Fine Structure of 5,10,15,20-Tetrakis(*m*-hydroxyphenyl)chlorin (*m*-THPC): a ^1H, ^{13}C and ^{15}N NMR Study

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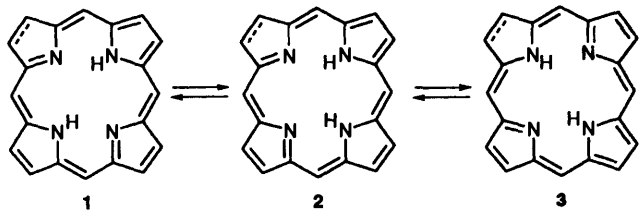
The ^1H, ^{13}C and natural abundance ^{15}N NMR spectra of tetrakis(*m*-hydroxyphenyl)chlorin (*m*-THPC) are assigned through the complementary analysis of the data from one-dimensional, and both homo- and hetero-nuclear two-dimensional NMR experiments. The analysis of the ^1H and ^{13}C spectra showed that the symmetry of the structure includes an effective mirror plane, σ_v, and the ^1H–^{15}N coupling constant of 99 Hz (measured from the 'inverse-mode' ^1H–^{15}N 2D experiment) showed that the central imino protons undergo slow intramolecular tautomeric exchange. The single ^{15}N chemical shift (δ 111.8 relative to $^{15}NH_4^+$) of the proton-bearing nitrogens is characteristic of a 'pyrrole' type, and the long range coupling ^1H chemical shift correlation (2D) spectrum showed that, on the NMR time scale, the imino hydrogens are localised on five-membered rings that are not in the σ_v plane. Taken together these data prove that the fine structure of *m*-THPC is correctly represented with the imino hydrogens placed on opposite rings which are not reduced, as shown in structure **4**.

The imino tautomerism of porphyrins and related compounds, commonly referred to as the problem of the fine structure of porphyrins,[1] was largely impenetrable in the solution state until the advent of NMR spectroscopy. Storm and Teklu[2] carried out variable temperature ^1H NMR studies with both porphyrins and chlorins which they interpreted in terms of the equilibria in Scheme 1.



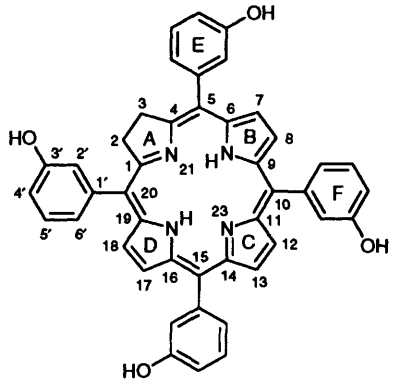
1 **2** **3**

Scheme 1

For porphyrins (– – – is a full bond), the opp-tautomers **1** and **3** were detected, while the intermediacy of the adj-tautomer **2** was inferred. For the chlorins (– – – is absent) the opp-tautomer **1** was detected (although incompletely justified at that stage), while **2** and **3** were inferred. Subsequent studies[3-12] have confirmed and considerably expanded these results, and there is now extensive kinetic data including H/D kinetic isotope effects which support the stepwise proton transfer pathway **1**⇄**2**⇄**3**.[7-12]

In recent years, it has been shown that certain chlorins are satisfactory sensitisers in the photodynamic therapy of cancer.[13] One of the most promising compounds is 5,10,15,20-tetrakis(*m*-hydroxyphenyl)chlorin (**4**, *m*-THPC),[14] the first clinical results on which have recently appeared.[15] Although the fine structure of *meso*-tetraphenylchlorin has been studied,[12] it was considered that the phenolic hydroxy groups of **4** might perturb the equilibrium and it was in any case desirable to ascertain the tautomeric situation for a potential drug.

Here we report the solution of this problem using a variety of NMR approaches involving ^1H, ^{13}C and natural abundance ^{15}N nuclei.



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Experimental

5,10,15,20-Tetrakis(*m*-hydroxyphenyl)chlorin **4** was made by the reduction of the corresponding porphyrin by diimide[14] and was >99% pure (HPLC). The initial ^1H and ^{15}N experiments described here used Bruker AM-250 and AMX-600 spectrometers and were carried out with a 7.35 × 10^{-3} mol dm^{-3} solution (5 mg in 1 cm^3 of [$^2H_6$]Me_2SO) which was sealed *in vacuo* (three freeze–thaw cycles). When not being studied, this solution was kept in darkness at 4 °C. Subsequent ^{13}C spectra were obtained with a Bruker AMX-400 spectrometer after the sample tube had been opened to the atmosphere. The state of the sample was monitored periodically by recording the ^1H NMR spectrum. This did not change to any significant degree over a period of three months while the various NMR studies were being carried out. The only minor change in the ^1H spectrum was an increase, with time, in the H_2O impurity resonance (at δ 3.34) which was accompanied by a sharpening of the O*H* resonances.

The procedures for the various 2D NMR experiments and the ^{13}C DEPT experiments employed here have been described in detail elsewhere.[16] The parameters for the ^1H 250 MHz long range COSY spectrum were a spectrum width of 3205 Hz, an acquisition time 0.32 s, relaxation delay 3 s, a delay of 0.08 s to enhance the long range correlations, and 48 transients were acquired (2 dummy scans) for each of 256 spectra. For the 600 MHz phase sensitive (tppi mode) NOESY spectrum the spectrum width was 9615 Hz, acquisition time 0.21 s, relaxation delay 3 s, mixing time 0.5 s, and 32 transients were acquired (4 dummy scans) for each of 512 spectra. The inverse mode

Table 1 ^{1}H Chemical shifts[a] and assignments for *m*-THPC

δ	Integral	Multiplicity[b]	Assignment
−1.64	2 H	s	NH
4.14	4 H	s	2,3H
7.08	2 H	d, d, d; J = 8.4, 2.5, 1.0 Hz	4'H (E)
7.15	2 H	d, d, d; J = 7.5, 2.4, 2.1 Hz	4'H (F)
7.26	2 H	m	2'H (E)
7.29	2 H	m	6'H (E)
7.45	2 H	m	2'H (F)
7.50	6 H	m	6'H (F), 5'H (E,F)
8.25	2 H	d; J = 5.0 Hz	7,18 H
8.40	2 H	s	12,13 H
8.65	2 H	d; J = 5.0 Hz	8,17 H
9.79	2 H	s	OH (E)
9.84	2 H	s	OH (F)

[a] Chemical shifts in ppm to high frequency of TMS. [b] s = singlet; d = doublet; m = multiplet.

^{1}H–^{15}N long range coupling chemical shift correlation pulse sequence assumed a one bond ^{1}H–^{15}N coupling constant of 95 Hz and a long range coupling constant of 5 Hz: the ^{1}H spectra were acquired without ^{15}N decoupling, and a relaxation delay of 2.0 s was used. The ^{1}H spectrum width was 9091 Hz and the ^{15}N spectrum width was 10 944 Hz. 228 ^{1}H spectra were acquired, each with 96 scans, and the ^{15}N domain was zero-filled to 512 before Fourier transformation (FT). A sine-bell window function was used on both ^{1}H and ^{15}N directions prior to FT. The inverse mode ^{1}H–^{15}N one bond coupling correlation experiment used similar parameters to those used in the long range experiment.

The parameters used on the AMX-400 for the inverse mode one bond ^{1}H–^{13}C chemical shift correlation included an assumed value of 140 Hz for the coupling constant, and ^{13}C globally optimised alternating-phase rectangular pulses (GARP) decoupling[17] was used. 64 Scans were accumulated, with a relaxation delay of 0.9 s, for each of 128 ^{1}H spectra, and this f_1 domain was zero-filled to 512 prior to FT. Sine-bell squared window functions were used. The inverse mode long range coupling ^{1}H–^{13}C correlation was run without ^{13}C decoupling, used an assumed value of 140 Hz for the one bond coupling and was repeated assuming different values for the long range coupling *viz.* 3.5, 7.0 and 12.0 Hz. 1024 Scans were accumulated, with a relaxation delay of 0.9 s, for each of 128 ^{1}H spectra, and this was zero-filled to 512 prior to FT. Sine-bell window functions were used.

Results and Discussion

NMR Spectroscopy.—Unambiguous assignment of the structure of *m*-THPC as a single observable tautomer was achieved by complete assignment of the ^{1}H, ^{13}C and ^{15}N NMR spectra. This assignment is described below, and is shown to be consistent with just one of the possible tautomers, and not to be consistent with rapid exchange between two or more of these tautomers. The deduction of this particular tautomeric structure was made from a preliminary assignment of the 1D ^{1}H and ^{13}C spectra, the ^{13}C DEPT spectra, a homonuclear ^{1}H long range COSY spectrum and a one-bond ^{1}H–^{13}C 2D chemical shift correlation. However, there remained some uncertainties in the assignments of the resonances from the five-membered rings and within the phenyl rings. These were largely removed by analysis of the ^{1}H NOESY spectrum and the long range ^{1}H–^{13}C 2D chemical shift correlation.

Preliminary assignments. The high frequency region of the ^{1}H NMR spectrum is shown in Fig. 1 (see also Table 1). In addition there is a four-proton singlet at δ 4.14 due to the protons on the reduced pyrrole ring A, a two-proton singlet at δ −1.64 due to the inner N*H* protons of the macrocycle, and two two-proton singlets at δ 9.79 and 9.84 due to the O*H* protons. The ^{13}C spectrum shows 22 resolved resonances for the 44 carbons of the molecule, and these were assigned as non-protonated, >CH–, or –CH_2– (see Table 2) through use of the DEPT experiment (see Experimental section). These observations accord with either a slowly exchanging symmetrical structure for *m*-THPC (**4** or **6**) with the inner hydrogens on opposite nitrogens, or rapid tautomeric equilibrium between **4** and **6**. The spectra do not accord with the less symmetrical structure **5**, as such, but do not exclude its participation as a short lived component of an exchange process.

In the ^{1}H spectrum the AX spin system at δ 8.25, 8.65, with J = 4.9 Hz has been attributed[18] to β-pyrrole protons H(7,18),

Table 2 ^{13}C and ^{15}N Chemical shifts[a] and assignments for *m*-THPC

δ	n[b]	Preliminary assignment[c]	Final assignment[d]
35.36	2	C2,3	C2,3
112.09	0	C5,20	C5,20
114.69	1	C4'	C4' (E)
114.89	1	C4'	C4' (F)
119.19	1	C2'	C2' (E)
121.02	1	C2'	C2' (F)
121.98	0	C10,15	C10,15
122.99	1	C5' or 6'	C6' (E)
123.56	1	C7,18 or 8,17	C7,18
124.93	1	C5' or 6'	C6' (F)
127.84	1	C5' or 6'	C5' (E)*
128.04	1	C8,17 or 7,18	C8,17
129.16	1	C5' or 6'	C5' (F)*
131.74	1	C12,13	C12,13
134.11	0	C6,19 or C9,16	C6,19†
139.76	0	C9,16 or C6,19	C9,16†
142.42	0	C1'	C1' (E)‡
143.40	0	C1'	C1' (F)‡
151.45	0	} C11,14 and C3'	C11,14
155.81	0		C3' (F)
156.99	0	}	C3' (E)
167.61	0	C1,4	C1,4
111.8[e]		*N*H	

[a] ^{13}C Spectra measured at 100.6 MHz; chemical shifts to high frequency of TMS. [b] Number of directly bonded protons, determined from DEPT experiment. [c] Based upon the presumption of structure **4**. [d] Assignments which are labelled *, † or ‡ may be interchanged. [e] ^{15}N Chemical shift in ppm to high frequency of NH_4^+, measured at 60.8 MHz.

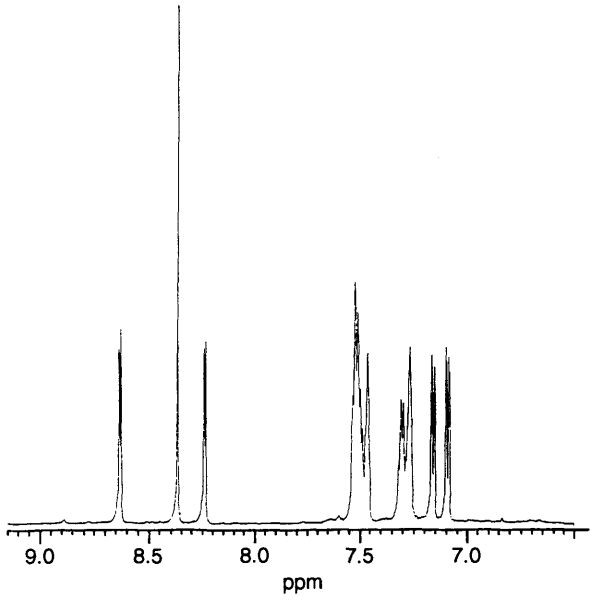
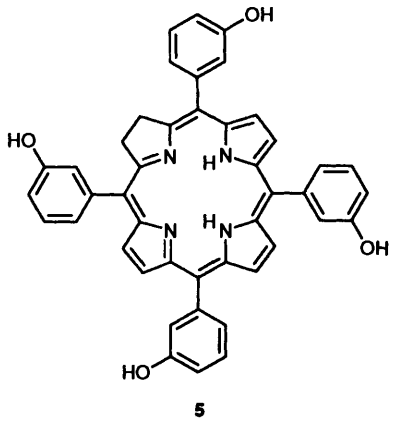


Fig. 1 High frequency region of the 600 MHz ^{1}H NMR spectrum of *m*-THPC



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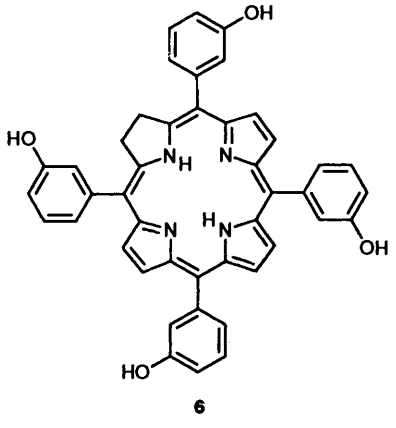

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(8,17) and the 2 H singlet at δ 8.40 to H(12,13). A preliminary selection in favour of structure **4** can be made from the appearance of a coupling correlation (four-bond) in the long range COSY spectrum (see Experimental section and Fig. 2) between the 'inner' N*H* proton resonance and both β-pyrrole resonances at δ 8.25 and 8.65. Structure **6** would require the correlation to be between the N*H* resonance and the singlet at δ 8.40, which was not found.

The starting point for the assignment of the ^{13}C chemical shifts is the DEPT result (*vida supra*, see Table 2). A single methylene ^{13}C resonance at δ 35.56 is not consistent with a static 'adjacent' structure (*e.g.* **5**) but is consistent with either static structures **4** or **6**, or with rapidly exchanging tautomers. The second step in the assignment process uses the ^{1}H–^{13}C one bond coupling chemical shift correlation experiment. The ^{1}H singlets at δ 4.14 (CH_2) and δ 8.40 (12,13H) correlated with ^{13}C resonances at δ 35.36 and 131.74 respectively and the β-pyrrole signals at δ 8.25 and 8.65 (7,8H) correlated with ^{13}C chemical shifts at δ 123.5 and 128.04, respectively. The third step in the assignment process is to assign the 12 signals from the hydroxyphenyl substituents, and these chemical shifts were predicted from the phenyl ring chemical shifts found[4] for *meso*-tetraphenylporphyrin (TPP) corrected for the effect of the hydroxy substituent[19] on the benzene ring as shown in Fig. 3.

Comparison of these predicted shifts with those observed allowed the following assignments: the C4′ carbons at δ 114.69 and 114.89 (predicted 114.5); the C2′ carbons at δ 119.91 and 121.02 (predicted 121.1); the C5′ and C6′ carbons at δ 122.99, 124.93, 127.84 and 129.16 (predicted 126.5 and 127.6); the C1′ carbons at δ 142.42 and 143.40 (predicted 142.4); and the C3′ carbons at two of the shifts δ 151.45, 155.81 and 156.99 (predicted 153.0). The α-carbon resonances for rings B, C and D of *m*-THPC, C(6,19), C(9,16) and C(11,14) may be assigned by

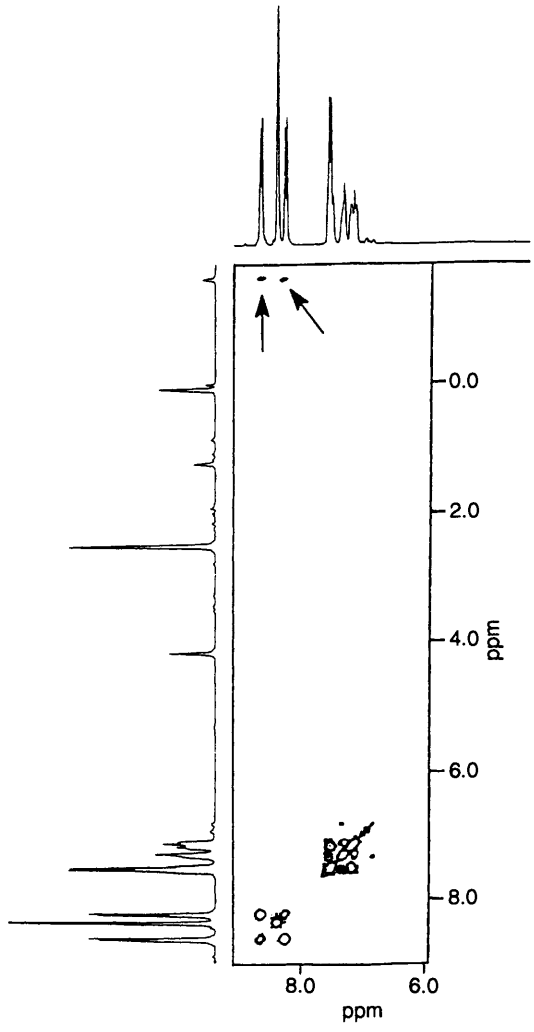


Fig. 2 Part of the 250 MHz ^{1}H long range COSY spectrum of *m*-THPC. The arrows indicate the correlations between the N*H* proton and the β-pyrrole proton signals.

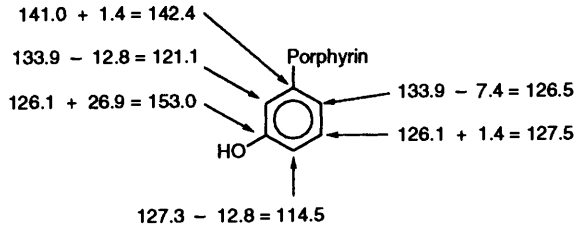


Fig. 3 Predicted ^{13}C chemical shifts for phenyl substituents of *m*-THPC. For each carbon the first number is the shift[4] for TPP, the increment is taken from Pretsch *et al.*[19] and the final figure is that predicted for *m*-THPC.

comparison with the ^{13}C assignments[4] for TPP at low temperature (slow N–H tautomerism), for which the ^{13}C signal for the α-pyrrole carbons was at δ 137.1 and for the α-pyrrolenine carbons at δ 154.0. Clearly the signals at δ 134.11 and 139.76 for *m*-THPC may be assigned to α-pyrrole carbons, and one of the three signals between δ 151 and 157 is due to a α-pyrrolenine type. The remaining highest frequency signal at δ 167.61 must be due to the second α-pyrrolenine carbon, either C1,4 in structure **4**, or either C6,19 or C9,16 in structure **6**, although at this point there is no obvious reason why an α-pyrrolenine carbon should appear at such a high frequency. Therefore we tentatively assign this signal to C1,4 in structure **4**. The remaining two signals at δ 112.09 and 121.98 are assigned

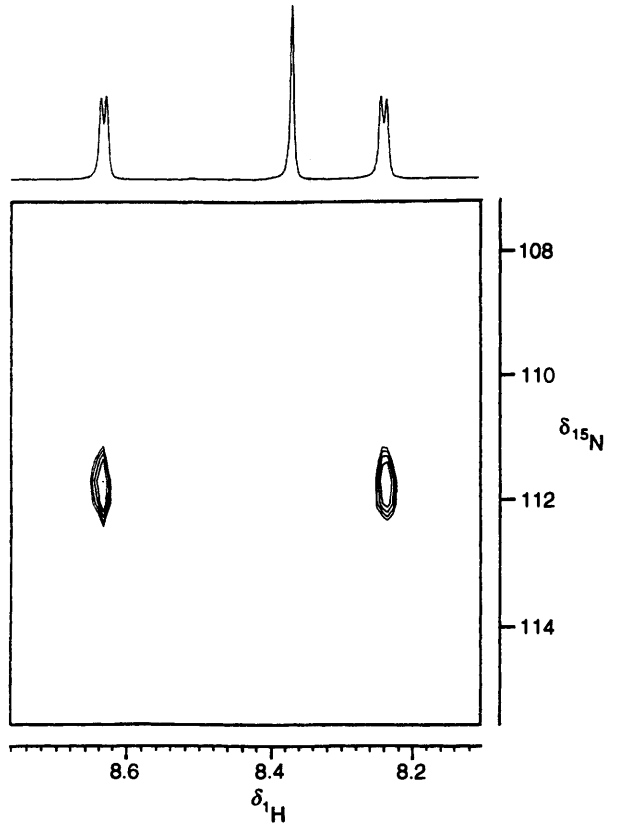


Fig. 4 Inverse mode ^{1}H–^{15}N 2D chemical shift correlation for *m*-THPC. The ^{1}H and ^{15}N frequencies are 600 and 60.8 MHz, respectively, and the experiment was optimised for an assumed long range coupling constant of 5 Hz.

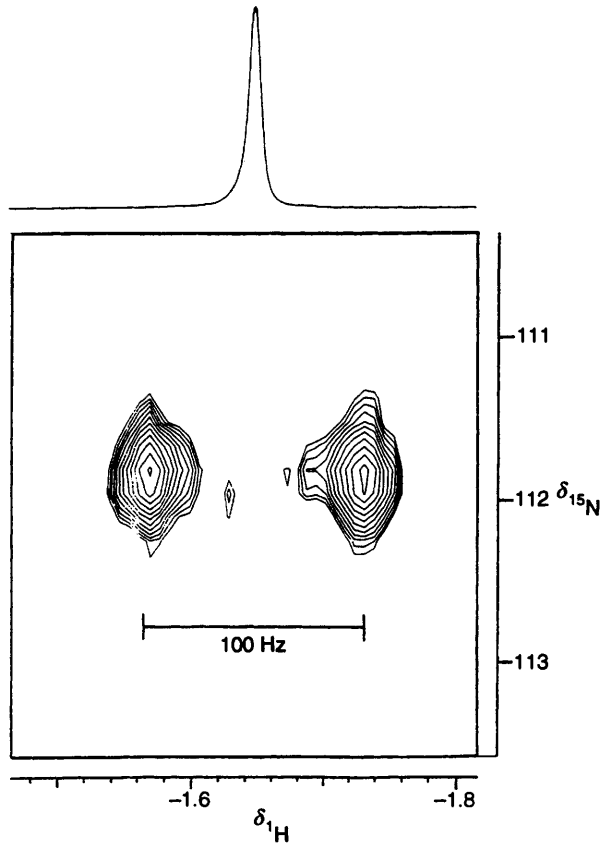


Fig. 5 Inverse mode ^{1}H–^{15}N 2D chemical shift correlation for *m*-THPC. The ^{1}H and ^{15}N frequencies are 600 and 60.8 MHz, respectively, and the experiment was optimised for the one-bond coupling assumed to be 90 Hz.

to the *meso*-carbons, the latter signal being assigned to C10,15 by comparison with that[4] for TPP at δ 119.5. The above arguments lead to the preliminary assignments given in Table 2.

The ^{1}H–^{15}N 2D long range coupling heteronuclear chemical shift correlation spectrum (see Fig. 4) gave correlations between both β-pyrrole proton resonances at δ 8.25 and 8.65 and a single ^{15}N chemical shift at δ 111.8.

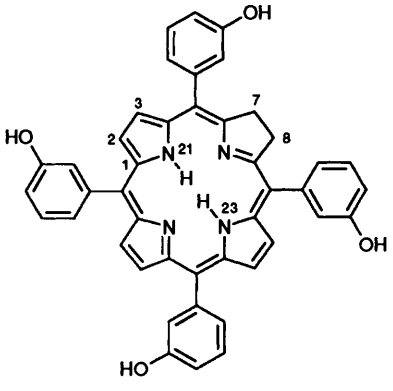
Final assignments. Definitive assignments were achieved by consideration of the long range ^{1}H–^{13}C coupling correlation experiment which should correlate ^{1}H and ^{13}C separated by 2–4 bonds, and the homonuclear ^{1}H NOESY spectrum which shows spatial proximity between proton pairs. The methylene ^{1}H resonance correlated with the ^{13}C signal at δ 112.09 confirming this as C5,20. The N*H* resonance at δ −1.6 correlated with four signals at δ 123.56, 128.04, 134.11 and 139.76 which were those tentatively assigned above to the α- and β-carbon resonances of the NH-bearing rings in structure **4**. These N*H* correlations do not support structure **6**. The ^{1}H singlet at δ 8.40 (12,13H) correlates with the ^{13}C signal at 151.45, confirming this as C11,14. Benzenoid ^{1}H and ^{13}C shifts could be grouped into two sets (rings E and F) by a combination of the following one-bond and long range ^{1}H–^{13}C connections: Ring E δ 114.69 (C4′)↔δ 7.08 (4′H)↔δ 119.19 (C2′)↔δ 7.26 (2′H)↔δ 112.09 (C5,20)↔δ 7.29 (6′H)↔δ 122.9 (C6′) and δ 7.08 (4′H)↔δ 156.99 (C3′); Ring F δ 114.89 (C4′)↔δ 7.15 (4′H)↔δ 121.02 (C2′)↔δ 7.45 (2′H) and δ 155.81 (C3′)↔δ 7.15 (4′H)↔δ 124.93 (C6′). The only ambiguities which remain in the ^{13}C assignments are between the two C1′ resonances at δ 142.42 and 143.40, between the two C5′ resonances at δ 127.84 and 129.16, and between the β-pyrrole carbon resonances at δ 123.56 and 128.04. Variation of the delay used in the long range coupling correlation to match ^{1}H–^{13}C couplings in the range 3.5 to 12 Hz did not reveal additional correlations which would remove the ambiguities.

The phenyl rings E and F were assigned as substituted at C5,20 and C10,15 respectively on the basis of the interproton NOEs from the NOESY spectrum (see Experimental section). The methylene group (ring A) is shown to be near to phenyl ring E (and not ring F) by the appearance of strong NOE cross peaks between the methylene resonance and the benzenoid chemical shifts at δ 7.08 (4′H), 7.26 (2′H) and 7.29 (6′H) from ring E, but not to δ 7.15 (4′H) from ring F. To substantiate this point further the β-pyrrole singlet at δ 8.40 (12,13H) shows an NOE cross peak to δ 7.15 (4′H) of ring F, but not to δ 7.08 (4′H) of ring E. The NOESY data also allow the specific assignment between the β-pyrrole protons 7 and 8H: the β-pyrrole doublet at δ 8.25 is due to 7,18H since it gives correlations with 2′H, 4′H and 6′H of ring E, whereas the doublet at δ 8.65 is due to 8,17H since it gives a correlation with 4′H of ring F. The O*H* resonance at δ 9.79 correlates with 4′H of ring E, and the other O*H* at δ 9.84 correlates with 4′H of ring F. The one bond ^{1}H–^{13}C chemical shift correlation, in conjunction with the above assignment for the β-pyrrole protons, gives the assignment for C7,18 at δ 123.56 and C8,17 at δ 128.04.

Evidence for slow exchange. The assignment of the ^{13}C chemical shifts for the α-pyrrole carbons at δ 134.11 and 139.76, and the α-pyrrolenine carbon of ring C at δ 151.45 is entirely consistent with the corresponding shifts found[4] for TPP in the low temperature (slow exchange) limit. Rapid exchange between different tautomers for TPP resulted[4] in an average shift for the α-carbons at δ 145.8. The ^{1}H–^{15}N 2D correlation experiment revealed a single ^{15}N chemical shift at δ 111.8. This is precisely the chemical shift region predicted (δ 112 to 116)[5,6] for a 'pyrrole' *N*H group, and strongly suggests that this

chemical shift is representative of a single nitrogen environment which is not undergoing rapid exchange with an appreciable proportion of a pyrrolenine site (for which the ^{15}N shift is expected to be in the region δ 221 to 223).[5,6] The final question concerns the possible mutual intramolecular exchange (concerted or stepwise) of the two N*H* protons. The symmetry of tautomer **4** requires that both fast and slow exchange of these protons gives rise to a single chemical shift. However, it has been shown by Limbach *et al.*[9,10,12] for the case of ^{15}N-enriched chlorins that in the slow exchange limit the N*H* proton resonance is a doublet with a ^{1}H–^{15}N coupling constant in the region 95 to 100 Hz, whereas in the fast intramolecular exchange situation the proton resonance is a triplet, equally coupled to two nitrogens but with the coupling constant exactly halved. The ^{1}H–^{15}N coupling is shown in this study (see Fig. 5), with ^{15}N at the natural abundance level, to be a doublet with *ca.* 99 Hz splitting. Therefore at the temperature of our measurement (303 K) the pyrrole protons are in the slow to intermediate exchange rate regime.

Finally, a point of nomenclature.[9] Chlorins have often been represented with the 'extra' hydrogens at C2 and C3 (giving lowest numbers) for synthetic compounds, and at C17 and C18 for compounds related to chlorophyll (since the 'extra' hydrogens are at C17 and C18 in chlorophyll a in semi-systematic nomenclature). Where fine structure is not known (as is often the case) the imino hydrogens are represented by convention at N21 and N23 for nomenclature purposes.[20] Thus *m*-THPC has often been represented heretofore as shown in **6**. Now that the predominant tautomer of *m*-THPC in solution at ambient temperature is identified as **4**, the systematic IUPAC name becomes 7,8-dihydro-5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin; represented by structure **7**, following the rule that 'indicated' hydrogens (implied as conventional here) take numerical precedence[21] and therefore must occupy the N21 and N23 positions.



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Acknowledgements

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