second *product*, tentatively formulated as (44), was eluted with benzene–chloroform (1 : 2) and crystallised from chloroform–benzene as dark purple needles (83 mg, 42%), m.p. 256—257° (Found: C, 67·1; H, 6·1; N, 9·35%); $\lambda_{max.}$ 258, 296, 330, 434·5, 581, and 609sh nm (ε 16,850, 15,250, 12,740, 124,000, 18,410, and 6830); τ ($CDCl_3$–TFA) −0·11 (2 × *meso*-H, s), 5·28 (4H, q, ester CH_2·CH_3), 6·65 (6H, s, 2 × CH_3), 6·7 (4H, q, nuclear CH_2·CH_3), 6·93 (6H, s, 2 × CH_3), 8·39 (6H, t, ester CH_2·CH_3), and 8·59 (6H, t, nuclear CH_2·CH_3).

(*b*) 3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18-tetramethyl-10,20-dithiaphlorin (100 mg) was thermolysed, under nitrogen, in 1,2,4-trichlorobenzene (100 ml) containing triphenylphosphine (1 g) for 10 h. Isolation of the product in the usual way gave dark blue needles (40 mg, 42%) (from chloroform–light petroleum). The n.m.r. spectrum ($CDCl_3$–TFA) indicated that the isomer ratio was not significantly different from that in the product obtained by thermolysis of the zinc complex.

Corroles

Thermolysis of Compound (26; R = Me).—(*a*) The macrocycle (50 mg) was dissolved in air-free, dry *o*-dichlorobenzene (50 ml) in an atmosphere of nitrogen and heated under reflux for 1 h. The solvent was evaporated off under reduced pressure and the residue chromatographed on

alumina. Chloroform–benzene (1 : 1) eluted red material which had a characteristic octa-alkylcorrole electronic spectrum. The product was identified as 8,12-*diethyl*-2,3,7,13,17,18-*hexamethylcorrole* (t.l.c. and mass spectrum) and the yield was estimated, by spectroscopic examination of the purified chromatography fractions, as 2%.

(*b*) The reaction was repeated but in the presence of triphenylphosphine (400 mg); the yield of corrole was increased to 15%.

3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18-*tetramethylcorrole* (35; R = R^1 = H).—3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18-tetramethyl-20-thiaphlorin (200 mg) was dissolved in air-free *o*-dichlorobenzene (200 ml) in an atmosphere of nitrogen. The solution was heated under reflux for 2 h, then the solvent was evaporated off under reduced pressure, and the residue chromatographed on alumina. Chloroform eluted a blue band, identified as starting material, which crystallised from chloroform–methanol as purple-brown needles (30 mg, 15%), m.p. >300°. A second band (purple-blue) was then eluted; crystallisation from chloroform–methanol gave 3,17-*bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18-*tetramethylcorrole* as purple-blue needles (80 mg, 42·5%), m.p. 210—212° [Found: C, 71·1; H, 6·75; N, 9·95%; *M* (mass spec.), 554. $C_{33}H_{38}N_4O_4$ requires C, 71·45; H, 6·9; N, 10·1%; *M*, 554]; $\lambda_{max.}$ 402·5, 420, 510sh, 571sh, 590, and 618 nm (ε 69,000, 55,490, 15,860, 19,300, 28,200, and 32,280); τ 1·5 (2H) and 2·5 (3 × *meso*-H, both vbr, s), 5·4 (4H, q, ester CH_2·CH_3), 6·4—7·6 (16H, nuclear CH_2·CH_3 and Me, vbr), 8·33 (6H, t, ester CH_2·CH_3), 8·61 (6H, br, t, nuclear CH_2·CH_3), and 13·3 (3 × NH, br, s). The broadness of the signals due to protons close to the ' aromatic π-system ' may be due to the formation of radical species by aerial oxidation [31] or the presence of a low-lying triplet state.[32]

The thermolysis experiments were repeated but in the presence of hydroquinone (4 mg per ml; 2 h heating) and t-butylcatechol (8 mg per ml; 12 h heating); the yields of corrole were 36 and 40%, respectively. When the reaction was carried out in the presence of triphenylphosphine (10 mg per ml) the yield was 60%.

Methylation of 3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18-*tetramethylcorrole*.—The corrole (80 mg) was dissolved in acetone (25 ml), di-isopropylethylamine (2 ml) was added, and the solution was heated under reflux for 1 h. The solvent was removed and the residue chromatographed on alumina with benzene as eluant. The first fraction (blue-red) yielded bronze plates (23 mg, 27%), m.p. 207—208° (from light petroleum) of 3,17-*bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18,21-*pentamethylcorrole* (35; R = Me, R^1 = H) (Found: C, 71·8; H, 6·75; N, 9·75. $C_{34}H_{40}N_4O_4$ requires C, 71·85; H, 7·1; N, 9·85%); $\lambda_{max.}$ 270, 293, 356sh, 402·5, 423, 552·5, and 594 nm (ε 19,940, 18,270, 23,750, 52,200, 30,880, 21,060, and 34,810); τ 0·81, 1·1, and 2·1 (3 × *meso*-H, all s), 5·29 and 5·48 (4H, m, ester C*H*·CH_3), 6·55 (3H, s, 18-CH_3), 6·63 (4H, m, nuclear CH_2·CH_3), 6·97 (3H, s, 2-CH_3), 7·08 (6H, s, 7- and 13-CH_3), 8·45 (12H, m, ester and nuclear CH_2·CH_3), 9·3 (NH, br, s), and 11·03 (3H, s, NMe).

[31] W. Ij Aalbersberg, J. Gaaf, and E. L. Mackor, *J. Chem. Soc.*, 1961, 905.

Chloroform–benzene (2 : 1) eluted the second fraction (deep blue-green) which was identified as 3,17-*bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18,22-*pentamethylcorrole* (35; R = H, R^1 = Me). It crystallised from chloroform–methanol as purple plates (36 mg, 46%), m.p. 225—227° (Found: C, 71·65; H, 6·8; N, 9·8. $C_{34}H_{40}N_4O_4$ requires C, 71·85; H, 7·1; N, 9·85%); $\lambda_{max.}$ 282·5, 300, 425, 433·5sh, 620·5, and 650·5 nm (ε 21,900, 21,040, 89,000, 81,050, 33,320, and 21,500); τ 0·07, 0·5, and 1·17 (3 × *meso*-H, all s), 5·25 (4H, q, ester CH_2·CH_3), 6·32 and 6·4 (6H, 2- and 18-CH_3, both s), 6·72 and 6·9 (6H, 7- and 13-CH_3, both s), 8·3 (12H, m, ester and nuclear CH_2·CH_3), 9·25 (NH, br, s), 11·73 (NH, br, s), and 13·57 (3H, s, NMe).

3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18,21-*pentamethylcorrole* (35; R = Me, R^1 = H).—3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18,21-pentamethyl-20-thiaphlorin (50 mg) was heated under nitrogen in boiling 1,2,4-trichlorobenzene (100 ml) containing triphenylphsphine (1 g) for 3 h. Isolation of the product in the usual way gave 3,17-bisethoxycarbonyl-8,12-diethyl-2,7,13,18,21-pentamethylcorrole (85%), identical with the sample already prepared.

Palladium 3,17-*Bisethoxycarbonyl*-8,12-*diethyl*-2,7,13,18,21-*pentamethylcorrole* (36).—(*a*) 3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18,21-pentamethylcorrole (100 mg) was dissolved in glacial acetic acid (50 ml) and palladium acetate (60 mg) was added. The solution was heated under reflux for 5 min and poured into water (200 ml). The complex was extracted into chloroform and the chloroform solution washed with dilute aqueous ammonia, dried ($MgSO_4$), and evaporated. The residue was chromatographed on alumina with chloroform as eluant. A trace of starting material was eluted first, followed by bright green material which was collected and crystallised from ether–light petroleum. The *product* formed dark purple prisms (72 mg, 60%), m.p. 185—186° (Found: C, 61·2; H, 5·65; N, 8·3. $C_{34}H_{38}N_4O_4Pd$ requires C, 60·7; H, 5·7; N, 8·3%); $\lambda_{max.}$ 253·5, 296·5, 353, 413·5sh, 436·5, 615, and 658·5 nm (ε 19,790, 19,310, 15,690, 39,200, 68,570, 18,900, and 30,170); τ 0·05, 0·39, and 1·4 (3 × *meso*-H, all s), 5·3 (4H, m, ester CH_2·CH_3), 6·2 (3H, s, 18-CH_3), 6·45 (4H, m, nuclear CH_2·CH_3), 6·58 (3H, s, 2-CH_3), 6·87 (6H, s, 7- and 13-CH_3, s), 8·35 (12H, m, nuclear and ester CH_2·CH_3), and 11·33 (3H, s, NMe).

(*b*) 3,17-Bisethoxycarbonyl-8,12-diethyl-2,7,13,18,21-pentamethyl-20-thiaphlorin (100 mg) was dissolved in glacial acetic acid (10 ml) and palladium acetate (80 mg) was added. The solution was boiled for 2 min, cooled, and poured into water (200 ml). After work-up in the usual way, the product (31 mg, 27%) crystallised from chloroform–light petroleum as dark purple prisms, m.p. 185—186°, and was identical with that prepared in (*a*).

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