The Synthesis of a New 22 π-Electron Macrocycle: Pentaphyrin

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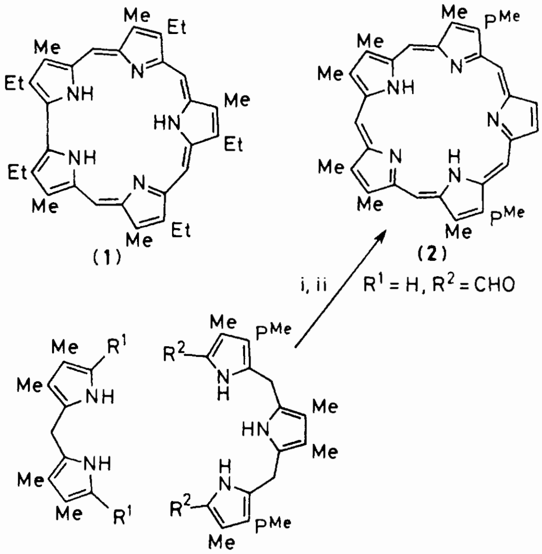
The first synthesis of a pentapyrrole macrocycle analogous to the porphyrins is described.

In contrast to the enormous amount of work on porphyrin chemistry,[1] only a few attempted syntheses of pyrrole macrocycles with more than four rings have been published until now.[2] In 1966 Woodward[3] reported the first example of this kind of compounds for which he coined the name sapphyrins. However, experimental details concerning the synthesis of the sapphyrin derivative (**1**) were not published until six years later by Johnson *et al.*[4] We now report the synthesis of compound (**2**) which is the first example of a 22 π-electron macrocycle analogous to the porphyrins (*i.e.* bearing five pyrrole rings and five methine bridges).† Thus, condensation of the known dipyrrylmethane (**3a**)[5] with the dialdehyde (**4c**) in the presence of 33% hydrobromic acid in acetic acid afforded, after oxidation with chloranil, the pentaphyrin (**2**) in 31% overall yield.‡

The dialdehyde (**4c**) was prepared from the corresponding dibenzyl ester (**4a**)[6] by hydrogenolytic cleavage of the benzyl ester groups and successive treatment of the dicarboxylic acid (**4b**) obtained with trifluoroacetic acid and triethyl orthoformate (*cf.* ref. 7).



(**3**)a; $R^1 = H$ (**4**)a; $R^2 = CO_2CH_2Ph$

b; $R^1 = CHO$ b; $R^2 = CO_2H$

c; $R^2 = CHO$

$P^{Me} = CH_2CH_2CO_2Me$

Reagents: i, HBr–AcOH; ii, chloranil.

It is noteworthy that the condensation of the dialdehyde (**3b**)[8] with the dicarboxylic acid (**4b**) in the presence of 33% hydrobromic acid in acetic acid yielded a porphyrin, instead of a pentapyrrole macrocycle, as the product. In fact, the latter approach has been found to be unsuccessful for synthesizing pentapyrrole macrocycles by other authors also.[2,9]

The structure of (**2**) was confirmed, *inter alia*, by fast-atom bombardment mass spectrometry,§ and u.v.–visible and ^1H and ^{13}C n.m.r. spectroscopy. In particular, the presence of three singlets (at δ 12.44, 12.46, and 12.55) for the methine protons with relative intensities 1 : 2 : 2 as well as three signals (at δ 99.864, 100.276, and 100.535 p.p.m.) for the methine C-atoms in the ^1H and ^{13}C n.m.r. spectra respectively¶ rules out isomeric structures with a lower symmetry than that corresponding to the point group C_{2v}. Moreover, the extremely high chemical shifts of the protons of the methine bridges and the peripheral methyl groups (δ 4.88, 4.86, and 4.84) agree with the postulation of a diamagnetic ring current within a delocalized 22 π-electron perimeter system. Like the sapphyrins, compound (**2**) displays an exceptionally strong visible absorption [λ_{max} (CH_2Cl_2): 367, 458, 642, and 695 nm; ϵ_{max} = 5 480, 238 000, 5 990, and 3 540 respectively].

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† In the phthalocyanine series, however, the synthesis of the uranyl chelate of a five-membered macrocycle corresponding to (**2**) has been reported (V. W. Day, T. J. Marks, and W. A. Wachter, *J. Am. Chem. Soc.*, 1975, **97**, 4519; T. J. Marks and D. R. Stojakovič, *ibid.*, 1978, **100**, 1695; E. A. Cuellar and T. J. Marks, *Inorg. Chem.*, 1981, **20**, 3766). Attempts to demetallate the complex led, unexpectedly, to the formation of phthalocyanine with loss of a phthalonitrile unit.

‡ In view of the synthesis of further polypyrrole macrocycles of the type described in this work, we suggest the trivial name pentaphyrin for the unsubstituted ring system corresponding to (**2**).

§ Using trifluoroacetic anhydride–glycerine as solvent: m/z 673 and 672 corresponding to $M^+ + 2$ and $M^+ + 1$ respectively.

¶ The 110.6 MHz ^{13}C and 400 MHz ^1H n.m.r. spectra were recorded in trifluoroacetic acid and in trifluoroacetic acid containing 1% $CDCl_3$ respectively.