New Macrocyclic Aromatic Systems Related to Porphins

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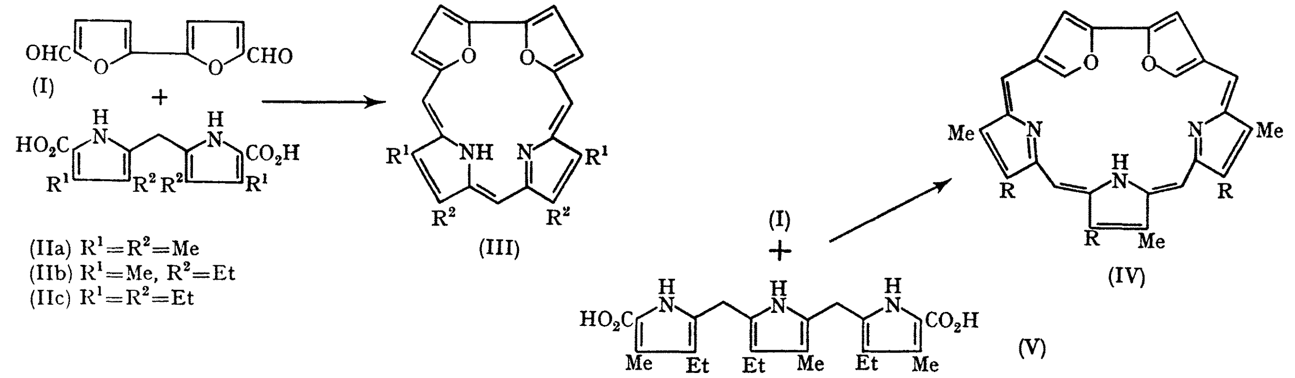
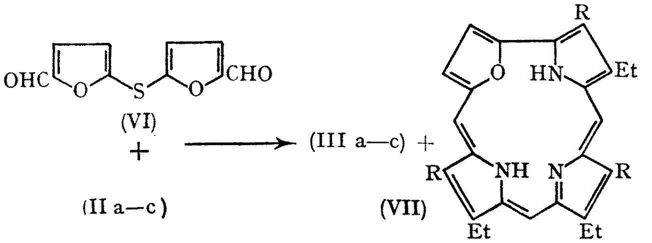
THE validity of Hückel's rule in polypyrrolic macrocycles such as porphins and corroles has been amply demonstrated by both their physical (*e.g.* n.m.r.) and their chemical properties. More recently a number of polyfuran[1] and furan–thiophen[2] macrocycles have been prepared, some of which show evidence of π-electron delocalisation and aromaticity.



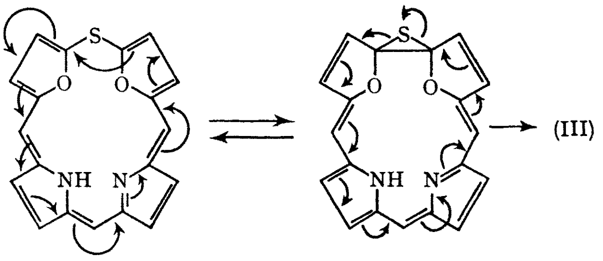
(IIa) $R^1 = R^2 = Me$
(IIb) $R^1 = Me$, $R^2 = Et$
(IIc) $R^1 = R^2 = Et$

We now report the first examples of furan–pyrrole macrocycles.† A projected rational synthesis of the macrocycle(III) by acid-catalysed condensation of the bifuran dialdehyde (I) with the dipyrrolylmethane diacid (IIa) gave a low yield (7%) of the expected product (IIIa) together with another macrocycle (5%), the n.m.r. spectrum of which clearly demonstrated the presence of three pyrrole and two furan rings. A similar product (9%) containing three pyrrole and two furan rings was obtained from the condensation of (I) and (IIb). The structures of these by-products, which had clearly arisen from a cleavage-recombination reaction, were tentatively formulated as (IV; R = Me or Et). The structure of (IV; R = Et) was confirmed by a rational synthesis involving acid-catalysed condensation of the di(pyrrolylmethyl)pyrrole diacid (V) and bifuran dialdehyde (I).[3]



An improved synthesis (27—30%) of (IIIa—c) was achieved by acid-catalysed condensation of the diformyldifuryl sulphide (VI) with the dipyrrolylmethane diacids (IIa—c). By-products isolated in low yield (1—2%) in reactions involving (IIb) and (IIc) were assigned the structure (VII; R = Me or Et) on the basis of their spectral characteristics (u.v., n.m.r., and mass) and microanalyses.

The extrusion of sulphur in the formation of (IIIa—c) from the difuryl sulphide (VI) could be analogous to the extrusion of nitrogen from ring-expanded porphins[4] and of sulphur from certain corrin intermediates.[5] A Hückel molecular orbital calculation‡ on the non-aromatic 20π-electron system (VIII), a probable precursor of (III), indicates that the highest filled molecular orbital has the correct symmetry for a disrotatory ring closure to the valence tautomer (IX), which could then lose sulphur (IX; arrows) to generate the 18π-electron aromatic system (III).



The n.m.r. spectra ($CDCl_3$) of the furan–pyrrole macrocycles provide compelling evidence for their aromaticity (Table).

The n.m.r. spectrum of the 22π-electron macrocycle (IV) was of particular interest in view of the prediction[6] that

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† T. J. King and J. McC. Gourley of this department have prepared an analogue of the porphins containing two furan and two pyrrole rings (J. McC. Gourley, Ph.D. Thesis, Nottingham, 1967), but the finer structural details of this macrocycle are still being investigated.

‡ The parameters used were $h_{\ddot{S}} = h_{\ddot{N}} = 1{\cdot}5$, $h_{\dot{N}} = 0{\cdot}5$, $h_{\ddot{O}} = 2$, $k_{C-N} = 1$, $k_{C-O} = k_{C\cdot S} = 0{\cdot}8$.

TABLE

	N.m.r. signals (τ values) of *meso*-protons
(III; R^1 = Me, R^2 = Et)	0·75(s,2H), 0·82(s,1H)
(VII; R = Me)	0·51(s,1H), 0·67(s,1H), 0·76(s,1H)
(IV; R = Et)*	−2·28 (s,4H).

* Solution in deuteriochloroform–trifluoroacetic acid 4 : 1.

[4*n* + 2]annulenes should be aromatic up to and including [22]annulene whereas [26]annulene should be non-aromatic. The NH protons of the monoprotonated macrocycle (IV; R = Et) in deuteriochloroform–trifluoroacetic acid (4 : 1) resonated at τ 15·5 and 16·8, further demonstrating the large ring current in this macrocycle.

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[1] J. A. Elix, *Chem. Comm.*, 1968, **343**; G. M. Badger, J. A. Elix, and G. E. Lewis, *Austral. J. Chem.*, 1966, **19**, 1221.

[2] G. M. Badger, G. E. Lewis, and U. P. Singh, *Austral. J. Chem.*, 1966, **19**, 1461.

[3] R. B. Woodward (Aromaticity Conference, Sheffield, 1966) reported the preparation of a macrocycle analogous to (IV) but containing five pyrrole rings.

[4] R. Grigg, *Chem. Comm.*, 1967, 1238.

[5] A. Fischli and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1967, **6**, 866.

[6] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1965, **87**, 685.