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CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF PORPHIN AND SOME RELATED COMPOUNDS

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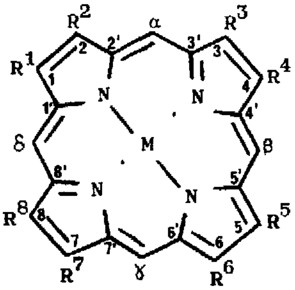
Carbon-13 NMR studies of the pyrrole-derived pigments continue to be of biological and theoretical interest.[1] For example, the nature of the rearrangement process central to the biogenesis of the type-III porphyrinogen skeleton has been delineated[2] using this technique, the critically important meso carbon assignments in protoporphyrin-IX being established using carbon-13 labelled compounds from an impressive synthetic programme. On the theoretical side, carbon-13 NMR arguments[3] for the 16-membered π-delocalisation pathway,[4] against which we have argued,[5] continue to be advanced.[6] In this letter we report the carbon-13 NMR spectra of porphin (**1**) (the basic porphyrin skeleton, free from extraneous substituent effects), and some derivatives (Figure); the spectrum of porphin in particular is of fundamental importance in our longer term aim to obtain a unique and unambiguous method for assignment of all carbon atoms in porphyrins, and as a basis for any future theoretical developments. Moreover, these shifts provide yet more evidence against the 16-membered pathway for π-electron delocalisation in the porphyrin nucleus.

With the exception of porphin (**1**), all spectra were run on the Varian XL-100 spectrometer in $CDCl_3$ containing a slight excess of pyrrolidine. Because of its low solubility (saturated solution, ca. 5 x 10^{-5}M), the proton NMR spectrum of porphin (**1**) was measured only recently;[7] the carbon-13 spectrum was therefore determined using the Bruker WH 180 spectrometer, operating at 44.28 MHz and using a 25 mm sample tube.[8]



(1) M = 2H; R$^{1-8}$ = H

(2) M = Zn; R$^{1-8}$ = H

(3) M = Zn; R^{1,4,5,8} = Me; R^{2,3} = H; R^{6,7} = P

(4) M = Zn; R^{1,3,5,8} = Me; R^{2,4} = H; R^{6,7} = P

P = $CH_2CH_2CO_2Me$

FIGURE

TABLE: Carbon-13 Chemical Shifts (δ, p.p.m. downfield from internal tetramethylsilane) of Porphyrins in $CDCl_3$ Solution.

Compound	α-Pyrrole	β-Pyrrole	meso	Me	Me(5,8)	CH_2 - CH_2 - CO_2-Me
(1)	[a]	131.5	104.4			
(2)[b]	149.3	131.7	104.3			
(3)[b]	148.8(2',3')	129.2(2,3)	103.0(α)	13.7 (1,4)	11.8	22.2, 37.4, 173.5, 51.5
	148.0(1',4',5',8')	140.4(1,4)	96.9(β)			
		136.7(5,8)	96.2(γ)			
	147.3(6',7')					
		138.7(6,7)	96.9(δ)			
(4)[b]	148.8	129.2 129.1 (2,4)	100.4(α)	13.7 (1,3)	11.7	22.2, 37.4, 173.6, 51.5
	148.7		99.2(β)			
	148.5	140.6 140.3 (1,3)	95.9(γ)			
	148.1					
	147.9	138.7 138.5 (6,7)	97.2(δ)			
	147.5					
		136.8(5,8)				

[a] Not observed. [b] Excess pyrrolidine added. Numbers in parentheses refer to carbon atoms indicated in Figure.

Although zinc(II) porphin (2) was virtually insoluble in $CDCl_3$, addition of ca. 2 equiv. of pyrrolidine dramatically increased the solubility and a spectrum was readily obtained on the XL-100 with 10 mg dissolved in ca. 0.5 ml $CDCl_3$. For consistency, the spectra of zinc(II) deuteroporphyrin-III (3) and zinc(II) deuteroporphyrin-IX (4) were obtained under similar conditions in presence of pyrrolidine, even though these compounds were considerably more soluble in $CDCl_3$ than was zinc(II) porphin (2). The importance of the addition of pyrrolidine to obtain spectra of metalloporphyrins in the "disaggregated" state has been discussed elsewhere.[9]

The assignments (Table) in the spectra of (1) and (2) are straightforward; the α-pyrrole carbon resonances in (1) were not observed, presumably due to broadening through NH tautomerism.[10] Assignments in (3) were aided by the molecular symmetry. For example, the two isochronous meso carbons must be the β and δ carbons. The almost complete assignments in (3) and (4) follow by comparison with other zinc(II) porphyrins.[9,11]

The shifts observed are of considerable interest. We note that the β-pyrrole and meso carbon atoms of zinc(II) porphin (2) (with added pyrrolidine) are identical with those of the free base (1), and this provides a theoretical rationale[12] for our use of these operating conditions in porphyrin NMR. The meso carbon chemical shifts can be differentiated simply by steric shifts caused by abutting peripheral substituents. With alkyl groups (methyl or propionate) the chemical shift is 96-97 δ, with one alkyl and a hydrogen it is 99-100 δ, and for two unsubstituted peripheral positions the shift is 103-104 δ. The low field shifts of the meso carbons in (1) and (2) provide further support for our earlier rejection[5] of the carbon-13 NMR evidence cited[3] in favour of the 16-membered pathway for π-electron delocalisation in the porphyrin nucleus, inasmuch as the suggestion[3] was based on the difference in chemical shifts of the β-pyrrole and meso carbons. The spectra herein reveal that 10 p.p.m. of this difference is simply due to the alkyl substituents commonly encountered in the porphyrin ring. The fundamental carbon-13 shifts of the porphyrin skeleton presented in the spectra of (1) and (2) provide no support for the 16-membered pathway hypothesis.

Acknowledgements

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References and Notes

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8. 25 ml of a saturated solution of porphin in $CDCl_3$ was used; this corresponds to only 0.5 mg porphin (**1**).
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12. We presume that the zinc(II) atom coordinates with one molecule of pyrrolidine, and that there is a concomitant change in geometry to square pyramidal, *cf.* J.L. Hoard, in Ref. 1, p. 345.