^{13}C Nuclear Magnetic Resonance Spectra of Coproporphyrins

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Summary Complete assignments of the ^{13}C n.m.r. spectra of the tetramethyl esters of the four coproporphyrin type-isomers are presented, together with analyses of the spectra of the zinc(II) and thallium(III) chelates of coproporphyrin-I tetramethyl ester.

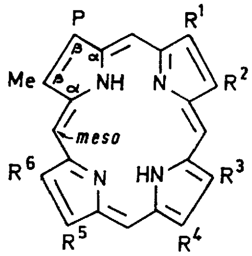
We present the complete spectral assignments for the ^{13}C n.m.r. spectra of the tetramethyl esters of the four coproporphyrin type-isomers[1] (Table). Previous studies of more diversely substituted porphyrins[2,3] have given only incomplete assignments, and sometimes incomplete spectra.[3]

Table. ^{13}C *Chemical shifts*[a] *for coproporphyrins*

	Nuclear carbon atoms				Side-chain carbon atoms				
	C_α	C_β–Me	C_β–P	*meso*[d]	CH_3	CH_2–CH_2–CO–OCH_3			
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 96·0	11·6	21·8	36·8	172·8	51·5
Copro-III	144·0[b]	135·8	137·8	96·4 (1) 96·0 (3)	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 (1) 95·8 (3)	11·5 11·3	21·6	36·8	172·7	51·4
Copro-I Tl(OH,H_2O)	147·5, 146·6	138·4	139·9	98·1	11·7	22·2	36·9	173·0	51·8
J[c]	18 19	109	106	147	15	12	—	—	—
Copro-I Zn	146·6, 145·6	135·9	137·7	96·0	11·5	21·8	36·9,	172·8	51·5

[a] δ, Relative to internal Me_4Si, measured at 25·2 MHz. [b] Broad (30—50 Hz) weak signals. [c] Tl-^{13}C couplings, ± 1 Hz. [d] Numbers in parentheses refer to relative signal intensities.

Our assignments for the side-chains and *meso*-carbon atoms agree with these previous studies; however, we have in addition assigned the broad low field signals (δ 143—144) to the α-carbon resonances of the "pyrrole" rings, which in our compounds are quite distinct from the β-carbon resonances (δ 136—138). The α-carbon resonances were presumably not reported by the earlier workers[2,3] on account of the broadening, which we ascribe to N–H tautomerism† in the porphyrin ring,[4] rather than to nitrogen quadrupole effects.



	R^1	R^2	R^3	R^4	R^5	R^6
Copro-I	Me	P	Me	P	Me	P
Copro-II	P	Me	Me	P	P	Me
Copro-III	Me	P	Me	P	P	Me
Copro-IV	P	Me	P	Me	Me	P

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

The appearance of the α-carbon atoms at similar chemical shifts to the β-carbons (Table) throws some doubt on the recent suggestion of Doddrell and Caughey[3] that the ^{13}C n.m.r. spectra of porphyrins afford evidence in favour of the "16-membered inner-pathway"[5] for delocalisation of the π-electrons. This suggestion was put forward because the porphyrin β-carbon atoms appeared in the usual olefinic region, whereas the *meso*-carbons were considerably upfield, at chemical shifts comparable with carbon atoms of simple unsubstituted pyrroles. They concluded that the *meso*-carbon atoms were experiencing strong resonance effects due to delocalisation *via* the 16-membered inner-ring pathway, with the β-carbons left as pure double bonds. On this basis, however, the α-carbons should resonate in a similar position to the *meso*-carbons, whereas in fact they are very similar to the β-carbon atoms (Table). We conclude that there is little evidence for a 16-membered inner pathway from the ^{13}C shifts.

We have further separated the β-carbons into those bearing methyl (Me) or propionic ester (P) substituents. Our assignment of the C_β–Me carbon to higher field is supported by the similar effects found in the benzene series (*e.g.* C_1 in toluene, δ 137·3; C_1 in methyl 3-phenylpropionate, δ 140·1).

The *meso*- and β-carbon atoms show additional fine structure in some of the type-isomers, thereby enabling ^{13}C n.m.r. to be used for differentiation of the type-isomers. The appearance of single resonances for C_β–Me (or C_β–P) in copros-I and -II, and two resonances for copro-IV can be predicted from the influence of the nearest substituent on the adjacent "pyrrole" ring. This differentiation of the *meso*- and β-carbons in the type-isomers is, however, not much greater and less unequivocal than that obtained[6] from their ^{1}H n.m.r. spectra.

In complete contrast, we find that the constancy of the carbon shifts provides a solid base from which the assignment of the zinc(II) and thallium(III) porphyrins can be made. In these compounds, the sharper signals of the α-carbons are further resolved, showing the different *ortho*

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† The α-carbon atoms in zinc(II) and thallium(III) coproporphyrins, and in coproporphyrin-I tetramethyl ester measured in trifluoroacetic acid, gave sharp signals.

substituent effects of the methyl and propionic ester substituents; again, the assignment follows by analogy with the benzene series (*e.g.* C_2 in toluene, δ 128·6; C_2 in methyl 3-phenylpropionate δ 127·9).

Thallium(III) coproporphyrin-I tetramethyl ester[1] shows extensive thallium–carbon splittings‡ which were only differentiated from chemical shifts by observation of the ^{13}C spectrum at 22·6 MHz. The interesting feature of these couplings is the small (18 Hz) two-bond coupling (*cf.* 107 and 147 Hz to the β- and *meso*-carbons respectively), and the comparable four-bond coupling (*ca.* 14 Hz) to the side-chain carbons. This has analogies in other ^{13}C–metal couplings[8] and also in ^1H–^1H couplings (*cf.* $^2J_{HH}$ *vs.* $^3J_{HH}$ in olefins), and supports the analogy of thallium and proton couplings, made originally by Evans.[7]

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‡ No differentiation between ^{203}Tl-^{13}C and ^{205}Tl-^{13}C splittings was observed, and we follow previous practice[7] in referring to these as Tl-^{13}C couplings.

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