The Nuclear Magnetic Resonance Spectra of Porphyrins. Part VIII.[1] The ^{13}C Nuclear Magnetic Resonance Spectra of Some Porphyrins and Metalloporphyrins [2]

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The ^{13}C n.m.r. spectra of the methyl esters of the four coproporphyrin type-isomers and deuteroporphyrin-IX, and of octaethylporphyrin, and the zinc(II), thallium(III), and some diprotonated derivatives are reported and assigned. An immediate differentiation between the coproporphyrin type-isomers is provided by the spectra; the shifts of the *meso* and ' pyrrole ' ring carbons are influenced by the adjacent peripheral substituents. The pattern of these carbon chemical shifts, when taken with other evidence, supports the 18 atom π-electron delocalisation pathway in these molecules. This conclusion is contrary to that of other workers, and illustrates the dangers of relying solely on ^{13}C shifts. A novel phenomenon in the spectra is line-broadening of the ' α-pyrrole ' carbon resonances in the neutral molecules, but not in the diprotonated or metal derivatives. This is attributed to NH tautomerism, and support for this is obtained from the spectra of the *N*-deuteriated species. Protonation of coproporphyrins gives upfield shifts of the ' α-pyrrole ' carbons and downfield shifts of the ' β-pyrrole ' and *meso*-carbon resonances; analogous behaviour has been observed earlier in other nitrogen heterocycles. The thallium(III) derivatives show extensive Tl–^{13}C couplings, the two-bond Tl–' α-pyrrole ' carbon couplings (15—20 Hz) being substantially less than the three-bond Tl–' β-pyrrole ' carbon (104—109 Hz) and Tl–*meso*-carbon (145—147 Hz) couplings; comparisons can again be drawn with other metal–carbon couplings. These couplings appear to be primarily due to the contact mechanism.

THE ^{13}C n.m.r. spectra of porphyrins are of considerable current interest. Recent studies have been concerned with the preferred pathway for electron delocalisation in the porphyrin ring,[2,3] pathways of biosynthesis,[4,5] and mechanisms of unpaired spin delocalisation in para-

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[1] Part VII, R. J. Abraham, G. H. Barnett, E. S. Bretschneider, and K. M. Smith, *Tetrahedron*, 1973, **29**, 553.

[2] Preliminary communication, R. J. Abraham, G. E. Hawkes, and K. M. Smith, *J.C.S. Chem. Comm.*, 1973, 401.

[3] D. Doddrell and W. S. Caughey, *J. Amer. Chem. Soc.*, 1972, **94**, 2510.

[4] A. R. Battersby, J. Moron, E. McDonald, and J. Feeney, *J.C.S. Chem. Comm.*, 1972, 920.

[5] A. R. Battersby, G. L. Hodgson, M. Ihara, E. McDonald, and J. Saunders, *J.C.S. Chem. Comm.*, 1973, 442.

magnetic metalloporphyrins.[6] We present here an extension of our preliminary communication,[2] aimed at establishing ^{13}C n.m.r. as an aid in the elucidation of structure and electronic configuration in this important class of compounds. The ^{13}C n.m.r. of the methyl esters of the coproporphyrins, deuteroporphyrin-IX, and of octaethylporphyrin and some dications and metal chelates are discussed, and detailed assignments are made.

EXPERIMENTAL

^{13}C N.m.r. spectra were obtained with modest quantities (20—100 mg) of samples dissolved in deuteriochloroform (1·5 ml) (*i.e.* 0·03—0·1M). The spectrometer was the Varian XL-100 instrument, operating at 25·2 MHz, in the Fourier transform mode, usually with noise modulated ^1H decoupling (3 kHz bandwidth), and in certain cases with single frequency off-resonance ^1H decoupling (s.f.o.r.d.). The sample temperature was *ca.* 35°. Spectra were usually obtained over a 5 kHz spectral width, with 2048 real points in the transformed spectrum. Pulse widths 35 μs (*ca.* 30° flip angle) were employed throughout. 12 mm Sample tubes were used, carrying an inner 5 mm tube of deuterium oxide for the field-frequency lock. Spectra at 22·6 MHz were provided by Dr. E. W. Randall, Queen Mary College.

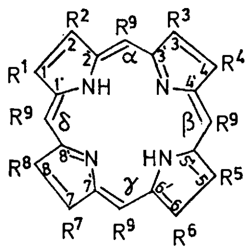
Details of the synthesis of the coproporphyrin esters,[1] their thallium(III) [1] and zinc(II) chelates,[7] and thallium(III) [8] and zinc(II) octaethylporphyrin [7] are already available in the literature.

*Aquo-*6,7-*bis*(2-*methoxycarbonylethyl*)-1,3,5,8-*tetramethylporphinatothallium*(III) *Hydroxide* [' *Thallium*(III) *Deuteroporphyrin-IX Dimethyl Ester* (OH,H_2O) '].—Deuteroporphyrin-IX dimethyl ester (60 mg) (Koch–Light; pre-purified) in hot chloroform (35 ml) was treated with a solution of thallium(III) acetate (62 mg) in hot methanol (*ca.* 5 ml). The solution was heated under reflux during 20 min, after which time visible absorption spectroscopy showed metal insertion to be complete. After pouring the mixture into water and methylene chloride, the organic phase was washed twice with water, dried (Na_2SO_4), and evaporated to dryness. The residue was chromatographed (Merck neutral alumina, Brockmann Grade III), eluting initially with chloroform containing 2% methanol (to accomplish ligand exchange) and then with pure methylene chloride. The porphyrinic eluates were evaporated to dryness and the residue was crystallised from methylene chloride–n-hexane, to give the *thallium*(III) *chelate* (78 mg, 90%), m.p. 258—260° (Found: C, 49·3; H, 4·4; N, 7·1. $C_{32}H_{35}N_4O_6Tl$ requires C, 49·5; H, 4·55; N, 7·2%), *m/e* [9] 946 (3%), 944 (2), 942 (0·5), 776 (4), 774 (2), 741 (3), 739 (1), 538 (100), and 465 (50), $\nu_{max.}$ (KBr) 1721 cm^{-1} (C=O), $\lambda_{max.}$ (CH_2Cl_2) 415 (ε 313,500), 542 (30,100), and 580 nm (16,000).

This compound was not sufficiently soluble in $CDCl_3$ for a ^1H n.m.r. spectrum to be obtained and because of this, the ^{13}C n.m.r. spectrum was only partially satisfactory.

RESULTS AND DISCUSSION

^{13}C *Resonance Assignments for the Tetramethyl Esters of Coproporphyrins* I—IV.—The ^{13}C chemical shifts and assignments for the tetramethyl esters of coproporphyrins I—IV (copros I—IV) are shown in Table 1; the side-chain methyl and methyl propionate resonances were assigned with the aid of s.f.o.r.d. and by comparison with ^{13}C chemical shift correlations from standard sources.[10] The *meso*-carbon signals characteristically appear in the region *ca.* 96 p.p.m. downfield from tetramethylsilane.[3-5] The ^{13}C spectra of the different type-isomers are immediately distinguished by the *meso*-carbon fine structure, in a very similar manner to the ^1H spectra.[11] However, in contrast to the ^1H spectra of the neutral porphyrins, in which the fine structure of the *meso*-proton region disappeared upon dilution,[11] no such concentration effects were observed for the ^{13}C spectra. The number of, and relative intensity of the *meso*-carbon signals, apparently depends upon the *meso*-carbons being differentiated by the nearest substituents (Me, P) on the two adjacent ' pyrrole ' rings. Both copro-III and copro-IV have *meso*-carbons flanked by nearest ' pyrrole ' ring substituents Me–P, Me–P, Me–Me, and P–P, and two *meso*-carbon signals with a 3 : 1 intensity ratio are observed. For copro-II the pattern is Me–Me, Me–Me, P–P, and P–P and two *meso*-carbon signals of approximately equal intensity are observed. Our main problem was to distinguish between the resonances for the α- and β-' pyrrole ' type carbons * in the region 135—145 p.p.m.



	R¹	R²	R³	R⁴	R⁵	R⁶	R⁷	R⁸	R⁹
Copro-I	Me	P	Me	P	Me	P	Me	P	H
Copro-II	Me	P	P	Me	Me	P	P	Me	H
Copro-III	Me	P	Me	P	Me	P	P	Me	H
Copro-IV	Me	P	P	Me	P	Me	Me	P	H
OEP [a]	Et	Et	Et	Et	Et	Et	Et	Et	H
TPP [b]	H	H	H	H	H	H	H	H	Ph
Deut-IX [c]	Me	H	Me	H	Me	P	P	Me	H

$P = CH_2{\cdot}CH_2{\cdot}CO_2Me$

[a] Octaethylporphyrin. [b] *meso*-Tetraphenylporphyrin. [c] Deuteroporphyrin-IX dimethyl ester.

The 135—145 p.p.m. region of the spectra usually consisted of sharp, well defined resonances to higher field and a broad, weak resonance to lower field. Under certain conditions (*vide infra*) this broad resonance could be partially resolved. Battersby and his co-workers [4] have reported weak resonances in this same region. We assign the broad lower field resonances to the ' α-pyrrole ' carbon atoms. This is confirmed by (*a*) the similar

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* Carbon atoms 1—8 will be referred to as ' β-pyrrole ' and 1'—8' as ' α-pyrrole.'

[6] K. Wüthrich and R. Baumann, *Helv. Chim. Acta*, 1973, **56**, 585.

[7] G. H. Barnett, M. F. Hudson, S. W. McCombie, and K. M. Smith, *J.C.S. Perkin I*, 1973, 691.

[8] R. J. Abraham, G. H. Barnett, and K. M. Smith, *J.C.S. Perkin I*, 1973, 2142.

[9] *Cf.* K. M. Smith, *Org. Mass Spectrometry*, 1972, **6**, 1401.

[10] J. B. Stothers, ' Carbon-13 N.M.R. Spectroscopy,' Academic Press, London, 1972.

[11] R. J. Abraham, P. Burbidge, A. H. Jackson, and D. B. MacDonald, *J. Chem. Soc.* (*B*), 1966, 620.

TABLE 1

^{13}C Chemical shifts of some porphyrins and metalloporphyrins [a]

	Nuclear carbon atoms				Side-chain carbon atoms				
	Cα	$C_{\beta\text{-Me}}$	$C_{\beta\text{-P}}$	*meso*	Me	CH_2—	CH_2—	CO_2—	Me
Copro-I	143·5 [b]	136·2	137·9	96·4	11·8	22·0	37·1	173·0	51·8
Copro-II	144·2 [b]	135·9	137·9	96·4 (β, δ) 96·0 (α, γ)	11·6	21·8	35·8	172·8	51·5
Copro-III	144·0 [b]	135·8	137·8	96·4 (δ) 96·0 (α, β, γ)	11·4	21·7	36·8	172·8	51·5
Copro-IV	143·4 [b]	135·8 135·5	137·7 137·3	96·0 (γ) 95·8 (α, β, δ)	11·5 11·3	21·6	36·8	172·7	51·4
Zn(II)copro-I	146·6 145·6	135·9	137·7	96·0	11·5	21·8	36·9	172·8	51·5
Tl(III)copro-I (OH,H_2O)	147·5 (18) 146·5 (20)	138·4 (109)	139·9 (106)	98·1 (147)	11·7 (15)	22·2 (12)	36·9	173·0	51·8
Tl(III)copro-II (OH,H_2O)	147·3 (18) 146·5 (20)	138·0 (107)	139·9 (106)	98·0 (145)	11·8 (15)	21·9 (15)	36·6	172·7	51·5
Tl(III)copro-III (OH,H_2O)	148·4 (18) 148·2 (18) 147·6 (18) 147·4 (15)	138·1 (108) 139·2 (108)	140·6 (106) 140·9 (106)	97·9 (147)	11·8 (15)	21·9 (13)	36·6	172·7	51·6
Tl(III)copro-IV (OH,H_2O)	147·3 (17) 147·1 (17) 146·6 (18) 146·4 (19)	138·0 (108) 138·2 (108)	139·6 (105) 139·9 (106)	97·9 (β, γ, δ) (147) 98·1 (α) (145)	11·8 (15)	21·9 (13)	36·6	172·7	51·5
Copro-I (2H+) [c]	144·1 143·4	142·6	142·7	101·2	12·7	23·4	37·3	178·6	54·6
Deut-IX	143·3 144·2	135·8 (5, 8) 139·2 } (1, 3) 139·5 } 128·0 (2, 4)	137·4 } (6, 7) 137·7 }	95·1 } (γ, δ) 96·2 } 98·7 } (α, β) 99·5 }	11·3 (5, 8) 13·4 (1, 3)	21·5	36·7	172·8	51·4
Tl(III)deut-IX (OH,H_2O) [d]		129·8 (2, 4) (110)		97·5 } (150) } (γ, δ) 98·5 } (143) } 100·7 } (145) } (α, β) 101·5 } (145) }	11·9 (5, 8) (12) 13·8 (1, 3) (10)	22·0 (12)	36·6	172·8	51·6
OEP	?	140·9		96·0	19·7 (CH_2)	18·3 (CH_3)			
OEP [e]	142·2	141·1		96·8	19·8	18·0			
Zn(II)OEP [f]	146·7	141·1		96·2	19·8	18·8			
Tl(III)OEP (OH,H_2O)	146·6 (18)	142·7 (104)		97·7 (147)	19·9 (13)	18·4			
OEP(2H+) [c]	143·1	147·0		100·3	21·4	18·1			

[a] Solutions in $CDCl_3$, unless otherwise stated. Chemical shifts in p.p.m. downfield from internal tetramethylsilane (±0·1 p.p.m.). Values in parentheses beside chemical shifts are probable assignments and those beneath are Tl—^{13}C coupling constants in Hz (±2 Hz). [b] Broad (25—50 Hz), weak signals. [c] Solution in trifluoroacetic acid. [d] Owing to low solubility (*cf.* Experimental section) quaternary α- and β-' pyrrole ' signals were indistinguishable from baseline noise. [e] In presence of trifluoroacetic acid. [f] In presence of pyrrolidine (8 mg) to aid solubility.

TABLE 2

^{13}C Chemical shifts [a]

	C-1	C_{ortho}	C_{meta}	C_{para}	Substituents
C_6H_6	127·9				
$C_6H_5{\cdot}CH_3$	137·3	128·6	127·8	124·9	21·3
$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$	140·1	128·0 *	127·8 *	125·7	31·0, 35·8, 172·1, 60·1, 14·2
$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$ [b]	140·7	129·6 *	129·1 *	127·7	32·4, 37·8, 179·8, 64·4, 14·1

^{13}C Chemical shift substituent parameters [c]

	C-1	C_{ortho}	C_{meta}	C_{para}
$\cdot CH_3$	9·4	0·7	−0·1	−3·0
$\cdot CH_2{\cdot}CH_2{\cdot}CO_2Et$	12·2	0·1	−0·1	−2·2

[a] Chemical shifts in p.p.m. downfield from internal tetramethylsilane, measured on 1M solutions in $CDCl_3$. For assignments see D. Laver, E. L. Motell, D. D. Traficante, and G. E. Maciel, *J. Amer. Chem. Soc.*, 1972, **94**, 5335; G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972. [b] 1M Solution in trifluoroacetic acid. [c] Relative to benzene, positive values indicate resonance is to lower field in the substituted benzene.

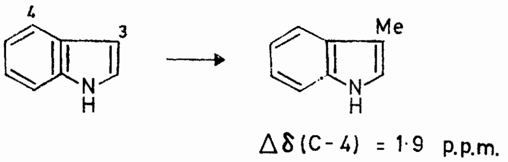
* These assignments may be interchanged.

assignment in TPP, which is unambiguous (from s.f.o.r.d. spectra), where the 'α-pyrrole' carbon (145·8 p.p.m.) shows a broad weak signal and the 'β-pyrrole' carbon resonates at 130·6 p.p.m. On this basis we might expect the 'α-pyrrole' carbon signals of other porphyrins to be broad. (*b*) The shifts produced by introducing a zinc atom; comparing the shifts obtained by Wüthrich and Baumann[6] for zinc(II)TPP (α and β-'pyrrole' carbons at 150·8 and 132·5 p.p.m. respectively) with those for TPP, the introduction of the zinc atom increases the shift differential between the α- and β-'pyrrole' carbon atoms by 3 p.p.m. This is exactly analogous to the case with copro-I (Table I), where the relative α,β-'pyrrole' carbon shift is increased by 2·5 p.p.m. with zinc.

In view of the substantial (*ca.* 2 p.p.m.) difference between the 'β-pyrrole' carbon resonances, we considered it reasonable to differentiate them as carrying a methyl or methyl propionate substituent. The basis for our assignment comes from comparison of the ^{13}C shifts in toluene and ethyl 3-phenylpropionate when compared to benzene; the ethyl propionate substituent is reasonably assumed to affect the benzene ring ^{13}C chemical shifts in the same manner as methyl propionate. The relevant chemical shifts and chemical shift substituent parameters are shown in Table 2.

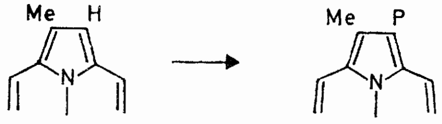
Assuming that similar substituent effects as determined for the benzene ring will apply to the porphyrin ring, the 'β-pyrrole' carbon with the propionate substituent is predicted to appear at *ca.* 3 p.p.m. lower field than that with the methyl substituent. The observed differential (Table 1) is *ca.* 2 p.p.m. This type of treatment assumes additivity of the substituent shift parameters and that any steric shift (induced by crowding of the Me and P groups) at the 'β-pyrrole' type carbons carrying the Me and P substituents is experienced equally by these two carbon atoms.

^{13}C *Resonance Assignments for Deuteroporphyrin-IX Dimethyl Ester and Octaethylporphyrin.*—Deuteroporphyrin-IX dimethyl ester was introduced into this study to elucidate the pattern of thallium–carbon couplings (*vide infra*). The ^{13}C spectrum of this molecule has been reported by other workers[3,4] but only partial assignments were given. From the assignments of the coproporphyrins, we are able to further assign the resonances of Deut-IX. The assignments in Table 1 for the side-chain methyl and methyl propionate carbons, and the 2- and 4-(unsubstituted) carbons are the same as reported by these previous workers.[3,4] The *meso*-carbon resonances may be divided into two groups, 95·1 and 96·2 p.p.m. and 98·7 and 99·5 p.p.m. The former range is close to that observed for the *meso*-carbon signals in the coproporphyrins, and accordingly, the high-field pair are assigned to the γ- and δ-*meso*-carbons. This assignment shows that substitution (by Me or P) at a neighbouring 'β-pyrrole' position shifts the *meso*-carbon signal upfield by *ca.* 3·5 p.p.m. This is comparable in magnitude and direction to the substituent induced shift at C-4 of indole[12] when a methyl group is substituted at C-3.



The quaternary pyrrole carbon region (135—145 p.p.m.) may be subdivided; the higher field portion (135—140 p.p.m.) showed five resonances in three groups, 135·8; 137·4 and 137·7; and 139·2 and 139·5 p.p.m., with each group of approximately equal intensity. These resonances are assigned to the six quaternary 'β-pyrrole' carbons and the two higher field groups have chemical shifts very close to those for the 'β-pyrrole' carbons C_β–Me and C_β–P of the coproporphyrins (*ca.* 136 and *ca.* 137·8 p.p.m. respectively); on this basis, the assignments in Table 1 are made. Comparison of these assignments indicates that for the substitution (1) the carbon carrying the methyl group experiences an upfield shift (*ca.* 4 p.p.m.), possibly steric in origin. In this context, both quaternary carbons of *ortho*-xylene (compared with benzene) experience an upfield shift contribution of *ca.* 2·3 p.p.m. not accountable by additivity of two methyl substituent induced shifts.[13]

The remaining portion of the spectrum, a broad partially resolved (maxima at 143·3 and 144·2 p.p.m.) signal, was assigned to the eight quaternary 'α-pyrrole' carbon atoms



(1)

For OEP, only one resonance was observed in the 135—145 p.p.m. region, and this was assigned to the 'β-pyrrole' type carbons. The 'α-pyrrole' carbon is presumably considerably broadened (Battersby and his co-workers[4] reported a weak resonance at 143·5 p.p.m.). Addition of a small quantity of trifluoroacetic acid (TFA) revealed two signals for this region, and increasing amounts of TFA resulted in a cross-over of these two signals ('β-pyrrole' carbon moves downfield, 'α-pyrrole' carbon upfield).

The spectrum of Zn(II)OEP was assigned, by analogy, without difficulty.

The Question of the Preferred Delocalisation Pathway.—Doddrell and Caughey[3] recently presented ^{13}C n.m.r. evidence for a preferred delocalisation pathway in porphyrins. As we intend to question their conclusions, we briefly outline available evidence on this topic.

Two extreme proposals for the aromatic delocalisation pathway in porphyrins are currently under consideration.[14] These are represented as structures A and B.

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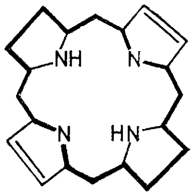
[12] R. G. Parker and J. D. Roberts, *J. Org. Chem.*, 1970, **35**, 996.

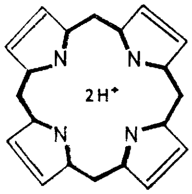
[13] W. R. Woolfenden and D. M. Grant, *J. Amer. Chem. Soc.*, 1966, **88**, 1496.

[14] E. B. Fleischer, *Accounts Chem. Res.*, 1970, **3**, 105.

For proposal A, there is an 18 atom pathway with the additional possibility of two or more tautomeric forms governed by the positions of the inner hydrogens. Proposal B features [15] a 16 atom pathway dianion (18 π-electrons) and the bonding to the inner hydrogens being ionic or dative through nitrogen. This latter proposal was consistent with the observation from *X*-ray crystallographic data that the four ' pyrrole ' rings were essentially equivalent, with the C_β–C_β bonds as almost pure double bonds, and that the two central hydrogen atoms were not localised to specific nitrogen atoms. Support for this proposal lies in the theoretical calculations of Gouterman [16] and others, on the electronic spectra of porphyrins. A third possibility is of course some hybrid of A and B. However, more recent *X*-ray studies [17] have shown two central hydrogens bonded to opposite nitrogens (N–H bond length *ca.* 0·86 Å) and also that opposite rings differ structurally from the other two. This would appear to favour proposal A. A further recent piece of evidence for proposal A comes from the variable temperature ^{1}H n.m.r. spectrum (100 MHz) of TPP in which two distinct types of ' β-pyrrole ' proton were observed [18] at −80°. These signals coalesced to a single line at 30°. More recently still, *X*-ray photoelectron spectroscopy has shown [19] two kinds of nitrogen in TPP.



A



B

Doddrell and Caughey [3] argue that since *meso*-carbon shifts (*ca.* 96—100 p.p.m.) are similar to shifts for β-carbons in simple unsubstituted pyrroles and the ' β-pyrrole ' carbons of porphyrins resonate in a normal olefinic range, this is evidence for the ' β-pyrrole ' type carbons to lie outside, and the *meso*-carbons to be in an aromatic delocalisation pathway. This would favour proposal B. Also, the bridging olefinic carbon of a pyrromethene resonates [3] *ca.* 20 p.p.m. to lower field than the *meso*-carbons of the porphyrins.

These data are very strong evidence for the *meso*-positions to be in the π-delocalisation pathway, but in no way do they exclude the ' β-pyrrole ' type carbons from the same pathway. For example, the ' α-pyrrole ' carbons resonate in the region 5—10 p.p.m. to lower field from the quaternary ' β-pyrrole ' carbons (Table 1); the shift difference between the α- and β-carbons of pyrrole itself [20] is *ca.* 10 p.p.m. in the same sense. If we were to follow this line of argument through, then we would arrive at the conclusion that the α- and β-' pyrrole ' type carbons of porphyrins must be in the same delocalisation pathway (proposal A). Thus it would seem that the majority of the available evidence now favours proposal A. The above discussion illustrates the dangers of using ^{13}C chemical shifts, without supporting evidence, to determine a subtle chemical problem such as aromatic delocalisation.

Line Broadening of the ' α-Pyrrole ' Carbon Signals.—Certain previous reports [2,4] of the ^{13}C n.m.r. spectra of porphyrins have noted the broad peaks due to the ' α-pyrrole ' carbons. Indeed, in some cases (*vide supra*) these are broadened beyond detection. This occurred also in our investigation and a typical example is shown in Figure 1. As yet there has been no quantitative explanation for this phenomenon.

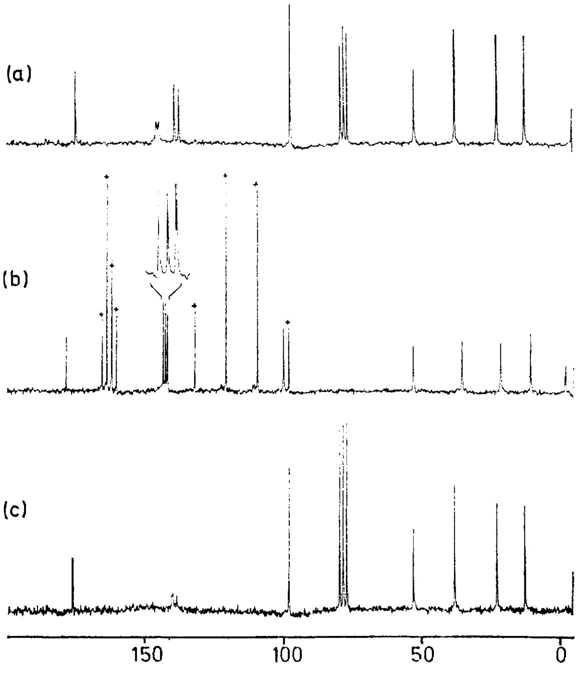


FIGURE 1 The ^{13}C spectrum of coproporphyrin-I tetramethyl ester: (a) 95 mg in 1·5 ml $CDCl_3$ (solvent passed through a short column of alumina); (b) 80 mg in 1·3 ml TFA, solvent peaks marked +; (c) *NN'*-dideuterio-species in $CDCl_3$

^{13}C Spectra of copro-I determined under certain conditions showed a partial resolution of the ' α-pyrrole ' carbon signal, with a chemical shift between the two maxima of *ca.* 0·8 p.p.m. (Figure 1). Taking the full linewidth of the unresolved band normally observed (*ca.* 40 Hz) to be the sum of two Gaussian line shapes superposed at a separation of 20 Hz (0·8 p.p.m.) yields an

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[15] E. L. Webb and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1965, **87**, 667.

[16] See M. Zerner and M. Gouterman, *Theor. Chim. Acta*, 1966, **4**, 44.

[17] S. J. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, 1967, **89**, 3331; B. M. L. Chen and A. Tulinsky, *ibid.*, 1972, **94**, 4144; P. W. Codding and A. Tulinsky, *ibid.*, p. 4151; for similar results using octaethylporphyrin see J. W. Lauher and J. A. Ibers, *ibid.*, 1973, **95**, 5148.

[18] C. B. Storm and Y. Teklu, *J. Amer. Chem. Soc.*, 1972, **94**, 1745.

[19] M. V. Zeller and R. G. Hayes, *J. Amer. Chem. Soc.*, 1973, **95**, 3855.

[20] T. F. Page, jun., T. Alger, and D. M. Grant, *J. Amer. Chem. Soc.*, 1965, **87**, 5333.

approximate value of 15—20 Hz for the full linewidth of each ' α-pyrrole ' carbon signal (*cf. ca.* 2 Hz for other ^{13}C resonances in the spectrum); thus, we are looking for a mechanism which may contribute *ca.* 40—55 s^{-1} to the ' α-pyrrole ' carbon spin–spin relaxation rate. This mechanism must be absent for the metalloporphyrins and diprotonated species, because for these, sharp ' α-pyrrole ' carbon signals are observed.

We have considered two principal sources for the broadening of the ' α-pyrrole ' carbon signals in the porphyrin free bases. The first is ' scalar relaxation of the second kind ' at carbon induced by rapid quadrupolar relaxation of the nitrogen. To estimate this effect we first require an approximation of the ^{14}N relaxation time (T_1^{N}); the quadrupolar relaxation rate is given[21] by equation (2) in the limit of ' extreme

$$\frac{1}{T_{1Q}^{N}} = \frac{1}{T_{2Q}^{N}} = \frac{3}{40}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2\tau_c \quad (2)$$

narrowing ' and assuming isotropic reorientation; η is the field gradient asymmetry parameter, which usually has values $\lesssim 10\%$, and we shall neglect this completely. e^2qQ/h is the quadrupole coupling constant, and τ_c the reorientational correlation time. As order of magnitude estimates, we take the value for e^2qQ/h in the range[22] 4—5 MHz, and the correlation time τ_c in the range[23] 100—200 × 10^{-12} s. These values in equation (2) yield $T_{1Q}^{N} = T_{2Q}^{N} = 1{\cdot}4$—$4{\cdot}2 \times 10^{-5}$ s. The effect upon the ^{13}C spin–spin relaxation rate, by the scalar coupling mechanism of the second kind is given by equation (3)

$$\frac{1}{T_{2SC}^{C}} = \frac{A^2}{3} I(I+1)\left(T_1^{N} + \frac{T_2^{N}}{1+(\Delta\omega T_2^{N})^2}\right) \quad (3)$$

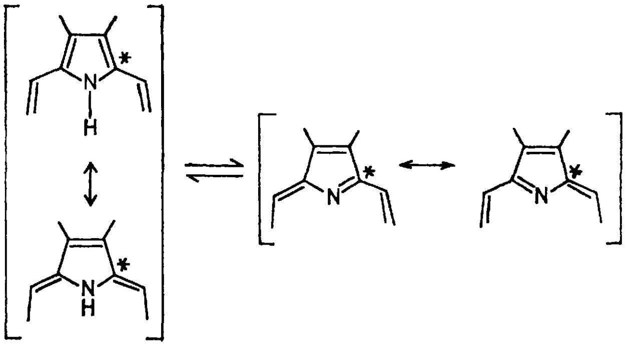
$$\frac{1}{T_1^{N}}, \frac{1}{T_2^{N}} \gg A$$

where A (radian s^{-1}) is the ^{14}N–^{13}C coupling constant and $I = 1$ is the spin of the ^{14}N nucleus; $\Delta\omega$ (radian s^{-1}) is the frequency separation of the ^{14}N and ^{13}C resonances (*ca.* 18 MHz). As an estimate for A we take the value $^{1}J_{^{14}\mathrm{N}-^{13}\mathrm{C}}$ found for the pyridinium ion (*ca.* 5 Hz).[24] This yields [equation (3)] an upper limit for the ^{13}C spin–spin relaxation rate $1/T_{2SC}^{C}$ of *ca.* 0·03 s^{-1}, *i.e.* a negligible contribution to the ^{13}C linewidth of *ca.* 0·02 Hz.

The second possible relaxation mechanism, scalar relaxation of the first kind *via* the $J_{^{1}\mathrm{H}-^{13}\mathrm{C}}$ coupling, has been shown to be inoperative with noise modulated proton decoupling.[25]

We are therefore led to the conclusion that the most likely explanation for the broad ' α-pyrrole ' carbon signal is that the ^{13}C spectrum is approaching coalescence for exchange between the two distinct sites (Scheme).

In an attempt to corroborate the above postulate, we measured the ^{13}C n.m.r. spectra of [^{2}H$_2$]copro-I and [^{2}H$_2$]TPP wherein the central protons are replaced by deuterons. Storm and Teklu[18] found coalescence for the ' β-pyrrole ' protons of [^{2}H$_2$]TPP at *ca.* 0° in the ^{1}H n.m.r. spectrum, compared with *ca.* —40° for the protio-compound, thereby indicating a large isotope effect upon the rate of tautomerism. From the spectra shown in Figures 1 and 2, it is apparent that the ' α-pyrrole '



SCHEME

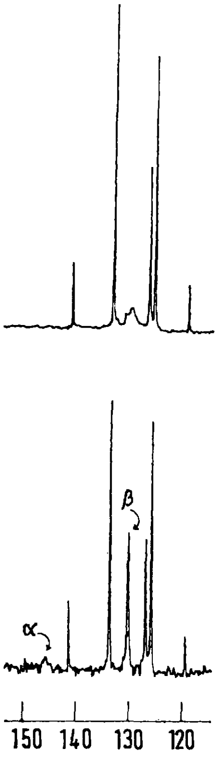


FIGURE 2 The ^{13}C spectrum of *meso*-tetraphenylporphyrin (lower), and the *NN'*-dideuterio-species (upper), 35 mg in 1·5 ml CDCl$_3$

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[21] For a discussion of factors contributing to relaxation rates see T. C. Farrar and E. D. Becker, ' Pulse and Fourier Transform N.M.R.', Academic Press, New York, 1971.

[22] This range includes cyclic secondary amines and pyridines, A. Colligiani, R. Ambrosetti, and R. Angelone, *J. Chem. Phys.*, 1970, **52**, 5022; E. Schempp and P. J. Bray, *ibid.*, 1968, **49**, 3450.

[23] For a medium size molecule this seems a reasonable value; for cholesteryl chloride $\tau_c \approx 9{\cdot}0 \times 10^{-12}$ s was estimated by A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 1971, **55**, 189.

[24] H. H. Mantsch and I. C. P. Smith, *Canad. J. Chem.*, 1973, **51**, 1384.

[25] For a recent discussion see R. A. Cooper, R. L. Lichter, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1973, **95**, 3724.

carbon signals are broadened beyond detection, and for $[^{2}H_{2}]$copro-I the ' β-pyrrole ' carbon signals are reduced in intensity and the $[^{2}H_{2}]$TPP ' β-pyrrole ' carbon atoms are considerably broadened. This is consistent with the broadening being due to exchange of the carbon atoms between the two sites if the chemical shift between the ' β-pyrrole ' carbon sites is smaller than the corresponding difference for the ' α-pyrrole ' carbons. We are reasonably confident at eliminating ^{13}C–^{2}H coupling as the source of this additional broadening because these couplings should be very small [26] ($\lesssim$1 Hz), a value well within the linewidths of resonances due to carbons elsewhere within the molecule.

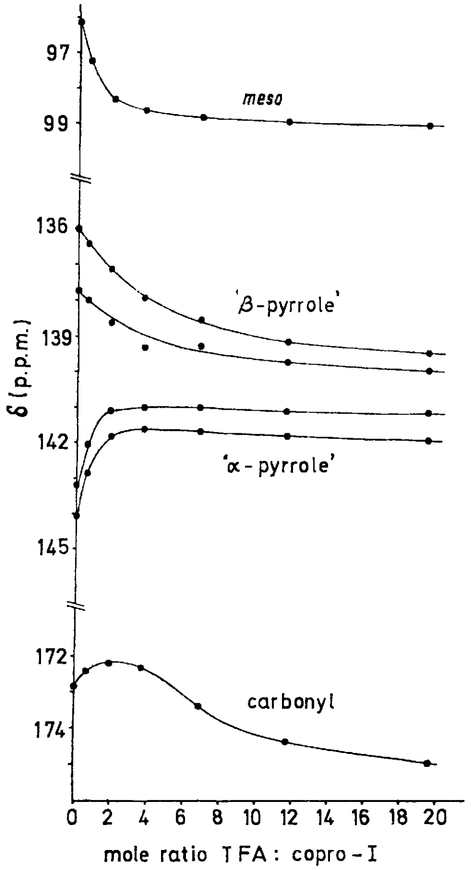

FIGURE 3 The ^{13}C chemical shifts (δ) of coproporphyrin-I tetramethyl ester with added TFA

^{13}C *N.m.r. Spectra from Protonated Coproporphyrin-I.*—The spectrum of coproporphyrin-I tetramethyl ester was determined in TFA solution. Assignments were made by adding incremental quantities of TFA to a solution of copro-I in $CDCl_3$ up to a ratio of $CDCl_3$: TFA of *ca.* 3 : 1 by (v/v) (Figure 3). The ' α-pyrrole ' carbons shift initially to higher field, up to a molar ratio of TFA : copro-I of *ca.* 3 : 1, but at higher acid concentrations, a weak shift to low field occurs. In contrast, the ' β-pyrrole ' and *meso*-carbon signals are initially quite strongly shifted to lower field, while at TFA : copro-I ratios $\gtrsim$3, the slopes of the titration curves are much smaller, and similar to the slopes of the ' α-pyrrole ' carbon curves in this region. This suggests to us a combination of factors involved, initial protonation shifts are upfield at ' α-pyrrole ' carbon and downfield at the *meso*- and ' β-pyrrole ' carbons. At TFA : copro-I ratios $\gtrsim$3, protonation is essentially complete at nitrogen and a bulk solvent effect and/or protonation at the ester carbonyls takes over, imparting a weak downfield shift at these positions. This effect has analogy in the shifts in the ^{13}C n.m.r. spectra of other nitrogen heterocycles upon protonation,[27] where carbons α and β to nitrogen experience upfield and downfield shifts respectively upon protonation. There is a pronounced hump in the plot for the ester group carbonyl carbon atom; the marked downfield shift at higher acid concentrations is consistent with increased protonation of the ester carbonyl.[28] The ^{13}C spectrum of ethyl 3-phenylpropionate exhibits a similar downfield shift for the carbonyl carbon in TFA compared to solution in $CDCl_3$ (Table 2).

In TFA solution, the mean shift between the α- and β-' pyrrole ' carbons for copro-I is 1·1 p.p.m., compared with 6·4 p.p.m. for the base, and 9·3 p.p.m. for Zn(II)-copro-I. Such a gradation in relative shifts on passing from dicationic to neutral to ' dianionic ' species could prove to be of great utility in assigning this potentially complex spectral region for other porphyrins (*cf.* Figure 4).

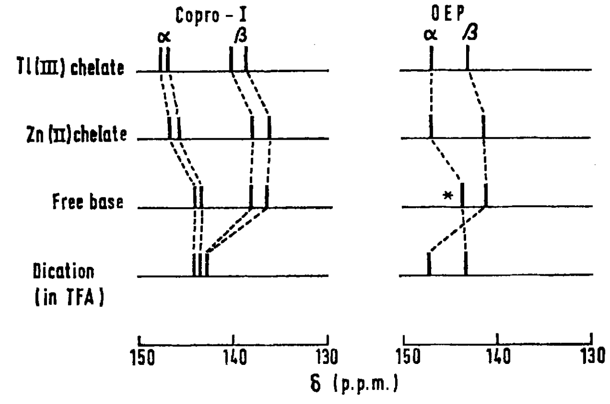

FIGURE 4 The ^{13}C chemical shifgs (δ) of ' pyrrole ' carbons in porphyrins. * = Assumed value from ref. 4

^{13}C *Chemical Shifts and Coupling Constants in the Thallium*(III) *Coproporphyrin Tetramethyl Esters.*—Introduction of a thallium atom into a porphyrin nucleus results in a ^{13}C n.m.r. spectrum showing extensive thallium–^{13}C coupling. For Tl(III)copro-I † and the OEP chelate, the ^{13}C spectra were analysed with the aid of spectra determined at 22·6 MHz, the 10% field difference between these spectra and those measured at 25·2 MHz was sufficient to identify the Tl–^{13}C couplings.

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† All thallium porphyrins discussed have OH and H_2O axial ligands.

[26] The best comparison with two and three bond ^{13}C–^{1}H couplings across nitrogen that we could find is in simple amides, where these couplings are generally $\gtrsim$6 Hz, D. E. Dorman and F. A. Bovey, *J. Org. Chem.*, 1973, **38**, 1719.

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[28] G. E. Maciel and D. D. Traficante, *J. Phys. Chem.*, 1965, **69**, 1030.

The chemical shifts and couplings are shown in Table 1. The *meso*-carbon signals for the Tl(III)copros were readily identified (s.f.o.r.d. spectra) and show a low field shift of *ca.* 1·8 p.p.m. compared with the porphyrin free bases. A similar shift was expected for the ' β-pyrrole ' carbons, to which are assigned the resonances in the 139 p.p.m. region. Thus, the resonances in the 146 p.p.m. region are assigned to the ' α-pyrrole ' carbon atoms, which therefore show a shift to lower field of *ca.* 3·5 p.p.m. upon introduction of thallium.

The Tl–^{13}C couplings are of interest, the two bond coupling to the ' α-pyrrole ' carbon being substantially smaller than the three bond couplings to the ' β-pyrrole ' and *meso*-carbon atoms, in agreement with other X–H [29,30] and X–^{13}C couplings.[31,32]

Maher and Evans [33] showed that the Tl–^{1}H couplings in a variety of organothallium compounds closely paralleled the corresponding H–H couplings, being *ca.* 60 times larger in the R_2Tl^+ compounds, *e.g.* $^2J_{Tl-H}$ +842, *cis*-$^3J_{Tl-H}$ +805, and *trans*-$^3J_{Tl-H}$ +1618 Hz in divinylthallium perchlorate, $^4J_{Tl-H}$ −94 and −47 Hz in *cis*- and *trans*-diprop-1-enylthallium cation. In the coproporphyrins, the coupling to the *meso*-carbons involves two equivalent *cis*-three bond pathways, and thus we assign a value of *ca.* 74 Hz to *cis*-$^3J_{Tl-^{13}C}$, and (to the ' β-pyrrole ' carbons) *trans*-$^3J_{Tl-^{13}C}$ 109 Hz. Thus, the thallium–carbon couplings, *trans*-^3J > *cis*-$^3J \gg {}^4J$, agree with the crude analogy given above with thallium–proton couplings, but $^2J_{Tl-H}$ seems anomalously large. This latter conclusion was also reached by Maher and Evans.[33] The relative Tl–^{13}C couplings are well reproduced by the corresponding H–H couplings in the propenyl system [34] where *trans*-$^3J_{H-H}$ > *cis*-$^3J_{H-H}$ > $^2J_{H-H} \approx {}^4J_{H-H}$. This is strong evidence for the dominance of the contact interaction and σ-mechanism for the Tl–^{13}C couplings in these systems.

Conclusions.—^{13}C N.m.r. assignments offer considerable promise in aiding structural assignment of porphyrins, even when unsymmetrical molecules are considered. Further studies on the influence of substituents upon porphyrin ring ^{13}C chemical shifts are immediately indicated. The ^{13}C chemical shifts do not present a basis upon which to discuss preferred delocalisation pathways in porphyrins, but unusual line-widths observed for the ' α-pyrrole ' type carbon signals are corroborative evidence for the tautomeric model of the porphyrin ring. The mean chemical shift separation between the α- and β-' pyrrole ' type quaternary carbons in copro-I is dependent upon the state of the porphyrin, *i.e.* mean separations *ca.* 8, 6·5, and 2 p.p.m. (in TFA) were observed for the dianion (metalloporphyrin), free base, and dication respectively. Studies of the porphyrins in these different forms may provide aid in resonance asssignments.

The pattern of thallium–carbon coupling constants in the coproporphyrin tetramethyl ester chelates is similar to that found for inter-proton couplings. This is evidence in favour of similar mechanisms (Fermi contact) operative for these two types of couplings.

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[3/1949 *Received*, 24*th September*, 1973]

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[31] F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, 1973, **12**, 313.

[32] D. Doddrell, M. L. Bullpitt, C. J. Moore, C. W. Fong, W. Kitching, W. Adcock, and B. D. Gupta, *Tetrahedron Letters*, 1973, 665.

[33] J. P. Maher and B. F. Evans, *J. Chem. Soc.*, 1964, 637.

[34] See L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry,' Pergamon, London, 1969, ch. 4.