Preparation of Some Sulphur-containing Polypyrrolic Macrocycles. Sulphur Extrusion from a *meso*-Thiaphlorin

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Summary The preparation of a *meso*-thiaphlorin, *meso*-thiaporphin, and a porphin analogue containing two thiophen rings is described together with several examples of extrusion of sulphur from polypyrrole macrocycles.

IN a previous communication[1] we described a reaction involving loss of sulphur, which may have proceeded *via* a non-aromatic 20 π-electron macrocyclic intermediate (I; X = O), capable of extruding sulphur by a disrotatory cyclisation (I) followed by a cheletropic reaction (Ib; arrows) generating an aromatic product (II; X = O). This combination of pericyclic processes occurs in other heterocyclic systems.[2] The oxidation level of the suggested intermediate (I) is that of a dihydroporphin (phlorin) and Hückel molecular orbital calculations for the *meso*-thiaphlorin (I; X = NH) and the thiophen analogue (I; X = S) indicated a similar extrusion process was allowed from orbital symmetry considerations. The synthesis and isolation of a stable *meso*-thiaphlorin has now been achieved and extrusion of sulphur observed. The formylpyrrole (III) reacted with sulphur dichloride in boiling ethylene dichloride to give the dipyrrolyl sulphide (IV; 50%), m.p. 264—267°.† The sulphide (IV) was condensed with the dipyrromethane (V) in chloroform at 0°, using dry hydrogen chloride as catalyst, to give a blue, air-stable, crystalline product formulated as the *meso*-thiaphlorin (VI; R = H; 52%), m.p. > 300°, $\lambda_{\max}$ ($CHCl_3$) 249, 315, 396, and 639 nm, ϵ 24,400, 19,700, 46,700, and 15,400, respectively.

Evidence for the non-aromatic *meso*-thiaphlorin structure was provided by the n.m.r. spectrum ($CDCl_3$) in which the *meso*-proton signals occurred at τ 2·43 (2H) and 3·7 (1H) and the imino-proton signals at τ 5·44 demonstrating the absence of a diamagnetic ring current. Alkylation of (VI; R = H) with methyl iodide in the presence of di-isopropylethylamine gave the *N*-methyl compound (VI; R = Me; 75%), m.p. 220—222° (d), [$\lambda_{\max}$ ($CHCl_3$) 248·5,

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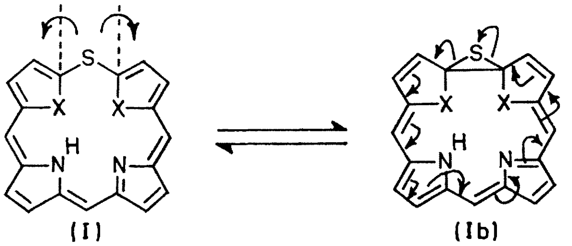
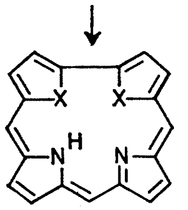
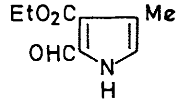
† Satisfactory microanalytical and mass-spectral data have been obtained for all new compounds.

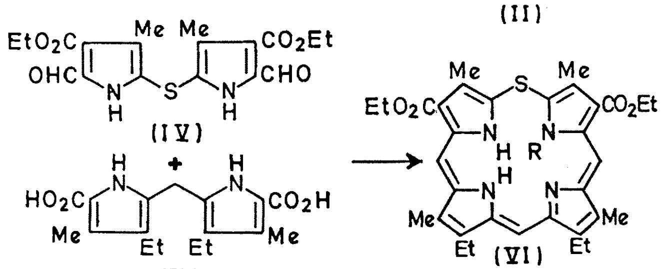
390, and 617 nm, ϵ 24,040, 28,250, and 16,590, respectively; λ_{infl} 353·5 nm, ϵ, 22,510] in which the *N*-methyl group resonated at τ 7·08 in the n.m.r. spectrum ($CDCl_3$) and the *meso*-protons at τ 2·17 (1H), 3·16 (1H), and 3·94 (1H); providing further evidence for the absence of a ring current.

(I) (Ib) (II)



(III)

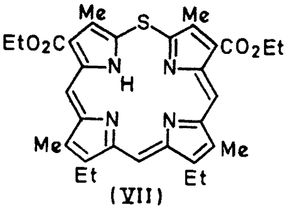


(IV) (V) (VI)

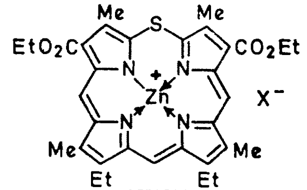
Alkylation on the ring adjacent to the sulphur bridge was indicated by an upfield shift, in the n.m.r. spectrum, of one β-methyl group and an ester ethyl group. Shifts of this nature are characteristic for *N*-alkylated macrocycles.[3] The mass spectra of (VI; R = H or Me) exhibited parent ions at *m/e* 586 and *m/e* 600, respectively, as required by the thiaphlorin formulation. However, this was not regarded as conclusive owing to the tendency of some polypyrrolic macrocycles to give strong $P + 2$ ions.[4]

Confirmation of the phlorin oxidation level of (VI; R = H) was obtained by oxidation of (VI; R = H) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone which caused an immediate colour change, in the cold, from blue to green giving an unstable solution of the *meso*-thiaporphin (VII). The visible spectrum of (VII) was very similar, apart from a bathochromic shift caused by the ester substituents, to that reported by Harris[5] for an unstable *meso*-thiaporphin. A stable cationic zinc complex (VIII; 75%), m.p. > 300°, could be prepared from solutions of the unstable *meso*-thiaporphin. The same zinc complex could be prepared from the *meso*-thiaphlorin in the presence of air, but not in the absence of air, implicating an oxidation step. The zinc complex (VIII) had a typically aromatic n.m.r. spectrum [$CDCl_3$; *meso*-protons at τ −0·47 (2H) and 0·36 (1H)].

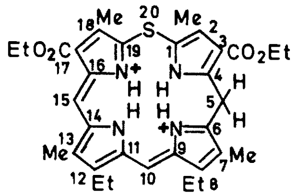
The electronic spectrum of the *meso*-thiaphlorin monocation (*N*-protonation) was similar to that of phlorin monocations (Figure) but addition of a second proton (trifluoroacetic acid) occurred at the *meso*-position adjacent to the sulphur bridge (IX), τ 1·7, 2·42 (C-10 and C-15 protons), and 4·95 (C-5 protons), in contrast to phlorins which are reported[6] to give (X). Rapid exchange of all the *meso*-protons of (VI; R = H) occurs in deuteriotrifluoroacetic acid in less than 10 min.



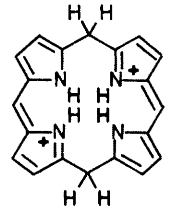
(VII)



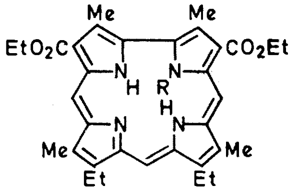
(VIII)



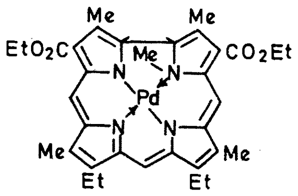
(IX)



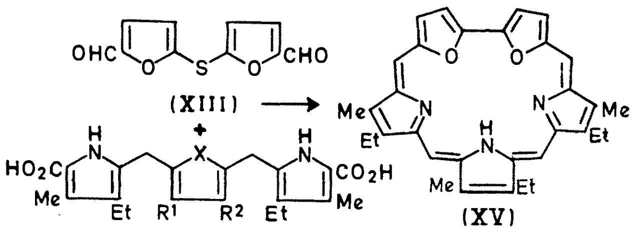
(X)



(XI)



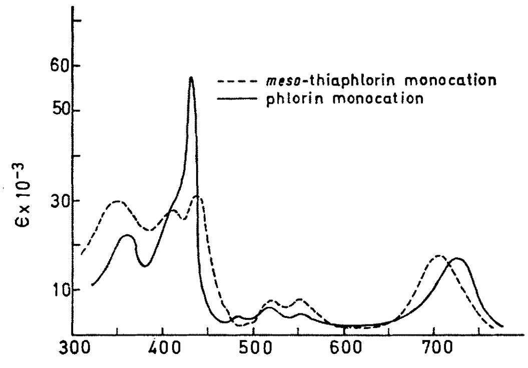
(XII)



(XIII) (XV)

(XIV) (a) X = NH, R^1 = Me, R^2 = Et

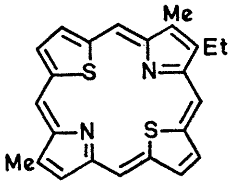
(b) X = S R^1 = R^2 = H



FIGURE

When the *meso*-thiaphlorin (VI; R = H) was heated in *o*-dichlorobenzene for 2 hr. the expected sulphur extrusion was realised, generating the corrole (XI; R = H; 40%), m.p. 210—212°; $\lambda_{\max}$ (CHCl$_3$) 402·5, 420, 590, and 618 nm, ϵ 69,000, 55,490, 28,200, and 32,280, respectively; λ_{infl} 510 and 571 nm; ϵ 15,860 and 19,300, respectively. When the reaction was repeated in the presence of a large excess of hydroquinone or of 4-t-butylcatechol there was no diminution in the yield of corrole, which militates against a radical process. In contrast, addition of triphenylphosphine increased the yield of corrole (XI; R = H) to 60%. The *N*-methylthiaphlorin (VI; R = Me) extruded sulphur, in boiling *o*-dichlorobenzene, at a much slower rate than (VI; R = H) and a considerable amount of (VI; R = Me) could be recovered after 12 hr. at 180°. This reflects the steric influence of the *N*-methyl group, but also indicates the stability of the sulphide linkage to radical cleavage. When (VI; R = Me) was heated for 3 hr. at 213° (trichlorobenzene) in the presence of triphenylphosphine, the *N*-methyl-corrole (XI; R = Me; 85%) was obtained, m.p. 207—208°; τ (CDCl$_3$) 0·81, 1·1, 2·1 (all s, *meso*-protons) and 11·03 (s, 3H, N–Me). Extrusion of sulphur from (VI; R = Me) occurs rapidly in boiling acetic acid in the presence of palladium acetate to afford some palladium *N*-methylcorrole (XII; *ca.* 30%), m.p. 185—186°; no extrusion occurs in the absence of palladium acetate. The n.m.r. spectrum of (XII) contained *inter alia* resonances at τ 0·05, 0·39, 1·40 (all s, *meso*-protons), and 11·33 (s, 3H, N–Me).

(XVI)



(XVII)

What may be an analogous case of sulphur extrusion occurs when the diformyl-difuryl sulphide (XIII) is condensed with the di(pyrrolylmethyl)pyrrole diacid (XIVa), in the presence of hydrogen bromide, followed by oxidation with iodine. The product (XV; 20%) is identical with that prepared by a rational synthesis.[1]

Aromatic macrocycles in which sulphur is present in thiophen rings embedded in the π-electron chromophore are more stable than the *meso*-thiaporphins. We previously reported two macrocycles containing one thiophen ring[7] and have now prepared a porphin analogue containing two thiophen rings. Condensation of the diformylthiophen (XVI) with the di(pyrrolylmethyl)thiophen diacid (XIVb) gave the macrocycle (XVII; 11%), m.p. > 300°, as grey-brown needles. The macrocycle (XVII) exhibited a Soret band in its electronic spectrum [*i.e.* (pyridine) $\lambda_{\max}$ 402, ϵ 64,900; (trifluoroacetic acid) $\lambda_{\max}$ 412, ϵ 156,200] and the *meso*-protons resonated, in the n.m.r. spectrum, at the low τ values [CDCl$_3$; −0·71 (2H), −0·68 (1H)] characteristic of an aromatic macrocycle of this type.

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[3] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.

[4] M. J. Broadhurst, R. Grigg, G. Shelton, and A. W. Johnson, *Chem. Comm.*, 1970, 231.

[5] R. L. N. Harris, *Tetrahedron Letters*, 1969, 3689. We thank Dr. Harris for his interest and for a copy of his manuscript before publication.

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[7] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *Chem. Comm.*, 1969, 1480.