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A *Meso*THIAPORPHYRIN

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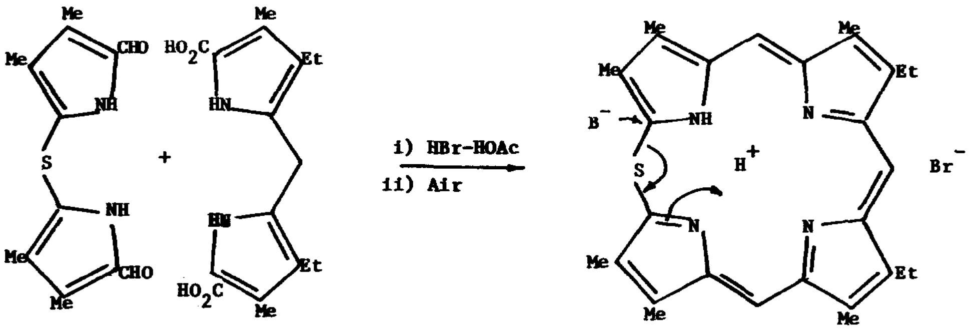
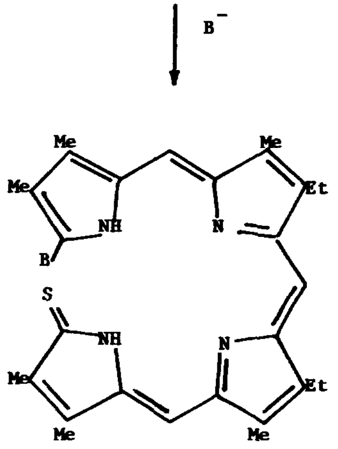
Analogues of the porphyrins in which one or more of the methene bridges is replaced by nitrogen (the azaporphyrins) have been known for many years[1] and a rational synthesis of monoazaporphyrins has been described recently.[2] This communication reports the synthesis of a monothiaporphyrin in which one methene bridge is replaced by sulphur.

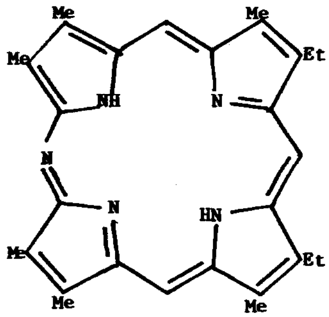
Reaction of 3,4-dimethyl-2-formylpyrrole[3] with one half mole equivalent of sulphur dichloride in dry ether gave poor yields of the dipyrrolyl monosulphide dialdehyde (I) (Anal. Found: C,61.1; H, 5.8; N, 10.4. $C_{14}H_{16}O_2N_2S$ requires C, 60.8; H, 5.8; N, 10.1%. Mol. wt. (mass spectrum) 276). This dialdehyde was condensed with the dipyrrolylmethane diacid (II)[4] in glacial acetic acid - hydrobromic acid, the solution buffered by the addition of anhydrous sodium acetate and aerated to give the thiaporphyrin (III) in 25-30% yield. The product crystallised from the reaction mixture as its monohydrobromide (Anal. Found: C, 63.2; H, 6.0; N, 10.2; S, 6.3; Br, 13.9. $C_{29}H_{33}N_4SBr$ requires C, 63.4; H, 6.0; H, 10.2; S, 5.8; Br, 14.6%. λ_{max} ($CHCl_3$) 309, 390, 529, 566, 610 sh and 666 mμ. ε 19750, 62600, 3570, 3200, 5160, 7150 and 30800 respectively). The insolubility of (III) precluded the measurement of its n.m.r. spectrum and a mass spectrum could not be obtained because of decomposition at elevated temperatures (sulphur detected). Attempts to prepare the free base by treatment of the hydrobromide salt (III) with methanolic ammonia gave as the major product a green crystalline compound formulated as the bilatriene (IV, B=MeO). (Anal. Found: C, 71.7; H, 7.4; N, 10.8; S, 6.5. $C_{30}H_{36}N_4SO$ requires C, 72.0; H, 7.2; N, 11.0; S, 6.4%). λ_{max} ($CHCl_3$) 323, 337 sh, 412 and 732 mμ, ε 40000, 38500, 47900 and 9000 respectively). The n.m.r. spectrum ($CDCl_3$) showed signals at δ1.15 (T, 6 protons, CH_3 of β-ethyl groups of pyrrole nuclei), δ1.52 and 2.09 (S and M respectively, 6 β-CH_3 groups of pyrrole nuclei), δ2.6 (Q, 4 protons, CH_2 of β-ethyl groups of pyrrole nuclei), δ3.7 (S, 3 protons, CH_3 of methoxy group) and δ6.02, 6.45 and 6.85 (3S, 3 *meso*protons). The two exchangeable NH protons were not detected even in scans 500 cps above or below TMS, but exchanged on deuteration. The mass spectrum



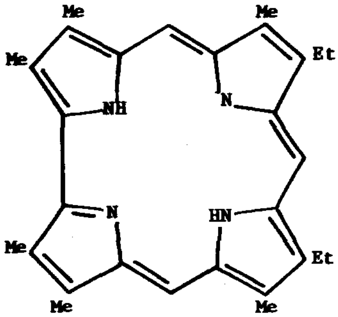
I II III



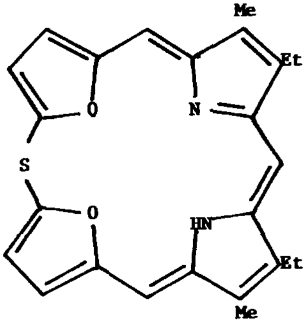
IV



V



VI



VII

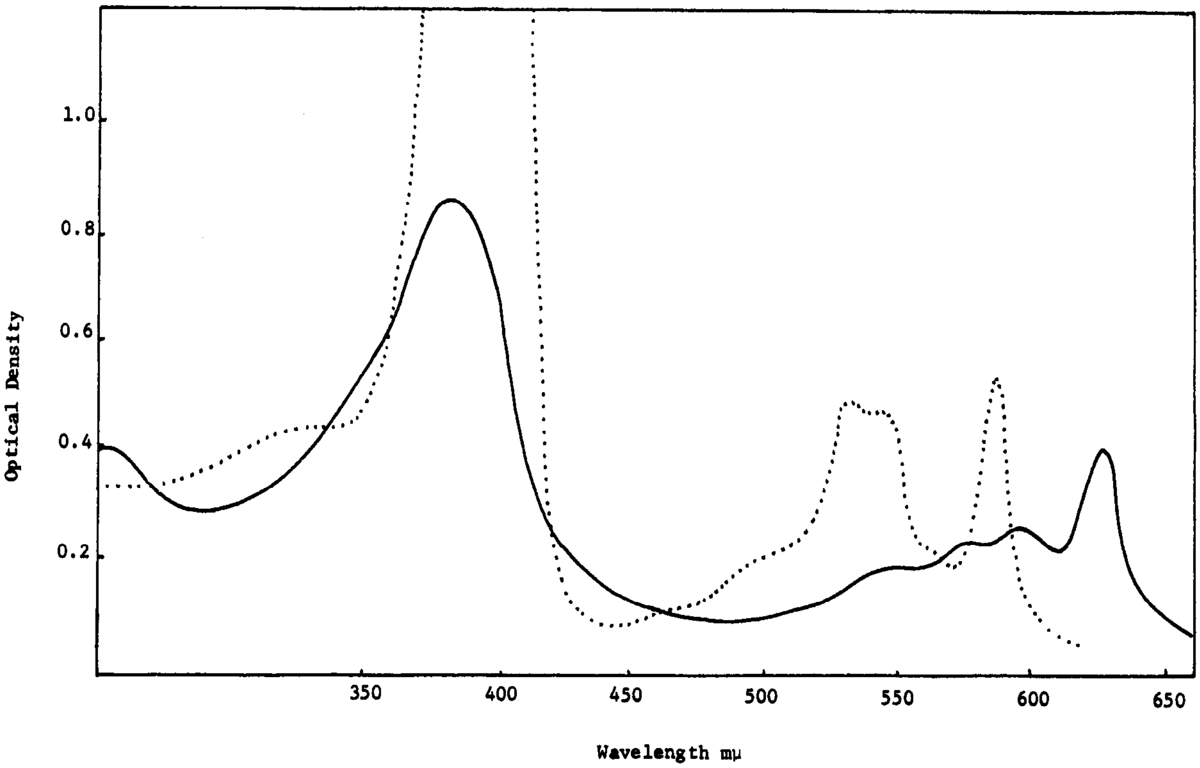


Fig. 1

Electronic Absorption Spectra of Thiaporphyrin (III) Free Base (——) and Corrole (VI) Free Base (·····) both at 2 x 10^{-5}M.

showed a molecular ion at m/e 500 and fragment ions corresponding to the loss of Me, S and ethylene. The spectral evidence is consistent with the bilatriene structure (IV, B=MeO). A minor by-product obtained in the methanolysis reaction was identified as the azaporphyrin (V), characterised by UV spectra (λ_{max} in $CHCl_3$ 375, 506, 536, 561 and 612 mμ[5]) and conversion to the copper complex, mol. wt. (mass spectrum) 512. The ring-opening of the thiaporphyrin is assumed to involve attack by base at the sulphide bridge (III → IV); when the base is methoxide the product is the methoxybilatriene (IV, B=MeO), and when the base is ammonia the corresponding aminobilatriene (IV, $B=NH_2$) is formed and recyclises with elimination of hydrogen sulphide to give the azaporphyrin (V).

Treatment of a suspension of the thiaporphyrin hydrobromide in dry chloroform with anhydrous triethylamine gave the corresponding free base in solution (λ_{max} ($CHCl_3$) 304, 384, 558, 578, 599 and 629 mμ, ε 21400, 47250, 8130, 10450, 14000 and 22300. Addition of hydrobromic acid in acetic acid regenerated the hydrobromide. The UV spectrum of the free base is similar to that of hexamethyldiethylcorrole (VI)[6] except that maxima in the visible region show a bathochromic shift of 40-50 mμ (Fig. 1). Attempts to isolate this free base in the pure state have so far been unsuccessful.

A recent communication[7] describes the synthesis of a furan-pyrrole macrocycle related to corrole involving extrusion of sulphur from an intermediate 20 π-electron sulphur-bridged system (VII, not isolated). Unlike (VII) the thiaporphyrin (III) is an 18 π-electron macrocycle, and this may explain why extrusion of sulphur in a similar manner to give the corresponding corrole (VI) was not observed.

References

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5. cf. the UV spectra of other monoazaporphyrins - refs. 1 and 2 above. The spectra contain four characteristic bands in the visible region, the intensity order being I (longest wavelength) > III >> II > IV
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