18- and 22-π-Electron Macrocycles Containing Furan, Pyrrole, and Thiophen Rings

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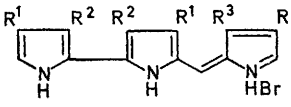
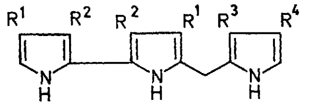
Summary The preparation of a number of novel aromatic macrocycles related to porphins, but containing furan and thiophen rings in addition to pyrrole rings, is described, together with deuterium exchange studies on some of the macrocycles.

PERTURBATIONS of the aromatic π-electron system in porphins by *meso*-, nitrogen-, and β-substituents has been the subject of both experimental[1] and theoretical[2] investigations. The effect of substituting other hetero-atoms for the pyrrole nitrogen atoms, increased ring size, and replacement of methine bridges by direct links is virtually unexplored.[3] Structural variations of this type should provide further insights into the chemistry of large macrocycles of the porphin type and several new macrocycles of this kind have now been prepared.

Borohydride reduction of the pyrrolyldipyrromethenes (Ia and b) gave the corresponding pyrrolyldipyrromethanes (IIa and b) which were condensed, without isolation, with the bifuran dialdehyde (III) in the presence of hydrogen bromide. The macrocycles (IVa and b) which were produced (15—20%) had typically aromatic spectra [*e.g.* (IVa);

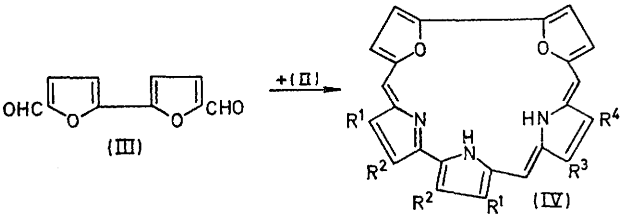


(I)



(II)

(a) $R^1 = R^3 = R^4 = Me, R^2 = H$
(b) $R^1 = R^3 = Me, R^2 = R^4 = Et$



λ_{max} (pyridine) 352, 442, 518, 547, 591, 655, 666, and 730 nm; ϵ 20,400, 201,200, 5340, 10,160, 39,390, 4540, 3970, and 9660 respectively; λ_{infl} 407 and 432 nm; ϵ 55,760 and 153,100; n.m.r. see Table 1].

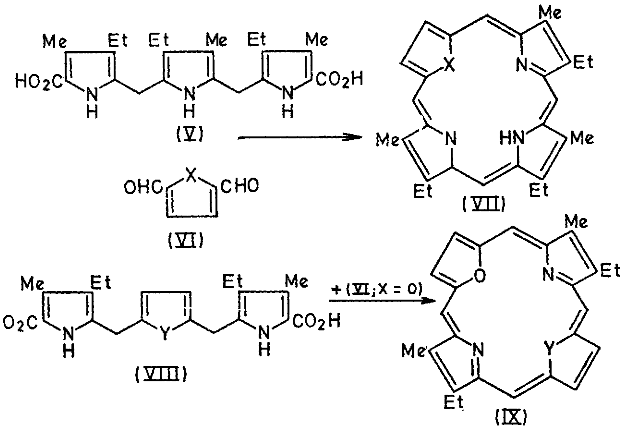
TABLE 1

N.m.r. signals (τ values)

	meso-protons	Furan/ thiophen protons	NH
(IVb)	−0·52(t, 1H), −0·06(s, 2H)	0·42(AB, 4H)	14·85(2H)
(VII; X = O)	−0·12(s, 2H), 0·02(s, 2H)	0·31(s, 2H)	not observed
(VII; X = S)	−0·06(s, 2H), 0·00(s, 2H)	0·02(s, 2H)	14·98(1H)
(IX; Y = O)†	−1·71(s, 4H)	−0·98(s, 4H)	—
(IX; Y = S)	−0·59(s, 2H), −0·05(s, 2H)	−0·01 (s, 2H), 0·31(s, 2H)	—

† Dihydrobromide in trifluoroacetic acid solution.

A number of synthetic approaches to the construction of the porphin ring have been successful.[4] For the synthesis of porphins in which one or more pyrrole rings have been replaced by furan or thiophen rings we have found the hitherto unreported 3 + 1 approach most useful. Thus, acid-catalysed condensation of the di(pyrrolylmethyl)-pyrrole diacid (V) with the dialdehydes (VI; X = O or S)



gave the macrocycles (VII; X = O, 25%; X = S, 12%). Similarly, the di(pyrrolylmethyl)furan and thiophen diacids (VIII; Y = O or S) reacted with the dialdehyde (VI); X = O) to give the related macrocycles (IX; Y = O, 21%; Y = S, 5%). The di(pyrrolylmethyl)furan diacid (VIII; Y = O) was prepared by Friedel–Crafts reaction of the furan (X) and the pyrrole (XI) followed by saponification. A similar series of reactions gave the thiophen analogue (VIII; Y = S).

The n.m.r. spectra ($CDCl_3$) of the new macrocycles (as free bases) convincingly demonstrates their ability to sustain a large induced diamagnetic ring current (Table 1) and all exhibited intense Soret bands (Table 2, free bases in pyridine).

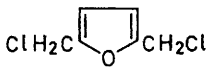
Preliminary studies show that (VII; X = O) forms charged nickel, copper, and zinc complexes, and (VII; X = S) forms a somewhat unstable zinc complex. Deuterium exchange studies in deuteriotrifluoroacetic acid (0·25 M-solutions) at 100° highlighted reactivity differences between the various macrocycles. In contrast to alkylcorroles[5] (XII; X = NH, $R^1 = R^2$ = alkyl) in which the *meso*-protons exchange rapidly at 35°, the *meso*-protons of (XII; X = O, R^1 = H, R^2 = Et)[3] were unchanged at 35°. Virtually complete exchange occurred, however, after 1 hr.

TABLE 2

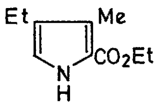
	Soret band(s) nm	ϵ
(VII; X = O)	374, 398	92,500, 92,500
(VII; X = S)	403	117,200
(IX; Y = O)‡	380	187,700
(IX; Y = S)	391	100,400

‡ Dihydrobromide in ethanol solution.

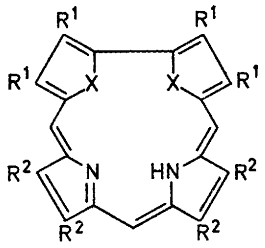
at 100° but no exchange of the β-protons of the furan rings had occurred after 100 hr. at 100°. No detectable exchange of *meso*- or β-protons of (VII; X = O) had occurred after 100 hr. at 100° whereas in the 22-π-electron macrocycle[3]



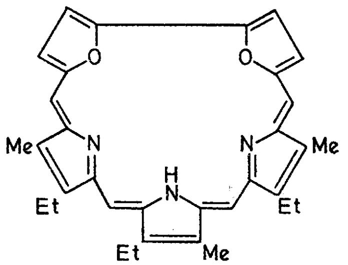
(X)



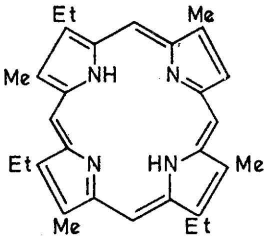
(XI)



(XII)



(XIII)



(XIV)

(XIII) two of the *meso*-protons exchanged with $t_{\frac{1}{2}} = 2·2$ hr. Exchange of the remaining two *meso*-protons had proceeded to only a small extent after 100 hr. at 100° and no exchange of the β-protons on the furan rings was observed.

The slow exchange of the *meso*-protons of porphins in deuteriated acids is well known, but bromination studies have indicated that the β-positions of the pyrrole rings in porphins are much more reactive. To provide a direct comparison with our new macrocycles we looked at the exchange rate of the β-proton in (XIV) and found no detectable exchange had occurred in deuteriotrifluoroacetic acid (0·25 M-solution) after 100 hr. at 100°. We were unable to study exchange rates of (IV) and (VII; X = S) in deuteriotrifluoroacetic acid owing to marked broadening of the spectra presumably due to formation of radical species.[6]

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