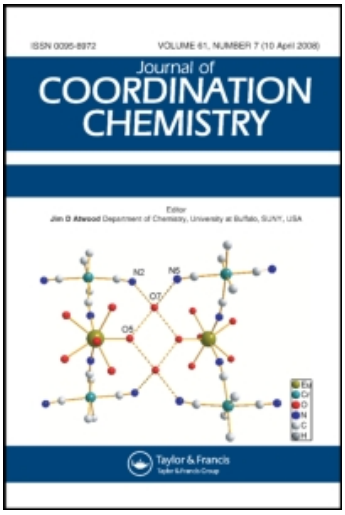

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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João Rocha[a]; Waclaw Kolodziejski[a]; José A. S. Cavaleiro[b]; Jacek Klinowski[a]
[a] Department of Chemistry, University of Cambridge, Cambridge, UK [b] Department of Chemistry, University of Aveiro, Aveiro, Portugal

To cite this Article Rocha, João , Kolodziejski, Waclaw , Cavaleiro, José A. S. and Klinowski, Jacek(1992) 'A High-Resolution ^{13}C Solid-State NMR Study of *meso*-Tetraphenylporphyrin and its Zinc(II) Complex', Journal of Coordination Chemistry, 25: 3, 205 — 210
To link to this Article: DOI: 10.1080/00958979209409192
URL: http://dx.doi.org/10.1080/00958979209409192

J. Coord. Chem. 1992, Vol. 25. pp. 205–210
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A HIGH-RESOLUTION ^{13}C SOLID-STATE NMR STUDY OF *meso*-TETRAPHENYLPORPHYRIN AND ITS ZINC(II) COMPLEX

JOÃO ROCHA,[a] WACLAW KOLODZIEJSKI,[a] JOSÉ A. S. CAVALEIRO[b] and JACEK KLINOWSKI[a]*

[a] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.*
[b] *Department of Chemistry, University of Aveiro, 3800 Aveiro, Portugal*

(Received July 7, 1991)

High-resolution ^{13}C solid-state NMR spectra of *meso*-tetraphenylporphyrin (TPP) and its zinc(II) complex (ZnTPP) are assigned by reference to low-temperature solution NMR results and using ^{1}H- ^{13}C cross-polarization magic-angle-spinning (CP/MAS). The splittings of the signals from pyrrole carbons in TPP are attributed to kinetic solid-state effects involved in the migration of the central hydrogen atom.

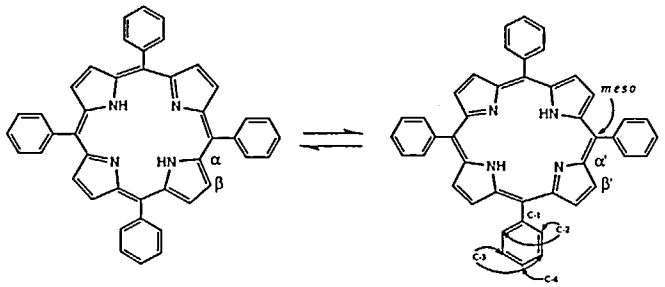
Keywords: *meso*-tetraphenylporphyrin, Zn(II) complex, solid-state ^{13}C NMR

INTRODUCTION

Because of their exciting chemical properties and biological importance, porphyrins and metalloporphyrins are among the most interesting natural products. Examples[1,2] include metalloporphyrins and their vital functions in the haemoproteins, cytochromes, catalases, peroxidases, reductases, chlorophylls and bacteriochlorophyll Factor F430 (from methanogenic bacteria). Chemists and biologists have often attempted to mimic the biological properties of such natural systems. Porphyrins may act as photosensitive agents to trap energy. Several studies have shown that some *meso*-unsubstituted porphyrins may be used as anticancer materials. A porphyrinic drug, Photofrin II®, is on the market.[3] Detoxification processes, through hydroxylation or other mono-oxygenations, are performed in nature by cytochrome P_{450}. During the last decade there have been many attempts to use analogues of biological systems for the functionalization of cheap substrates in catalytic transformations, giving novel value-added compounds. *Meso*-tetraphenylporphyrins and some TPP derivatives have been the porphyrins of choice, since they are readily available and some of their metal complexes have shown high efficiency in such catalytic oxidation, mainly when the complexes are supported on an appropriate polymer.[4]

NMR is a powerful technique for the characterization of porphyrins. Although extensive reviews of solution NMR of these compounds are available,[1,2] only a few high-resoltuion ^{13}C solid-state NMR studies of porphyrins[5-7] and metalloporphyrins[5] have been measured. We wish to report the first high-resolution solid-state ^{13}C NMR spectra of a tetraarylporphyrin, TPP (see Figure 1) and its Zn(II) complex (ZnTPP).

* Author for correspondence.



1 2

FIGURE 1 NH tautomerism in *meso*-tetraphenylporphyrin (TPP) showing the labelling of carbon atoms.

EXPERIMENTAL

The synthesis of TPP and ZnTPP has been described previously.[8] ^{13}C CP/MAS NMR spectra were recorded at 100.613 MHz on a Bruker MSL-400 spectrometer at 25°C using single contacts with contact times of 4 ms and 40 μs. The length of the ^{1}H $\pi/2$ pulse was 2.8 μs, the recycle delay 10 s and the spinning rates were in the range 8–12 kHz. Dipolar dephased[9] (DD) spectra were recorded with a 50 μs delay prior to acquisition.

RESULTS AND DISCUSSION

The dipolar dephased spectrum of TPP shown in Figure 2 reveals only the carbons which have no attached protons. It follows that the signals at 153.0, 142.2, 139.0 and 118.5 ppm must be assigned to C_{α}, *meso* and phenyl C-1 carbons. A comparison with the chemical shifts and assignments for TPP low-temperature (−60°C) solution spectra listed in Table I, allows the assignment of the 142.2 and 118.5 ppm resonances to phenyl C-1 and *meso* carbons, respectively. The splittings of the TPP pyrrole signals in solution (see Table I) are due to the quenching of the NH tautomerism.[10] Similar effects have been observed[5–7] in the solid-state NMR spectra of porphyrins (see below). Accordingly, we assign the resonances at 153.0 and 139.0 ppm to $C_{\alpha'}$ and C_{α} carbons, respectively.

When the CP/MAS spectrum is recorded with a contact time of 40 μs [Figure 2(c)] only the CH carbons are monitored. The TPP signal centred at 135.6 ppm is therefore assigned, by reference to solution spectra, to the $C_{\beta'}$ and phenyl C-2 carbons. The three signals which overlap in the range 120–130 ppm must be associated with C_{β} and phenyl C-3 and C-4 carbons. Our spectra, recorded with very different contact times, always showed the central signal at 127.5 ppm to be much more intense than the two others. We therefore assign it to the more numerous phenyl C-3 carbons. The assignment of the signals at 130.0 and 124.1 ppm to individual C_{β} and C-4 nuclei is still an open question.

In accordance with solution NMR evidence (see Table I), no splitting of the C_{α} and C_{β} carbons is observed in the ZnTPP spectra. The DD spectrum [Figure 3(b)]

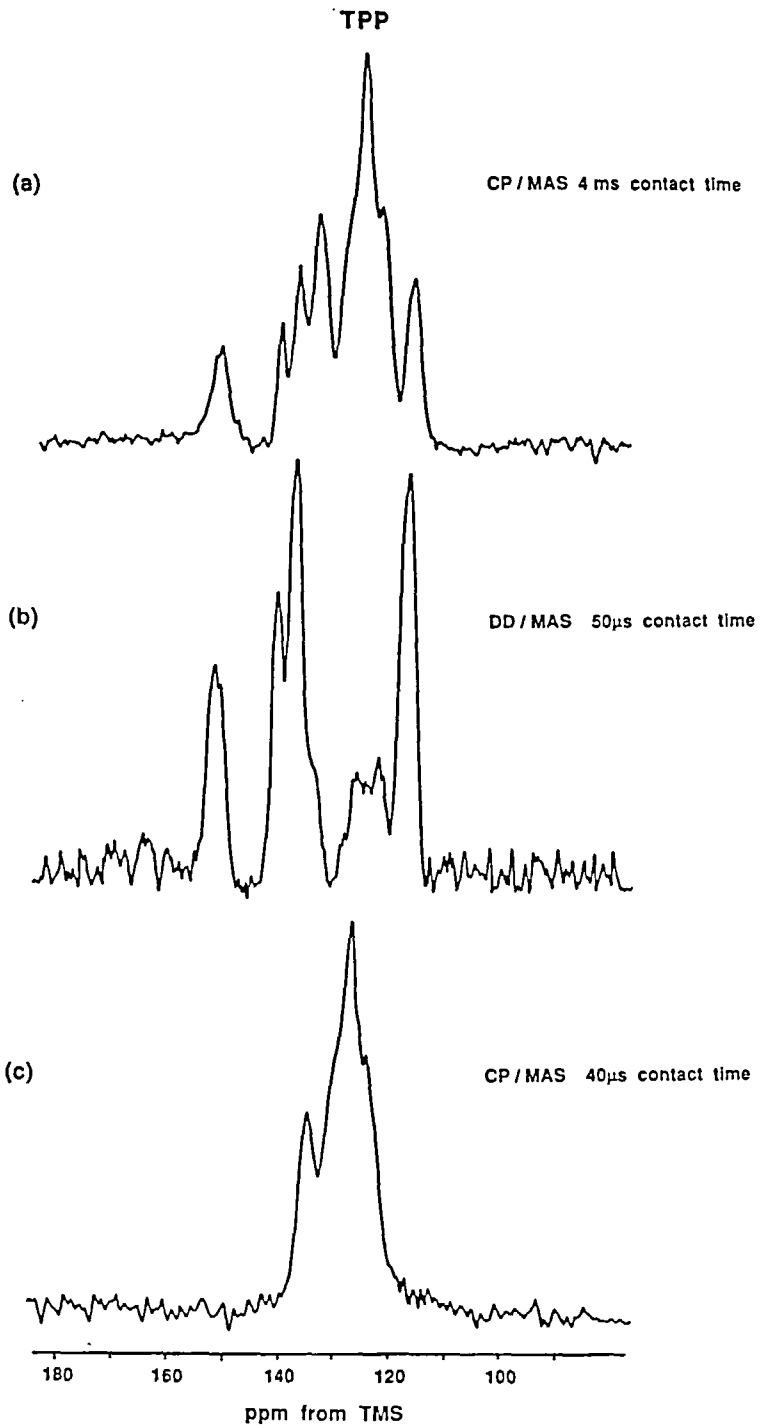


FIGURE 2 ^{13}C CP/MAS NMR spectra of TPP recorded with (a) contact time of 4 ms; (b) dipolar dephasing (DD) delay of 50 μs before acquisition, to monitor C_α $C_{\alpha'}$, *meso* and phenyl C-1 carbons only; (c) contact time of 40 μs which allows only the C_β, $C_{\beta'}$, and phenyl C-2, C-3 and C-4 carbons to cross-polarize.

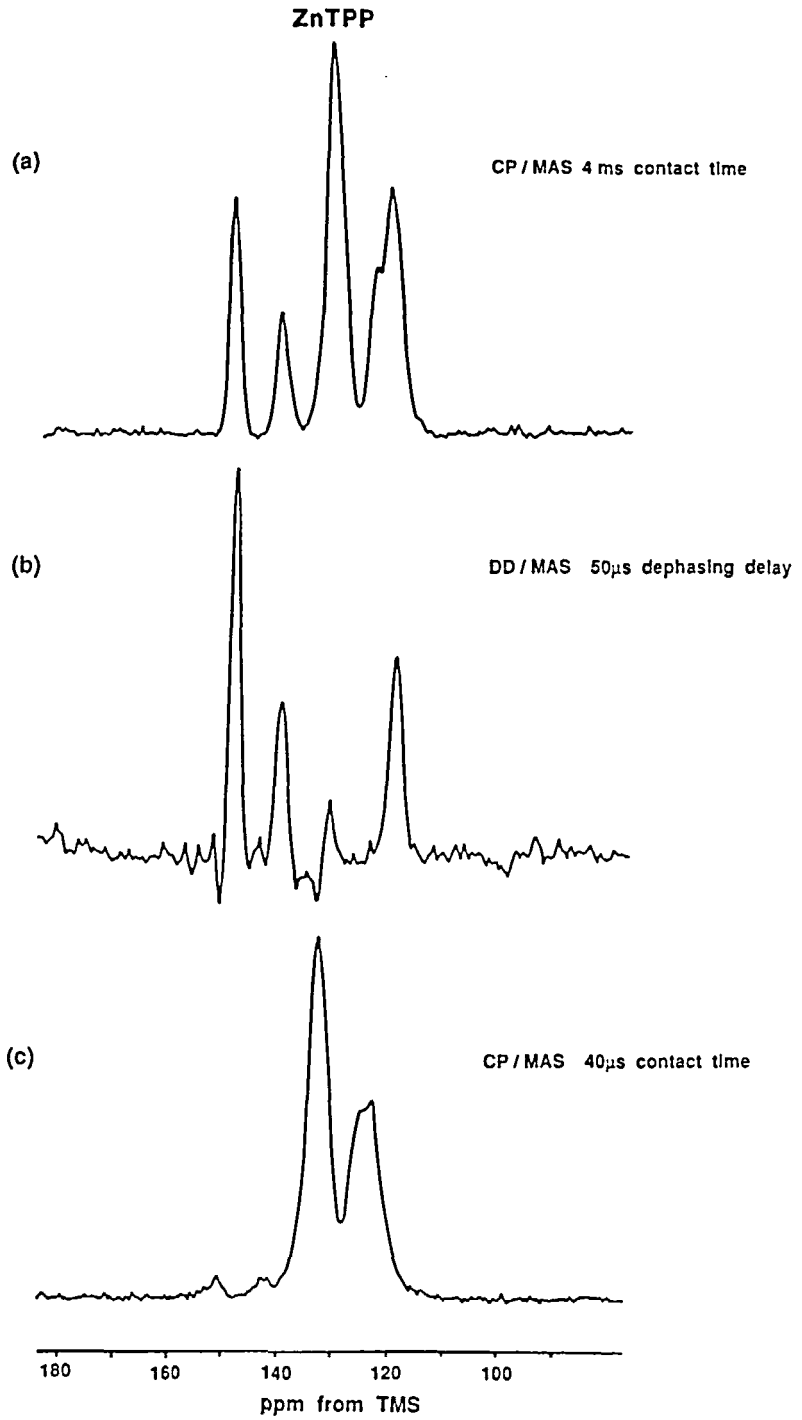


FIGURE 3 ^{13}C CP/MAS NMR spectra of ZnTPP.

readily allows the assignment of the signals at 150.4, 142.0 and *ca* 122 ppm to C_α, phenyl C-1 and *meso* carbons, respectively. Note that the phenyl C-1 carbons of ZnTPP and TPP resonate at very similar frequencies of 142.0 and 142.2 ppm, respectively, a fact which supports our assignment. The CP/MAS spectrum recorded with a contact time of 40 μs [Figure (3)] and evidence from solution NMR suggests that the signal at 132.7 ppm should be assigned to C_β and phenyl C-2 and the signal at *ca* 125 ppm to phenyl C-3 and C-4 carbons. The assignments of the different TPP and ZnTPP ^{13}C CP/MAS resonances are summarized in Table I.

TABLE I
^{13}C NMR chemical shifts and assignments of TPP and ZnTPP.

	$C_{\alpha',\alpha}$	$C_{\beta',\beta}$	C_{meso}	C-1	C-2	C-3	C-4
TPP solution[b]	154.0 137.1	133.9 127.0	119.5	141.0	133.9	126.1	127.3
TPP solid[c]	153.0 139.0	135.6 (d)	118.5	142.2	135.6	127.5	(d)
ZnTPP solution[a]	150.8	132.5	121.6	143.3	134.9	127.5	128.0
ZnTPP solid[c]	150.4	132.7	122.0	142.0	132.7	125.0	125.0

[a] Solutions in $CDCl_3$. Chemical shifts in ppm from internal TMS.[10] [b] At −60°C. [c] Chemical shifts in ppm from external TMS. [d] Assignment of $C_{\beta'}$ and phenyl C-4 carbons in solid TPP is uncertain (see text).

The C_α and C_β splittings observed in the ^{13}C CP/MAS NMR spectrum of TPP could in principle arise from chemically equivalent nuclei in isolated molecules which become crystallographically inequivalent in the crystal lattice. However, the magnitudes of the splittings suggest that their origin is related to perturbations of the tautomeric process **1** ⟷ **2** in the solid.[6] Indeed, a variable-temperature ^{15}N CP/MAS NMR study using isotopically enriched compounds reveals that TPP tautomerism is influenced by crystal packing forces which modify the rate constants, shifting the equilibrium towards one of the tautomers.[11] In addition, intermolecular ring-current shifts are also known to contribute to the splittings of the resonances in the solid-state ^{13}C NMR spectra of porphyrins.[5] Although these shifts are usually negligible in solution, less motion and small intermolecular distances (3–4 Å) in solid porphyrins cooperate so as to produce appreciable shifts in ^{13}C CP/MAS NMR spectra.

ACKNOWLEDGEMENTS

We are grateful to Unilever Research, Port Sunlight, the University of Aveiro, Portugal, and INIC for support.

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